Electronic Supporting Information

for

Synthesis of nucleoside and nucleotide conjugates of bile acids and polymerase construction of bile acid-functionalized DNA

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Table of contents:

General

NMR spectra were measured on a Bruker Avance 600 (600.1 MHz for ^{1}H and 150.9 MHz for ^{13}C nuclei) and a Bruker Avance 500 (500.1, 500.0, 499.8 MHz for ^{1}H, 125.7 MHz for ^{13}C and 202.3 for ^{31}P nuclei) in $CDCl_3$ (referenced to solvent signals δ_H = 7.26 ppm, δ_C = 77.0 ppm), CD_3OD (referenced to solvent signals δ_H = 3.31 ppm, δ_C = 69.3 ppm) and D_2O (reference to dioxane as an internal standard, δ_H = 3.75 ppm, δ_C = 69.3 ppm, standard for ^{31}P NMR was external H_3PO_4). Chemical shifts are given in ppm (δ-scale), and coupling constants (*J*) in Hz. Mass spectra were measured on LCQ classic (Thermo/Finnigan) spectrometer using ESI. Preparative HPLC separations were performed on a column packed with 10 µm C18 reversed phase (Phenomenex, Luna C18(2).

Synthesis

Starting compound **2b** was prepared as described previously.[1] Triphosphorylation of iododeoxynucleosides (**dA$^{\mathbf{I}}$TP** and **dC$^{\mathbf{I}}$TP**) were performed utilizing known procedures.[2]

Synthesis of Bile acid acetylenes

Method A: Bile acid 1 (10.0 mmol) and Cs_2CO_3 (15.0 mmol) suspensed with 35 mL of DMF were stirred at rt for 1 h. Propargyl bromide (80 % in toluene, 20.0 mmol) was added and the stirring continued for 20 hours. Mixture was dissolved in 100 mL of $CHCl_3$ and washed with 3x50 mL of H_2O and 50 mL of Brine, dried over anhydrous Na_2SO_4 and evaporated to give oily crude product which was purified by column chromatography. Products were crystallized from CH_3CN as white solids which were dried in *vacuo.*

Method B: Bile acid 1 (10.0 mmol) was suspended with dry dioxane, triethyl amine (1.53 mL, 11.0 mmol) was added and the mixture cooled to 10^{o}C. Through a dropping funnel ethyl chloroformate (1.05 mL, 11.0 mmol) was added dropwice after which the stirring was continued for 30 min at 10 ^{o}C. Propargyl amide (1.23 mL, 20 mmol) in 10 mL of dioxane was added dropwise to the reaction mixture and the mixture was allowed to spontaneously reach room temperature after which the stirring was continued for another 20 h. Mixture was then evaporated and the residue dissolved in 200 mL of $CHCl_3$, washed with 100 mL of H_2O, 4x50 mL of 0.1 M HCl, 2x100 mL H_2O and 100 mL of Brine, dried over anhydrous Na_2SO_4 and evaporated to give crude product which was purified by column chromatography.

Propargyl 3α,7α,12α-trihydroxy-5β-cholan-24-oate (2a)[1]

Prepared by Method A from **1a** and purified by column chromatography using CH_3OH (2-20 % gradient) in CH_2Cl_2 as an eluent. Yield 73 % of **2a** as white solid. δ_H (500.1 MHz; $CDCl_3$) ppm: 0.68 (s, 3H, 18''CH_3), 0.89 (s, 3H, 19''CH_3), 0.98 (d, *J*=6.0, 3H, 21''CH_3), 0.98-2.46 (steroidal -CH_2- and -CH-, 3''C-O*H*, 7''C-O*H*, 12''C-O*H*, 23''CH_2, 27''CH), 3.44 (m, 1H, 3''CH), 3.85 (br.s, 1H, 7''CH), 3.96 (br.s, 1H, 12''CH), 4.65 (s, 2H, 25''CH_2); δ_C (125.8 MHz; $CDCl_3$) ppm:12.5 (C18''), 17.3 (C21''), 22.5 (C19''), 23.2 (C15''), 26.6 (C9''), 27.4 (C16''), 28.3 (C11''), 30.6 (C2''), 30.8 (C22''), 31.0 (C23''), 34.7 (C6'' and C10''), 35.1 (C20''), 35.3 (C1''), 39.6 (C8''), 39.7 (C4''), 41.5 (C5''), 41.9 (C14''), 46.5 (C13''), 47.1 (C17''), 51.7 (C25''), 68.4 (C12''), 71.9 (C3''), 73.0 (C7''), 74.7 (C27''), 77.9 (C26''), 173.3 (C24''); MS (ES^+): found m/z: 469.3 ($[M+Na]^+$), 485.3 ($[M+K]^+$).

Propargyl 3α,7α-dihydroxy-5β-cholan-24-oate (2c)

Bile acid **1c** (3.93 g, 10.0 mmol) and Cs_2CO_3 (4.89 g, 15.0 mmol) suspensed with 35 mL of DMF were stirred at rt for 1 h. Propargyl bromide (2.97 g, 80 w% in toluene, 20.0 mmol) was added and the stirring continued for 20 hours. Mixture was dissolved in 100 mL of $CHCl_3$ and washed with 3x50 mL of H_2O and 50 mL of Brine, dried over anhydrous Na_2SO_4 and evaporated to give oily crude product which was purified by column chromatography using CH_3OH (2-10 %) in CH_2Cl_2 as an eluent. Product was crystallized from CH_3CN and dried *in vacuo* to give **2c** (1.95 g, 45 %) as a white solid. Found: C, 75.2; H, 9.7. ($C_{27}H_{42}O_4$ requires C, 75.3; H, 9.8); ν(KBr)/cm^{-1}: 3429, 3310, 2931, 2866, 2129, 1743, 1638, 1626, 1466, 1449, 1418, 1377, 1328, 1307, 1244, 1161, 1078, 1030, 1001, 980, 899, 859, 764; δ_H (500.1 MHz; $CDCl_3$) ppm: 0.64 (s, 3H, 18''CH_3), 0.89 (s, 3H, 19''CH_3), 0.91 (d, J=6.5, 3H, 21''CH_3), 0.92-2.42 (steroidal -CH_2- and -C*H*-, 3''C-O*H*, 7''C-O*H*, 23''CH_2), 2.37 (t, J=5 Hz, 1H, 27''CH), 3.43 (m, 1H, 3''CH), 3.83 (m, 1H, 7''CH), 4.65 (m, 2H, 25''CH_2); δ_C (126 MHz; $CDCl_3$) ppm: 11.7 (C18''), 18.2 (C19''), 20.6 (C11''), 22.7 (C21''), 23.6 (C15''), 28.1 (C16''), 30.7 (C6''), 30.8 (C22''), 30.9 (C23''), 32.8 (C8''), 34.6 (C2''), 35.0 (C10''), 35.3 (C1'' and C20''), 39.4 (C5''), 39.6 (C12''), 39.8 (C4''), 41.5 (C9''), 42.7 (C13''), 50.4 (C14''), 51.7 (C25''), 55.8 (C17''), 68.4 (C3''), 71.9 (C7''), 74.6 (d, C27''), 77.9 (C26''), 173.3 (C24''); MS (ES^+): found m/z: 453.3 ($[M+Na]^+$), 469.3 ($[M+K]^+$).

***N*-Propargyl 3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-amide (2d)**[3]

Prepared by method b from **1d** and purified by column chomatography using CH_3OH (20 %) in CH_2Cl_2 as an eluent. Yield 49 % of **2d** as white solid. δ_H (500.1 MHz; CD_3OD) ppm: 0.67 (s, 3H, 18''CH_3), 0.88 (s, 3H, 19''CH_3), 0.99 (d, *J*=6.5, 3H, 21''CH_3), 0.95-2.60 (steroidal -CH_2- and -CH-), 2.08-2.28 (m, 2H, 23''CH_2), 2.54 (t, *J*=2.5, 1H, 27''CH), 3.53 (m, 1H, 3''CH), 3.93 (d, *J*=2.5, 2H, 25''CH_2), 3.95 (m, 1H, 12''CH); δ_C (125.8 MHz; $CDCl_3$) ppm: 12.5 (C18''), 17.5 (C21''), 22.5 (C19''), 23.3 (C15''), 26.5 (C9''), 27.6 (C16''), 28.2 (C11''), 29.1 (C25''), 30.5 (C2''), 31.4 (C22''), 32.8 (C23''), 34.7 (C6''), 34.7 (C10''), 35.3 (C1''), 35.3 (C20''), 39.5 (C8''), 39.7 (C4''), 41.5 (C5''), 41.8 (C14''), 46.5 (C13''), 46.6 (C17''), 68.4 (C12''), 71.3 (C27''), 71.9 (C3''), 73.1 (C7''), 79.9 (C26''), 173.6 (C24''); MS (ES^+): found m/z: 468.4 ($[M+Na]^+$), 484.4 ($[M+K]^+$).

_N_-Propargyl 3α,12α-dihydroxy-24-oxo-5β-cholan-24-amide (2e)[3]

Prepared by method b and purified by column chromatography using CH_3OH (2-6 % gradient) in CH_2Cl_2 as an eluent. Yield 50 % of **2e** as white solid. δ_H (500.1 MHz; $CDCl_3$) ppm: 0.71 (s, 3H, 18''CH_3), 0.93 (s, 3H, 19''CH_3), 1.02 (d, *J*=6.5, 3H, 21''CH_3), 0.93-1.90 (steroidal -CH_2- and –CH-, 23''CH_2) 2.23 (t, J=2.5, 27''CH), 2.77 (br. s, 3H, 3''C-O*H*, 7''C-O*H*, 12''C-O*H*), 3.34 (m, 1H, 3''CH), 3.83 (br.s, 1H, 7''CH), 3.96 (br.s, 1H, 12''H), 4.04 (m, 2H, 25''CH_2), 6.28 (br.s, 1H, N*H*); δ_C (125.8 MHz; $CDCl_3$) ppm: 13.3 (C18''), 17.8 (C21''), 23.8 (C19''), 25.0 (C15''), 27.6 (C16''), 28.6 (C7''), 28.8 (C6''), 29.5 (C25''), 30.1 (C11''), 31.3 (C2''), 33.3 (C22''), 34.0 (C23''), 35.0 (C9''), 35.5 (C10''), 36.6 (C1''), 36.9 (C20''), 37.4 (C4''), 37.6 (C8''), 43.8 (C5''), 47.7 (C13''), 48.3 (C17''), 49.5 (C14''), 72.1 (C27''), 72.7 (C3''), 74.2 (C12''), 80.9 (C26''), 176.6 (C24''); MS (ES^+): found m/z: 452.4 ($[M+Na]^+$), 468.3 ($[M+K]^+$).

Synthesis of modified nucleosides – Sonogashira cross-coupling – General procedure:

Water/acetonitrile mixture (1.5 mL) was added through a septum to argon-purged vial containing halogenated nucleoside **3-5**, acetylene **2** (1.2-1.5 eqv. to nucleoside), and CuI (10 mol %). In a separate vial $Pd(OAc)_2$ (5 mmol %) and $P(Ph\text{-}SO_3Na)_3$ (5 eqv. to Pd) were combined under argon with 0.5 mL of H_2O-CH_3CN. After dissolution of the solids, the catalyst solution was added to the reaction mixture followed by addition of EtN(*i*-Pr)2 (10 eqv.). Reaction mixture was stirred under argon at 65-75 °C for 12-120 min. Mixture was then concentrated and purified by column chromatography and dried *in vacuo* to give **6a-8e**.

7-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)oxy]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosine (6a)

Reaction from **2a** (60.0 mg, 0.13 mmol) and **3** (29.6 mg, 0.08 mmol) with CuI (1.9 mg, mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (130 µL, 0.75 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 12 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:2) as an eluent and dried in vacuo to yield 37.7 mg (69 %) of **6a** as slightly yellowish solid. NMR: Tables S1 and S2. ν(KBr)/cm^{-1}: 3434, 2936, 2868, 2231, 1733, 1626, 1590, 1571, 1538, 1464, 1450, 1377, 1300, 1196, 1169, 1092, 1077, 1043, 980, 914, 797; MS (ES^+): found m/z: 695.4 ($[M+H]^+$), 717.4 ($[M+Na]^+$), 1411.0 ($[2M+Na]^+$); HRMS (ES^-): found m/z: 695.4018 ($C_{38}H_{55}O_8N$ requires 695.4014).

7-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)oxy]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosine (6b)

Reaction from **2b** (51.7 mg, 0.12 mmol) and **3** (30.1 mg, 0.08 mmol) with CuI (1.5 mg, 0.008 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), TPPTS (11.2 mg, 0.02 mmol), EtN(*i*-Pr)$_2$ (140 μL, 0.8 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 20 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0.5-10:4) as an eluent and dried *in vacuo* to yield 19.1 mg (35 %) of **6b** as a slightly yellowish solid. NMR: Tables S1 and S2. ν(KBr)/cm^{-1}:3440, 2936, 2865, 2231, 1732, 1626, 1591, 1573, 1537, 1449, 1376, 1300, 1203, 1166, 1094, 1044, 996, 943, 798; MS (ES^+): found m/z: 679 ($[M+H]^+$), 701 ($[M+Na]^+$), 1379 ($[2M+Na]^+$); HRMS (ES^+): found m/z: 679.4069 ($C_{38}H_{55}O_7N_4$ requires 679.4065).

7-{[(3α,7α-dihydroxy-24-oxo-5β-cholan-24-yl)oxy]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosine (6c)

Reaction from **2c** (53.3 mg, 0.12 mmol) and **3** (29.6 mg, 0.08 mmol) with CuI (1.4 mg, 0.007 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), TPPTS (11.3 mg, 0.02 mmol), EtN(*i*-Pr)$_2$ (140 μL, 0.8 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 15 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:4) as an eluent and dried *in vacuo* to yield 23.6 mg (45 %) **6c** as a slightly yellowish solid. NMR: Tables S1 and S2. ν(KBr)/cm^{-1}: 3442, 2932, 2867, 2231, 1734, 1626, 1591, 1572, 1537, 1463, 1453, 1376, 1301, 1201, 1164, 1095, 1079, 1059, 798; MS (ES^+): found m/z: 679.5 ($[M+H]^+$), 701.4 ($[M+Na]^+$), HRMS (ES^-): found m/z: 679.4069 ($C_{38}H_{55}O_7N_4$ requires 679.4065)

7-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosine (6d)

Reaction from **2d** (42.5 mg, 0.10 mmol) and **3** (30.6 mg, 0.08 mmol) with CuI (2.2 mg, 0.012 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), TPPTS (11.4 mg, 0.02 mmol), EtN(*i*-Pr)$_2$ (140 μL, 0.8

mmol), in H_2O-CH_3CN (2:1) at 75 °C for 60 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:1-10:4) as an eluent and dried *in vacuo* to yield 38.3 mg (69 %) of **6d** as slightly yellowish solid. NMR: Tables S1 and S2. ν(KBr)/cm^{-1}: 3422, 2933, 2863, 2230, 1625, 1590, 1571, 1533, 1449, 1417, 1377, 1301, 1201, 1173, 1090, 1040, 941, 797; MS (ES^+): found m/z: 694.4 ($[M+H]^+$), 716.5 ($[M+Na]^+$), 1409.2 ($[2M+Na]^+$), HRMS (ES^+): found m/z: 694.4177 ($C_{38}H_{56}N_5O_7$ requires 694.4174).

7-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosine (6e)

Reaction from **2e** (43.5 mg, 0.10 mmol) and **3** (31.9 mg, 0.08 mmol) with CuI (2.2 mg, 0.012 mmol), $Pd(OAc)_2$ (0.9 mg, 0.004 mmol), TPPTS (11.3 mg, 0.02 mmol), EtN(*i*-Pr)$_2$ (140 μL, 0.8 mmol), in H_2O-CH_3CN (2:1) at 75 °C for 60 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:2) as an eluent and dried *in vacuo* to yield 37.5 mg (65 %)of **6e** as a slightly yellowish solid. NMR: Tables S1 and S2. ν(KBr)/cm^{-1}: 3430, 2934, 2866, 2230, 1626, 1591, 1571, 1533, 1461, 1450, 1377, 1301, 1198, 1174, 1090, 1076, 1043, 981, 914, 858, 797; MS (ES^-): found m/z: 676.3 ($[M-H]^-$); HRMS (ES^-): found m/z: 676.4067 ($C_{38}H_{54}N_5O_6$ requires 676.4074).

5-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)oxy]prop-1-yn-1-yl}-2'-deoxycytidine (7a)

Reaction from **2a** (60.2 mg, 0.13 mmol) and **4** (37.4 mg, 0.11 mmol) with CuI (1.9 mg, 0.01 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 12 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0.5-10:3) as an eluent and dried *in vacuo* to yield 28.0 mg (39 %) **7a** as a white solid. NMR: Tables S3 and S4. ν(KBr)/cm^{-1}: 3393, 2935, 2868, 1650, 1601, 1506, 1417, 1303, 1259, 1232, 1193, 1092, 1077, 1046, 981, 950, 914, 853, 785; MS (ES^+): found m/z: 672.3 ($[M+H]^+$), 694.4 ($[M+Na]^+$), 1343.4 ($[2M+H]^+$), 1365.5 ($[2M+Na]^+$), MS (ES^-): found m/z: 670.1 $[M-H]^-$, 716.1 $[M+OH]^-$; HRMS (ES^-): found m/z: 670.3702 ($C_{36}H_{52}O_9N_3$ requires 670.3709).

5-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)oxy]prop-1-yn-1-yl}-2'-deoxycytidine (7b)

Reaction from **2b** (64.6 mg, 0.15 mmol) and **4** (35.9 mg, 0.10 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 20 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0.5-10:4) as an eluent and dried *in vacuo* to yield 57.9 mg (88 %) of **7b** as a slightly yellowish solid. NMR: Tables S3 and S4. ν(KBr)/cm^{-1}: 3411, 2934, 2864, 1650, 1602, 1505, 1449, 1417, 1356, 1304, 1258, 1191, 1092, 1043, 945, 851, 785; MS (ES^+): found m/z: 656.3 ($[M+H]^+$), 678.4 ($[M+Na]^+$), 1311.4 ($[2M+H]^+$), 1333.4 ($[2M+Na]^+$); HRMS (ES^-): found m/z: 653.3919 ($C_{36}H_{54}N_4O_7$ requires 653.3914).

5-{[(3α,7α-dihydroxy-24-oxy-5β-cholan-24-yl)oxo]prop-1-yn-1-yl}-2'-deoxycytidine (7c)

Reaction from **2c** (64.6 mg, 0.15 mmol) and **4** (35.7 mg, 0.10 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 20 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:4) as an eluent and dried *in vacuo* to yield 59.2 mg (90 %) of **7c** as a white solid. NMR: Tables S3 and S4. ν(KBr)/cm^{-1}: 3425, 2936, 2868, 2232, 1732, 1649, 1602, 1505, 1447, 1416, 1377, 1306, 1259, 1236, 1190, 1153, 1092, 1078, 1045, 1000, 982, 951, 914, 858, 786 ; MS (ES^+): found m/z: 656.2 ($[M+H]^+$), 678.4 ($[M+Na]^+$), 694.3 ($[M+K]^+$), 1311.4 ($[2M+H]^+$), 1334.3 ($[2M+Na]^+$); HRMS (ES^+): found m/z: 656.3909 ($C_{36}H_{54}O_8N_3$ requires 656.3905).

5-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxycytidine (7d)

Reaction from **2d** (53.8 mg, 0.12 mmol) and **4** (36.9 mg, 0.10 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (2:1) at 75 °C for 60 min yielded product which was purified by column chromatography using $CHCl_3$-CH_3OH (10:2) as an eluent and dried *in vacuo* to yield 44.6 mg (66 %) of **7d** as a white solid. NMR: Tables S3 and S4. ν(KBr)/cm^{-1}: 3422, 2935, 2864, 2233, 1733, 1648, 1598, 1057, 1448, 1376, 1307, 1256, 1164, 1092, 1042, 967, 945, 851, 785; MS (ES^+): found m/z: 671.3 ($[M+H]^+$), 693.4 ($[M+Na]^+$), 791.0 ($[M+K]^+$), 1363.4 ($[2M+Na]^+$); HRMS (ES^-): found m/z: 699.3859 ($C_{36}H_{53}N_4O_8$ requires 669.3869).

5-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxycytidine (7e)

Reaction from **2e** (61.9 mg, 0.14 mmol) and **4** (42.0 mg, 0.12 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$, (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (2:1) at 75 °C for 120 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:1-10:4) as an eluent and dried *in vacuo* to yield 48.0 mg

(61 %) of **7e** as a slightly yellowish solid. NMR: Tables S3 and S4. ν(KBr)/cm^{-1}: 3419, 2829, 2866, 2359, 2341, 2233, 1732, 1649, 1598, 1506, 1448, 1416, 1376, 1308, 1260, 1163, 1091, 1078, 1050, 1000, 979, 955, 900, 860, 785; MS (ES$^+$): found m/z: 655.3 ([M+H]$^+$), 677.4 ([M+Na]$^+$), 1309.4 ([2M+H]$^+$), 1331.4 ([2M+Na]$^+$); HRMS (ES$^-$): found m/z: 653.3919 ($C_{36}H_{54}N_4O_7$ requires 653.3914).

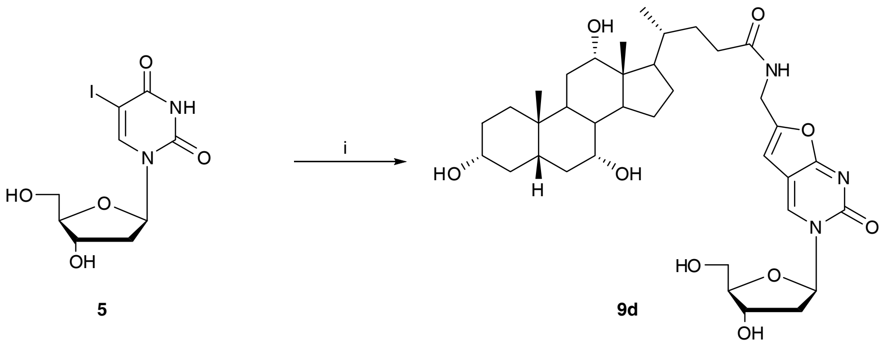
5-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxyuridine (8e) in aqueous phase

Reaction from **2e** (66.8 mg, 0.16 mmol) and **4** (35.4 mg, 0.10 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in H_2O-CH_3CN (1:1) at 65 °C for 20 min yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:4) as an eluent and dried *in vacuo* to yield 37.9 mg (58 %) of **7a** as a white solid. NMR: Tables S5 and S6. ν(KBr)/cm^{-1}: 3422, 3066, 2935, 2864, 2363, 2343, 1691, 1534, 1459, 1420, 1377, 1355, 1281, 1194, 1091, 1042, 986, 945, 922, 851, 774, 758; MS (ES$^+$): found m/z: 678.3 ([M+Na]), 1333.3 ([2M+Na]$^+$); HRMS (ES$^+$): found m/z: 656.3907 ($C_{36}H_{54}N_3O_8$ requires 656.3905).

5-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxyuridine (8e) under anhydrous conditions

Reaction from **2e** (55.0 mg, 0.13 mmol) and **4** (35.3 mg, 0.10 mmol) with CuI (1.9 mg, 0.010 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), TPPTS (14.2 mg, 0.025 mmol), EtN(*i*-Pr)$_2$ (174 μL, 1.0 mmol), in dry DMF at 80 °C for 3 h yielded product which was purified by column chromatography using EtOAc-CH_3OH (10:0-10:4) as an eluent and dried *in vacuo* to yield 22.1 mg (31 %) of **7a** as a white solid. NMR: Tables S5 and S6. ν(KBr)/cm^{-1}: 3419, 3063, 2936, 2865, 2357, 2339, 1694, 1537, 1463, 1416, 1376, 1357, 1282, 1194, 1092, 1042, 986, 946, 920, 852, 806, 776, 758; MS (ES$^+$): found m/z: 678.4 ([M+Na]$^+$), 1333.2 ([2M+Na]$^+$) HRMS (ES$^+$): found m/z: 678.3728 ($C_{36}H_{53}N_3O_8Na$ requires 678.3725).

