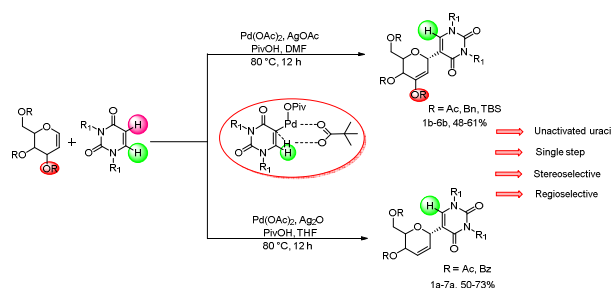


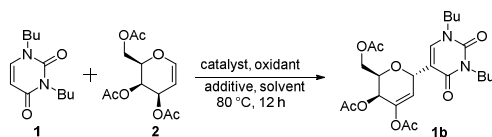
Pd catalyzed regio- and stereo-selective C-nucleoside synthesis from unactivated uracils and pyranoid glycals

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General information: All reactions were performed in a seal tube with teflon cap. ^1H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers with TMS as internal standard. Chemical shifts are expressed in parts per million (δ ppm). Signal multiplicities are represented by the following abbreviations: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet), coupling constant (J values) in Hz and integration. Silica gel coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. Exact mass of all products were analysed by using HRMS having QTOF analyser. Reagents used were mostly purchased from Sigma Aldrich.

Table1: Optimisation of β -C-nucleoside from glycal and 1,4-dibutyluracil^a

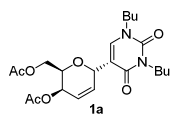
entry	catalyst	oxidant	additive	solvent	temp (°C)	yield (%)
1	Pd(TFA) ₂	Ag ₂ O	PivOH	DMF	80	23
2	PdCl ₂ (Ph ₃ P) ₂	Ag ₂ O	PivOH	DMF	80	35
3	PdCl ₂	Ag ₂ O	PivOH	DMF	80	27
4	Pd(OAc)₂	AgOAc	PivOH	DMF	80	57
5	Pd(OAc) ₂	Ag ₂ CO ₃	PivOH	DMF	80	13
6 ^b	Pd(OAc) ₂	AgOAc	PivOH	DMF	80	56

^a in all cases **1** (1 equiv), **2** (2 equiv), oxidant (2 equiv), additive (2 equiv), and Pd(OAc)₂ (10 mol %) in solvent were taken in a sealed tube and heated for 12 h. ^b using **1** (1 equiv), **2** (2 equiv), oxidant (2 equiv), PivOH (3 equiv) and Pd(OAc)₂ (10 mol %) in DMF.

General Procedure A for the Synthesis of Ferrier C-nucleosides (1a-7a): To a 20 mL oven dried seal tube, 1,3-dialkyl uracil (1 mmol), glycal (2 mmol), silver oxide (2 mmol), pivalic acid (2 mmol), THF (5 mL), and palladium(II)acetate (0.1 mmol) were successively added. The reaction mixture was stirred at 80 °C for 12-16 hours. After the completion of the reaction as checked by the TLC, the reaction mixture was then cooled, diluted with EtOAc (5 mL), and filtered over Celite. The filter cake was washed with EtOAc (20 mL). The filtrate was then concentrated under reduced pressure and purified by flash chromatography (30–40% EtOAc in petroleum ether) on silica gel to provide products generally as colorless oil.

General Procedure B for the Synthesis of β -hydride C-nucleosides (1b-6b): To a 20 mL oven dried seal tube, 1,3-dialkyl uracil (1 mmol), glycal (2 mmol), silver acetate (2 mmol), pivalic acid (2 mmol), DMF (3 mL), and palladium(II)acetate (0.1 mmol) were successively added. The reaction mixture was stirred at 80 °C for 12-16 hours. After the completion of the reaction as checked by the TLC, the reaction mixture was then cooled, diluted with EtOAc (5 mL), and filtered over Celite. The filter cake was washed with EtOAc (20 mL). The filtrate was then concentrated under reduced pressure and purified by flash chromatography (30–40% EtOAc in petroleum ether) on silica gel to provide products generally as colorless oil.

Characterization Data of Substrates:

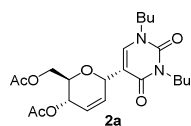


Prepared by the general procedure **A** using N,N-dibutyl uracil (224mg, 1mmol), tri-*O*-acetyl-D-galactal (544 mg, 2 mmol), Silver oxide (464 mg, 2mmol), Pivalic acid (226.67 μ L, 2mmol) and Pd(OAc)₂ (22.45 mg, 0.1 mmol) in THF (5mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **1a** in 73% (319mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 0.8 Hz, 1H), 6.30 (dd, J = 10.3, 2.6 Hz, 1H), 6.12-6.07 (m, 1H), 5.40 (s, 1H), 5.19 – 5.11 (m, 1H), 4.29 – 4.19 (m, 2H), 4.09 – 4.05 (m, 1H), 3.97 – 3.92 (m, 2H), 3.80 – 3.70 (m, 2H), 2.10 (s, 3H), 2.05 (s, 3H), 1.70 – 1.57 (m, 3H), 1.36 (dd, J = 15.0, 7.5 Hz, 4H), 1.25 (grease), 0.97 (t, J = 5.7 Hz, 3H), 0.93 (t, J = 5.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.48 (s), 170.47 (s), 161.94 (s), 151.03 (s), 139.84 (s), 131.83 (s), 123.56 (s), 110.21 (s), 68.90 (s), 68.18 (s), 63.76 (s), 62.72 (s), 49.87 (s), 41.38 (s), 31.15 (s), 29.66 (s), 20.84 (s), 20.71 (s), 20.21 (s), 19.76 (s), 13.70 (s), 13.59 (s).

HRMS (ESI⁺): m/z calcd for C₂₂H₃₃N₂O₇ (M+H)⁺ 437.2288, found 437.2280.



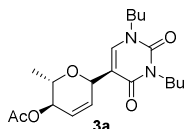
Prepared by the general procedure **A** using N,N-dibutyl uracil (50 mg, 0.223 mmol), tri-*O*-acetyl-D-glucal (121.4 mg, 0.446 mmol), Silver oxide (103.3, 0.446 mmol), Pivalic acid (50.5 μ L, 0.446 mmol) and Pd(OAc)₂ (5mg, 0.022 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **2a** in 71% (69.0 mg) mg as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 0.8 Hz, 1H), 6.15 (dd, J = 10.3, 2.6 Hz, 1H), 5.95-5.92 (m, 1H), 5.33 (d, J = 1.9 Hz, 1H), 5.17-5.15 (m, 1H), 4.26 (dd, J = 11.9, 6.7 Hz, 1H), 4.16 (dd, J = 11.9, 3.8 Hz, 1H), 3.98 – 3.91 (m, 3H), 3.78-3.73 (m, 2H), 2.08 (s, 3H),

2.07 (s, 3H), 1.71 – 1.65 (m, 2H), 1.62 – 1.55 (m, 2H), 1.39-1.33 (m, 4H), 1.25 (s, grease), 0.96 (t, $J = 6.1$ Hz, 3H), 0.93 (t, $J = 6.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.60 (s), 170.19 (s), 161.96 (s), 151.04 (s), 140.15 (s), 130.80 (s), 124.54 (s), 110.89 (s), 70.41 (s), 67.25 (s), 65.18 (s), 62.93 (s), 49.82 (s), 41.34 (s), 31.13 (s), 29.65 (s), 21.01 (s), 20.73 (s), 20.20 (s), 19.74 (s), 13.71 (s), 13.60 (s).

HRMS (ESI^+): m/z calcd for $\text{C}_{22}\text{H}_{33}\text{N}_2\text{O}_7$ ($\text{M}+\text{H}$) $^+$ 437.2288, found 437.2284.

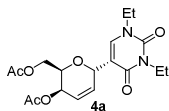


Prepared by the general procedure **A** using N,N-dibutyl uracil (50 mg, 0.223 mmol), di-*O*-acetyl-L-Rhamnal (95.4 mg, 0.446 mmol), Silver oxide (103.3, 0.446 mmol), Pivalic acid (50.5 μL , 0.446 mmol) and $\text{Pd}(\text{OAc})_2$ (5mg, 0.022 mmol) in THF (3 mL) at 80 $^\circ\text{C}$ for 12 h and purified by flash chromatography (30% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **3a** in 73% (61.5 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.22 (s, 1H), 6.12 – 6.08 (m, 1H), 5.92-5.89 (m, 1H), 5.29 (d, $J = 1.6$ Hz, 1H), 4.94 – 4.88 (m, 1H), 3.95 (dd, $J = 13.3, 6.5$ Hz, 3H), 3.77 – 3.73 (m, 2H), 2.09 (s, 3H), 1.68 (t, $J = 7.5$ Hz, 2H), 1.62 – 1.56 (m, 2H), 1.38 (dd, $J = 7.4, 1.9$ Hz, 2H), 1.35 (dd, $J = 7.5, 1.9$ Hz, 2H), 1.30 (d, $J = 6.6$ Hz, 3H), 0.96 (t, $J = 5.1$ Hz, 3H), 0.93 (t, $J = 5.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.52 (s), 162.14 (s), 151.08 (s), 140.11 (s), 131.76 (s), 123.31 (s), 111.60 (s), 69.53 (s), 69.20 (s), 65.37 (s), 49.78 (s), 41.33 (s), 31.13 (s), 29.65 (s), 21.18 (s), 20.22 (s), 19.74 (s), 16.60 (s), 13.73 (s), 13.61 (s).

HRMS (ESI^+): m/z calcd for $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_5$ ($\text{M}+\text{H}$) $^+$ 379.2233, found 379.2231.



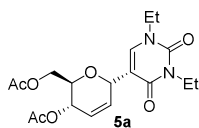
Prepared by the general procedure **A** using N,N-diethyl uracil (30 mg, 0.178 mmol), tri-*O*-acetyl-D-galactal (97.1 mg, 0.357 mmol), Silver oxide (82.7mg, 0.357 mmol), Pivalic acid (40.5 μL , 0.357 mmol) and $\text{Pd}(\text{OAc})_2$ (4mg, 0.017 mmol) in THF (3 mL) at 80 $^\circ\text{C}$ for 12 h

and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **4a** in 51% (34.4 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 0.9 Hz, 1H), 6.32 (dd, *J* = 10.3, 3.2 Hz, 1H), 6.12-6.08(m, 1H), 5.41 (s, 1H), 5.18 – 5.12 (m, 1H), 4.30-4.19 (m, 2H), 4.10 – 4.06 (m, 1H), 4.05 – 3.99 (m, 2H), 3.83 (dt, *J* = 13.9, 6.8 Hz, 2H), 2.11 (s, 3H), 2.06 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.53 (s), 170.51 (s), 161.81 (s), 157.22 (s), 139.43 (s), 131.82 (s), 123.57 (s), 110.52 (s), 68.88 (s), 68.19 (s), 63.75 (s), 62.69 (s), 45.08 (s), 36.63 (s), 29.69 (s), 20.86 (s), 20.74 (s), 14.41 (s), 12.80 (s).

HRMS (ESI⁺): *m/z* calcd for C₁₈H₂₅N₂O₇ (M+H)⁺ 381.1662, found 381.1664.

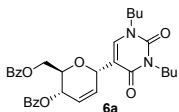


Prepared by the general procedure **A** using N,N-diethyl uracil (30 mg, 0.178 mmol), tri-*O*-acetyl-D-glucal (97.1 mg, 0.357 mmol), Silver oxide (82.7mg, 0.357 mmol), Pivalic acid (40.5 μL, 0.357 mmol) and Pd(OAc)₂ Pd(OAc)₂ (4mg, 0.017 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **5a** in 51% (34.4 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 0.9 Hz, 1H), δ 6.15-6.11 (m, 1H), 5.96 – 5.86 (m, 1H), 5.32 (d, *J* = 1.8 Hz, 1H), 5.14 (m, 1H), 4.28 – 4.22 (m, 1H), 4.15 (dd, *J* = 12.0, 3.8 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.96 – 3.92 (m, 1H), 3.86 – 3.76 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.23 (bs, grease peak) 1.31 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). 0.86-0.80 (m, grease peak)

¹³C NMR (101 MHz, CDCl₃) δ 170.62 (s), 170.21 (s), 161.80 (s), 150.67 (s), 139.75 (s), 130.77 (s), 124.52 (s), 111.19 (s), 70.39 (s), 67.19 (s), 65.13 (s), 62.86 (s), 45.04 (s), 36.56 (s), 29.65 (s, grease peak) 21.00 (s), 20.72 (s), 14.38 (s), 12.77 (s).

HRMS (ESI⁺): *m/z* calcd for C₁₈H₂₅N₂O₇ (M+H)⁺ 381.1662, found 381.1659.

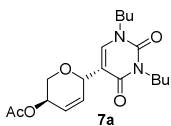


Prepared by the general procedure **A** using N,N-dibutyl uracil (50 mg, 0.223 mmol), tri-*O*-benzoyl-D-glucal (204.4 mg, 0.446 mmol), Silver oxide (103.3mg, 0.446 mmol), Pivalic acid (50.5 μ L, 0.446 mmol) and Pd(OAc)₂ (5mg, 0.022 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **6a** in 64% (79.9 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.98 (m, 4H), 7.59 – 7.52 (m, 2H), 7.40 (dd, J = 15.2, 7.6 Hz, 4H), 7.31 (s, 1H), 6.26 (ddd, J = 10.3, 2.6, 1.3 Hz, 1H), 6.27 – 6.25 (m, 1H), 5.52 (s, 1H), 5.54 – 5.48 (m, 1H), 5.46 (d, J = 1.8 Hz, 1H), 4.60 – 4.53 (m, 2H), 4.29 (dd, J = 10.8, 6.1 Hz, 1H), 3.97 – 3.89 (t, J = 7.4 Hz, 2H), 3.71 (t, J = 7.4 Hz, 2H), 1.63 – 1.57 (m, 4H), 1.39 – 1.29 (m, 4H), 0.96 – 0.93 (m, 3H), 0.93 – 0.90 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 166.25 (s), 165.87 (s), 161.98 (s), 151.04 (s), 140.13 (s), 133.34 (s), 133.15 (s), 131.07 (s), 129.80 (s), 129.76 (s), 129.70 (s), 128.45 (s), 128.39 (s), 124.61 (s), 110.96 (s), 70.56 (s), 67.51 (s), 66.31 (s), 63.83 (s), 49.84 (s), 41.35 (s), 31.14 (s), 29.69 (s), 20.23 (s), 19.71 (s), 13.72 (s), 13.62 (s).

HRMS (ESI⁺): m/z calcd for C₃₂H₃₇N₂O₇ (M+H)⁺ 561.2601, found 561.2613.

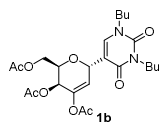


Prepared by the general procedure **A** using N,N-dibutyl uracil (50 mg, 0.223 mmol), di-*O*-acetyl-D-xylal (89.2 mg, 0.446 mmol), Silver oxide (103.3, 0.446 mmol), Pivalic acid (50.5 μ L, 0.446 mmol) and Pd(OAc)₂ (5mg, 0.022 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (30% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **7a** in 50% (40.5 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.26 (s, 1H), 6.19 (d, J = 10.2 Hz, 1H), 6.00 (t, J = 22.9 Hz, 1H), 5.14 (t, J = 37.6 Hz, 2H), 4.10 (d, J = 12.9 Hz, 1H), 2.09 (s, 3H), 1.69 – 1.64 (m, 2H), 1.61 – 1.56 (m, 2H), 1.36 (dd, J = 14.5, 7.2 Hz, 4H), 0.94 (dd, J = 15.9, 7.8 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 170.63 (s), 161.97 (s), 151.04 (s), 139.83 (s), 134.25 (s), 122.50 (s), 111.92 (s), 69.50 (s), 67.92 (s), 64.45 (s), 49.83 (s), 41.29 (s), 31.13 (s), 29.68 (s), 29.65 (s), 21.16 (s), 20.21 (s), 19.75 (s), 13.71 (s), 13.61 (s).

HRMS (ESI⁺): m/z calcd for C₁₉H₂₉N₂O₅ (M+H)⁺ 365.2076, found 365.2073.

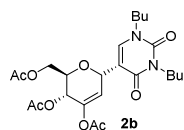


Prepared by the general procedure **B** using N,N-dibutyl uracil (224mg, 1mmol), tri-*O*-acetyl-D-galactal (544 mg, 2 mmol), Silver acetate (464 mg, 2mmol), Pivalic acid (226.7μL, 2 mmol) and Pd(OAc)₂ (22.4 mg, 0.1) in THF (5 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **1b** in 59% (290.7 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.35 (s, 1H), 5.83 (d, *J* = 3.7 Hz, 1H), 5.64 (d, *J* = 3.7 Hz, 1H), 5.35 (d, *J* = 2.5 Hz, 1H), 4.17 (s, 1H), 4.15 (s, 1H), 4.08 – 4.06 (m, 1H), 3.93 (t, *J* = 7.6 Hz, 2H), 3.76 (dd, *J* = 13.8, 6.9 Hz, 2H), 2.15 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H), 1.69 (dd, *J* = 7.4, 2.3 Hz, 2H), 1.61 – 1.58 (m, 2H), 1.38 – 1.32 (m, 4H), 1.25 (grease), 0.96 (t, *J* = 5.8 Hz, 3H), 0.92 (t, *J* = 5.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.44 (s), 170.25 (s), 169.79 (s), 161.92 (s), 151.02 (s), 144.25 (s), 141.64 (s), 119.35 (s), 108.70 (s), 68.46 (s), 67.86 (s), 63.86 (s), 61.94 (s), 49.90 (s), 41.44 (s), 30.93 (s), 29.63 (s), 20.63 (s), 20.57 (s), 20.19 (s), 19.67 (s), 13.69 (s), 13.53 (s).

HRMS (ESI⁺): m/z calcd for C₂₄H₃₅N₂O₉ (M+H)⁺ 495.2343, found 495.2347.

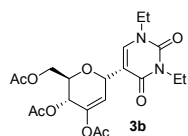


Prepared by the general procedure **B** using N,N-dibutyl uracil (50 mg, 0.223 mmol), tri-*O*-acetyl-D-glucal (121.4 mg, 0.446), Silver acetate (74.5 mg, 0.446 mmol), Pivalic acid (50.5 μL, 0.446 mmol) and Pd(OAc)₂ (5 mg, 0.022 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **2b** in 56% (61.6 mg) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.45 (s, 1H), 5.83 (d, $J = 2.4$ Hz, 1H), 5.51 (s, 1H), 5.35 (d, $J = 4.1$ Hz, 1H), 3.98 – 3.86 (m, 4H), 3.77 (t, $J = 7.4$ Hz, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.71 – 1.67 (t, 2H), 1.61-1.57 (t, 2H), 1.37 – 1.33 (m, 4H), 0.95 – 0.91 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.44 (s), 169.25 (s), 168.79 (s), 160.92 (s), 150.02 (s), 143.25 (s), 140.64 (s), 118.35 (s), 107.70 (s), 67.46 (s), 66.86 (s), 62.86 (s), 60.94 (s), 48.90 (s), 40.44 (s), 29.93 (s), 28.63 (s), 19.63 (s), 19.57 (s), 19.19 (s), 18.67 (s), 12.69 (s), 12.53 (s).

