Supporting Information for

N^2-modified 2-aminopurine ribonucleosides as minor-groove-modulating adenosine replacements in duplex RNA

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General.
All reagents were obtained from commercial sources (Sigma/Aldrich or Fisher Scientific) and were used without further purification unless noted otherwise. Glassware for all reactions was oven dried overnight and cooled in a desiccator prior to use. Reactions were carried out under an atmosphere of dry nitrogen or argon. Liquid reagents were introduced via dry glass syringes. To monitor the progress of reactions, thin layer chromatography (TLC) was performed with Merck silica gel 60 F_{254} precoated plates. Yields were calculated for material that appeared as a single spot by TLC and homogenous by ^{1}H and ^{13}C NMR. Flash chromatography was carried out either manually, using Sorbent silica gel (230-400 mesh) and pressurized air, or with the Combiflash Companion instrument (Teledyne Isco), using RediSep Rf normal phase columns. Radial chromatography was performed using the Chromatotron instrument (Harrison Research) and silica plates. Nuclear magnetic resonance spectra were acquired on Varian spectrometers at the frequencies indicated. Chemical shifts for proton and carbon NMR are reported in parts per million in reference to the solvent peak. The abbreviations s, d, dd, dt, t, td, q, qd, m, and brs stand for singlet, doublet, doublet of doublets, doublet of triplets, triplet, triplet of doublets, quartet, quartet of doublets, multiplet, and broad singlet, respectively. Distilled, deionized water was used for all aqueous reactions and dilutions. High resolution electrospray ionization (ESIHRMS) and fast atom bombardment (FABHRMS) mass spectra were obtained at the University of California, Davis Mass Spectrometry facility or at the Department of Chemistry, University of Utah.

2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-6-chloro-2-amino-purine (1) was synthesized according to a literature procedure. Spectroscopic data agreed with reported values[1].

2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-2-amino-purine (2). 2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-2-amino-6-chloro-9-purine **(1)** (3.75 g, 8.77 mmol) was dissolved in anhydrous MeOH/THF (9:1, 160 mL). Palladium (10% on carbon) (1.5 g) and sodium acetate (1.58 g, 19.3 mmol) were added under inert atmosphere. The atmosphere was replaced with 60psi H_2 and the mixture was shaken at rt for 15 h. The catalyst was removed by filtration (celite) and the filtrate was concentrated under reduced pressure. The residue was diluted with EtOAc (150 mL) and H_2O (150 mL) and the aqueous layer was separated and extracted with EtOAc (150 mL). The combined organic layers were washed with saturated aqueous NaCl (150 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash chromatography (0 → 5% MeOH in CH_2Cl_2) afforded **2** as a white foam (2.90 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.83 (s, 1H), 6.01 (d, J = 4.8 Hz, 1H), 5.97 (t, J = 5.1 Hz, 1H), 5.79 (t, J = 5.1 Hz, 1H), 5.08 (brs, 2H), 4.46 – 4.40 (m, 2H), 4.35 (dd, J = 11.6, 4.5 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 169.8, 169.6, 160.2, 152.8, 150.6, 140.9, 128.8, 86.4, 80.1, 73.0, 70.7, 63.2, 20.9, 20.7, 20.6. ESIHRMS: calcd for $C_{16}H_{19}N_5O_7$ $(M + H)^+$: 394.1357, obsd 394.1354.

2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-2-fluoro-purine (3). 2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-2-amino-purine **(2)** (2.42 g, 6.14 mmol) was dissolved in 15 mL 60% HF/pyridine in a 50 mL polypropylene centrifuge tube at -40°C. The 60% HF/pyridine solution was generated immediately before use by diluting 70% HF/pyridine with anhydrous pyridine in a separate polypropylene tube. t-Butyl nitrite (1.3 g, 13mmol) was added dropwise. The headspace was filled with Ar and the cap was loosely fastened. After stirring for 3.5 h at -40°C, the reaction mixture was diluted with 20mL CH_2Cl_2, poured slowly onto 25 g solid K_2CO_3 and diluted with a further 50 mL CH_2Cl_2 and 50 mL H_2O. The aqueous layer was separated and extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL) and H_2O (100 mL), dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash chromatography (0 → 5% MeOH in CH_2Cl_2) afforded **3** as a white foam (2.26 g, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.22 (s, 1H), 6.17 (d, *J* = 5.6 Hz, 1H), 5.83 (t, *J* = 5.6 Hz, 1H), 5.57 (dd, *J* = 5.4, 4.5 Hz, 1H), 4.45 (dd, *J* = 7.3, 4.1 Hz, 1H), 4.41 (dd, *J* = 12.4, 3.0 Hz, 1H), 4.37 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 169.7, 169.5, 159.7, 158.3, 153.5, 151.6, 144.4, 133.7, 86.4, 80.8, 73.2, 70.7, 63.1, 20.9, 20.7, 20.5. ESIHRMS: calcd for $C_{16}H_{17}FN_4O_7$ $(M + H)^+$: 397.1154, obsd 397.1156.

General procedure for the synthesis of N^2-substituted 2-aminopurine ribonucleoside derivatives 4-6. 2',3',5'-Tri-*O*-acetyl-9-(β-D-ribofuranosyl)-2-fluoro-purine **(3) (**594 mg, 1.50 mmol) was dissolved in 2.0 mL anhydrous DMF or THF as indicated below, treated with the appropriate amine (5 equiv) and stirred. Disappearance of the SM to give highly fluorescent compounds of lower Rf (TLC, 10% MeOH in CH_2Cl_2) indicates completion of the substitution reaction. At this point, 10 mL NH_3/MeOH (saturated solution) was added. After 15 h at RT, TLC showed a single component, indicating that acetyl deprotection was complete, and the reaction mixture was concentrated under reduced pressure, absorbed onto silica gel, and purified by flash chromatography (10% MeOH in CH_2Cl_2).

9-(β-D-Ribofuranosyl)-2-propylamino-purine (4). Amine: Propylamine (443 mg, 7.5 mmol). Solvent: DMF. Reaction for 30 min at RT before addition of NH_3/MeOH. A white solid (362 mg, 78%). ^{1}H NMR (600 MHz, CD_3OD) δ 8.54 (s, 1H), 8.24 (s, 1H), 5.96 (d, *J* = 5.5 Hz, 1H), 4.78 (t, *J* = 5.4 Hz, 1H), 4.37 (dd, *J* = 5.1, 4.0 Hz, 1H), 4.11 (dd, *J* = 7.3, 3.7 Hz, 1H), 3.86 (dd, *J* = 12.1, 3.3 Hz, 1H), 3.76 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.36 (dd, *J* = 11.5, 4.3 Hz, 2H), 1.68 – 1.62 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 161.3, 154.4, 150.3, 143.3, 128.2, 90.1, 87.2, 75.2, 72.4, 63.3, 44.7, 23.8, 11.9. ESIHRMS: calcd for $C_{13}H_{19}N_5O_4$ $(M + H)^+$: 310.1510, obsd 310.1509.

9-(β-D-Ribofuranosyl)- 2-cyclopentylamino-purine (5). Amine: Cyclopentylamine (639 mg, 7.5 mmol). Solvent: DMF. Reaction for 30 min at RT before addition of NH_3/MeOH. A white foam (423 mg, 84%). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.62 (s, 1H), 8.26 (s, 1H), 7.10 (brs, 1H), 5.83 (d, *J* = 5.9 Hz, 1H), 5.42 (d, *J* = 6.1 Hz, 1H), 5.16 (d, *J* = 4.8 Hz, 1H), 4.95 (t, *J* = 5.1 Hz, 1H), 4.63 (brs, 1H), 4.21 – 4.12 (m, 2H), 3.89 (q, *J* = 4.4 Hz, 1H), 3.64 (dt, *J* = 11.7, 4.9 Hz, 1H), 3.53 (dt, *J* = 10.3, 4.8 Hz, 1H), 1.95 – 1.88 (m, 2H), 1.71 – 1.65 (m, 2H), 1.57 – 1.44 (m, 4H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$) δ 159.2, 152.9, 149.2, 141.0, 126.9, 86.7, 85.3, 73.0, 70.5, 61.6, 52.6, 32.2, 23.4. ESIHRMS: calcd for $C_{15}H_{21}N_5O_4$ $(M + H)^+$: 336.1667, obsd 336.1668.

9-(β-D-Ribofuranosyl)- 2-propargylamino-purine (6). Amine: Propargylamine (413 mg, 7.5 mmol). Solvent: THF. Reaction for 3 h at 65°C before addition of NH_3/MeOH. A white solid (327 mg, 71%). ^{1}H NMR (600 MHz, $(CD_3)_2SO$) δ 8.70 (s, 1H), 8.34 (s, 1H), 7.45 (brs, 1H), 5.86 (d, *J* = 5.9 Hz, 1H), 5.43 (d, *J* = 6.1 Hz, 1H), 5.17 (d, *J* = 4.8 Hz, 1H), 4.96 (t, *J* = 5.4 Hz, 1H), 4.62 (d, *J* = 4.9 Hz, 1H), 4.16 (dd, *J* = 8.5, 4.8 Hz, 1H), 4.11 – 4.07 (m, 2H), 3.91 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.65 (dt, *J* = 11.6, 4.9 Hz, 1H), 3.55 (dt, *J* = 11.4, 4.8 Hz, 1H), 2.98 (d, *J* = 1.62 Hz, 1H). ^{13}C NMR

(151 MHz, CD_3OD) δ 160.6, 154.2, 150.3, 143.8, 128.9, 90.2, 87.1, 82.3, 75.2, 72.3, 71.5, 63.3, 32.2. ESIHRMS: calcd for $C_{13}H_{15}N_5O_4$ $(M + H)^+$: 306.1020, obsd 306.1018.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-amino-purine (7) was synthesized according to a literature procedure. Spectroscopic data agreed with reported values.[2]

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-bromo-purine (8). A solution of 2',3',5'-tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-amino-purine **(7)** (145 mg, 0.24 mmol) in CH_2Br_2 (15 mL) was treated with *t*BuONO (565 µL, 4.8 mmol) and TMSBr (123 µL, 0.95 mmol). The reaction mixture was allowed to stir at 0 °C for 1 hour and for an additional 3 hours at room temperature. The resulting reaction mixture was concentrated to dryness under reduced pressure, re-dissolved in CH_2Cl_2 (20 mL), and washed with saturated aqueous NaCl (10 mL). The organic portion was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2) to afford **9** as a yellow foam (109 mg, 68 %). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.90 (s, 1H), 8.50 (s, 1H), 6.04 (d, *J* = 4.6 Hz, 1H), 4.61-4.58 (m, 1H), 4.34-4.31 (m, 1H), 4.17 (dd, *J* = 3.9, 2.7 Hz, 1H), 4.07-3.79 (m, 2H), 0.96 (s, 9 H), 0.94 (s, 9 H), 0.82 (s, 9 H), 0.16 (s, 3H), 0.15 (s, 3H), 0.13 (s, 3H), 0.11 (s, 3H), 0.00 (s, 3H), -0.20 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 153.2, 150.7, 145.3, 145.2, 134.9, 89.3, 86.2, 76.7, 72.3, 62.9, 26.4, 26.2, 26.0, 19.0, 18.5, 18.3, -4.0, -4.3, -4.4, -4.8, -5.1, -5.2. FABHRMS: calcd. for $C_{28}H_{54}BrN_4O_4Si_3$ $(M + H)^+$ 673.2636, obsd. 673.2650.

General procedure for the synthesis of 2',3',5'-tri-*O*-*tert*-butyldimethylsilyl-N^2–substituted 2-aminopurine ribonucleoside derivatives 9-14.
A solution of 2',3',5'-tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-bromo-purine **(8)** (68.4 mg, 0.10 mmol) in DMF (1.5 mL) was treated with the appropriate amine (10 equiv) and resulting reaction mixture was stirred at 75-80 °C. Upon completion of the reaction, the mixture was cooled to RT and dissolved in Hexanes/EtOAc 3:7 (25 mL). The organic portion was washed with water (15 mL) and aqueous saturated NaCl (15 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude material was purified by column chromatography with the solvent systems indicated.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-butylamino-purine (9). Amine: Butylamine (73.1 mg, 1.0 mmol). Reaction for 2.5 h. Chromatography: 30% EtOAc in hexanes. A slightly yellow foam (66%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.58 (s, 1H), 8.04 (s, 1H), 5.96 (d, *J* = 4.88 Hz, 1H), 5.17 (brs, 1H), 4.59 (t, *J* = 4.64 Hz, 1H), 4.33-4.31 (m, 1H), 4.12-4.10 (m, 1H), 4.00-3.78 (m, 2H), 3.46-3.39 (m, 2H), 1.66-1.56 (m, 4H), 1.49-1.36 (m, 3H), 0.95 (s, 9H), 0.94 (s, 9 H), 0.81 (s, 9H), 0.13-0.11 (m, 12H), 0.02 (s, 3H), -0.17 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.5, 153.6, 150.2, 140.8, 128.5, 88.0, 85.5, 76.2, 72.5, 63.1, 42.2, 32.3, 26.4, 26.2, 26.1, 20.8, 18.9, 18.5, 18.4, 14.3, -4.1, -4.3, -4.4, -4.6, -5.0, -5.1. FABHRMS: calcd. for $C_{32}H_{64}N_5O_4Si_3$ $(M + H)^+$ 666.4266, obsd. 666.4242.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-cyclohexylamino-purine (10). Amine: Cyclohexylamine (99.2 mg, 1.0 mmol). Reaction for 3.5 h. Chromatography: Hexanes/EtOAc 5:1. A white foam (78%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.57 (s, 1H), 8.05 (s, 1H), 5.99 (d, *J* = 4.88 Hz, 1H), 5.22 (brs, 1H), 4.51 (t, *J* = 4.5, 1H), 4.34-4.31 (m, 1H), 4.11-4.08 (m, 1H), 4.00-3.79 (m, 2H), 2.06-1.19 (m, 11H), 0.96 (s, 9H), 0.95 (s, 9H), 0.81 (s, 9H), 0.14- 0.12 (m, 12H), 0.01 (s, 3H), -0.16 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 159.7, 153.7, 150.2, 140.6, 128.3, 87.6, 85.5, 76.5, 72.4, 63.1, 50.4, 33.8, 26.4, 26.3, 26.2, 26.0, 25.6, 25.5, 18.9, 18.5, 18.3, -4.1, -4.3, -4.5, -5.0, -5.1. FABHRMS: calcd. for $C_{34}H_{66}N_5O_4Si_3$ $(M + H)^+$ 692.4422, obsd. 691.4338.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-benzylamino-purine (11). Amine: Benzylamine (107 mg, 1.0 mmol). Reaction for 5 h. Chromatography: Hexanes/EtOAc 5:1. A white straw foam (64%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.61 (s, 1H), 8.09 (s, 1H), 7.38-7.25 (m, 5H), 5.96 (d, *J* = 5.13 Hz, 1H), 5.55 (brs, 1 H), 4.69-4.64 (m, 2H), 4.55 (t, *J* = 4.64, 1H), 4.32-4.30 (m, 1H), 4.11-4.08 (m, 1H), 3.99-3.78 (m, 2H), 0.94 (s, 9 H), 0.94 (s, 9 H), 0.79 (s, 9 H), 0.12-0.11 (s, 12H), -0.05 (s, 3H), -0.22 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.1, 150.2, 141.1, 140.2, 129.0, 128.0, 127.6, 87.9, 85.7, 76.3, 72.5, 63.1, 46.4, 26.4, 26.2, 26.0, 18.9, 18.5, 18.3, -4.1, -4.3, -4.4, -4.7, -5.1. FABHRMS: calcd. for $C_{35}H_{62}N_5O_4Si_3$ (M + H)$^+$ 700.4109, obsd. 700.4089.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-(6''-hydroxyhexyl)amino-purine (12). Amine: Hexylamine (101 mg, 1.0 mmol). Reaction for 1 h. Chromatography: Hexanes/EtOAc 1:1. A white foam (80%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.58 (s, 1H), 8.08 (s, 1H), 5.97 (d, *J* = 4.98 Hz, 1H), 5.55 (brs, 1 H), 4.60-4.56 (m, 1H), 4.33-4.31 (m, 1H), 4.12-4.09 (m, 1H), 4.00-3.79 (m, 1H), 3.61-3.56 (m, 2H), 3.52-3.34 (m, 2H), 2.28 (s, 1H), 1.66-1.40 (m, 8H), 0.96 (s, 9 H), 0.94 (s, 9 H), 0.82 (s, 9 H), 0.14 (s, 6H), 0.13 (s, 3H), 0.12 (s, 3H), 0.01 (s, 3H), -0.15 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.4, 153.6, 150.1, 140.9, 128.3, 88.0, 85.5, 76.3, 72.4, 63.1, 63.0, 42.4, 33.4, 30.1, 27.4, 26.4, 26.2, 26.1, 18.9, 18.5, 18.3, -4.0, -4.3, -4.4, -4.5, -5.0, -5.1. ESIHRMS: calcd. for $C_{34}H_{68}N_5O_5Si_3$ (M + H)$^+$ 710.4528, obsd. 710.4526.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-cyclopentylamino-purine (13). Amine: Cyclopentylamine (85.2 mg, 1.0 mmol). Reaction for 2.5 h. Chromatography: Hexanes/EtOAc 5:1. A white foam (77%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.58 (s, 1H), 8.04 (s, 1H), 5.96 (d, *J* = 5.28 Hz, 1H), 5.29-5.27 (brs, 1 H), 4.60 (t, *J* = 4.8 Hz, 1H), 4.34-4.28 (m, 1H), 4.12-4.08 (m, 1H), 4.00-3.80 (m, 2H), 3.62-3.58 (m, 2H), 2.12-1.47 (m, 9H), 0.96 (s, 9 H), 0.95 (s, 9 H), 0.81 (s, 9 H), 0.14-0.12 (m, 12H), 0.01 (s, 3H), -0.17 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.0, 153.6, 150.2, 140.8, 128.4, 87.9, 85.6, 76.1, 72.5, 63.1, 33.8, 26.4, 26.2, 26.0, 24.3, 24.2, 18.9, 18.5, 18.3, -4.1, -4.4, -4.6, -5.0, -5.1. ESIHRMS: calcd. for $C_{33}H_{64}N_5O_4Si_3$ (M + H)$^+$ 678.4266, obsd. 678.4267.

