Supplemental Information

Syntheses of 5-Formyl- and 5-Carboxyl-dC Containing DNA Oligos as Potential Oxidation Products of 5-Hydroxymethylcytosine in DNA

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3',5'-*O*-Di-*tert*-butylsilyl-5-iodo-2'-deoxycytidine (**2**)

To a cloudy solution of **1** (690 mg, 1.95 mmol) in DMF (15 mL) at 0 °C was added di-*tert*-butylsilyl-bis(trifluoromethanesulfonate) (0.81 mL, 1.1 equiv). After stirring at 0 °C for 10 min, ice-water bath was removed to allow the temperature going back to rt. imidazole (332 mg, 2.5 equiv) was then added and the mixture was stirred at rt for 0.5 h. After removal of DMF under high vacuum, the residue was dissolved in ethyl acetate, washed with water, 5% $NaHCO_3$ solution and brine, and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by silica gel chromatography, eluting with 3-6% MeOH in CH_2Cl_2, to give **2** (913 mg, 95%) as white foam. ^{1}H NMR (500.1 MHz) ($CDCl_3$) δ: 8.86 (br., 1H), 7.67 (s, 1H), 6.08 (m, *J*=5.0 Hz, 1H), 5.72 (br., 1H), 4.49 (m, 1H), 3.99-4.10 (m, 2H), 3.74 (m, 1H), 2.37 (m, 2H), 1.07 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (125.8 MHz) ($CDCl_3$) δ: 164.8, 155.3, 146.9, 86.4, 79.2, 75.3, 68.4, 57.6, 40.4, 28.4, 28.1, 23.6, 21.1. HRMS calculated for $C_{17}H_{29}IN_3O_4Si$, [MH^+] 494.0972 (calcd.), 494.0967 (found).

3',5'-*O*-Di-*t*-butylsilyl-5-formyl-2'-deoxycytidine (**3**)

To a solution of **2** (897 mg, 1.82 mmol) in anhydrous THF (50 mL) in a flask with a self-contained glass coupling apparatus equipped with a pressure equalizing addition funnel were added Ph_3P (286 mg, 0.6 equiv) and $Pd_2(dba)_3$ (166 mg, 0.10 equiv). The apparatus was charged with 50 psi of CO and heated to 70 °C and Bu_3SnH (0.53 mL, 1.05 equiv) was added slowly with a syringe within 1 h. After that, the mixture was kept on stirring for 2 h at 70 °C. After cooled to rt, the small amount of solid was removed by filtration. The solvent of filtrate was removed under reduced pressure and the residue was purified

by silica gel chromatography, eluting with 2-5% MeOH in CH_2Cl_2, to give **3** (563 mg, 78%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CHO=1665.2 cm^{-1}. ^1H NMR (500.1 MHz) ($CDCl_3$) δ: 9.48 (s, 1H), 8.18 (br., 1H), 8.06 (s, 1H), 7.50 (br., 1H), 6.08 (m, 1H), 4.51 (m, 1H), 4.03 (m, 2H), 3.81 (m, 1H), 2.46 (m, 2H), 1.05 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (125.8 MHz) ($CDCl_3$) δ: 188.1, 163.7, 153.9, 152.9, 106.2, 87.2, 79.4, 75.1, 68.3, 40.4, 23.6, 21.1. HRMS calculated for $C_{18}H_{29}N_2O_6Si$, [MH^+] 397.1795 (calcd.), 397.1789 (found).

3',5'-*O*-Di-*t*-butylsilyl-N^4-acetyl-5-formyl-2'-deoxycytidine (**4**)

To a solution of **3** (521 mg, 1.32 mmol) in anhydrous DMF (8 mL) in a flask was added acetic anhydride (0.15 mL, 1.2 equiv) and the mixture was stirred overnight at rt. MeOH (0.5 mL) was added to quench the reaction. After the mixture was stirred for additional 15min, the solvents were removed under reduced pressure. The residue was purified by silica gel chromatography, eluting with 2-4% MeOH in CH_2Cl_2, to give **4** (520 mg, 90%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CHO=1664.6 cm^{-1}. ^1H NMR (500.1 MHz) ($CDCl_3$) δ: 10.70 (br., 1H), 9.52 (s, 1H), 8.31 (s, 1H), 6.08 (m, 1H), 4.54 (m, 1H), 4.06 (m, 2H), 3.86 (m, 1H), 2.52 (m, 2H), 1.04 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (125.8 MHz) ($CDCl_3$) δ: 188.2, 172.5, 159.9, 154.2, 153.1, 106.1, 87.7, 79.7, 74.9, 68.2, 40.2, 23.6, 21.1. HRMS calculated for $C_{20}H_{32}N_3O_6Si$, [MH^+] 438.2060 (calcd.), 438.2055 (found).

N^4-Acetyl-5-formyl-2'-deoxycytidine (**5**)

To a solution of **4** (500 mg, 1.14 mmol) in THF (20 mL) were added HF in pyridine (1.0 equiv) under argon and the mixture was stirred at rt for 1 h. Silica gel (4.0 g) was added and the solvent was removed under reduced pressure. The residue was purified by silica

gel chromatography, eluting with 8-12% MeOH in CH_2Cl_2, to give **5** (319 mg, 94%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CHO=1666.5 cm^{-1}. ^1H NMR (500.1 MHz) ($CDCl_3$) δ: 9.25 (s, 1H), 9.05 (s, 1H), 5.90 (m, 1H), 4.12 (m, 1H), 3.79 (m, 1H), 3.69 (dd, *J*=12.5, 2.5 Hz, 1H), 3.52 (dd, *J*=12.0, 2.5 Hz, 1H), 2.35 (m, 1H), 2.31 (s, 3H), 2.00 (m, 1H). ^{13}C NMR (125.8 MHz) ($CDCl_3$) δ: 193.4, 177.0, 163.9, 160.3, 158.4, 110.3, 93.0, 92.9, 73.8, 65.2, 46.5, 31.4. HRMS calculated for $C_{12}H_{16}N_3O_6$, [MH^+] 298.1039 (calcd.), 298.1034 (found).

5'-*O*-(4,4'-Dimethoxytrityl)-N^4-acetyl-5-formyl-2'-deoxycytidine (**6**)

To a solution of **5** (237 mg, 0.80 mmol) in pyridine (8 mL) was added DMTr-Cl (324 mg, 1.2 equiv) under argon. The mixture was stirred overnight at rt. MeOH (1 mL) was added to quench the reaction. After concentrated to dryness, the residue was dissolved in CH_2Cl_2 (100 mL) and the mixture was washed with 5% $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel chromatography, eluting with 1-3% MeOH in CH_2Cl_2, to give **6** (437 mg, 91%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CHO=1663.4 cm^{-1}. ^1H NMR (500 MHz) (CD_3CN) δ: 10.68 (br., 1H), 8.72 (s, 1H), 8.52 (s, 1H), 7.44 (m, 2H), 7.27-7.35 (m, 7H), 6.88 (m, 4H), 6.06 (m, 1H), 4.55 (m, 1H), 4.08 (m, 1H), 3.78 (s, 6H), 3.42 (m, 1H), 3.36 (m, 1H), 2.55 (m, 1H), 2.50 (s, 3H), 2.44 (m, 1H). ^{13}C NMR (125.8 MHz) (CD_3CN) δ: 189.4, 171.9, 160.0, 159.9, 159.8, 155.9, 153.5, 145.5, 136.7, 136.4, 131.1, 131.0, 129.1, 129.0, 128.1, 114.2, 105.6, 88.8, 87.6, 87.4, 70.2, 63.3, 55.9, 41.9, 27.1. HRMS calculated for $C_{33}H_{34}N_3O_8$, [MH^+] 600.2346 (calcd.), 600.2340 (found).