HRMS (ESI^+): m/z calcd for $\text{C}_{24}\text{H}_{35}\text{N}_2\text{O}_9(\text{M}+\text{H})^+$ 495.2343, found 495.2345.

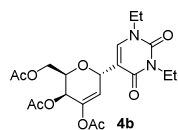


Prepared by the general procedure **B** using N,N-diethyl uracil (30 mg, 0.178 mmol), tri-*O*-acetyl-D-glucal (97.1 mg, 0.357 mmol), Silver acetate (59.6 mg, 0.357 mmol), Pivalic acid (40.5 μL , 0.357 mmol) and $\text{Pd}(\text{OAc})_2$ (4 mg, 0.017 mmol) in THF (3 mL) at 80 $^\circ\text{C}$ for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **3b** in 48% (37.4 mg) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 7.48 (s, 1H), 5.84 (s, 1H), 5.52 (s, 1H), 5.36 (s, 1H), 4.34 (d, $J = 6.7$ Hz, 1H), 4.21 – 4.14 (m, 2H), 4.02 – 3.99 (m, 2H), 3.85-3.83 (m, 2H), 2.14 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 1.36-1.33 (m, 3H), 1.23-1.20 (m, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 170.68 (s), 170.23 (s), 169.02 (s), 161.70 (s), 150.68 (s), 142.42 (s), 140.95 (s), 119.28 (s), 110.75 (s), 72.33 (s), 66.30 (s), 64.83 (s), 61.97 (s), 45.15 (s), 36.63 (s), 20.90 (s), 20.81 (s), 20.73 (s), 14.40 (s), 12.83 (s).

HRMS (ESI^+): m/z calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_9(\text{M}+\text{H})^+$ 439.1717, found 439.1719.



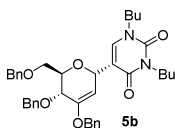
Prepared by the general procedure **B** using N,N-diethyl uracil (30 mg, 0.178 mmol), tri-*O*-acetyl-D-galactal (97.1 mg, 0.357 mmol), Silver acetate (59.6 mg, 0.357 mmol), Pivalic acid (40.5 μL , 0.357 mmol) and $\text{Pd}(\text{OAc})_2$ (4 mg, 0.017 mmol) in THF (3 mL) at 80 $^\circ\text{C}$ for 12 h

and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **3b** in 49% (38.2 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.39 (s, 1H), 5.86 (d, *J* = 3.7 Hz, 1H), 5.66 (d, *J* = 3.6 Hz, 1H), 5.37 (d, *J* = 1.5 Hz, 1H), 4.19 (d, *J* = 6.6 Hz, 2H), 4.10 (t, *J* = 5.5 Hz, 1H), 4.02 (dd, *J* = 13.6, 6.7 Hz, 2H), 3.91 – 3.79 (m, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 2.02 (s, 3H), 1.35-1.33 (m, 3H), 1.26-1.22 (m, 3H), 0.87 (m, grease).

¹³C NMR (101 MHz, CDCl₃) δ 170.52 (s), 170.38 (s), 169.96 (s), 161.81 (s), 150.71 (s), 144.28 (s), 141.15 (s), 119.36 (s), 109.06 (s), 68.42 (s), 67.87 (s), 63.82 (s), 61.92 (s), 45.12 (s), 36.73 (s), 29.70 (s), 20.71 (s), 20.66 (s), 14.31 (s), 12.81 (s).

HRMS (ESI⁺): *m/z* calcd for C₂₀H₂₇N₂O₉ (M+H)⁺ 439.1717, found 439.1719.

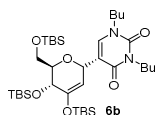


Prepared by the general procedure **A** using N,N-dibutyl uracil (50 mg, 0.223 mmol), tri-*O*-benzyl-D-glucal (121.4 mg, 0.446 mmol), Silver acetate (74.5 mg, 0.446 mmol), Pivalic acid (50.5 μL, 0.446 mmol) and Pd(OAc)₂ (5 mg, 0.017 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (30% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **2b** in 61% (86.7 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.38-7.36 (m, 4H), 7.33-7.31 (m, 4H), 7.30-7.28 (m, 5H), 7.26-7.24 (m, 3H), δ 5.40 (d, *J* = 1.5 Hz, 1H), 5.11 (d, *J* = 3.1 Hz, 1H), 4.87 – 4.80 (m, 3H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.55 (bs, 2H), 4.13 (t, *J* = 5.4 Hz, 1H), 4.00 (d, *J* = 4.9 Hz, 1H), 3.97 – 3.92 (m, 2H), 3.67-3.58 (m, 4H), 1.63-1.59 (m, 7.8 Hz, 4H), 1.38 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.30 – 1.25 (m, 2H), 0.94 (dd, *J* = 15.1, 7.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) 162.33 (s), 152.47 (s), 151.14 (s), 140.16 (s), 138.30 (s), 138.03 (s), 136.76 (s), 128.48 (s), 128.41 (s), 128.32 (s), 128.10 (s), 127.88 (s), 127.84 (s), 127.74 (s), 127.71 (s), 127.37 (s), 112.72 (s), 98.15 (s), 74.28 (s), 73.55 (s), 73.20 (s), 71.75 (s), 69.06 (s), 69.02 (s), 66.88 (s), 49.69 (s), 41.24 (s), 31.08 (s), 29.69 (s), 20.26 (s), 19.71 (s), 13.76 (s), 13.63 (s).

HRMS (ESI⁺): *m/z* calcd for C₃₉H₄₇N₂O₆ (M+H)⁺ 639.3434, found 639.3439.



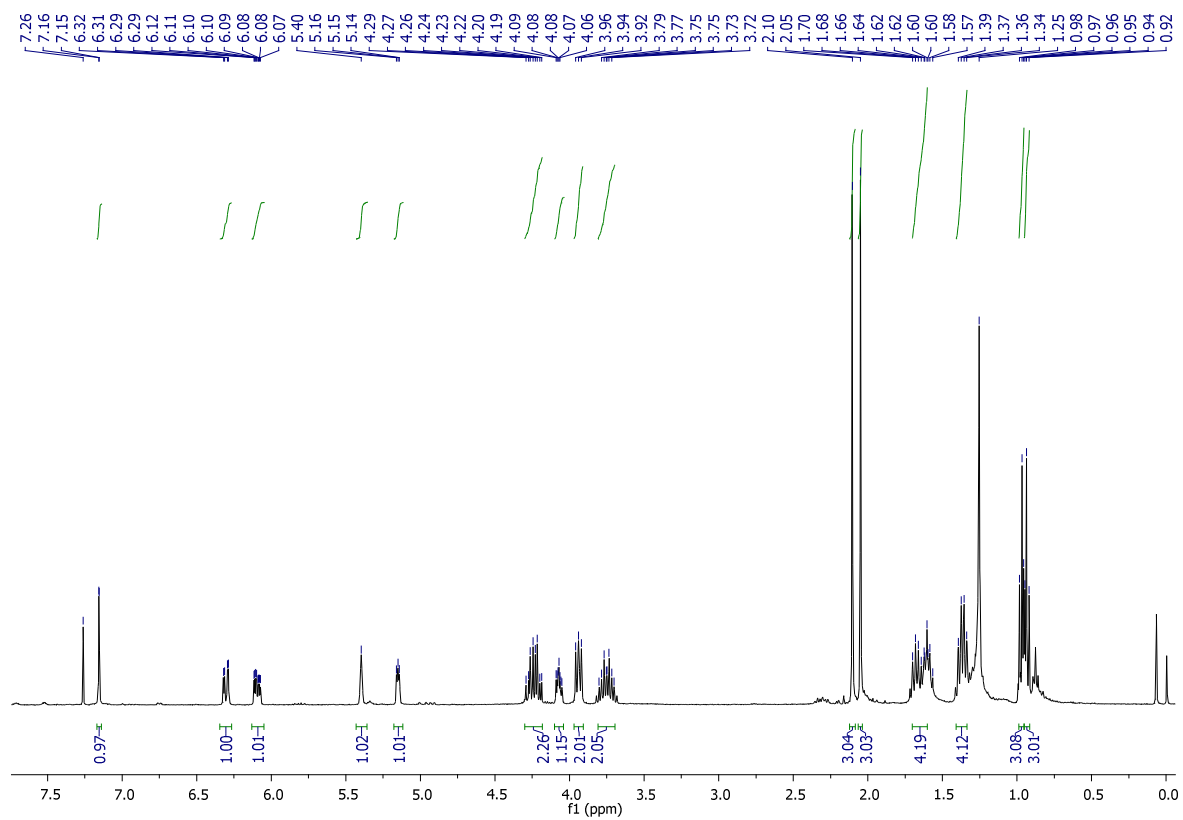
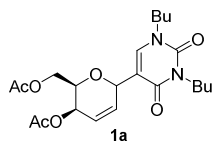
Prepared by the general procedure **B** using N,N-dibutyl uracil (50 mg, 0.223 mmol), tri-*O*-tert-butyldimethylsilyl-D-glucal (121.4 mg, 0.446 mmol), Silver acetate (74.5 mg, 0.446 mmol), Pivalic acid (50.5 μ L, 0.446 mmol) and Pd(OAc)₂ (5 mg, 0.017 mmol) in THF (3 mL) at 80 °C for 12 h and purified by flash chromatography (40% EtOAc/Petroleum ether) on silica gel (mesh size 100-200) to obtain **6b** in 52% (82.3 mg) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 5.27 (d, *J* = 1.2 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 4.02 (s, 1H), 3.96 – 3.90 (m, 3H), 3.77 – 3.68 (m, 4H), 1.67-1.57 (m, 5H), 1.40 – 1.30 (m, 5H), 1.26 (s, 2H), 0.95 (d, *J* = 2.8 Hz, 2H), 0.93 (s, 9H), 0.92 (s, 9H), 0.89 (s, 9H), 0.17 (d, *J* = 4.9 Hz, 6H), 0.12 (d, *J* = 3.6 Hz, 6H), 0.05 (s, 6H).

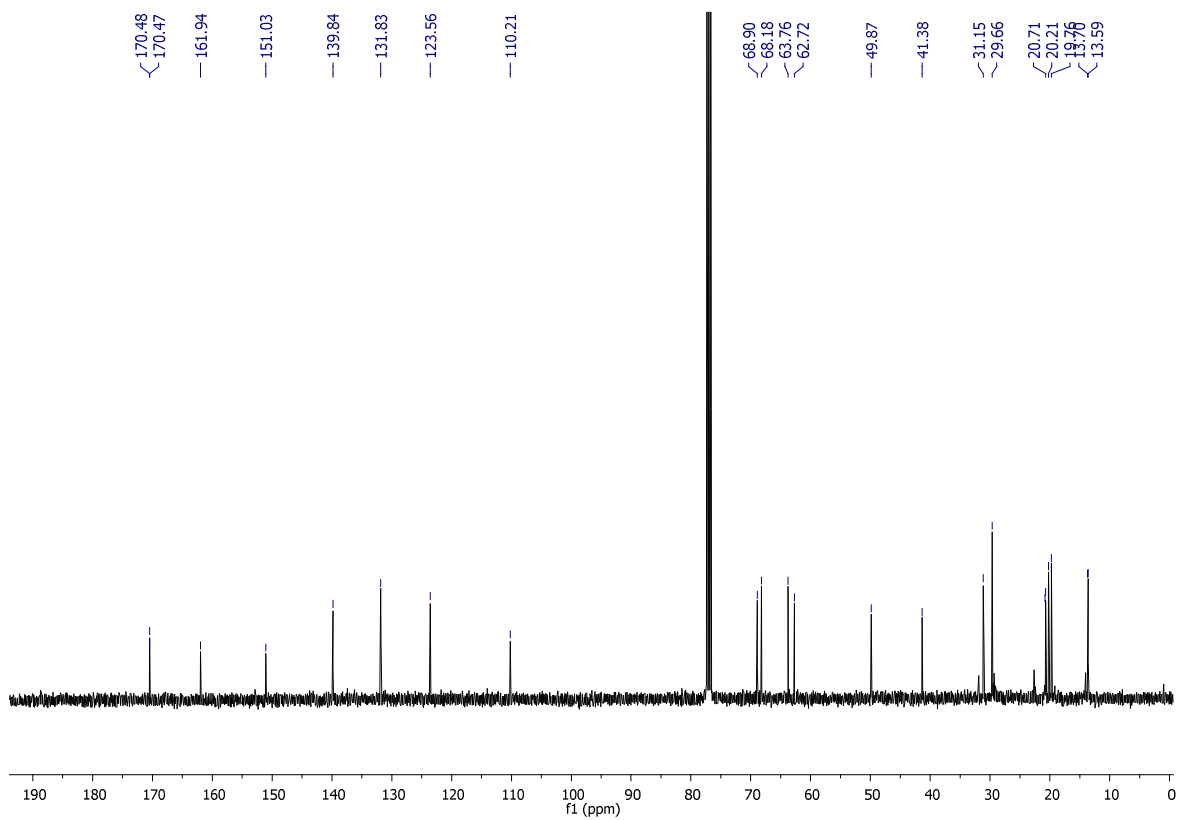
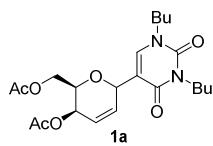
¹³C NMR (101 MHz, CDCl₃) δ 162.21 (s), 151.14 (s), 148.21 (s), 140.51 (s), 114.11 (s), 104.99 (s), 79.93 (s), 67.25 (s), 65.80 (s), 62.08 (s), 49.70 (s), 41.17 (s), 31.13 (s), 29.68 (s), 25.91 (s), 25.89 (s), 25.85 (s), 20.20 (s), 19.78 (s), 18.29 (s), 18.21 (s), 18.07 (s), 13.73 (s), 13.59 (s), -4.14 (s), -4.18 (s), -4.64 (s), -5.42 (s), -5.50 (s).

HRMS (ESI⁺): *m/z* calcd for C₃₆H₇₁N₂O₆Si₃ (M+H)⁺ 711.4620, found 711.4623.

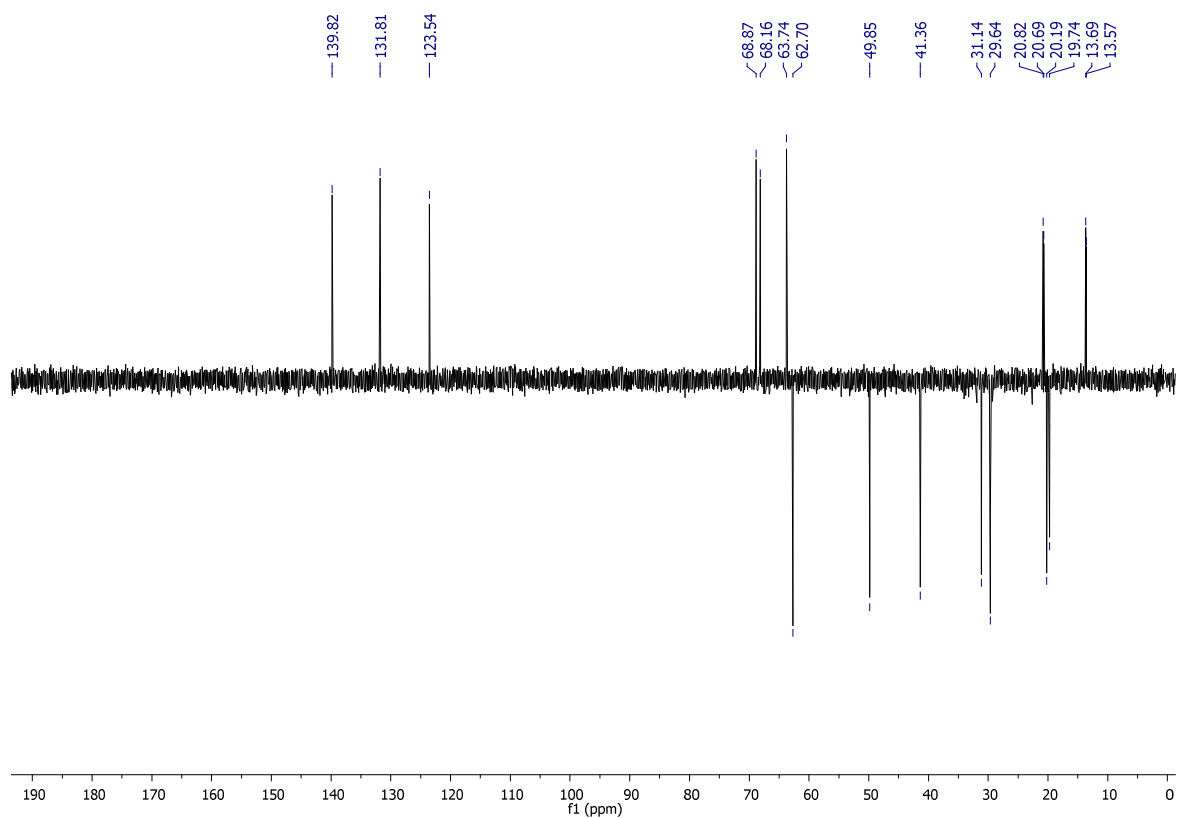
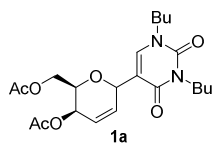
¹H NMR of 1a



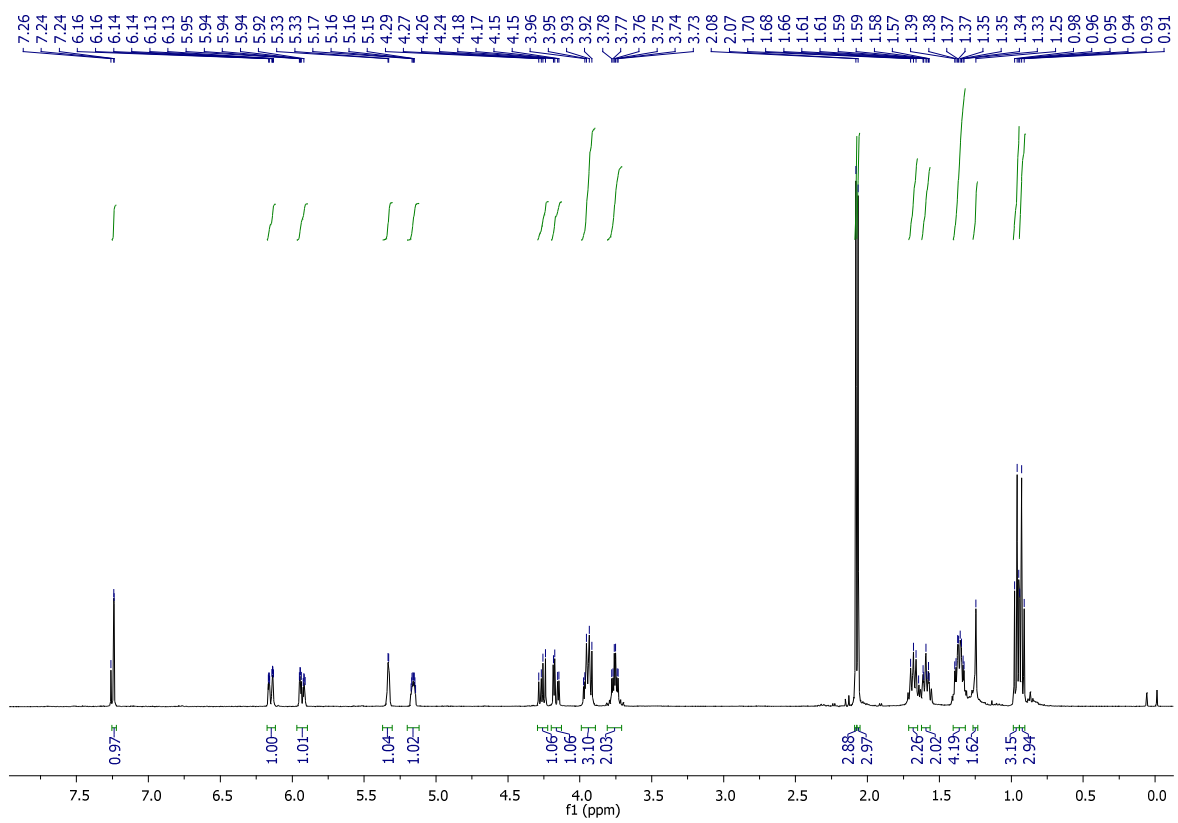
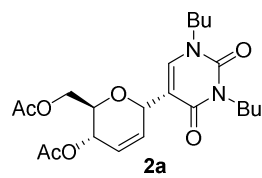
¹³C NMR of **1a**