2',3',5'-Tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-piperidino-purine (14). Amine: Piperidine (85.2 mg, 1.0 mmol). Reaction for 1 h. Chromatography: Hexanes/EtOAc 9:1. A white foam (54%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.63 (s, 1H), 8.05 (s, 1H), 5.95 (d, *J* = 4.68 Hz, 1H), 4.65-4.62 (m, 1H), 4.34 (t, *J* = 4.1 Hz, 1H), 4.11-4.08 (m, 1H), 4.00-3.79 (m, 4H), 1.68-1.60 (m, 6H), 0.96 (s, 9 H), 0.95 (s, 9 H), 0.83 (s, 9 H), 0.14-0.12 (m, 12H), 0.01 (s, 3H), -0.15 (s, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 159.7, 153.6, 149.6, 141.2, 127.8, 88.2, 85.3, 75.9, 72.3, 63.1, 46.0, 26.4, 26.3, 26.2, 26.1, 25.5, 18.9, 18.5, 18.4, -4.0, -4.3, -4.4, -4.6, -5.0, -5.1. ESIHRMS: calcd. for $C_{33}H_{64}N_5O_4Si_3$ (M + H)$^+$ 678.4266, obsd. 678.4258.

9-(β-D-Ribofuranosyl)-2-benzylamino-purine (15). 1.0 M TBAF/THF (1.3 ml, 1.3 mmol) was added to a solution of 2',3',5'-tri-*O*-*tert*-butyldimethylsilyl-9-(β-D-ribofuranosyl)-2-benzylamino-purine **(11)** (300 mg, 0.43 mmol) in THF (4 mL) cooled in an ice-bath. The resulting reaction mixture was warmed to room temperature and stirred for 2 hours. The reaction mixture was pre-absorbed on silica gel, and purified by flash column chromatography (Hexanes/EtOAc 1:1 followed by 8% CH_3OH/CH_2Cl_2) to give a white foam (139 mg, 91%). ^{1}H NMR (CD_3OD, 300 MHz): δ 8.52 (s, 1H), 8.23 (s, 1H), 7.36–7.15 (m, 5H), 5.94 (d, *J* = 5.6 Hz, 1H), 4.73-4.69 (m, 1H), 4.60 (s, 2H), 4.33-4.30 (m, 1H), 4.09-4.05 (m, 1H), 3.82-3.65 (m, 2H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 161.1, 154.2, 150.3, 143.4, 141.2, 129.5, 128.5, 128.0, 90.1, 87.0, 75.1, 72.2, 63.2, 46.5. FABHRMS: calcd. for $C_{17}H_{20}N_5O_4$ (M + H)$^+$ 358.1515, obsd. 358.1516.

General procedure for the synthesis of 5'-*O*-DMTr ribonucleoside derivatives 16-18. DMTrCl (1.1 eq) and DMAP (0.1 eq) were added to a solution of free ribonucleoside derivative **(4-6)** in anhydrous pyridine. The reaction mixture was stirred at RT for 4h. It was then diluted with EtOAc (25 mL) and washed with saturated aqueous $NaHCO_3$ (2 x 40 mL). The organic layer was

dried (Na_2SO_4), and concentrated under reduced pressure. Purification by flash chromatography (CH_2Cl_2/MeOH/Et_3N 98:1:1). Et_3N was removed from combined column fractions as an azeotrope with acetonitrile.

5'-*O*-(4,4'-Dimethoxytrityl)- 9-(β-D-ribofuranosyl)-2-propylamino-purine (16). Ribonucleoside: **4** (282 mg, 0.91 mmol). Volume of solvent: 2 mL. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.60 (s, 1H), 7.88 (s, 1H), 7.35 – 7.13 (m, 9H), 6.76 (dd, *J* = 8.9, 6.3 Hz, 4H), 5.88 (d, *J* = 5.9 Hz, 1H), 4.82 (t, *J* = 5.6 Hz, 1H), 4.41 (dd, *J* = 5.2, 2.5 Hz, 1H), 4.34 (dd, *J* = 6.3, 3.8 Hz, 1H), 3.75 (s, 6H), 3.40 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.32 – 3.24 (m, 3H), 1.65 – 1.56 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.8, 159.2, 150.7, 145.2, 140.5, 136.1, 136.0, 130.5, 130.5, 128.5, 128.4, 127.4, 113.6, 90.5, 87.0, 86.2, 75.7, 73.0, 64.4, 55.7, 44.3, 23.1, 11.8. ESIHRMS: calcd for $C_{34}H_{37}N_5O_6$ $(M + H)^+$: 612.2816, obsd 612.2814.

5'-*O*-(4,4'-Dimethoxytrityl)- 9-(β-D-ribofuranosyl)-2-cyclopentylamino-purine (17). Ribonucleoside: **5** (436 mg, 1.30 mmol). Volume of solvent: 4 mL. A white foam (564 mg, 68%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.62 (s, 1H), 7.88 (s, 1H), 7.35 – 7.16 (m, 9H), 6.78 – 6.74 (m, 4H), 5.87 (d, *J* = 5.8 Hz, 1H), 5.65 (brs, 1H), 4.83 (t, *J* = 5.5 Hz, 1H), 4.42 (d, *J* = 5.0 Hz, 1H), 4.35 – 4.34 (m, 1H), 4.14 (d, *J* = 5.7 Hz, 1H), 3.76 (s, 6H), 3.41 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.29 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.09 – 1.98 (m, 2H), 1.77 – 1.60 (m, 4H), 1.54 – 1.45 (m, 2H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 159.5, 159.1, 153.0, 150.3, 145.2, 140. 7, 136.2, 136.1, 130.5, 128.5, 128.4, 127.4, 113.6, 90. 1, 86.9, 85.8, 75.2, 72.7, 64.5, 55.7, 53.9, 33.6, 24.3. ESIHRMS: calcd for $C_{36}H_{39}N_5O_6$ $(M + H)^+$: 638.2973, obsd 638.2977.

5'-*O*-(4,4'-Dimethoxytrityl)- 9-(β-D-ribofuranosyl)-2-propargylamino-purine (18). Ribonucleoside: **6** (550 mg, 1.30 mmol). Volume of solvent: 4 mL. A white solid (777 mg, 71%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.65 (s, 1H), 7.91 (s, 1H), 7.42 – 7.15 (m, 9H), 6.78 (dd, *J* = 8.6, 4.1 Hz, 4H), 5.94 (d, *J* = 5.3 Hz, 1H), 5.73 (brs, 1H), 4.89 (t, *J* = 5.3 Hz, 1H), 4.49 (t, *J* = 4.2 Hz, 1H), 4.32 (d, *J* = 3.6 Hz, 1H), 4.15 – 4.08 (m, 2H), 3.76 (s, 6H), 3.44 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.37 (dd, *J* = 10.4, 4.5 Hz, 1H), 2.22 (s, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 159.5, 159.2, 153.2, 150.6, 145. 4, 141.7, 136.5, 130.7, 129.2, 128.9, 128.5, 127.6, 113.9, 90.4, 87.3, 85.7, 81.5, 75.4, 72.8, 71. 3, 64.7, 55.9, 32.4. ESIHRMS: calcd for $C_{34}H_{33}N_5O_6$ $(M + H)^+$: 608.2503, obsd 608.2506.

General procedure for the synthesis of 5'-*O*-DMTr, 2'-*O*-TBDMS ribonucleoside derivatives 19-21.
Triethylamine (2.0 eq), TBDMSCl (1.1 eq) and $AgNO_3$ (1.1 eq) were consecutively added to a solution of 5'-*O*-DMTr protected derivative **16-18** in anhydrous THF. The resulting reaction mixture was stirred at RT for 12 h. It was then diluted with EtOAc (25 mL), filtered, and washed with saturated aqueous $NaHCO_3$ (1 x 30 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude products were purified by radial chromatography, eluting with the solvents indicated. The identity of 2'-O-/3'-O-TBDMS regioisomers was confirmed by COSY NMR. The 3'-O-TBDMS side-product was re-equilibrated (3% triethylamine in MeOH, overnight, RT) to yield 2'-O- and 3'-O-TBDMS isomers, which was concentrated and fractioned again to yield additional 2'-O-TBDMS product.

5'-*O*-(4,4'-Dimethoxytrityl)- 2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-propylamino-purine (19). DMTr derivative: **16** (353 mg, 0.58 mmol). Volume of solvent: 3 mL. Chromatography: 20 → 60% EtOAc in hexanes. A white foam (243 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.85 (s, 1H), 7.48 – 7.16 (m, 9H), 6.78 (dd, *J* = 8.9, 1.4 Hz, 4H), 5.92 (d, *J* = 5.2 Hz, 1H), 4.98 (brs, 2H), 4.36 (dd, *J* = 8.0, 3.8 Hz, 1H), 4.20 (dd, *J* = 7.1, 3.6 Hz, 1H), 3.75 (s, 6H), 3.49 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.36 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.32 – 3.18 (m, 2H), 2.70 (d, *J* = 3.9 Hz, 1H), 1.49 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.32 – 1.20 (m, 3H), 0.84 (s, 9H), -0.01 (s, 3H), -0.15 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 158.8, 153.3, 150.2, 144.9, 140.7, 135.9, 130.3, 128.4, 128.1, 127.2, 113.4, 87.9, 86.8, 84.1, 71.7, 63.9, 55.4, 43.9, 25.8, 22.9, 18.1, 11.6, -

4.7, -4.9. ESIHRMS: calcd for $C_{40}H_{51}N_5O_6Si$ $(M + H)^+$: 726.3681, obsd: 726.3668.

5'-*O*-(4,4'-Dimethoxytrityl)- 2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-cyclopentylamino-purine (20). DMTr derivative: **17** (388 mg, 0.61 mmol). Volume of solvent: 3 mL. Chromatography: 20 → 60% EtOAc in hexanes. A white foam (256 mg, 56%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.63 (s, 1H), 7.85 (s, 1H), 7.49 – 7.18 (m, 9H), 6.82 – 6.78 (m, 4H), 5.92 (d, *J* = 4.8 Hz, 1H), 5.18 (brs, 1H), 5.02 (brs, 1H), 4.39 (d, *J* = 4.3 Hz, 1H), 4.21 – 4.09 (m, 2H), 3.77 (s, 6H), 3.46 – 3.32 (m, 2H), 2.74 (d, *J* = 4.1 Hz, 1H), 1.99 – 1.86 (m, 2H), 1.70 – 1.51 (m, 4H), 1.41 – 1.32 (m, 2H), 0.87 (s, 9H), 0.03 (s, 3H), -0.09 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 159.7, 158.9, 153.2, 150.0, 145.1, 140.6, 135.9, 130.3, 130.2, 128.3, 128.0, 127.1, 113.3, 88.3, 86.6, 84.0, 75.1, 71.6, 64.0, 55.4, 33.4, 33.3, 25. 6, 23.9, 18.0, -5.0, -5.2. ESIHRMS: calcd for $C_{42}H_{53}N_5O_6Si$ $(M + H)^+$: 752.3838, obsd: 752.3848.

5'-*O*-(4,4'-Dimethoxytrityl)- 2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-propargylamino-purine (21). DMTr derivative: **18** (293 mg, 0.48 mmol). Volume of solvent: 2 mL. Chromatography: 30 → 70% EtOAc in hexanes. A white foam (177 mg, 51%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.70 (s, 1H), 7.91 (s, 1H), 7.49 – 7.15 (m, 9H), 6.85 – 6.77 (m, 4H), 5.93 (d, *J* = 5.0 Hz, 1H), 5.43 (brs, 1H), 4.99 (t, *J* = 5.1 Hz, 1H), 4.39 (q, *J* = 4.3 Hz, 1H), 4.21 (q, *J* = 4.0 Hz, 1H), 4.12 – 4.05 (m, 2H), 3.77 (s, 6H), 3.43 (qd, *J* = 10.4, 4.1 Hz, 2H), 2.74 (d, *J* = 4.6 Hz, 1H), 2.20 (t, *J* = 2.4 Hz, 1H), 0.86 (s, 9H), 0.02 (s, 3H), -0.12 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 159.2, 153.3, 150.5, 145. 4, 141.6, 136.2, 136.1, 130.6, 128.6, 128.4, 127.4, 113.6, 88.7, 87.0, 84.4, 81.6, 75.5, 72.0, 70.9, 64.2, 55.7, 32.1, 25.9, 18.3, -4.6, -4.8. ESIHRMS: calcd for $C_{40}H_{47}N_5O_6Si$ $(M + H)^+$: 722.3368, obsd: 722.3366.

General procedure for the synthesis of 5'-*O*-DMTr, 3' *O*-[(2-cyanoethoxy)(*N*,*N*-diisopropylamino)phosphino], 2'-O-TBDMS ribonucleoside derivatives 22-24. *N,N*-Diisopropylethylamine (6 eq) and 2-cyanoethyl-(*N,N*-diisopropylamino)chlorophosphite (1.1 eq) were consecutively added to a solution of 5'-O-DMTr, 2'-O-TBDMS protected derivative **19-21** in 1 mL anhydrous THF. The reaction mixture was stirred for 5 h. It was then diluted with EtOAc (25mL) and washed with 5% (w/v) aqueous $NaHCO_3$ (2 x 15 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. Purification by flash chromatography (30 → 70% EtOAc in hexanes).

5'-*O*-(4,4'-Dimethoxytrityl)-3'-*O*-[(2-cyanoethoxy)(*N*,*N*-diisopropylamino)phosphino]-2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-propylamino-purine (22). DMTr/TBDMS derivative: **19** (123 mg, 0.17 mmol). A white foam (127 mg, 81%). ^{31}P NMR (121 MHz, $CDCl_3$) δ 152.27, 150.16. ESIHRMS: calcd for $C_{49}H_{68}N_7O_7PSi$ $(M + H)^+$: 926.4760, obsd: 926.4789.

5'-*O*-(4,4'-Dimethoxytrityl)- 3'-*O*-[(2-cyanoethoxy)(*N*,*N*-diisopropylamino)phosphino]-2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-cyclopentylamino-purine (23). DMTr/TBDMS derivative: **20** (112 mg, 0.15 mmol). A white foam (118 mg, 83%). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 151.91, 150.14. ESIHRMS: calcd for $C_{51}H_{70}N_7O_7PSi$ $(M + H)^+$: 952.4916, obsd: 952.4914.

5'-*O*-(4,4'-Dimethoxytrityl)- 3'-*O*-[(2-cyanoethoxy)(*N*,*N*-diisopropylamino)phosphino]-2'-*O*-(*tert*-butyldimethylsilyl)-9-(β-D-ribofuranosyl)-2-propargylamino-purine (24). DMTr/TBDMS derivative: **21** (99.0 mg, 0.14 mmol). A white foam (98.6 mg, 78%). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 151.74, 150.19. ESIHRMS: calcd for $C_{49}H_{64}N_7O_7PSi$ $(M + H)^+$: 922.4447, obsd: 922.4455.

Synthesis of RNAs.
RNA oligonucleotides were synthesized on an ABI 394 synthesizer (DNA/Peptide Core Facility, University of Utah) at 1.0 μmol scale using 5'-DMTr, 2'-OTBDMS protected β-cyanoethyl phosphoramidites. Deprotection was carried out as previously described[3].

RNA purification and quantification.
RNAs were purified by urea-polyacrylamide gel electrophoresis (PAGE) (19%). After electrophoresis, the RNA bands were visualized by UV shadowing (254 nm light, F_{254} TLC plate as a backing), and extracted from the gel via the crush and soak method at 4°C overnight in to 0.5 M NH_4OAc containing 0.1 mM EDTA. Polyacrylamide particles were removed using a Centrex filter (0.2 μm) and the oligonucleotide solution was desalted using C_{18} Sep-Pak cartridges, eluting with 1:1 CH_3CN/H_2O. The oligonucleotide solutions were lyophilized to dryness, resuspended in H_2O and quantified by absorbance measurements at 260 nm. The extinction coefficients for the oligonucleotides were calculated as the sum of the extinction coefficients of the component nucleotides using adenosine as a replacement for all modifications.

Mass spectrometery analysis of RNAs.
Mass spectra were obtained on a LTQ-Orbitrap instrument (Thermo-Fisher Scientific, San Jose, CA) by loop injection of a 10-20 μM RNA sample (in 1:1 CH_3CN/H_2O or H_2O) into a 100 μl/min flow of 1:1 MeOH/(200mM hexafluoroisopropanol/Et_3N in H_2O, pH 7.9) using the IonMax source. Spectra were recorded between 400 and 1700 m/z in negative ion mode at 15,000 resolution with standard source conditions and deconvoluted using MassLynx software.

Preparation of Tris-[1-(3-hydroxypropyl)-1H-[1,2,3]triazol-4-yl)methyl]amine (ligand for CuAAc)[4]
3-Azido-1-propanol (prepared according to a literature procedure[5]) (1.33 g, 13.2 mmol) was dissolved in 6 mL 1:1 $tBuOH/H_2O$. Tripropargylamine (393 mg, 3.00 mmol) was added, followed by $CuSO_4.5H_2O$ (75 mg, 0.30 mmol) and sodium ascorbate (119 mg, 0.60 mmol). The solution was stirred at ambient temperature for 20 h, at which point TLC (1/1 EtOAc/hex, permanganate stain) showed consumption of the tripropargylamine. The mixture was evaporated to a thick oil, resuspended in a small volume of MeOH and absorbed onto silica gel. The MeOH was removed from the silica gel under vacuum. Flash chromatography (10%→50% MeOH in CH_2Cl_2, RediSep Rf normal phase column) yielded the title compound (815 mg, 63%) as a white solid. A 100mM solution was prepared in H_2O for use in CuAAC reactions. ^1H NMR (600 MHz, CD_3OD) δ 7.98 (s, 3H), 4.51 (t, J = 7.0 Hz, 6H), 3.75 (s, 6H), 3.57 (t, J = 6.0 Hz, 6H), 2.13 – 2.09 (m, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 145.46, 125.82, 59.47, 48.88, 48.44, 34.11. ESIHRMS: calcd for $C_{18}H_{30}N_{10}O_3$ $(M + H)^+$: 435.2575, obsd: 435.2578.

CuAAC Reaction on RNAs.
A solution of RNA in H_2O was treated sequentially with tris-[1-(3-hydroxypropyl)-1H-[1,2,3]triazol-4-yl)methyl]amine ligand (100 mM solution in H_2O), $CuSO_4$ (100 mM solution in H_2O), sodium ascorbate (200 mM solution in H_2O) and the corresponding azide* (10mM solution in H_2O for all azides apart from AZT, which was a 10 mM solution in 40% DMSO), appropriate volumes indicated below. The solution was incubated for 4 h at room temp. The reaction mixture was diluted to 2x the original volume with PAGE loading buffer (80% formamide containing 10 mM EDTA). The RNA was PAGE-purified, quantified and analyzed by ESIHRMS according to the procedures above. For the 12-mers, the slower moving gel band corresponded to the click products. For the 21-mer, the slower moving band corresponded to the di-click product and the faster moving band corresponded to the mono-click product. Lypholization gave white pellets, which were fully soluble in H_2O.