5'-*O*-(4,4'-Dimethoxytrityl)-N^4-Acetyl-5-formyl-2'-deoxycytidine 3'-*O*-(2-cyanoethyl-*N,N*-diisopropyl)phosphoramidite (III)

To a stirring solution of **6** (120 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) were added *N,N*-diisopropylethylamine (0.24 mL) under argon followed by 2-cyanoethyl *N,N*-diisopropylchlorophosphoramidite (71.7 mg, 0.30 mmol). After the reaction mixture was stirred at room temperature for 0.5 h, CH_2Cl_2 (80 mL) was added. The mixture was washed with 5% aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel chromatography, eluting with 6-9% acetone in CH_2Cl_2 containing 0.2% Et_3N, to give **III** (141 mg, 88%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CHO=1664.8 cm^{-1}. ^1H NMR (500.1 MHz) (CD_3CN) δ: 10.66 (br., 1H), 8.74 (s, 0.5H), 8.47 (s, 0.5H), 8.43 (s, 1H), 7.43 (m, 2H), 7.27-7.34 (m, 7H), 6.88 (m, 4H), 6.08 (m, 1H), 4.71 (m, 1H), 4.18 (m, 1H), 3.74 (s, 6H), 3.70 (m, 4H), 3.42 (m, 2H), 2.67 (m, 1H), 2.55 (m, 1H), 2.50 (s, 3H). 1.06-1.20 (m, 12H). ^{13}C NMR (125.8 MHz) (CD_3CN) δ: 189.4, 171.9, 160.0, 159.9, 159.8, 155.8, 145.4, 145.3, 136.4, 136.3, 131.1, 129.2, 129.1, 129.0, 128.2, 114.2, 105.8, 88.8, 88.7, 87.7, 86.7, 86.4, 62.962.7, 59.3, 55.9, 44.1, 44.0, 41.2, 40.8, 27.1. 24.9, 24.8, 21.0. ^{31}P NMR (202.5 MHz) (CD_3CN) 148.47, 148.35 ppm. HRMS calcd. for $C_{42}H_{51}N_5O_9P$, $[MH]^+$ 800.3424 (calcd.), 800.3419 (found).

5-Methoxycarbonyl-2'-deoxycytidine (7)

To a solution of **1** (540 mg, 1.53 mmol) in DMF (20 mL) were added Ph_3P (242 mg, 0.92 mmol, 0.6 equiv), Et_3N (377 μL, 2.0 equiv.) and $Pd_2(dpa)_3$ (140 mg, 0.1 eq.) and MeOH (1 mL). The mixture was stirred at 50 °C under CO atmosphere overnight. After cooling to rt, the solid was removed by filtration. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel chromatography, eluting with 5-15% MeOH in CH_2Cl_2, to give **7** (406 mg, 93%) as white solid. IR (MeOH) $\nu_{(C=O)}$ of CO_2Me

=1644.1 cm^{-1}. ^1H NMR (500.1 MHz) (DMSO-d_6) δ: 8.96 (s, 1H), 7.96 (br., 1H), 7.64 (br., 1H), 6.07 (t, *J*=6.5 Hz, 1H), 5.24 (d, *J*=4.5 Hz, 1H), 5.08 (t, *J*=4.5 Hz, 1H), 4.21 (m, 1H), 3.85 (s, 1H), 3.74 (s, 3H), 3.63 (m, 1H), 3.58 (m, 1H), 2.26 (m, 1H), 2.04 (m, 1H). ^{13}C NMR (125.8 MHz) (DMSO-d_6) δ: 166.6, 164.4, 154.7, 150.1, 95.9, 89.1, 87.6, 71.1, 62.0, 53.2, 42.7. HRMS calculated for $C_{11}H_{16}N_3O_6S$ [MH^+] 286.1039 (calcd.), 286.1034 (found).

5-Methoxycarbonyl-*N*^{4}-acetyl-2'-deoxycytidine (8)

To a solution of **7** (200 mg, 0.70 mmol) in DMF (8 mL) was added Ac_2O (79 μL, 1.2 equiv) and the mixture was stirred overnight. MeOH (100 μL) was added to quench the reaction. The solvents were removed under reduced pressure and the residue 10-14% MeOH in CH_2Cl_2, to give **8** (202 mg, 88%) as white solid. IR (MeOH) $\nu_{(C=O)}$ of CO_2Me=1642.5 cm^{-1}. ^1H NMR (500 MHz) (DMSO-d_6) δ: 10.62 (br., 1H), 9.23 (s, 1H), 6.03 (t, *J*=6.0 Hz, 1H), 5.28 (d, *J*=4.5 Hz, 1H), 5.17 (t, *J*=4.5 Hz, 1H), 4.24 (m, 1H), 3.90 (s, 1H), 3.78 (s, 3H), 3.68 (m, 1H), 3.61 (m, 1H), 2.41 (s, 3H), 2.35 (m, 1H), 2.14 (m, 1H). ^{13}C NMR (125.8 MHz) (DMSO-d_6) δ: 172.2, 166.5, 160.4, 154.1, 151.3, 98.0, 89.4, 88.6, 70.5, 61.5, 53.8, 42.5, 27.5. HRMS calculated for $C13H_{17}N_3O_7$, [MH^+] 328.1145 (calcd.), 328.1139 (found).

5'-*O*-(4,4'-Dimethoxytrityl)- 5-methoxycarbonyl-*N*^{4}-acetyl-2'-deoxycytidine (9)

To a stirring solution of **8** (120 mg, 0.37 mmol) in pyridine (8 mL) was added DMTr-Cl (149 mg, 1.2 equiv) under argon. The mixture was stirred overnight at rt. MeOH (1 mL) was added to quench the reaction. After concentrated to dryness, the residue was dissolved in CH_2Cl_2 (100 mL) and the mixture was washed with 5% $NaHCO_3$ and brine,

dried over Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel chromatography, eluting with 1-3% MeOH in CH_2Cl_2, to give **9** (196 mg, 85%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CO_2Me=1640.4 cm^{-1}. ^1H NMR (500.1 MHz) (CD_3CN) δ: 10.71 (br., 1H), 8.92 (s, 1H), 7.46 (m, 2H), 7.24-7.34 (m, 7H), 6.86 (m, 4H), 6.05 (m, 1H), 4.36 (m, 1H), 4.06 (m, 1H), 3.75 (s, 6H), 3.58 (m, 1H), 3.42 (m, 1H), 3.24 (m, 1H), 3.18 (s, 3H), 2.50 (m, 4H), 2.35 (m, 1H). ^{13}C NMR (125.8 MHz) (CD_3CN) δ: 171.9, 166.4, 160.6, 159.7,2, 159.71, 154.1, 150.0, 145.8, 136.8, 131.0, 129.0, 128.8, 127.9, 114.0, 97.0, 88.8, 87.7, 87.3, 71.0, 63.6, 55.9, 52.7, 41.2, 27.1. (CD_3CN) δ: HRMS calculated for $C_{34}H_{36}N_3O_9$, [MH^+] 630.2452 (calcd.), 630.2446 (found).

5'-*O*-(4,4'-Dimethoxytrityl)-5-methoxycarbonyl-*N*^{4}-acetyl-2'-deoxycytidine (9) 3'-*O*-(2-cyanoethyl-*N,N*-diisopropyl)phosphoramidite (V)