6-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl]aminomethyl}-3-(2'-β-D-deoxyribofuranosyl)-furo[2,3-*d*]pyrimidin-2(3*H*)-one nucleoside (9d)



Scheme S1. (i) CuI (10 mol%), $Pd(OAc)_2$ (5 mol%), $P(Ph\text{-}SO_3Na)_3$ (5 eq. to Pd), EtN(*i*-Pr)$_2$ (10 eq.), H_2O-CH_3CN (2:1), 75 ^oC, 60 min.

Water/acetonitrile mixture (1.5 mL) was added through a septum to argon-purged vial containing **5** (36.9 mg, 0.10 mmol), **2d** (53.8 mg, 0.12 mmol), and CuI (2.1 mg, 0.01 mol). In a separate vial $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) and TPPTS (14.2 mg, 0.025 mmol) were combined under argon with 0.5 mL of H_2O-CH_3CN (2:1). After dissolution of the solids, the catalyst solution was added to the reaction mixture followed by addition of EtN(*i*-Pr)$_2$ (174 µL, 1.0 mmol). Reaction mixture was stirred under argon at 75 ^oC for 60 min. Mixture was then concentrated and purified by column chromatography twice, first with EtOAc-CH_3OH (5:2) and again with $CHCl_3$-CH_3OH (10:1-10:4 gradient) and dried *in vacuo* to give 17.7 mg (26 %) of **9d** as yellowish oil. λ_{max} (MeOH)/nm 202 (ε/dm^3 mol^{-1} cm^{-1} 11300), 240 (ε/dm^3 mol^{-1} cm^{-1} 4900), 327 (ε/dm^3 mol^{-1} cm^{-1} 2200); NMR. ESI MS+: Found: 694.4 [M+Na], 792.1 [M+K], 1365.4 [2M+Na]. HRMS (ES$^-$): found m/z: 670.3704 ($C_{36}H_{52}N_3O_9$ requires 670.3709).

Synthesis of modified dNTPs – Sonogashira cross-coupling – General procedure:
Water/acetonitrile mixture (1.5 mL) was added through a septum to argon-purged vial containing halogenated nucleoside triphophate **dA$^{\mathbf{I}}$TP** or **dC$^{\mathbf{I}}$TP**, acetylene **2** (1.5 eqv.), and CuI (10 mol %). In a separate vial $Pd(OAc)_2$ (5 mmol %) and TPPTS (5 eqv. to Pd) were combined under argon with 0.5 mL of H_2O-CH_3CN. After dissolution of the solids, the catalyst solution was added to the reaction mixture followed by addition of EtN(*i*-Pr)$_2$ (10 eqv.). Reaction mixture was stirred under argon at 75 ^oC for 45 min. The product was isolated from the crude reaction mixture by HPLC on a C18 column using two-step linear gradient from 0.1 M TEAB (triethylammonium bicarbonate) in H_2O to 0.1 M TEAB in H_2O/MeOH (1:1) and from 0.1 M TEAB in H_2O/MeOH (1:1) to MeOH as an eluent. Several co-distillations from water and conversion to sodium salt form (Dowex 50WX8 in Na^+ cycle) followed by freeze drying gave products as white solids.

7-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosinetriphosphate (dA^{CA}TP)

Prepared from **dA^{I}TP** and **2d**, yield 44 %.

MS (ES^{-}): found m/z: 465.8 ([M-2H]$^{2-}$); HRMS (ES^{-}): found m/z: 465.6470 ($C_{38}H_{56}N_5O_{16}P_3$, z=2 requires 465.6473). NMR: Tables S1 and S2.

7-{[(3α,12α-dihydroxy-24-oxy-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-7-deaza-2'-deoxyadenosinetriphosphate (dA^{DCA}TP)

Prepared from **dA^{I}TP** and **2d**, yield 57 %.

NMR; MS (ES^{-}): found m/z: 457.8 ([M-2H]$^{2-}$); HRMS (ES^{-}): found m/z: 457.6502 ($C_{38}H_{56}N_5O_{15}P_3$, z=2 requires 454.1393). NMR: Tables S1 and S2.

5-{[(3α,7α,12α-trihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxycytidinetriphosphate (dC^{CA}TP)

Prepared from **dA^{I}TP** and **2d**, yield 32 %.

NMR; MS (ES^{-}): found m/z: 414.3 ([M-PO_3-2H]$^{2-}$), 454.3 ([M-2H]$^{2-}$); HRMS (ES^{-}): found m/z: 454.1385 ($C_{36}H_{55}N_4O_{17}P_3$, z=2 requires 454.1393). NMR: Tables S3 and S4.

5-{[(3α,12α-dihydroxy-24-oxo-5β-cholan-24-yl)amino]prop-1-yn-1-yl}-2'-deoxycytidinetriphosphate (dC^{DCA}TP)

Prepared from **dA^{I}TP** and **2d**, yield 53 %.

MS (ES^{-}): found m/z: 406.3 ([M-PO_3-2H]$^{2-}$), 446.3 ([M-2H]$^{2-}$); HRMS (ES^{-}): found m/z: 446.1413 ($C_{36}H_{55}N_4O_{16}P_3$, z=2 requires 446.1418). NMR: Tables S3 and S4.

Primer extension, purification and analysis of the PEX products

Materials: Synthetic ONs were purchased from either VBC genomics (Austria) or from Sigma Aldrich. Primer: 5′-CAT GGG CGG CAT GGG-3′; Templates: 5′-**CTA GCA TGA GCT CAG T**CC CAT GCC GCC CAT G-3′ (temp^{md16}), 5′-**CCC G**CC CAT GCC GCC CAT G-3′ (temp^{1C}), 5′-**CCC T**CC CAT GCC GCC CAT G-3′ (temp^{1A}), 5′-**GCG ACG AAG AGC TT**C CCA TGC CGC CCA TG-3′ (temp^{AA}), 5′-**TTA TAT TTA TA**C CCA TGC CGC CCA TG-3′ (temp^{3A}), 5′-**TAT ATA TAT AT**C CCA TGC CGC CCA TG-3′ (temp^{rep}) (segments forming a duplex with the primer are underlined, the replicated segments are in bold). Template temp^{1C} used in experiment involving the DBstv magnetoseparation procedure was biotinylated at its 5‘ ends.

Dynabeads M-270 strepavidin (DBstv) were obtained from Dynal A.S. (Norway), DyNAzyme II and Phusion DNA Polymerases from Finnzymes (Finland), Pwo DNA Polymerase from PeqLab (Germany), unmodified nucleoside triphosphates (dATP, dTTP, dCTP, and dGTP) from Fermentas (USA), Vent (exo-) DNA Polymerase and T4 polynucleotide kinase from New England Biolabs (Great Britain) and γ-^{32}P-ATP from Izotop, Institute of isotopes Co, Ltd. (Hungary).

Primer extension experiments: The reaction mixture (20 μL) contained DNA polymerase (2 U), dNTPs (either natural or modified, 200 μM; composition of the dNTP is specified in the text and Figure legends for individual experiments), primer (150 nM) and ON template (225 nM) in the reaction buffer. For polyacrylamide gel electrophoresis (PAGE) experiments, the primer was labeleled using [γ^{32}P]-ATP according to standard techniques. Reaction mixtures were incubated at 60 ^{o}C for 30 min and at 95 ^{o}C for 5 min in a thermal cycler and were stopped by addition of stop solution (40 μL, 80 % [v/v] formamide, 20 mM EDTA, 0.025% [w/v] bromophenol blue, 0.025% [w/v] xylene cyanol). Reaction mixture was subjected to gel electrophoresis in 12.5 % denaturating polyacrylamide gel containing 1×TBE buffer (ph 8) and 7 % urea at 50-60 W for ~60 min. Gels were dried and phosphoroimaged.

Polymerase chain reactions: The PCR reaction mixture (20 μL) contained DNA polymerase Phusion (2 U, Finnzymes, Finland), dNTPs (either natural (200 μM) or modified (600 μM)), DMSO (5 %), formamide (0.25 %), betaine (37.5 mM) and tetramethylammoniumchloride (2.5 mM) primers LT25TH (400 nM, 5'-CAAGGACAAAATACCTGTATTCCTT-3') and L20- (400 nM, 5'-GACATCATGAGAGACATCGC-3'), template (25 nM, 5'-
GACATCATGAGAGACATCGCCTCTGGGCTAATAGGACTACTTCTAATCTGTAAGAGCA
GATCCCTGGACAGGCAAGGAATACAGGTATTTGTCCTTG-3'
),in the Phusion reaction buffer HF 5× supplied by the manufacturer. 30 PCR cycles were run under the following conditions: denaturation for 1 min at 94 ^{o}C, annealing for 1 min at 55 ^{o}C, extension for 1.5 min at 72 ^{o}C, followed by final extension step of 5 min at 72 ^{o}C. PCR products were analyzed on a 2 % agarose gel in 0.5×TBE buffer, followed by staining with GelRed™.

Thermal denaturation studies: Double stranded ONs were prepared by PEX-reaction in 500 μL scale using primer (2 μM), template (2 μM), Phusion DNA polymerase (0.2 U), and dNTPs (200 μM) in the reaction buffer. The PEX-products were purified using QIAquick Nucleotide Removal Kit Protocol (Qiagen). The melting temperature of oligonucleotides containing modified base or bases hybridized with natural DNA template were measured. The melting temperature of the control unmodified duplex was also determined in each case. The DNA duplexes were dissolved in 160 μL of phosphate buffer (10mM) and 1M NaCl (pH 7) and further diluted to final duplex concentrations of 0.73 ± 0.3 μM with the buffer. Melting curves were recorded on a Cary 100 bio UV/Vis instrument with temperature controller (Varian). Melting temperatures (T_m values in ^{o}C) were obtained by plotting temperature versus absorbance and by applying a sigmoidal curve fit and results are averages of 4-6 measurements.

MALDI-TOF experiment (ssDNA)

The reaction mixture (200μL) of Phusion DNA Polymerase (Finnzymes, 10 units, 5μL), dNTP (either natural or functionalized, 4mM, 10μL), primer (10μM, 80μL, 3'-GGGTACGGCGGGTAC-5'), and 19-mer biotinylated template (10μM, 40μL, temp^{1C}-bio: 5′-**CCCG**CCCATGCCGCCCATG-3′) in Phusion reaction buffer HF 5× (40μL) supplied by the manufacturer. Reaction mixtures were incubated for 30 min at 60°C in a thermal cycler. The separation on magnetic beads (100μM, Sigma-Aldrich) were carried out according to standard techniques. As matrix for MALDI-TOF measurement was used a mixture of 3-hydroxypicolinic acid (HPA)/picolinic acid (PA)/ammonium tartrate in ratio 9/1/1 respectively. Then 2μL of the matrix and 0.5μL of the sample were mixed on target by use of anchor-chip desk. The crystallized spots were washed once by 0.1% formic acid and once by water. The acceleration tension in reflectron mode was 19.5kV and range of measurement 3–13kDa.

a) Mass (ssDNA: natural dNTPs): calculated: 5950.9 Da; found: 5953.9 Da; Δ = 3 (Figure S1)

b) Mass (ssDNA: **dC^{CA}TP**, dGTP, dATP, TTP): calculated: 6394.5 Da; found: 6394.3 Da; Δ = 0.2 (Figure S1)

c) Mass (ssDNA: **dC^{DCA}TP**, dGTP, dATP, TTP): calculated: 6378.5 Da; found: 6379.2 Da; Δ = 0.7 (Figure S1)

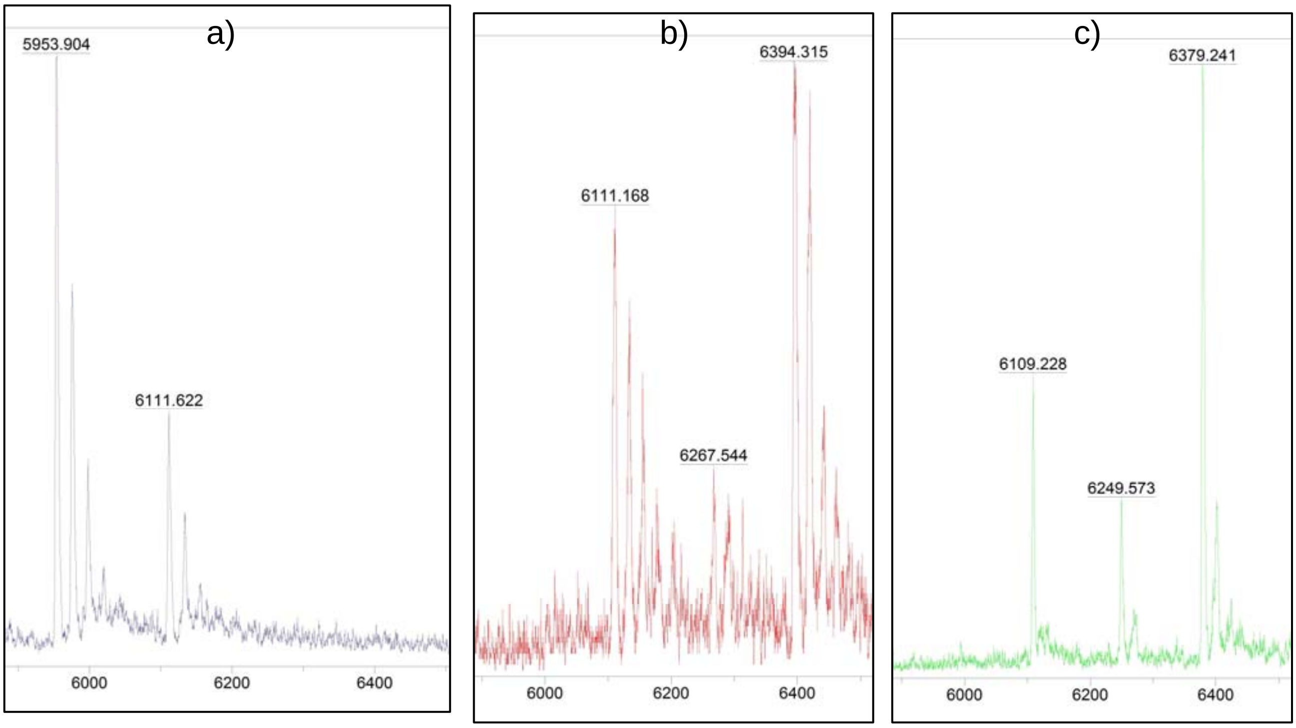


Figure S1: MALDI-TOF spectra of PEX products with temp^{1C}-bio and with a) +: natural dNTPs; b) C^{CA}: dC^{CA}TP, dTTP, dATP, dGTP; c) C^{DCA}: dC^{DCA}TP, dTTP, dATP, dGTP

Sequence analysis of PCR products

The products of PCR with natural dNTPs and with dC^{CA}TP were purified by QIAquick PCR purification kit (Qiagen). Concentrations of products were measured on Nanodrop 1000 Spectrophotometer (+: 6.9 ng/ µl ; C^{CA}: 3.3 ng/ µl) . 0.5 µl of natural DNA + and 1 µl of DNA containing dC^{CA} was used as template for new PCR reaction using natural dNTPs employing forenamed procedure (Figure S2). 3 ng of DNA were mixed with L20- (230 nM) and completed to 14 µl. Sequence analysis (Figure S3) were done by Seqlab (Charles University, Prague).

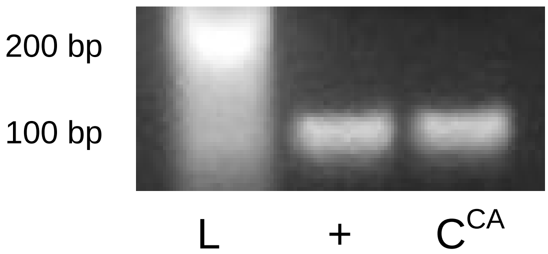


Figure S2: Agarose gel electrophoresis analysis of PCR products prepared from natural dNTPs and templates purified from previous PCR (+: natural template, C^{CA}: template containing dC^{CA} instead of natural dC)

98-mer template:

5´GACATCATGAGAGACATCGCCTCTGGGCTAATAGGACTACTTCTAATCTG**TAAGAGCAGATCCCTGGACAGGCAAGGAATA CAGGTATTTTGTCCTTG** 3´

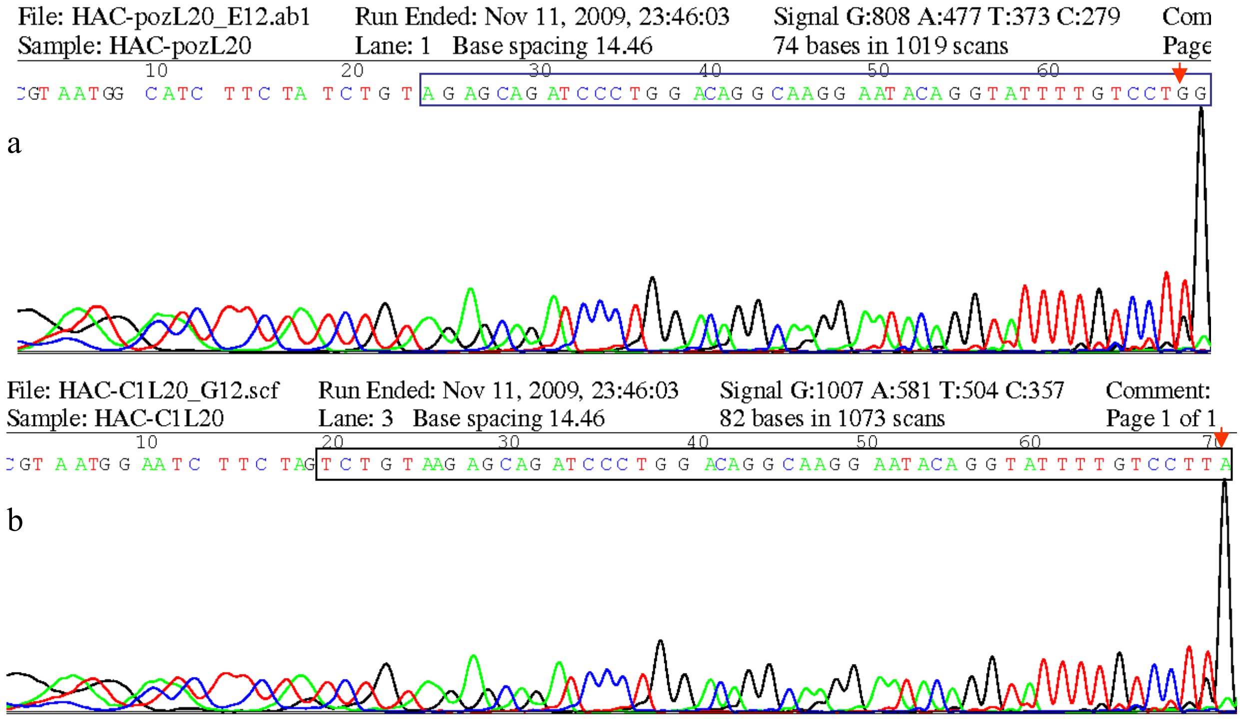


Figure S3: Sequence analysis of DNA prepared from natural dNTPs and natural (a) or modified template containing dC^{CA} instead of natural dC (b). Determined sequence is red in original template and in the frames in the graphs of sequence analysis.

Supplementary results – PAGE of PEX:

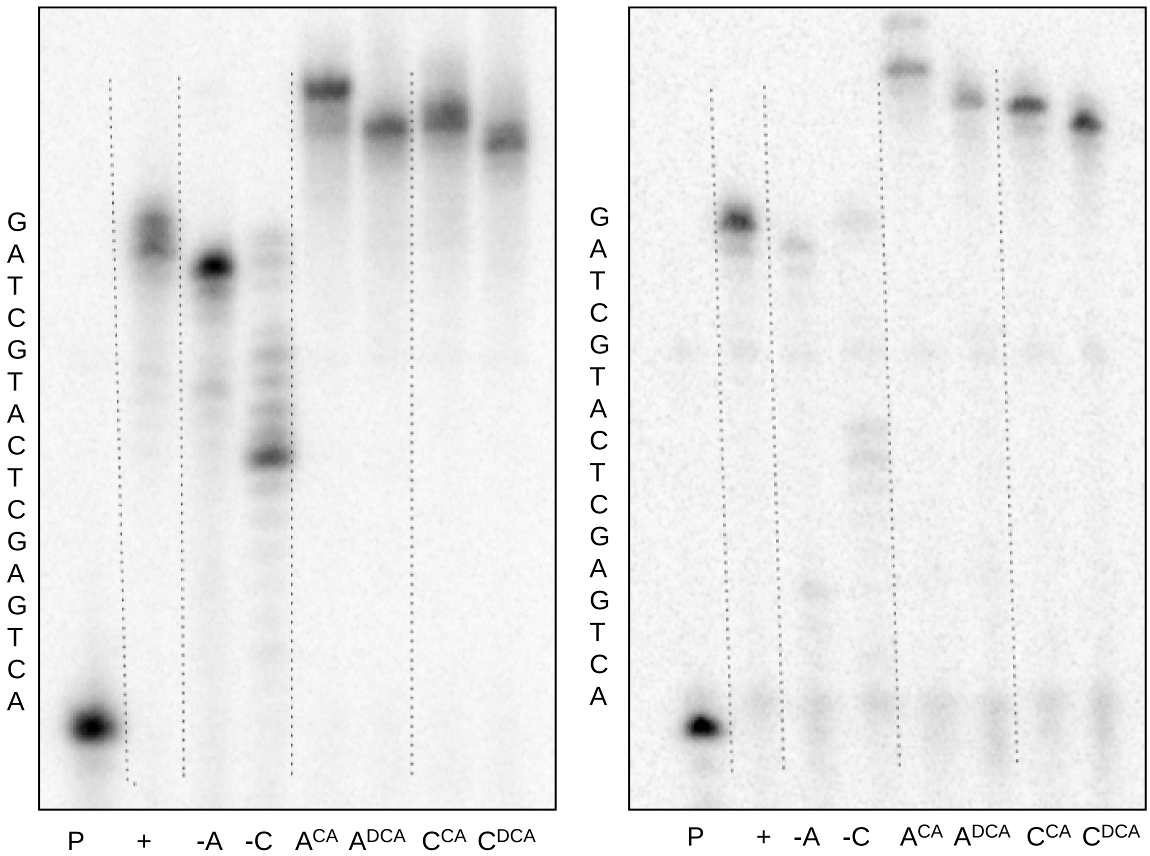


Figure S4. Denaturating PAGE analysis of PEX products synthesized on a temp^{md16} with Vent (exo-) (a) and DyNAzyme (b) DNA polymarases. 5-^{32}P-end-labeled primer-template was incubated with different combinations of natural and functionalized dNTPs. P=Primer; +: natural dNTPs; -A: dTTP, dCTP, dGTP; -C: dATP, dTTP, dGTP; A^{CA}: **dA^{CA}TP**, dTTP, dCTP, dGTP; A^{DCA}: **dA^{DCA}TP**, dTTP, dCTP, dGTP; C^{CA}: **dC^{CA}TP**, dATP, dTTP, dGTP; C^{DCA}: **dC^{DCA}TP**, dATP, dTTP, dGTP.