*Man-2 and ManNAc azides were obtained from the Xi Chen Lab, UC Davis.

RNA 1 (12-mer): 5'-CAU UA**X** GGU GGG-3'

RNA: 20 nmol in 30.0 μL H_2O; Ligand: 5.0 μL; $CuSO_4$: 2.5 μL; Sodium ascorbate: 2.5 μL; Azide: 10 μL.

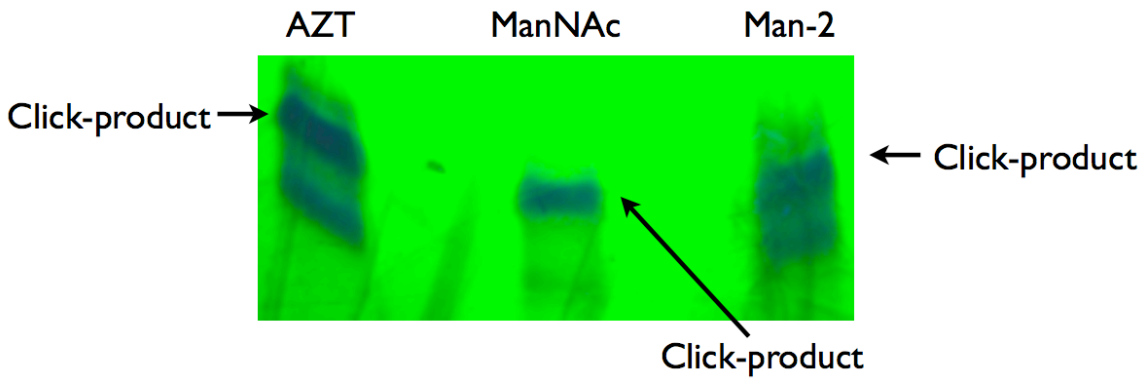
R = **Man-2:** Recovered yield after PAGE: 6.1 nmol; Calcd M: 4116.64; Obsd M: 4116.64
R = **ManNAc:** Recovered yield after PAGE: 4.0 nmol; Calcd M: 4173.66; Obsd M: 4173.66
R = **AZT:** Recovered yield after PAGE: 8.3 nmol; Calcd M: 4178.67; Obsd M: 4178.67

RNA 2: (21-mer): 5'-GGA AAU GC**X** AGA G**X**A ACU GdTdT-3'

RNA: 3 nmol in 6.0 μL H_2O; Ligand: 1.0 μL; $CuSO_4$: 0.5 μL; Sodium ascorbate: 0.5 μL; Azide: 2 μL.

R = **ManNAz:**Recovered yield after PAGE: 0.17 nmol; Calcd M: 7400.24; Obsd M: 7400.53

Representative PAGE UV-Shadow after CuAAC reaction on 12-mer RNA:



Preparation of Duplex RNAs and Tm analysis.
Duplexes were formed by hybridizing 975 pmol complementary strands in 975 μL TE buffer (10 mM Tris-HCl, pH 7.5, 0.1 mM EDTA) with 100 mM NaCl. The solution was heated at 95 ºC for 5 min and allowed to slow-cool over a period of 2 h to RT. These duplexes were directly used in Tm analyses.

Tm experiments were performed on a Beckmann DU 7400 spectrophotometer with a multi-cuvette temperature controller. Duplexes (325 pmol, 325 μL) were denatured in triplicate over a temperature range of 10 ºC to 80 ºC at 0.5 ºC/min. The absorbance at 260 nm was recorded every 0.5 ºC. The fraction of oligonucleotides in a duplex (*f*) was determined by fitting the data to the equation:

$$f = \frac{A - A_{ss}}{A_{ds} - A_{ss}}$$

Where: A = Absorbance of sample at each temperature
A_{ds}= Absorbance of double stranded oligo
A_{ss}= Absorbance of single stranded oligo

The *f* vs. temperature was graphed for the linear portion of the curve (range of values where $f \approx$

0.4 → 0.6). A linear regression was performed and the Tm is determined from the point on the line where *f* =0.5. The values reported represent the average of three experiments. The error bars on the graph and the ± values in the manuscript indicate ± standard deviation.

Tm Data:

X =	Y =	Ave Tm (°C)	Std Dev (°C)
A	U	40.7	0.8
	C	35.7	0.5
	A	32.4	0.2
	G	30.4	0.6
2AP	U	39.2	2.1
	C	34.0	1.2
	A	30.2	0.3
	G	29.4	0.5
Propyl	U	40.6	1.0
	C	33.4	0.6
	A	31.6	0.8
	G	30.1	0.2
Cyclopentyl	U	39.4	0.4
	C	30.6	0.6
	A	30.2	0.3
	G	28.5	1.0
Man-2 triazole	U	37.7	0.5
	C	34.0	0.9
	A	31.3	1.8
	G	29.5	0.7
ManNAc triazole	U	40.2	0.6
	C	35.6	0.6
	A	31.8	0.8
	G	29.6	1.1
AZT triazole	U	39.4	0.7
	C	36.1	0.3
	A	33.3	0.7
	G	28.8	1.0
Propargyl	U	36.2	0.6
	C	32.6	0.3
	A	29.8	1.1
	G	29.5	0.9