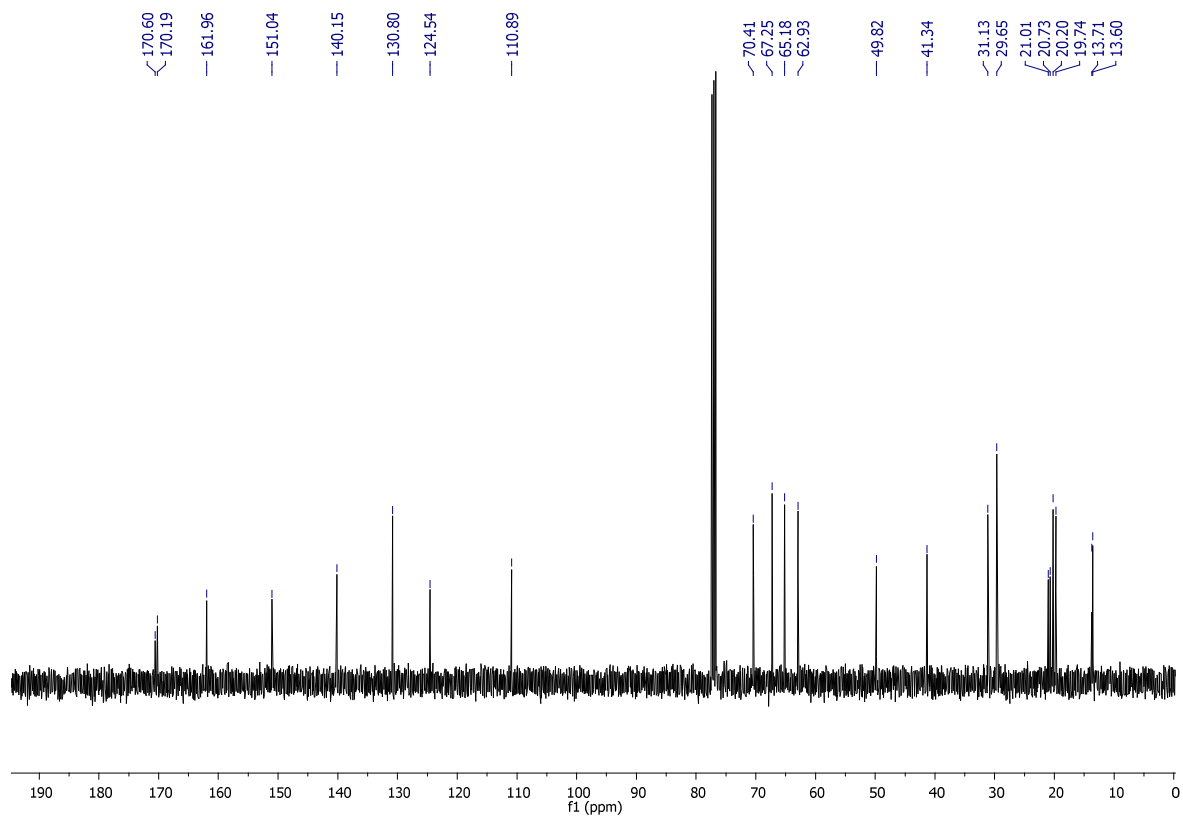
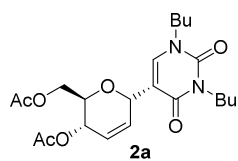
DEPTof 1a



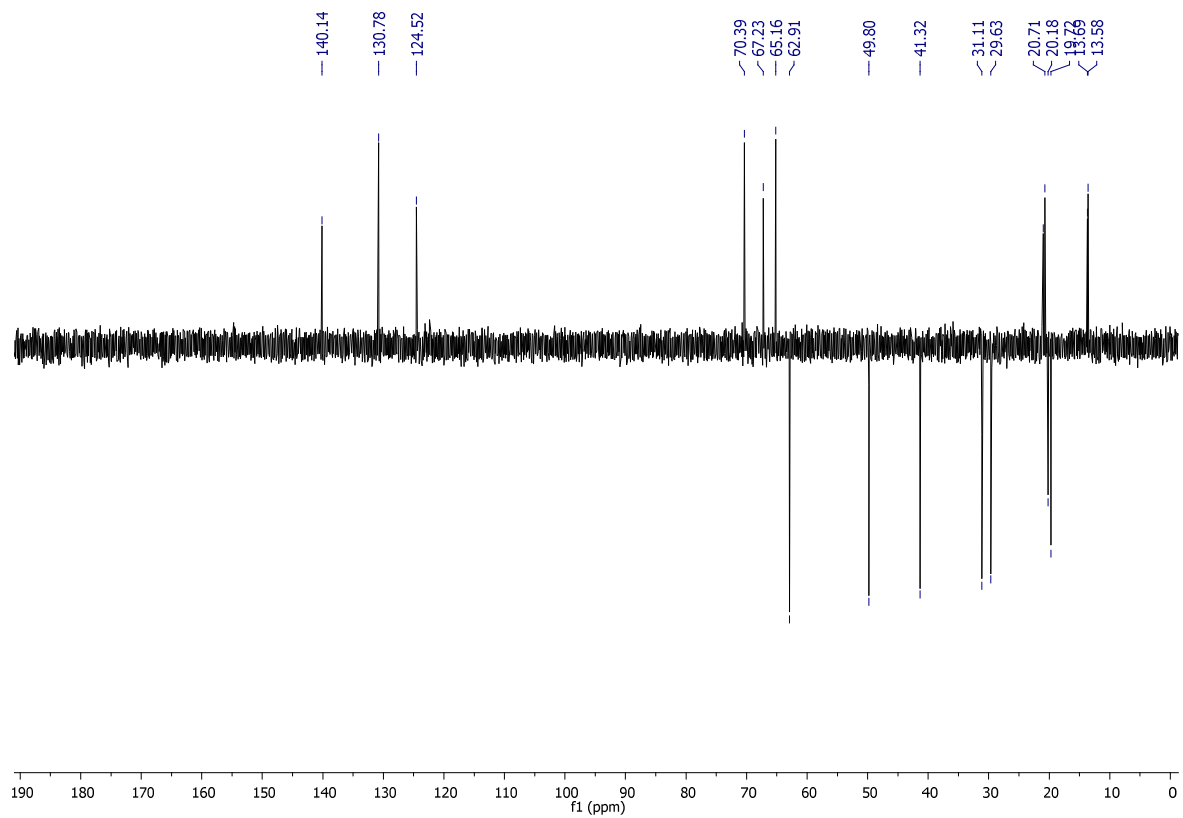
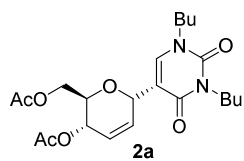
¹HNMR of 2a



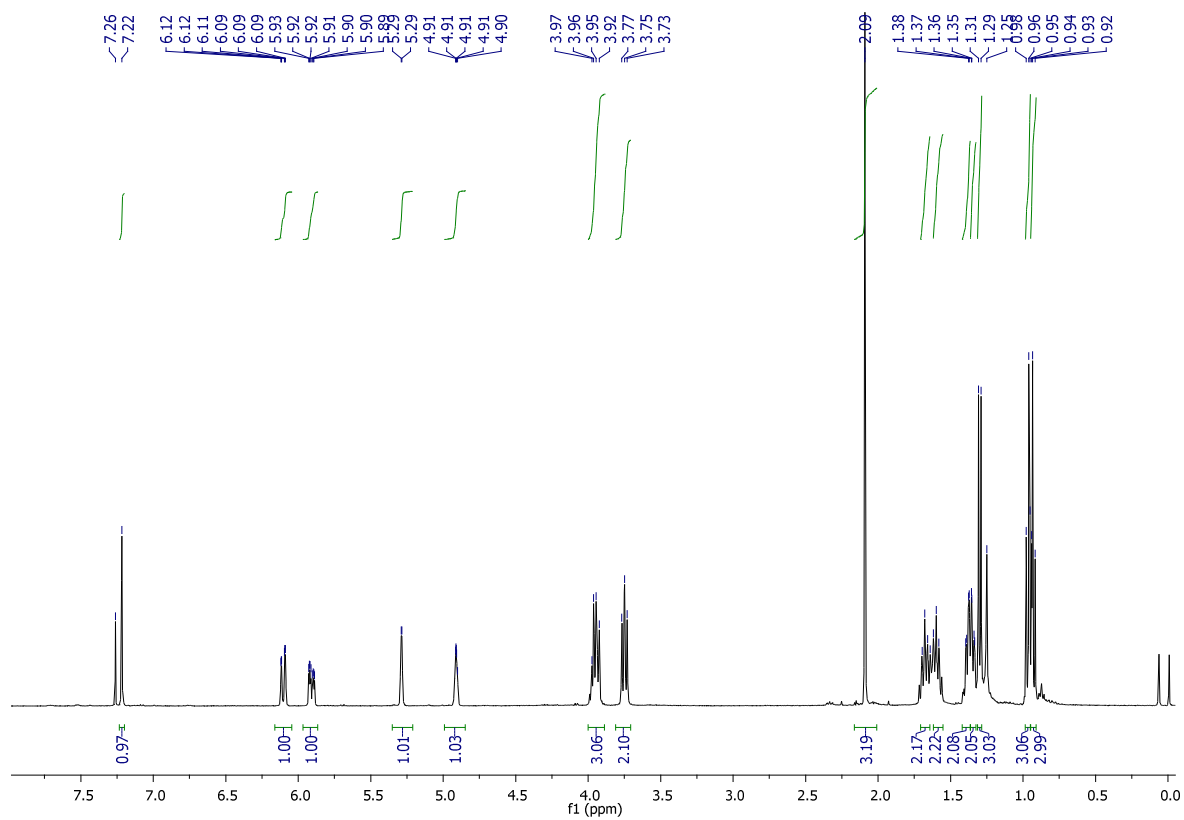
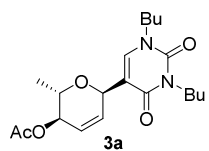
¹³C NMR of 2a



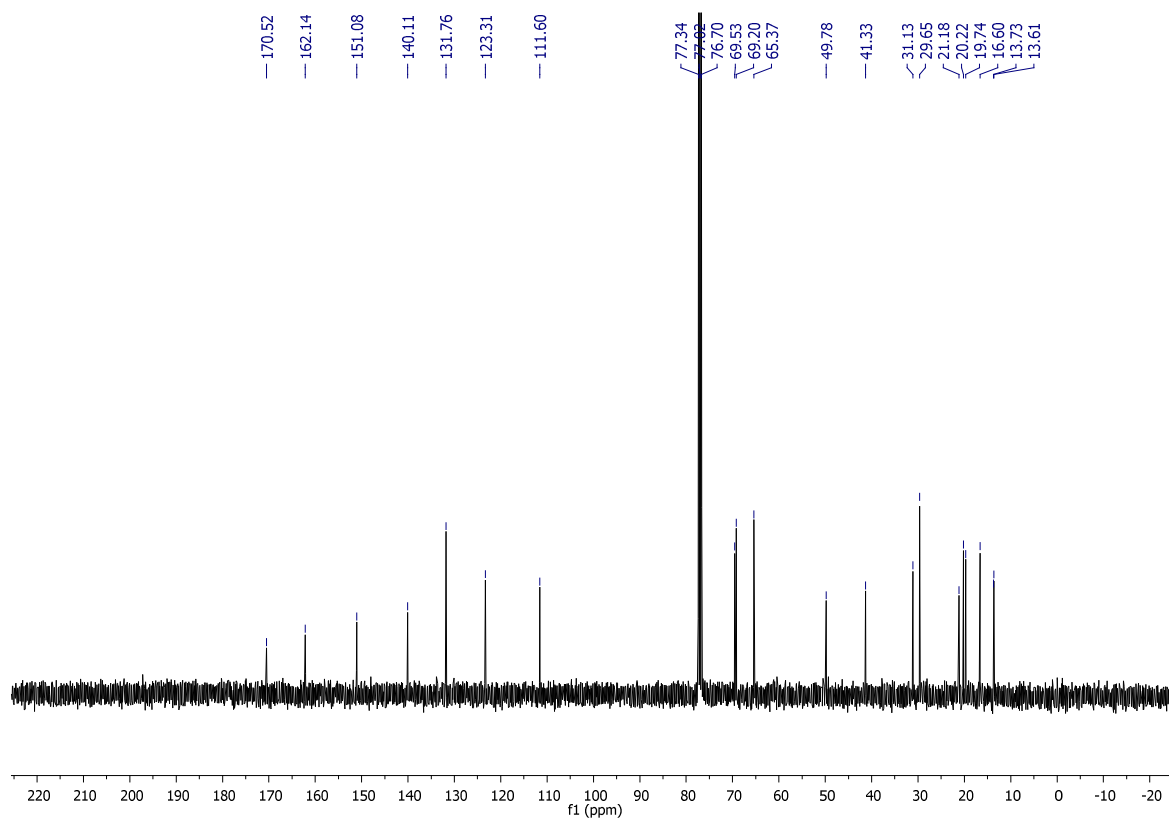
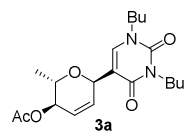
DEPT NMR of 2a



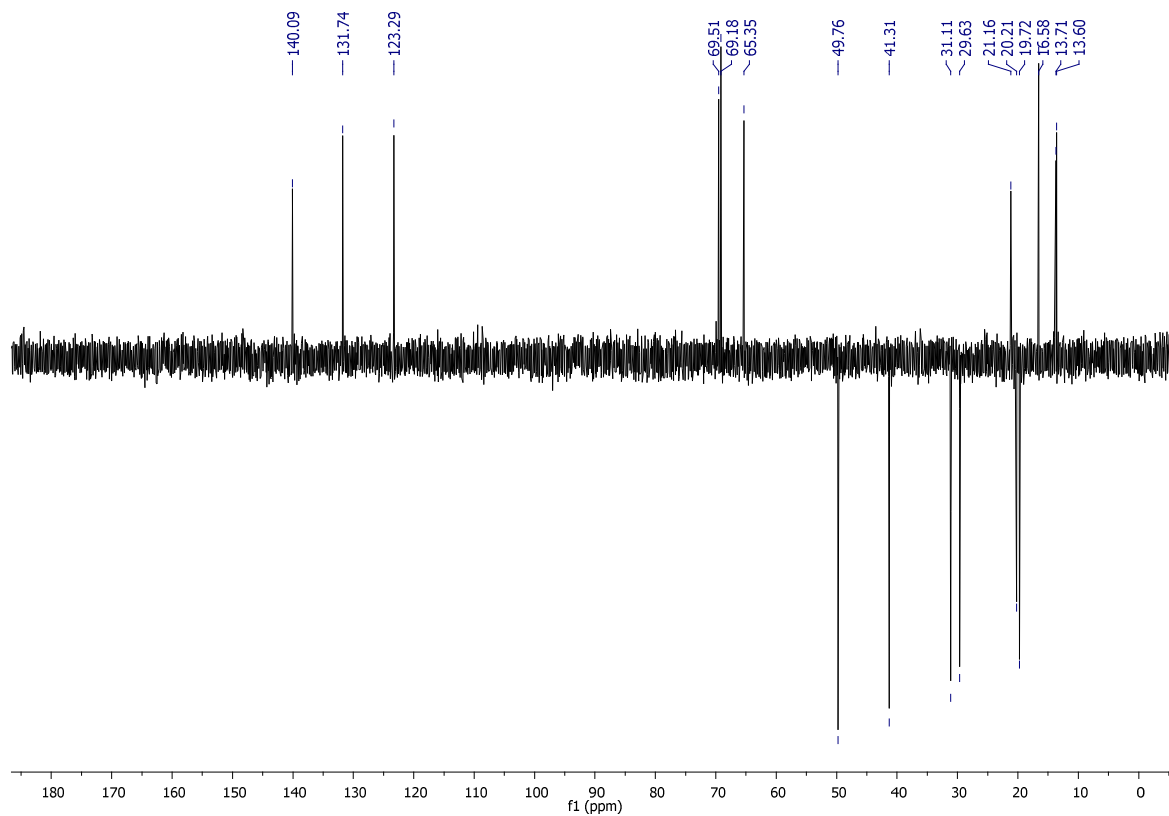
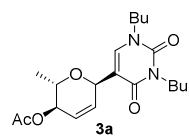
¹HNMR of 3a