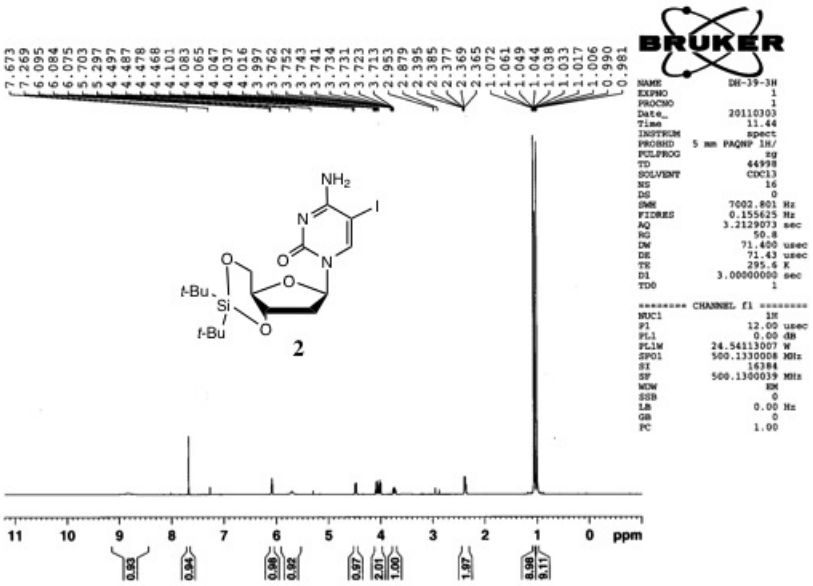
To a stirring solution of **9** (118 mg, 0.19 mmol) in CH_2Cl_2 (8 mL) were added *N,N*-diisopropylethylamine (0.22 mL) under argon followed by 2-cyanoethyl *N,N*-diisopropylchlorophosphoramidite (68 mg, 0.28 mmol). After the reaction mixture was stirred at room temperature for 0.5 h, CH_2Cl_2 (80 mL) was added. The mixture was washed with 5% aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by silica gel chromatography, eluting with 6-9% acetone in CH_2Cl_2 containing 0.2% Et_3N, to give **V** (127 mg, 82%) as white foam. IR (CH_2Cl_2) $\nu_{(C=O)}$ of CO_2Me =1641.8 cm^{-1}. ^1H NMR (500.1 MHz) (CD_3CN) δ: 10.76 (br., 1H), 8.99 (s, 0.5H), 8.96 (s, 0.5H), 7.46 (m, 2H), 7.22-7.36 (m, 7H), 6.86 (m, 4H), 6.10 (m, 1H), 4.56 (m, 1H), 4.18 (m, 1H), 3.78 (s, 6H), 3.60 (m, 4H), 3.24 (m, 1H), 3.10 (s, 1.5H), 3.07 (s, 1.5H), 2.65 (m, 2H), 2.50 (s, 3H), 2.45 (m, 1H), 1.01-1.16 (m, 12H). ^{13}C NMR (125.8 MHz) (CD_3CN) δ: 171.9, 167.2, 161.0, 159.8, 154.6, 150.4 145.7, 136.7,

136.6, 131.1 131.0, 129.1, 129.0, 128.8, 128.0, 127.9, 114.0, 98.1, 88.7, 87.6, 87.4, 73.2, 72.1, 62.8, 62.6, 59.5, 55.9, 52.6, 44.0, 41.8 41.2, 27.0, 24.9, 24.8, 24.7, 21.0, 20.9. ^{31}P NMR (202.5 MHz) (CD_3CN) 148.32, 148.06 ppm. HMRS calculated for $C_{43}H_{53}N_5O_{10}P$, [MH^+] 830.3530 (calcd.), 830.3525 (found).

DNA synthesis, deprotection, purification and characterization

Oligonucleotide synthesis was performed on an Expedite Nucleic Acid Synthesis System using standard DNA synthesis conditions (scale: 1 μM) except that the modified modifications **III** and **V** used double coupling to ensure good yields. Phosphoramidites for dA, dC, dG, dT and CPG carriers were obtained from *Glen Research*. The terminal DMTr protecting group was removed from the oligonucleotides by using the DMTr off mode. Then the resin containing oligos was transferred to a 2 mL vial. In general, two mild conditions were used for deprotection and cleavage of the **ODNs** from the resin with the oligos containing 5-fC and 5-hmC modifications. (1) The resin was treated with 1 mL 0.1 M K_2CO_3 in MeOH/H_2O (v/v, 1:1) for 2-4 h at r.t. ; (2) the resin was treated with 1 mL concentrated ammonium hydroxide for 4 h at r.t. For oligos containing 5-caC modification) the resin was treated with 1 mL 0.1 M K_2CO_3 in MeOH/H_2O (v/v, 1:1) overnight at 40 °C. After deprotection, filtration to get rid of the resin and the resin was rinsed with 0.5 mL the mixture of acetonitrile and water (v/v, 1:1). For the ammonium treatment, the filtrate was concentrated by speedvac. For the K_2CO_3 treatment, the filtrate was added AcOH to pH neutral and then was concentrated by speedvac. The dried **ODN** samples were then dissolved in deionized water (1mL) and were purified by C18 reverse phase HPLC with the applied buffer as 0-20% acetonitrile in 0.1 M triethylammoniumacetate in water. The fractions were checked for purity by analytical HPLC and MALDI-MS. The purified oligonucleotides were concentrated by speedvac.