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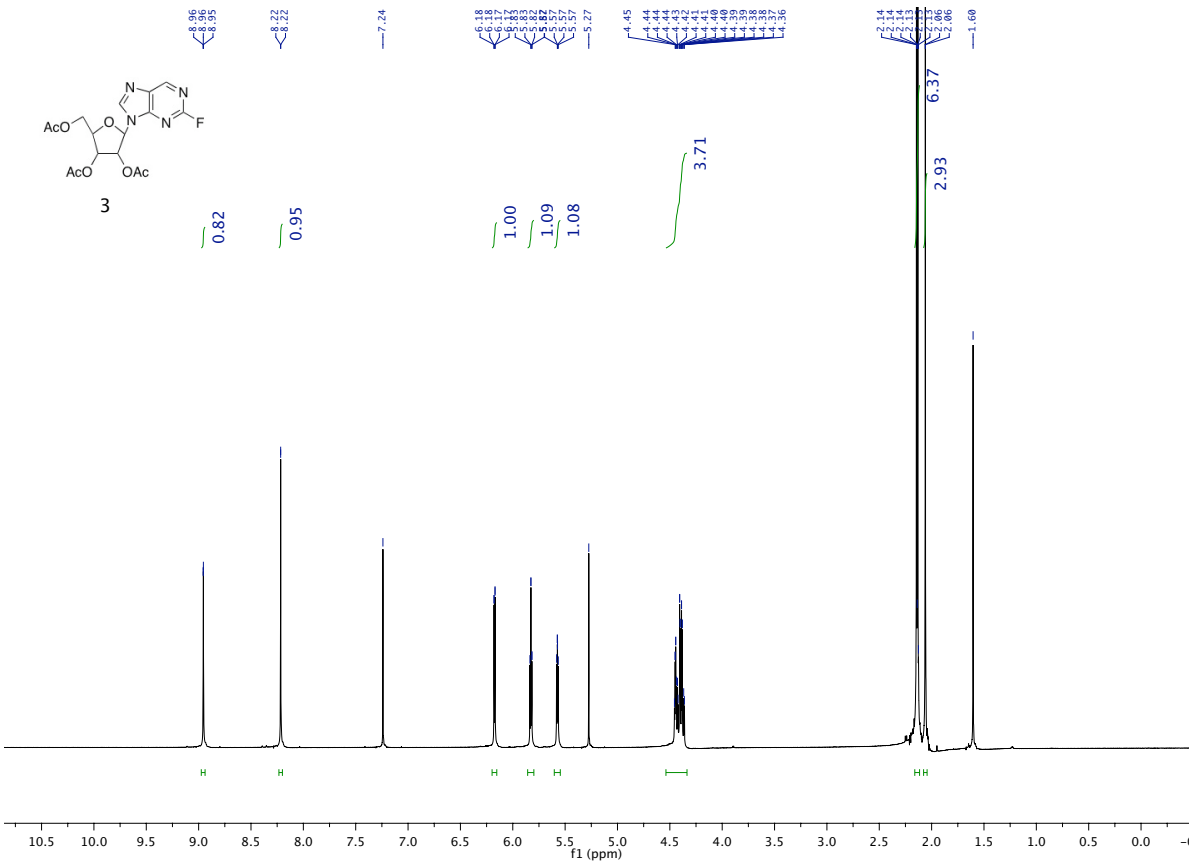
(5) Damien Quémener, T. P. D., Christopher Barner-Kowollik and Martina H. Stenzel *Chem. Commun.* **2006**, 5051-5053.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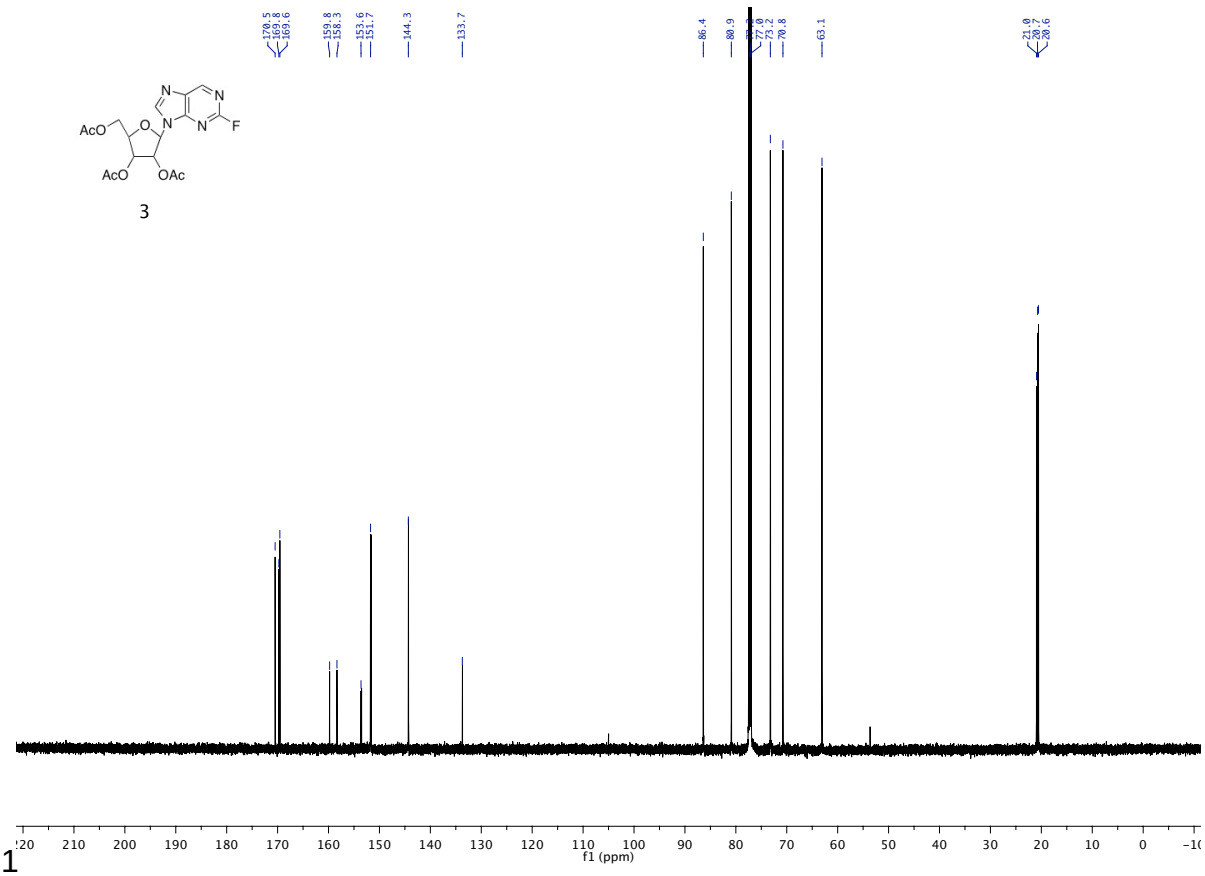
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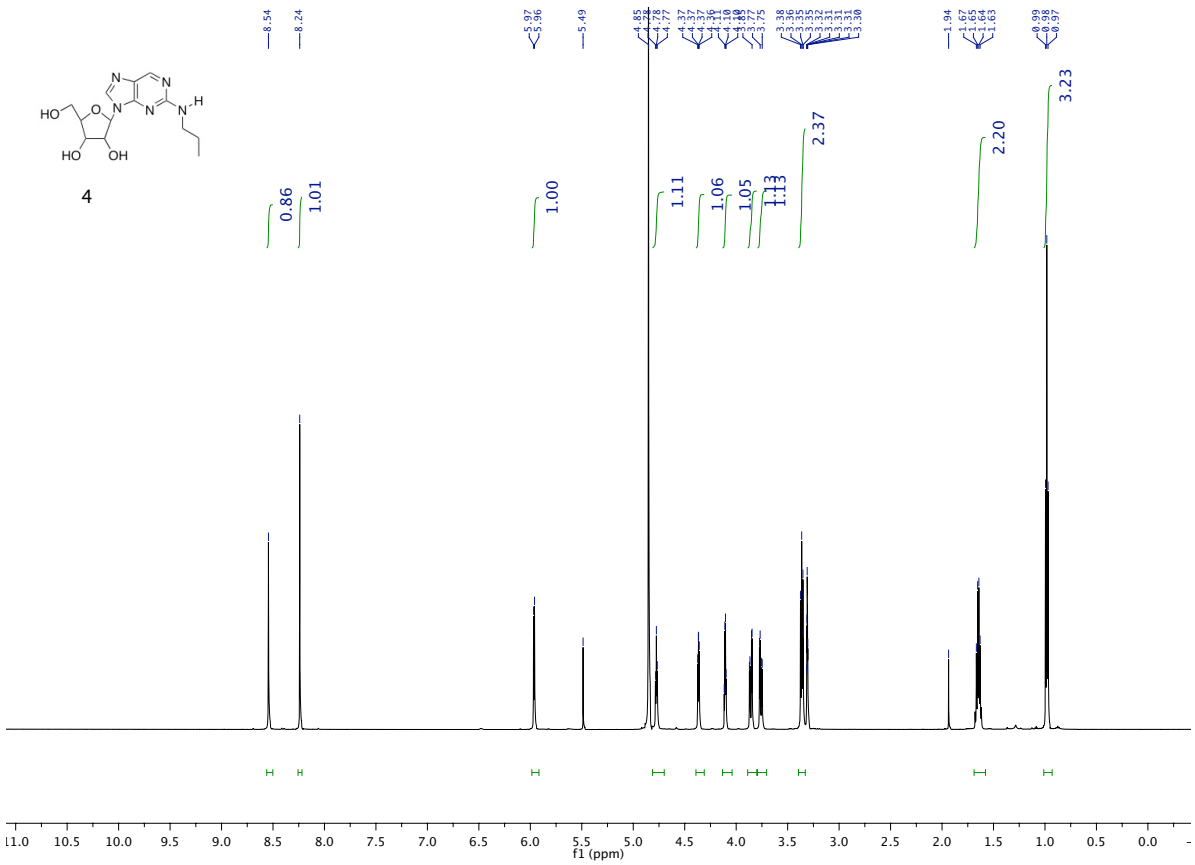
f1 (ppm)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1.64
1.63
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0.98
0.97
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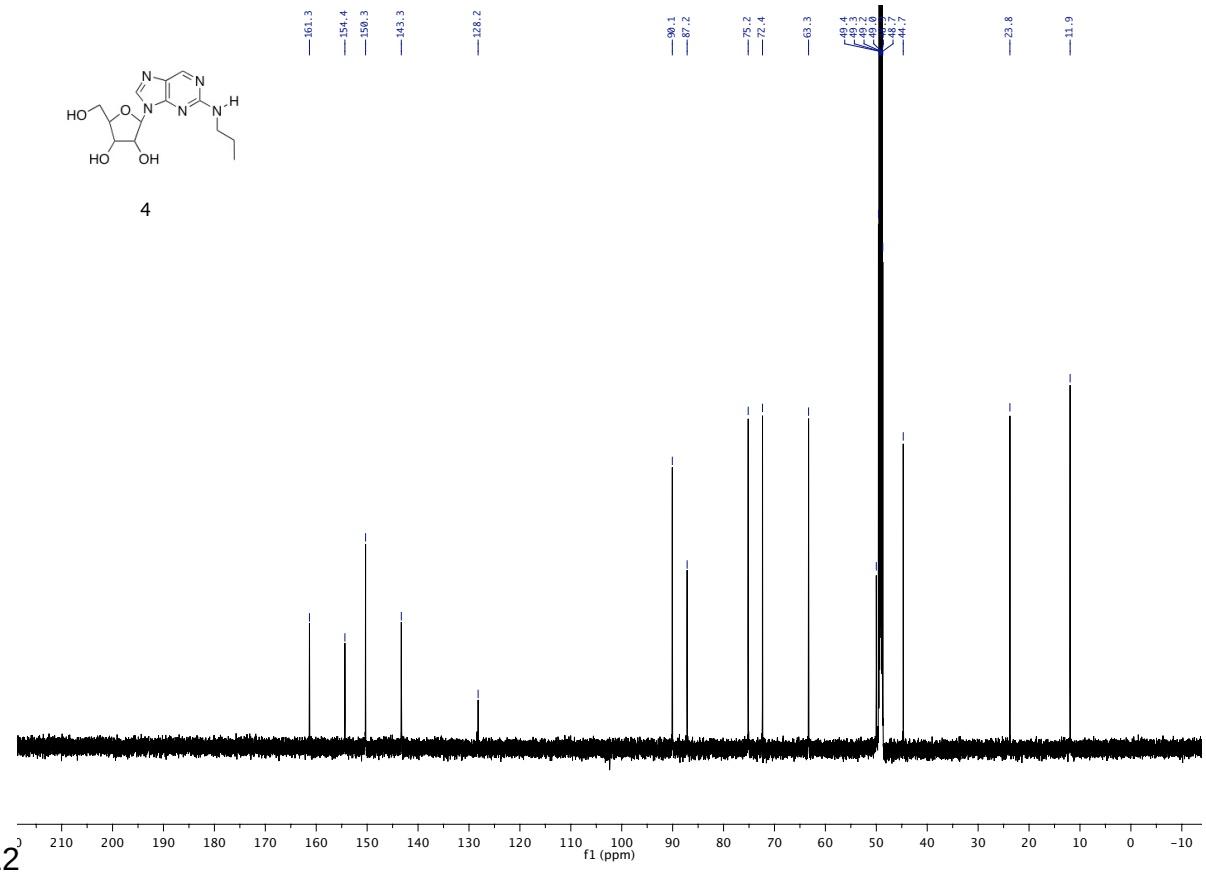
f1 (ppm)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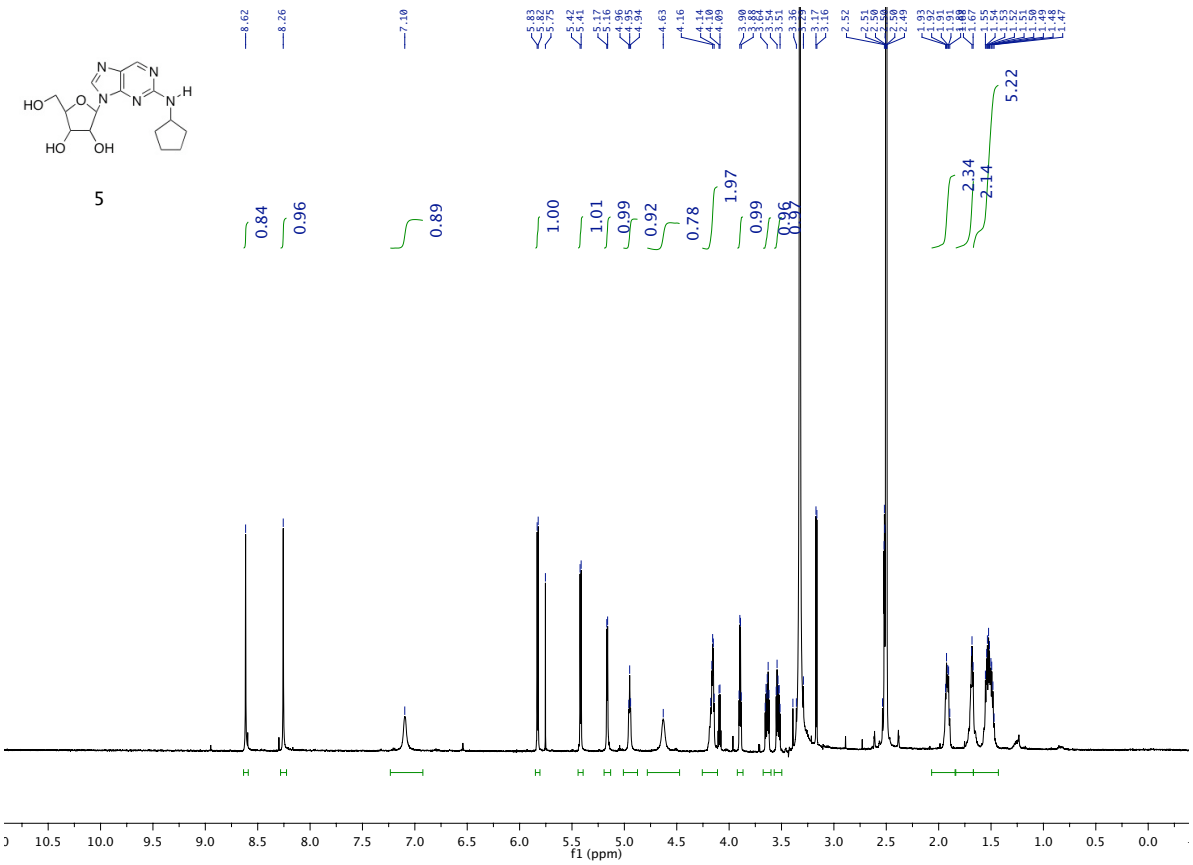
f1 (ppm)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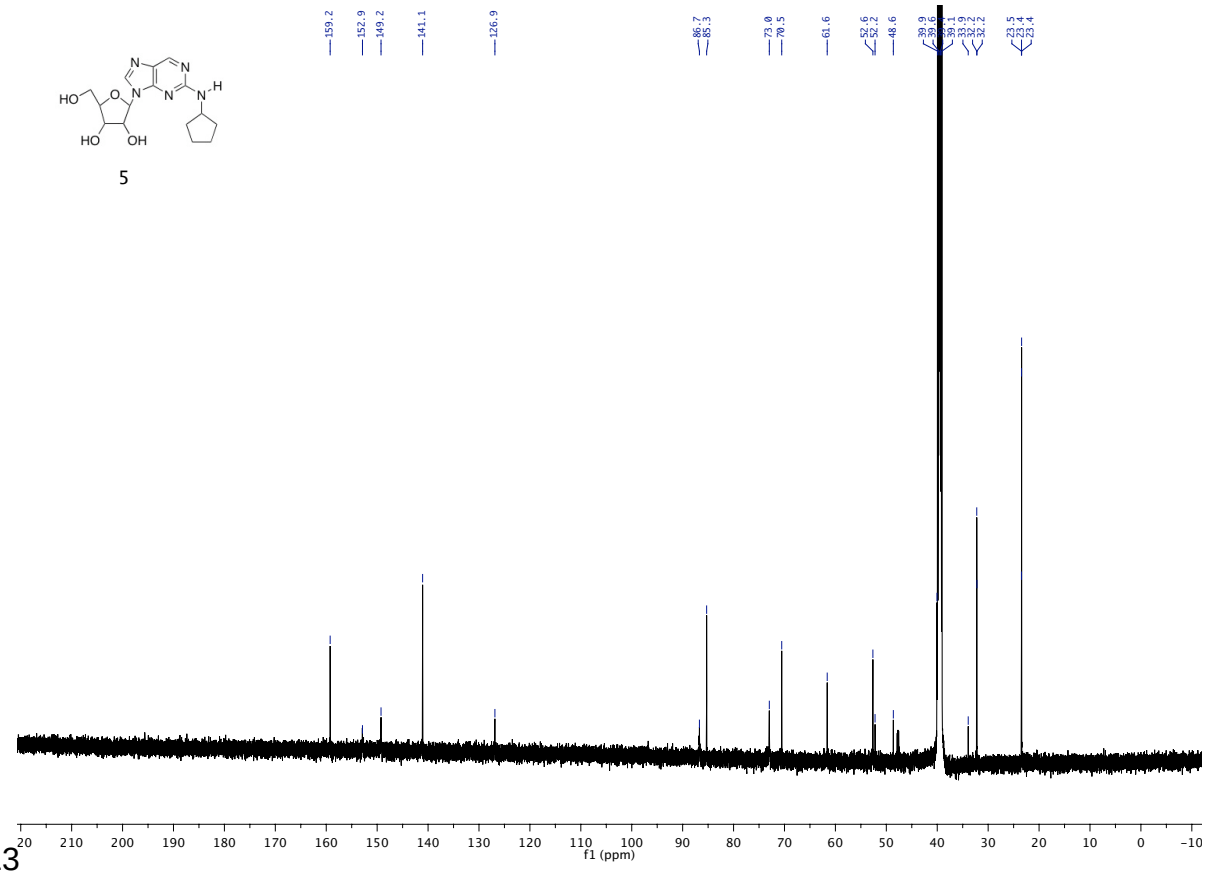
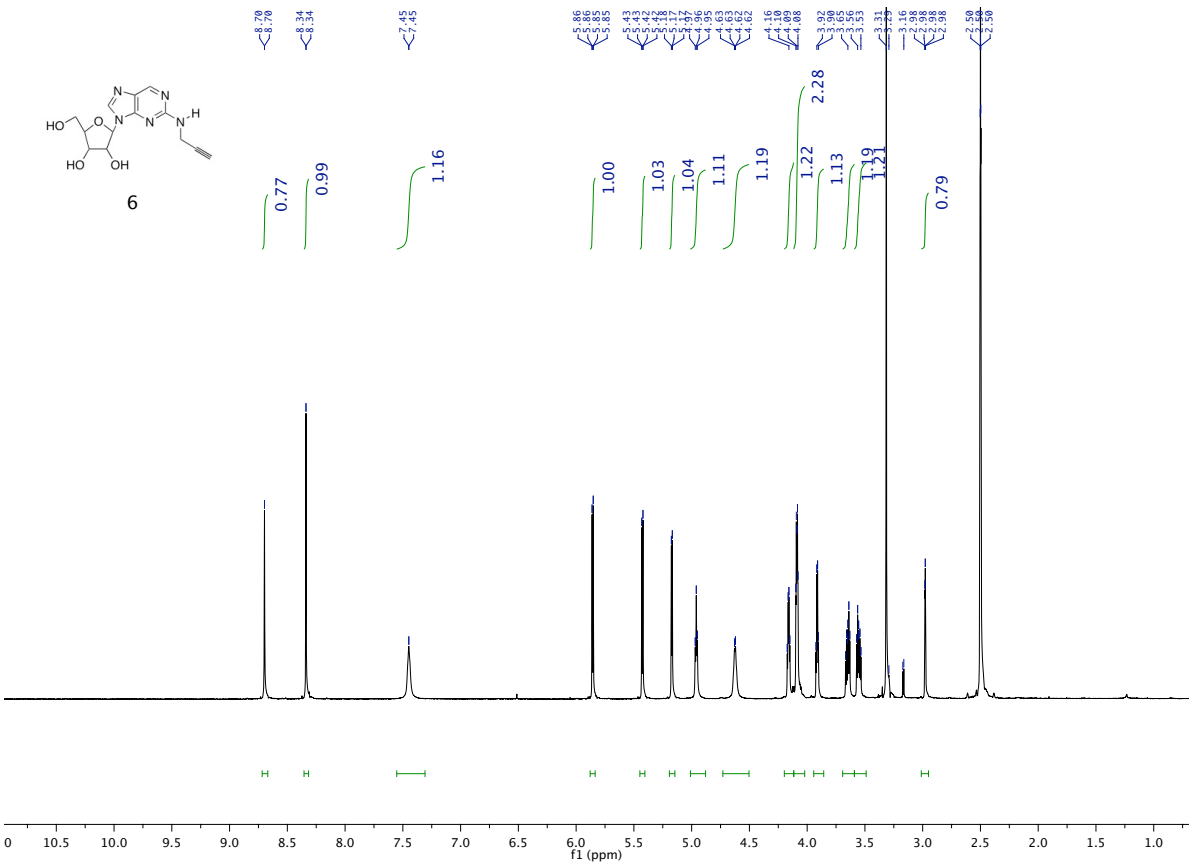
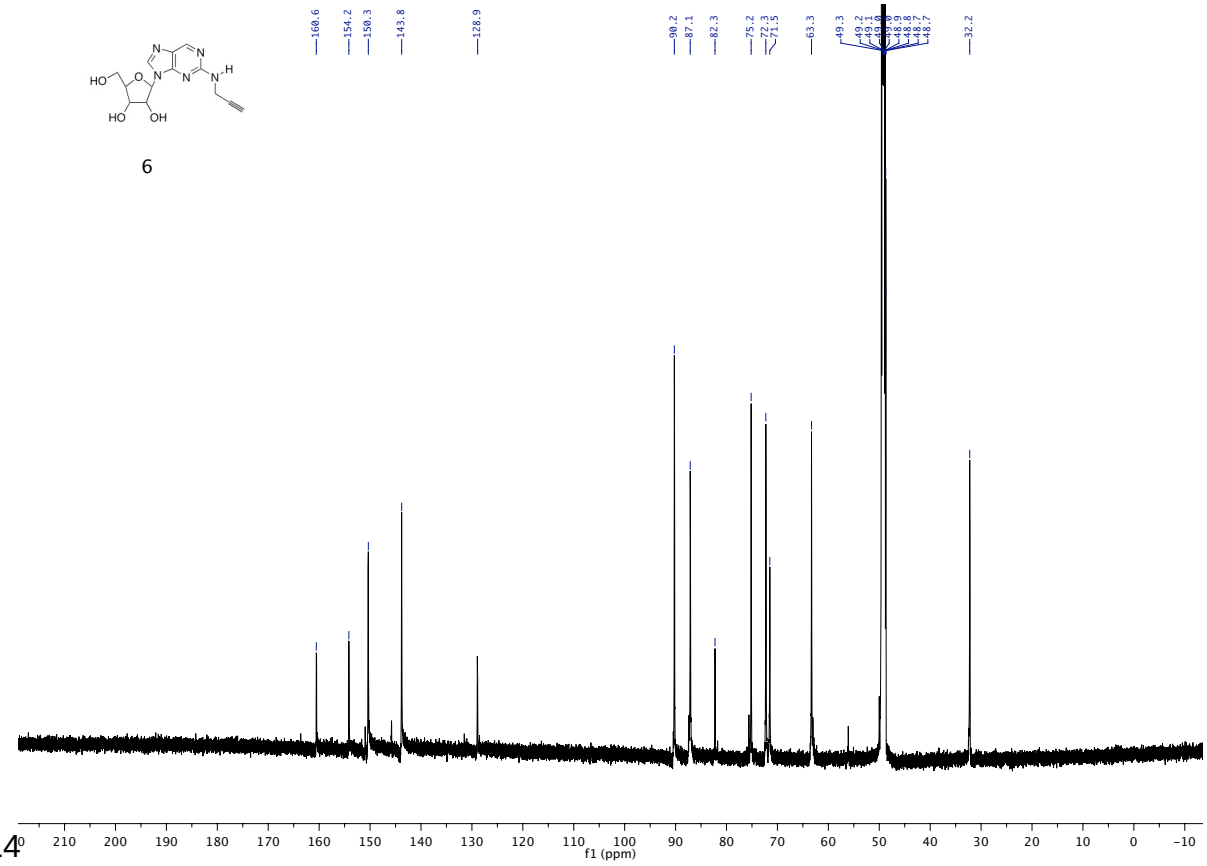
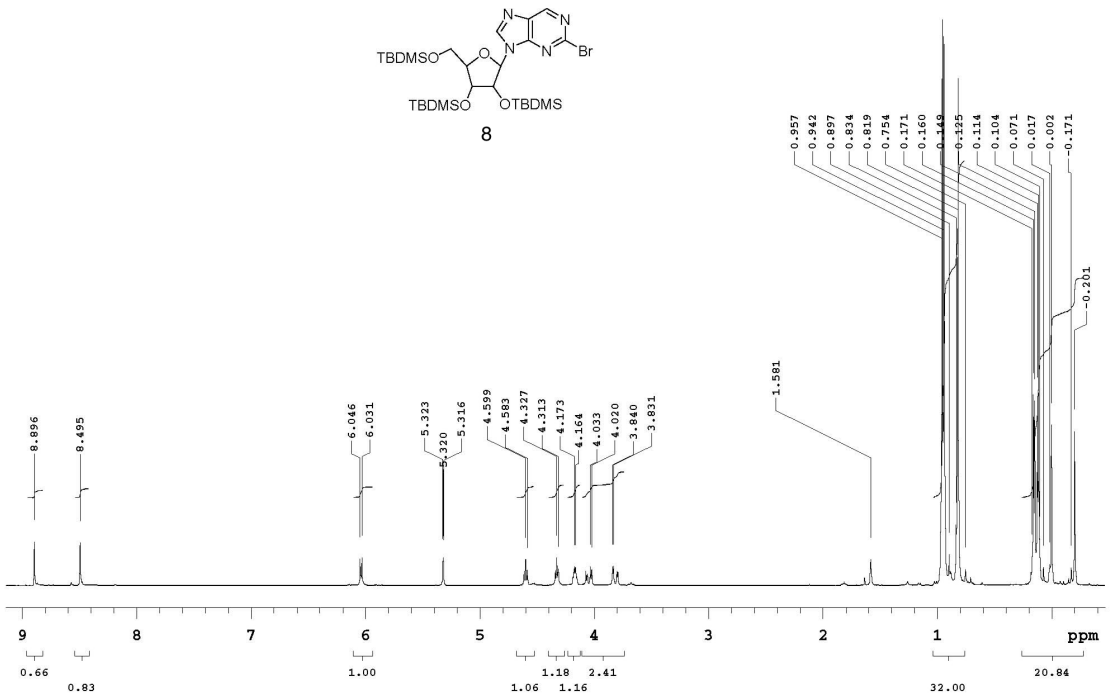
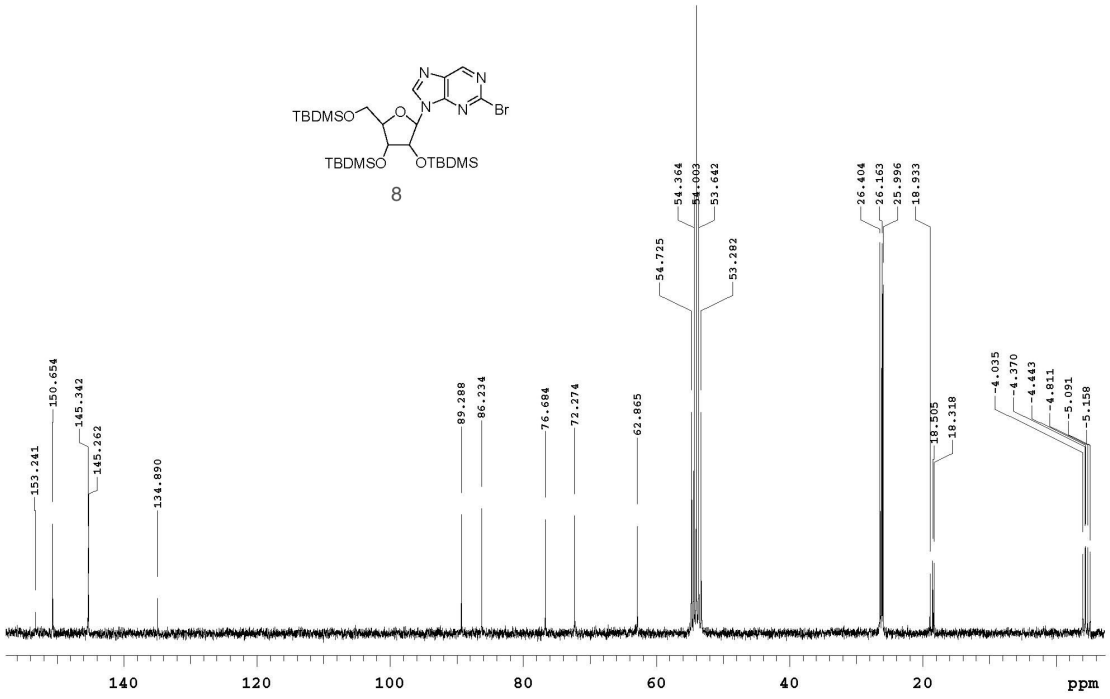
H
5
f1 (ppm)