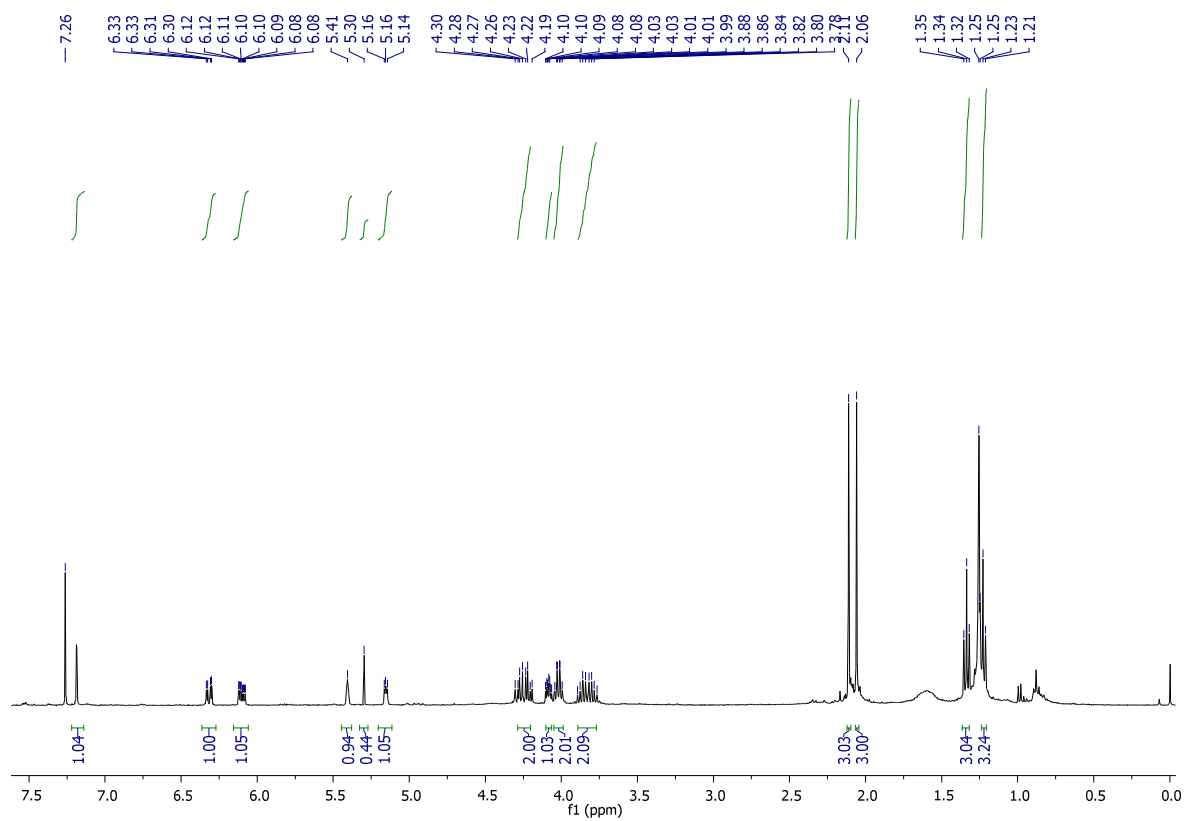
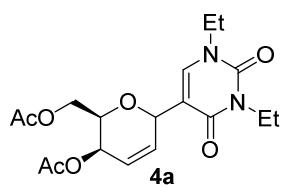
¹³CNMR of 3a



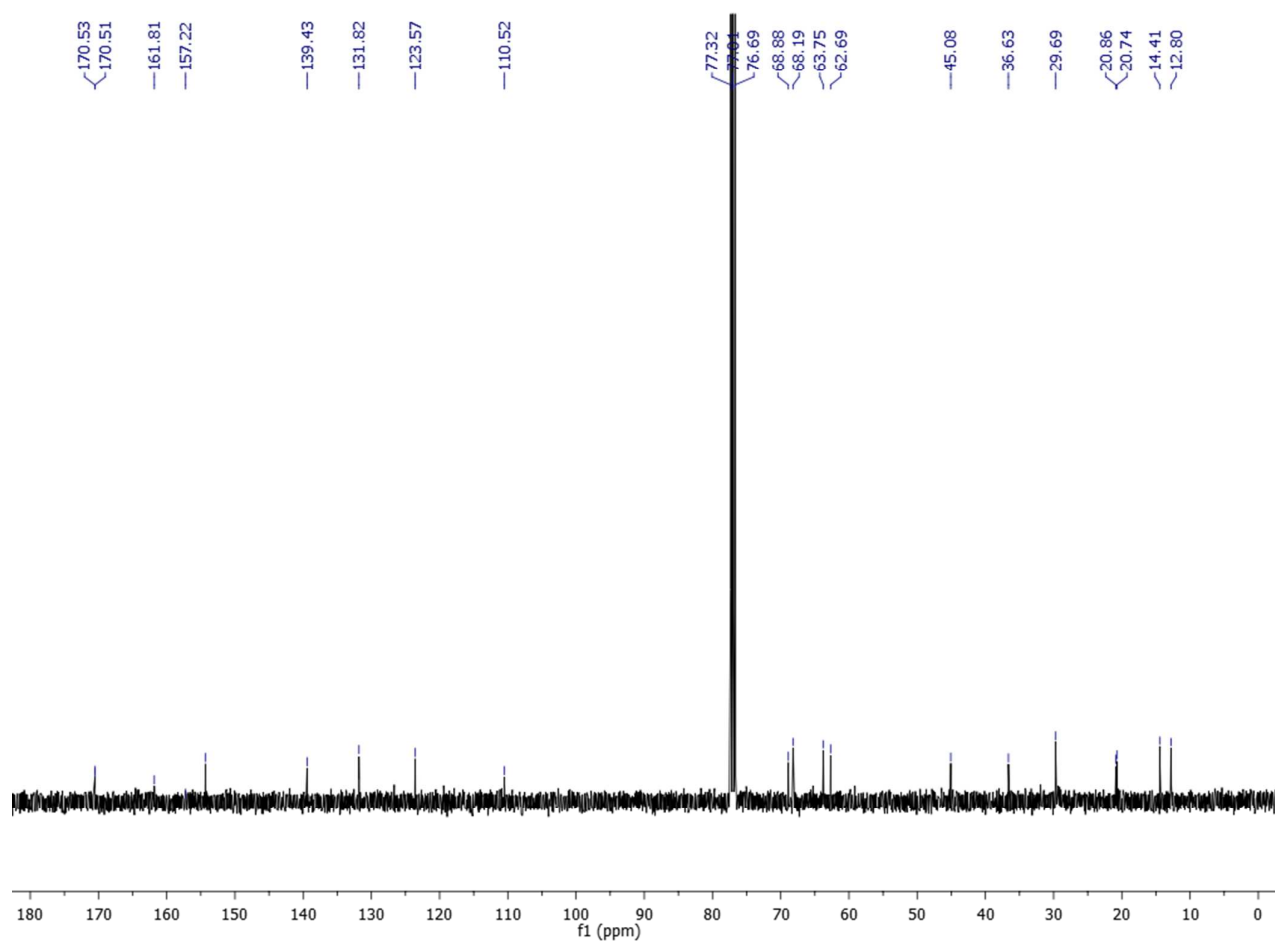
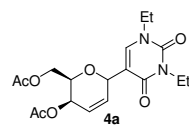
DEPT of 3a



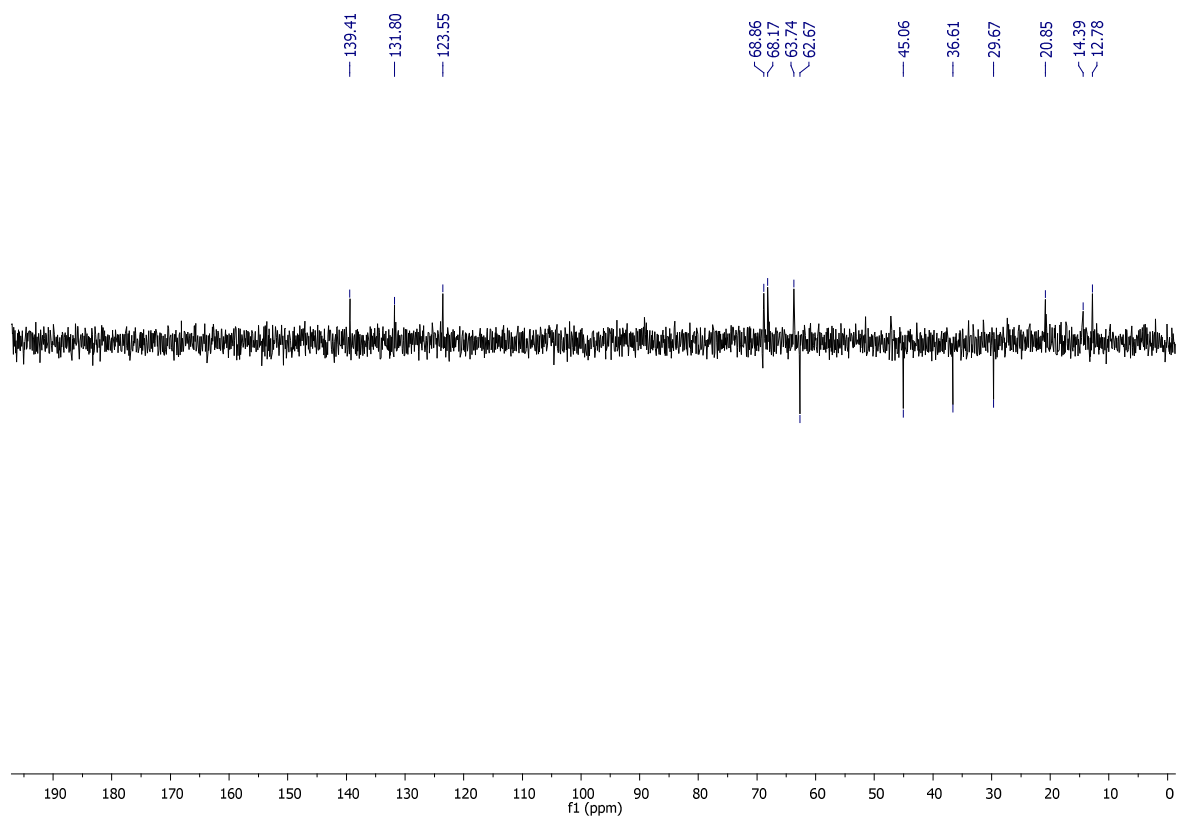
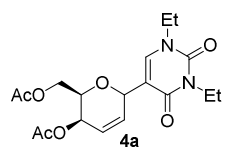
¹H NMR of 4a



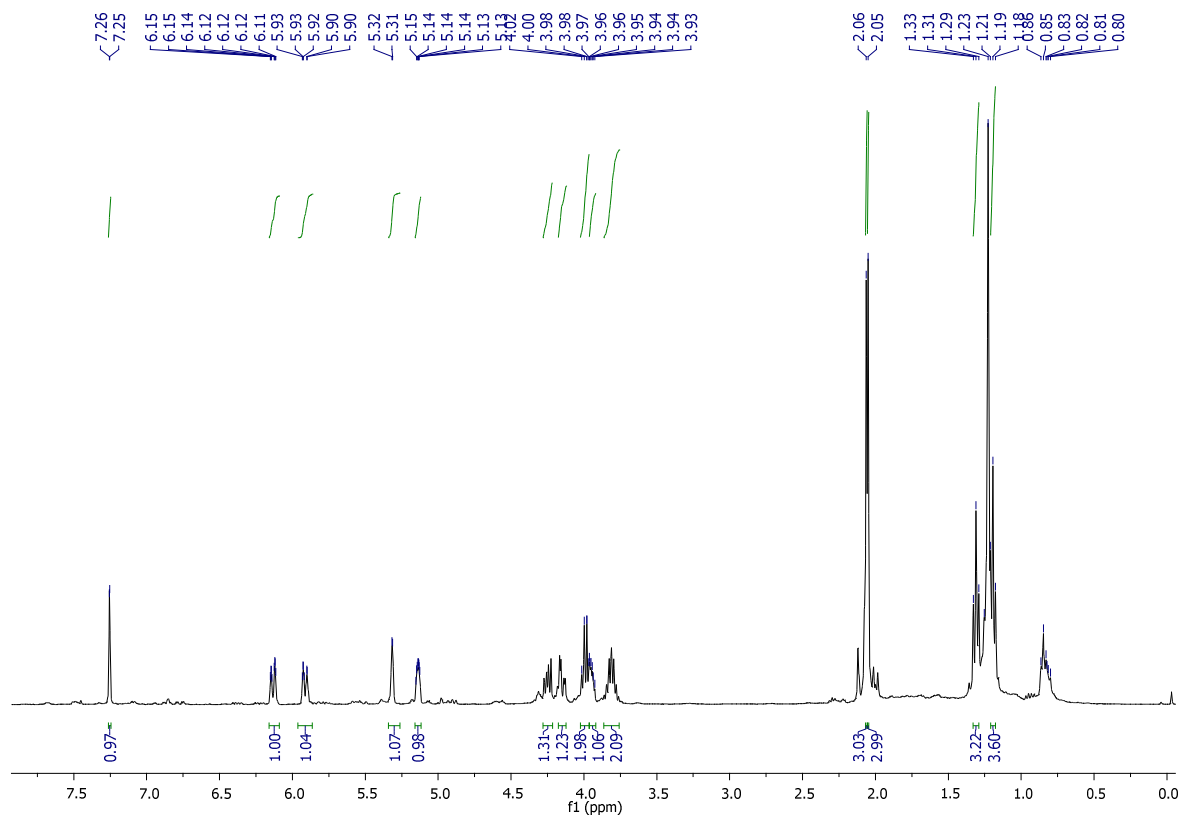
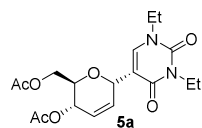
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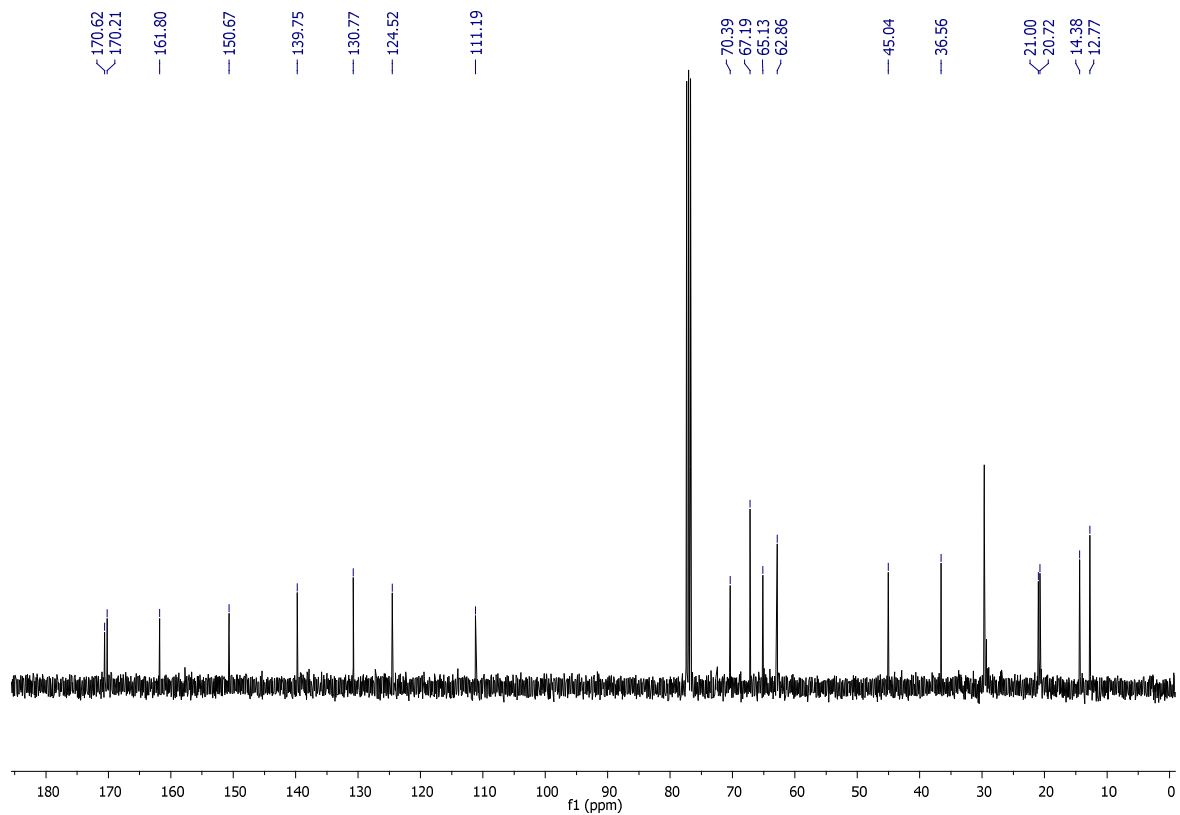
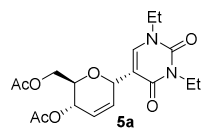
DEPT of 4a



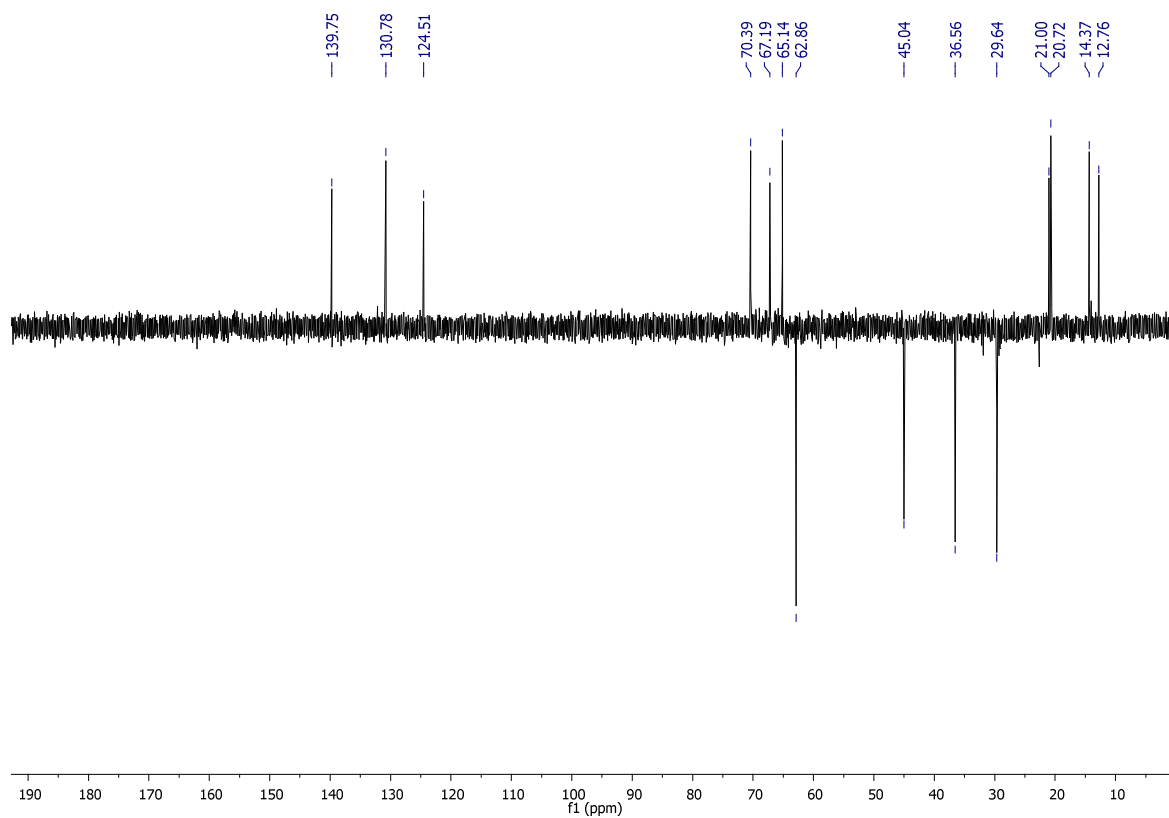
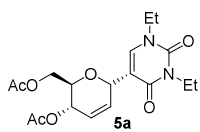
¹HNMR of 5a



