Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A three-component reagent system for rapid and mild removal of *O*-, *N*- and *S*-trityl protecting groups

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General Information

Optical rotations were measured at room temperature with a Perkin-Elmer 241 automatic polarimeter. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by UV-light (254 nm) and immersing into 5 vol.% ethanolic sulfuric acid or sulfuric acidic ammonium-molibdenate solution followed by heating. Column chromatography was performed on Silica gel 60 (Merck 0.040-0.063 mm). Organic solutions were dried over Na_2SO_4, and concentrated in vacuum. The ^1H NMR (360 and 400 MHz) and ^{13}C NMR (90 and 100 MHz) spectra were recorded with Bruker DRX-360 and DRX-400 spectrometers at 25 °C. Chemical shifts are referenced to Me_4Si (0.00 ppm for ^1H) and to the residual solvent signals ($CDCl_3$: 77.16, DMSO-d_6: 39.52 ppm for ^{13}C). MALDI-TOF MS analyses of the compounds were carried out in the positive reflectron mode using a BIFLEX III mass spectrometer (Bruker, Germany) equipped with delayed-ion extraction. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix and $F_3CCOONa$ as cationising agent in DMF. ESI-TOF MS spectra were recorded by a microTOF-Q type QqTOFMS mass spectrometer (Bruker) in the positive ion mode using MeOH as the solvent. Elemental analysis (C, H, N) was performed on an Elementar Vario MicroCube instrument.

Compound **12** and **13a** were purchased from Sigma-Aldrich.

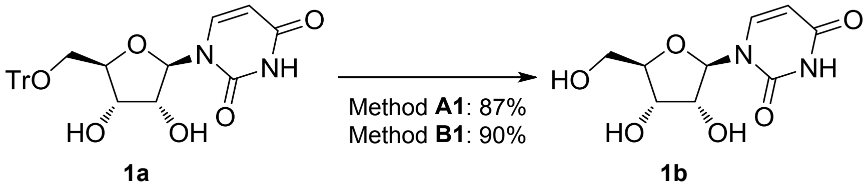
General method A for detritylation using $BF_3{\cdot}Et_2O$ as the Lewis acid

0.500 mmol of trityl, monomethoxytrityl or dimethoxytrityl derivative was added to the mixture of hexafluoroisopropanol (0.5 mL), $BF_3{\cdot}Et_2O$ (method **A1**: 0.2 equiv., method **A2**: 0.065 equiv.) and Et_3SiH (3.8 equiv., 300 µL). When the yellow colour of the solution was disappeared the reaction was monitored by TLC. After complete conversion of the starting compound (cc. 3-5 min) the reaction was quenched by saturated aqueous solution of $NaHCO_3$. The solvent was evaporated in *vacuo* and the residue was purified by flash column chromatography.

General method B for detritylation using $Cu(TfO)_2$ as the Lewis acid

0.500 mmol of trityl derivative was added to the mixture of hexafluoroisopropanol (0.5 mL), $Cu(TfO)_2$ (method **B1**: 0.2 equiv., method **B2**: 0.065 equiv., 100 mg in 50 mL $MeNO_2$) and Et_3SiH (3.8 equiv., 300 µL). When the yellow colour of the solution was disappeared the reaction was monitored by TLC. After complete conversion of the starting compound (cc. 3-5 min) the reaction was quenched by saturated aqueous solution of $NaHCO_3$. The solvent was evaporated in *vacuo* and the residue was purified by flash column chromatography.

Compound 1b

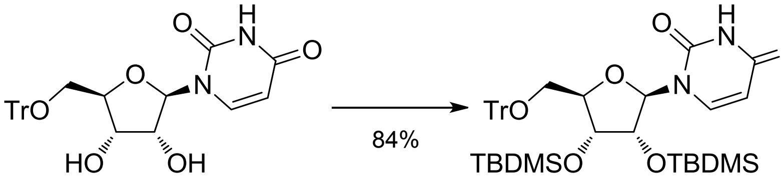


1a **1b**

Compound **1a**[1] (**A1**: 243 mg, 0.50 mmol; **B1**: 122 mg, 0.250 mmol) was converted to **1b** by method **A1** and **B1**. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH **A1**: 10:0 → 9:1 → 8:2, **B1**: 85:15 → 8:2) to yield **1b** (**A1**: 106 mg, 87%; **B1**: 56 mg, 90%) as a white solid. The spectral data were the same as those described in the literature. R_f= 0.14 (CH_2Cl_2/MeOH 9:1); ^1H NMR (400 MHz, DMSO-d_6 + one drop of D_2O) δ = 11.32 (s, 1H, N*H*), 7.89 (d, *J* = 8.1 Hz, 1H, CH_a uracil), 5.79 (d, *J* = 5.4 Hz, 1H, H-1), 5.67 (d, *J* = 8.1 Hz, 1H, CH_b uracil), 5.42 (s, 0.2H, O*H*), 5.17 (s, 0.4H, O*H*), 4.04 (t, *J* = 5.3 Hz, 1H, H-2), 3.98 (t, *J* = 4.4 Hz, 1H, H-4), 3.87 (q, *J* = 3.3 Hz, 1H, H-3), 3.63 (dd, *J* = 12.2

Hz, *J* = 3.0 Hz, 1H, H-5a), 3.60-3.54 (m, 1H, H-5b), 2.53 (s, 1H, O*H*); ^{13}C NMR (100 MHz, DMSO-d$_6$ + one drop of D$_2$O) δ = 163.5 (1C, C$_q$ uracil), 151.0 (1C, C$_q$ uracil), 141.1 (1C, *C*H$_a$ uracil), 102.0 (1C, *C*H$_b$ uracil), 87.9, 85.5, 73.7, 70.1 (4C, skeleton carbons), 61.0 (1C, C-5); ESI-TOF-MS: *m/z* calcd for $C_9H_{12}N_2NaO_6$ [M+Na]$^+$ 267.059, found 267.055.

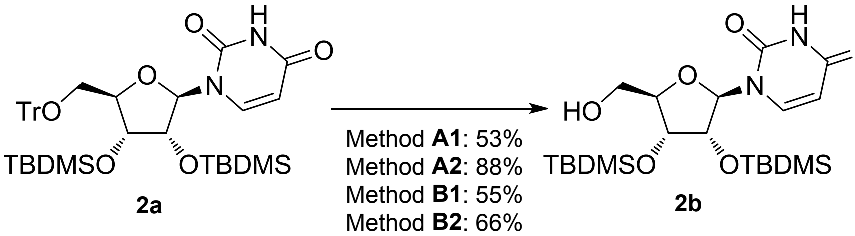
Compound 2a[2]



1a **2a**

Compound **1a** (9.1 g, 18.60 mmol) was dissolved in dry DMF (50 mL) and cooled to 0 °C. Imidazole (6.3 g, 93.0 mmol, 5.0 equiv.) and *tert*-butyldimethylsilyl chloride (9.0 g, 59.7 mmol, 3.2 equiv) were added to the reaction mixture and stirred overnight. The reaction was diluted with EtOAc and extracted with water. The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated. The crude product was purified by flash column chromatography (hexane/EtOAc 8:2) to yield **2a** (11.2 g, 84%) as a white foam. R$_f$= 0.41 (hexane/acetone 7:3); ^{1}H NMR (360 MHz, CDCl$_3$) δ = 9.25 (s, 1H, N*H*), 8.14 (d, *J* = 8.1 Hz, 1H, C*H*$_a$ uracil), 7.38-7.25 (m, 15H, arom.), 5.84 (s, 1H, H-1), 5.26 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1H, C*H*$_b$ uracil), 4.19 (s, 3H, H-2, H-3, H-4), 3.71 (d, *J* = 10.8 Hz, 1H, H-5a), 3.37 (d, *J* = 10.8 Hz, 1H, H-5b), 0.90, 0.77 (2 x s, 18H, 2 x *t*-Bu-C*H*$_3$), 0.17, 0.11, 0.02, -0.07 (4 x s, 12H, 4 x C*H*$_3$); ^{13}C NMR (90 MHz, CDCl$_3$) δ = 163.5 (1C, C$_q$ uracil), 150.4 (1C, C$_q$ uracil), 143.1 (3C, C$_q$ arom.), 140.4 (1C, *C*H$_a$ uracil), 129.1, 128.1, 127.7 (15C, arom.), 102.1 (1C, *C*H$_b$ uracil), 89.9, 83.0, 76.3, 70.9 (4C, skeleton carbons), 87.9 (1C, C$_q$ Tr), 61.9 (1C, C-5), 25.9 (6C, 2 x *t*-Bu-*C*H$_3$), 18.1 (1C, C$_q$ *t*-Bu), -3.9, -4.3, -4.7, -4.8 (4C, 4 x *C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_{40}H_{54}N_2NaO_6Si_2$ [M+Na]$^+$ 737.342, found 737.340.

Compound 2b[3]



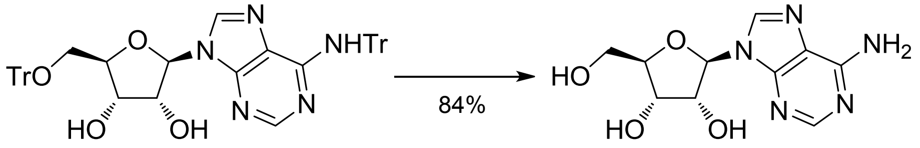
2a **2b**

Compound **2a** (**A1**, **A2**, **B1** and **B2**: 178 mg, 0.250 mmol) was converted to **2b** by method **A1**, **A2**, **B1** and **B2**. The crude product was purified by flash column chromatography (hexane/acetone 8:2) to yield **2b** (**A1**: 63 mg, 53%; **A2**:[a] 104 mg, 88%; **B1**: 65 mg, 55%; **B2**: 79 mg, 66%) as a white solid. R$_f$= 0.25 (hexane/acetone 7:3); ^{1}H NMR (360 MHz, CDCl$_3$) δ = 8.74 (s, 1H, N*H*), 7.73 (d, *J* = 8.1 Hz, 1H, C*H*$_a$ uracil), 5.84 (d, *J* = 8.0, 1H, C*H*$_b$ uracil), 5.58 (d, *J* = 5.3 Hz, 1H, H-1), 4.67 (t, *J* = 4.9 Hz, 1H), 4.29 (t, *J* = 3.9 Hz, 1H), 4.21 (s, 1H), 4.05 (d, *J* = 12.2 Hz, 1H, H-5a), 3.86-3.81 (m, 1H, H-5b), 3.12 (d, *J* = 4.7 Hz, 1H, O*H*), 1.03, 0.99 (2 x s, 18H, 2 x *t*-Bu-C*H*$_3$), 0.21, 0.20, 0.18, 0.15 (4 x s, 12H, 4 x C*H*$_3$); ^{13}C NMR (90 MHz, CDCl$_3$) δ = 163.9, 150.6 (2C, 2 x C$_q$ uracil), 143.1, 102.1 (2C, 2 x C*H* uracil), 93.6, 86.0, 74.0, 71.6 (C-1, C-2, C-3, C-4), 61.5 (1C, C-5), 26.0, 25.9 (6C, 2 x *t*-Bu-*C*H$_3$), 18.2, 18.1 (2C, 2 x C$_q$ *t*-Bu); MALDI-TOF-MS: *m/z* calcd for $C_{21}H_{40}N_2NaO_6Si_2$ [M+Na]$^+$ 495.23, found 495.33.

[a] The UV-active byproduct triphenylmethane was isolated from the reaction mixture (45 mg) and its structure was determined by NMR measurements: ^{1}H NMR (360 MHz, CDCl$_3$) δ =

7.28-7.10 (m, 15H, arom), 5.54 (s, 1H, C*H*); ^{13}C NMR (90 MHz, CDCl$_3$) δ = 144.1 (3C, 3 x C$_q$ arom), 129.6, 128.4, 126.4 (15C, arom), 100.0 (1C, C$_q$ trityl), 57.0 (1C, *C*H).