159.2
152.9
149.2
141.1
126.9
86.7
85.3
73.0
70.5
61.6
52.6
52.2
48.6
39.9
39.6
39.1
33.9
32.2
32.2
23.5
23.4
23.4
HO
HO
OH
N
N
N
N
H
5
f1 (ppm)


6
f1 (ppm)


6
f1 (ppm)


TBDMSO
TBDMSO
OTBDMS
Br
8
8.896
8.495
6.046
6.031
5.323
5.320
5.316
4.599
4.583
4.327
4.313
4.173
4.164
4.033
4.020
3.840
3.831
1.581
0.957
0.942
0.897
0.834
0.819
0.754
0.171
0.160
0.149
0.125
0.114
0.104
0.071
0.017
0.002
-0.171
-0.201
9
8
7
6
5
4
3
2
1
ppm
0.66
0.83
1.00
1.06
1.16
1.18
2.41
32.00
20.84


TBDMSO
TBDMSO
OTBDMS
Br
8
153.241
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145.342
145.262
134.890
89.288
86.234
76.684
72.274
62.865
54.725
54.364
54.003
53.642
53.282
26.404
26.163
25.996
18.933
18.505
18.318
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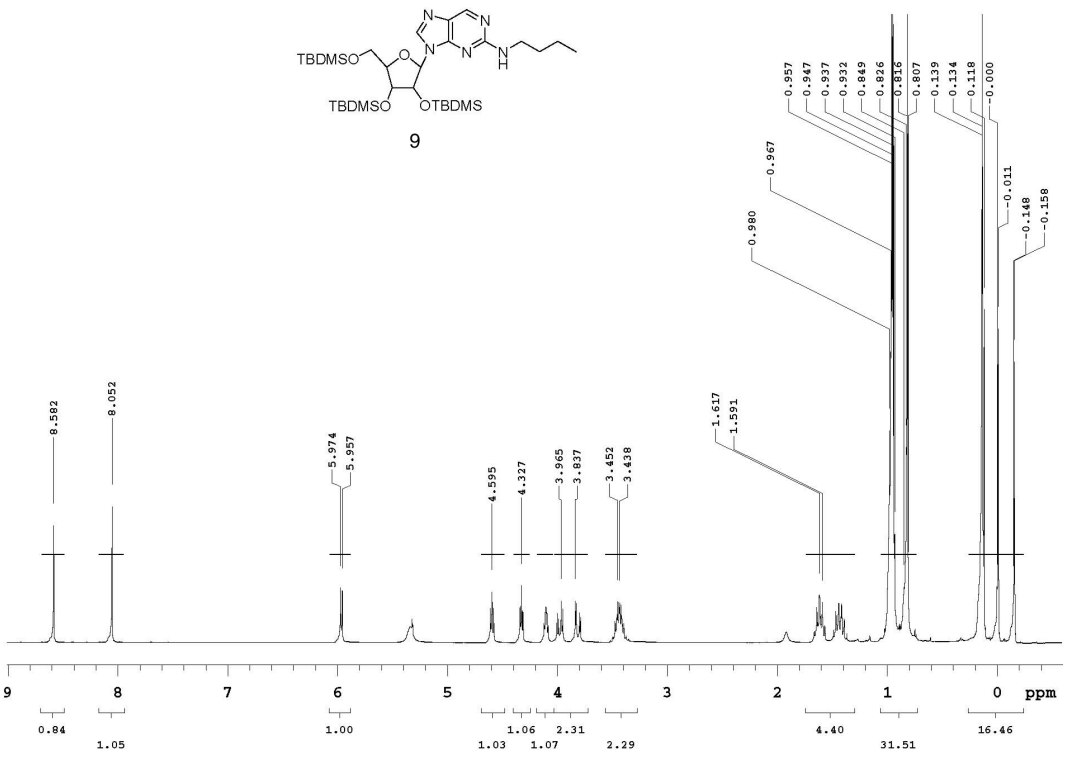
-4.370
-4.443
-4.811
-5.091
-5.158
140
120
100
80
60
40
20
ppm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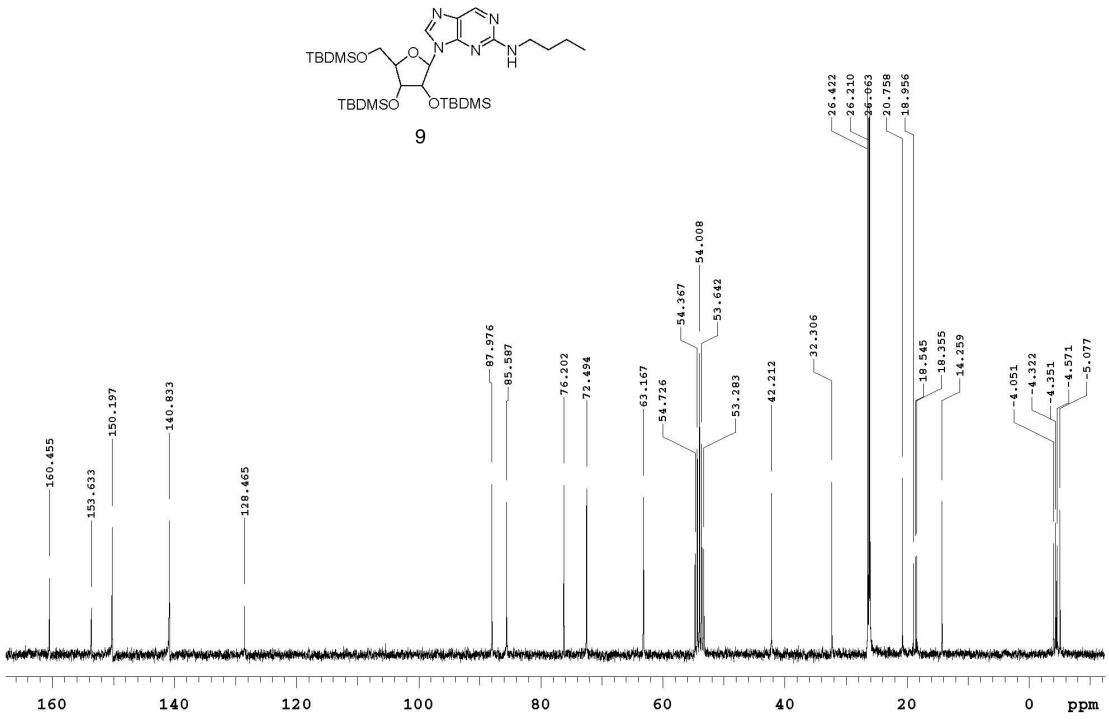
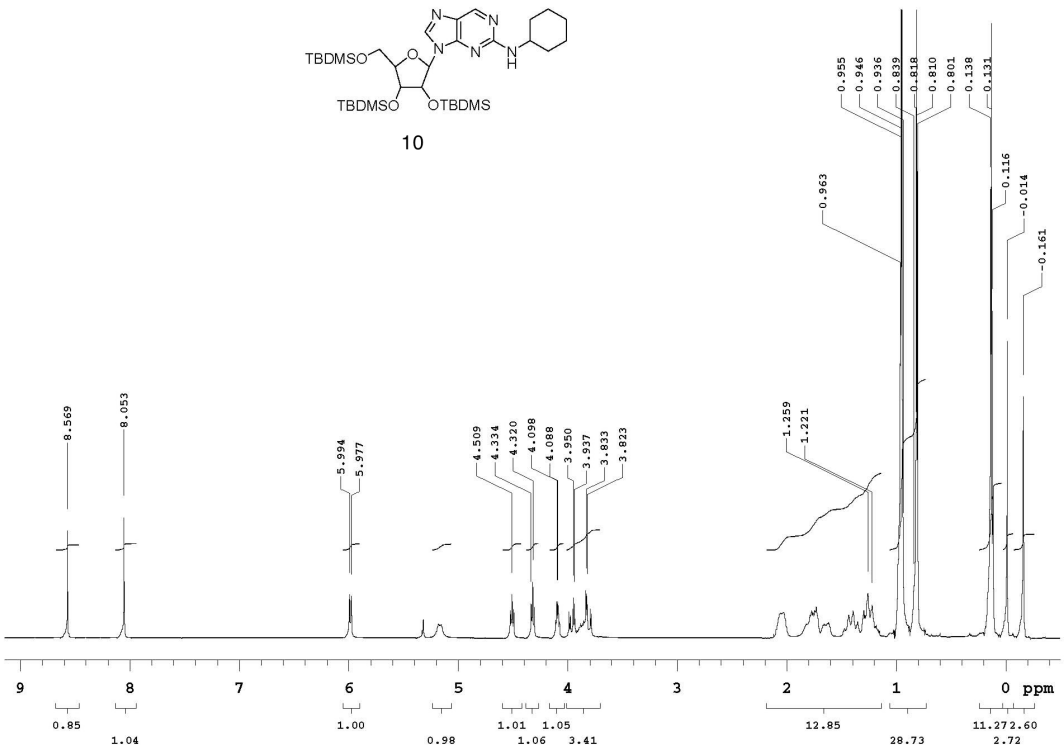
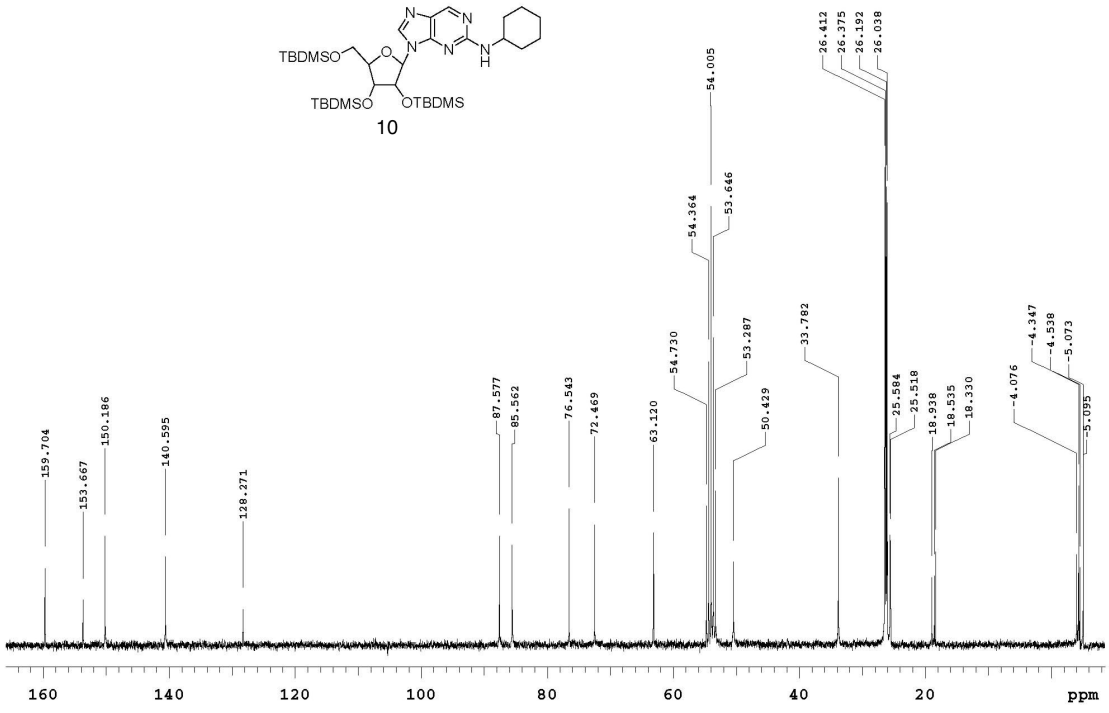
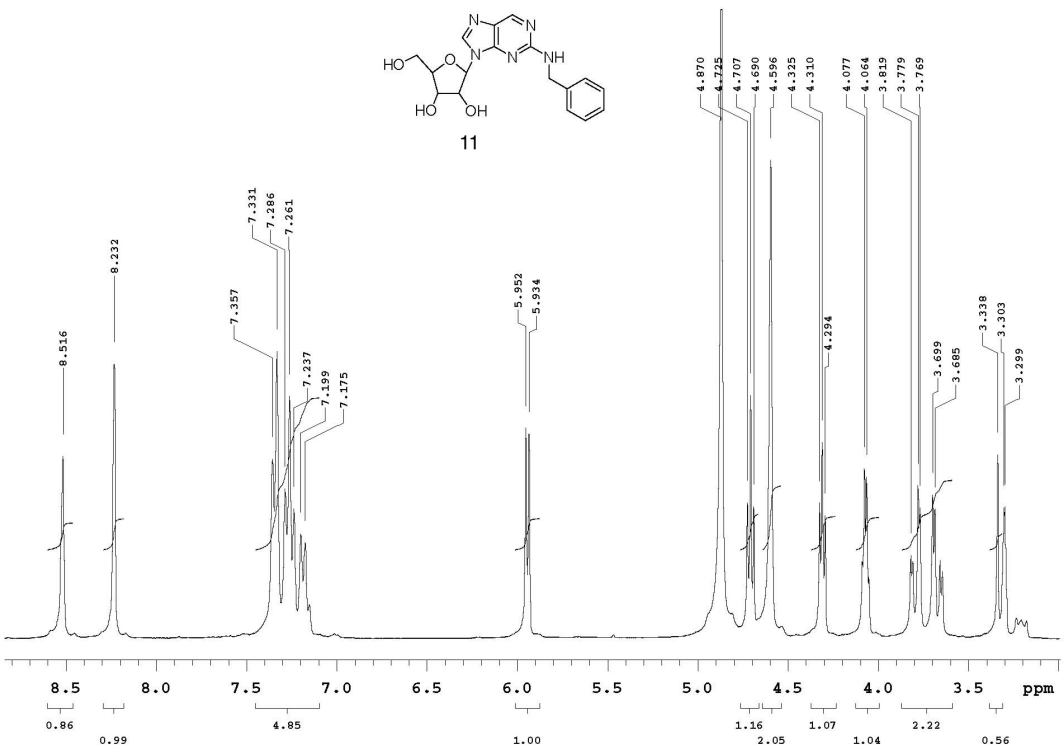
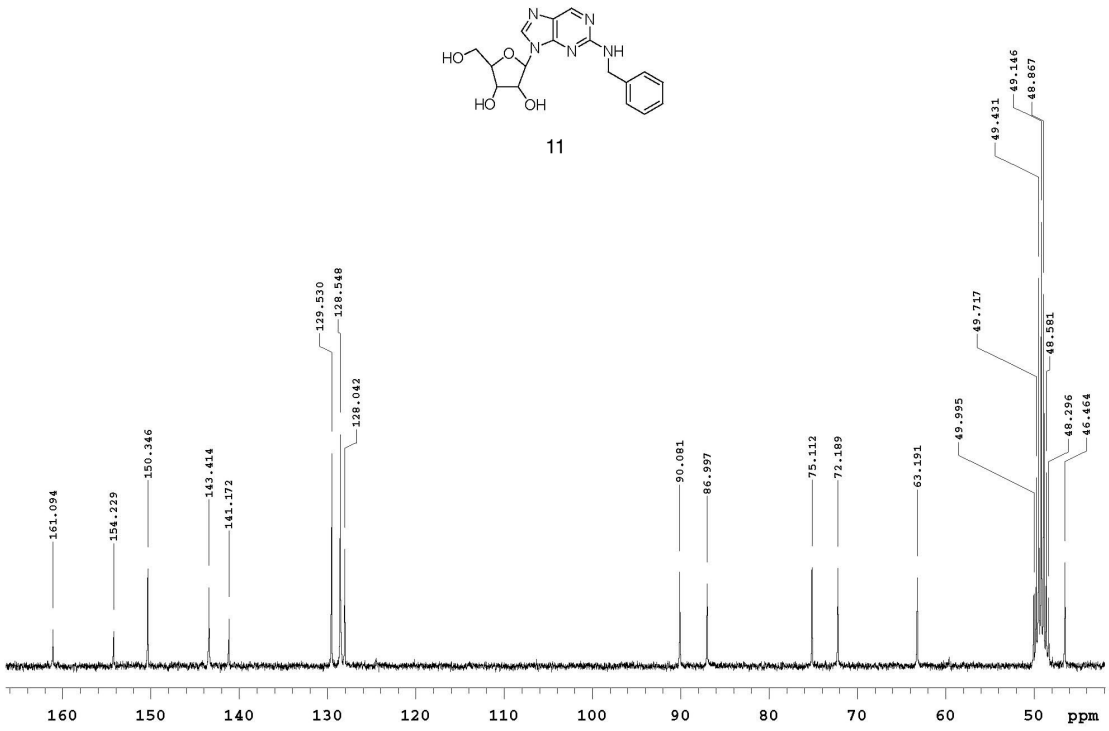
TBDMSO
OTBDMS
9
8.582
8.052
5.974
5.957
4.595
4.327
3.965
3.837
3.452
3.438
1.617
1.591
0.980
0.967
0.957
0.947
0.937
0.932
0.849
0.826
0.816
0.807
0.139
0.134
0.118
0.000
-0.011
-0.148
-0.158
9
8
7
6
5
4
3
2
1
0
ppm
0.84
1.05
1.00
1.03
1.06
1.07
2.31
2.29
4.40
31.51
16.46