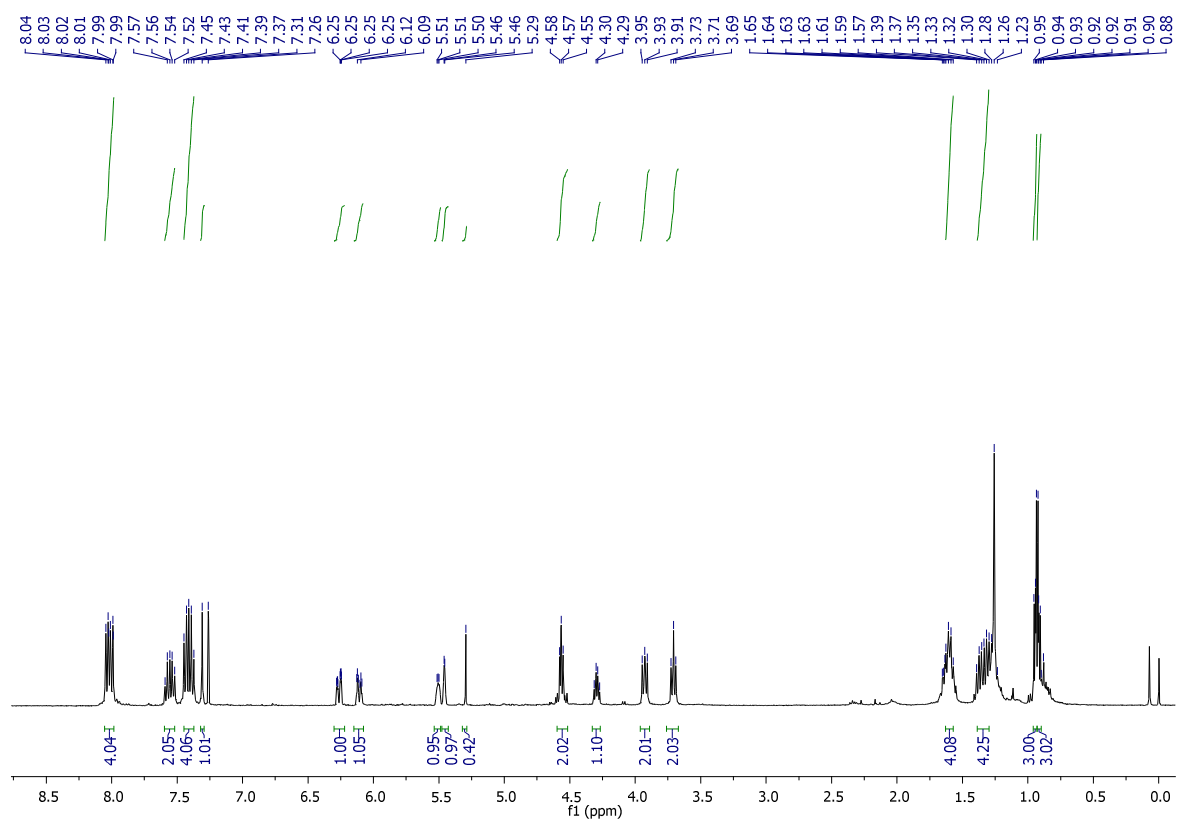
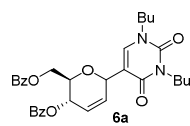
¹³C NMR of 5a



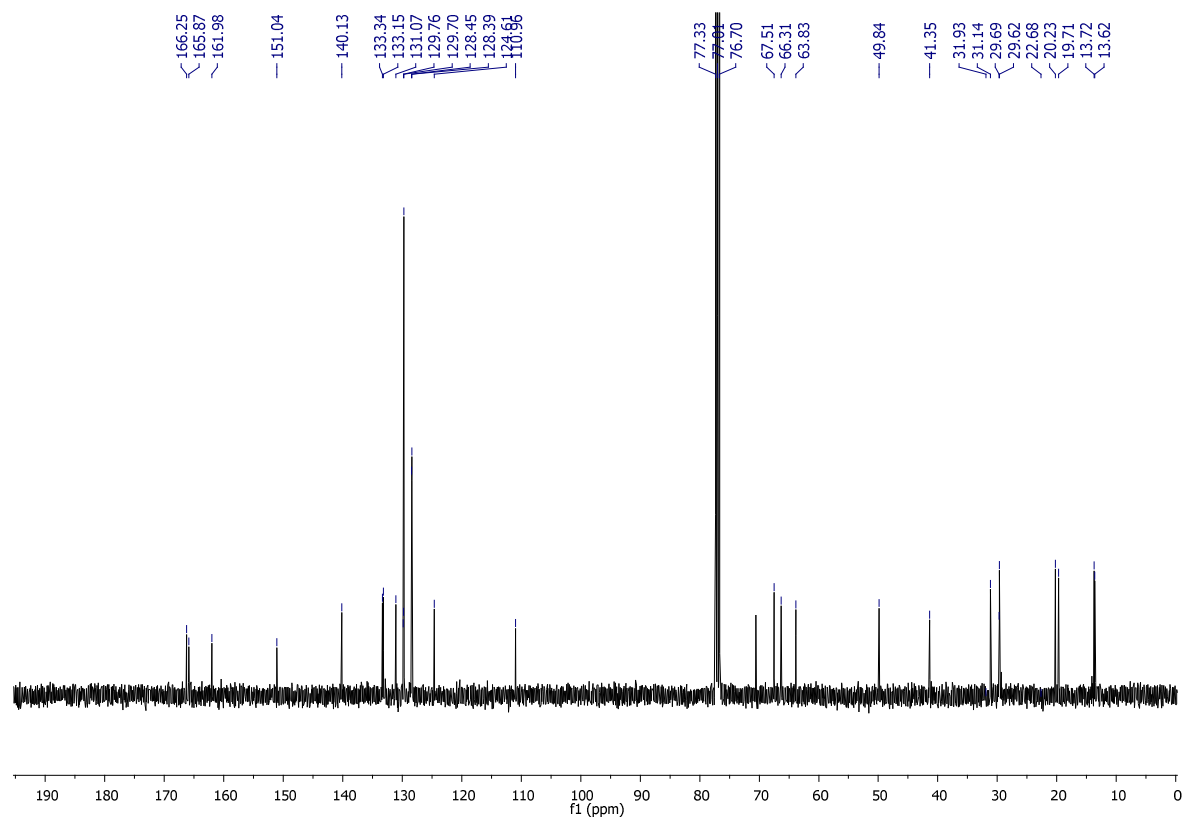
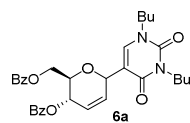
DEPT NMR of 5a



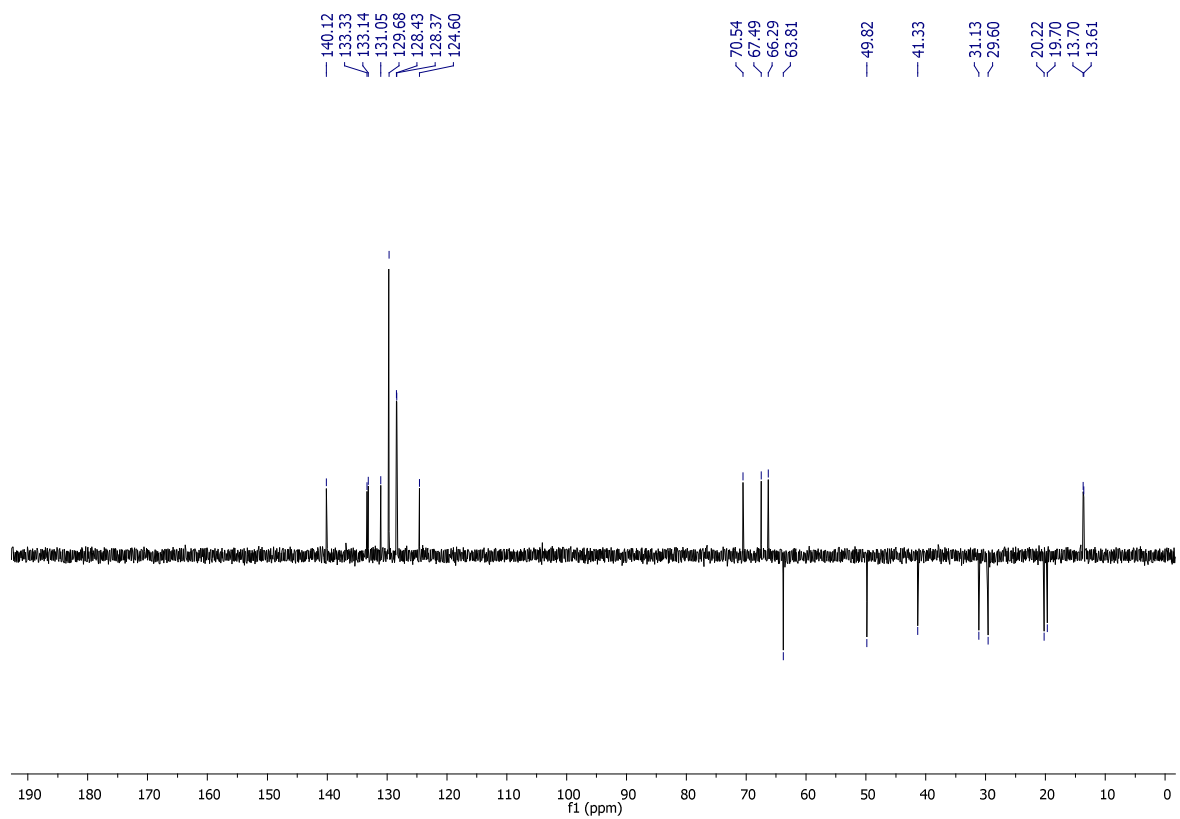
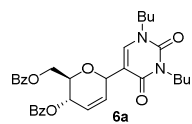
¹H NMR of 6a



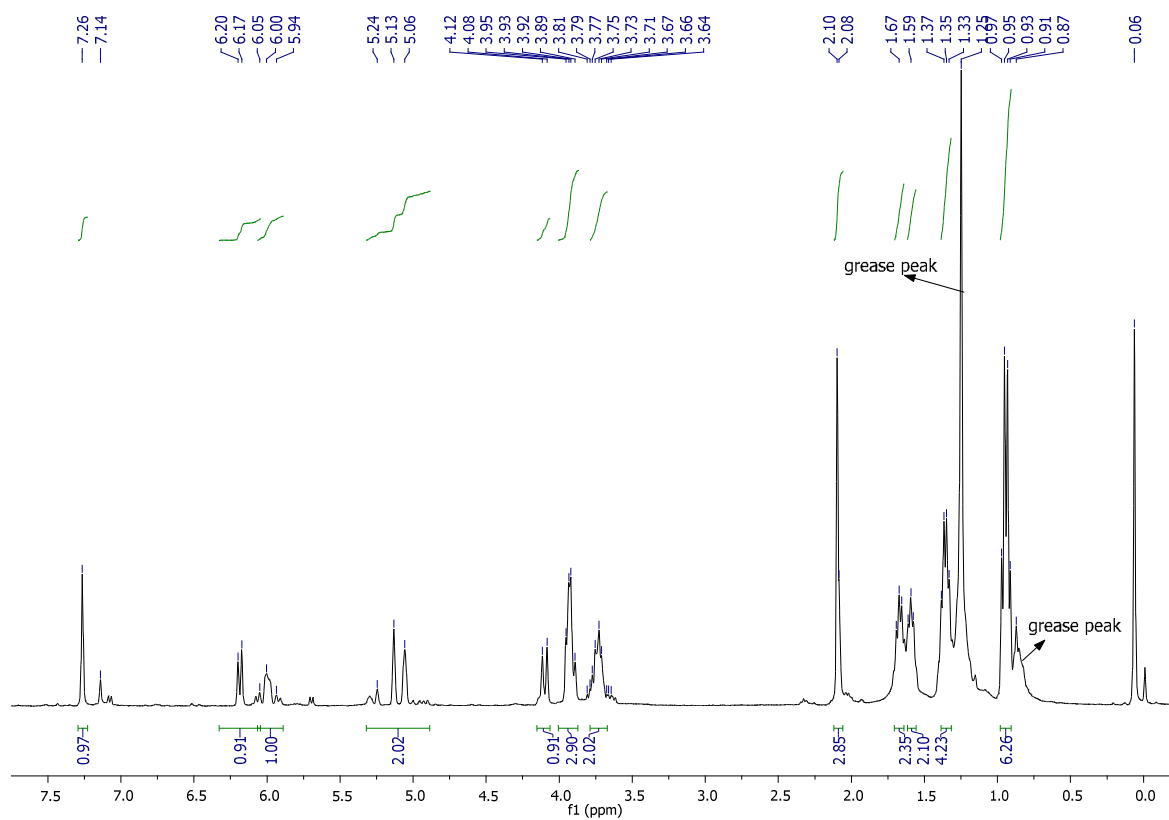
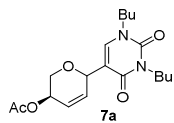
¹³C NMR of 6a



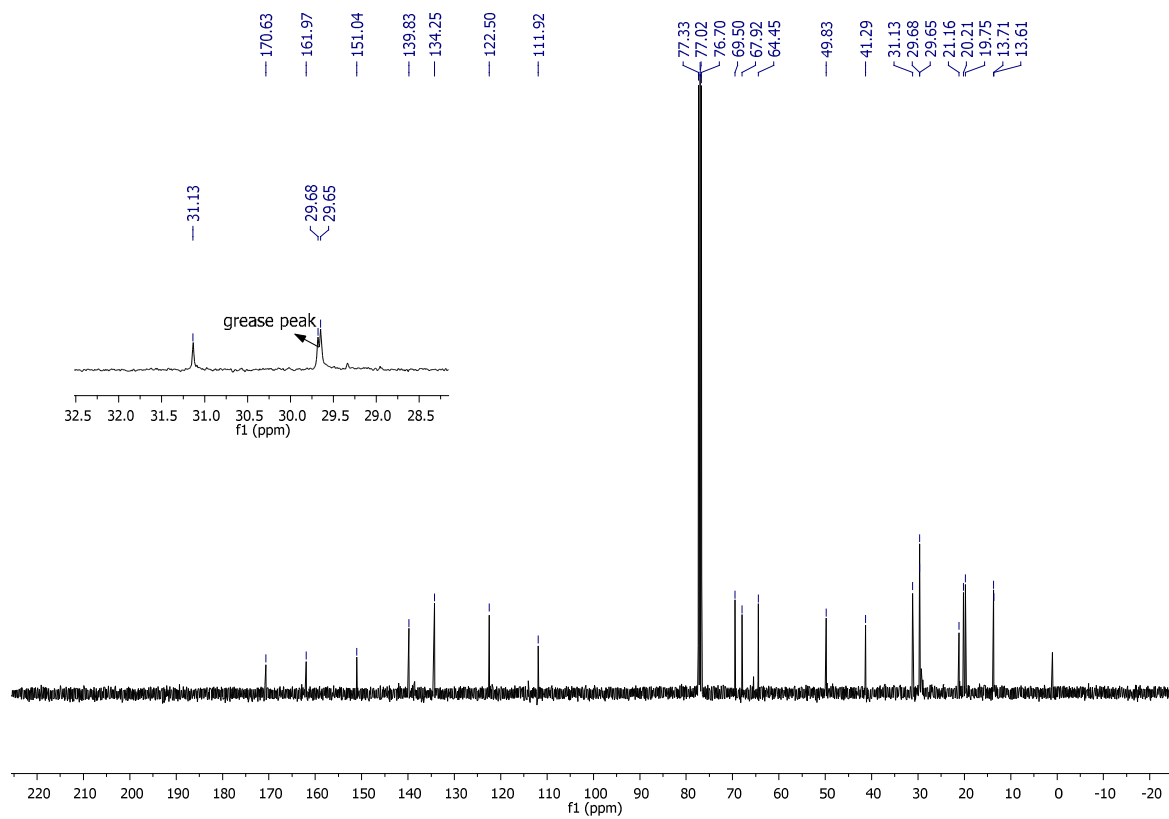
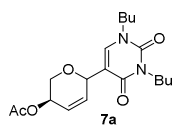
DEPT of 6a



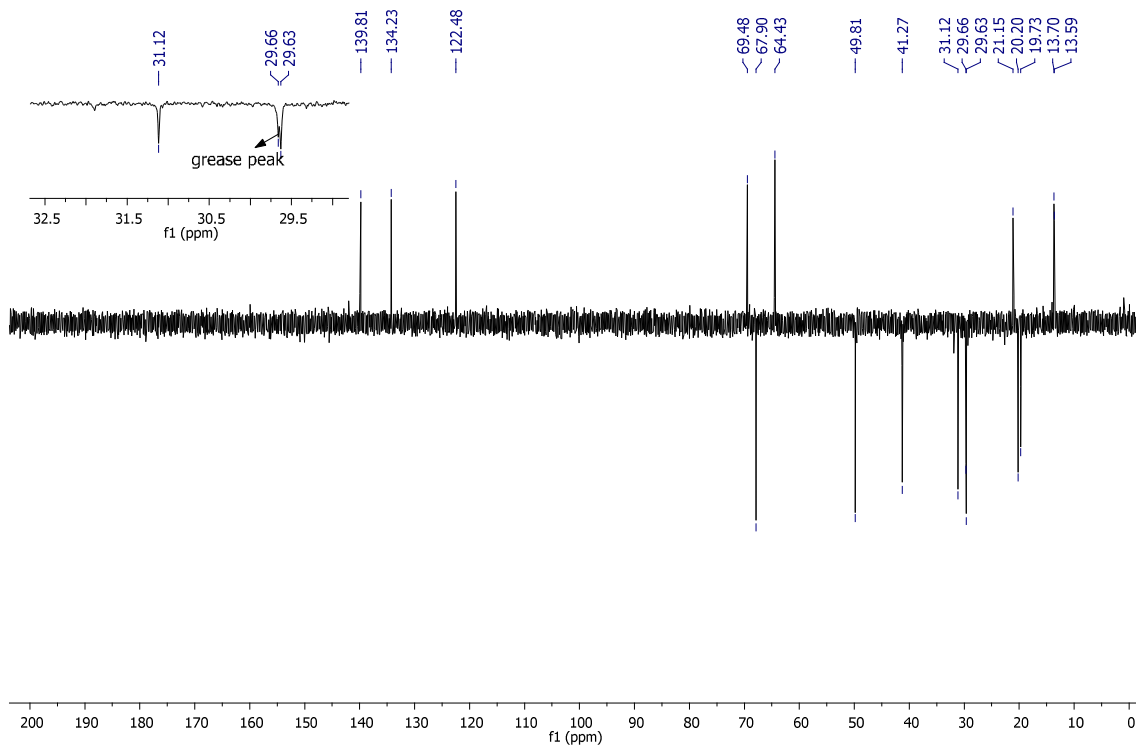
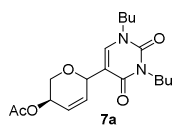
¹H of 7a