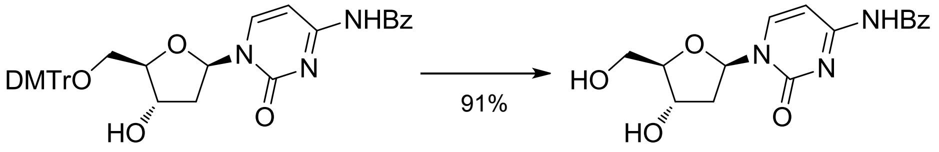
Compound 3b



3a **3b**

Compound **3a**[4] (376 mg, 0.500 mmol) was converted to **3b** by method **A1**. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 95:5 → 9:1 → 85:15) to yield **3b** (112 mg, 84%) as a white solid. The spectral data were the same as those described in the literature. R_f= 0.32 (CH$_2$Cl$_2$/MeOH 85:15); ^{1}H NMR (400 MHz, DMSO-d$_6$ + one drop of D$_2$O) δ = 8.38, 8.17 (2 x s, 2H, 2 x C*H* adenine), 7.37 (s, 2H, N*H*$_2$), 5.91 (d, *J* = 6.2 Hz, 1H, H-1), 5.52 (d, *J* = 6.1 Hz, 0.5H, O*H*), 5.27 (d, *J* = 4.2 Hz, 0.3H, O*H*), 4.63 (t, *J* = 5.5 Hz, 1H, H-4), 4.18-4.17 (m, 1H), 4.01 (q, *J* = 3.2 Hz, 1H), 3.70 (dd, *J* = 12.1 Hz, *J* = 3.3 Hz, 1H, H-5a), 3.58 (dd, *J* = 12.4 Hz, *J* = 3.7 Hz, 1H, H-5b), 2.53 (s, 0.3H, O*H*); ^{13}C NMR (100 MHz, DMSO-d$_6$ + one drop of D$_2$O) δ = 156.2 (1C, C$_q$ adenine), 152.6 (2C, 2 x *C*H adenine), 149.2 (1C, C$_q$ adenine), 119.5 (1C, C$_q$ adenine), 88.1, 86.0, 73.5, 70.7 (4C, skeleton carbons), 61.7 (1C, C-5); ESI-TOF-MS: *m/z* calcd for $C_{10}H_{13}N_5NaO_4$ [M+Na]$^+$ 290.087, found 290.086.

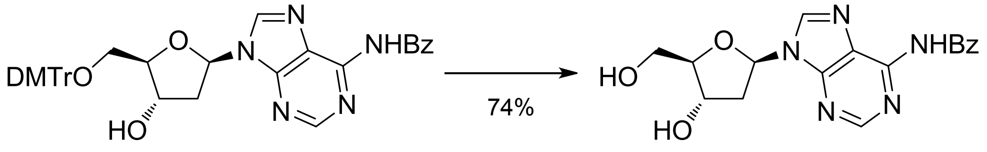
Compound 4b[5]



4a **4b**

Compound **4a**[6] (317 mg, 0.500 mmol) was converted to **4b** by method **A1**. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 95:5 → 9:1) to yield **4b** (150 mg, 91%) as a white solid. R_f= 0.44 (CH$_2$Cl$_2$/MeOH 9:1); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 11.24 (s, 1H, N*H*), 8.43 (d, *J* = 7.5 Hz, 1H, C*H*$_a$ cytosine), 8.04-7.37 (m, 6H, 5 x arom., C*H*$_b$ cytosine), 6.18 (t, *J* = 6.3 Hz, 1H, H-1), 5.33 (d, *J* = 4.2 Hz, 1H), 5.12 (t, *J* = 5.0 Hz, 1H), 4.31-4.27 (m, 1H), 3.94-3.91 (m, 1H), 3.67-3.63 (m, 2H, H-5a,b), 2.39-2.33 (m, 1H, H-2a), 2.13-2.06 (m, 1H, H-2b); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ = 163.0 (1C, C$_q$ cytosine), 154.5 (1C, C$_q$ cytosine), 145.0 (1C, *C*H$_a$ cytosine), 133.3 (1C, C$_q$ arom.), 132.7, 128.5 (5C, arom.), 96.2 (1C, *C*H$_b$ cytosine), 88.0, 86.3, 70.0 (3C, skeleton carbons), 61.0 (1C, C-5), 41.0 (1C, C-2); ESI-TOF-MS: *m/z* calcd for $C_{16}H_{17}N_3NaO_5$ [M+Na]$^+$ 354.107, found 354.104.

Compound 5b[5]

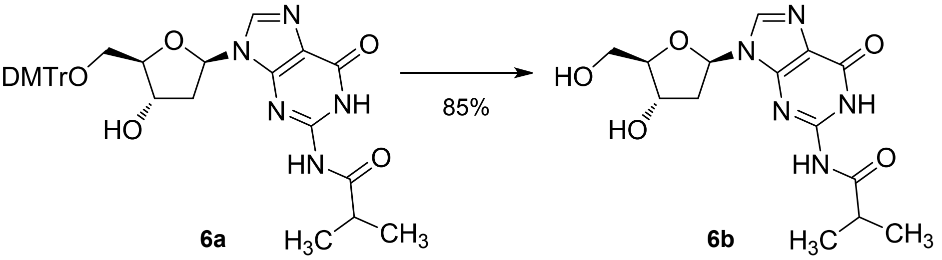


5a **5b**

Compound **5a**[5] (329 mg, 0.500 mmol) was converted to **5b** by method **A1**. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 95:5) to yield **5b** (131 mg, 74%) as a white solid. R_f= 0.33 (CH$_2$Cl$_2$/MeOH 9:1); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 11.23 (s, 1H, N*H*), 8.78 (s, 1H, C*H*$_a$ adenine), 8.72 (s, 1H, C*H*$_b$ adenine), 8.09-7.54 (m, 5H, arom.), 6.53 (t, *J* = 6.8 Hz, 1H, H-1), 5.42 (d, *J* = 2.8 Hz, 1H), 5.08 (t, *J* = 4.9 Hz, 1H), 4.50

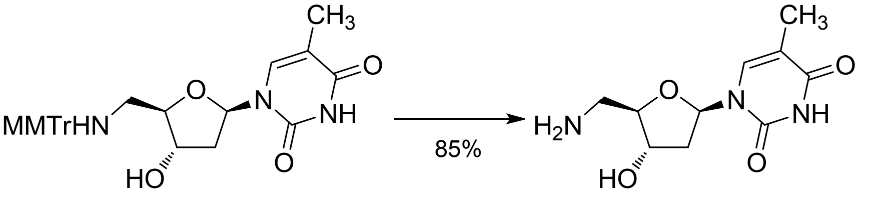
(d, J = 1.9 Hz, 1H), 3.95 (dd, J = 7.4 Hz, J = 4.4 Hz, 1H), 3.71-3.66 (m, 1H, H-5a), 3.61-3.56 (m, 1H, H-5b), 2.87-2.80 (m, 1H, H-2a), 2.43-2.38 (m, 1H, H-2b); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ = 152.0, 150.4, 125.9 (3C, C$_q$ adenine), 133.5 (1C, C$_q$ arom.), 132.5, 128.5 (5C, arom.), 88.1, 83.9, 70.8 (3C, skeleton carbons), 61.7 (1C, C-5), 39.4 (1C, C-2); ESI-TOF-MS: *m/z* calcd for $C_{17}H_{17}N_5NaO_4$ [M+Na]$^+$ 378.118, found 378.117.

Compound 6b[7]



Compound **6a**[8] (312 mg, 0.500 mmol) was converted to **6b** by method **A1**. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 95:5 → 9:1) to yield **6b** (144 mg, 85%) as a white solid. R$_f$= 0.20 (CH_2Cl_2/MeOH 9:1); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 12.09, 11.69 (s, 2H, 2 x N*H*), 8.25 (s, 1H, C*H* guanine), 6.23 (dd, J = 7.1 Hz, J = 6.3 Hz, 1H, H-1), 5.34 (d, J = 3.7 Hz, 1H), 4.98 (t, J = 5.3 Hz, 1H), 4.40 (dd, J = 5.1 Hz, J = 2.8 Hz, 1H), 3.86 (dd, J = 7.4 Hz, J = 4.4 Hz, 1H), 3.63-3.51 (m, 2H, H-5a,b), 2.82-2.75 (m, 1H, H-2a), 2.60-2.55 (m, 1H, H-2b), 2.33-2.28 (m, 1H, C*H*), 1.15, 1.13 (2 x s, 6H, 2 x CH_3); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ = 180.2 (1C, *C*O), 154.9, 148.4, 148.1, 120.2 (4C, C$_q$ guanine), 87.8, 83.0, 70.5 (3C, skeleton carbons), 61.5 (1C, C-5), 39.7 (1C, C-2), 34.8 (1C, *C*H), 18.9 (2C, 2 x *C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_{14}H_{19}N_5NaO_5$ [M+Na]$^+$ 360.128, found 360.127.

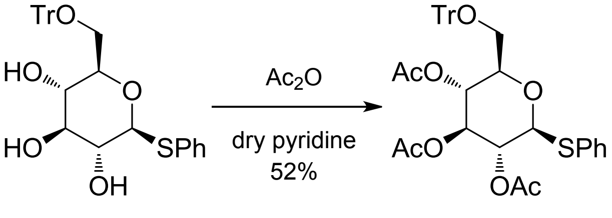
Compound 7b[9]



7a **7b**

Compound **7a**[10] (136 mg, 0.260 mmol) was converted to **7b** by method **A1**. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 1:1 + 0.1% of Et_3N) to yield **7b** (51 mg, 85%) as a yellow solid. R$_f$= 0.10 (CH_2Cl_2/MeOH 1:1 + 0.1% of Et_3N); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 7.64 (d, J = 1.0 Hz, 1H, C*H* thymine), 6.15 (t, J = 6.6 Hz, 1H), 4.70-4.38 (m, 5H), 4.21 (dt, J = 6.4 Hz, J = 3.4 Hz, 1H), 3.66 (dd, J = 8.6 Hz, J = 5.2 Hz, 1H), 2.74-2.73 (m, 2H), 2.18-2.11 (m, 1H, H-2a), 2.08-2.02 (m, 1H, H-2b), 1.80 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ = 164.0, 150.7, 109.6 (3C, 3 x C$_q$ thymine), 136.3 (1C, *C*H thymine), 87.8, 83.5, 70.8 (3C, skeleton carbons), 43.7 (1C, C-5), 39.0 (1C, C-2), 12.2 (1C, *C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_{10}H_{16}N_3O_4$ [M+H]$^+$ 242.114, found 242.114.

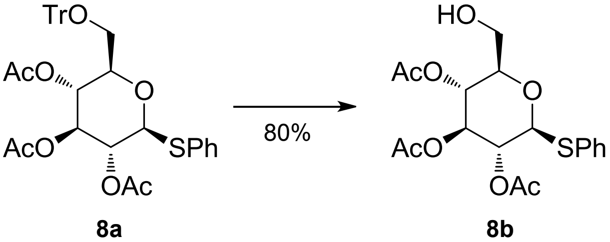
Compound 8a



8 **8a**

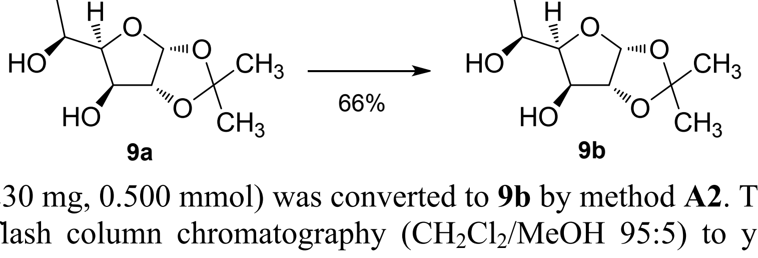
Compound **8** (800 mg, 1.55 mmol) was dissolved in dry pyridine (5 mL), Ac_2O (3.5 mL) was added to the mixture and stirred overnight. The solution was poured into ice-water, diluted with CH_2Cl_2 and extracted. The organic phase was extracted with diluted acetic acid, water, saturated aqueous $NaHCO_3$-solution and then dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/acetone 8:2 + 0.1 % of Et_3N) to afford **8a** (518 mg, 52%) as a white foam. R_f = 0.27 (hexane/acetone 8:2 + 0.1 % of Et_3N); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.64-7.14 (m, 20H, arom.), 5.16 (t, J = 9.2 Hz, 1H, H-3), 5.08 (t, J = 9.8 Hz, 1H, H-2), 5.03 (t, J = 8.7 Hz, 1H, H-4), 4.73 (d, J = 10.0 Hz, 1H, H-1), 3.58 (ddd, J = 9.8 Hz, J = 5.1 Hz, J = 1.9 Hz, 1H, H-5), 3.26 (dd, J = 10.6 Hz, J = 1.9 Hz, 1H, H-6a), 3.14 (dd, J = 10.6 Hz, J = 5.1 Hz, 1H, H-6b), 2.09, 1.96, 1.70 (3 x s, 9H, 3 x Ac-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.4, 169.4, 169.0 (3C, 3 x Ac-CO), 143.7 (3C,3 x C_q Tr-arom.), 133.3-127.1 (20C, arom.), 131.9 (1C, C_q SPh), 86.8 (1C, C_q Tr), 85.7 (1C, C-1), 77.7, 74.5, 70.2, 68.5 (4C, skeleton carbons), 62.1 (1C, C-6), 20.9, 20.7, 20.5 (3C, 3 x Ac-CH$_3$); Elemental analysis: calcd (%) for $C_{37}H_{36}O_8S$: C 69.36, H 5.66, S 5.00; found C 69.40, H 5.68, S 4.99.