The oligonucleotides were purified per preparative HPLC as described above.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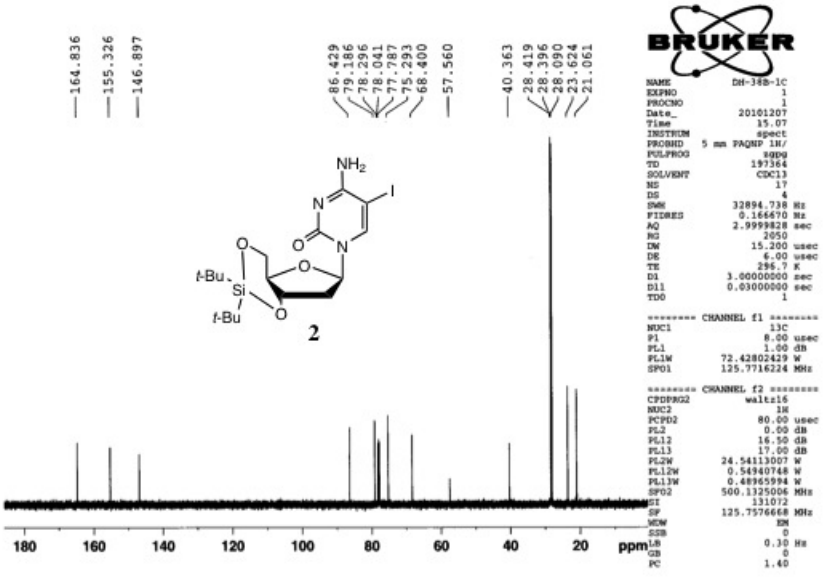
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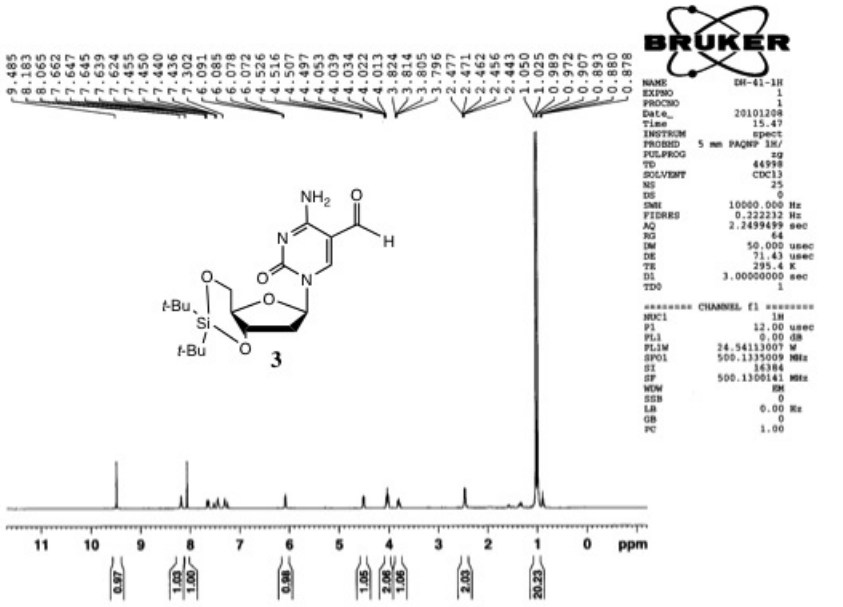
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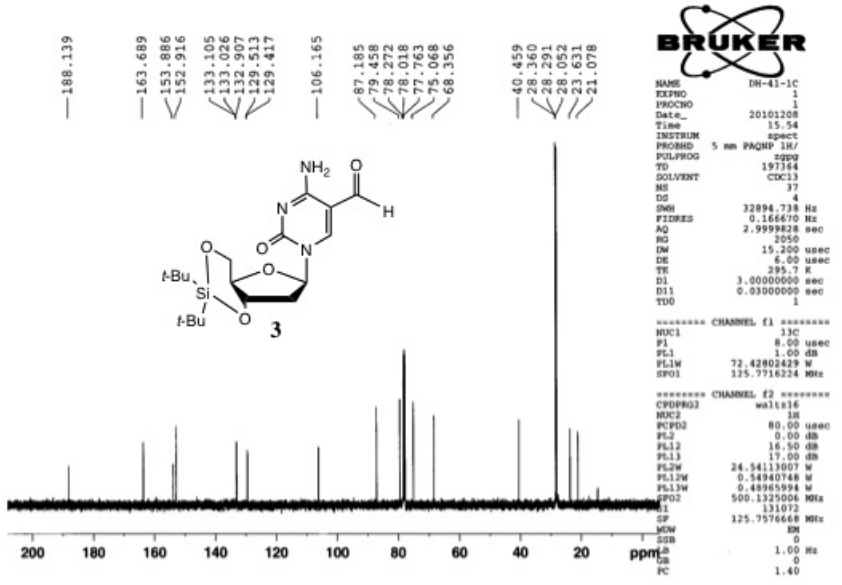
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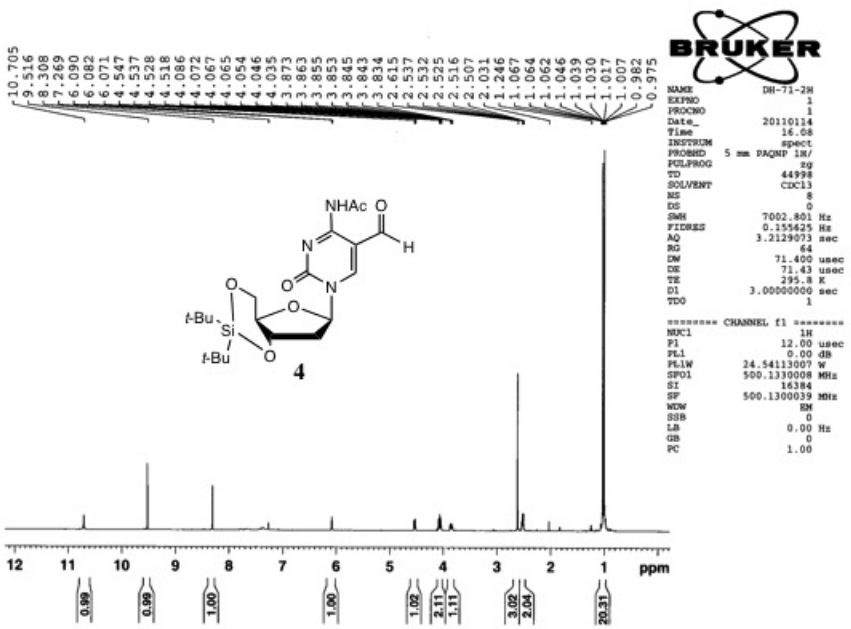
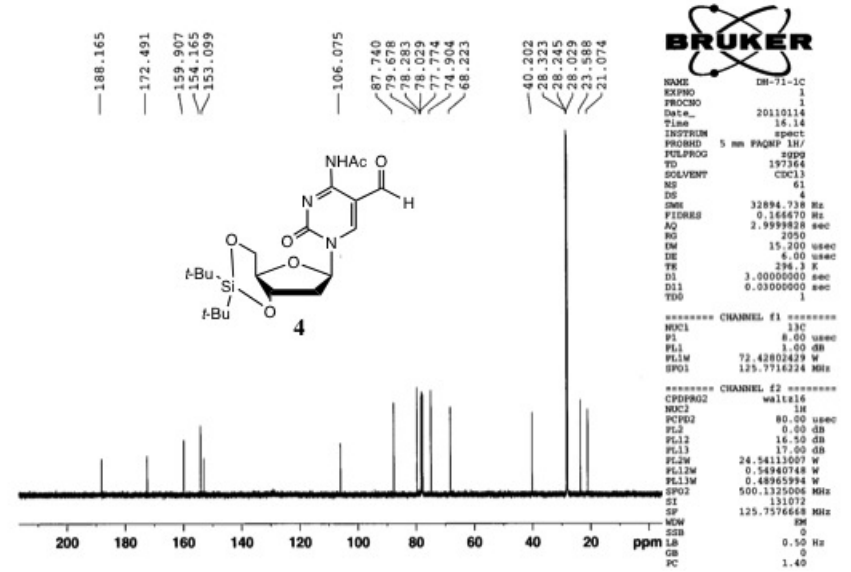
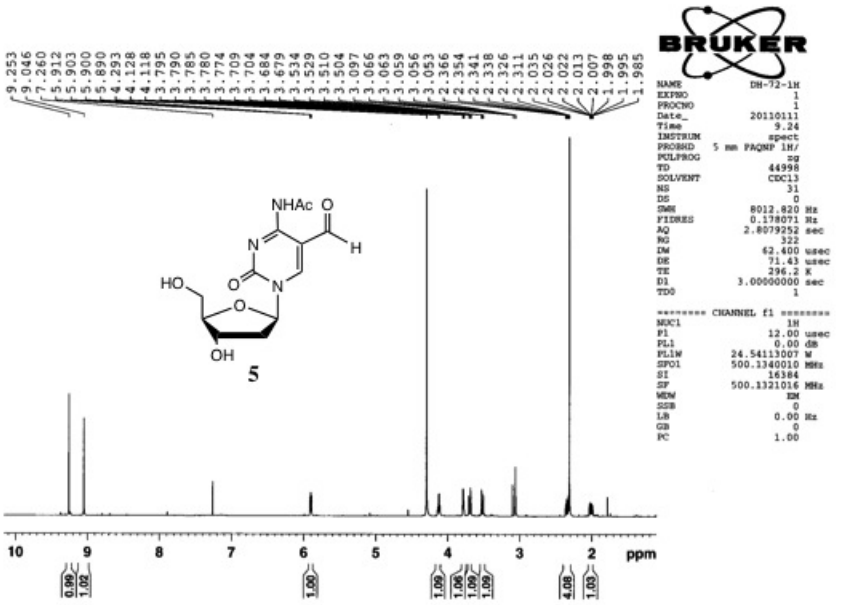
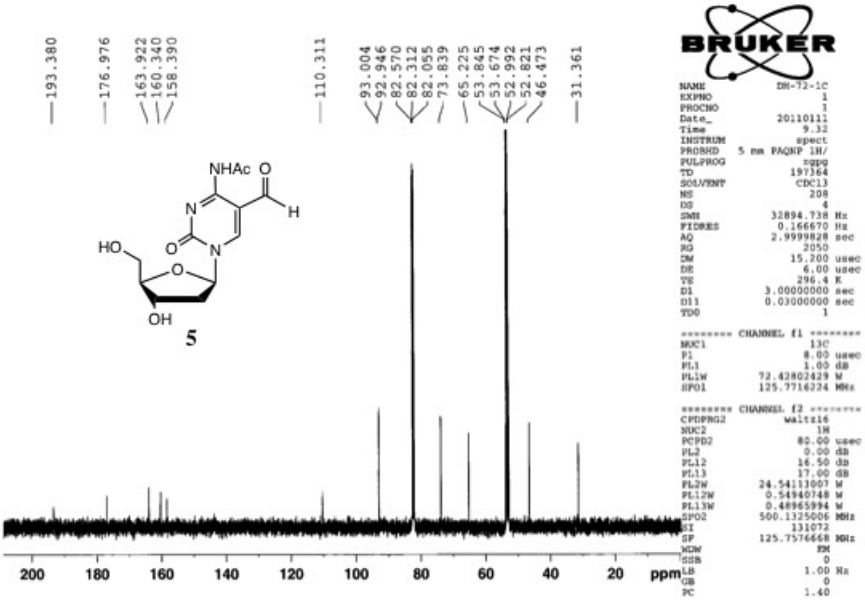
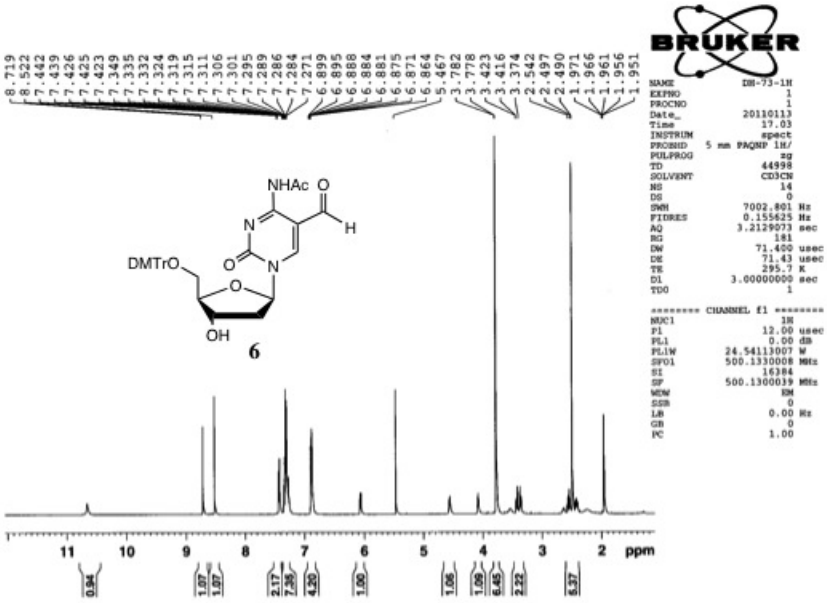
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 295.7 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