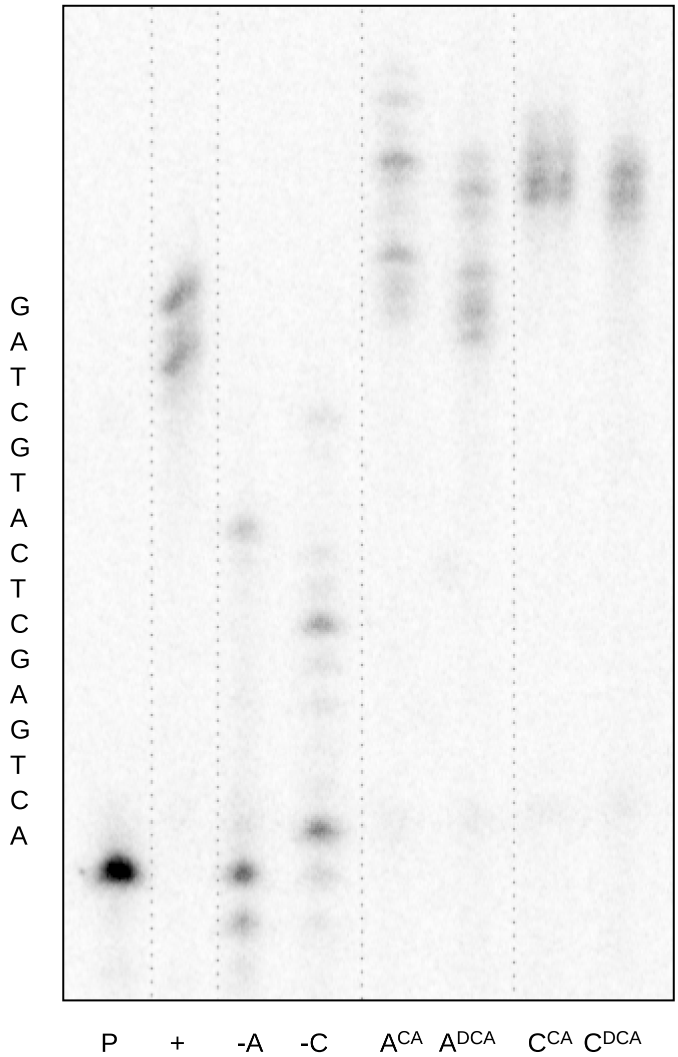


Figure S5. Denaturating PAGE analysis of PEX products synthesized on a temp^{md16} with Pwo DNA polymarase. 5-^{32}P-end-labeled primer-template was incubated with different combinations of natural and functionalized dNTPs. P=Primer; +: natural dNTPs; -A: dTTP, dCTP, dGTP; -C: dATP, dTTP, dGTP; A^{CA}: **dA^{CA}TP**, dTTP, dCTP, dGTP; A^{DCA}: **dA^{DCA}TP**, dTTP, dCTP, dGTP; C^{CA}: **dC^{CA}TP**, dATP, dTTP, dGTP; C^{DCA}: **dC^{DCA}TP**, dATP, dTTP, dGTP.

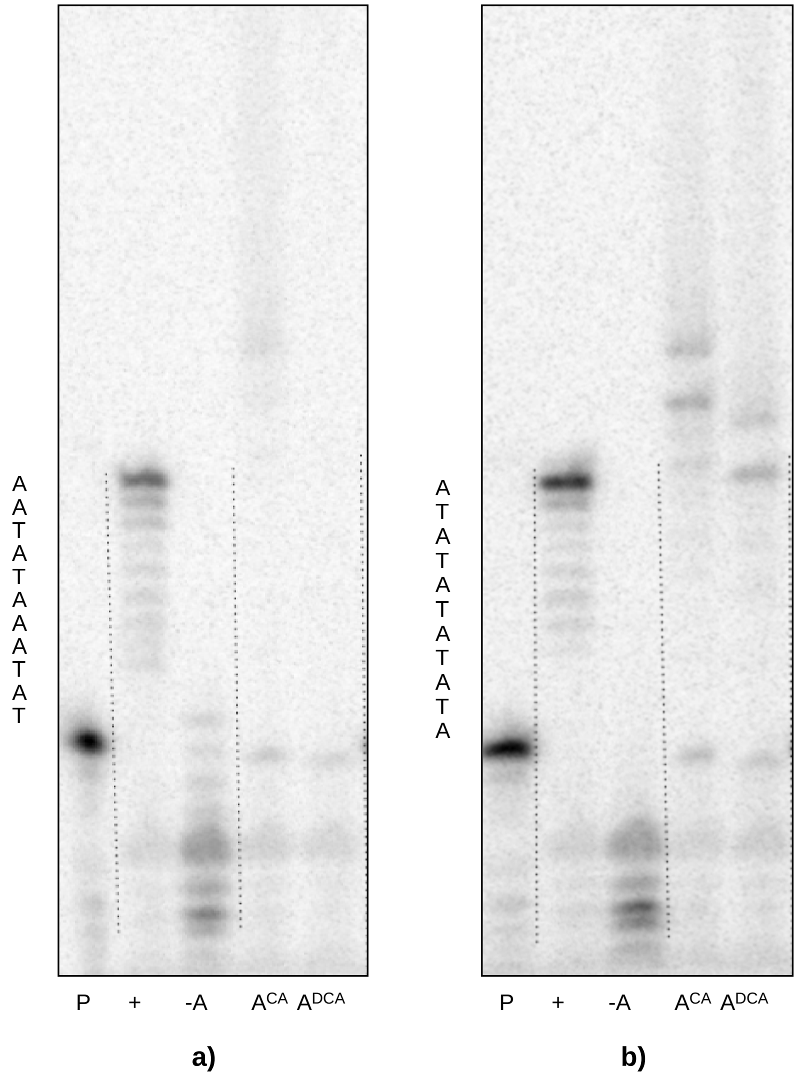


Figure S6. Denaturating PAGE analysis of PEX products synthesized on a temp^{3A} (a) and temp^{rep} (b) with Phusion DNA polymarase. 5-^{32}P-end-labeled primer-template was incubated with different combinations of natural and functionalized dNTPs. P=Primer; +: natural dNTPs; -A: dTTP, dCTP, dGTP; A^{CA}: **dA^{CA}TP**, dTTP, dCTP, dGTP; A^{DCA}: **dA^{DCA}TP**, dTTP, dCTP, dGTP.

References:

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2) P. Čapek, H. Cahová, R. Pohl, M. Hocek, C. Gloeckner, A. Marx, *Chem. Eur. J.* **2007**, *13*, 6196-6203. H. Cahová, L. Havran, P. Brázdilová, H. Pivoňková, R. Pohl, M. Fojta, M. Hocek, *Angew. Chem. Int. Ed.* **2008**, *47*, 2059-2062.

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Table S1. ^{1}H NMR of 7-deazaadenine - bile acids conjugates

Proton	Compound						
	6d 500.0 MHz CD_3OD	**6e** 500.0 MHz CD_3OD	**6a** 500.0 MHz CD_3OD	**6b** 600.1 MHz CD_3OD	**6c** 600.1 MHz CD_3OD	**dA^{CA}TP** 600.1 MHz D_2O[a]	**dA^{DCA}TP** 600.1 MHz D_2O[a]
1”α	1.77	1.73 dt (14.2, 3.2)	1.77 dt (14.4, 3.1)	1.76	1.80 dt (14.3, 3.6)	1.65 dt (14.6, 3.5)	1.60
1”β	0.96 td (14.2, 3.4)	0.96 td (14.2, 3.4)	0.95 td (14.4, 3.5)	0.95 td (14.2, 3.5)	0.96 td (14.3, 3.5)	0.95 td (14.6, 3.5)	0.88
2”α	1.40	1.40	1.41	1.39	1.29	1.23	1.23
2”β	1.58	1.59	1.58	1.59	1.58	1.59	1.58
3”β	3.36 tt (11.5, 4.1)	3.51 tt (11.2, 4.6)	3.35 tt (11.3, 4.5)	3.51 tt (11.2, 4.5)	3.35 tt (11.1, 4.1)	3.46 tt (11.1, 4.4)	3.58 bm
4”α	2.25	1.78	2.25 td (13.2, 11.3)	1.76	2.23 td (13.3, 11.3)	1.93 td (12.9, 11.7)	1.65
4”β	1.63	1.44	1.63	1.44	1.63	1.64	1.42
5”β	1.35	1.38	1.35	1.37	1.33	1.38	1.30
6”α	1.50	1.25	1.48 dt (14.7, 2.1)	1.24	1.49 dt (14.8, 2.3)	1.46 dt (15.0, 2.8)	1.16
6”β	1.92	1.86	1.92 ddd (14.7, 5.7, 3.1)	1.87	1.92 ddd (14.8, 5.5, 3.5)	1.88	1.69
7”α		1.11 qd 13.8, 3.7)		1.10 qd (13.8, 3.5)			0.93
7”β	3.71 q (3.2)	1.35	3.70 q (3.1)	1.34	3.70 q (3.0)	3.51 q (2.8)	1.19
8”β	1.39	1.33	1.38	1.31	1.37	0.89 dt (11.7, 2.8)	0.91
9”α	2.19	1.84	2.19 td (12.5, 4.6)	1.85	1.84	1.88	1.25
11”α	1.52	1.44	1.51	1.43	1.42	1.33	1.24
11”β	1.45	1.44	1.44	1.43	1.19 ddd (13.2, 12.4, 3.7)	1.21	1.14
12”α					1.12 ddd (13.4, 12.6, 4.0)		
12”β	3.88 t (2.9)	3.89 t (3.0)	3.86 t (3.1)	3.87 t (2.9)	1.91	3.81 t (2.9)	3.79 b
14”α	1.89	1.53	1.90	1.53	1.37	1.53	1.29
15”α	0.79 qd (11.6, 5.7)	0.80 qd (11.9, 5.8)	0.77 qd (12.2, 5.9)	0.79 qd (12.1, 6.1)	0.79 qd (11.8, 6.4)	0.01	0.28
15”β	1.59	1.47	1.59	1.46	1.59	1.53	1.30
16”α	1.82	1.81	1.82	1.81	1.84	1.75	1.74
16”β	1.24	1.25	1.24	1.24	1.27	1.05	1.05
17”α	1.80	1.78	1.79	1.77	1.10 q (9.6)	1.52	1.54
18”	0.51 s	0.52 s	0.47 s	0.48 s	0.46 s	0.06 s	0.18 s
19”	0.87 s	0.89 s	0.87 s	0.88 s	0.88 s	0.74 s	0.72 s
20”	1.39	1.40	1.39	1.38	1.43	1.22	1.26
21”	1.02 d (6.5)	1.01 d (6.5)	1.09 d (6.4)	0.99 d (6.5)	0.94 d (6.5)	0.92 d (6.2)	0.93 bd (5.0)
22”a	1.86	1.85	1.89	1.91	1.91	1.81 td (12.4)	1.77
22”b	1.29	1.31	1.31	1.32	1.98	1.19	1.26
23”a	2.27	2.29 dd (13.7, 8.4, 5.1)	2.44 ddd (14.9, 7.6, 5.1)	2.41 ddd (15.0, 7.9, 5.2)	2.43 ddd (14.9, 7.8, 5.2)	2.31 dt (13.5, 4.6)	2.31 bm
23”b	2.19	2.19 dt (13.7, 8.3)	2.36 ddd (14.9, 9.1, 7.3)	2.36 ddd (15.0, 8.9, 7.5)	2.35 ddd (14.9, 8.9, 7.4)	2.27 td (13.5, 12.4, 3.5)	2.23 bm
25”a	4.17 d (17.6)	4.16 d (17.6)	4.94 d (15.8)	4.93 d (15.8)	4.94 d (15.8)	4.22 d (17.8)	4.15 d (17.8)
25”b	4.10 d (17.6)	4.11 d (17.6)	4.90 d (15.8)	4.90 d (15.8)	4.90 d (15.8)	4.08 d (17.8)	4.10 d (17.8)
2	8.09 s	8.09 s	8.09 s	8.23 bs	8.09 bs	8.12 s	8.11 s
8	7.59 s	7.57 s	7.66 s	7.66 s	7.65 s	7.74 s	7.67
1’	6.47 dd (8.1, 6.0)	6.46 dd (8.3, 5.9)	6.47 dd (8.2, 5.9)	6.47 dd (8.2, 5.9)	6.46 dd (8.2, 6.0)	6.53 dd (7.9, 6.1)	6.52 bdd (8.0, 5.8)
2’a	2.61 ddd (13.4, 8.2, 5.8)	2.62 ddd (13.4, 8.3, 5.9)	2.61 ddd (13.4, 8.2, 5.8)	2.62 ddd (13.4, 8.2, 5.9)	2.61 ddd (13.6, 8.2, 5.9)	2.63 ddd (14.0, 7.9, 6.2)	2.63 bddd (13.6, 8.0, 5.8)
2’b	2.31 ddd (13.4, 6.0, 2.6)	2.31 ddd (13.4, 5.9, 2.6)	2.32 ddd (13.4, 5.9, 2.6)	2.33 ddd (13.4, 5.9, 2.5)	2.32 ddd (13.6, 6.0, 2.5)	2.40 ddd (14.0, 6.1, 3.1)	2.43 bddd (13.6, 5.8, 3.0)
3’	4.51 dt (5.8, 2.6)	4.51 dt (5.9, 2.6)	4.51 dt (5.8, 2.6)	4.51 dt (5.9, 2.5)	4.51 dt (5.9, 2.5)	4.74 ddd (6.2, 3.1, 2.7)	4.72 bdt (5.8, 3.1)
4’	4.00 td (3.4, 2.6)	4.01 td (3.4, 2.6)	4.01 td (3.4, 2.6)	4.01 td (3.3, 2.5)	4.01 td (3.3, 2.5)	4.21 tdd (3.7, 2.7, 1.5)	4.21 bm
5’a	3.79 dd (12.1, 3.4)	3.79 dd (12.2, 3.4)	3.80 dd (12.1, 3.4)	3.80 dd (12.1, 3.3)	3.80 dd (12.1, 3.3)	4.19 ddd (10.7, 6.2, 3.7)	4.16 bm
5’b	3.72 dd (12.1, 3.4)	3.72 dd (12.2, 3.4)	3.72 dd (12.1, 3.4)	3.72 dd (12.1, 3.3)	3.72 dd (12.1, 3.3)	4.11 ddd (10.7, 4.9, 3.7)	4.11 bm

[a] In phosphate buffer, pD = 7.1, referenced to 1,4-dioxane signal (3.75 ppm)

Table S2. ^{13}C NMR of 7-deazaadenine - bile acids conjugates

Carbon	Compound						
	6d 125.7 MHz CD_3OD	**6e** 125.7 MHz CD_3OD	**6a** 125.7 MHz CD_3OD	**6b** 150.9 MHz CD_3OD	**6c** 150.9 MHz CD_3OD	**dA^{CA}TP** 150.9 MHz D_2O^a	**dA^{DCA}TP** 150.9 MHz D_2O^a
1”	36.44	36.39	36.44	36.40	36.51	37.10	37.30
2”	31.14	31.03	31.14	31.04	31.32	31.83	31.75
3”	72.84	73.09	72.85	73.07	72.83	74.32	74.21
4”	40.42	37.16	40.42	37.17	40.44	40.99	37.81
5”	43.14	43.58	43.15	43.59	43.13	43.47	44.32
6”	35.81	28.38	35.80	28.39	35.85	36.41	29.55
7”	68.99	27.40	68.99	27.40	69.02	71.09	28.63
8”	40.89	37.34	40.90	37.34	40.66	41.77	38.41
9”	27.79	34.73	27.78	34.74	33.94	28.76	35.87
10”	35.86	35.27	35.86	35.28	36.19	36.92	36.40
11”	29.47	29.80	29.46	29.79	21.69	29.90	30.37
12”	73.99	74.00	73.94	73.96	40.91	75.75	75.87
13”	47.42	47.49	47.42	47.50	43.60	48.58	48.66
14”	42.86	49.29	42.85	48.86	51.42	43.67	49.98
15”	24.13	24.78	24.14	24.80	24.55	25.28	26.13
16”	28.76	28.72	28.72	28.69	29.26	30.03	30.11
17”	48.08	48.14	48.12	48.20	57.37	49.42	49.29
18”	12.90	13.11	12.84	13.05	12.01	14.31	14.76
19”	23.19	23.72	23.19	23.72	23.41	24.35	25.11
20”	36.43	36.39	36.38	36.35	36.39	36.46	36.92
21”	17.75	17.69	17.52	17.48	18.72	19.56	19.54
22”	33.37	33.34	32.54	32.49	32.54	34.65	34.55
23”	34.03	33.99	32.18	32.15	32.14	35.94	35.59
24”	177.10	177.08	175.68	175.68	175.65	180.24	180.17
25”	30.63	30.62	53.74	53.75	53.76	32.22	32.36
26”	89.89	89.74	88.09	88.07	88.05	91.89	91.75
27”	75.79	75.88	80.14	80.14	80.17	77.36	77.35
2	152.72	153.17	153.32	153.22	153.31	154.88	154.70
4	149.75	149.84	149.98	150.02	149.99	151.12	151.09
5	104.90	104.97	104.99	104.70	105.02	106.22	106.10
6	158.88	159.19	159.21	159.24	159.23	160.33	160.03
7	97.21	97.07	96.30	96.55	96.35	99.34	99.35
8	128.07	127.98	128.84	128.66	128.84	129.65	129.23
1’	86.78	86.84	86.91	86.92	86.94	85.71	85.67
2’	41.70	41.66	41.76	41.76	41.76	41.83	41.61
3’	73.08	72.51	73.08	72.52	73.08	73.91	73.83
4’	89.29	89.28	89.34	89.35	89.35	88.02 d (8.9)	87.92 d (9.1)
5’	63.64	63.66	63.64	63.64	63.65	68.24 d (5.9)	68.30 d (5.3)

[a] In phosphate buffer, pD = 7.1, referenced to 1,4-dioxane signal (69.3 ppm)

dA^{CA}TP ^{31}P NMR (202.3 MHz, D_2O, pD = 7.1, ref (phosphate buffer) = 2.35 ppm): -21.19 (t, J = 20, Pβ); -9.92 (d, J = 20, Pα); -7.29 (d, J = 20, Pγ).
dA^{DCA}TP ^{31}P NMR (202.3 MHz, D_2O, pD = 7.1, ref (phosphate buffer) = 2.35 ppm): -21.03 (t, J = 19, Pβ); -9.77 (d, J = 19, Pα); -7.37 (d, J = 19, Pγ).

Table S3. ^{1}H NMR of cytosine - bile acids conjugates

Proton	Compound **7d** 500.0 MHz CD_3OD	**7e** 499.8 MHz CD_3OD	**7a** 500.0 MHz CD_3OD	**7b** 500.0 MHz CD_3OD	**7c** 500.0 MHz CD_3OD	**dC^{CA}TP** 499.8 MHz D_2O[a]	**dC^{DCA}TP** 499.8 MHz D_2O[a]
1"α	1.80 dt (14.0, 3.2)	1.77 dt (14.1, 3.2)	1.80 dt (14.2, 3.3)	1.76 dt (14.2, 3.5)	1.84	1.76 dt (14.4, 3.1)	1.72
1"β	0.98 td (14.0, 3.4)	0.98 td (14.1, 3.5)	0.98 td (14.2, 3.5)	0.97 td (14.2, 3.5)	0.98 td (14.1, 3.2)	0.99 td (14.4, 3.2)	0.97 td (14.4, 3.4)
2"α	1.41	1.40	1.41	1.41	1.33	1.26	1.28
2"β	1.59	1.59	1.59	1.59	1.61	1.62	1.60
3"β	3.37 tt (11.0, 4.3)	3.52 tt (11.0, 4.7)	3.37 tt (11.1, 4.4)	3.52 tt (11.2, 4.7)	3.37 tt (11.2, 4.5)	3.49 tt (11.0, 4.5)	3.63 tt (10.9, 4.7)
4"α	2.26	1.79	2.27 td (13.2, 11.5)	1.80	2.25 td (13.3, 11.5)	1.99	1.72
4"β	1.64	1.44	1.65	1.45	1.65	1.67	1.47
5"β	1.37	1.38	1.37	1.38	1.37	1.43	1.40
6"α	1.52	1.26	1.52	1.26	1.52 dt (14.8, 2.3)	1.46	1.23
6"β	1.95	1.88	1.96	1.89	1.96	1.96	1.81
7"α		1.14 qd (13.4, 4.2)		1.15 qd (12.7, 4.1)			1.03
7"β	3.78 q (2.9)	1.42	3.78 q (3.0)	1.42	3.78 q (2.8)	3.75	1.29
8"β	1.51	1.46	1.52	1.47	1.48	1.43	1.31
9"α	2.23	1.88	2.13 dt (13.6, 6.5)	1.89	1.86	1.98	1.66
11"α	1.56	1.50	1.56	1.50	1.47	1.52	1.44
11"β	1.56	1.50	1.56	1.50	1.19	1.52	1.44
12"α					1.18 td (12.0, 4.0)		
12"β	3.93 t (3.2)	3.94 t (3.0)	3.93 t (3.1)	3.94 t (3.0)	1.98	3.99 t (2.9)	3.98 t (2.8)
14"α	1.96	1.59	1.97	1.59	1.48	1.68	1.39
15"α	1.03 qd (11.8, 5.5)	1.03	1.05 qd (12.1, 5.7)	1.02	1.04 qd (11.7, 6.3)	0.68 qd (11.9, 6.2)	0.64 qd (11.9, 6.5)
15"β	1.71	1.58	1.71	1.58	1.71	1.53	1.48
16"α	1.87	1.85	1.86	1.85	1.90	1.83	1.81
16"β	1.26	1.26	1.28	1.26	1.33	1.12	1.09
17"α	1.84	1.82	1.84	1.82	1.16 q (9.8)	1.60	1.58
18"	0.66 s	0.66 s	0.66 s	0.66 s	0.64 s	0.49 s	0.49 s
19"	0.91 s	0.92 s	0.91 s	0.92 s	0.92 s	0.88 s	0.88 s
20"	1.40	1.40	1.41	1.40	1.44	1.30	1.27
21"	1.02 d (6.5)	1.02 d (6.4)	1.01 d (6.4)	1.00 d (6.5)	0.96 d (6.6)	0.98 d (6.2)	0.96 d (6.0)
22"a	1.83	1.81	1.86	1.84	1.86	1.81	1.80
22"b	1.31	1.33	1.34	1.33	1.31	1.23	1.25
23"a	2.28	2.28 ddd (13.8, 9.2, 5.2)	2.44 ddd (15.3, 8.6, 5.2)	2.44 ddd (15.3, 8.8, 5.2)	2.43 ddd (15.3, 8.5, 5.2)	2.29 dd (8.6, 4.6)	2.28 dd (9.1, 4.3)
23"b	2.18	2.16 ddd (13.8, 8.8, 7.6)	2.34 dt (15.3, 7.9)	2.33 dt (15.3, 8.0)	2.33 dt (15.3, 8.2)		
25"a	4.16 d (17.7)	4.15 d (17.7)	4.94 d (15.9)	4.94 d (15.9)	4.94 d (15.9)	4.24 d (17.9)	4.22 d (17.8)
25"b	4.11 d (17.7)	4.12 d (17.7)	4.89 d (15.9)	4.89 d (15.9)	4.89 d (15.9)	4.05 bd (17.9)	4.06 d (17.8)
6	8.31 s	8.31 s	8.40 s	8.40 s	8.40	8.18	8.18
1'	6.20 dd (6.4,6.1)	6.20 t (6.2)	6.19 t (6.2)	6.20 t (6.3)	6.20 t (6.3)	6.21 t (6.2)	6.22 t (6.3)
2'a	2.39 ddd (13.6, 6.1, 3.8)	2.39 ddd (13.6, 6.2, 3.9)	2.39 ddd (13.6, 6.2, 4.0)	2.39 ddd (13.6, 6.3, 3.9)	2.39 ddd (13.6, 6.3, 3.6)	2.41 bm	2.43 ddd (14.1, 6.3, 4.6)
2'b	2.12 dt (13.6, 6.4)	2.12 dt (13.6, 6.2)	2.24 dt (13.6, 6.2)	2.13 dt (13.6, 6.3)	2.13 dt (13.6, 6.3)	2.25 bm	2.26 dt (14.1, 6.3)
3'	4.36 dt (6.4, 3.8)	4.36 dt (6.2, 3.9)	4.36 dt (6.2, 4.0)	4.37 dt (6.3. 3.9)	4.37 dt (6.3. 3.6)	4.62 bm	4.61 dt (6.3, 4.6)
4'	3.95 ddd (3.8, 3.6, 3.2)	3.95 ddd (3.9, 3.6, 3.2)	3.95 ddd (4.0, 3.5, 3.1)	3.95 ddd (3.9, 3.5, 3.2)	3.95 td (3.6, 3.1)	4.16 bm	4.17 bm
5'a	3.81 dd (12.1, 3.2)	3.81 dd (12.0, 3.2)	3.83 dd (12.0, 3.1)	3.83 dd (12.1, 3.2)	3.83 dd (12.1, 3.1)	4.25 bm	4.23 bm
5'b	3.73 dd (12.1, 3.6)	3.73 dd (12.0, 3.6)	3.74 dd (12.0, 3.5)	3.74 dd (12.1, 3.5)	3.74 dd (12.1, 3.6)	4.20 bm	4.20 bm