Compound 8b



Compound **8a** (80 mg, 0.125 mmol) was converted to **8b** by method **A2**. The crude product was purified by flash column chromatography (CH_2Cl_2/acetone 10:0 → 10:2) to yield **8b** (40 mg, 80%) as a white foam. R_f = 0.24 (CH_2Cl_2/acetone 98:2); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.49-7.31 (m, 5H, arom.), 5.27 (t, J = 9.4 Hz, 1H, H-3), 5.00 (t, J = 9.6 Hz, 1H, H-2), 4.95 (t, J = 9.4 Hz, 1H, H-4), 4.75 (d, J = 10.1 Hz, 1H, H-1), 3.76-3.73 (m, 1H, H-6a), 3.62-3.64 (m, 2H, H-5, H-6b), 2.27 (s, 1H, OH), 2.08, 2.04, 2.00 (3 x s, 9H, 3 x Ac-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.3, 170.1, 169.4 (3C, 3 x Ac-CO), 133.0, 129.2, 128.5 (5C, arom.), 131.7 (1C, C_q arom.), 85.8 (1C, C-1), 78.4, 73.9, 70.3, 68.6 (4C, skeleton carbons), 61.6 (1C, C-6), 20.8, 20.7 (3C, 3 x Ac-CH$_3$); Elemental analysis: calcd (%) for $C_{18}H_{22}O_8S$: C 54.26, H 5.57, S 8.05; found C 54.23, H 5.60, S 8.09.

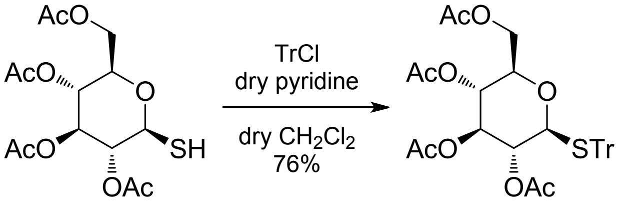
Compound 9b[11]



Compound **9a**[12] (230 mg, 0.500 mmol) was converted to **9b** by method **A2**. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 95:5) to yield **9b** (73 mg, 66%) as a white solid. The spectral data were the same as those described in the literature. R_f = 0.13 (CH_2Cl_2/MeOH 95:5); $[\alpha]_D$: -10.1 (c 0.13, MeOH); lit. [13]: $[\alpha]_D$: -11.6 (c 2.50, H_2O); ^1H NMR (400 MHz, DMSO-d_6 + one drop of D_2O) δ = 5.79 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.38 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-2), 4.03 (d, J = 2.4 Hz, 1H, H-3), 3.83 (dd, $J_{4,5}$ = 8.6 Hz, $J_{3,4}$ = 2.5 Hz, 1H, H-4), 3.68 (ddd, $J_{4,5}$ = 8.7 Hz, $J_{5,6b}$ = 6.2 Hz, $J_{5,6a}$ = 2.9 Hz, 1H, H-5), 3.55 (dd, J_{gem} = 11.2 Hz, $J_{5,6a}$ = 2.9 Hz, 1H, H-6a), 3.36 (dd, J_{gem} = 11.2 Hz, $J_{5,6b}$ = 6.2 Hz, 1H, H-6b), 1.37, 1.23 (2 x s, 6H, 2 x iP-CH_3); ^{13}C NMR (100 MHz, DMSO-d_6 + one drop of D_2O) δ = 110.6

(1C, C_q *i*P), 104.6 (1C, C-1), 84.8, 80.2, 73.3, 68.5 (4C, skeleton carbons), 63.7 (1C, C-6), 26.8, 26.2 (2C, 2 x *i*P-*C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_9H_{16}NaO_6$ $[M+Na]^+$ 243.084, found 243.081.

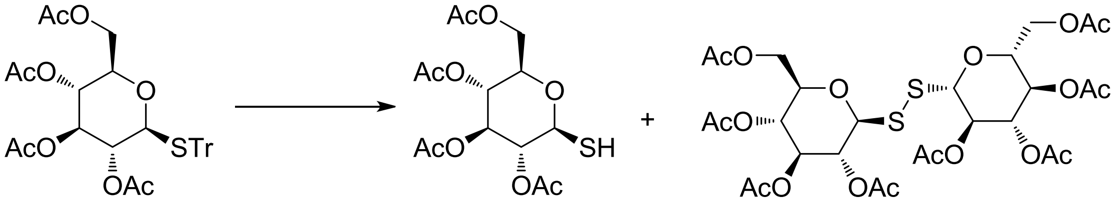
Compound 10a



10b **10a**

To a solution of compound **10b** (364 mg, 1.000 mmol) in dry CH_2Cl_2 (5 mL) dry pyridine (0.6 mL) and triphenylmethyl chloride (418 mg, 1.50 mmol, 1.5 equiv.) were added and stirred overnight under argon atmosphere. Next day the reaction mixture was diluted with CH_2Cl_2 and extracted with 10% aqueous $NaHSO_4$-solution then saturated aqueous $NaHCO_3$-solution. The organic phase was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl-acetate 8:2) to afford **10a** (461 mg, 76%) as a white solid. R_f= 0.40 (hexane/ethyl-acetate 7:3); $[\alpha]_D$: +1.64 (*c* 0.12, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ = 7.42-7.23 (m, 15H, arom.), 5.13-5.08 (m, 1H), 5.01-4.90 (m, 2H), 4.01 (dd, J = 12.2 Hz, J = 4.6 Hz, 1H), 3.78-3.72 (m, 2H), 2.90-2.87 (m, 1H), 2.07, 1.97, 1.96, 1.94 (4 x s, 12H, 4 x Ac-C*H*$_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ = 170.6, 170.3, 169.4, 169.3 (4C, 4 x Ac-*C*O), 144.5 (3C, 3 x C_q arom.), 130.1, 127.9, 127.1 (15C, arom.), 83.8 (1C, C-1), 75.4, 74.5, 69.9, 68.3 (4C, C-2, C-3, C-4, C-5), 68.9 (1C, C_q Tr), 61.9 (1C, C-6), 20.9, 20.8, 20.7, 20.6 (4C, 4 x Ac-*C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_{33}H_{34}NaO_9S$ $[M+Na]^+$ 629.182, found 629.180.

Compound 10b[14,15]



10a

10b
Method **A1**: 82%
Method **B2**: 54%

10c
Method **A1**: 0%
Method **B2**: 10%

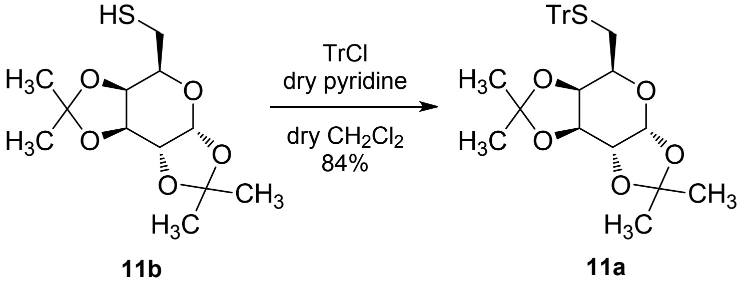
Compound **10a** (**A1** and **B2**: 151 mg, 0.250 mmol) was converted to **10b** by method **A1** and **B2**. The crude product was purified by flash column chromatography (hexane/acetone 8:2) to yield **10b** (**A1**: 75 mg, 82%; **B2**: 49 mg, 54%) and **10c**[16] (**B2**: 10%).

Compound **10b**: white foam, R_f= 0.24 (hexane/acetone 7:3); $[\alpha]_D$: +18.4 (*c* 0.13, $CHCl_3$); lit.[15]: $[\alpha]_D$: +11.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (360 MHz, $CDCl_3$) δ = 5.20 (t, J = 9.3 Hz, 1H), 5.11 (t, J = 9.7 Hz, 1H), 4.98 (t, J = 9.5 Hz, 1H), 4.56 (t, J = 9.8 Hz, 1H), 4.26 (dd, J = 12.4 Hz, J = 4.7 Hz, 1H, H-6a), 4.15-4.11 (m, 1H, H-6b), 3.76-3.72 (m, 1H, H-5), 2.33 (d, J = 9.9 Hz, 1H, S*H*), 2.10, 2.08, 2.03, 2.01 (4 x s, 12H, 4 x Ac-C*H*$_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ = 170.6, 170.1, 169.6, 169.4 (4C, 4 x Ac-*C*O), 78.7 (1C, C-1), 76.4, 73.6, 68.3 (4C, C-2, C-3, C-4, C-5), 62.1 (1C, C-6), 20.7, 20.6 (4C, 4 x Ac-*C*H$_3$); ESI-TOF-MS: *m/z* calcd for $C_{14}H_{20}NaO_9S$ $[M+Na]^+$ 387.073, found 387.069.

Compound **10c**: white foam, R_f= 0.49 (CH_2Cl_2/acetone 9:1); ^{1}H NMR (360 MHz, $CDCl_3$) δ = 5.36 – 4.95 (m, 6H,), 4.67 (d, J = 9.6 Hz, 2H, H-1), 4.43 – 4.06 (m, 4H, H-6), 3.83-3.76 (m, 2H, H-5), 2.14, 2.11, 2.03, 2.01 (4 x s, 24H, 8 x Ac-C*H*$_3$); ^{13}C NMR (90 MHz, $CDCl_3$) δ =

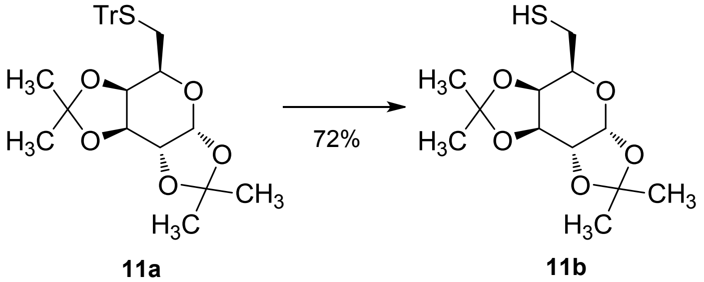
170.8, 170.2, 169.4, 169.2 (4C, 4 x Ac-*C*O), 87.3 (1C, C-1), 76.3, 74.0, 69.9, 68.0 (4C, C-2, C-3, C-4, C-5), 61.7 (1C, C-6), 20.8, 20.7, 20.6 (4C, 4 x Ac-*C*H$_3$).

Compound 11a



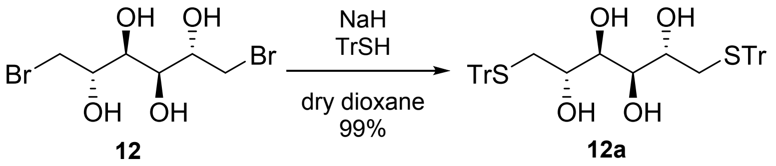
To a solution of compound **11b** (205 mg, 0.740 mmol) in dry CH$_2$Cl$_2$ (3 mL) dry pyridine (0.5 mL) and triphenylmethyl chloride (310 mg, 1.11 mmol, 1.5 equiv.) were added and stirred overnight under argon atmosphere. Next day the reaction mixture was diluted with CH$_2$Cl$_2$ and extracted with 10% aqueous NaHSO$_4$-solution then saturated aqueous NaHCO$_3$-solution. The organic phase was dried over Na$_2$SO$_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/Et$_2$O 98:2 → 95:5 → 9:1) to afford **11a** (324 mg, 84%). R$_f$= 0.53 (hexane/acetone 8:2); [α]$_D$: -70.3 (*c* 0.11, CHCl$_3$); ^{1}H NMR (360 MHz, CDCl$_3$) δ = 7.42-7.14 (m, 15H, arom.), 5.44 (d, *J* = 5.0 Hz, 1H, H-1), 4.52 (dd, *J* = 7.9 Hz, *J* = 2.3 Hz, 1H, H-3), 4.23 (dd, *J* = 5.0 Hz, *J* = 2.4 Hz, 1H, H-2), 4.10 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H, H-4), 3.63 (td, *J* = 7.0 Hz , *J* = 1.5 Hz, 1H, H-5), 2.50 (ddd, *J* = 27.4 Hz, *J* = 12.2 Hz, *J* = 7.1 Hz, 2H, H-6a,b), 1.48, 1.39, 1.32, 1.29 (4 x s, 12H, 4 x *i*P-C*H*$_3$); ^{13}C NMR (90 MHz, CDCl$_3$) δ = 145.0 (3C, 3 x C$_q$ arom.), 129.9, 128.0, 126.8 (15C, arom.), 109.3, 108.7 (2C, 2 x C$_q$-*i*P), 96.5 (1C, C-1), 72.0, 71.0, 70.6, 67.5 (4C, C-2, C-3, C-4, C-5), 67.1 (1C, C$_q$ Tr), 32.2 (1C, C-6), 26.3, 26.1, 25.0, 24.7 (4C, 4 x *i*P-*C*H$_3$); ESI-TOF-MS: *m/z* calcd for C$_{31}$H$_{34}$NaO$_5$S [M+Na]$^+$ 541.202, found 541.203.