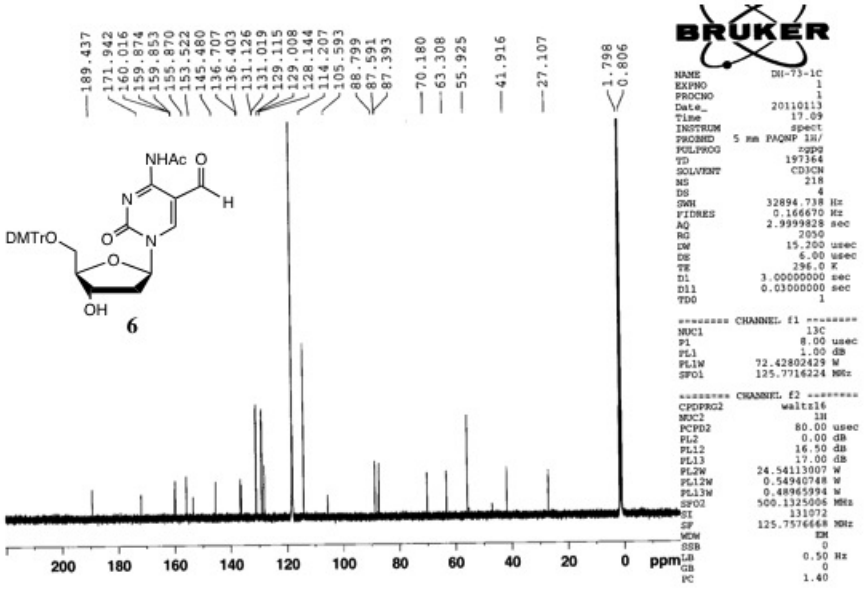

10.705
9.516
8.308
7.269
6.090
6.082
6.071
4.547
4.537
4.528
4.518
4.086
4.072
4.067
4.065
4.054
4.046
4.035
3.873
3.863
3.855
3.853
3.845
3.843
3.834
2.615
2.537
2.532
2.525
2.516
2.507
2.031
1.246
1.067
1.064
1.062
1.046
1.039
1.030
1.017
1.007
0.982
0.975
NHAc
O
N
H
O
N
O
O
t-Bu
Si
t-Bu
O
4
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
0.99
1.00
1.00
1.02
2.11
1.11
3.02
2.04
20.31
BRUKER
NAME DH-71-2H
EXPNO 1
PROCNO 1
Date_ 20110114
Time 16.08
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7002.801 Hz
FIDRES 0.155625 Hz
AQ 3.2129073 sec
RG 64
DW 71.400 usec
DE 71.43 usec
TE 295.8 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300039 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

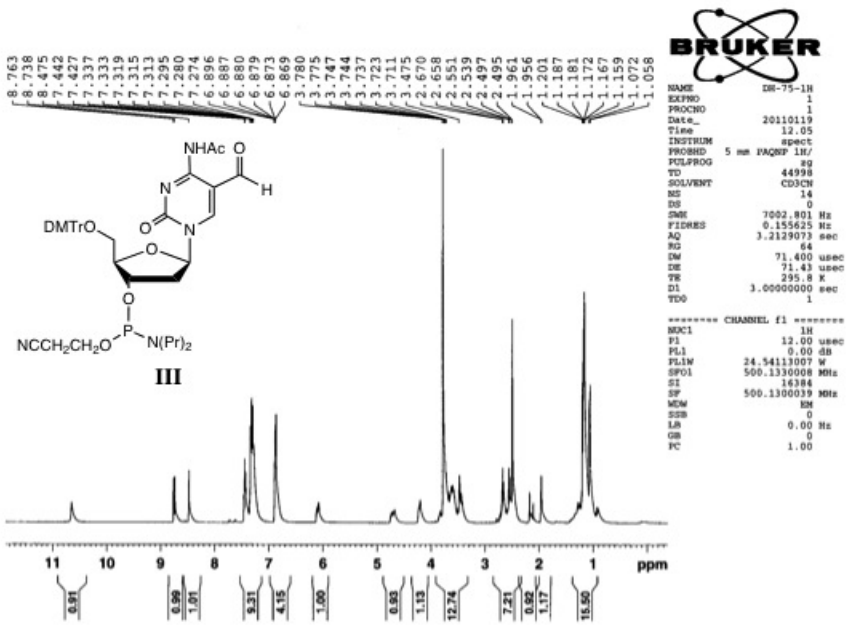

188.165
172.491
159.907
154.165
153.099
106.075
87.740
79.678
78.283
78.029
77.774
74.904
68.223
40.202
28.323
28.245
28.029
23.588
21.074
NHAc
O
N
H
O
N
O
O
t-Bu
Si
t-Bu
O
4
200
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME DH-71-1C
EXPNO 1
PROCNO 1
Date_ 20110114
Time 16.14
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CDCl3
NS 61
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.3 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54960748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40

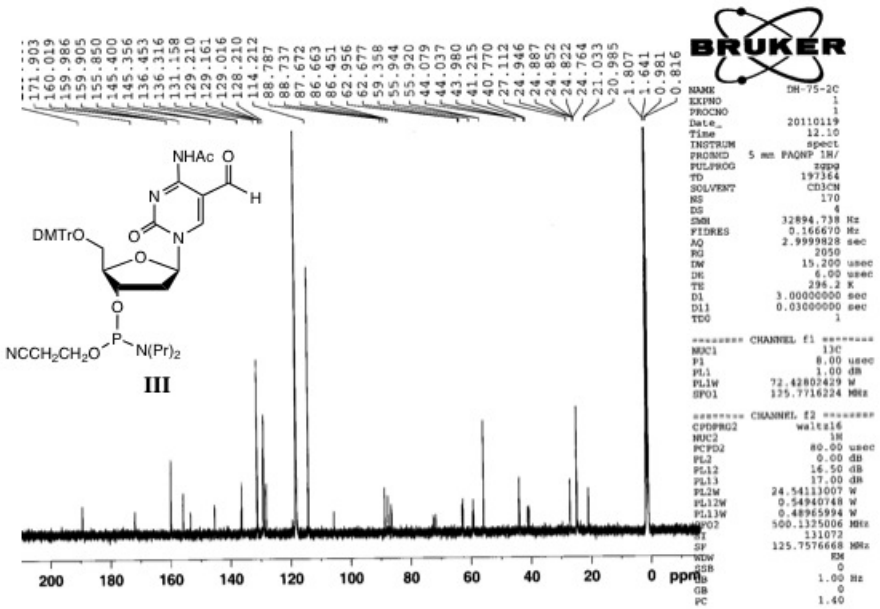

9.253
9.046
7.260
5.912
5.903
5.900
5.890
4.293
4.128
4.118
3.795
3.790
3.785
3.780
3.774
3.709
3.704
3.684
3.679
3.534
3.529
3.510
3.504
3.097
3.066
3.063
3.059
3.056
3.053
2.366
2.354
2.341
2.338
2.326
2.311
2.035
2.026
2.022
2.013
2.007
1.998
1.995
1.985
NHAc
O
N
H
HO
O
N
O
OH
5
10
9
8
7
6
5
4
3
2
ppm
0.99
1.02
1.00
1.09
1.06
1.09
1.09
4.08
1.03
BRUKER
NAME DH-72-1H
EXPNO 1
PROCNO 1
Date_ 20110111
Time 9.24
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 31
DS 0
SWH 8012.820 Hz
FIDRES 0.178071 Hz
AQ 2.8079252 sec
RG 322
DW 62.400 usec
DE 71.43 usec
TE 296.2 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1340010 MHz
SI 16384
SF 500.1321016 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