[a] In phosphate buffer, pD = 7.1, referenced to 1,4-dioxane signal (3.75 ppm)

Table S4. ^{13}C NMR of cytosine - bile acids conjugates

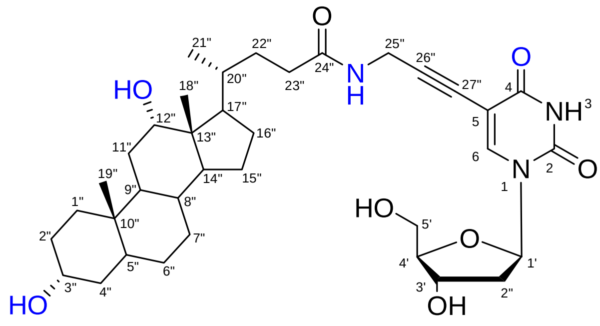
Carbon	Compound						
	7d	**7e**	**7a**	**7b**	**7c**	**dC^{CA}TP**	**dC^{DCA}TP**
	125.7 MHz	125.7 MHz	125.7 MHz	125.7 MHz	125.7 MHz	125.7 MHz	125.7 MHz
	CD_3OD	CD_3OD	CD_3OD	CD_3OD	CD_3OD	D_2O[a]	D_2O[a]
1"	36.46	36.42	36.46	36.40	36.52	37.20	37.29
2"	31.14	31.07	31.15	31.05	31.32	31.91	31.82
3"	72.86	72.53	72.86	72.52	72.83	74.41	74.37
4"	40.43	37.20	40.43	37.17	40.44	41.06	37.77
5"	43.15	43.62	43.15	43.59	43.13	43.57	44.39
6"	35.84	28.40	35.82	28.39	35.86	36.48	29.53
7"	69.07	27.46	69.07	27.45	69.06	71.23	28.60
8"	40.94	37.43	40.95	37.41	40.70	41.83	38.43
9"	27.84	34.81	27.84	34.78	34.01	29.01	36.04
10"	35.89	35.30	35.89	35.29	36.20	36.97	36.41
11"	29.53	29.89	29.53	29.87	21.75	30.13	30.49
12"	74.06	74.04	74.01	74.00	40.98	75.91	76.21
13"	47.49	47.57	47.50	47.56	43.68	48.92	48.92
14"	42.98	49.28	42.98	49.26	51.52	44.19	50.43
15"	24.29	24.91	24.29	24.92	24.67	25.76	26.42
16"	28.76	28.70	28.73	28.68	29.29	30.16	30.22
17"	48.03	48.12	48.07	48.14	57.30	49.52	49.58
18"	13.05	13.25	13.05	13.24	12.22	14.72	14.98
19"	23.17	23.72	23.17	23.71	23.40	24.39	25.04
20"	36.46	36.58	36.54	36.50	36.55	36.74	36.74
21"	17.74	17.70	17.54	17.49	18.74	19.59	19.56
22"	33.24	33.20	32.30	32.25	32.29	34.71	34.65
23"	33.93	33.92	32.03	32.00	31.99	35.89	35.85
24"	176.92	176.85	175.45	175.37	175.36	180.34	180.36
25"	30.54	30.54	53.51	53.51	53.53	32.15	32.15
26"	92.88	92.86	91.22	91.21	91.20	95.40	95.34
27"	74.46	74.47	78.40	78.36	78.39	75.52	75.48
2	156.70	156.71	156.65	156.69	156.68	158.44	158.51
4	166.57	166.56	166.50	166.48	166.48	168.00	168.01
5	92.38	92.36	91.64	91.67	91.66	95.40	85.15
6	145.85	145.83	146.76	146.74	146.75	148.01	148.01
1'	87.97	87.98	88.03	88.02	88.03	88.85	88.86
2'	42.43	42.44	42.48	42.48	42.47	42.38	42.36
3'	71.80	71.82	71.71	71.75	71.73	72.77	72.77
4'	89.08	89.11	89.10	89.14	89.12	88.24 br	88.19 d (9.0)
5'	62.48	62.52	62.40	62.42	62.41	67.70 br	67.71 d (4.7)

[a] In phosphate buffer, pD = 7.1, referenced to 1,4-dioxane signal (69.3 ppm)

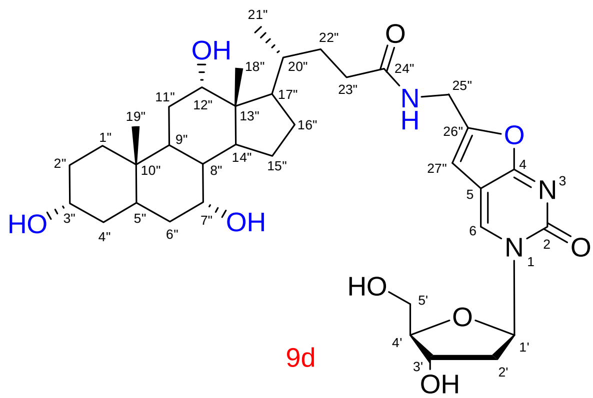
dC^{CA}TP ^{31}P NMR (202.3 MHz, D_2O, pD = 7.1, ref (phosphate buffer) = 2.35 ppm): -21.14 (br, Pβ); -10.34 (br, Pα); -6.82 (br, Pγ).
dC^{DCA}TP ^{31}P NMR (202.3 MHz, D_2O, pD = 7.1, ref (phosphate buffer) = 2.35 ppm): -21.34 (bdd, *J* = 19, 15, Pβ); -10.37 (d, *J* = 19, Pα); -7.23 (bd, *J* = 15, Pγ).

Table S5. ^{1}H NMR of uracil - bile acids conjugates

Proton	**9d**[a] 499.8 MHz DMSO-d_6	**8e** 500.0 MHz CD_3OD
1"α	1.64	1.77 dt (14.2, 3.4)
1"β	0.84	0.98 td (14.2, 3.5)
2"α	1.26	1.41
2"β	1.43	1.60
3"β	3.18	3.52 tt (11.1, 4.6)
4"α	2.21	1.80
4"β	1.44	1.46
5"β	1.24	1.39
6"α	1.36	1.27
6"β	1.78	1.88
7"α		1.17 qd (13.7, 4.6)
7"β	3.59	1.43
8"β	1.31	1.46
9"α	2.13	1.89
11"α	1.38	1.51
11"β	1.38	1.51
12"α		
12"β	3.76 q (3.6)	3.95 t (2.8)
14"α	1.95 td (11.4, 7.5)	1.60
15"α	0.90	1.07 qd (11.8, 5.7)
15"β	1.61	1.60
16"α	1.43	1.85
16"β	1.27	1.27
17"α	1.76	1.83
18"	0.51 s	0.69 s
19"	0.80 s	0.93 s
20"	1.21	1.43
21"	0.92 d (6.4)	1.02 d (6.4)
22"a	1.67	1.79
22"b	1.18	1.33
23"a	2.16	2.27 ddd (14.1, 9.7, 4.8)
23"b	2.05	2.13 ddd (14.1, 9.5, 7.2)
25"	4.26 td (5.8, 1.0)	4.13 s
27"	6.50 t (1.0)	-
6	8.74 s	8.32 s
1'	6.14 t (6.1)	6.24 dd (7.1, 6.3)
2'a	2.39 ddd (13.5, 6.1, 4.2)	2.31 ddd (13.6, 6.3, 3.6)
2'b	2.02 dt (13.5, 6.1)	2.21 ddd (13.6, 7.1, 6.1)
3'	3.22 m	4.40 ddd (6.1, 3.6, 3.2)
4'	3.91 q (3.8)	3.94 ddd (3.5, 3.2, 3.1)
5'a	3.66 ddd (12.1, 5.2, 3.8)	3.81 dd (12.0, 3.1)
5'b	3.60 ddd (12.1, 5.2, 3.8)	3.73 dd (12.0, 3.5)



8e

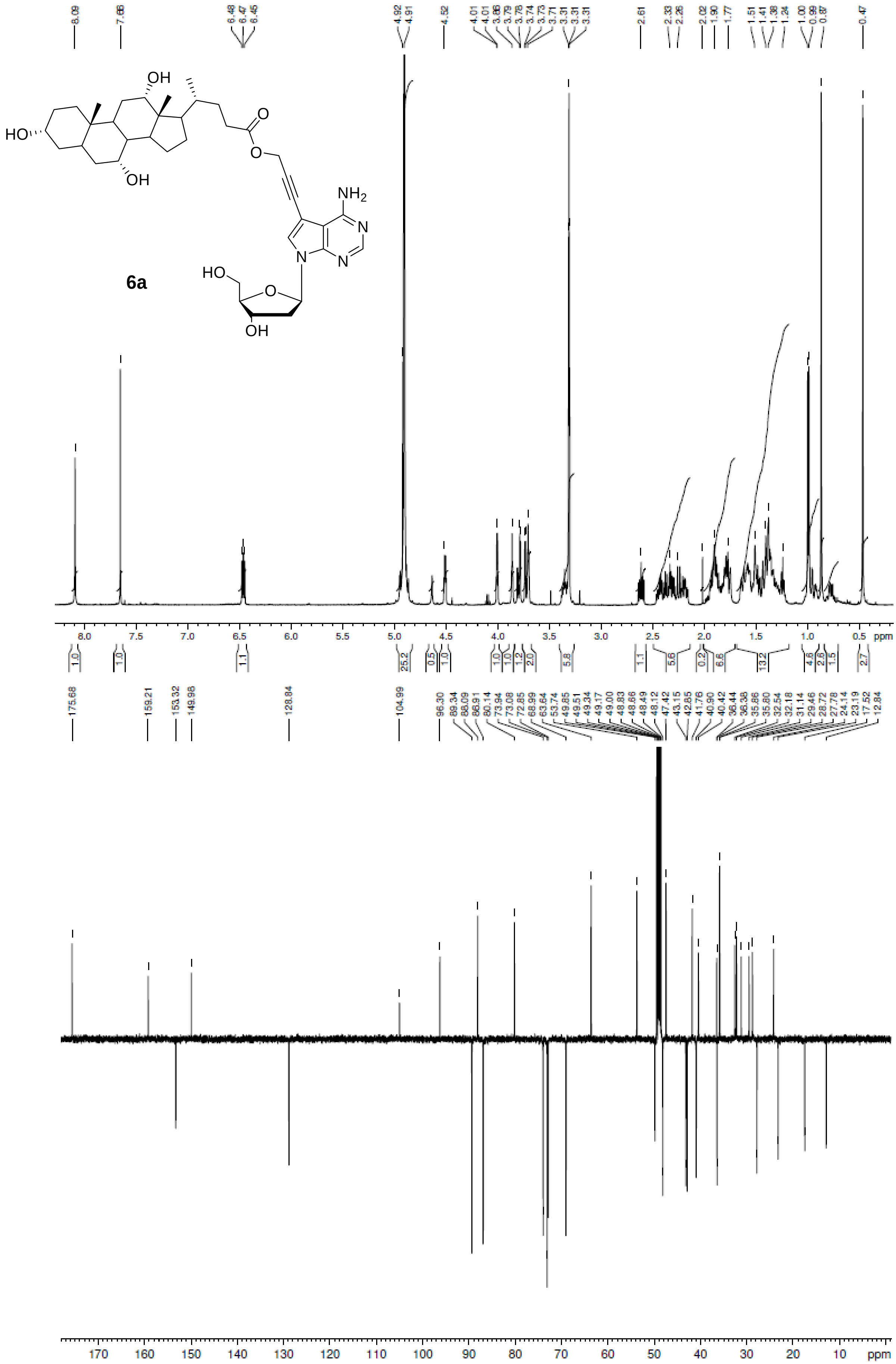


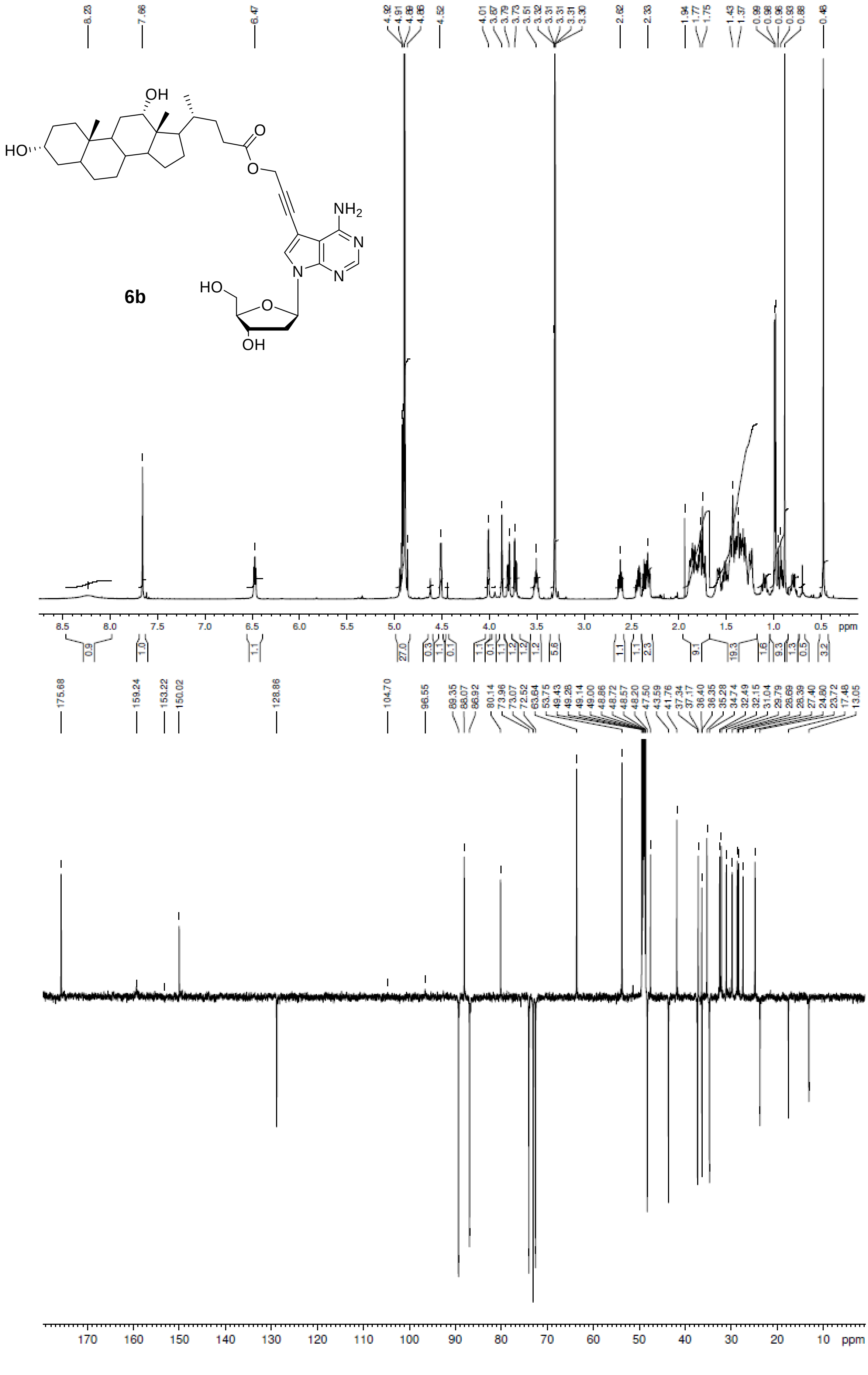
9d

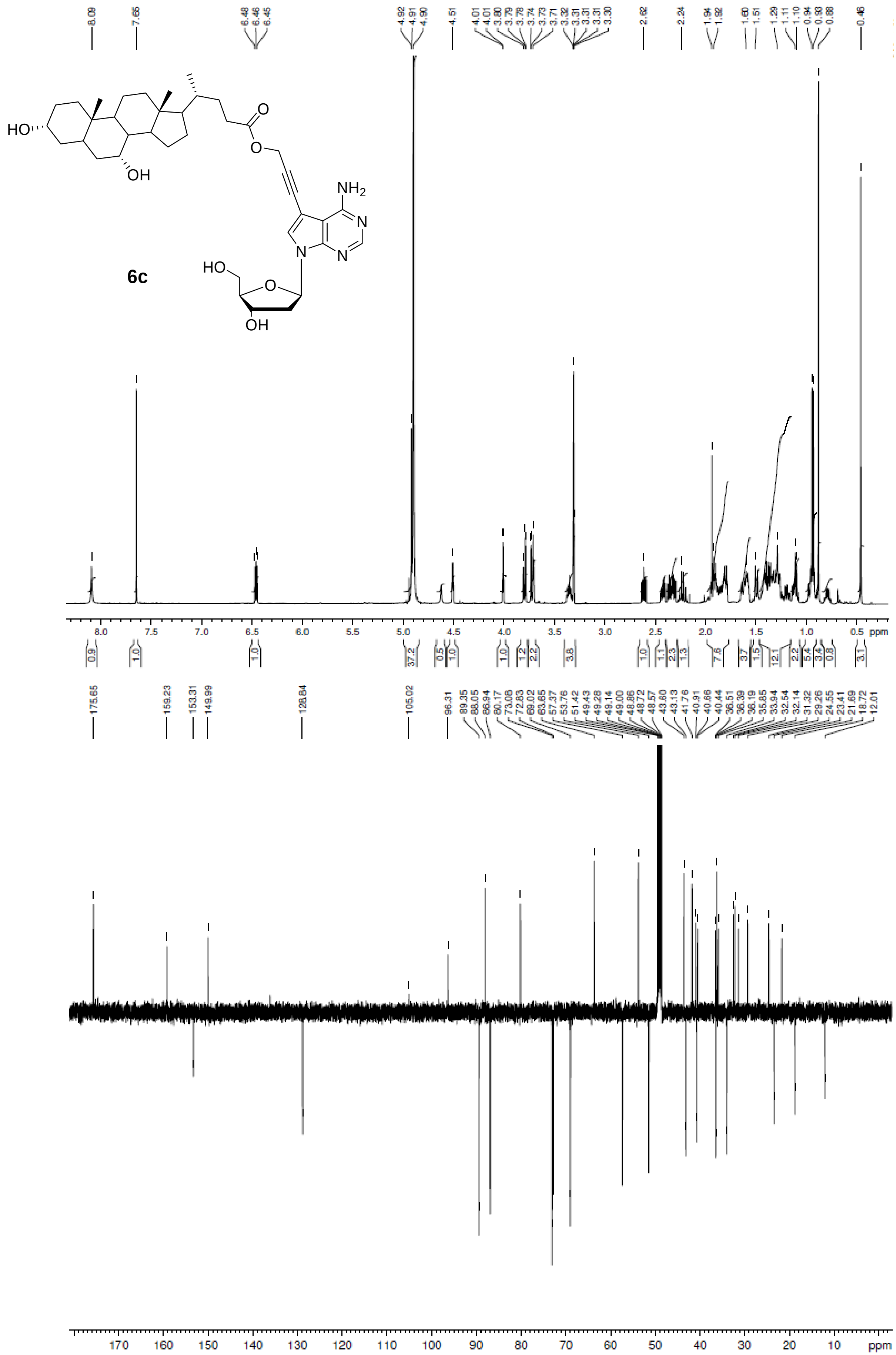
[a]Other signals: 3.09 (d, 1H, J = 3.5, OH-7"); 4.09 (d, 1H, J = 3.6, OH-12"); 4.32 (d, 1H, J = 4.4, OH-3"); 5.12 (t, 1H, J = 5.2, OH-5'); 5.29 (d, 1H, J = 4.3, OH-3'); 8.41 (t, 1H, J = 5.8, NH).

Table S6. ^{13}C NMR of uracil - bile acids conjugates

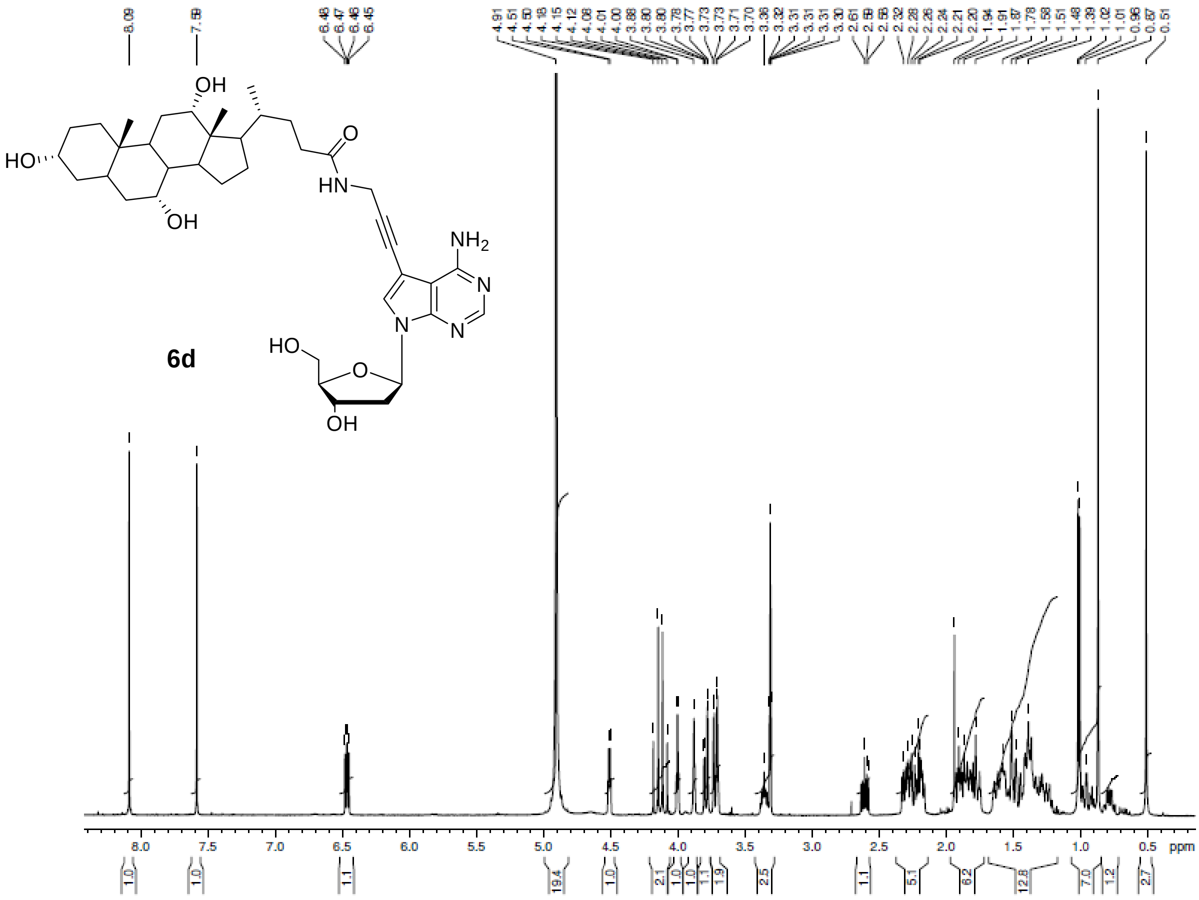
Carbon	Compound **9d** 125.7 MHz DMSO-d_6	**8e** 125.7 MHz CD_3OD
1"	35.51	36.42
2"	30.60	31.05
3"	70.64	72.53
4"	39.79	37.17
5"	41.72	43.61
6"	35.08	28.40
7"	66.44	27.47
8"	39.63	37.44
9"	26.40	34.79
10"	34.59	35.30
11"	27.54	29.87
12"	71.20	74.05
13"	45.91	47.56
14"	41.57	49.26
15"	22.99	24.92
16"	28.75	28.67
17"	46.32	48.07
18"	12.45	13.25
19"	22.83	23.71
20"	35.25	36.72
21"	17.27	17.69
22"	31.91	33.15
23"	32.55	33.91
24"	173.06	176.43
25"	35.74	30.36
26"	154.83	90.20
27"	101.34	75.03
2	153.96	151.17
4	171.38	164.61
5	106.07	99.99
6	138.06	145.45
1'	87.78	87.03
2'	41.44	41.73
3'	69.92	71.12
4'	88.43	89.18
5'	61.00	62.62