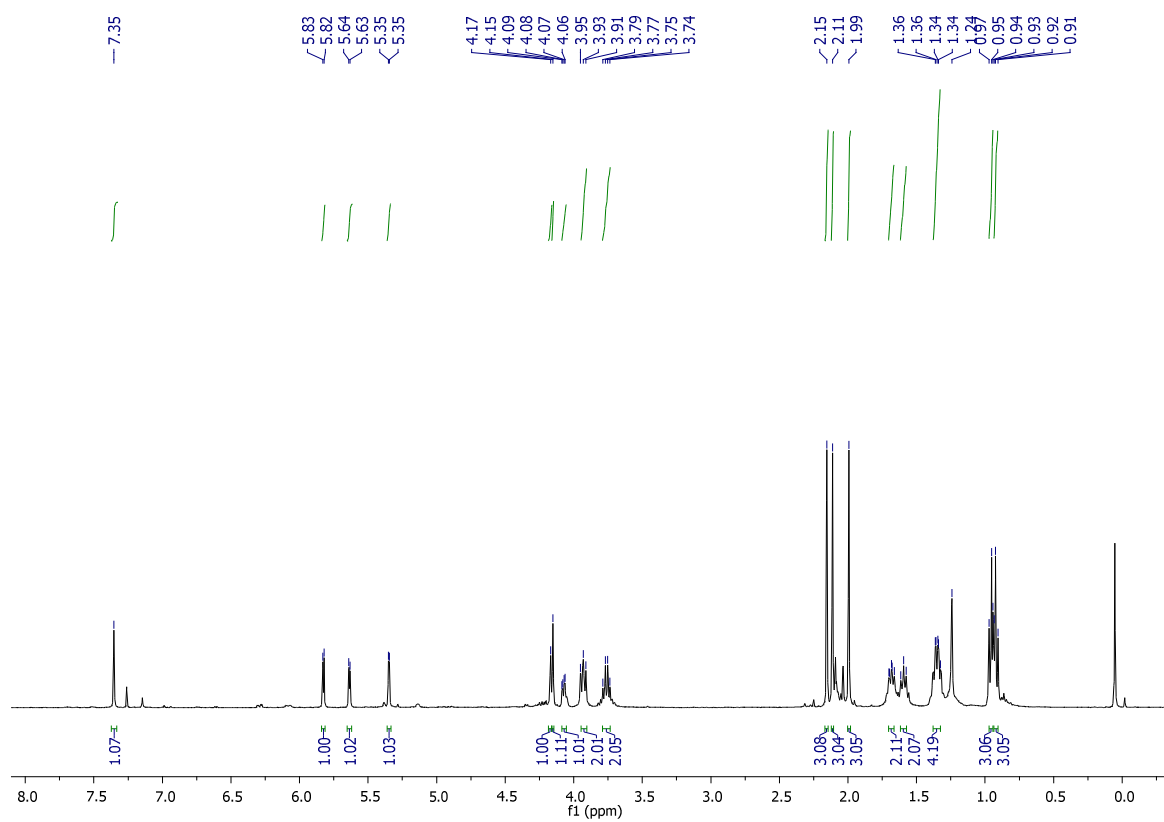
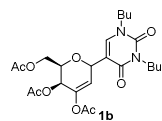
¹³C of 7a



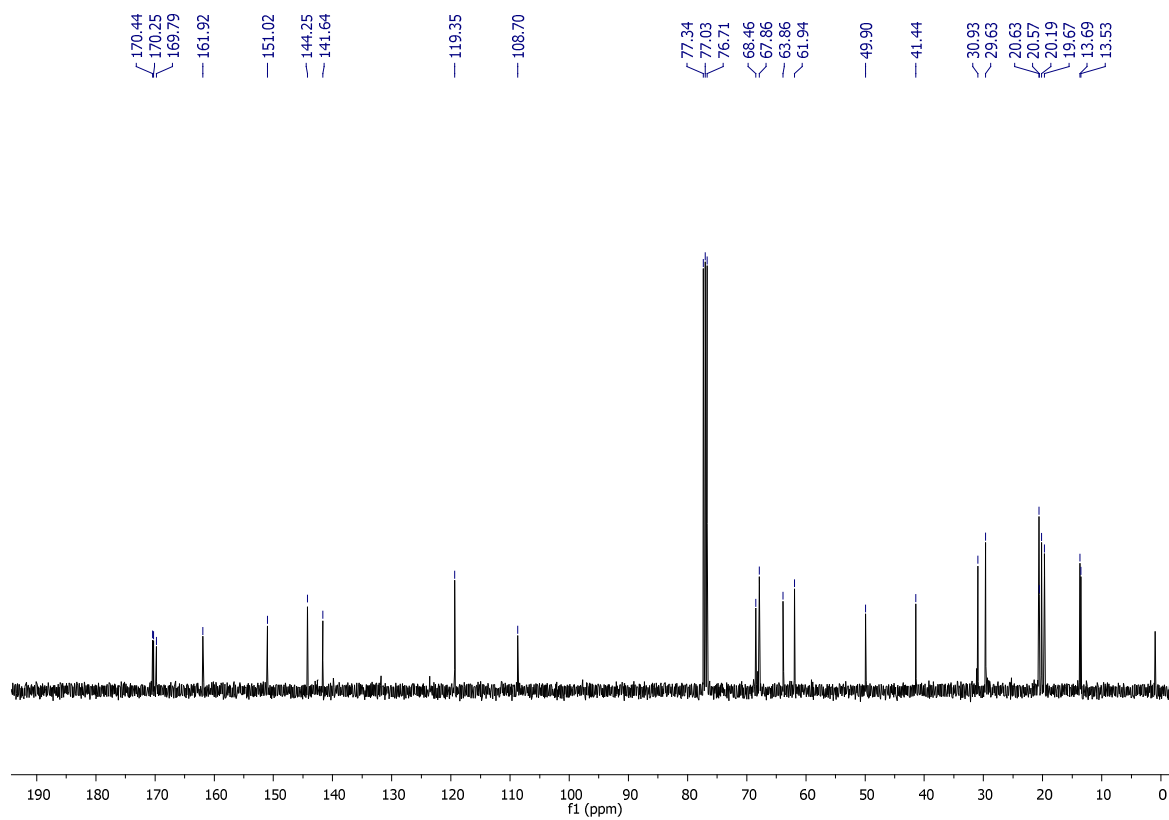
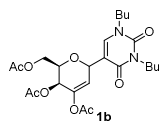
DEPT of 7a



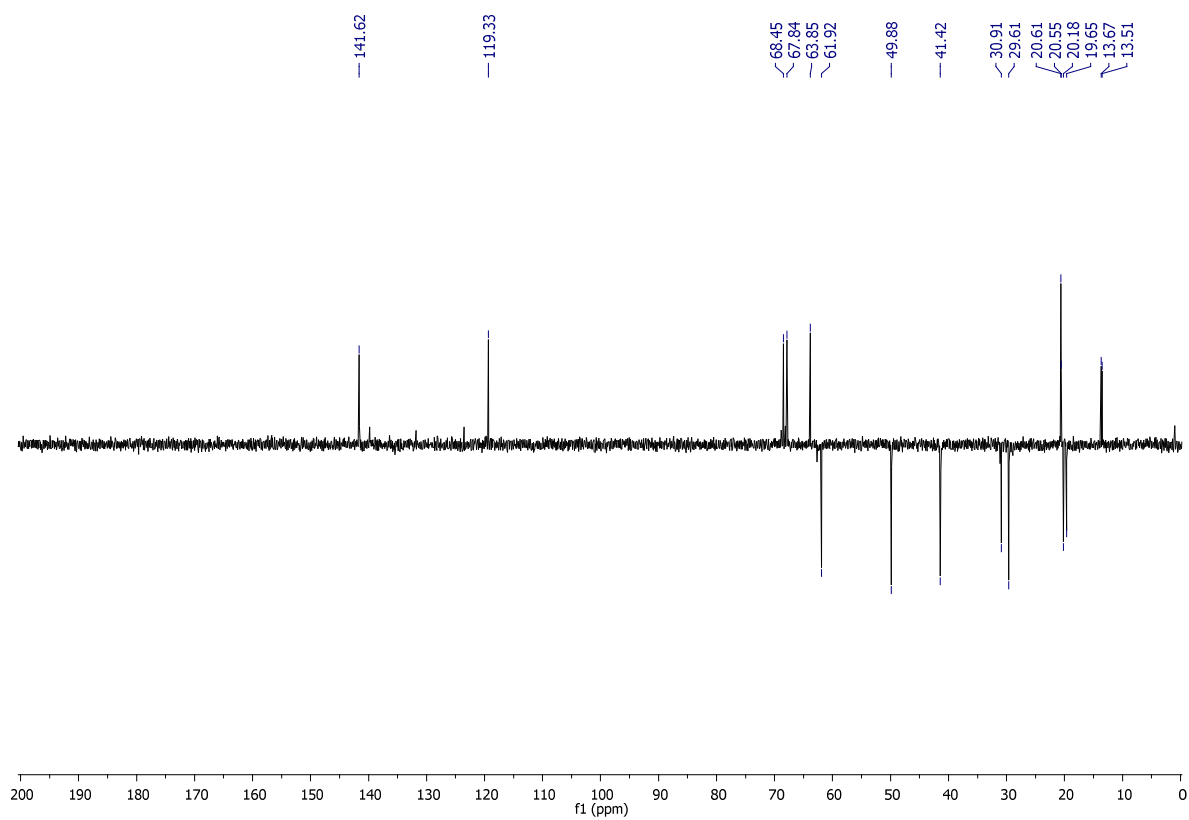
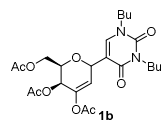
¹H NMR of 1b



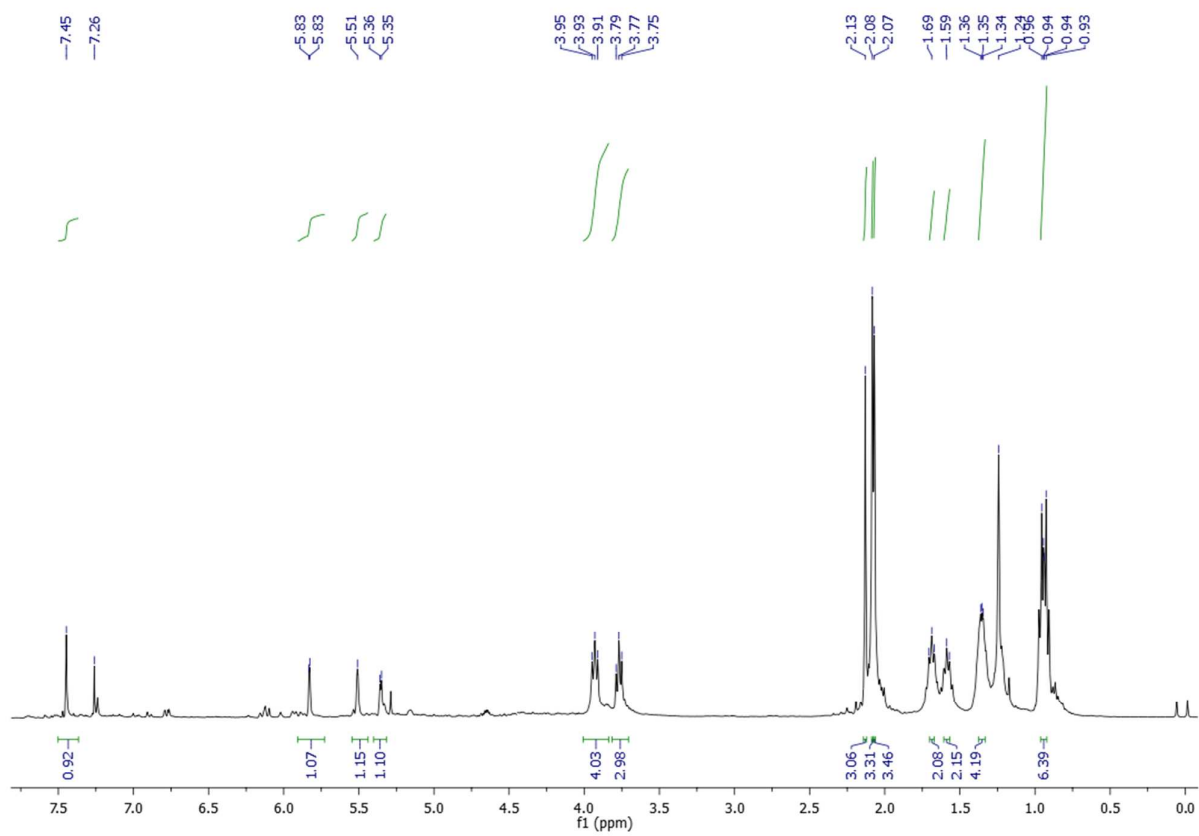
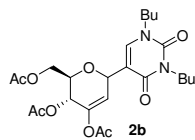
^{13}C NMR of 1b



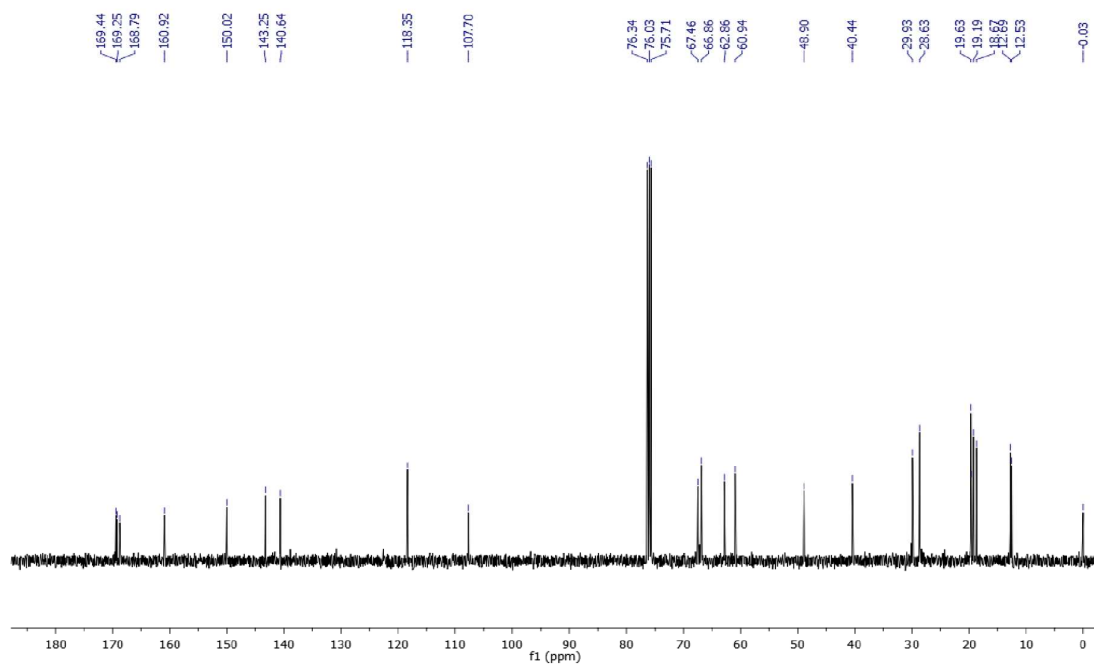
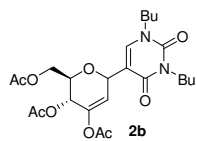
DEPT of 1b



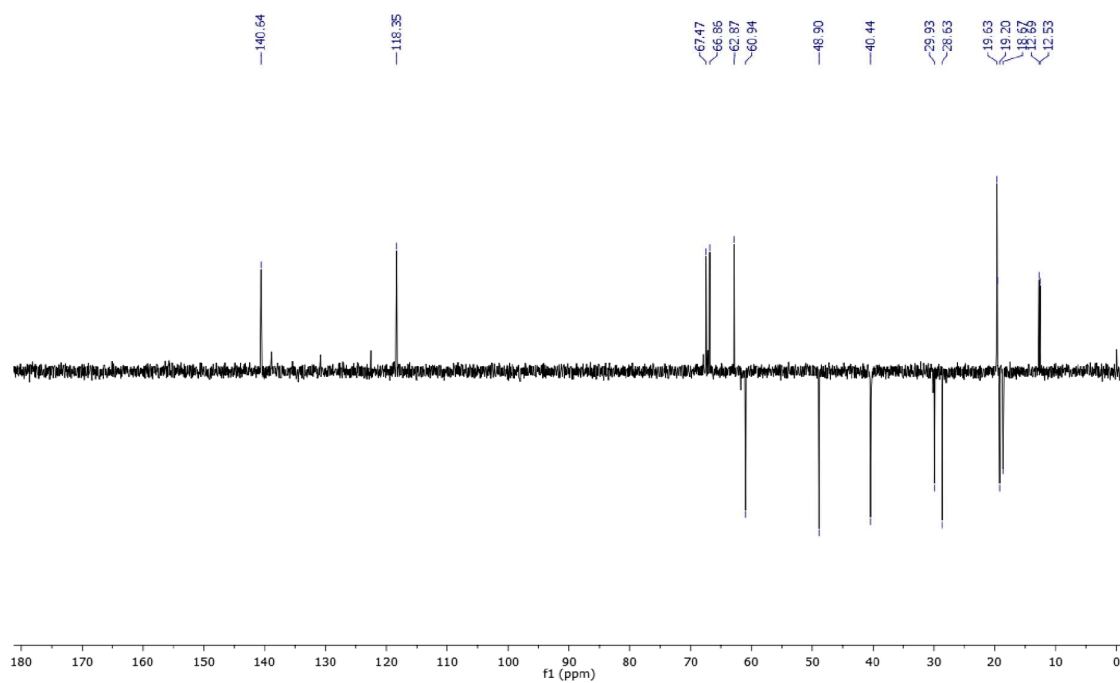
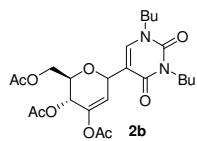
¹H of 2b



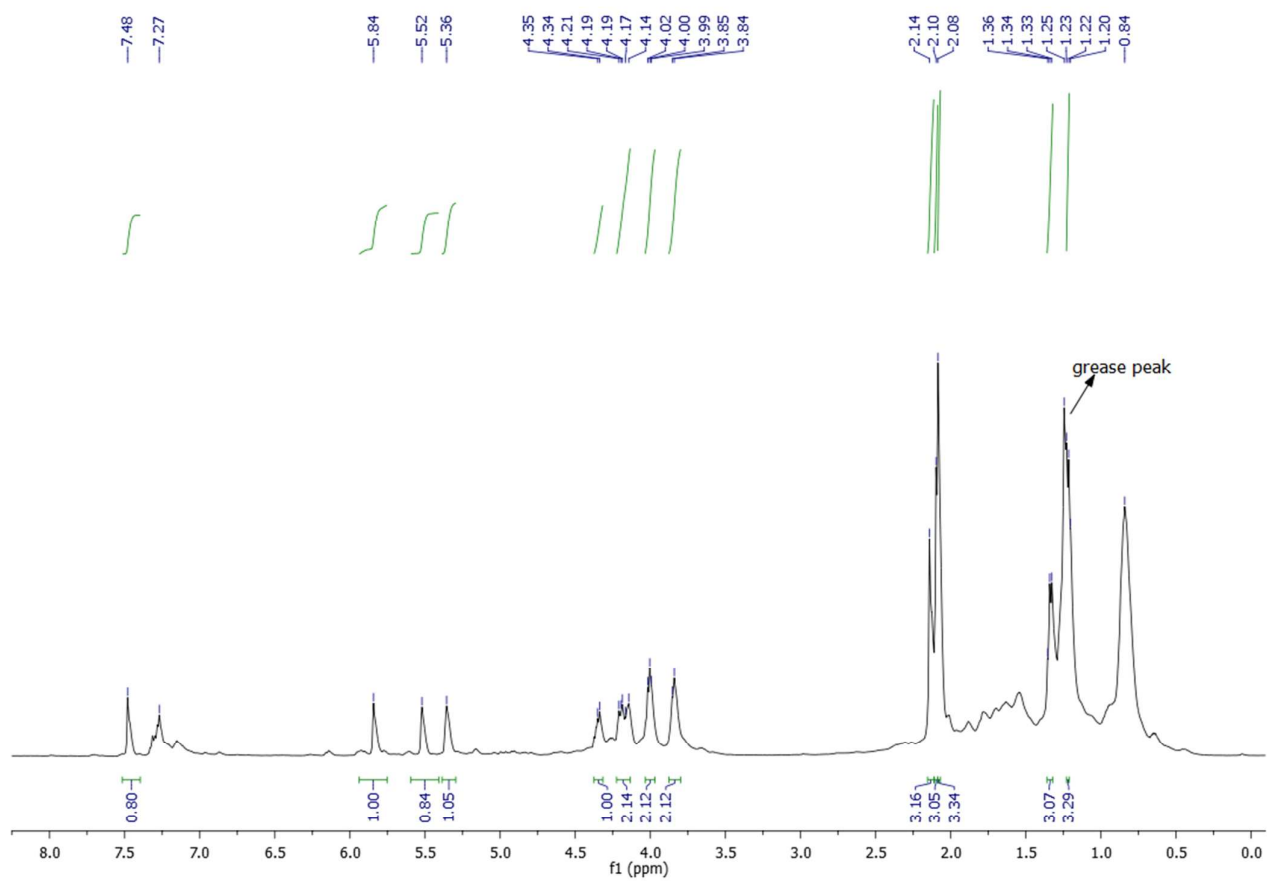
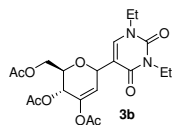
¹³C of 2b