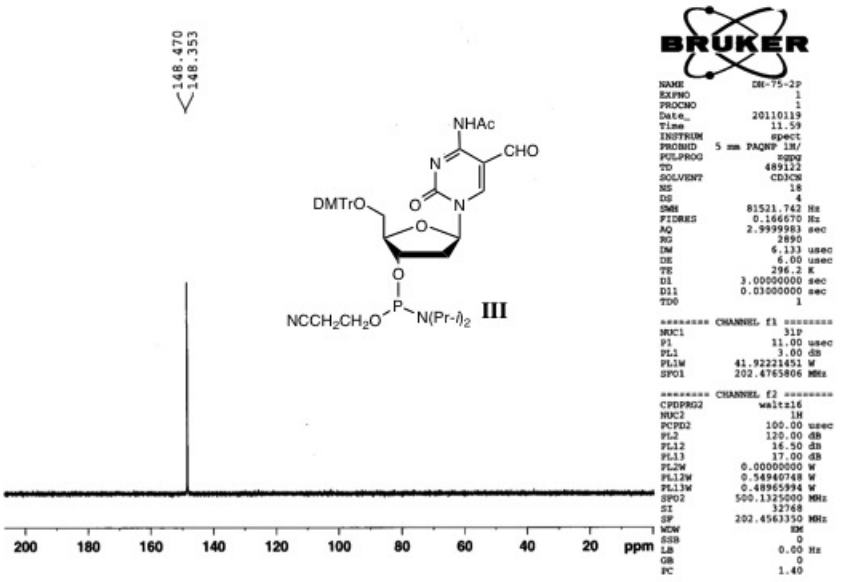

193.380
176.976
163.922
160.340
158.390
110.311
93.004
92.946
82.570
82.312
82.055
73.839
65.225
53.845
53.674
52.992
52.821
46.473
31.361
NHAc
O
N
H
HO
O
N
O
OH
5
200
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME DH-72-1C
EXPNO 1
PROCNO 1
Date_ 20110111
Time 9.32
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CDCl3
NS 208
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.99999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.4 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


8.719
8.522
8.442
7.439
7.426
7.425
7.423
7.349
7.335
7.332
7.324
7.319
7.315
7.311
7.306
7.301
7.295
7.289
7.286
7.284
7.271
6.899
6.895
6.888
6.884
6.881
6.875
6.871
6.864
5.467
3.782
3.778
3.423
3.416
3.374
3.344
2.542
2.497
2.490
1.971
1.966
1.961
1.956
1.951
NHAc
O
N
H
DMTrO
O
N
O
OH
6
11
10
9
8
7
6
5
4
3
2
ppm
0.94
1.07
1.07
2.17
2.26
4.20
1.00
1.06
1.09
6.45
2.22
6.37
BRUKER
NAME DH-73-1H
EXPNO 1
PROCNO 1
Date_ 20110113
Time 17.03
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CD3CN
NS 14
DS 0
SWH 7002.801 Hz
FIDRES 0.155625 Hz
AQ 3.2129073 sec
RG 181
DW 71.400 usec
DE 71.43 usec
TE 295.7 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300039 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


189.437
171.942
160.016
159.874
159.853
155.870
153.522
145.480
136.707
136.403
131.126
131.019
129.115
129.008
128.144
114.207
105.593
88.799
87.591
87.393
70.180
63.308
55.925
41.916
27.107
1.798
0.806
NHAc
O
N
H
DMTrO
O
N
O
OH
6
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
NAME DH-73-1C
EXPNO 1
PROCNO 1
Date_ 20110113
Time 17.09
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CD3CN
NS 218
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.0 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40

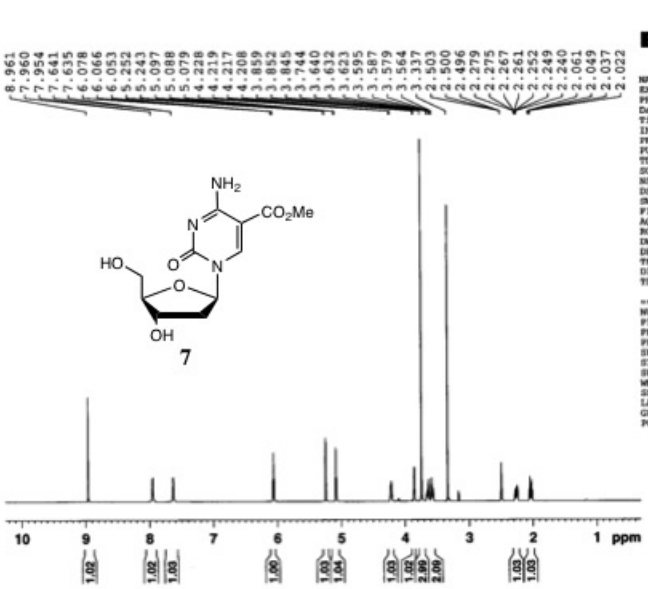

8.763 8.738 8.475 7.442 7.427 7.337 7.333 7.319 7.315 7.311 7.295 7.280 7.274 6.896 6.887 6.880 6.879 6.873 6.869 3.780 3.775 3.747 3.744 3.737 3.723 3.711 3.475 2.670 2.658 2.551 2.539 2.497 2.495 1.961 1.956 1.201 1.187 1.181 1.172 1.167 1.159 1.072 1.058
NHAc
O
N
H
DMTrO
O
N
O
O
P
NCCH2CH2O
N(Pr)2
III
11 10 9 8 7 6 5 4 3 2 1 ppm
0.91 0.99 1.01 9.31 4.15 1.00 0.83 1.13 12.74 7.21 0.82 1.17 15.50
BRUKER
NAME DH-75-1H
EXPNO 1
PROCNO 1
Date_ 20110119
Time 12.05
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CD3CN
NS 16
DS 0
SWH 7002.801 Hz
FIDRES 0.155625 Hz
AQ 3.2129073 sec
RG 64
DW 71.400 usec
DE 71.43 usec
TE 295.8 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300039 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


171.903 160.019 159.986 159.905 155.850 145.400 145.356 136.453 136.316 131.158 129.210 129.161 129.016 128.210 114.212 88.787 88.737 87.672 86.663 86.451 62.956 62.677 59.358 55.944 55.920 44.079 44.037 43.980 41.215 40.770 27.112 24.946 24.887 24.852 24.822 24.764 21.033 20.985 1.807 1.641 0.981 0.816
NHAc
O
N
H
DMTrO
O
N
O
O
P
NCCH2CH2O
N(Pr)2
III
200 180 160 140 120 100 80 60 40 20 0 ppm
BRUKER
NAME DH-75-2C
EXPNO 1
PROCNO 1
Date_ 20110119
Time 12.10
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT CD3CN
NS 170
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