Compound 11b



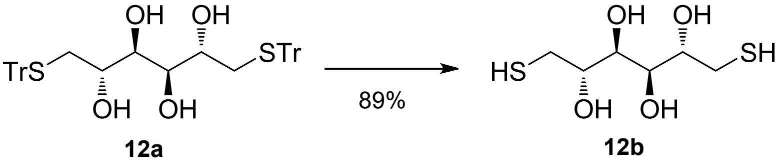
Compound **11a** (130 mg, 0.250 mmol) was converted to **11b** by method **A2**. The crude product was purified by flash column chromatography (hexane/Et$_2$O 95:5) to yield **11b** (50 mg, 72%) as a colourless syrup. R$_f$= 0.41 (hexane/acetone 95:5); [α]$_D$: -74.1 (*c* 0.16, CHCl$_3$); ^{1}H NMR (360 MHz, CDCl$_3$) δ = 5.53 (d, *J* = 5.0 Hz, 1H, H-1), 4.63 (dd, *J* = 7.9 Hz, *J* = 2.4 Hz, 1H, H-3), 4.35 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H, H-4), 4.32 (dd, *J* = 5.0 Hz, *J* = 2.4 Hz, 1H, H-2), 3.79 (td, *J* = 7.0 Hz, *J* = 1.6 Hz, 1H, H-5), 2.81 - 2.63 (m, 2H, H-6a,b), 1.62 (dd, *J* = 9.7 Hz, *J* = 7.5 Hz, 1H, S*H*), 1.55, 1.44, 1.35, 1.34 (4 x s, 12H, 4 x *i*P-C*H*$_3$); ^{13}C NMR (90 MHz, CDCl$_3$) δ = 109.5, 108.8 (2C, 2 x C$_q$-*i*P), 96.7 (1C, C-1), 71.4, 71.1, 70.7, 70.0 (4C, C-2, C-3, C-4, C-5), 26.2, 26.1, 25.0, 24.6 (4C, 4 x *i*P-*C*H$_3$), 24.5 (1C, C-6); ESI-TOF-MS: *m/z* calcd for C$_{12}$H$_{20}$NaO$_5$S [M+Na]$^+$ 299.093, found 299.089.

Compound 12a[17]



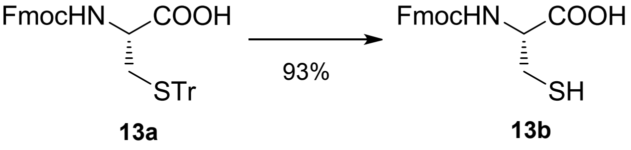
NaH (50% in oil) (940 mg, 19.58 mmol, 3.0 equiv.) was washed with hexane (2x5 mL) and dried under the stream of argon followed by suspension in dry dioxane (130 mL). Triphenylmethanethiol (4.50 g, 16.28 mmol, 2.5 equiv.) was added to the suspension and stirred for 10 minutes followed by addition of **12** (2.0 g, 6.49 mmol) and stirring was continued for additional 2 hours. After completion of the reaction, methanol (3 mL) was added to the reaction mixture and stirred for 30 minutes to quench the unreacted NaH. The solvent was evaporated in *vacuo* and the residue was purified by flash column chromatography (hexane/acetone 75:25) to yield compound **12a** (4.53 g, 99%) as a white foam. R_f= 0.35 (hexane/acetone 6:4); $[\alpha]_D$: -18.4 (*c* 0.30, CH_2Cl_2); ^1H NMR (360 MHz, $CDCl_3$) δ = 7.42-7.16 (m, 30H, arom.), 3.30 (t, J = 6.0 Hz, 2H), 3.23-3.20 (m, 2H), 2.65 (d, J = 5.7 Hz, 2H), 2.54-2.41 (m, 6H); ^{13}C NMR (90 MHz, $CDCl_3$) δ = 144.7 (6C, 6 x C_q arom.), 129.7, 128.1, 127.0 (30C, arom.), 71.8, 71.7 (4C, skeleton carbons), 67.2 (2C, 2 x C_q Tr), 36.2 (2C, C-1, C-1'); ESI-TOF-MS: *m/z* calcd for $C_{44}H_{42}NaO_4S_2$ $[M+Na]^+$ 721.242, found 721.244.

Compound 12b[17]



Compound **12a** (350 mg, 0.500 mmol) was added to the mixture of hexafluoroisopropanol (0.5 mL), $BF_3 \cdot Et_2O$ (0.2 equiv.) and Et_3SiH (3.8 equiv., 300 μL). After complete conversion of the starting compound (cc. 5 min) the solvent was evaporated in *vacuo* and the crude product was purified by trituration with dry Et_2O to yield compound **12b** (96 mg, 89%) as a white solid. R_f= 0.08 (hexane/acetone 1:1); $[\alpha]_D$: +7.9 (*c* 0.30, MeOH) ^1H NMR (360 MHz, $CDCl_3$) δ = 4.74 (s, 2H), 4.24 (d, J = 5.6 Hz, 2H), 3.53 (d, J = 4.4 Hz, 4H), 2.85-2.79 (m, 2H), 2.53 (dd, J = 12.7 Hz, J = 5.7 Hz, 3H), 1.99 (t, J = 7.8 Hz, 1H); ^{13}C NMR (90 MHz, DMSO-d_6) δ = 71.2, 70.7 (4C, skeleton carbons), 29.1 (2C, C-1, C-1'); ESI-TOF-MS: *m/z* calcd for $C_6H_{14}NaO_4S_2$ $[M+Na]^+$ 237.023, found 237.022.

Compound 13b[18]



Compound **13a** (250 mg, 0.427 mmol) was converted to **13b** by method **A1**. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 9:1 → 85:15) to yield **13b** (136 mg, 93%) as a white foam. R_f= 0.12 (CH_2Cl_2/MeOH 9:1); ^1H NMR (400 MHz, DMSO-d_6) δ = 7.90-7.18 (m, 9H, 8 x arom., 1 x N*H*), 4.36-4.23 (m, 3H), 4.09-4.07 (m, 1H), 3.20 (s, 1H), 2.95-2.82 (m, 2H, CH_2-SH), 1.21 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 155.8 (1C, *C*O), 144.0, 143.9, 140.8 (5C, 5 x C_q Fmoc), 127.7, 127.2, 125.3, 120.1 (8C, arom.), 65.7 (1C, *C*H_2-Fmoc), 57.2 (1C, *C*H), 46.8 (1C, *C*H-Fmoc), 26.6 (1C, *C*H_2-SH); ESI-TOF-MS: *m/z* calcd for $C_{18}H_{17}NNaO_4S$ $[M+Na]^+$ 366.078, found 366.071.

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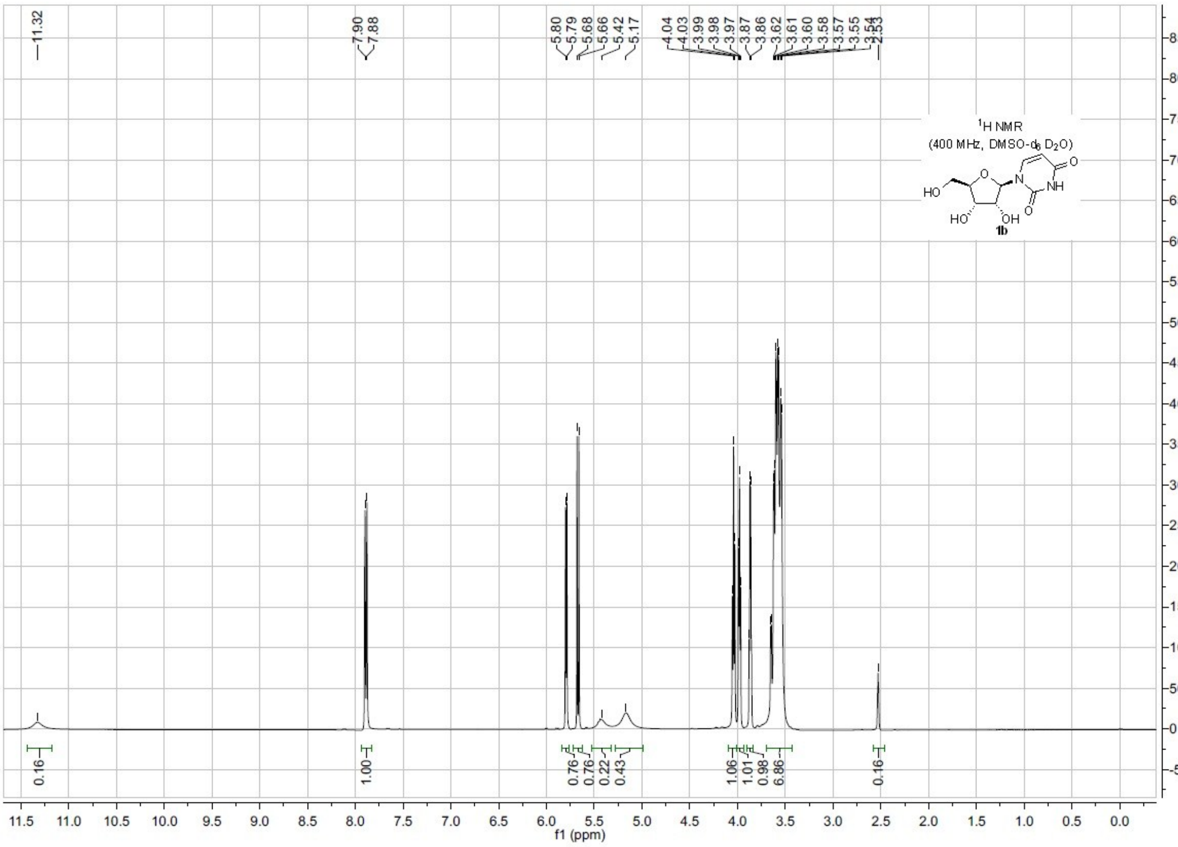
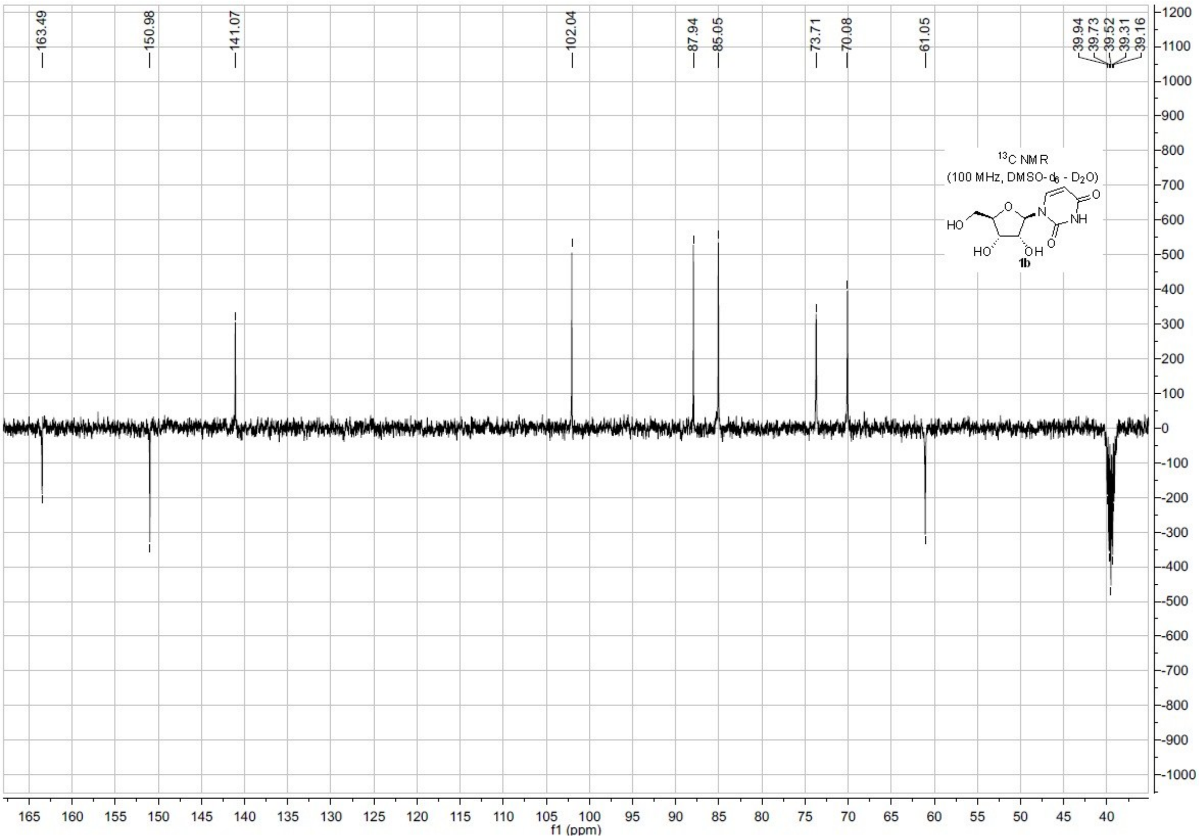
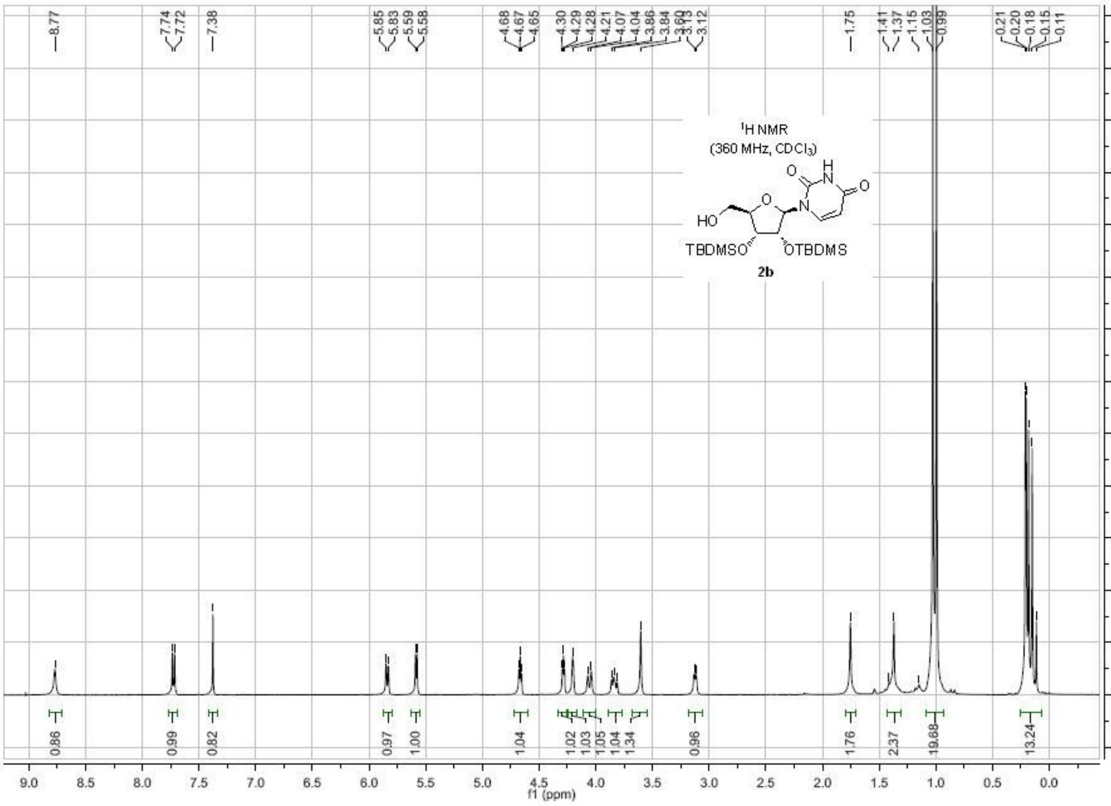
^{1}H and ^{13}C NMR spectra of the compounds