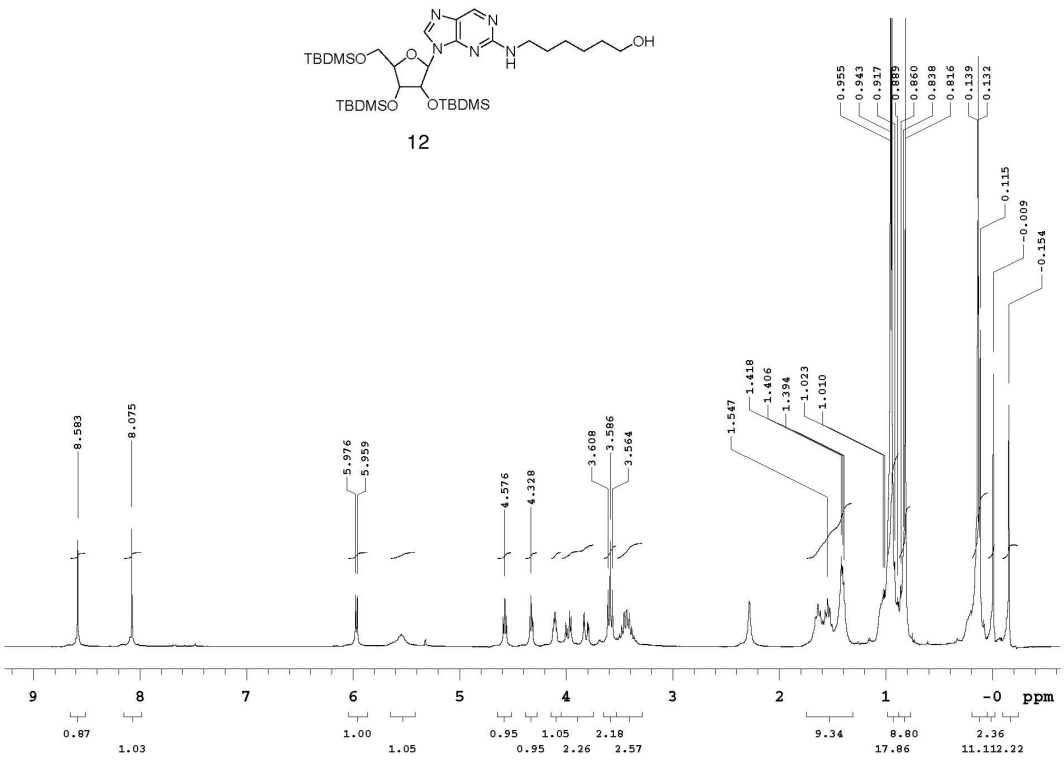

TBDMSO
TBDMSO
OTBDMS
9
160.455
153.633
150.197
140.833
128.465
87.976
85.587
76.202
72.494
63.167
54.726
54.367
54.008
53.642
53.283
42.212
32.306
26.422
26.210
26.063
20.758
18.956
18.545
18.355
14.259
-4.051
-4.322
-4.351
-4.571
-5.077
160
140
120
100
80
60
40
20
0
ppm

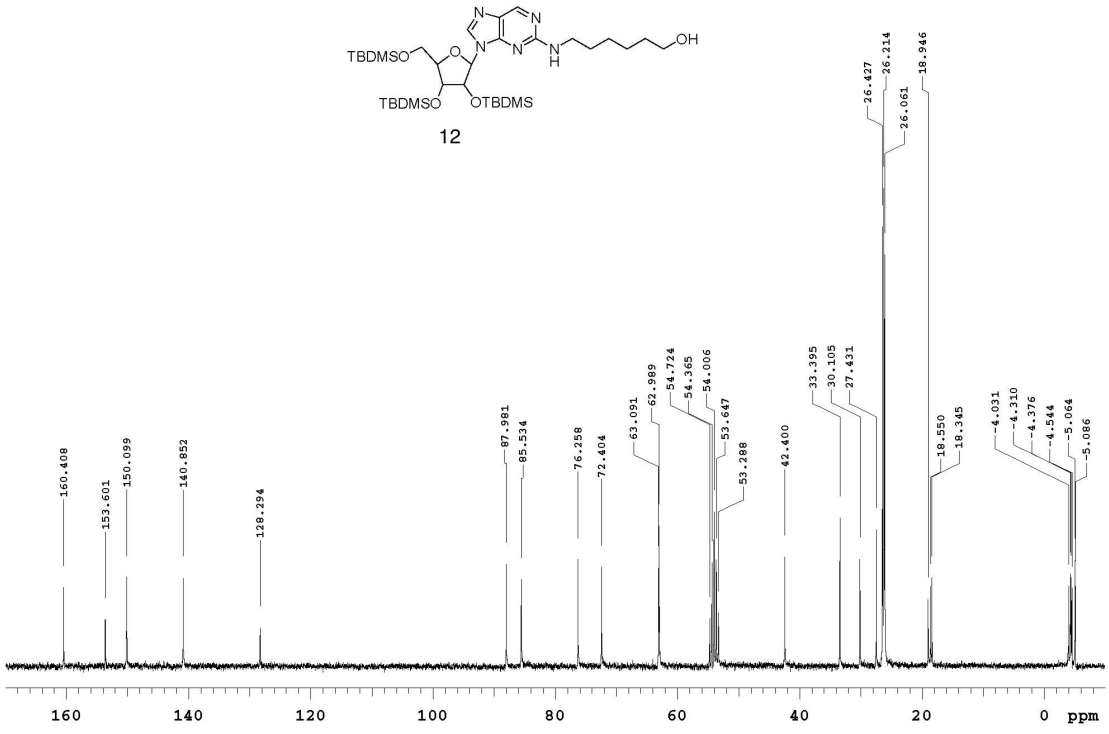

TBDMSO
TBDMSO
OTBDMS
10
8.569
8.053
5.994
5.977
4.509
4.334
4.320
4.098
4.088
3.950
3.937
3.833
3.823
1.259
1.221
0.963
0.955
0.946
0.936
0.839
0.818
0.810
0.801
0.138
0.131
0.116
-0.014
-0.161
9
8
7
6
5
4
3
2
1
0 ppm
0.85
1.04
1.00
0.98
1.01
1.06
1.05
3.41
12.85
28.73
11.27
2.72
2.60

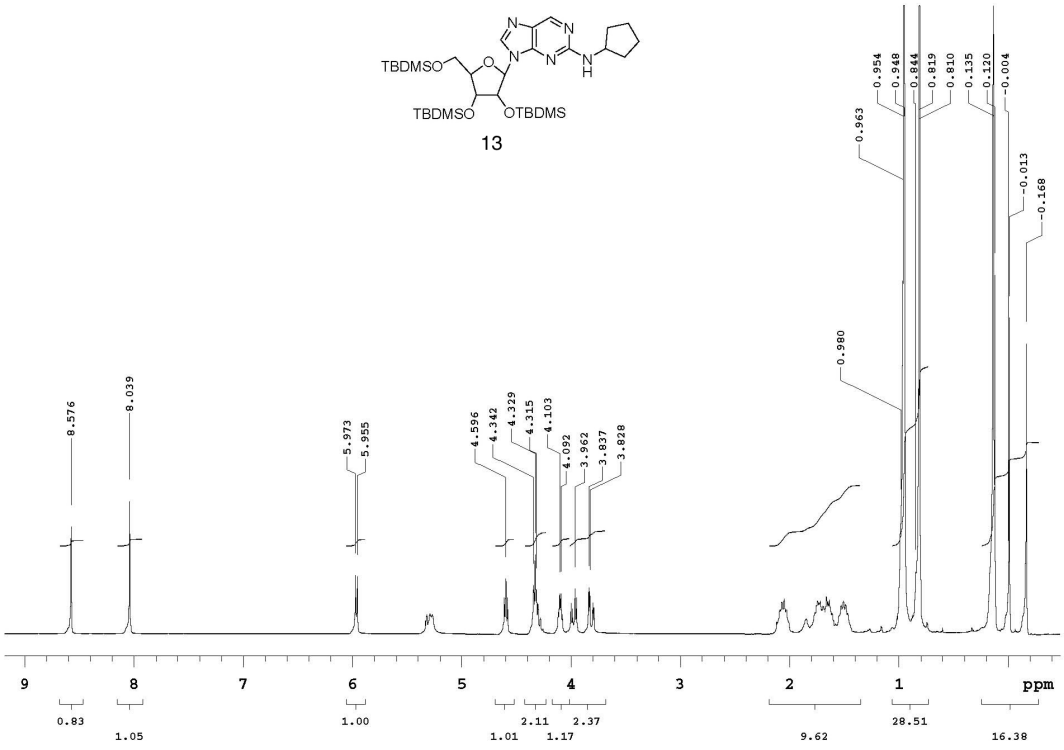

TBDMSO
TBDMSO
OTBDMS
10
159.704
153.667
150.186
140.595
128.271
87.577
85.562
76.543
72.469
63.120
54.730
54.364
54.005
53.646
53.287
50.429
33.782
26.412
26.375
26.192
26.038
25.584
25.518
18.938
18.535
18.330
-4.076
-4.347
-4.538
-5.073
-5.095
160
140
120
100
80
60
40
20
ppm

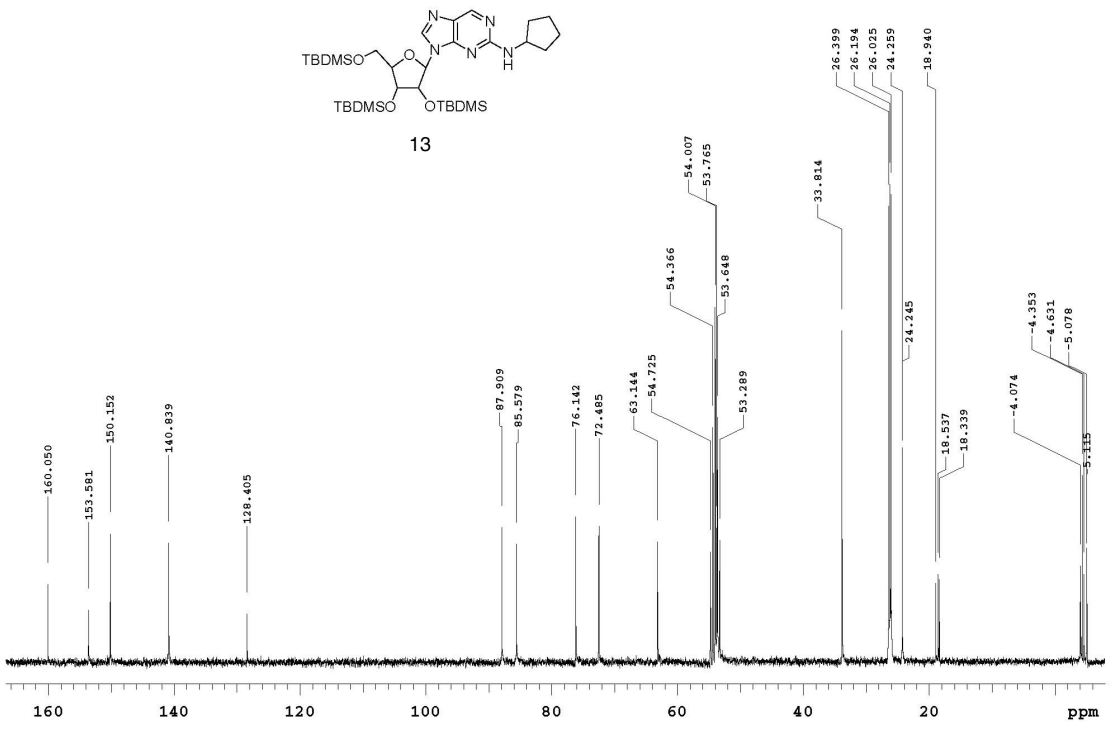

11
8.516
8.232
7.357
7.331
7.286
7.261
7.237
7.199
7.175
5.952
5.934
4.870
4.725
4.707
4.690
4.596
4.325
4.310
4.294
4.077
4.064
3.819
3.779
3.769
3.699
3.685
3.338
3.303
3.299
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
0.86
0.99
4.85
1.00
1.16
2.05
1.07
1.04
2.22
0.56


11
161.094
154.229
150.346
143.414
141.172
129.530
128.548
128.042
90.081
86.997
75.112
72.189
63.191
49.995
49.717
49.431
49.146
48.867
48.581
48.296
46.464
160
150
140
130
120
110
100
90
80
70
60
50
ppm


TBDMSO
TBDMSO
OTBDMS
OH
12
8.583
8.075
5.976
5.959
4.576
4.328
3.608
3.586
3.564
1.547
1.418
1.406
1.394
1.023
1.010
0.955
0.943
0.917
0.889
0.860
0.838
0.816
0.139
0.132
0.115
0.009
-0.154
ppm
0.87
1.03
1.00
1.05
0.95
0.95
1.05
2.26
2.18
2.57
9.34
8.80
17.86
2.36
11.11
2.22


TBDMSO
TBDMSO
OTBDMS
OH
12
160.408
153.601
150.099
140.852
128.294
87.981
85.534
76.258
72.404
63.091
62.989
54.724
54.365
54.006
53.647
53.288
42.400
33.395
30.105
27.431
26.427
26.214
26.061
18.946
18.550
18.345
-4.031
-4.310
-4.376
-4.544
-5.064
-5.086
ppm


TBDMSO
TBDMSO
OTBDMS
13
8.576
8.039
5.973
5.955
4.596
4.342
4.329
4.315
4.103
4.092
3.962
3.837
3.828
0.980
0.963
0.954
0.948
0.844
0.819
0.810
0.135
0.120
-0.004
-0.013
-0.168
9
8
7
6
5
4
3
2
1
ppm
0.83
1.05
1.00
1.01
2.11
1.17
2.37
9.62
28.51
16.38


TBDMSO
TBDMSO
OTBDMS
13
160.050
153.581
150.152
140.839
128.405
97.909
85.579
76.142
72.485
63.144
54.725
54.366
54.007
53.765
53.648
53.289
33.814
26.399
26.194
26.025
24.259
24.245
18.940
18.537
18.339
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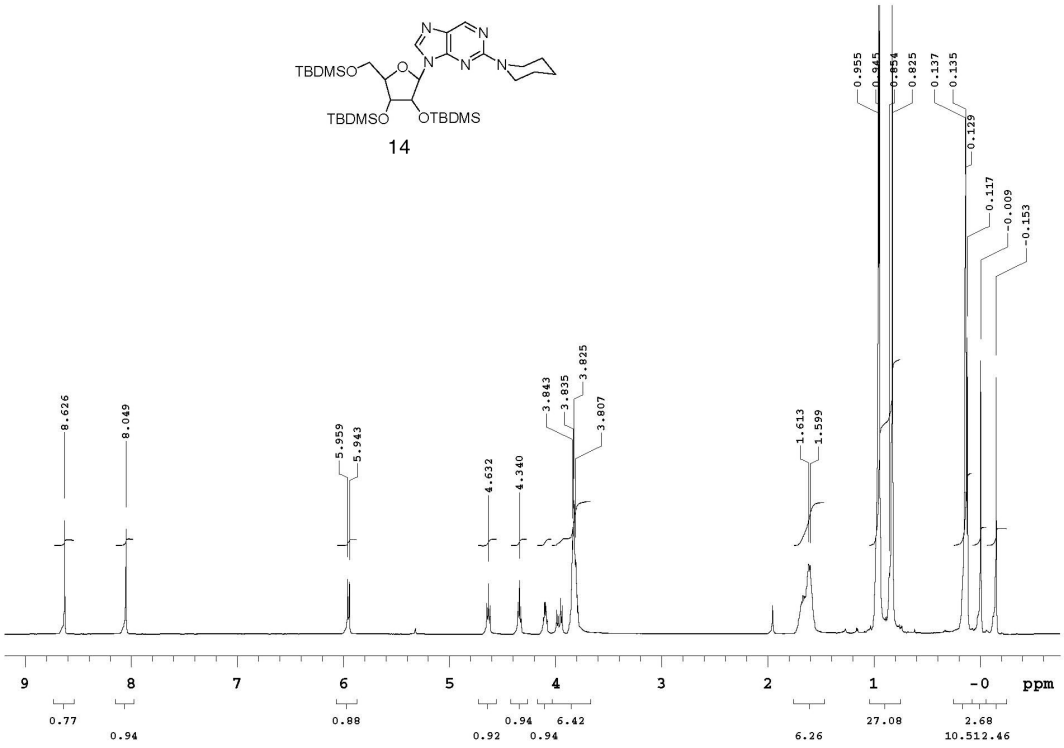
-4.353
-4.631
-5.078
-5.115
160
140
120
100
80
60
40
20
ppm


TBDMSO
TBDMSO
OTBDMS
14
8.626
8.049
5.959
5.943
4.632
4.340
3.843
3.835
3.825
3.807
1.613
1.599
0.955
0.945
0.854
0.825
0.137
0.135
0.129
0.117
0.009
-0.153
9
8
7
6
5
4
3
2
1
-0
ppm
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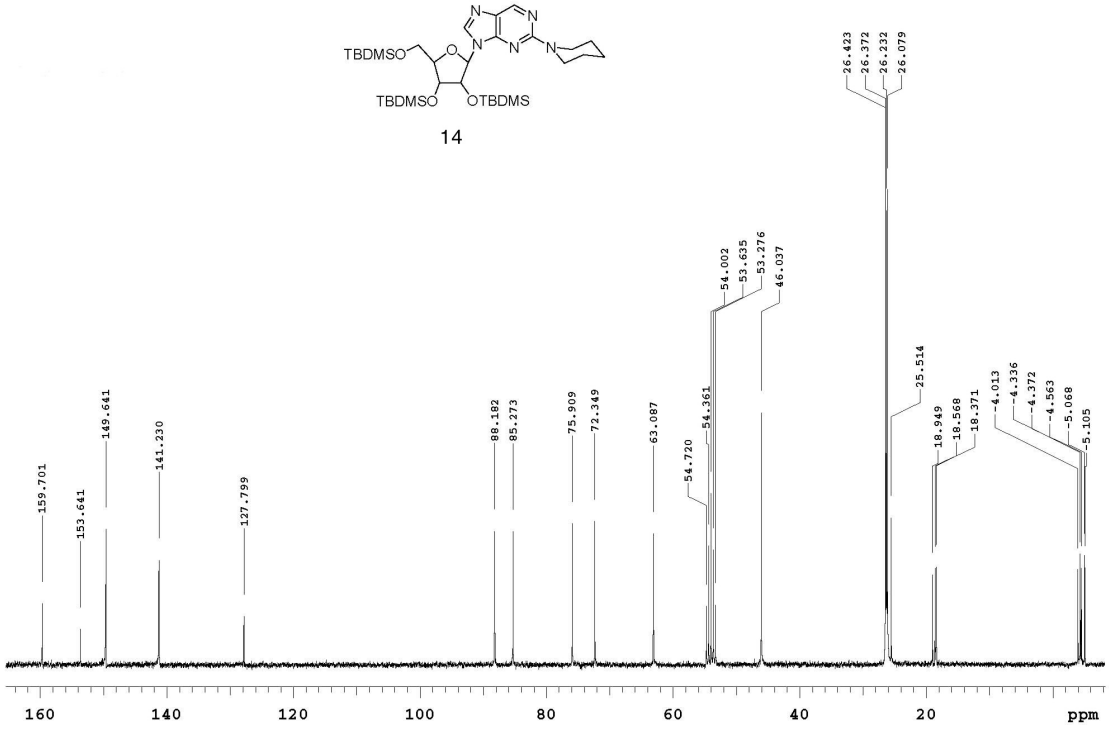
0.94
0.88
0.92
0.94
6.42
6.26
27.08
2.68
10.512.46