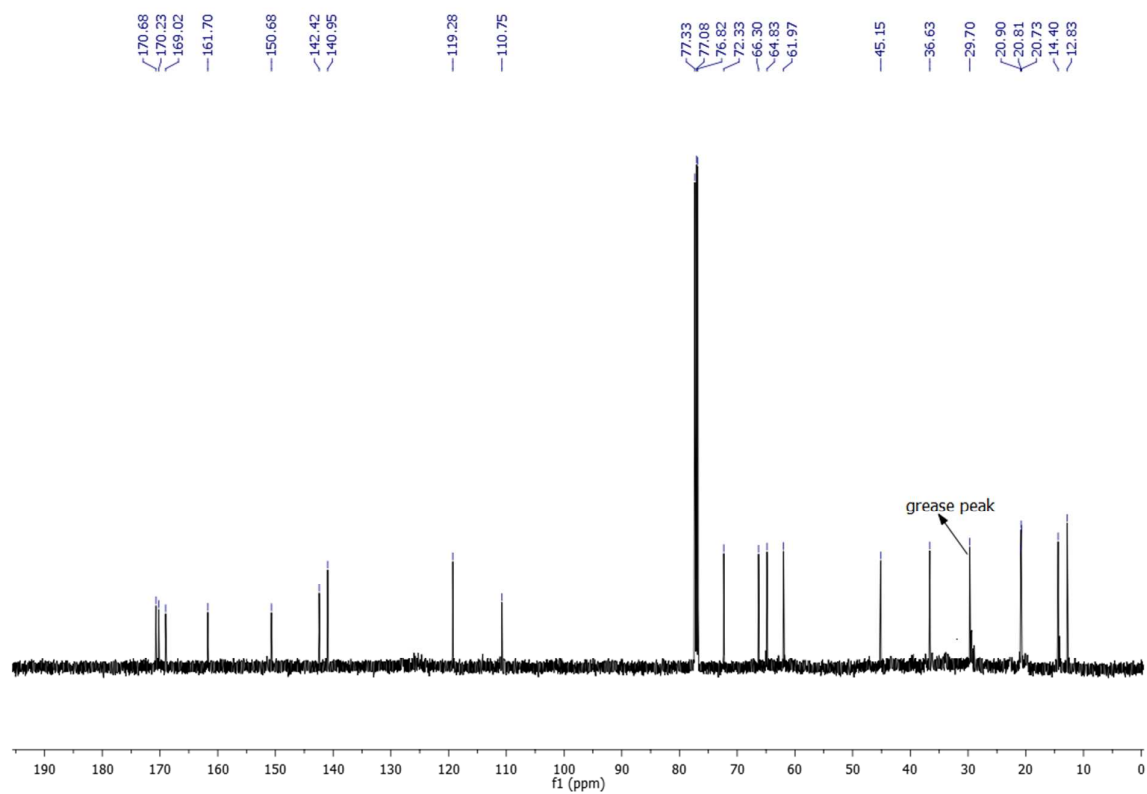
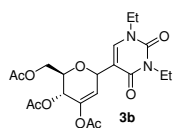
Dept of 2b



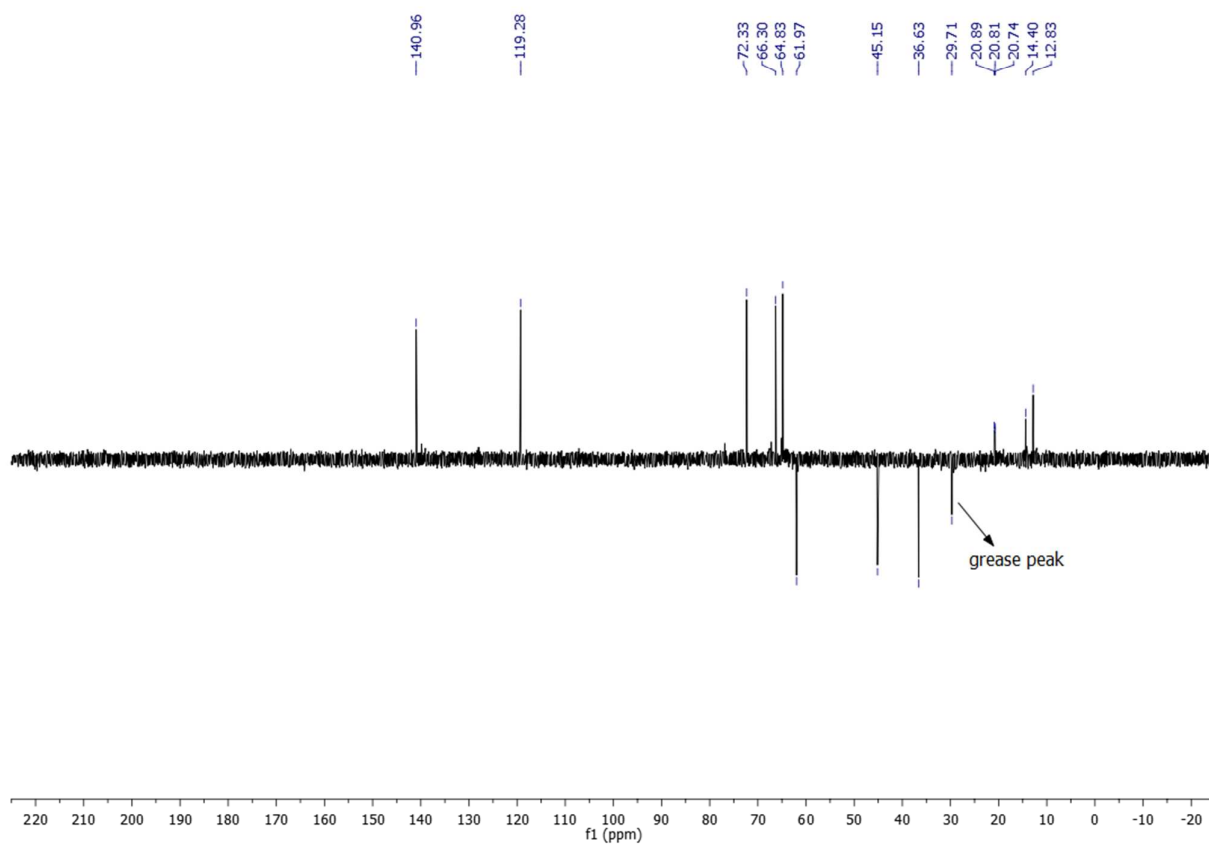
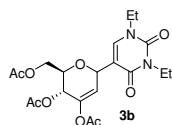
¹H of 3b



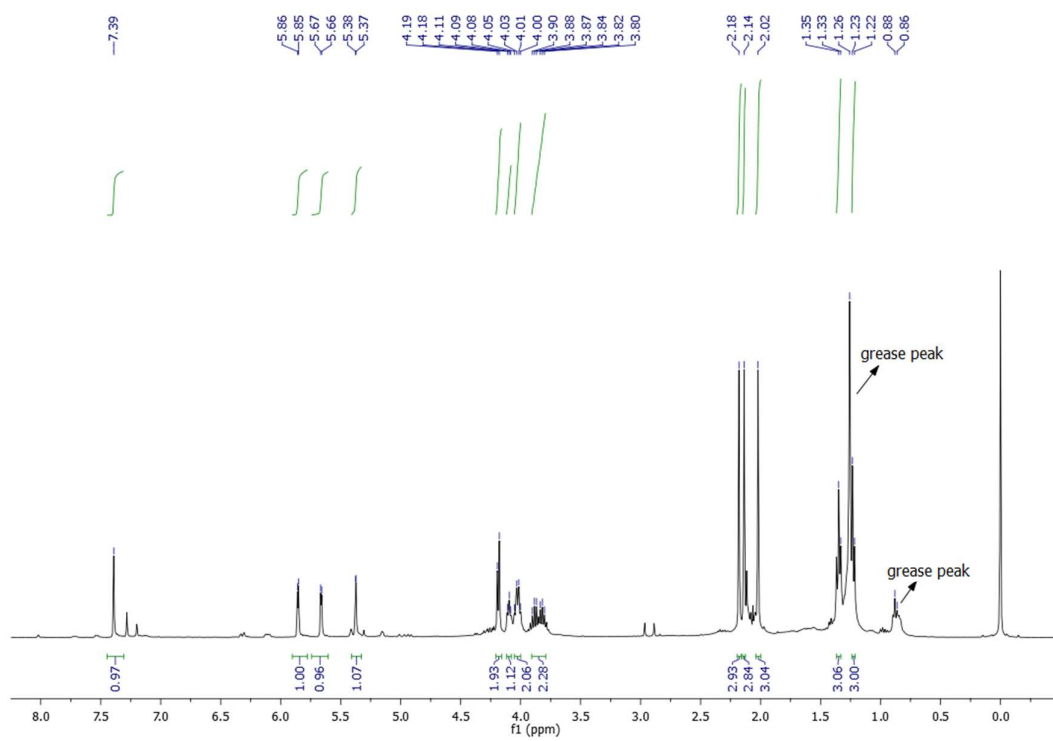
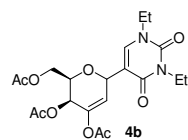
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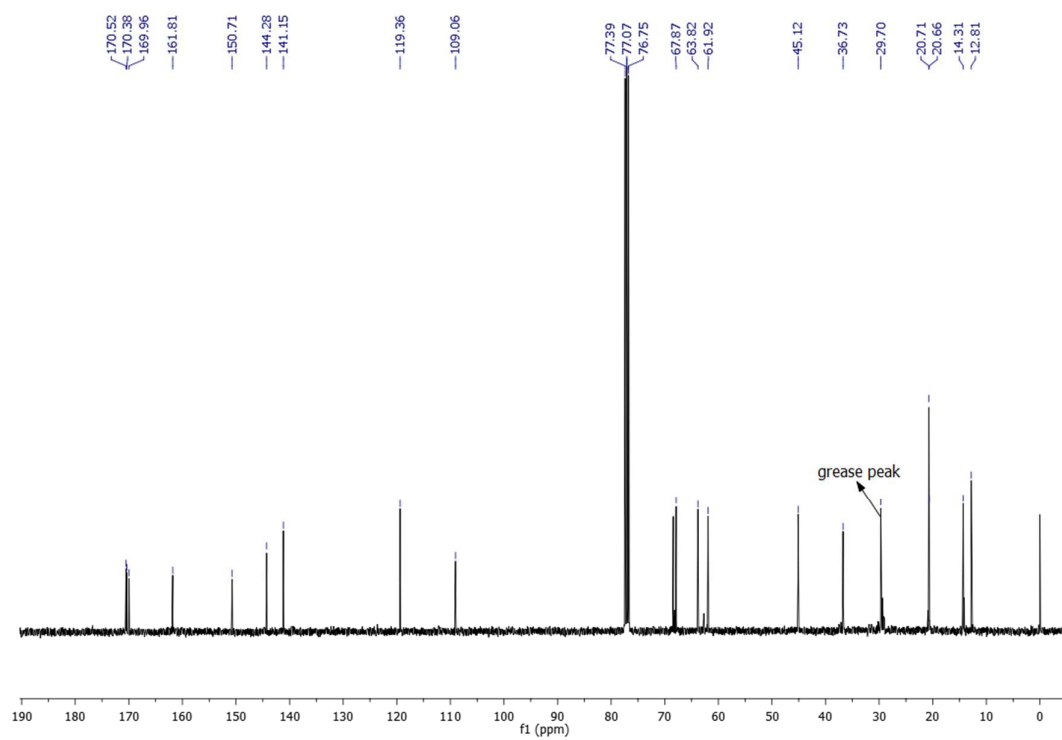
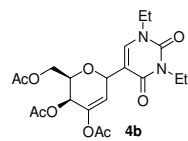
DEPT of 3b



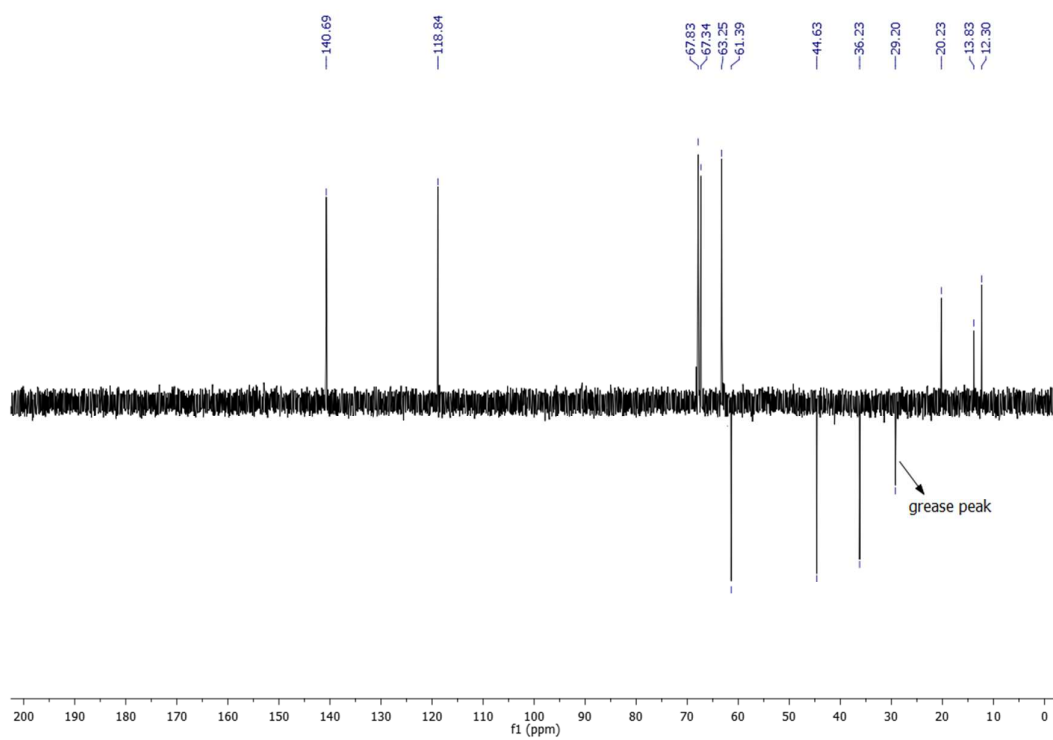
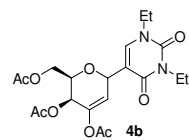
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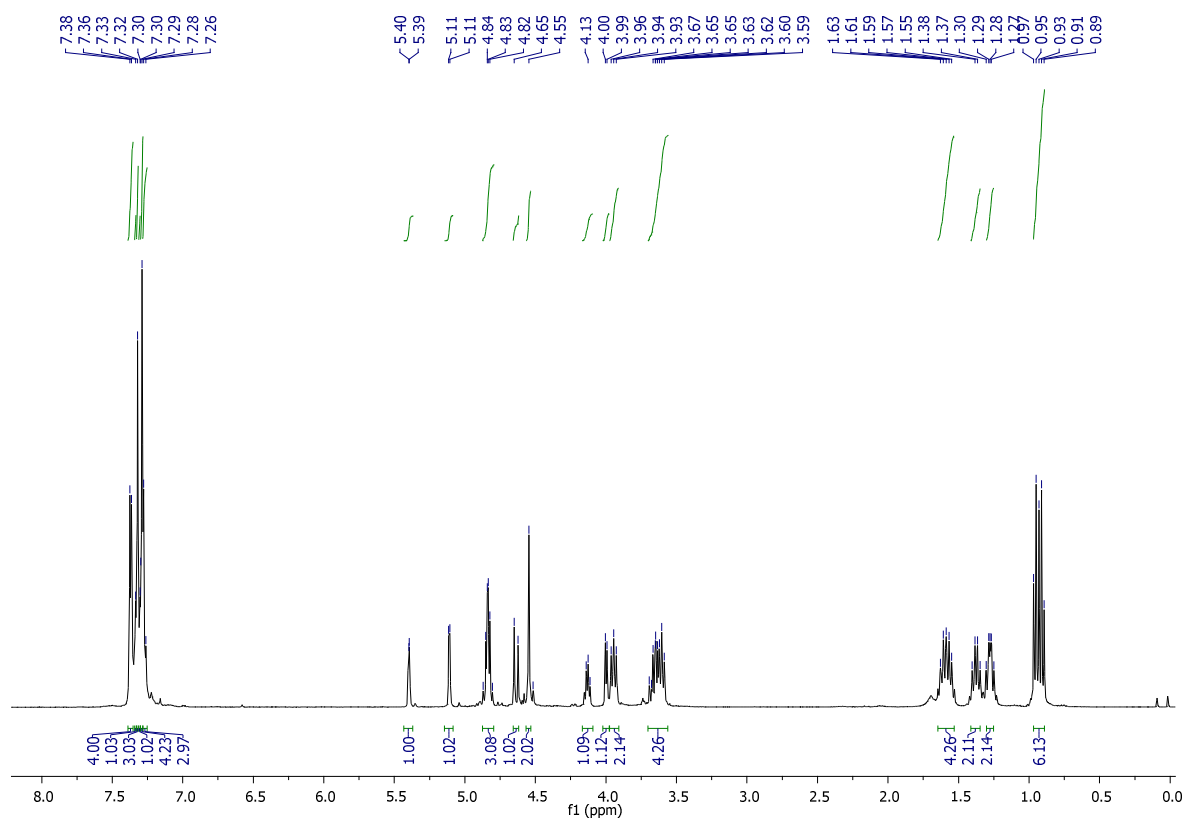
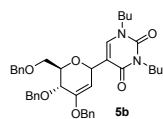
¹³C of 4b