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3.86
3.84
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1.03
0.99
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0.20
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^{1}H NMR
(360 MHz, CDCl$_3$)
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OTBDMS
O
N
H
2b
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0.99
0.82
0.97
1.00
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0.96
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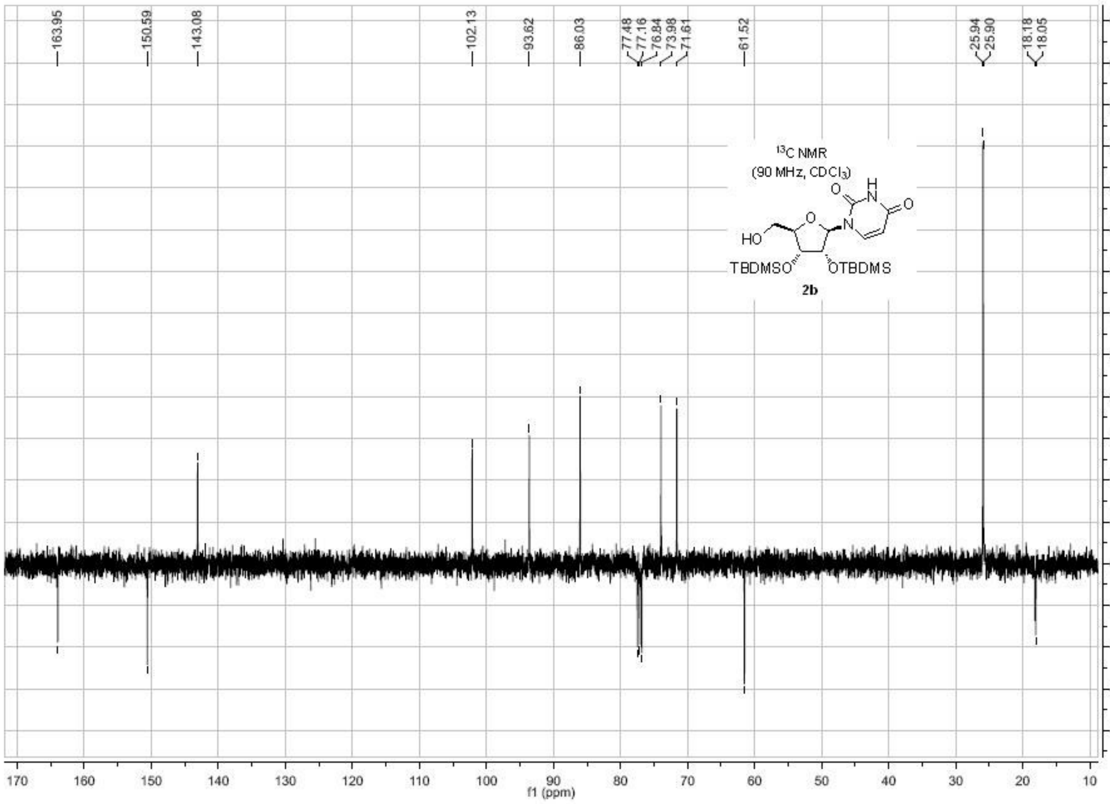
f1 (ppm)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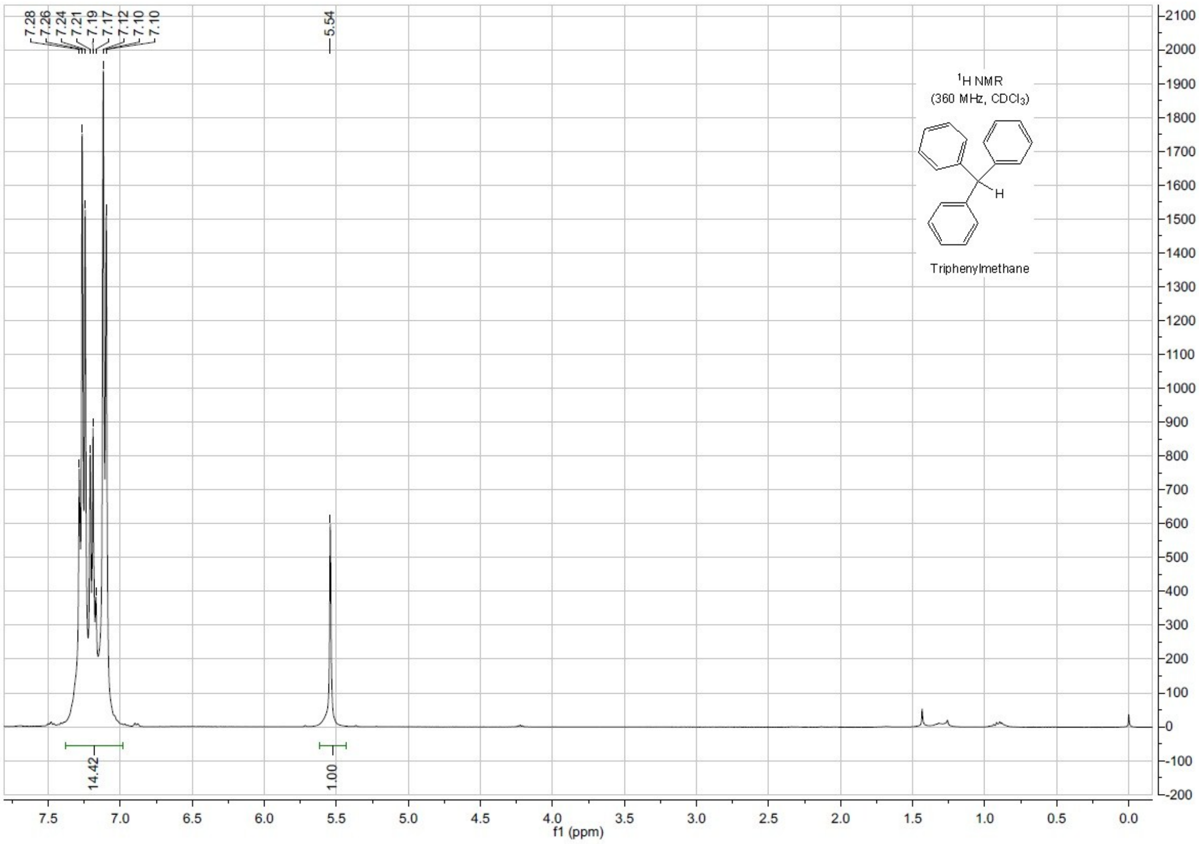
2b
f1 (ppm)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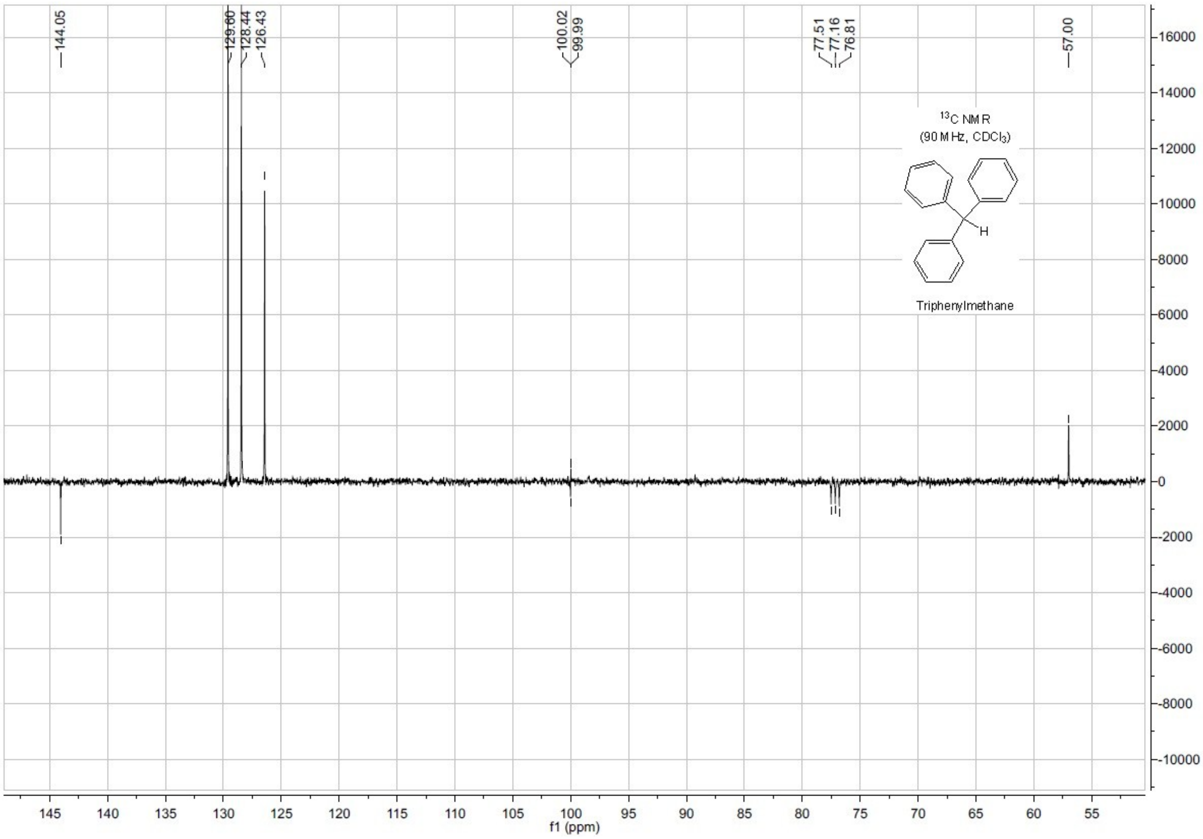
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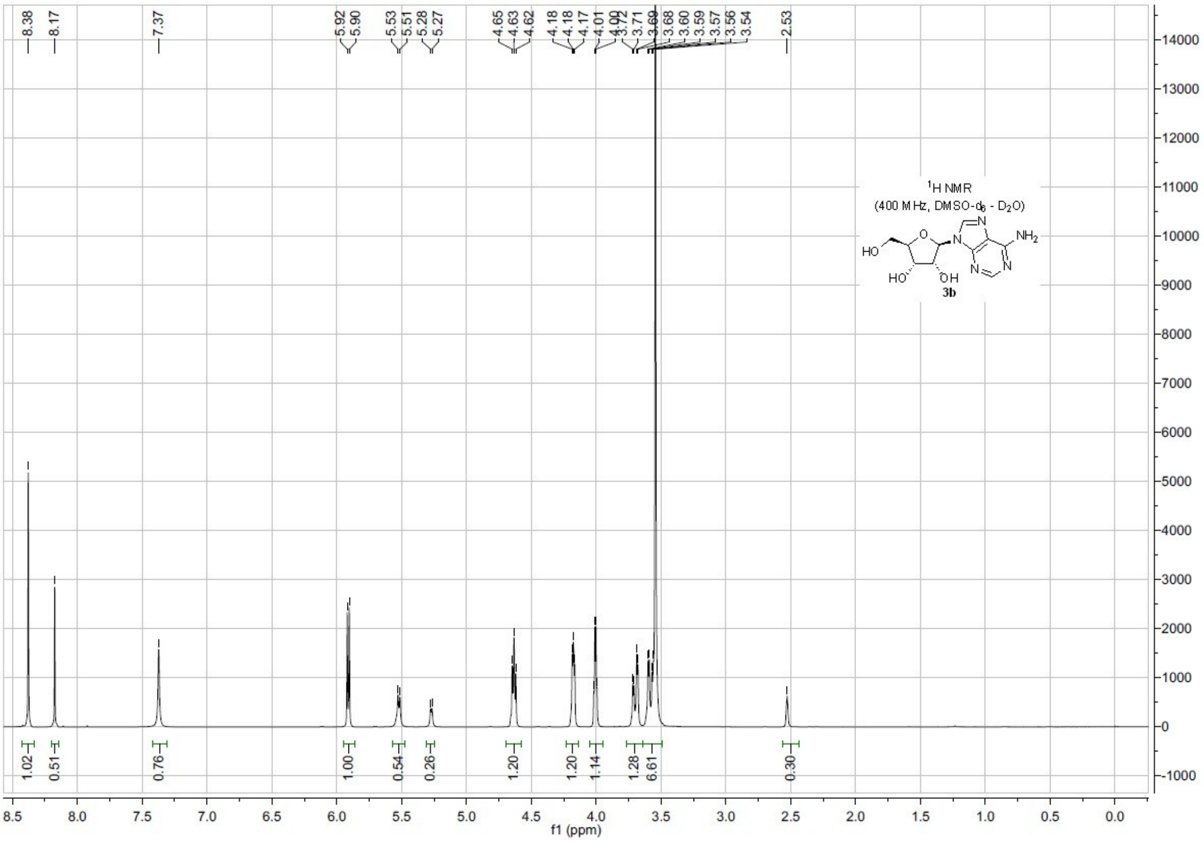