TBDMSO
TBDMSO
OTBDMS
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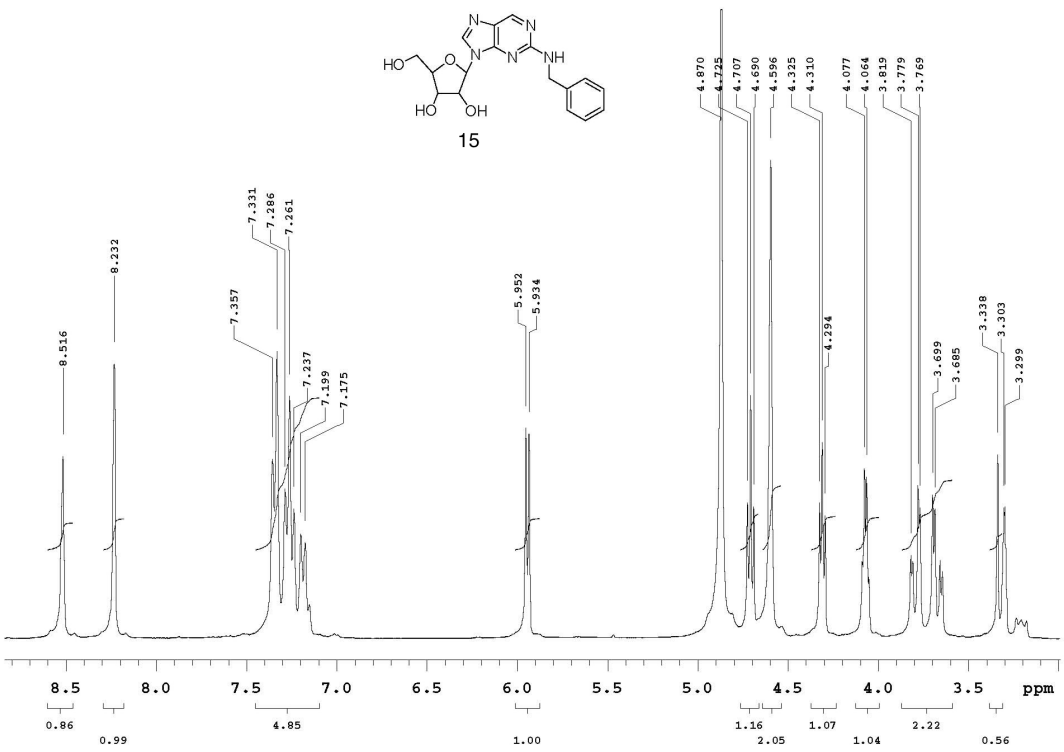
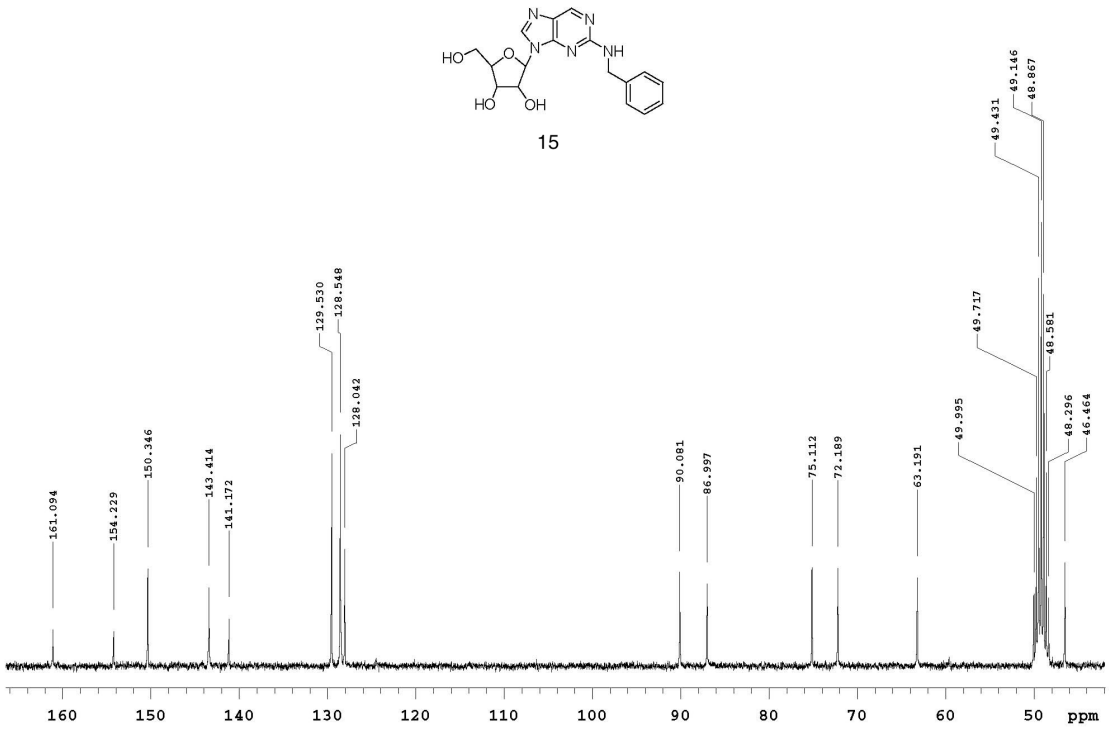
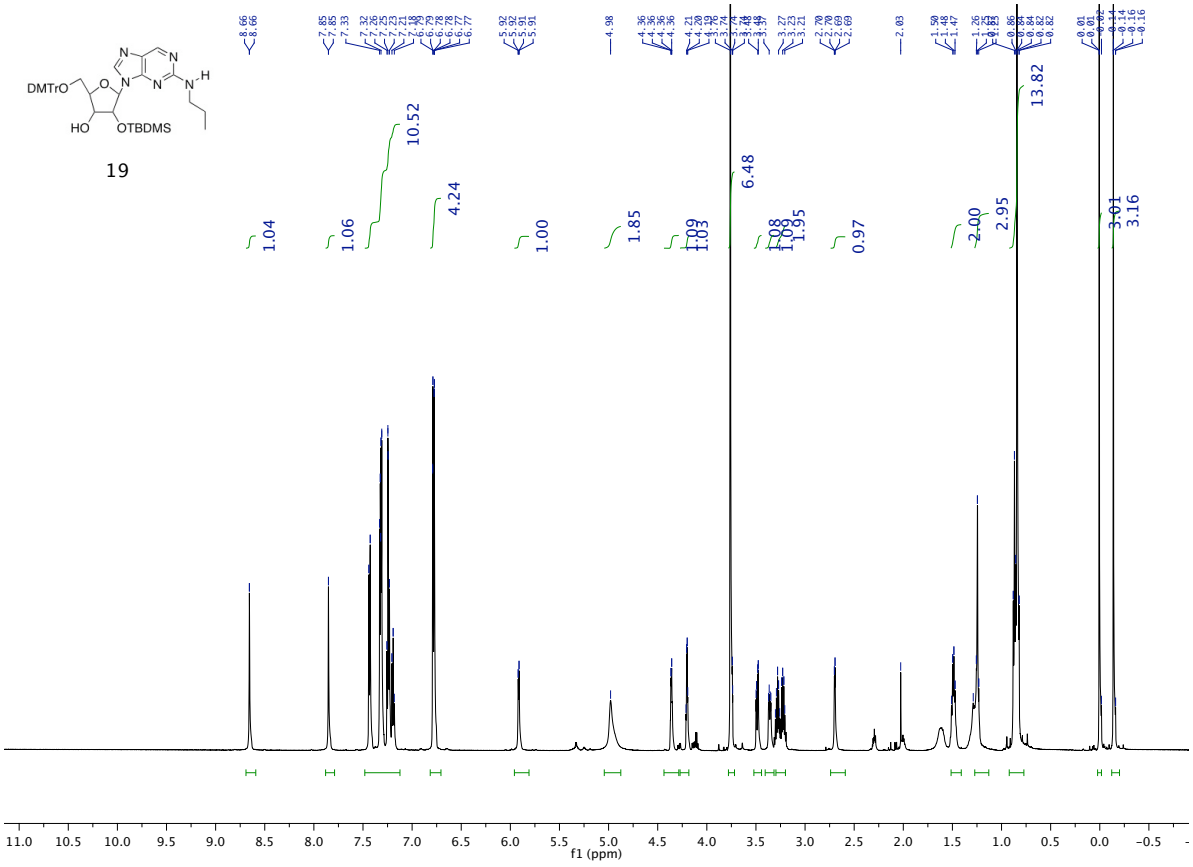
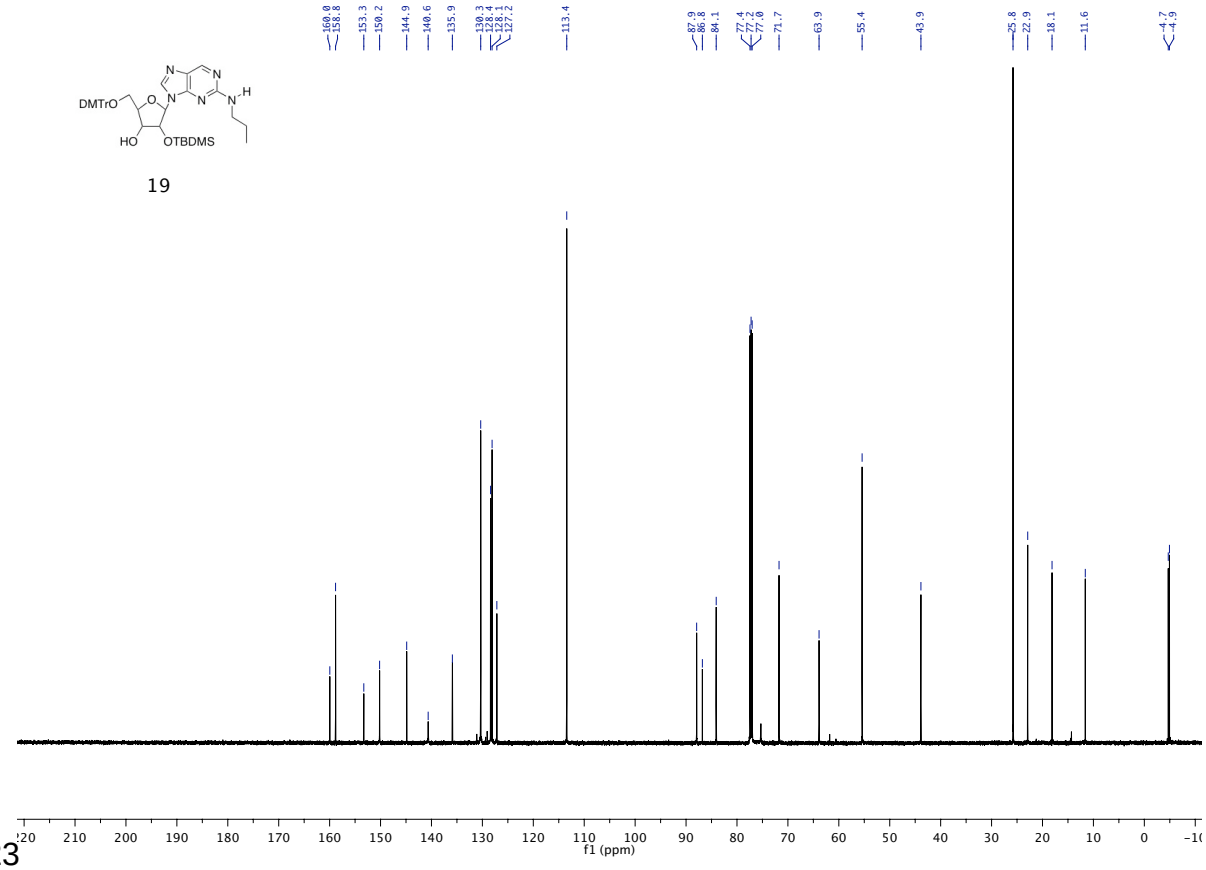
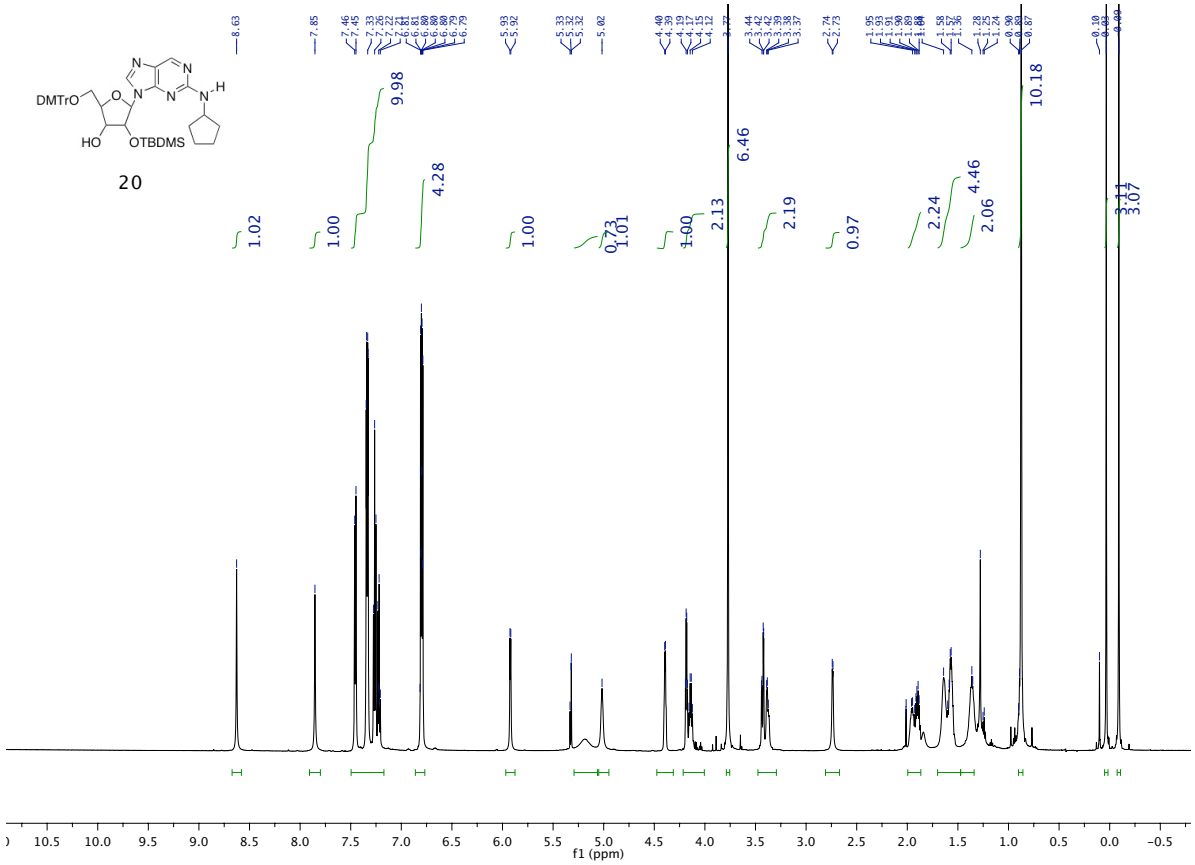
159.701
153.641
149.641
141.230
127.799
88.182
85.273
75.909
72.349
63.087
54.720
54.361
54.002
53.635
53.276
46.037
26.423
26.372
26.232
26.079
25.514
18.949
18.568
18.371
-4.013
-4.336
-4.372
-4.563
-5.068
-5.105
160
140
120
100
80
60
40
20
ppm

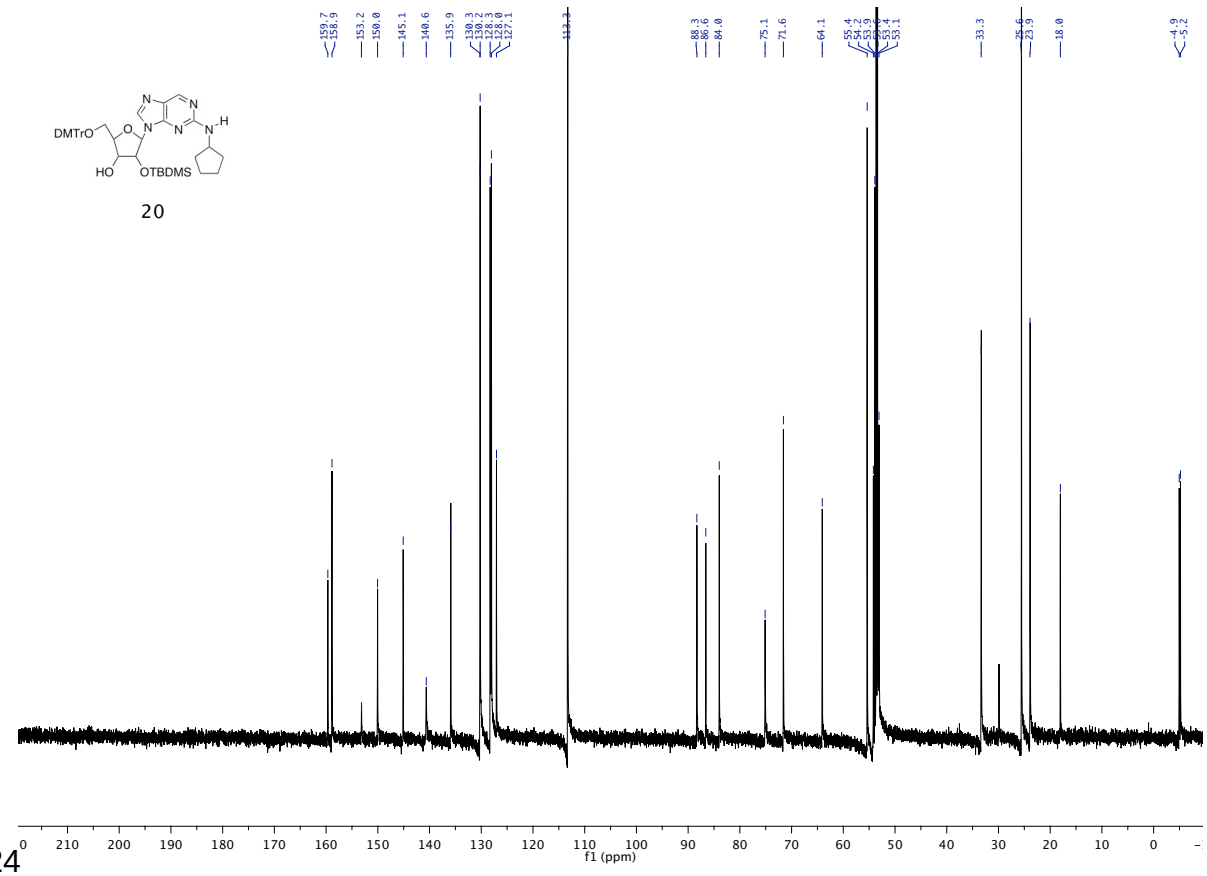

15
8.516
8.232
7.357
7.331
7.286
7.261
7.237
7.199
7.175
5.952
5.934
4.870
4.725
4.707
4.690
4.596
4.325
4.310
4.294
4.077
4.064
3.819
3.779
3.769
3.699
3.685
3.338
3.303
3.299
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
0.86
0.99
4.85
1.00
1.16
2.05
1.07
1.04
2.22
0.56