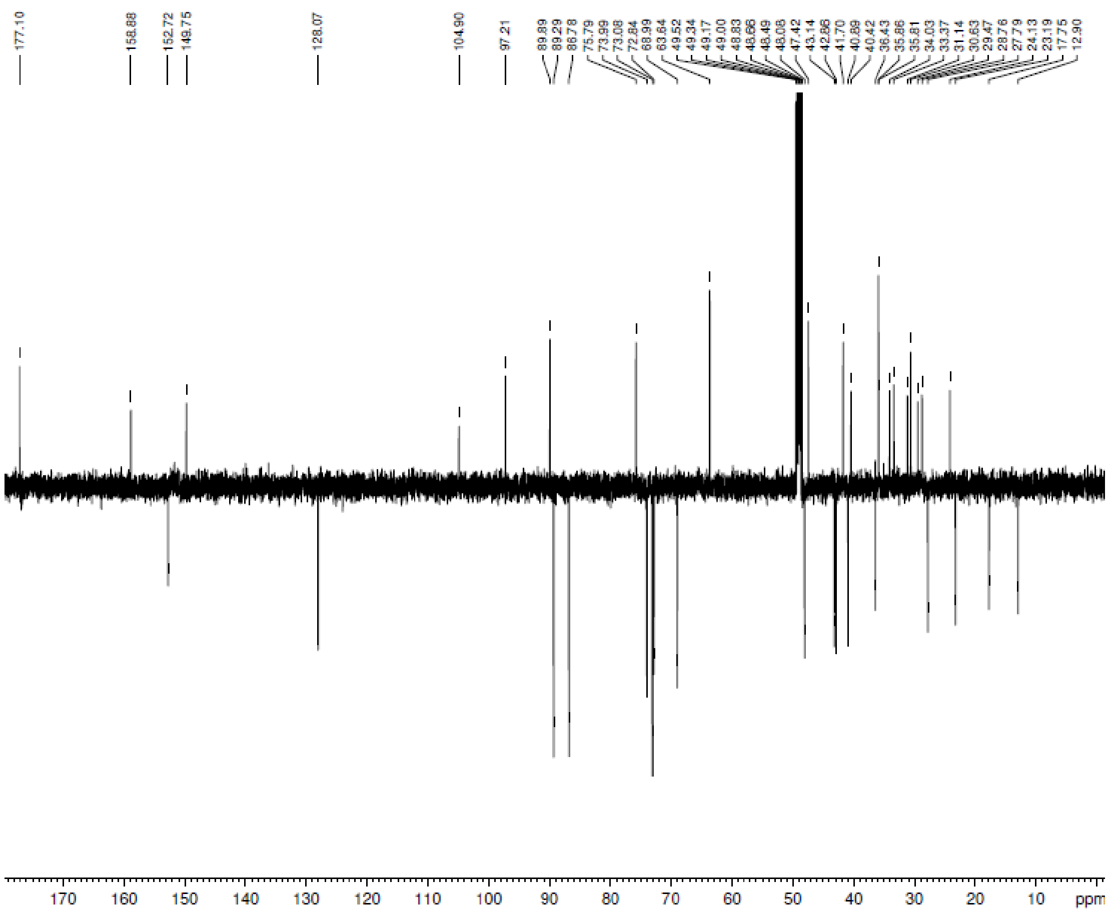

6a

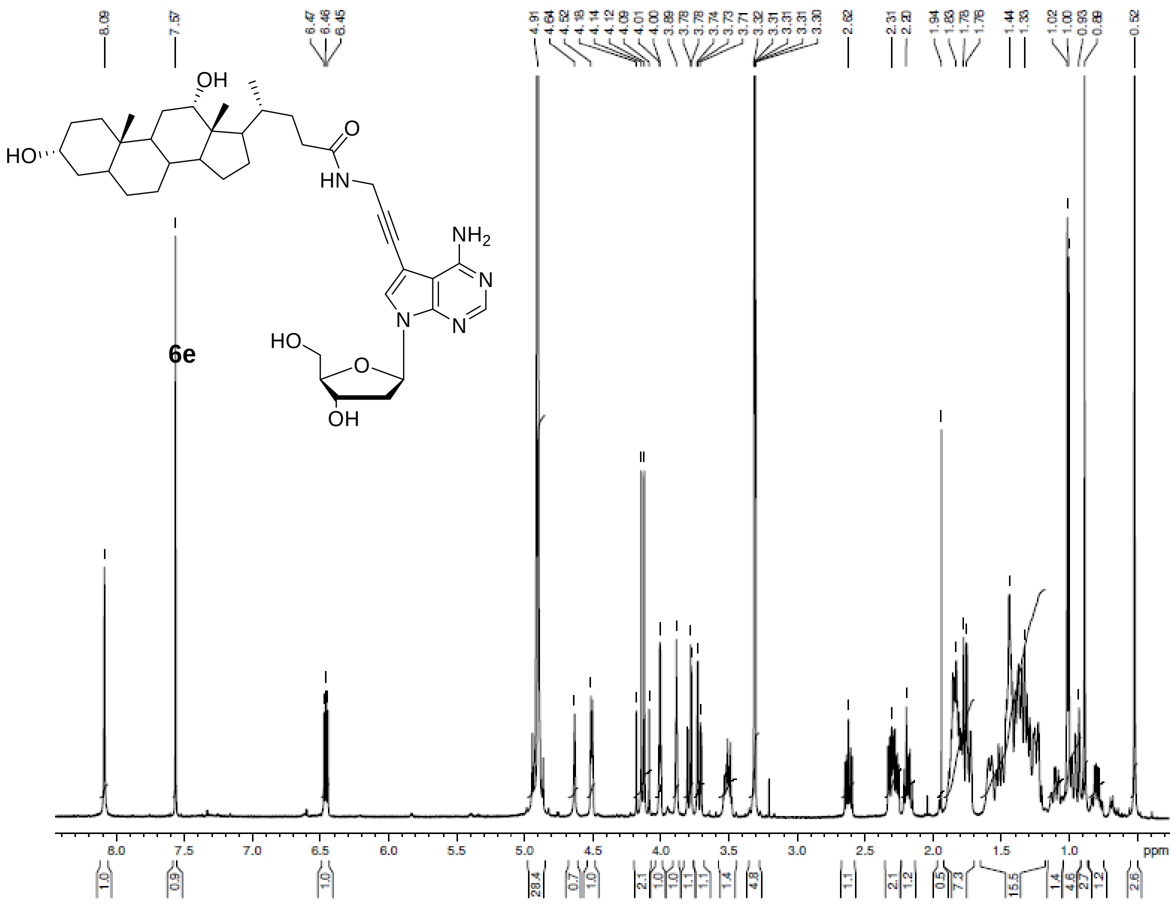

6b
ppm
ppm

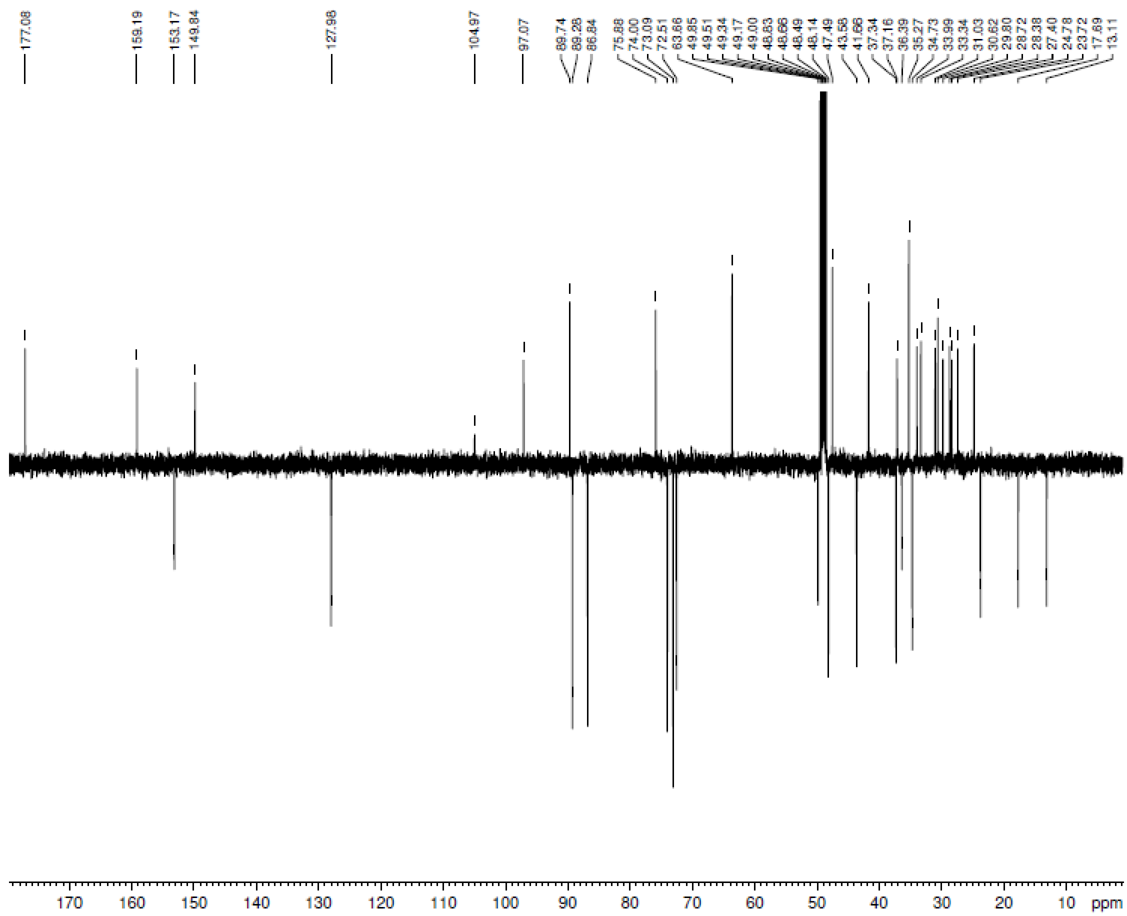

6c

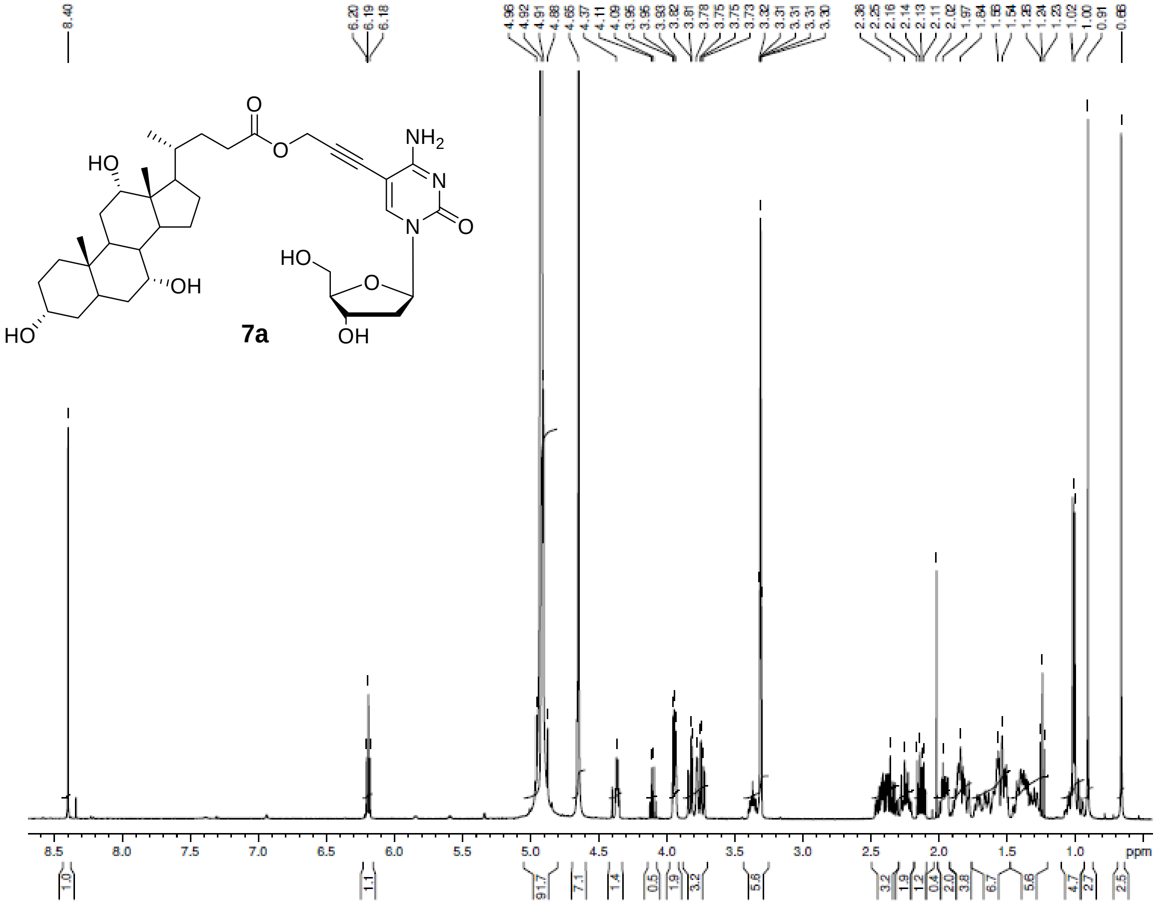
6d

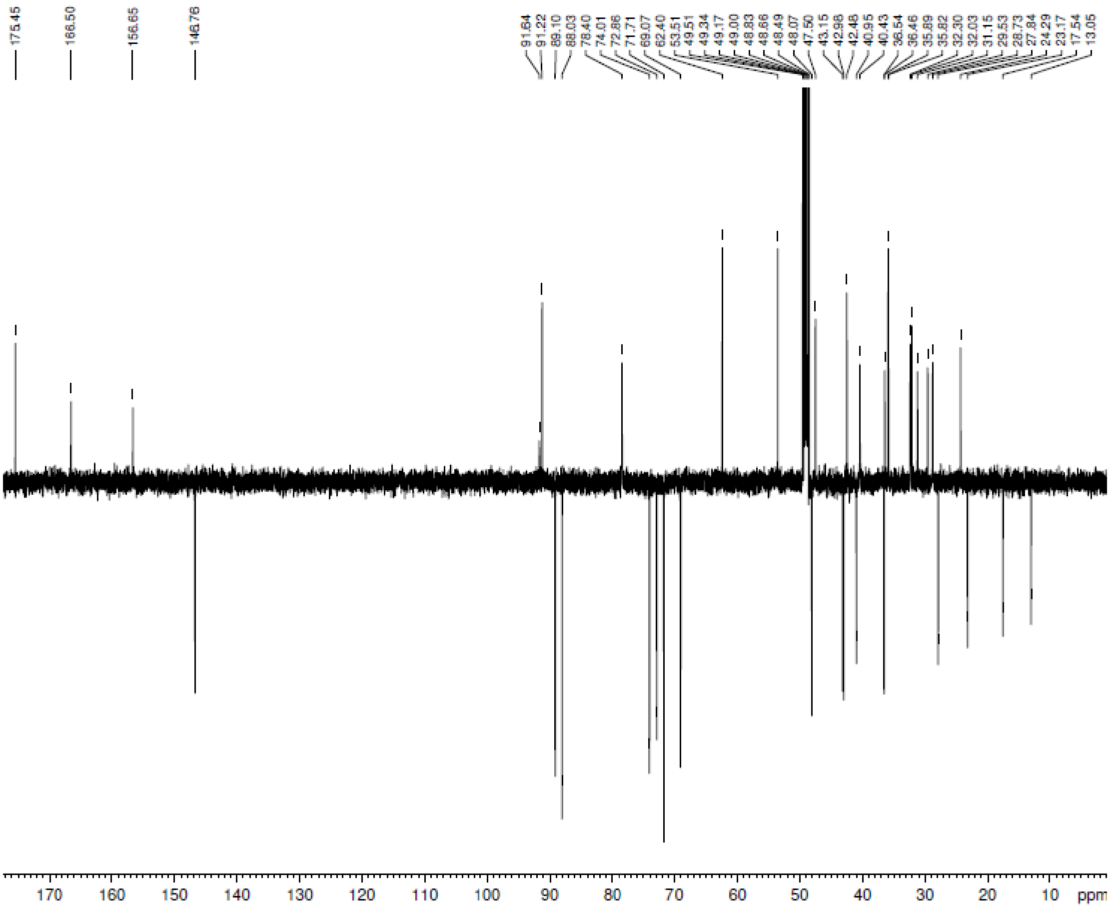


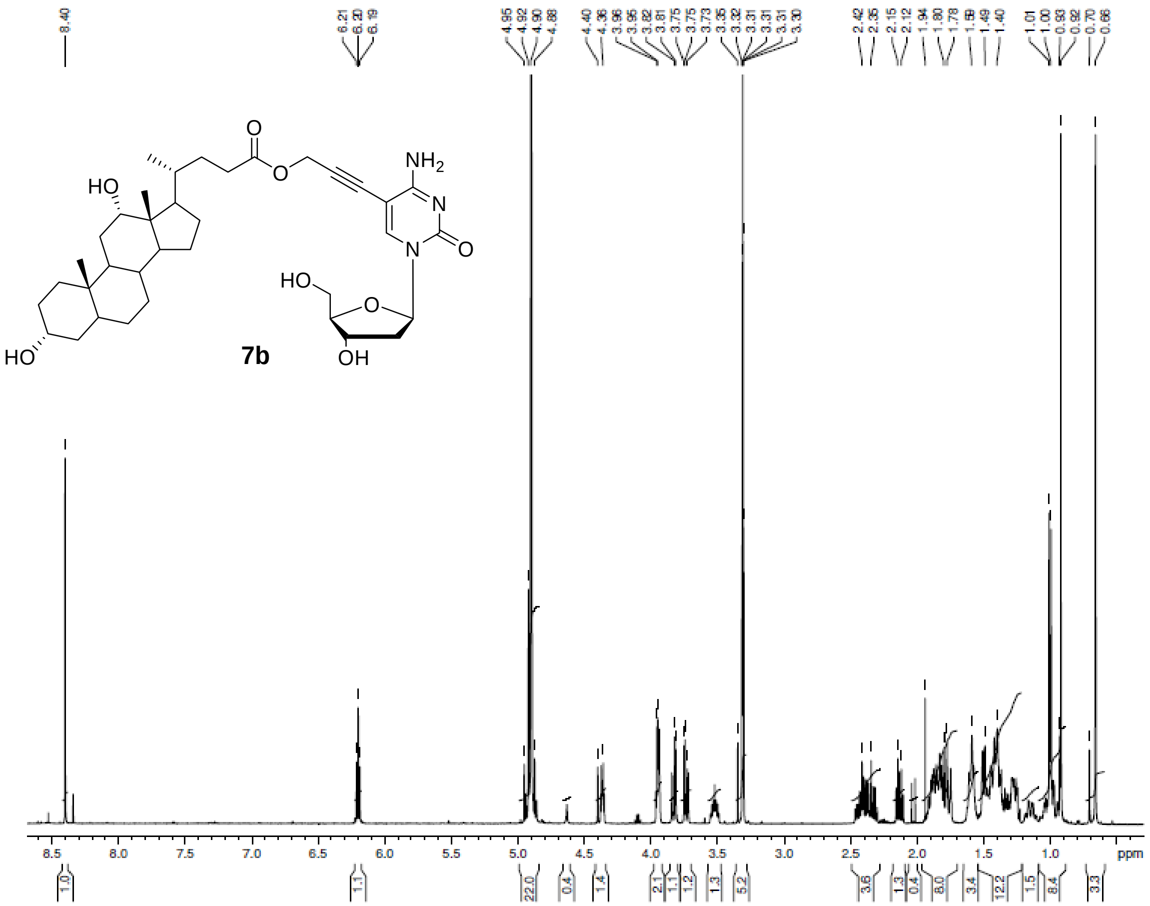






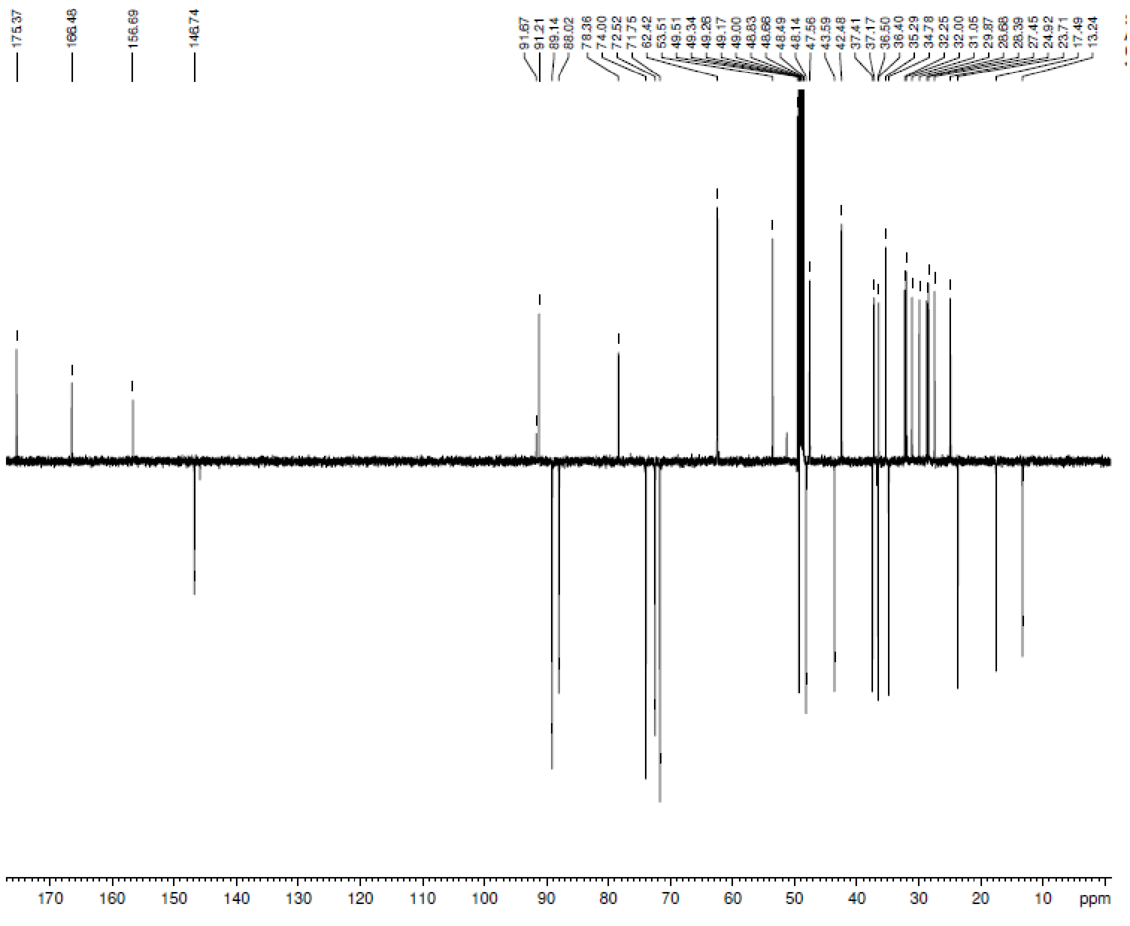

O
O
NH2
N
N
O
HO
HO
O
OH
OH
HO
7a
8.40
6.20
6.19
6.18
ppm


175.45
166.50
156.65
146.76
ppm

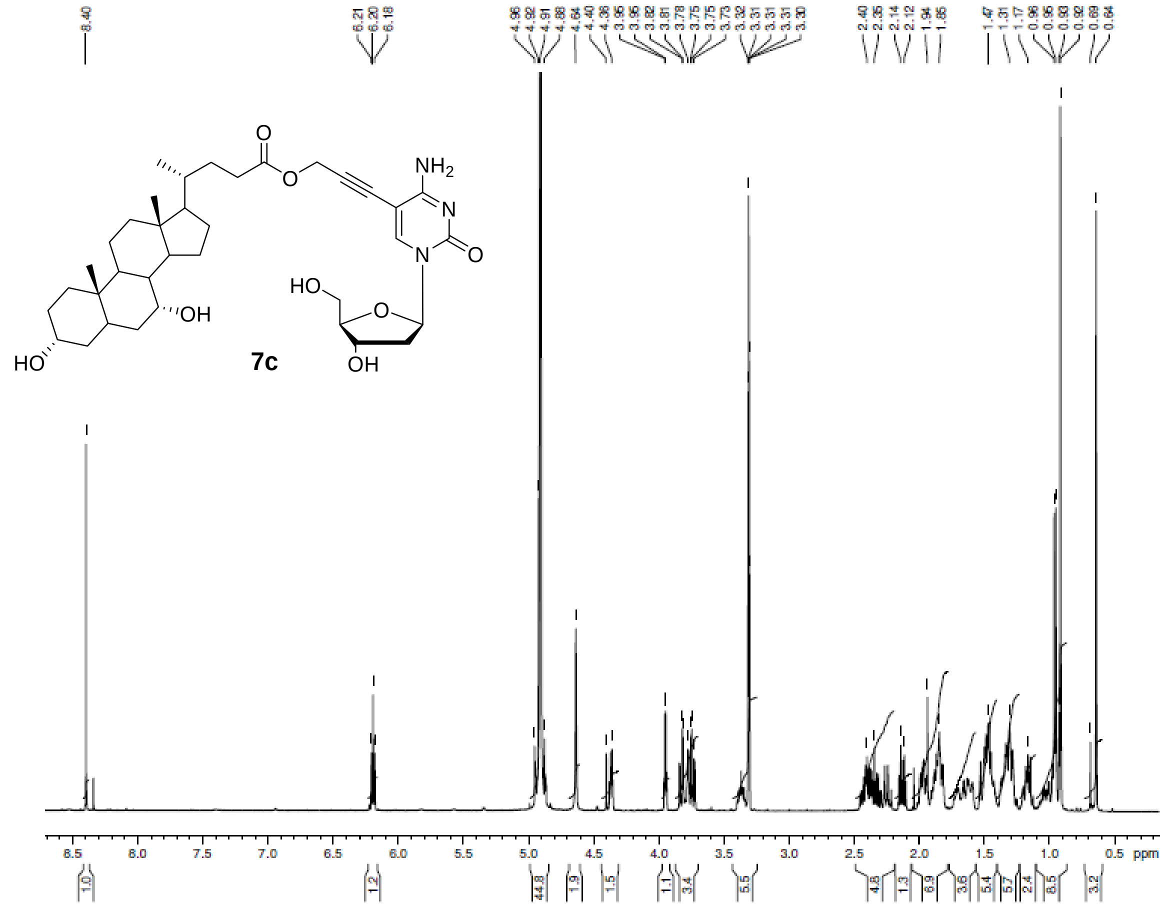


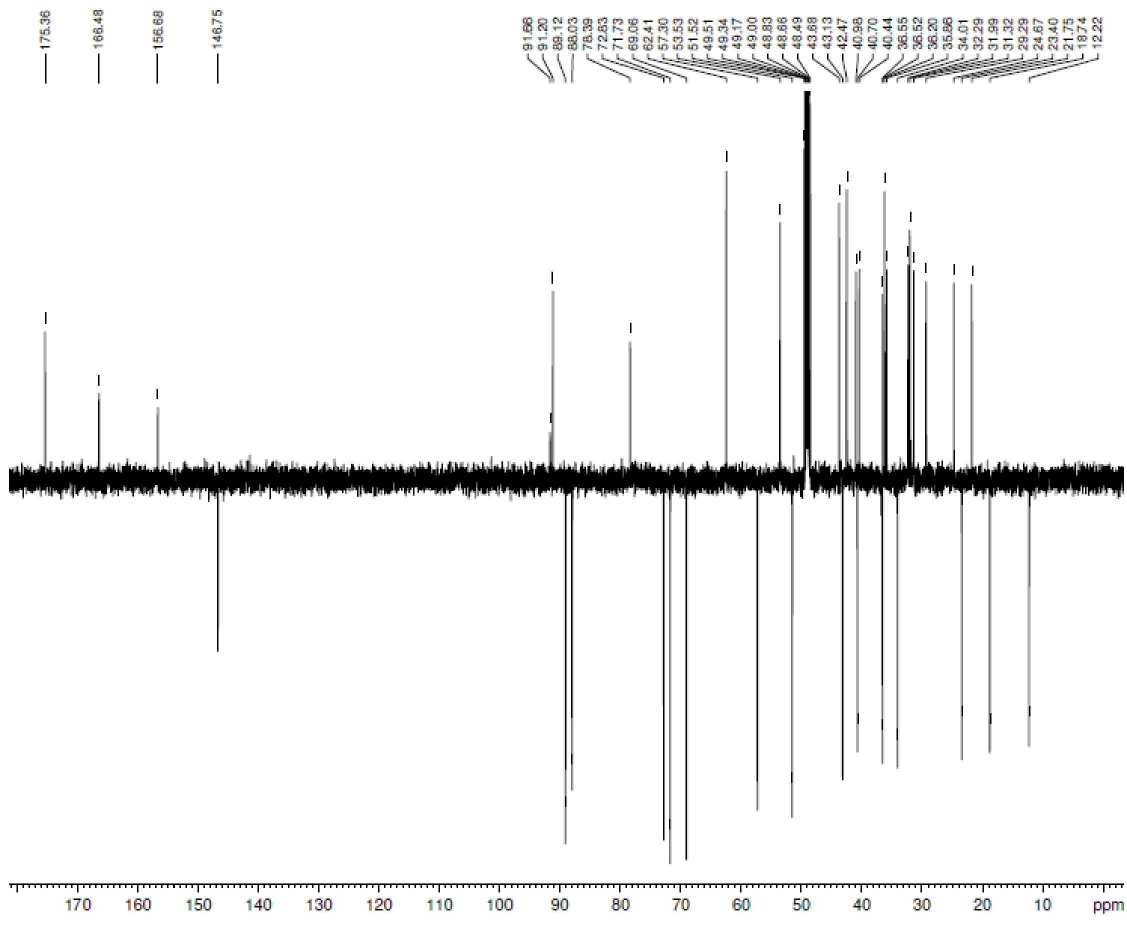
8.40
6.21 6.20 6.19
4.95 4.92 4.90 4.88
4.40 4.36 3.96 3.95 3.82 3.81 3.75 3.75 3.73 3.35 3.32 3.31 3.31 3.31 3.30
2.42 2.35 2.15 2.12 1.94 1.80 1.78 1.59 1.49 1.40
1.01 1.00 0.93 0.92 0.70 0.66
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.0 1.1 22.0 0.4 1.4 2.1 1.1 1.2 1.3 5.2 3.6 1.3 0.4 8.0 3.4 12.2 1.5 8.4 3.3
HO
HO
O
O
NH2
N
N
O
HO
O
OH
HO

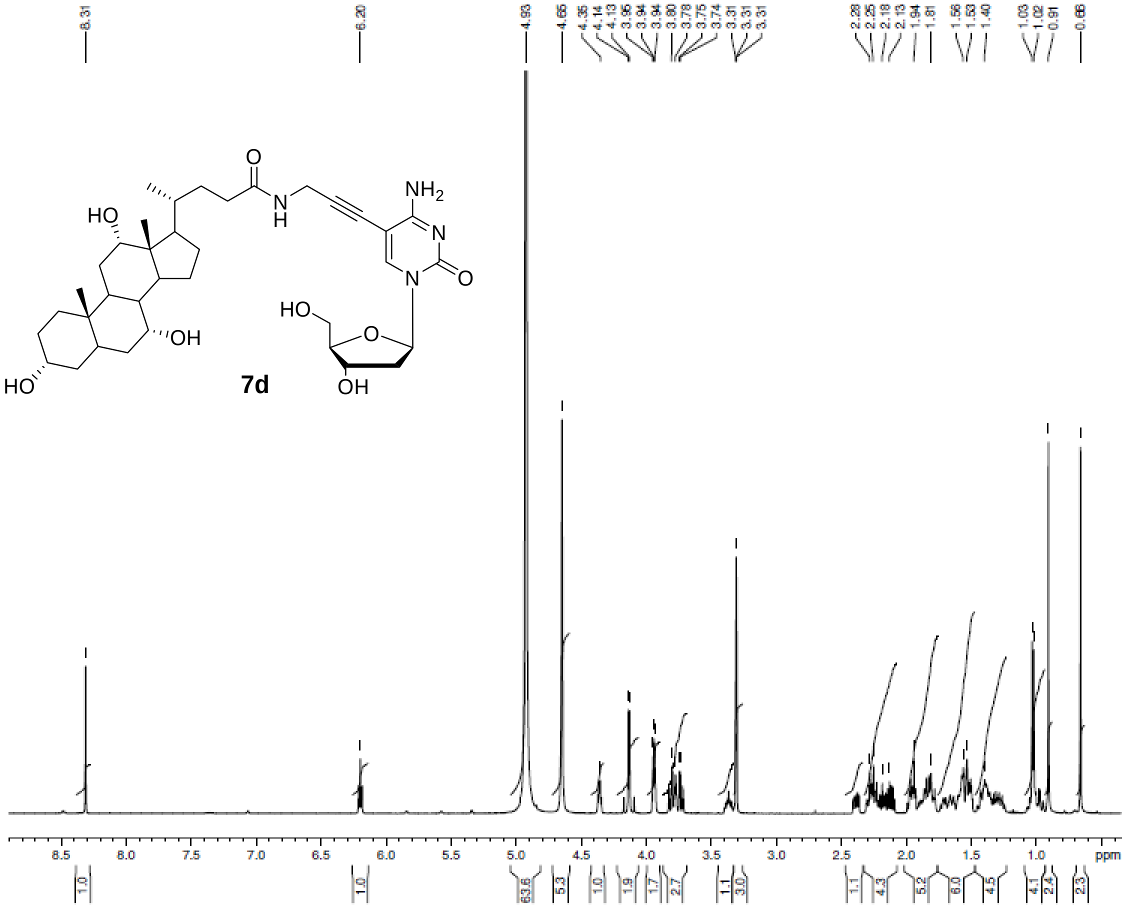
7b

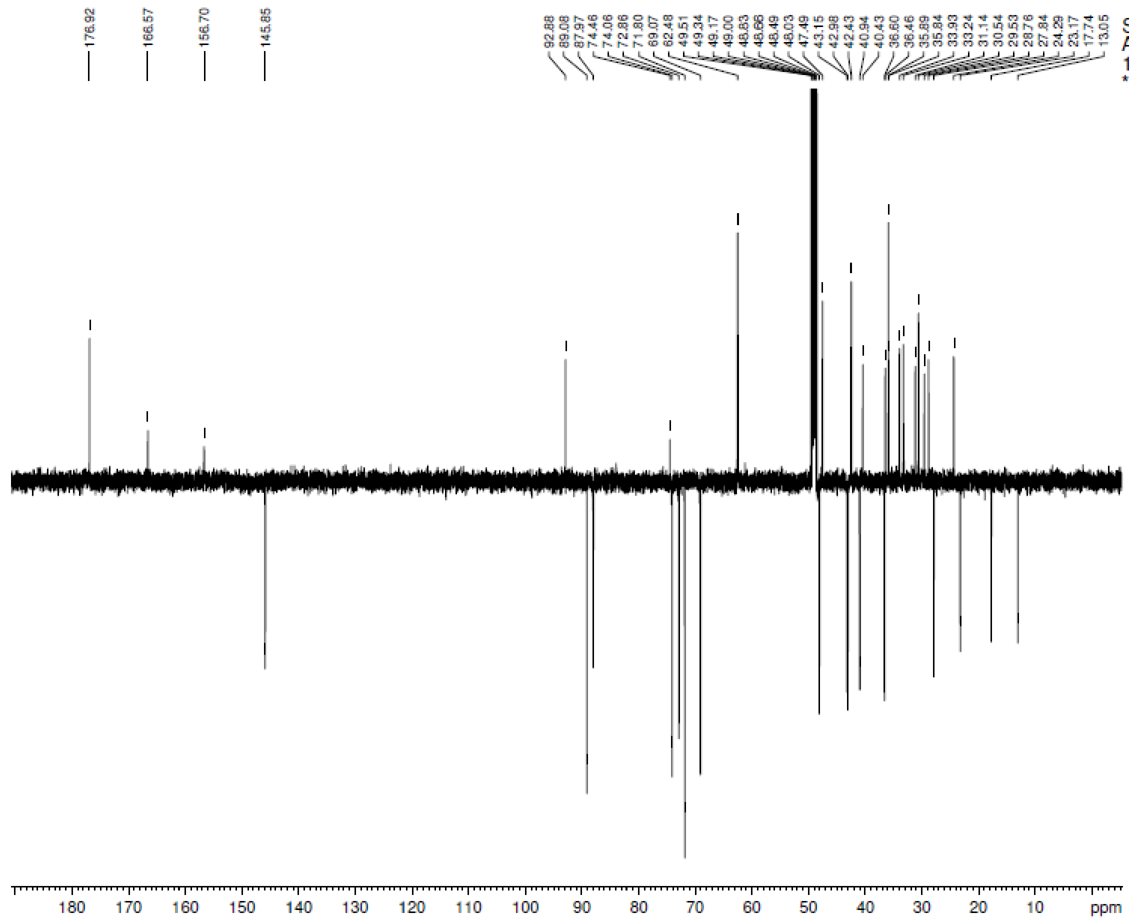