f1 (ppm)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3.59
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3.56
3.54
2.53
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N
NH$_2$
HO
OH
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N
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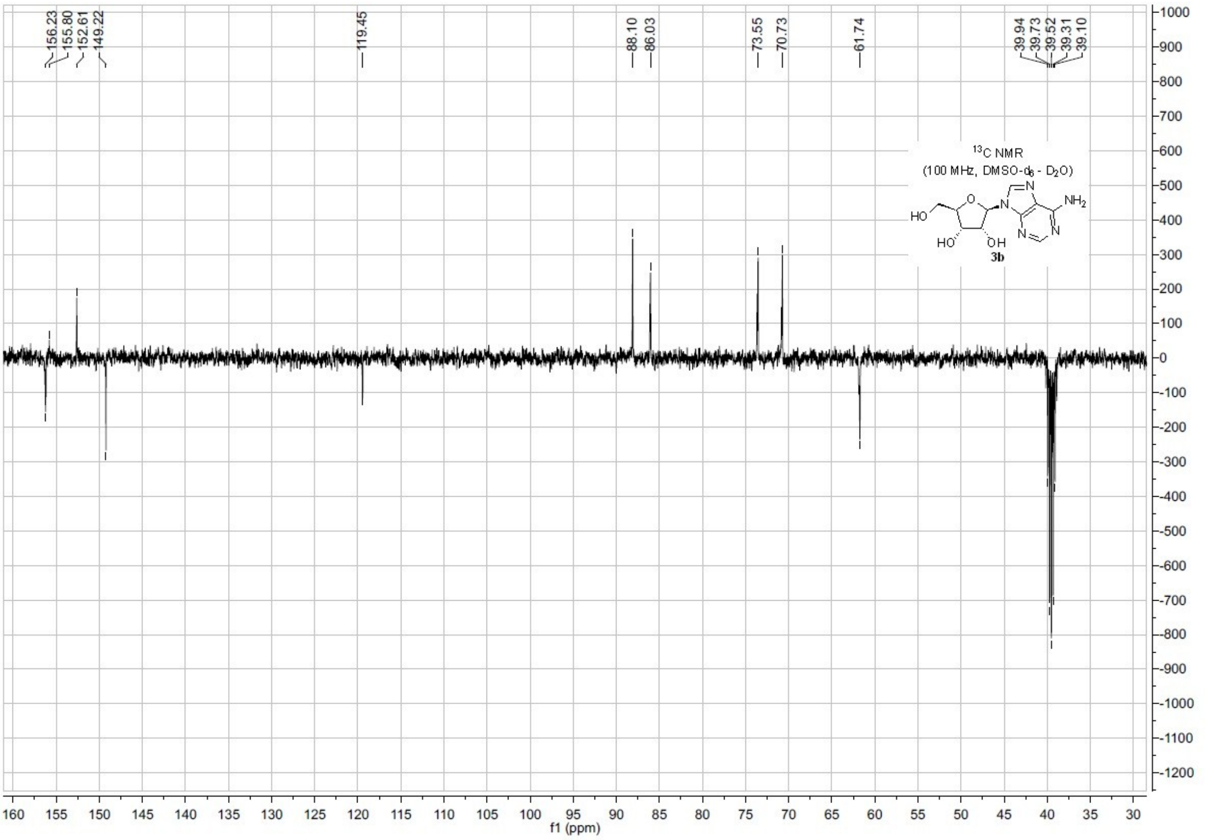
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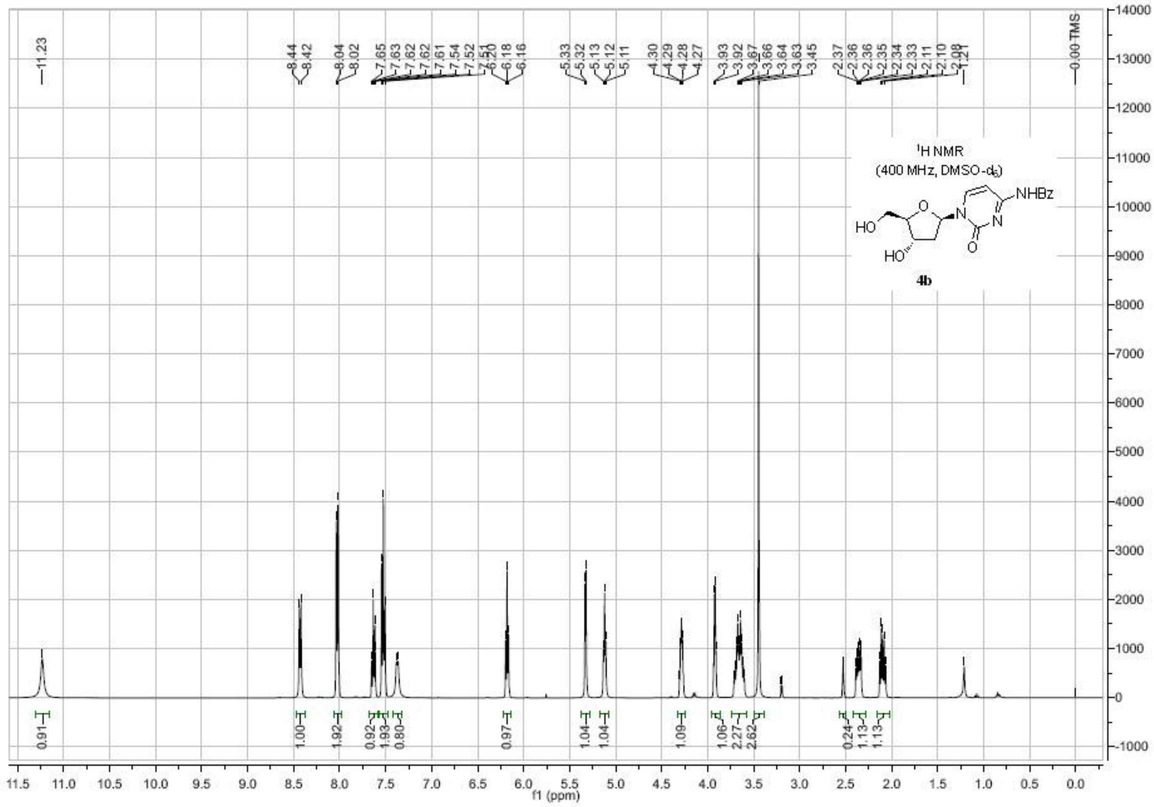
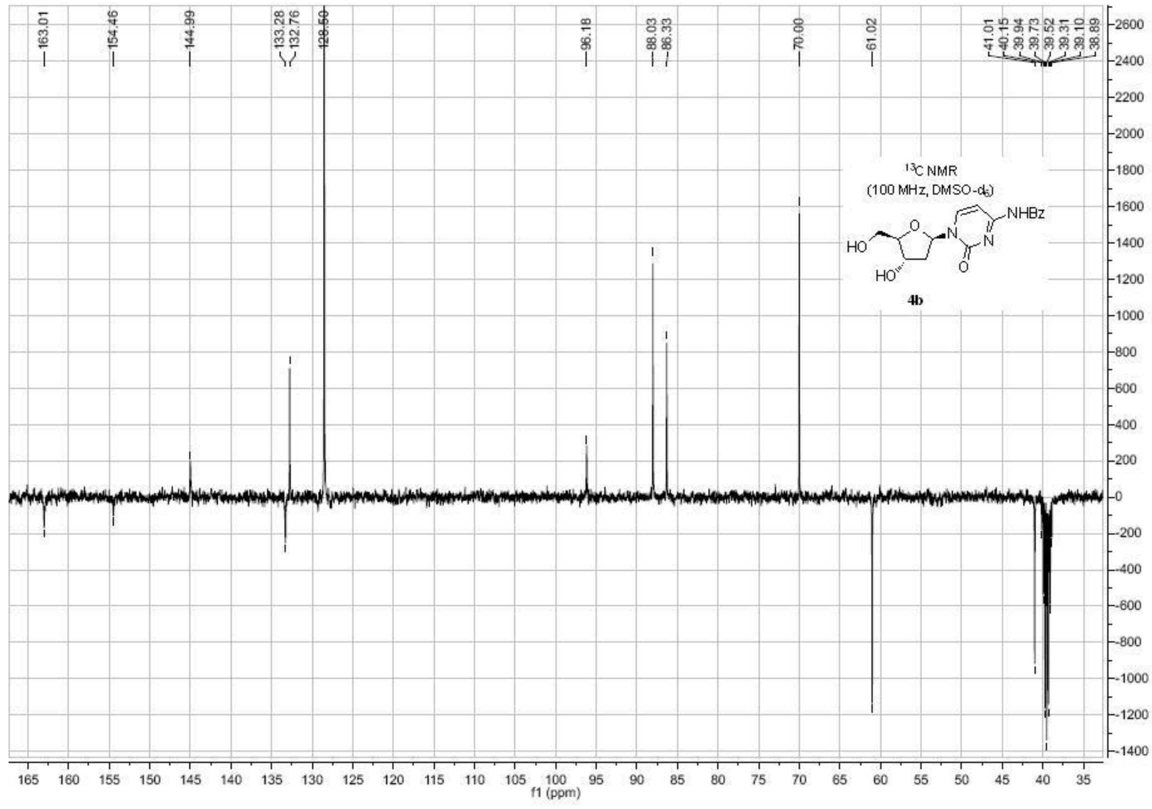
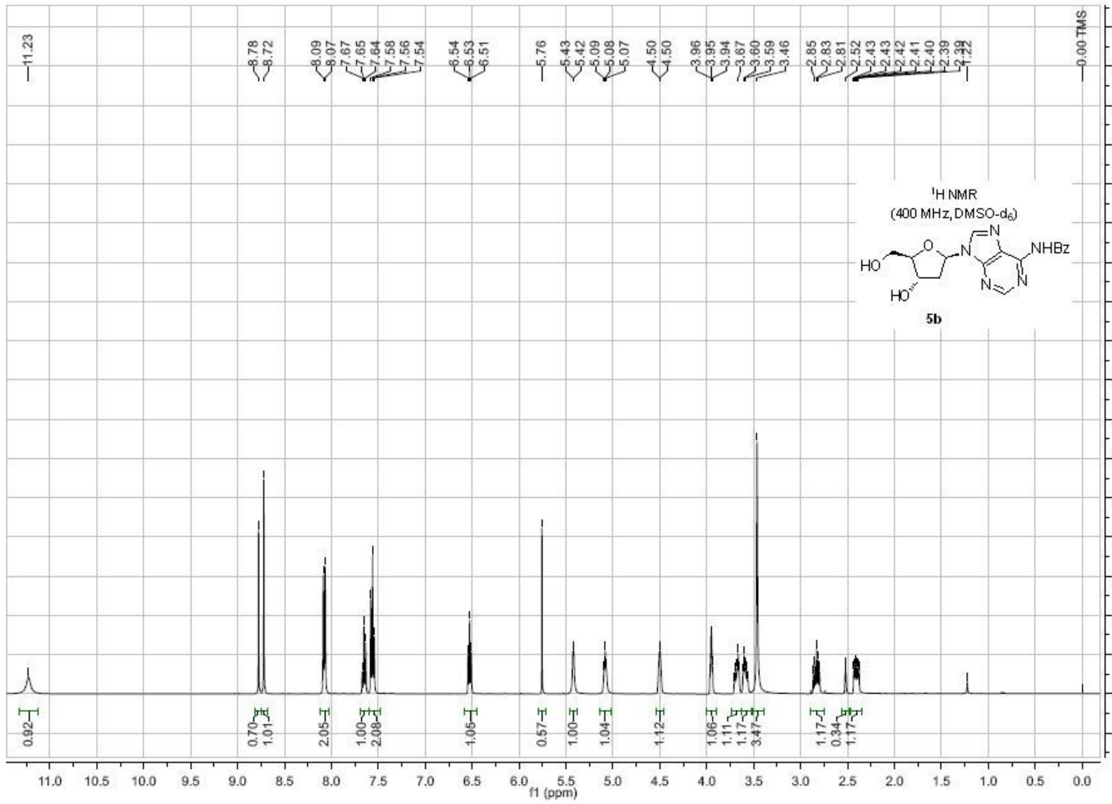
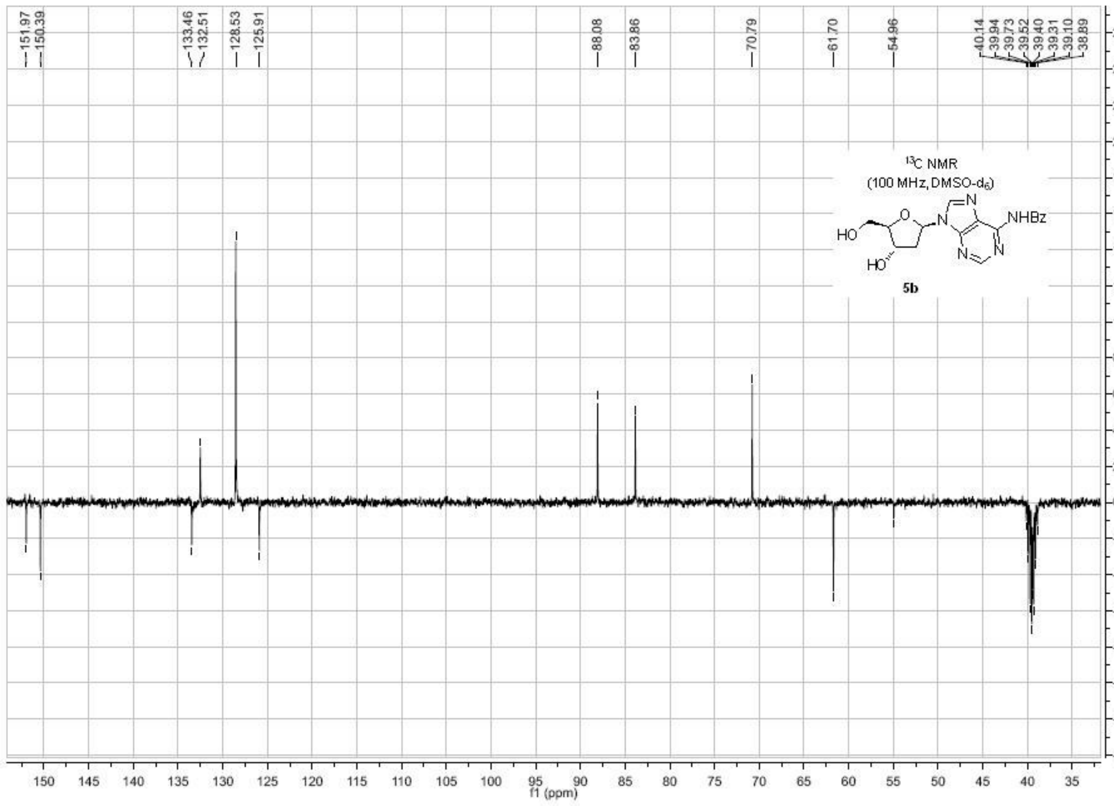
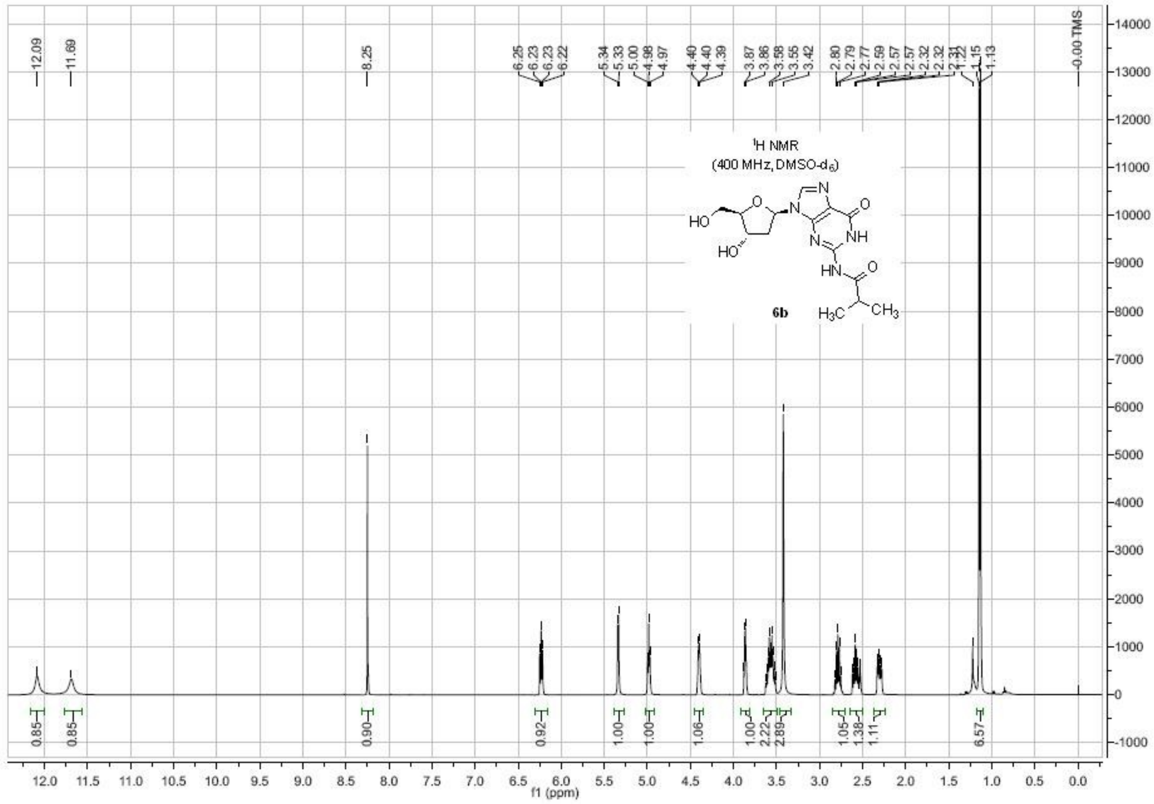
NH$_2$
HO
OH
N
N
3b
f1 (ppm)
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
1000 900 800 700 600 500 400 300 200 100 0 -100 -200 -300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200