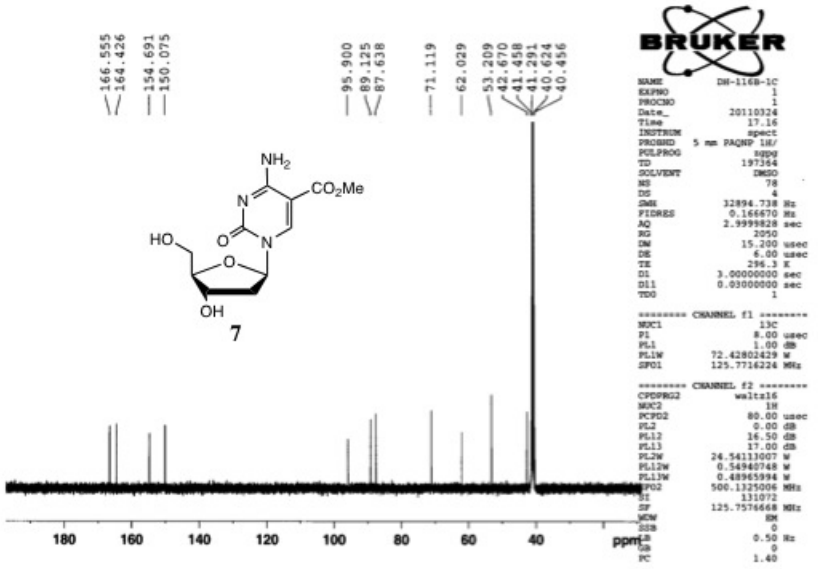
BRUKER

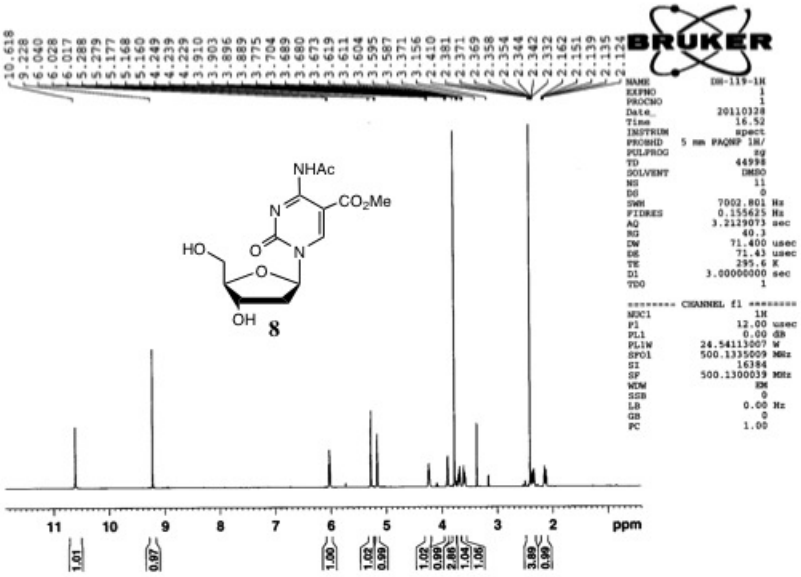
NAME	DM-75-2P
EXPNO	1
PROCNO	1
Date_	20110119
Time	11.59
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg2
TD	489122
SOLVENT	CDICN
NS	18
DS	4
SWH	81521.742 Hz
FIDRES	0.166670 Hz
AQ	2.9999983 sec
RG	2890
DW	6.133 usec
DE	6.00 usec
TE	296.2 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	11.00 usec
PL1	3.00 dB
PL1W	41.92221451 W
SFO1	202.4765806 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	120.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	0.00000000 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325000 MHz
SI	32768
SF	202.4563350 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

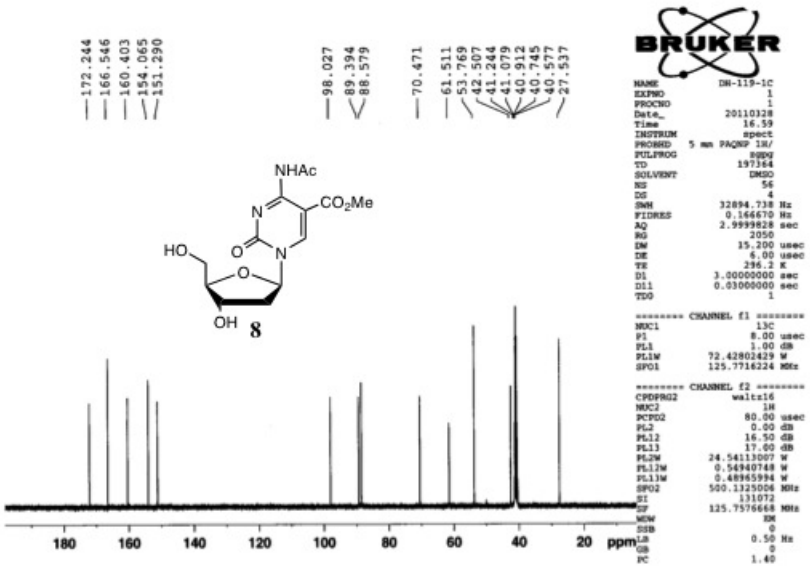


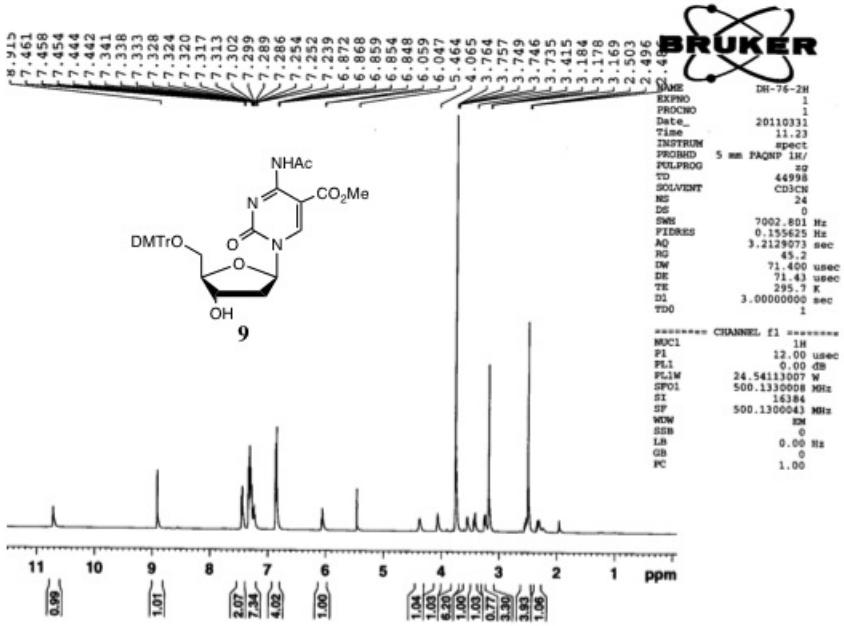
BRUKER

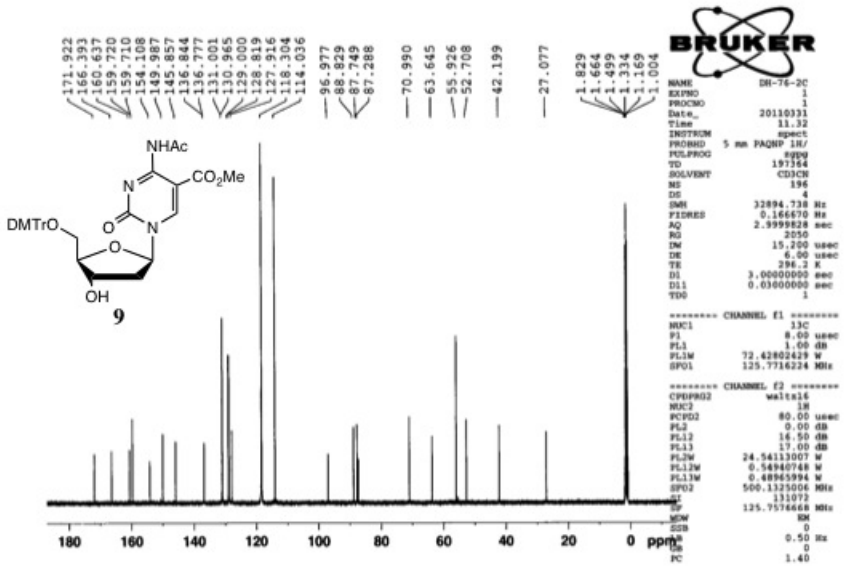
NAME	DM-116B
EXPNO	1
PROCNO	1
Date_	20110324
Time	17.09
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zg
TD	44998
SOLVENT	DMSO
NS	13
DS	0
SWH	7002.801 Hz
FIDRES	0.155625 Hz
AQ	3.2129073 sec
RG	161
DW	71.400 usec
DE	71.43 usec
TE	295.7 K
D1	3.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.00 usec
PL1	0.00 dB
PL1W	24.54113007 W
SFO1	500.1330008 MHz
SI	16384
SF	500.1300019 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