175.37
166.48
156.69
146.74
91.67 91.21 89.14 88.02 78.36 74.00 72.52 71.75 62.42 53.51 49.51 49.34 49.26 49.17 49.00 48.83 48.66 48.49 48.14 47.56 43.59 42.48 37.41 37.17 36.50 36.40 35.29 34.78 32.25 32.00 31.05 29.87 28.68 28.39 27.45 24.92 23.71 17.49 13.24
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

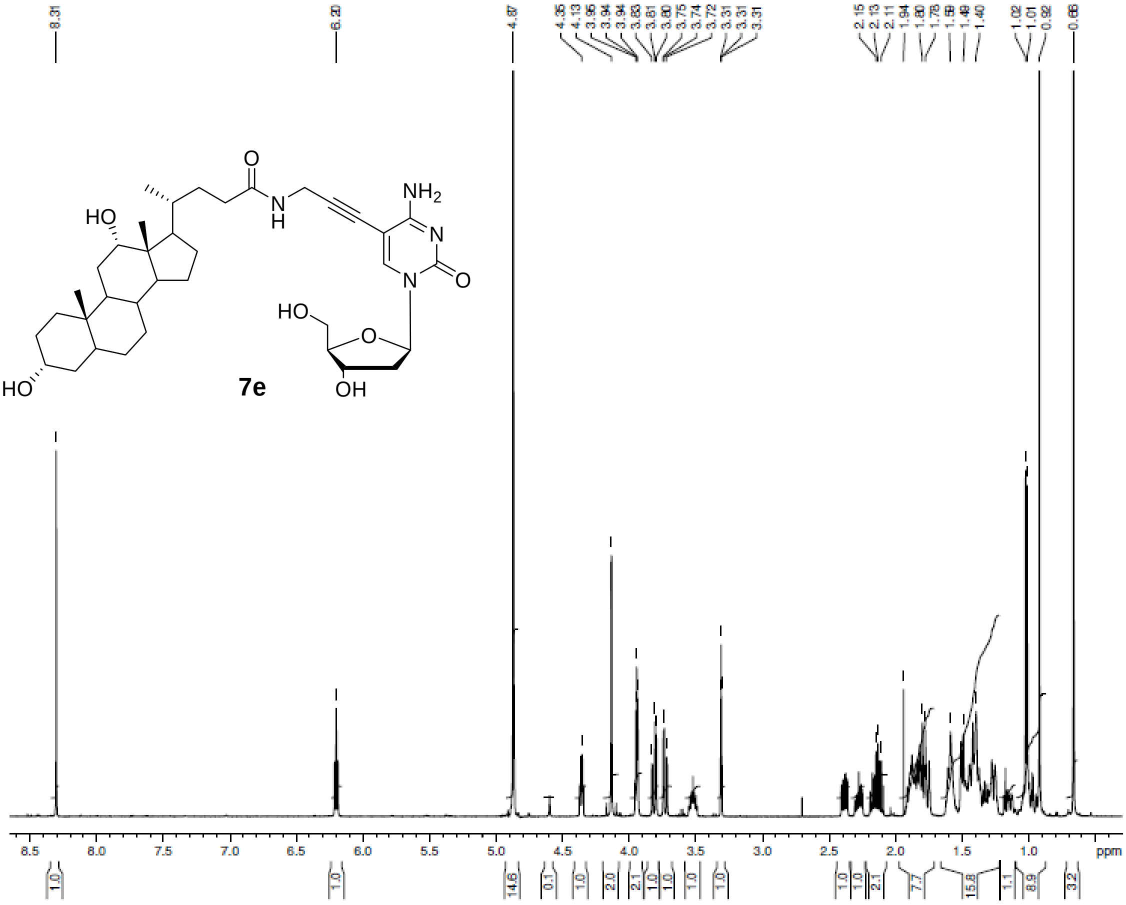

8.40
6.21
6.20
6.18
4.96
4.92
4.91
4.88
4.64
4.40
4.38
3.95
3.95
3.82
3.81
3.78
3.75
3.75
3.73
3.32
3.31
3.31
3.31
3.30
2.40
2.35
2.14
2.12
1.94
1.85
1.47
1.31
1.17
0.96
0.95
0.93
0.92
0.69
0.64
O
O
NH2
N
N
O
HO
O
OH
HO
OH
7c
ppm
1.0
1.2
44.8
1.9
1.5
1.1
3.4
5.5
4.8
1.3
6.9
3.6
5.4
5.7
2.4
8.5
3.2


175.36
166.48
156.68
146.75
91.66
91.20
89.12
88.03
78.39
72.83
71.73
69.06
62.41
57.30
53.53
51.52
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.68
43.13
42.47
40.98
40.70
40.44
36.55
36.52
36.20
35.86
34.01
32.29
31.99
31.32
29.29
24.67
23.40
21.75
18.74
12.22
ppm