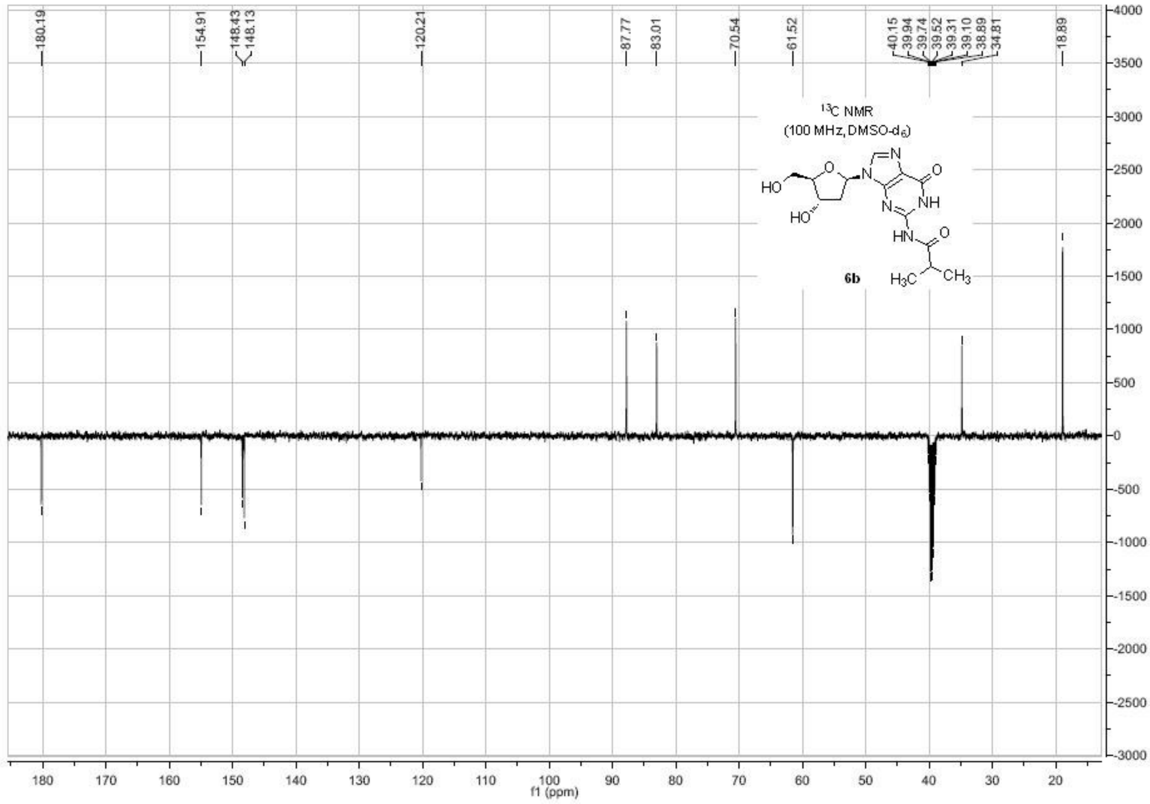

11.23
8.44
8.42
8.04
8.02
7.65
7.63
7.62
7.62
7.61
7.54
7.52
7.51
6.20
6.18
6.16
5.33
5.32
5.13
5.12
5.11
4.30
4.29
4.28
4.27
3.93
3.92
3.67
3.66
3.64
3.63
3.45
2.37
2.36
2.36
2.35
2.34
2.33
2.11
2.10
2.08
1.21
0.00 TMS
^{1}H NMR
(400 MHz, DMSO-d_6)
NHBz
HO
HO
O
N
N
O
4b
0.91
1.00
1.92
0.92
1.93
0.80
0.97
1.04
1.04
1.09
1.06
2.27
2.62
0.24
1.13
1.13
f1 (ppm)