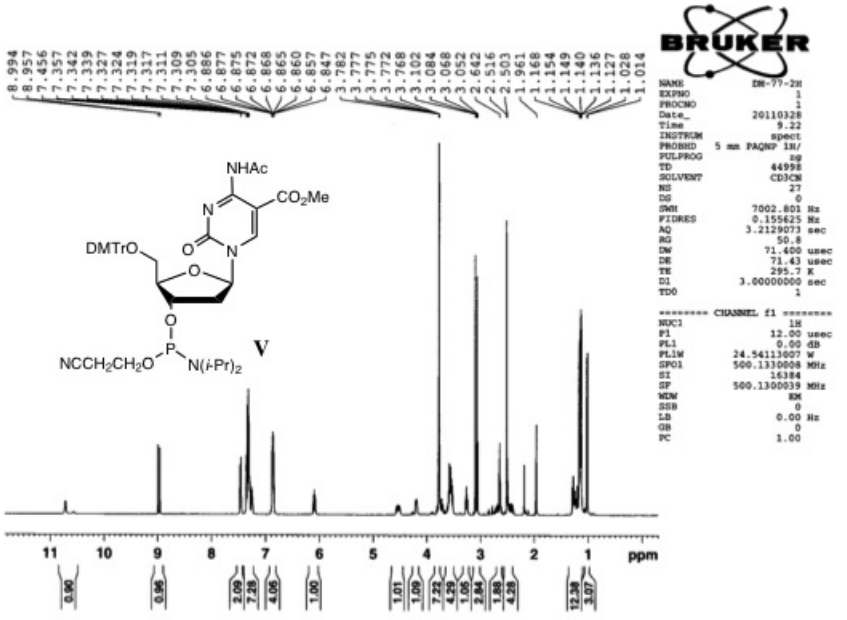

166.555
164.426
154.691
150.075
95.900
89.125
87.638
71.119
62.029
53.209
42.670
41.458
41.291
40.624
40.456
NH2
CO2Me
HO
OH
7
180
160
140
120
100
80
60
40
ppm
BRUKER
NAME DH-116B-1C
EXPNO 1
PROCNO 1
Date_ 20110324
Time 17.16
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT DMSO
NS 78
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.3 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40

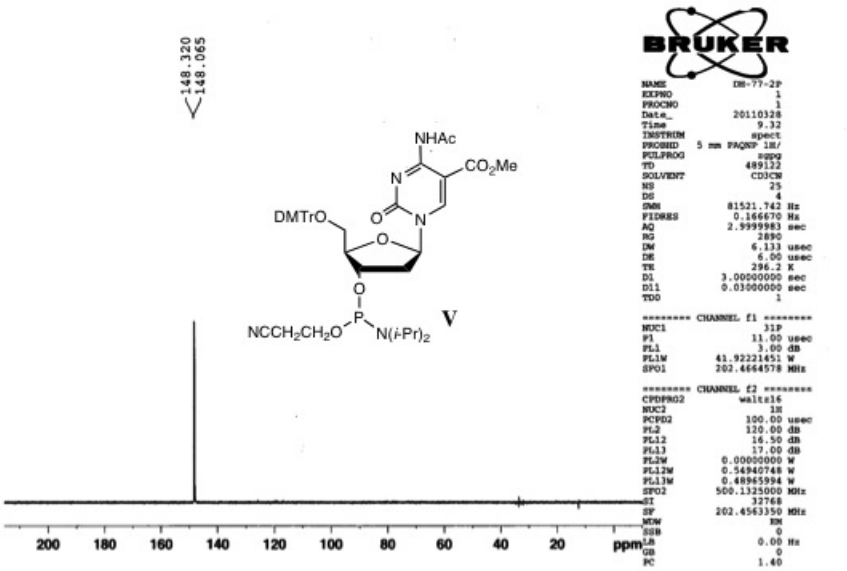

10.618
9.228
6.040
6.028
6.017
5.288
5.279
5.177
5.168
5.160
4.249
4.239
4.229
3.910
3.903
3.896
3.889
3.775
3.704
3.689
3.680
3.673
3.619
3.611
3.604
3.595
3.587
3.371
3.156
2.410
2.381
2.371
2.369
2.358
2.354
2.344
2.342
2.332
2.162
2.151
2.139
2.135
2.124
NHAc
CO2Me
HO
OH
8
11
10
9
8
7
6
5
4
3
2
ppm
1.01
0.97
1.00
1.02
0.99
1.02
0.99
2.86
1.04
1.06
3.89
0.99
BRUKER
NAME DH-119-1H
EXPNO 1
PROCNO 1
Date_ 20110328
Time 16.52
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT DMSO
NS 11
DS 0
SWH 7002.801 Hz
FIDRES 0.155625 Hz
AQ 3.2129073 sec
RG 40.3
DW 71.400 usec
DE 71.43 usec
TE 295.6 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300039 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

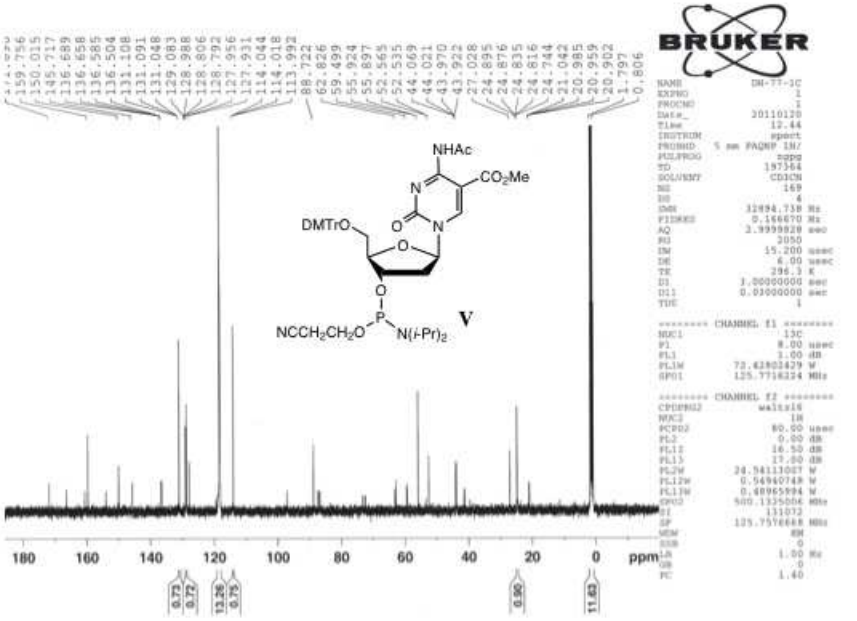

172.244
166.546
160.403
154.065
151.290
98.027
89.394
88.579
70.471
61.511
53.769
42.507
41.244
41.079
40.912
40.745
40.577
27.537
NHAc
CO2Me
HO
OH
8
180
160
140
120
100
80
60
40
20
ppm
BRUKER
NAME DN-119-1C
EXPNO 1
PROCNO 1
Date_ 20110328
Time 16.59
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 197364
SOLVENT DMSO
NS 56
DS 4
SWH 32894.738 Hz
FIDRES 0.166670 Hz
AQ 2.9999828 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 296.2 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7716224 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7576668 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40


8.415
7.461
7.458
7.454
7.444
7.442
7.341
7.338
7.333
7.328
7.324
7.320
7.317
7.313
7.302
7.299
7.289
7.286
7.254
7.252
7.239
6.872
6.868
6.859
6.854
6.848
6.059
6.047
5.464
4.065
3.764
3.757
3.749
3.746
3.735
3.415
3.184
3.178
3.169
2.503
2.496
NHAc
CO2Me
DMTrO
OH
9
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
1.01
2.07
7.34
4.02
1.00
1.04
1.03
6.20
1.00
1.03
0.77
3.30
3.03
1.00
BRUKER
NAME DH-76-2H
EXPNO 1
PROCNO 1
Date_ 20110331
Time 11.23
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CD3CN
NS 24
DS 0
SWH 7002.801 Hz
FIDRES 0.155625 Hz
AQ 3.2129073 sec
RG 45.2
DW 71.400 usec
DE 71.43 usec
TE 295.7 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1330008 MHz
SI 16384
SF 500.1300043 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


NHAc
CO2Me
DMTrO
OH
9
ppm


NHAc
CO2Me
DMTrO
NCCH2CH2O
N(i-Pr)2
V
ppm


148.320
148.065
NHAc
CO2Me
DMTrO
NCCH2CH2O
N(i-Pr)2
V
200
180
160
140
120
100
80
60
40
20
ppm


NHAc
CO2Me
DMTrO
NCCH2CH2O
N(i-Pr)2
V
180
160
140
120
100
80
60
40
20
0
ppm