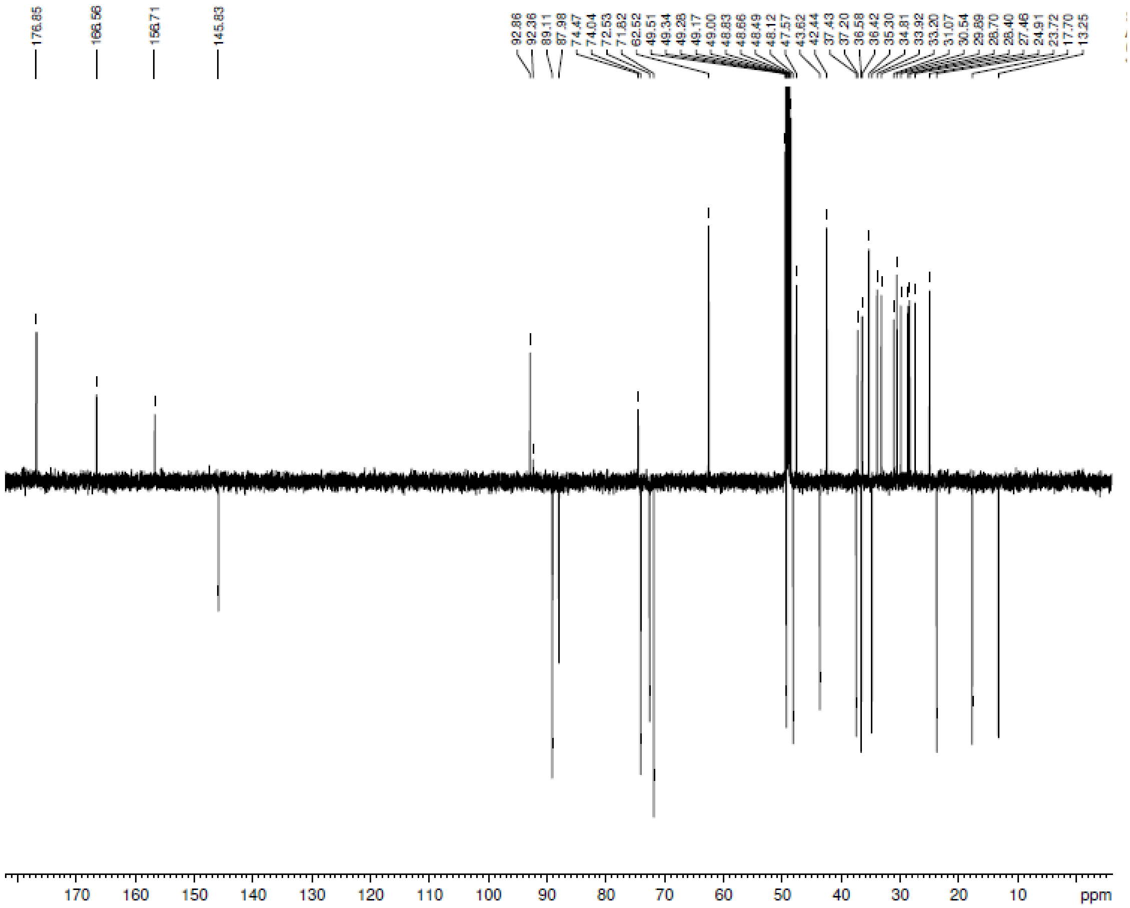

8.31
6.20
4.93
4.65
HO
OH
HO
O
N
H
NH2
N
N
O
HO
O
OH
7d
ppm

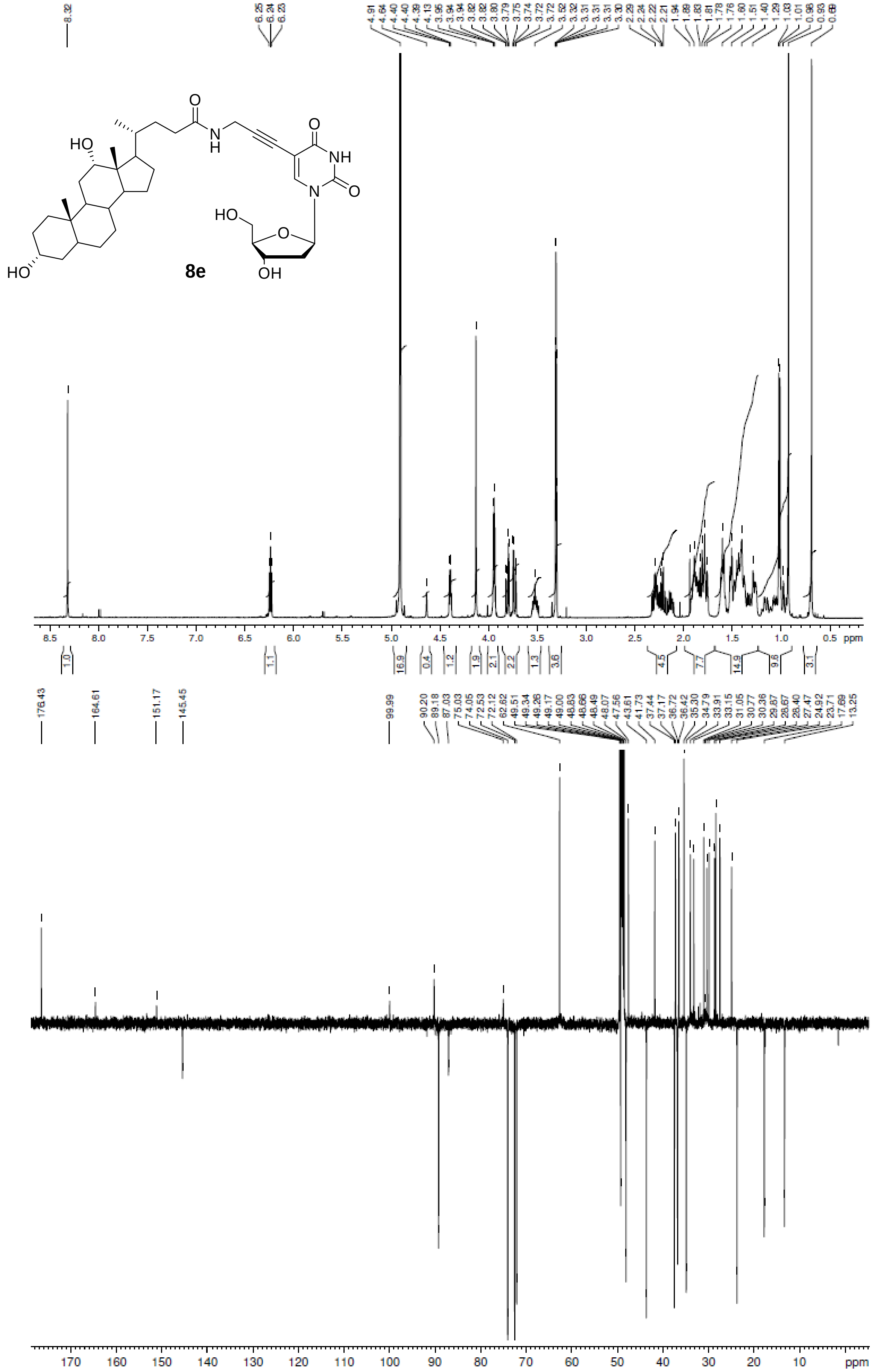

176.92
166.57
156.70
145.85
ppm

Supplementary Material (ESI) for Organic and Biomolecular Chemistry



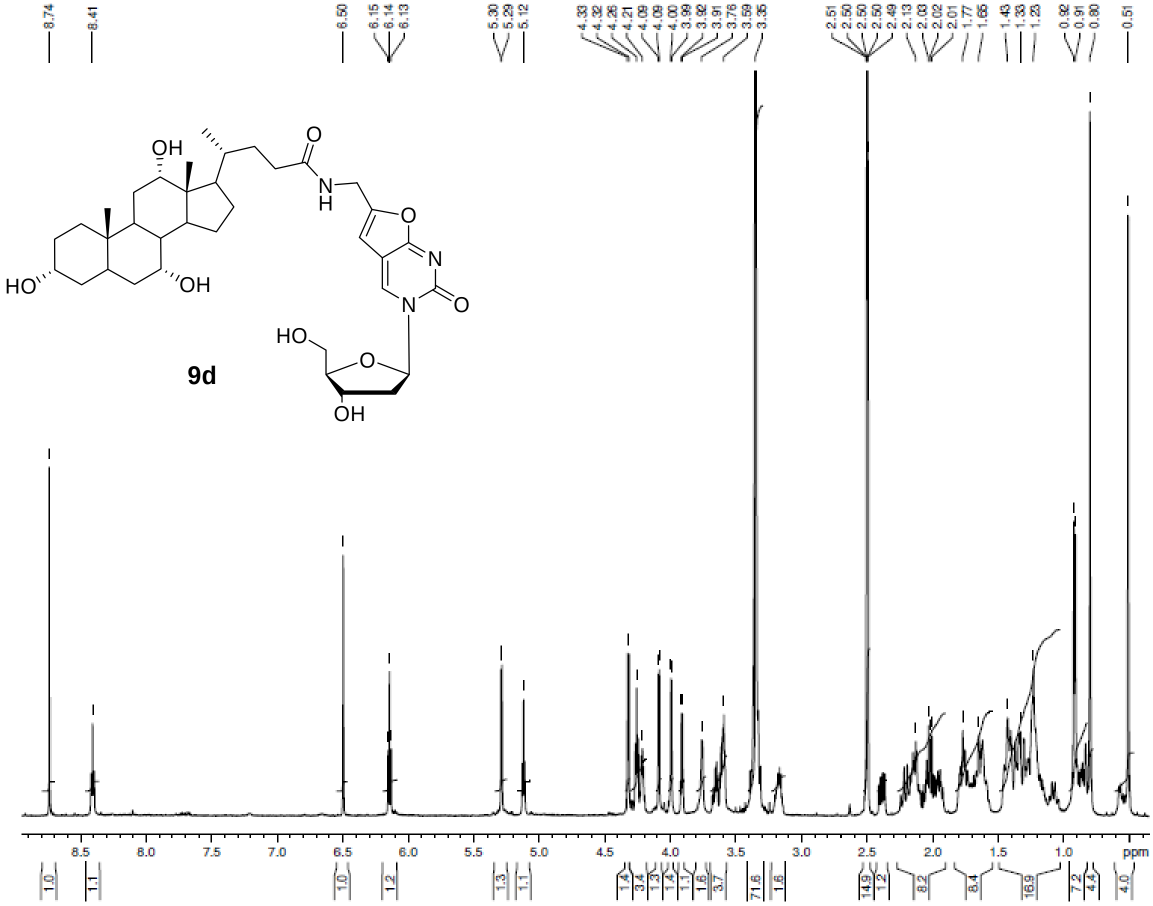
7e

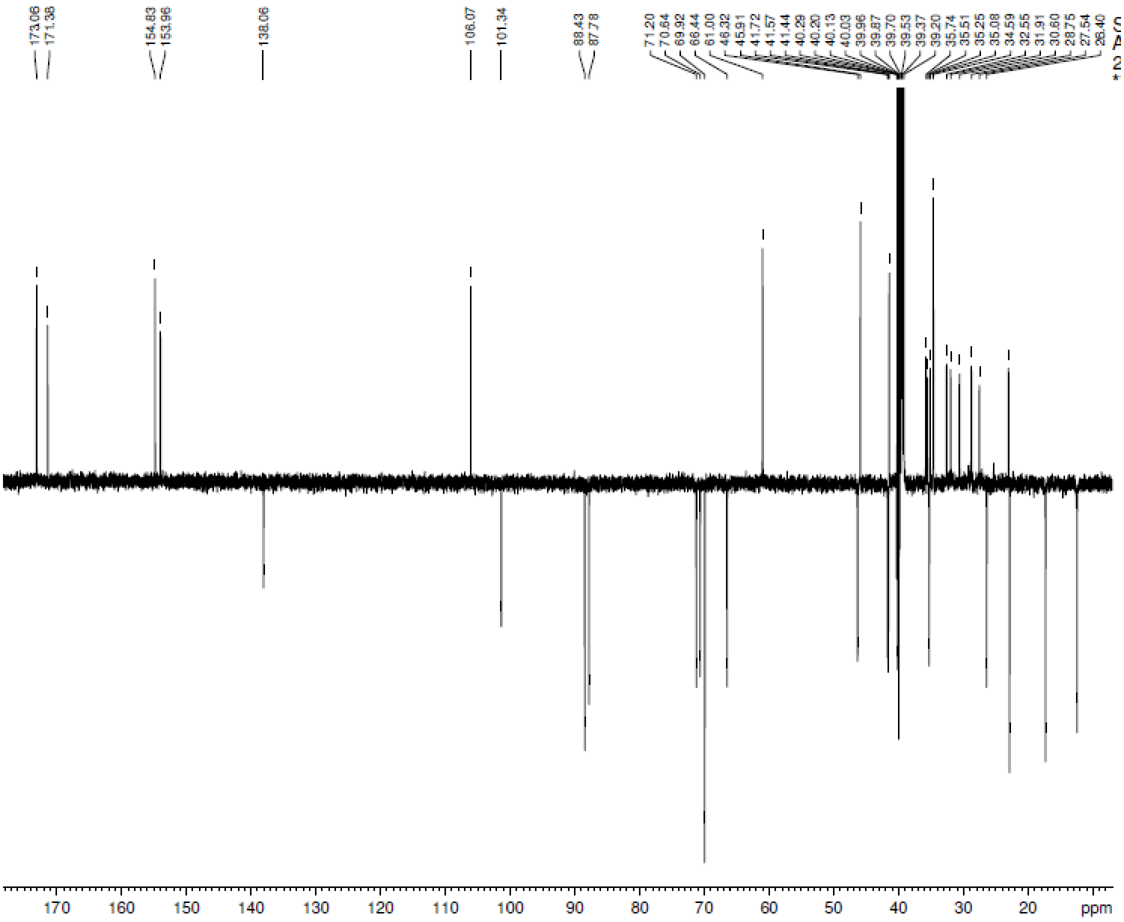


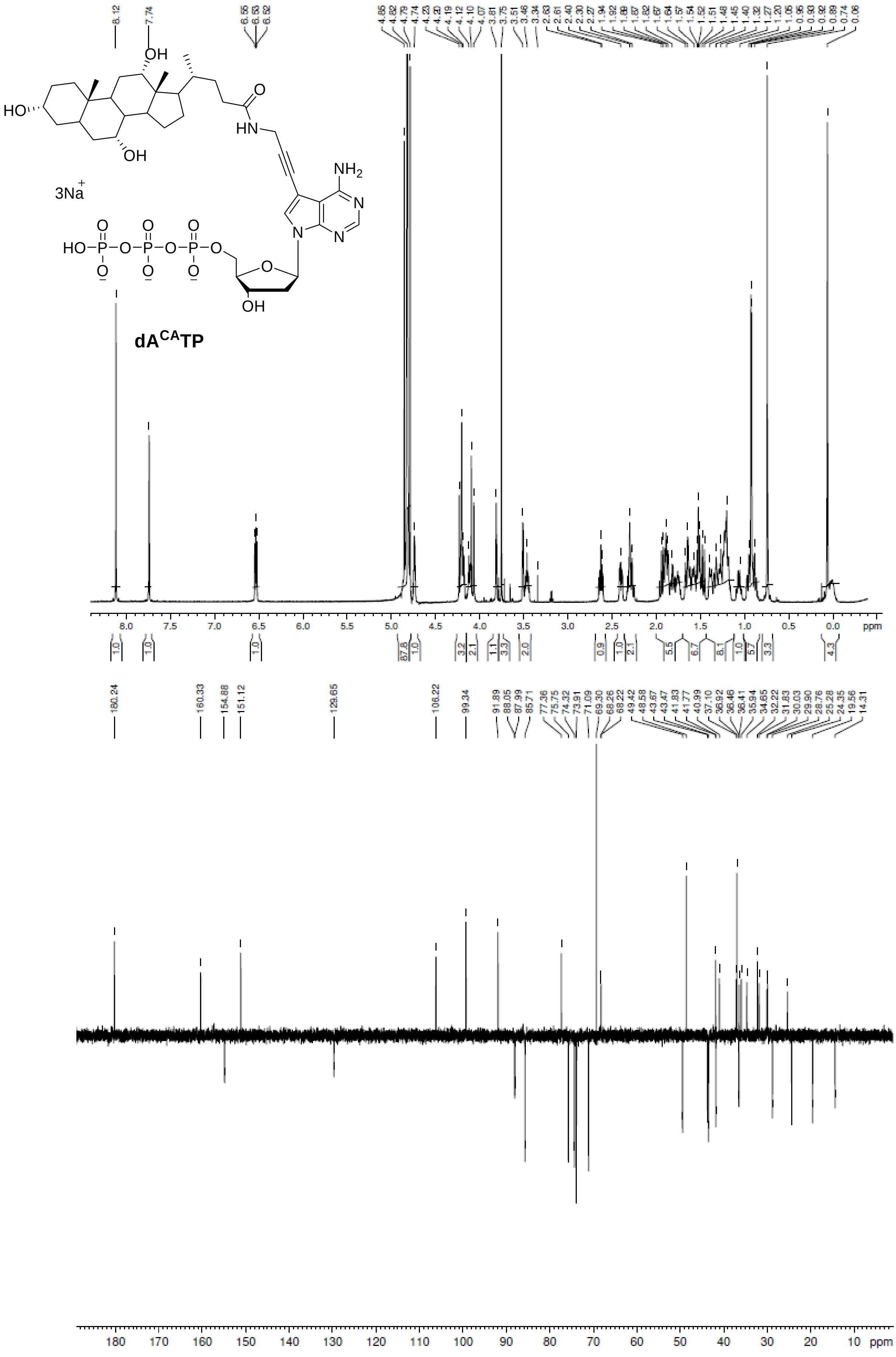


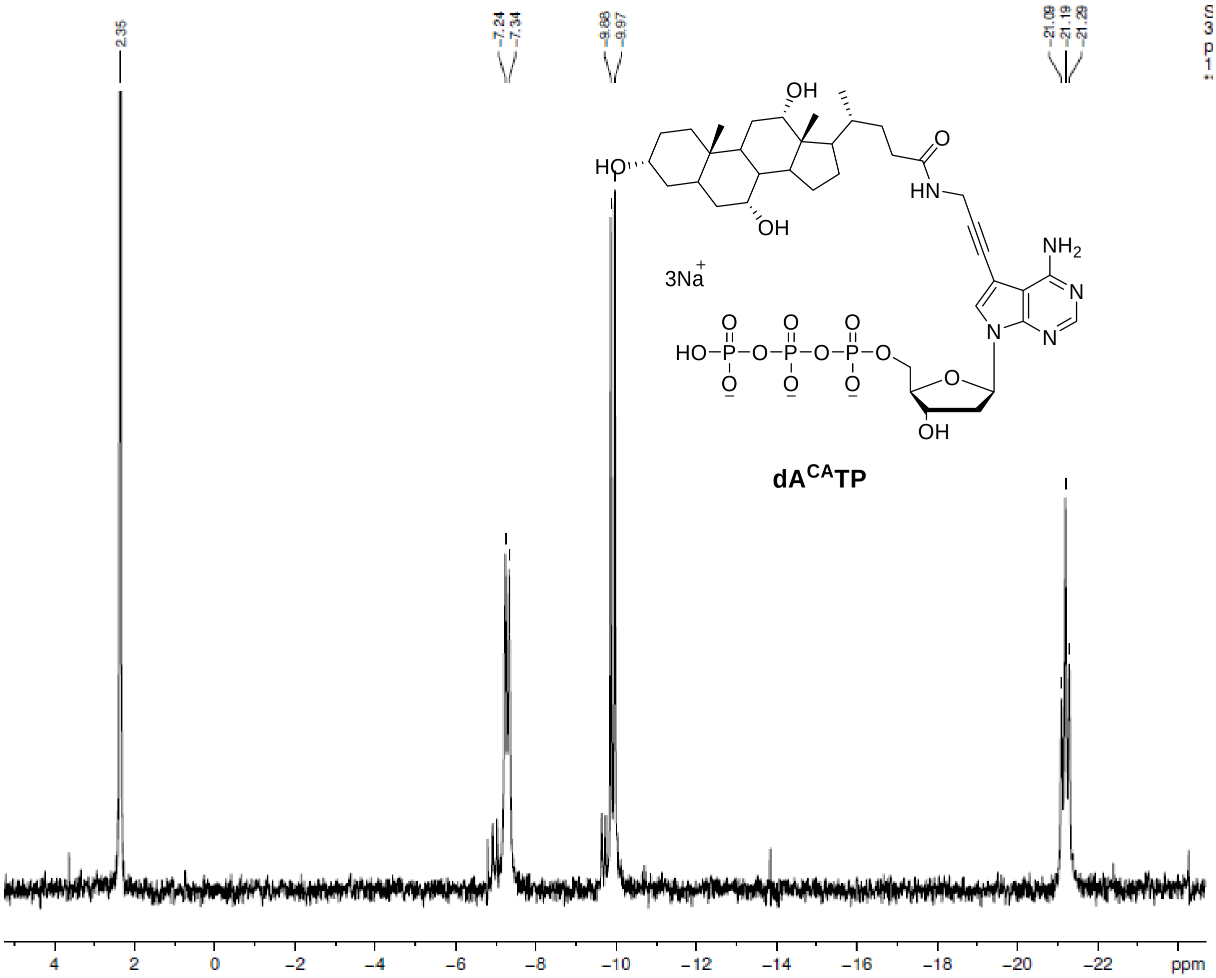
8e

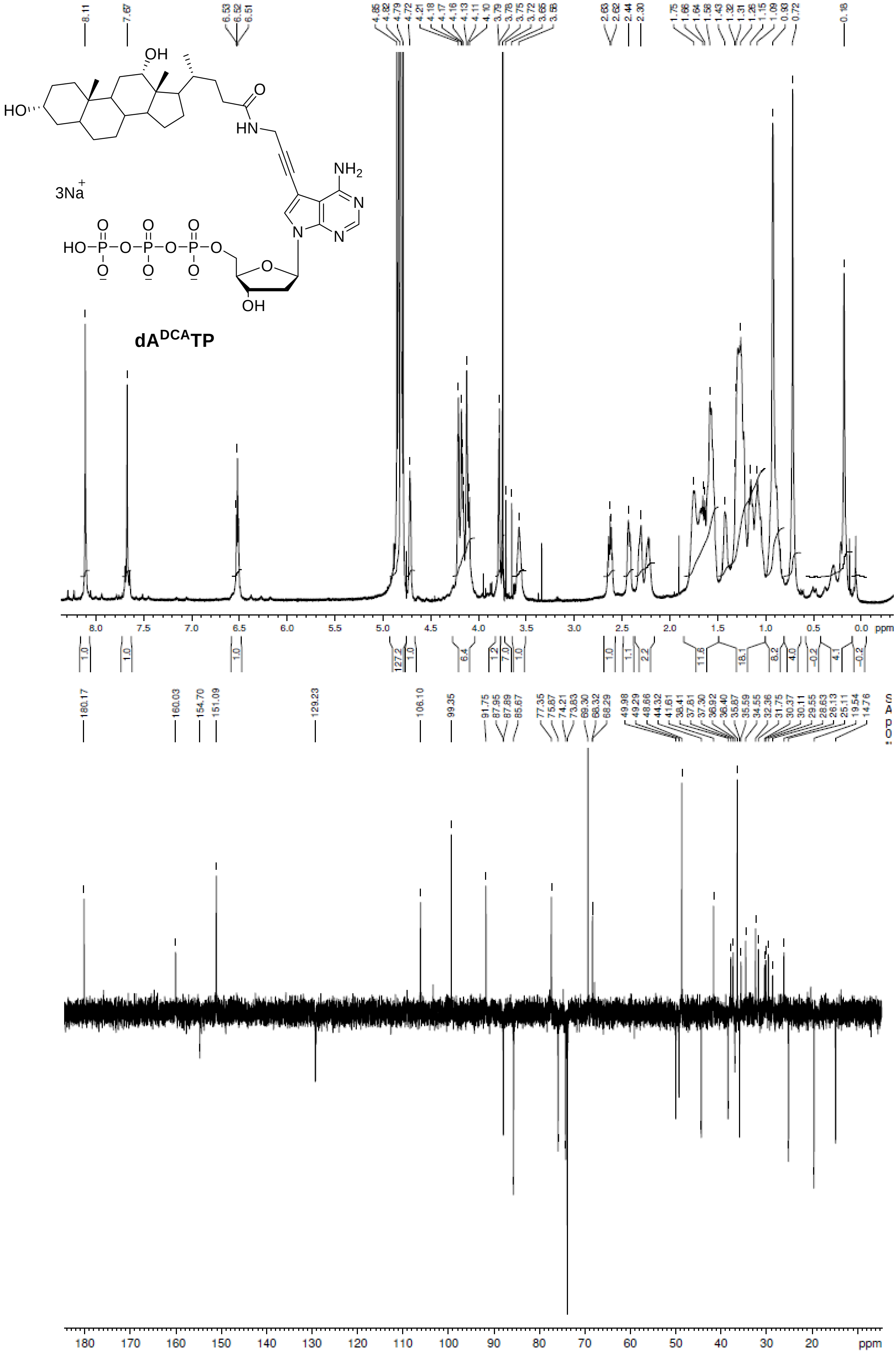
Supplementary Material (ESI) for Organic and Biomolecular Chemistry