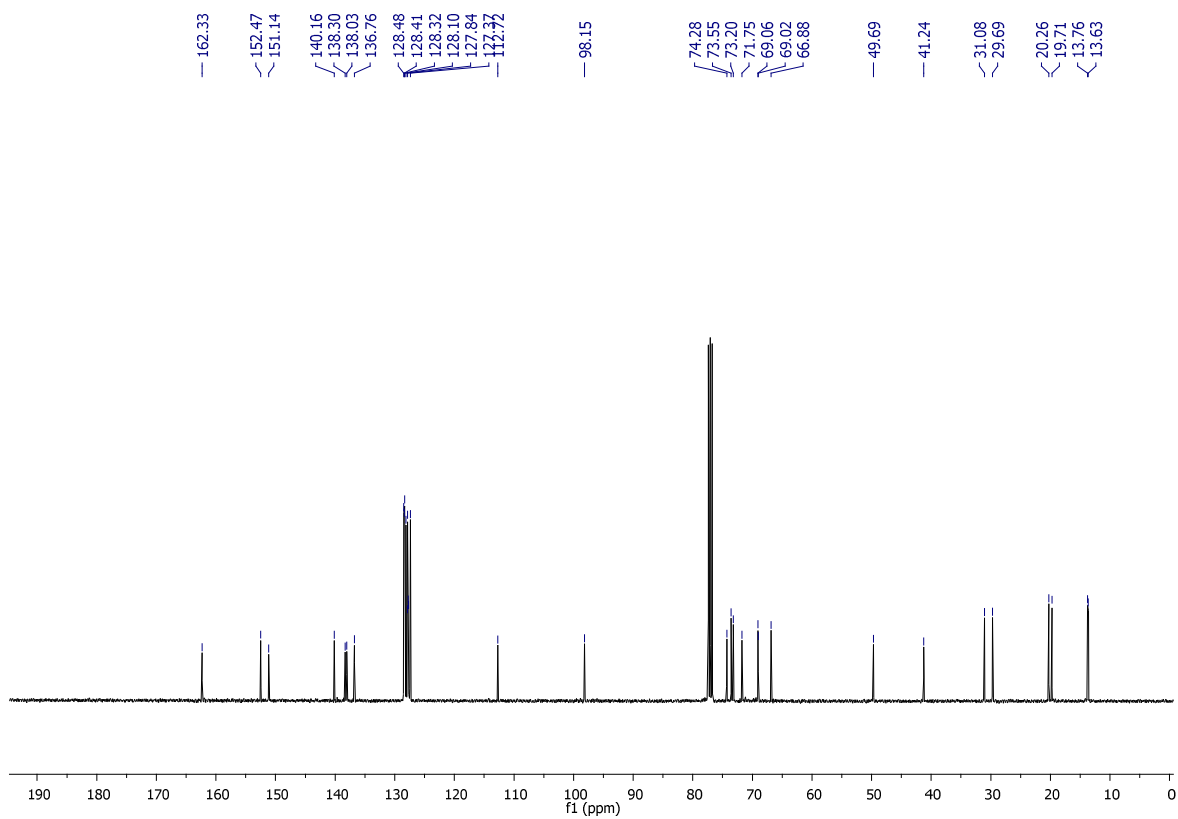
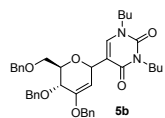
DEPT of 4b



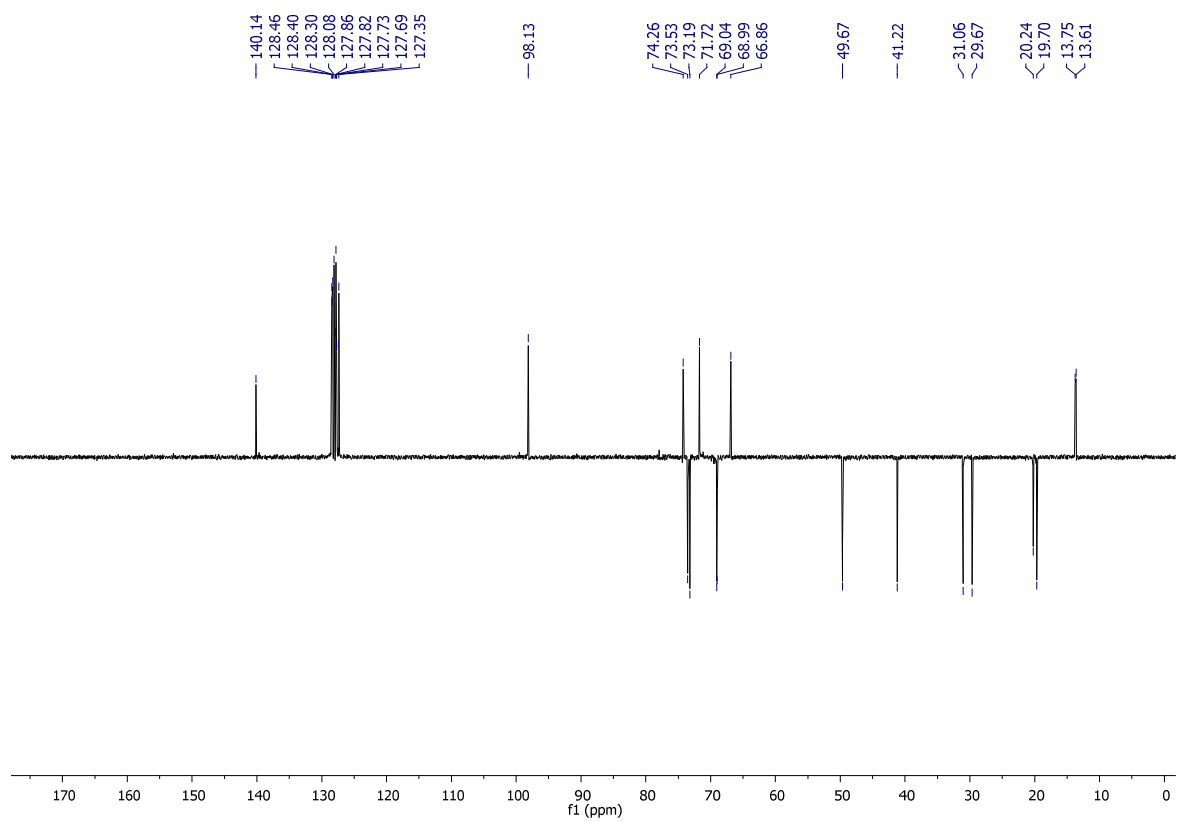
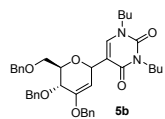
¹H NMR of 5b



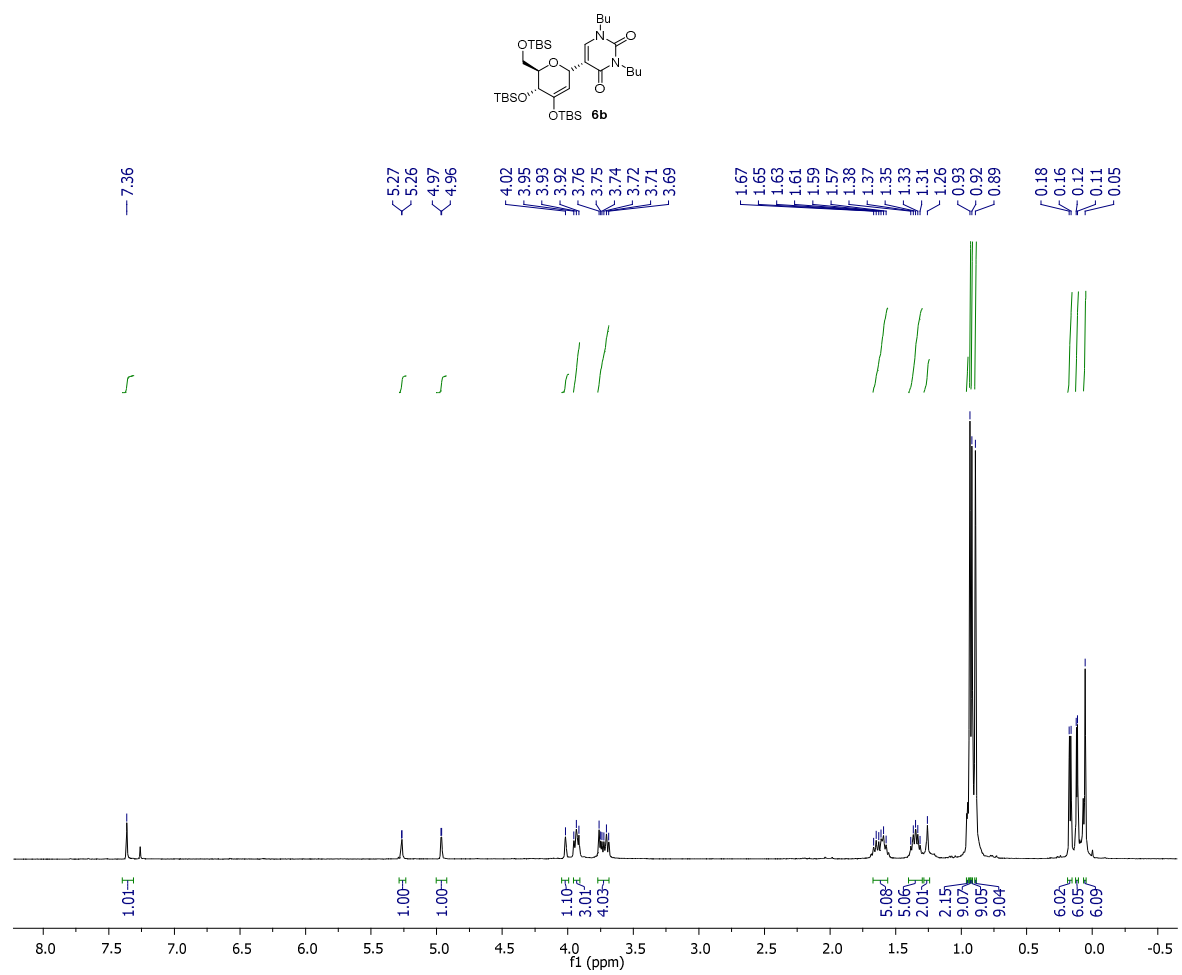
¹³C NMR of 5b



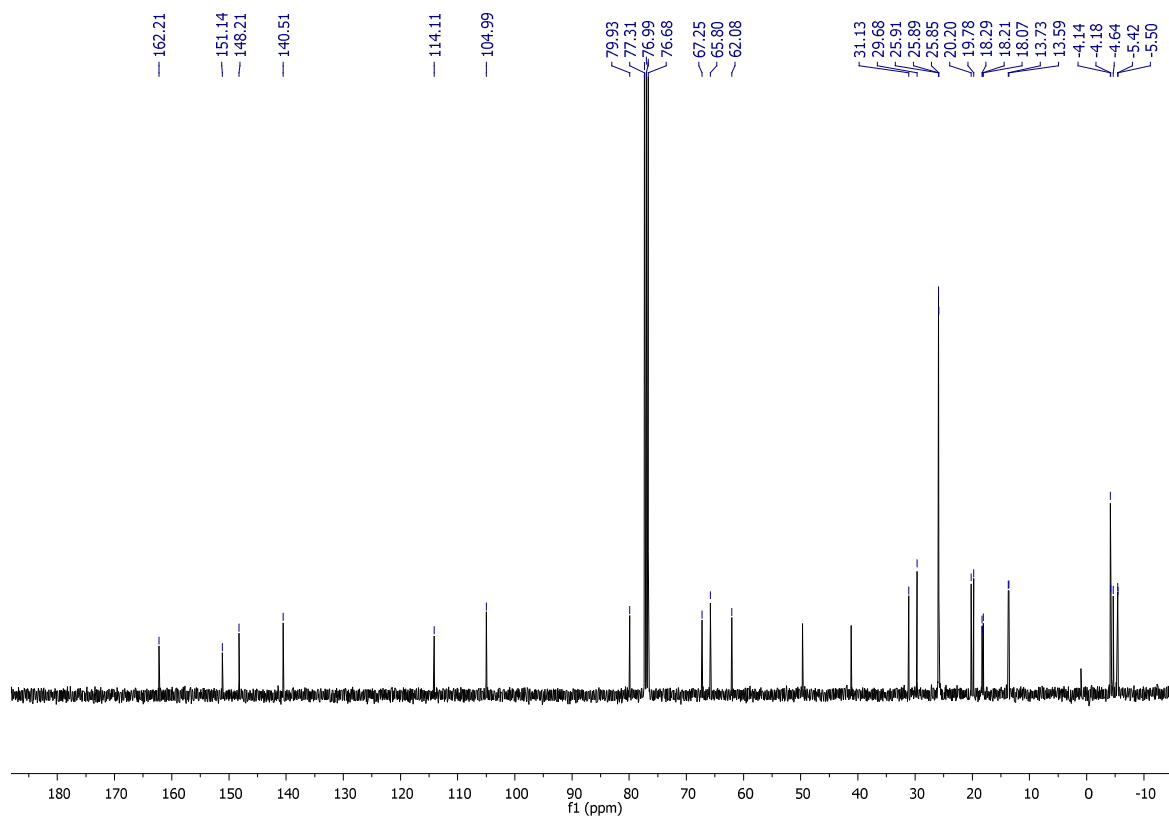
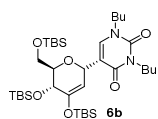
DEPT of 5b



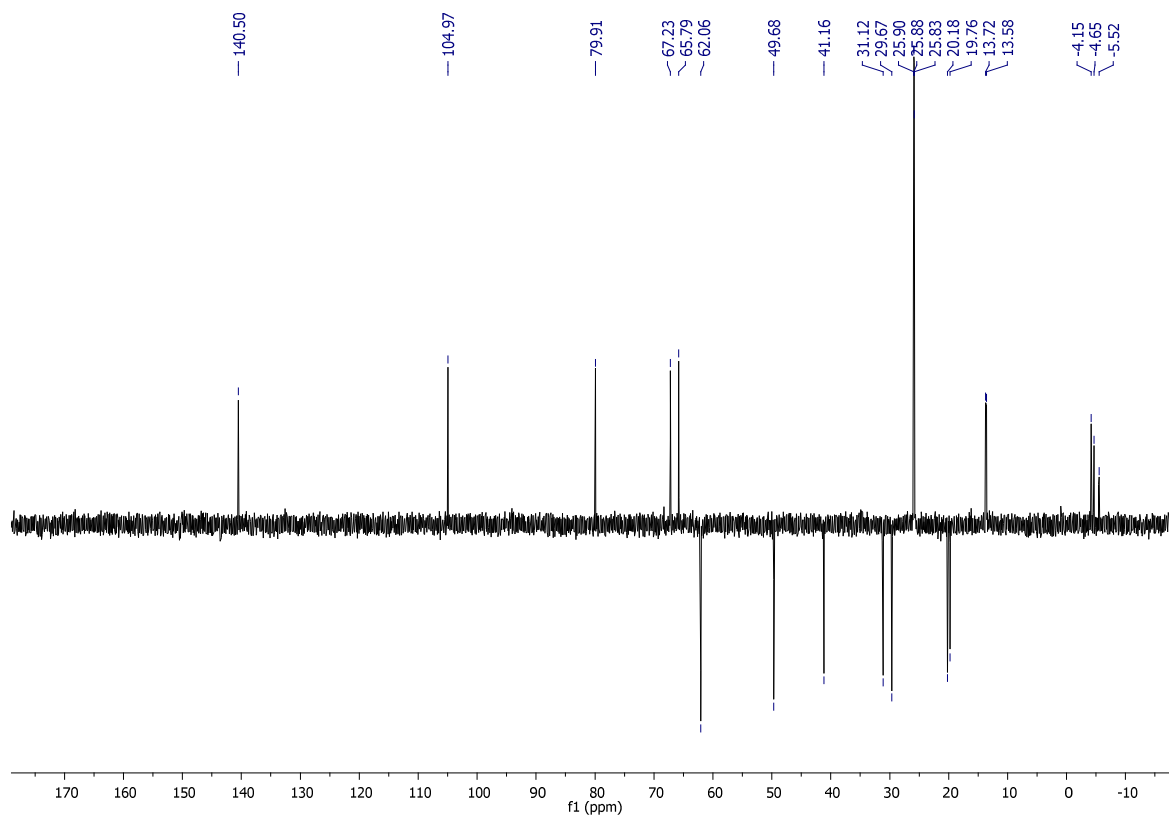
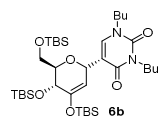
47

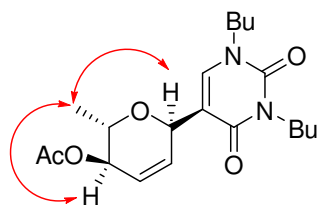


¹³C of 6b

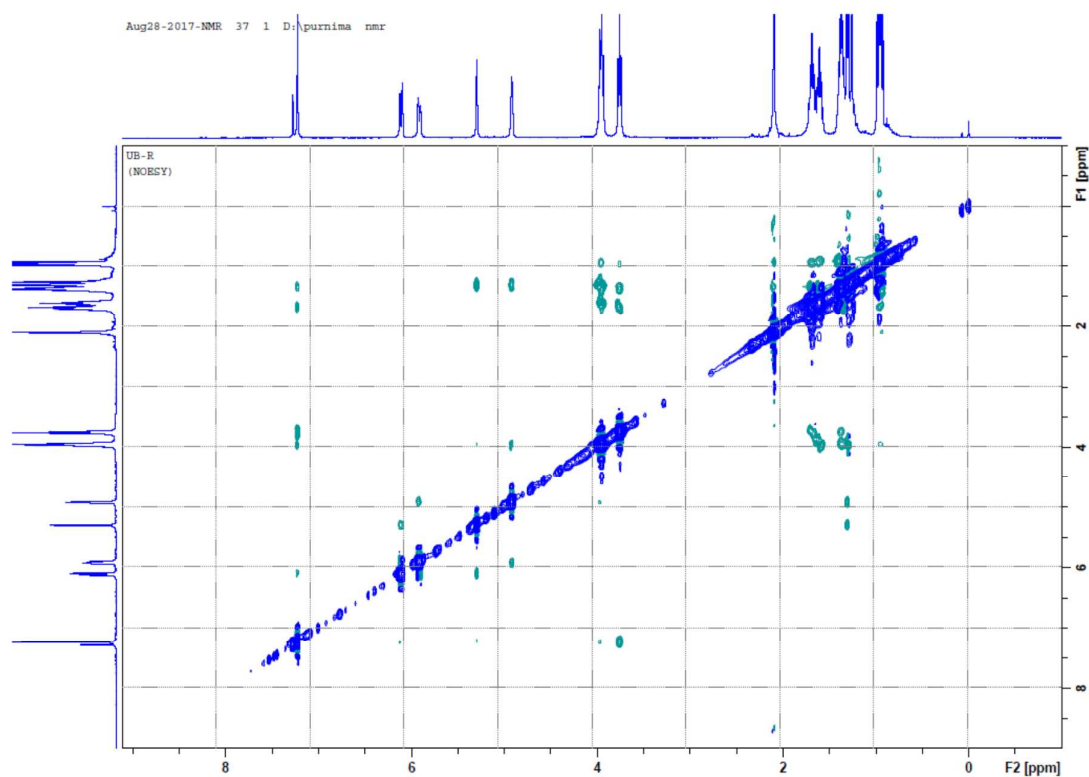


DEPT OF 6b





NOESY of Compound 3a



COSY of Compound 3a