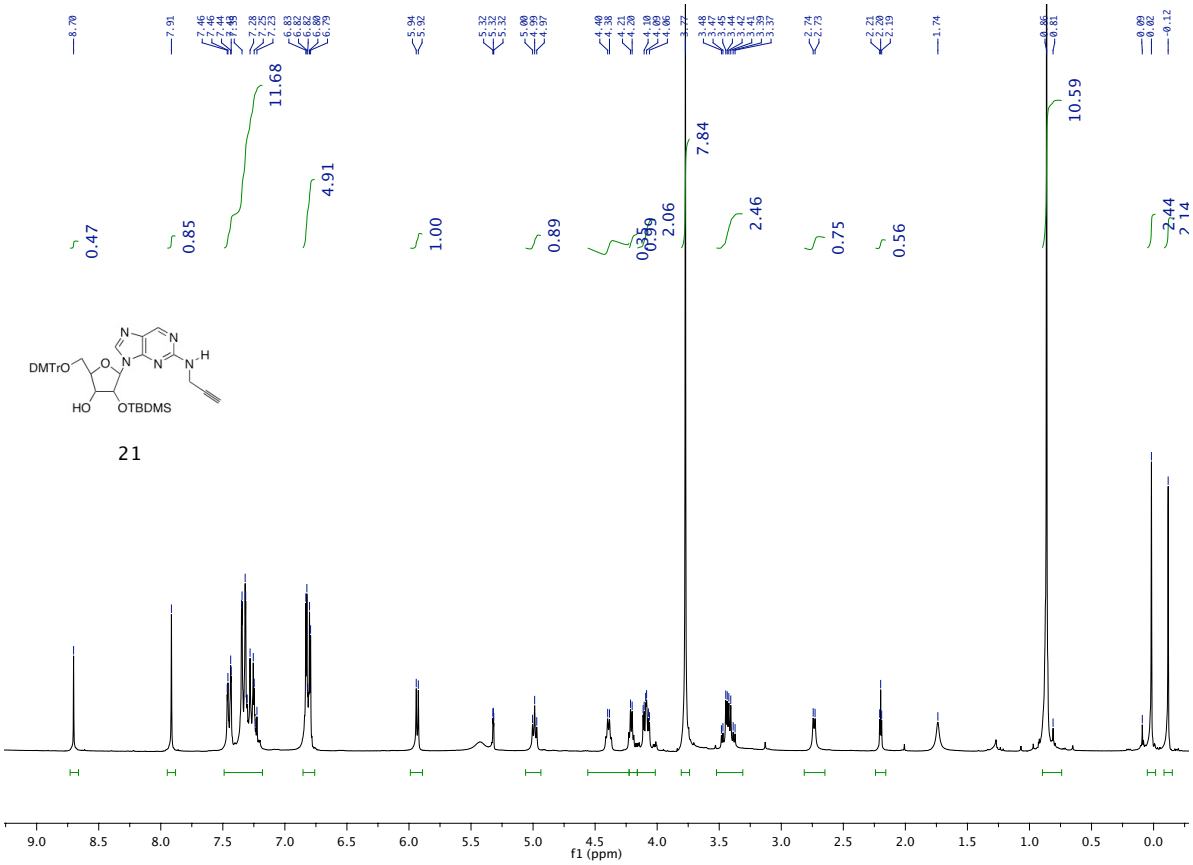

15
161.094
154.229
150.346
143.414
141.172
129.530
128.548
128.042
90.081
86.997
75.112
72.189
63.191
49.995
49.717
49.431
49.146
48.867
48.581
48.296
46.464
160
150
140
130
120
110
100
90
80
70
60
50
ppm


DMTrO
HO
OTBDMS
N
H
19
f1 (ppm)

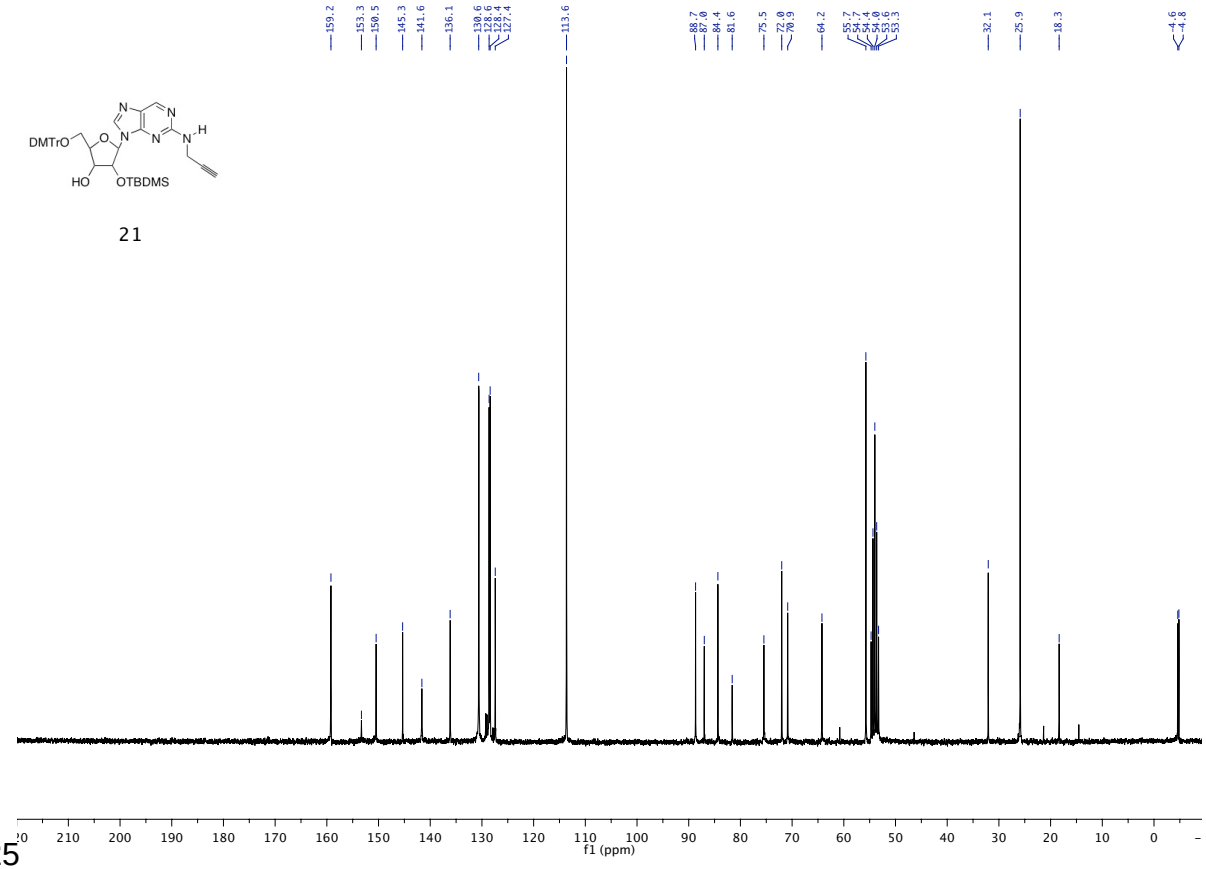

DMTrO
HO
OTBDMS
N
H
19
f1 (ppm)


DMTrO
HO
OTBDMS
N
H
20
f1 (ppm)

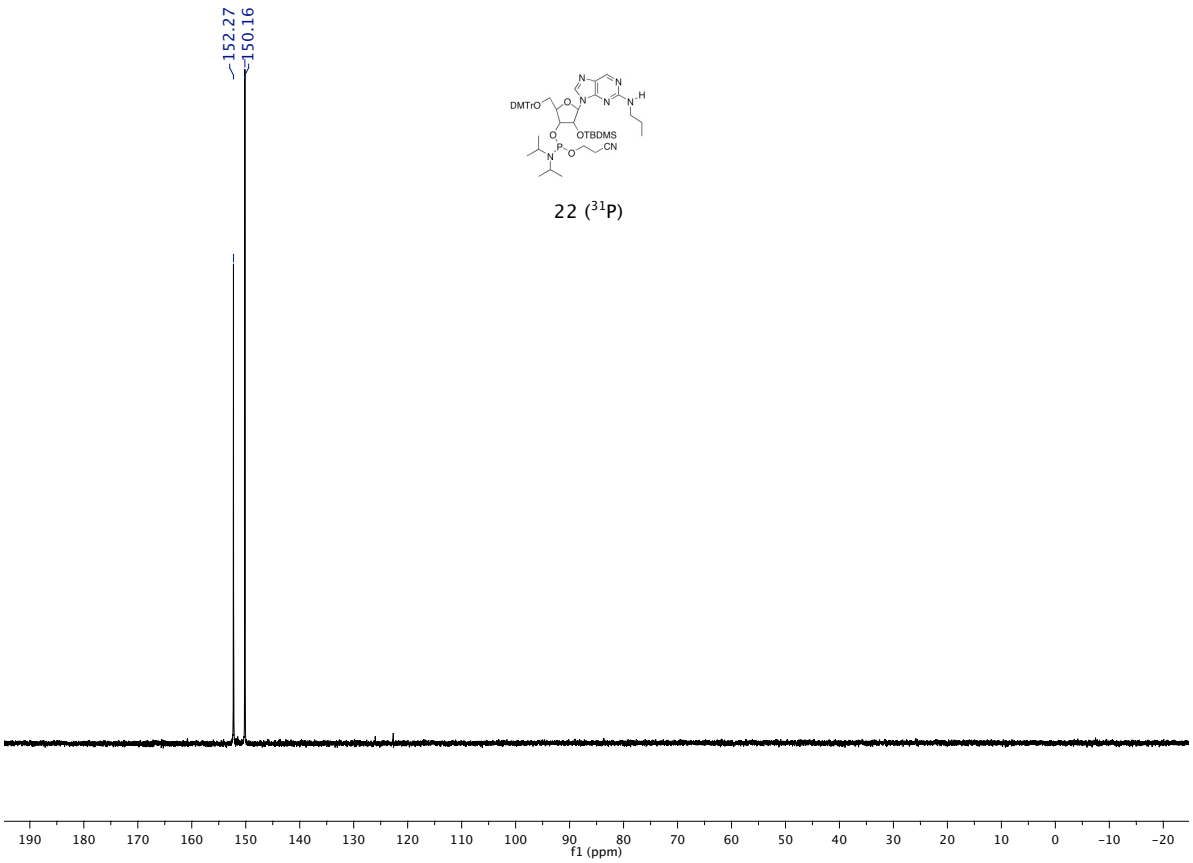

DMTrO
HO
OTBDMS
N
H
20
f1 (ppm)


DMTrO
HO
OTBDMS
N
H
11.68
4.91
1.00
0.89
0.35
0.39
2.06
7.84
2.46
0.75
0.56
10.59
2.44
2.14
0.47
0.85
f1 (ppm)

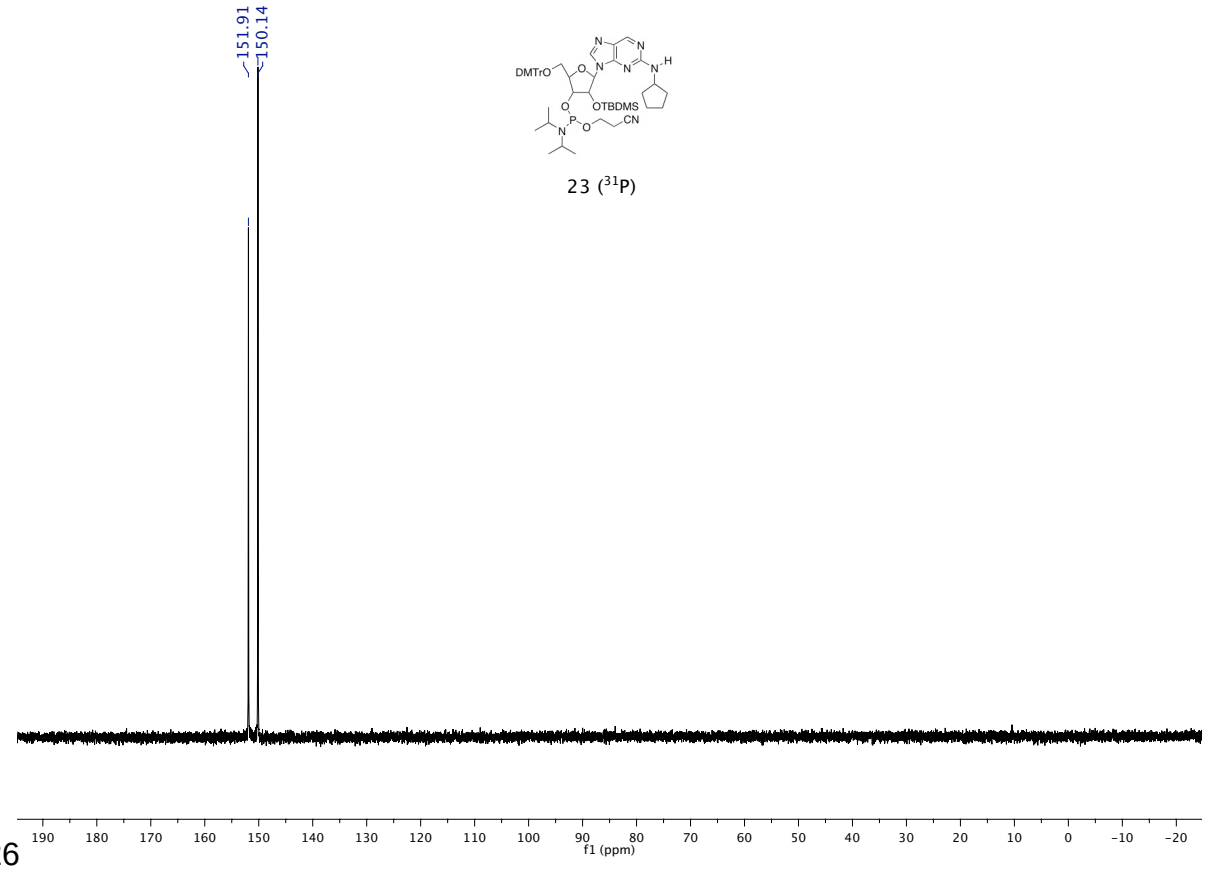
21


DMTrO
HO
OTBDMS
159.2
153.3
150.5
145.3
141.6
136.1
130.6
128.6
128.4
127.4
113.6
88.7
87.0
84.4
81.6
75.5
72.0
70.9
64.2
55.7
54.4
54.0
53.6
53.3
32.1
25.9
18.3
-4.6
-4.8
f1 (ppm)

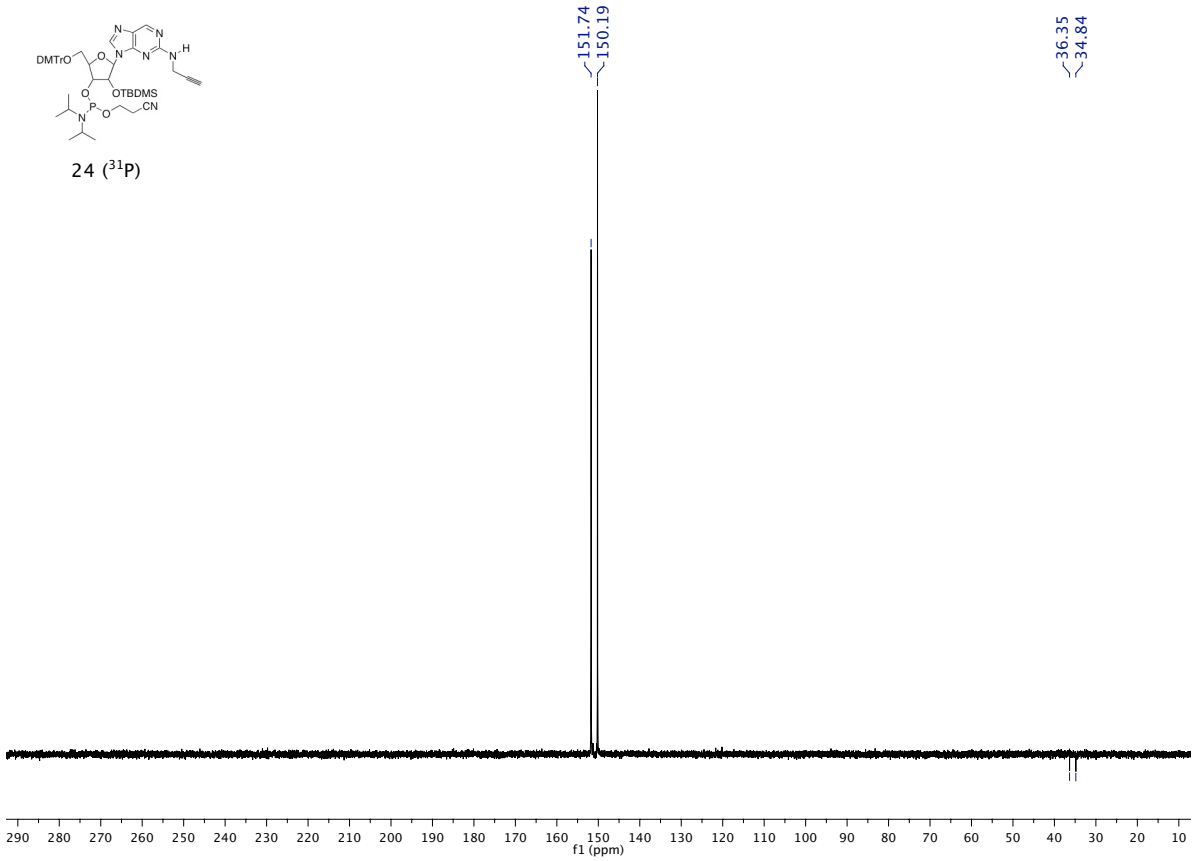
21


152.27
150.16
DMTrO
OTBDMS
CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

22 (^{31}P)


151.91
150.14
DMTrO
OTBDMS
CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

23 (^{31}P)


DMTrO
OTBDMS
CN
151.74
150.19
36.35
34.84
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

24 (^{31}P)