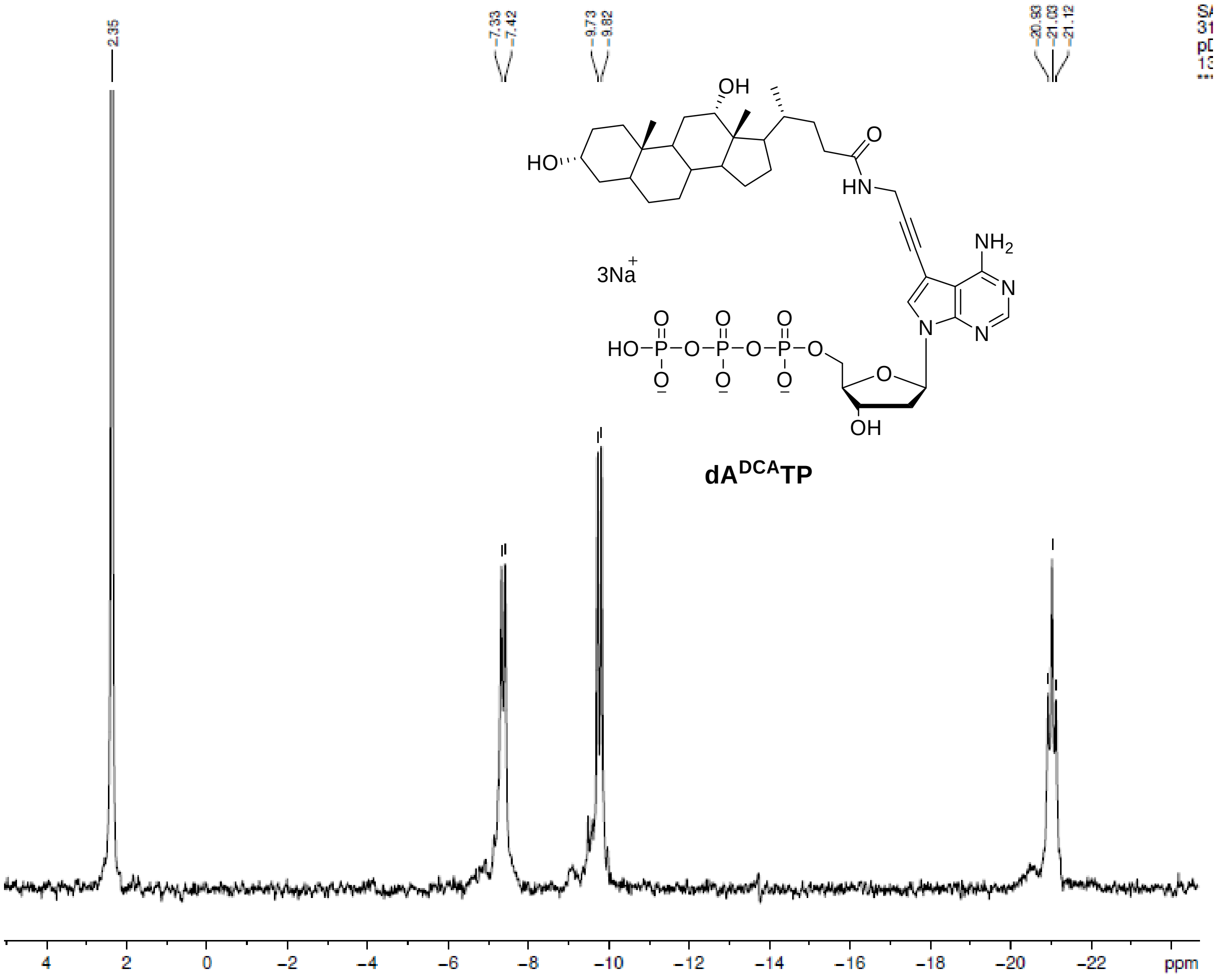


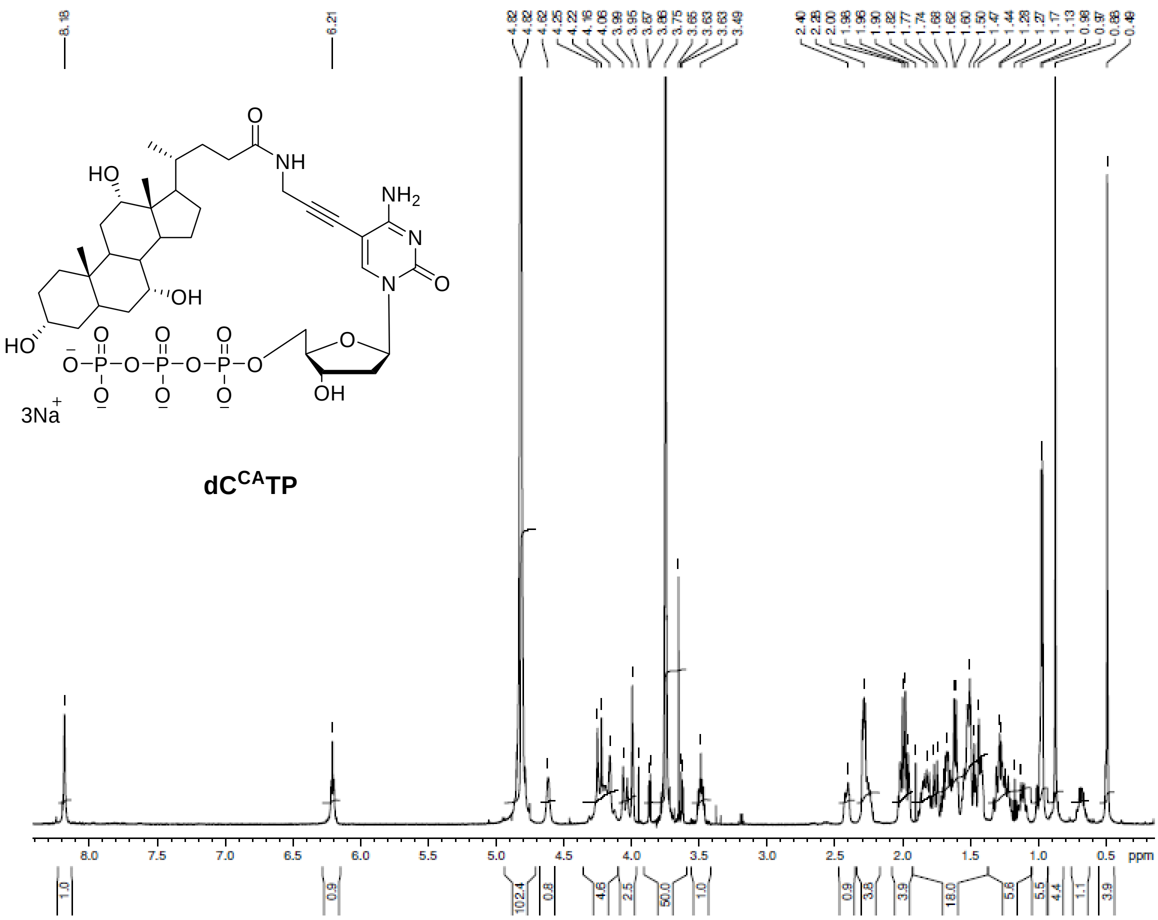


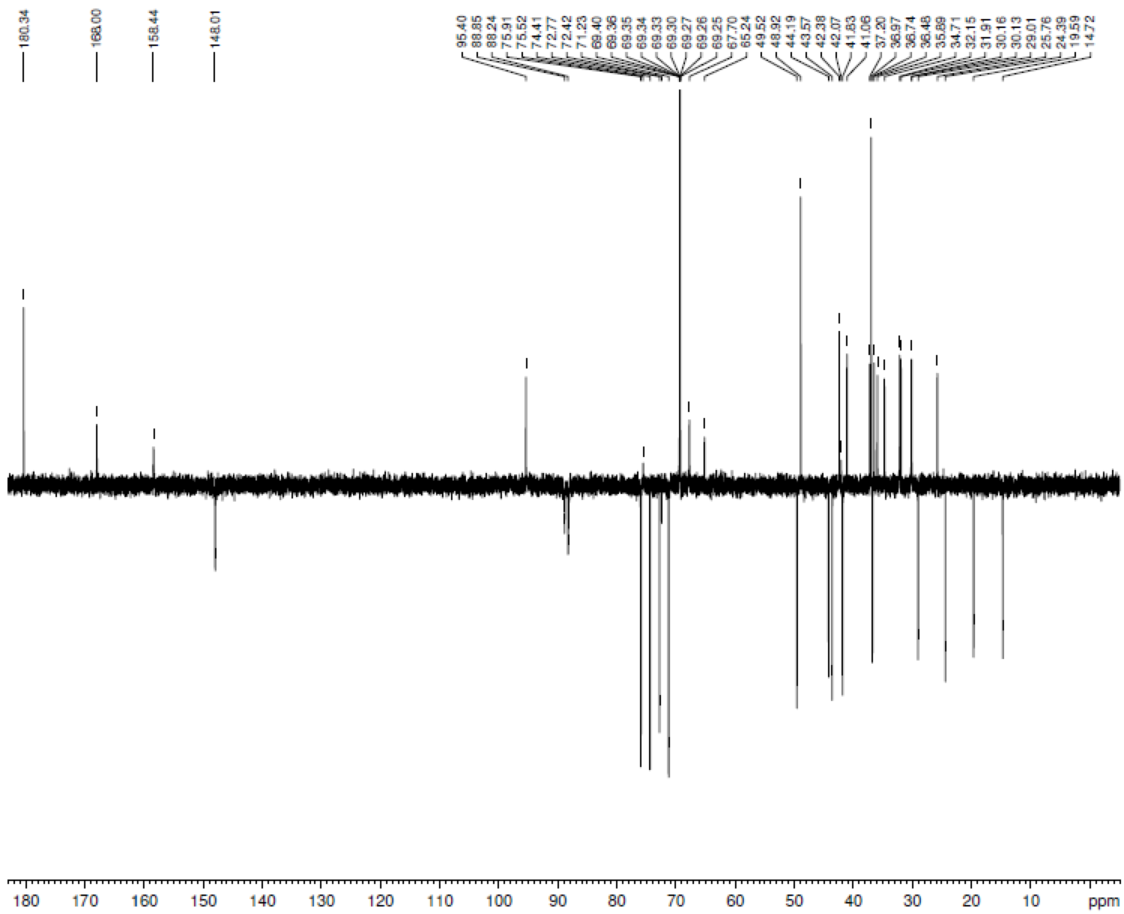

HO
OH
OH
O
HN
NH2
N
N
N
3Na+
HO-P-O-P-O-P-O
O
OH
dA^CA TP
8.12
7.74
6.55 6.53 6.52
4.85 4.82 4.79 4.74 4.23 4.20 4.19 4.12 4.10 4.07 3.81 3.75 3.51 3.48 3.34 2.63 2.61 2.40 2.30 2.27 1.94 1.92 1.89 1.87 1.82 1.67 1.64 1.57 1.54 1.52 1.51 1.48 1.45 1.40 1.32 1.27 1.20 1.05 0.95 0.93 0.92 0.89 0.74 0.06
ppm
1.0 1.0 1.0 57.8 1.0 3.2 2.1 1.1 3.3 2.0 0.9 1.0 2.1 5.5 6.7 8.1 1.0 5.7 3.3 4.3
180.24 160.33 154.88 151.12 129.65 106.22 99.34 91.89 88.05 87.99 85.71 77.36 75.75 74.32 73.91 71.09 69.30 68.26 68.22 49.42 48.58 43.67 43.47 41.83 41.77 40.99 37.10 36.92 36.46 36.41 35.94 34.65 32.22 31.83 30.03 29.90 28.76 25.28 24.35 19.56 14.31
ppm


2.35
-7.24
-7.34
-9.88
-9.97
-21.09
-21.19
-21.29
OH
HO
O
HN
OH
NH2
3Na+
N
N
N
HO
P
O
OH
dACATP
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
ppm

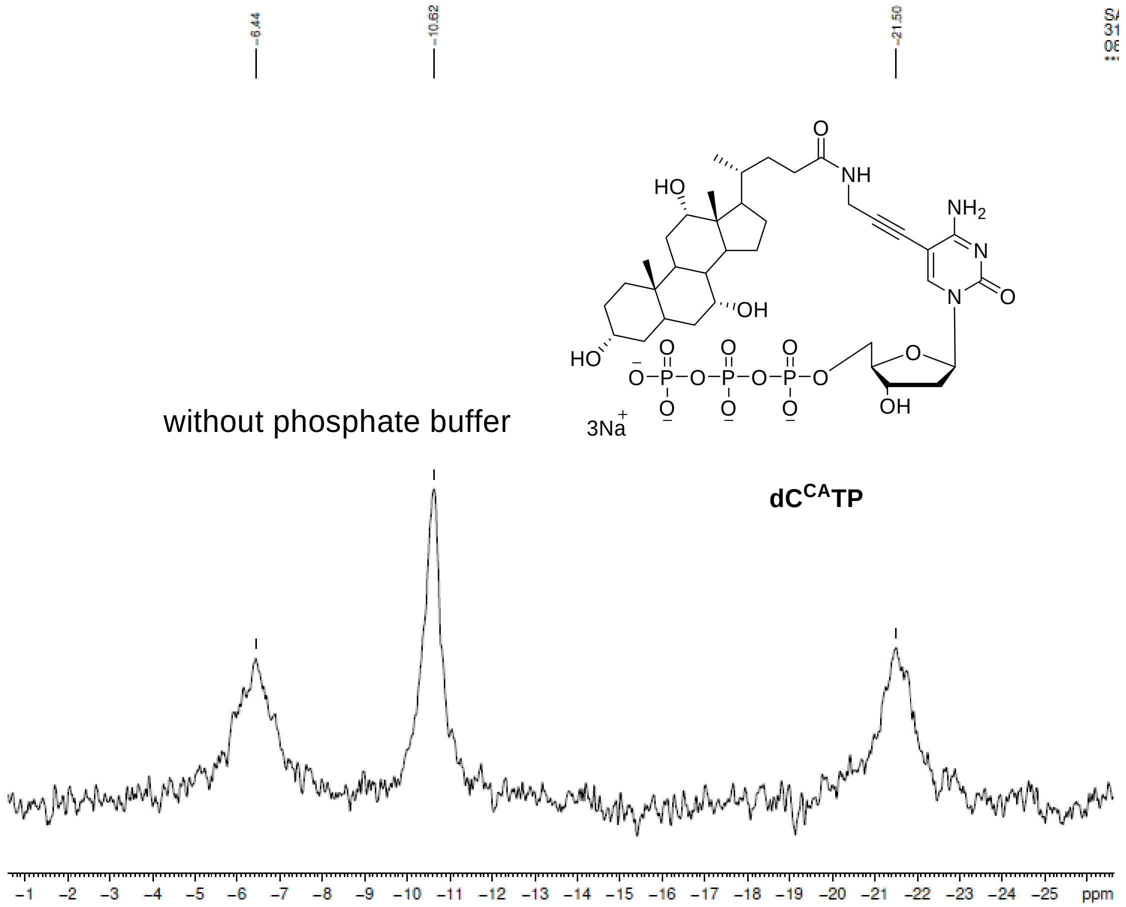

dA^DCA^TP
3Na+
NH2
HN
HO
OH
ppm
ppm

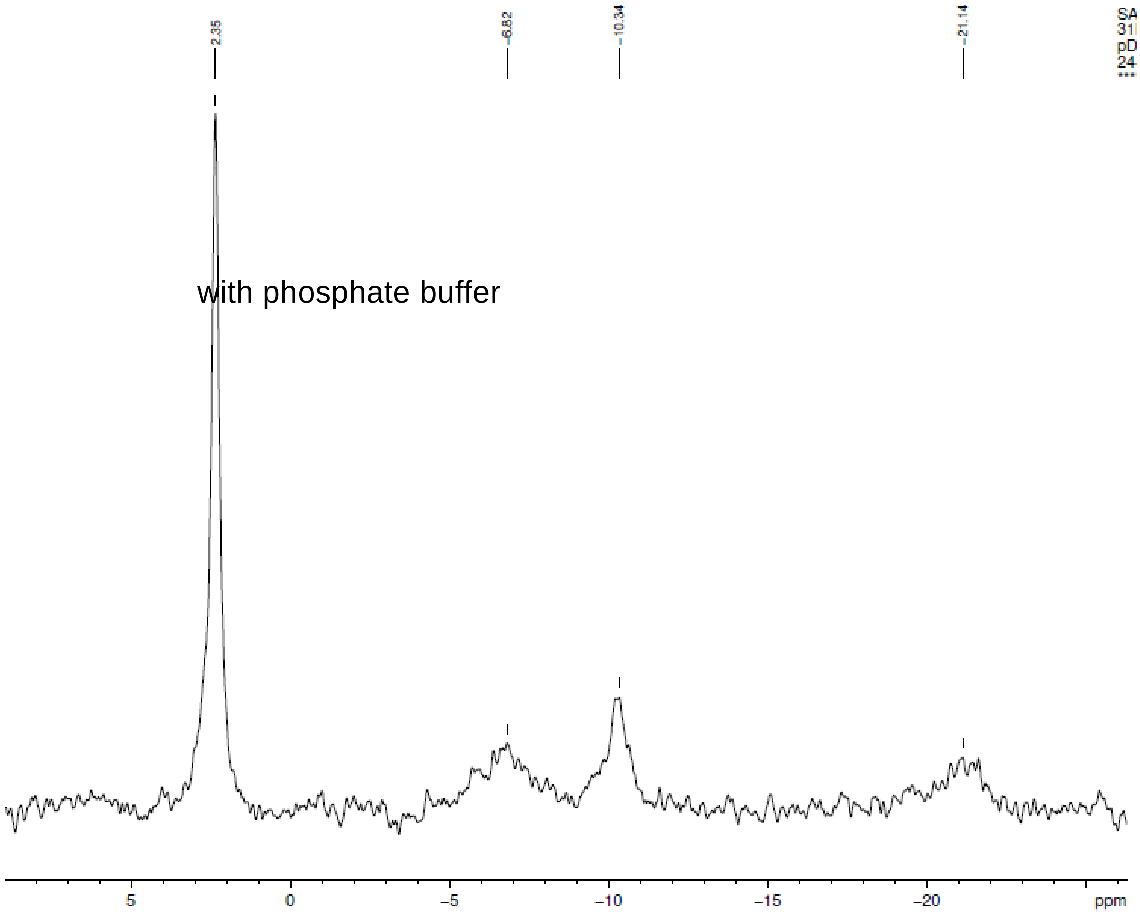

2.35
-7.33
-7.42
-9.73
-9.82
-20.93
-21.03
-21.12
OH
HO
O
HN
NH2
3Na+
N
HO-P-O-P-O-P-O
O
OH
dADCATP
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
−20
−22
ppm

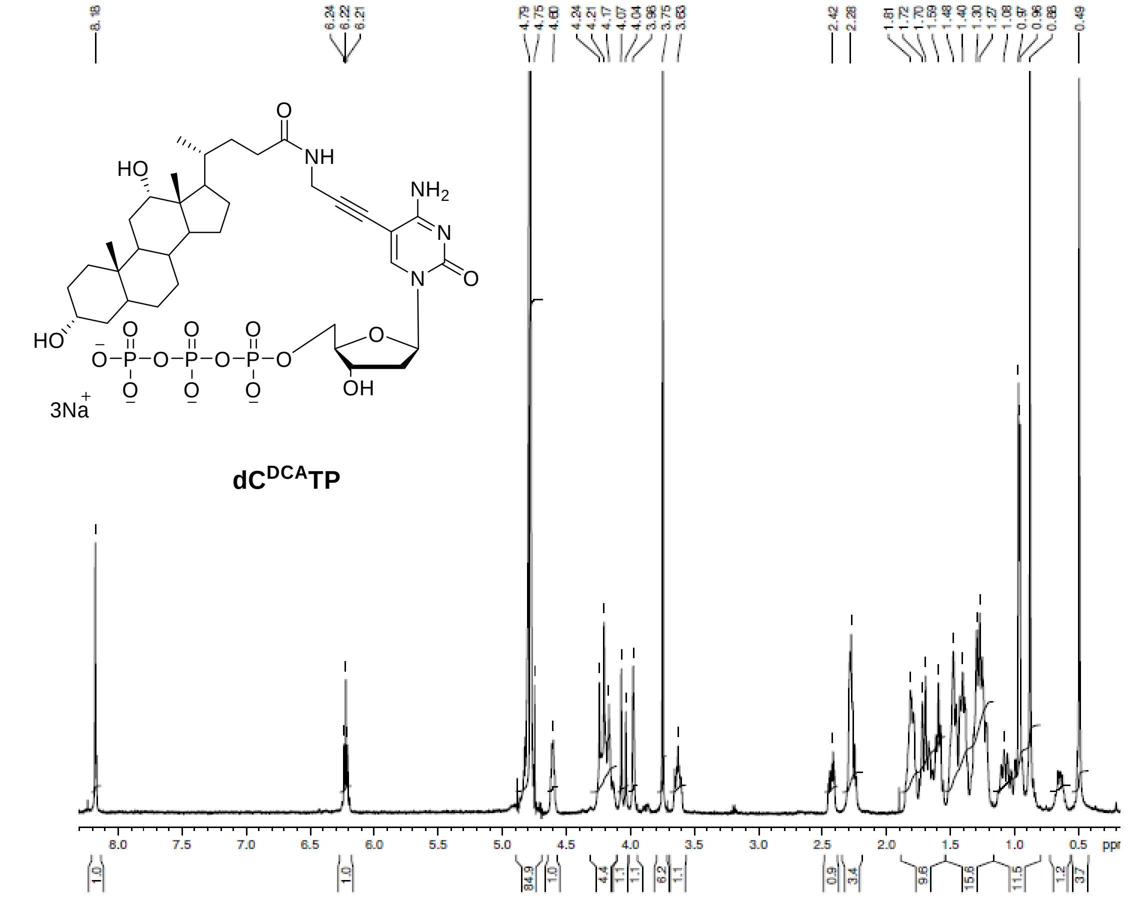

NH2
HO
OH
3Na+
dCCATP
ppm

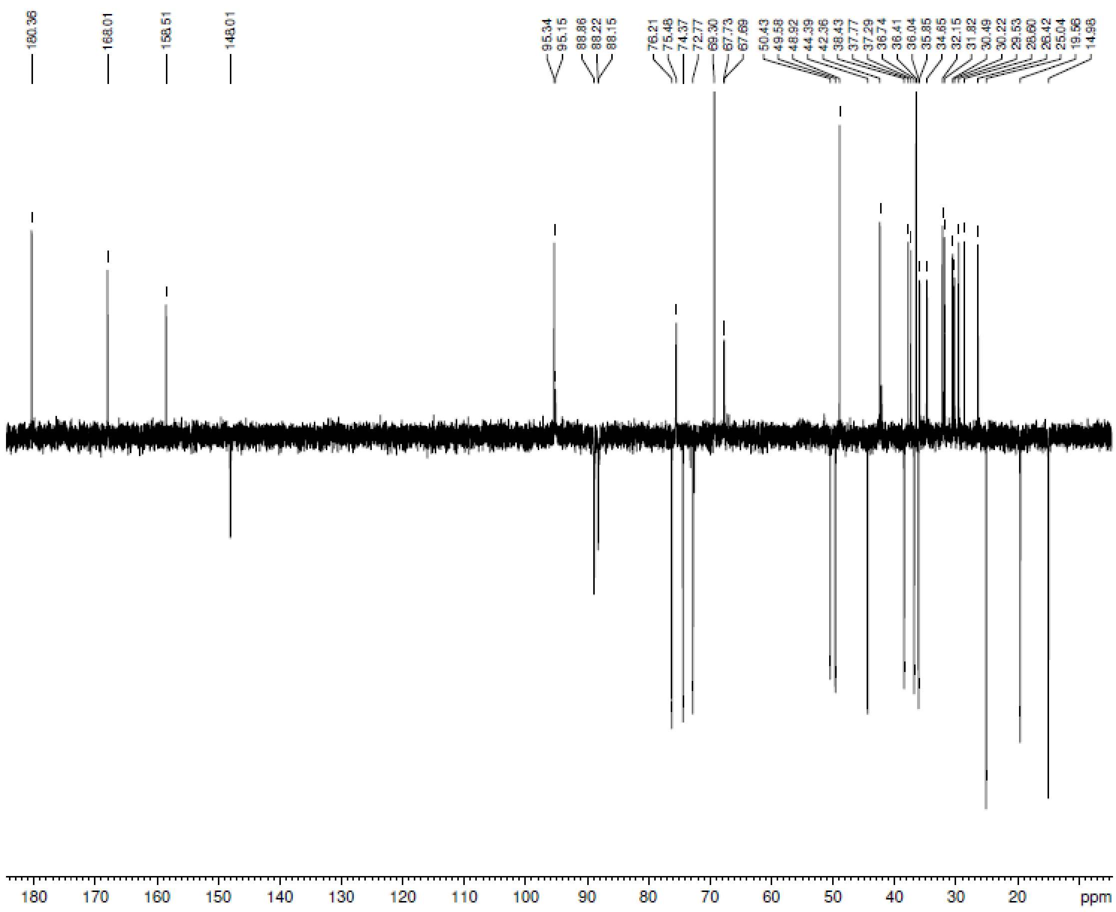

ppm

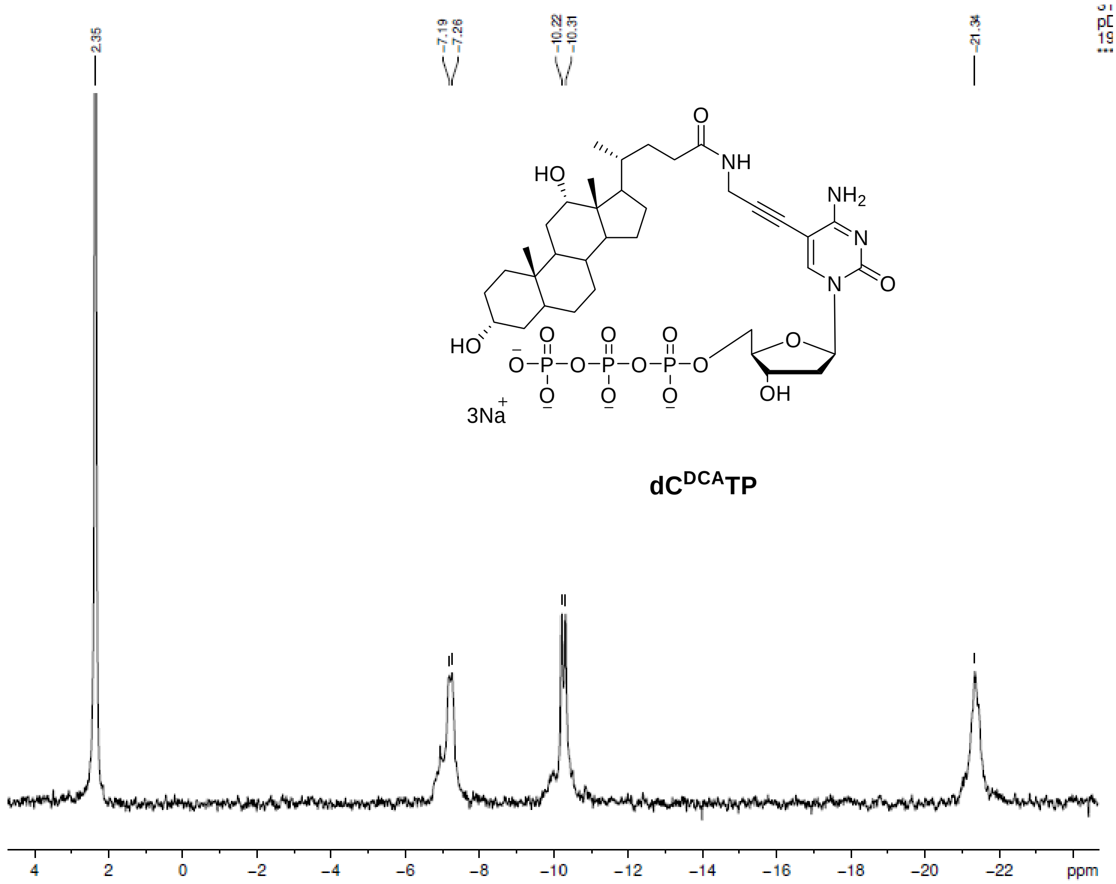
Supplementary Material (ESI) for Organic and Biomolecular Chemistry






dC^{DCA}TP
3Na^{+}




2.35
-7.19
-7.26
-10.22
-10.31
-21.34
O
NH
HO
NH_2
N
N
O
HO
O
O
O
O
OH
3Na
dC^{DCA}TP
4
2
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
−20
−22
ppm