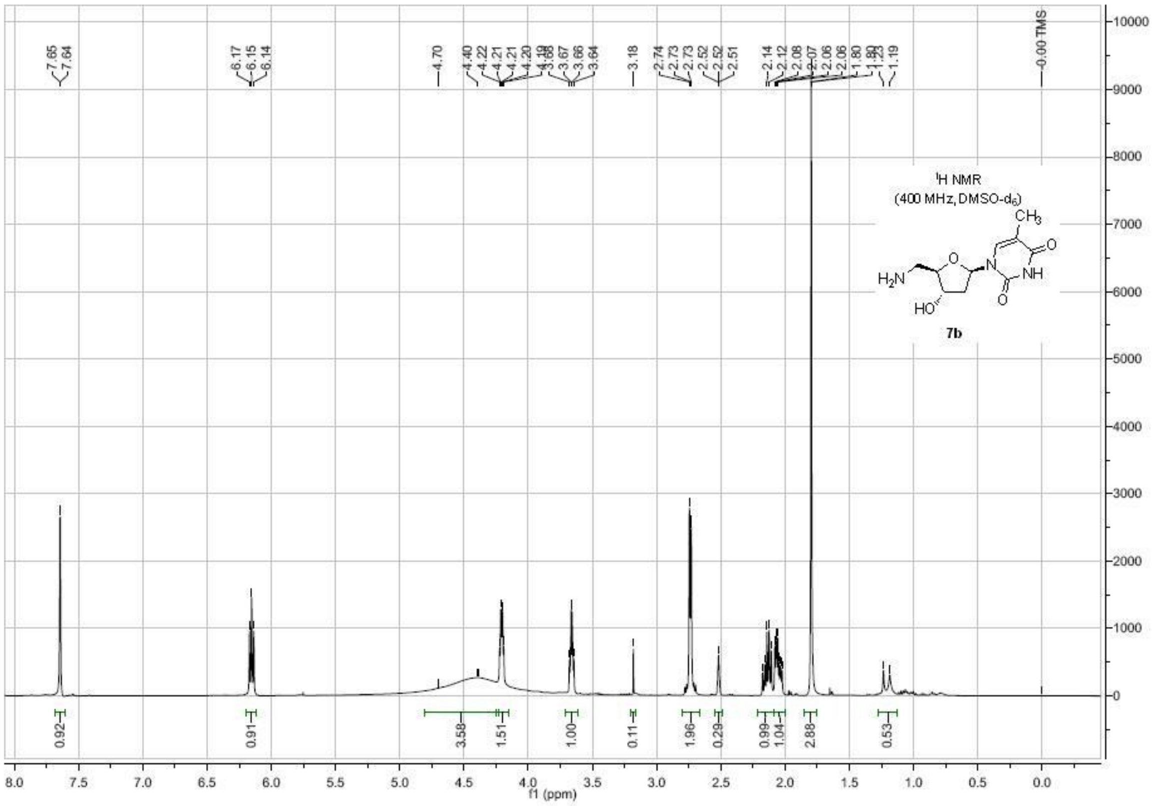

163.01
154.46
144.99
133.28
132.76
128.50
96.18
88.03
86.33
70.00
61.02
41.01
40.15
39.94
39.73
39.52
39.31
39.10
38.89
^{13}C NMR
(100 MHz, DMSO-d_6)
NHBz
HO
HO
O
N
N
O
4b
f1 (ppm)

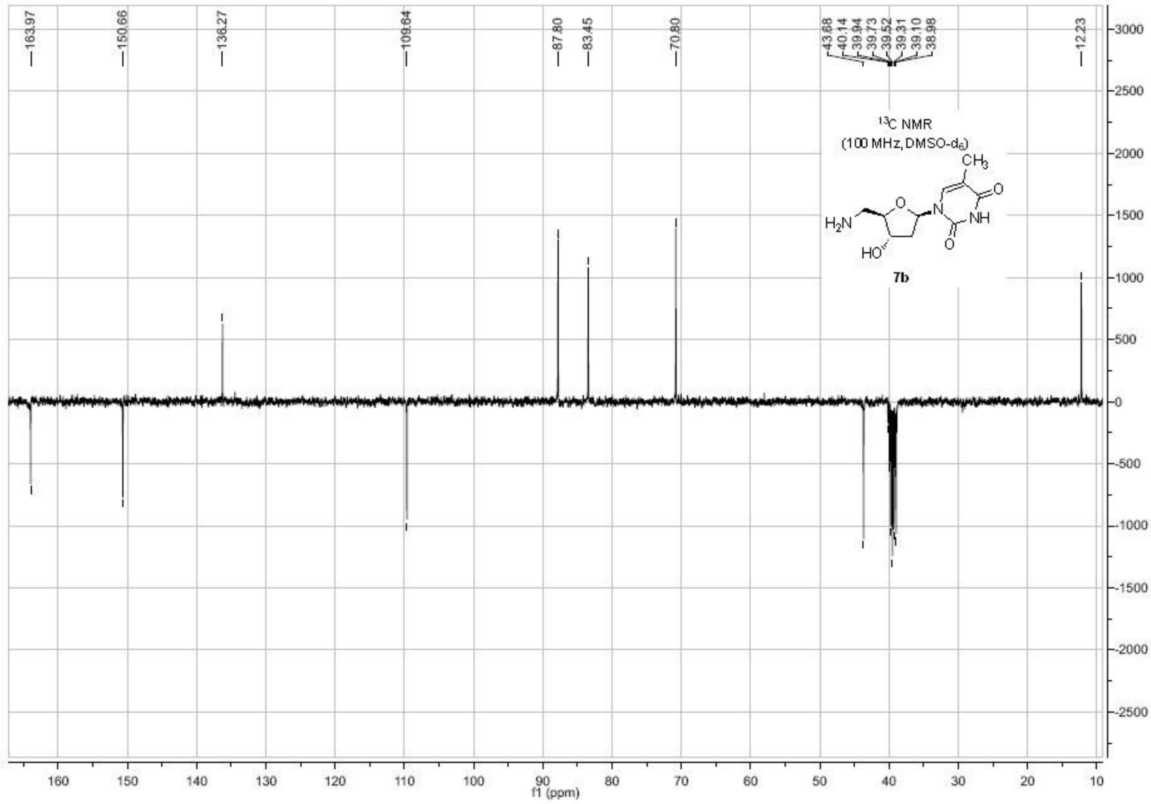

11.23
8.78
8.72
8.09
8.07
7.67
7.65
7.64
7.58
7.56
7.54
6.54
6.53
6.51
5.76
5.43
5.42
5.09
5.08
5.07
4.50
4.50
3.96
3.95
3.94
3.67
3.60
3.59
3.46
2.85
2.83
2.81
2.52
2.43
2.43
2.42
2.41
2.40
2.39
2.39
1.22
0.00 TMS
^{1}H NMR
(400 MHz, DMSO-d$_6$)
HO
HO
NHBz
N
N
N
N
O
5b
0.92
0.70
1.01
2.05
1.00
2.08
1.05
0.57
1.00
1.04
1.12
1.06
1.11
1.17
3.47
1.17
0.34
1.17
f1 (ppm)

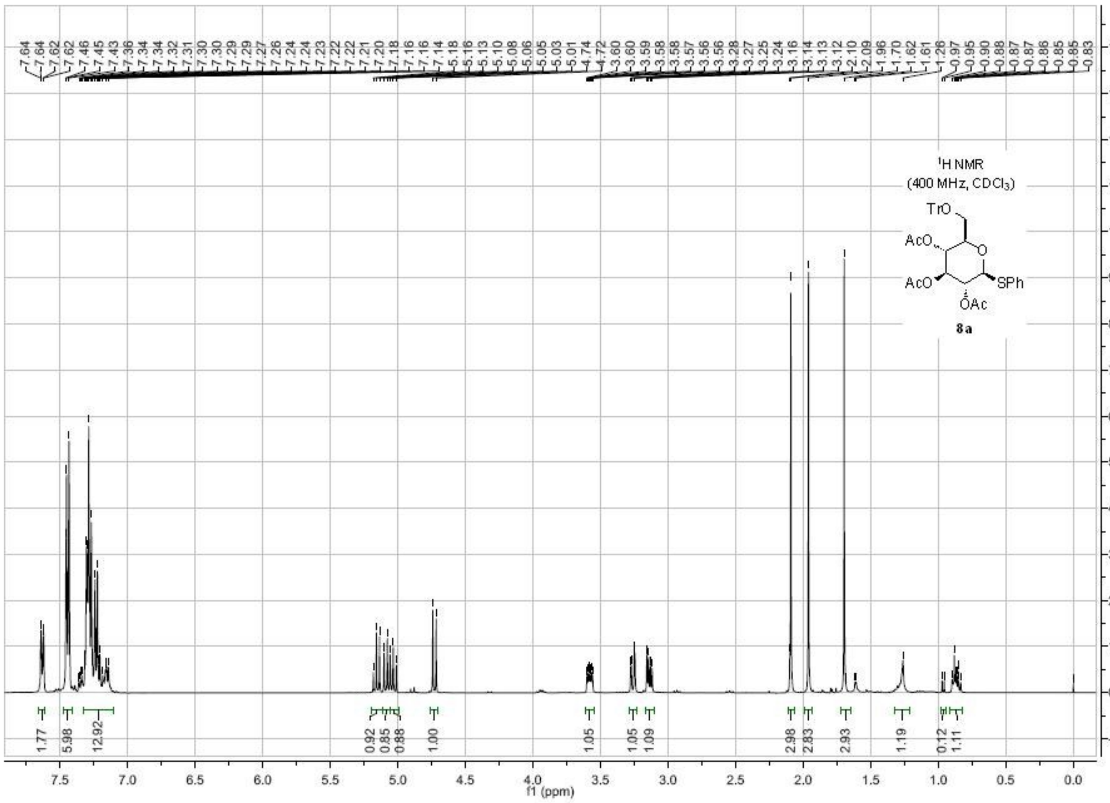

151.97
150.39
133.46
132.51
128.53
125.91
88.08
83.86
70.79
61.70
54.96
40.14
39.94
39.73
39.52
39.40
39.31
39.10
38.89
^{13}C NMR
(100 MHz, DMSO-d$_6$)
HO
HO
NHBz
N
N
N
N
O
5b
f1 (ppm)

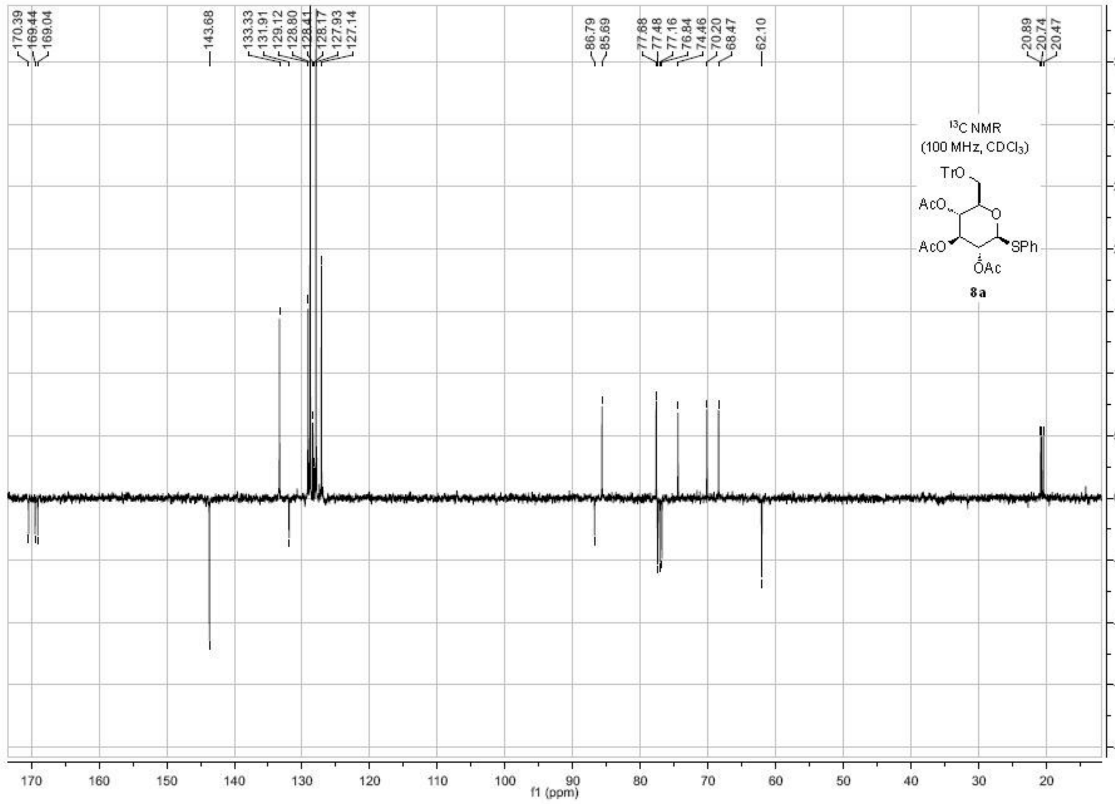

12.09
11.69
8.25
6.25
6.23
6.23
6.22
5.34
5.33
5.00
4.98
4.97
4.40
4.40
4.39
3.87
3.86
3.58
3.55
3.42
2.80
2.79
2.77
2.59
2.57
2.57
2.32
2.32
2.31
1.22
1.15
1.13
0.00 TMS
¹H NMR
(400 MHz, DMSO-d6)
HO
O
N
N
O
NH
HO
N
HN
O
6b
H3C
CH3
0.85
0.85
0.90
0.92
1.00
1.00
1.06
1.00
2.22
2.89
1.05
1.38
1.11
6.57
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

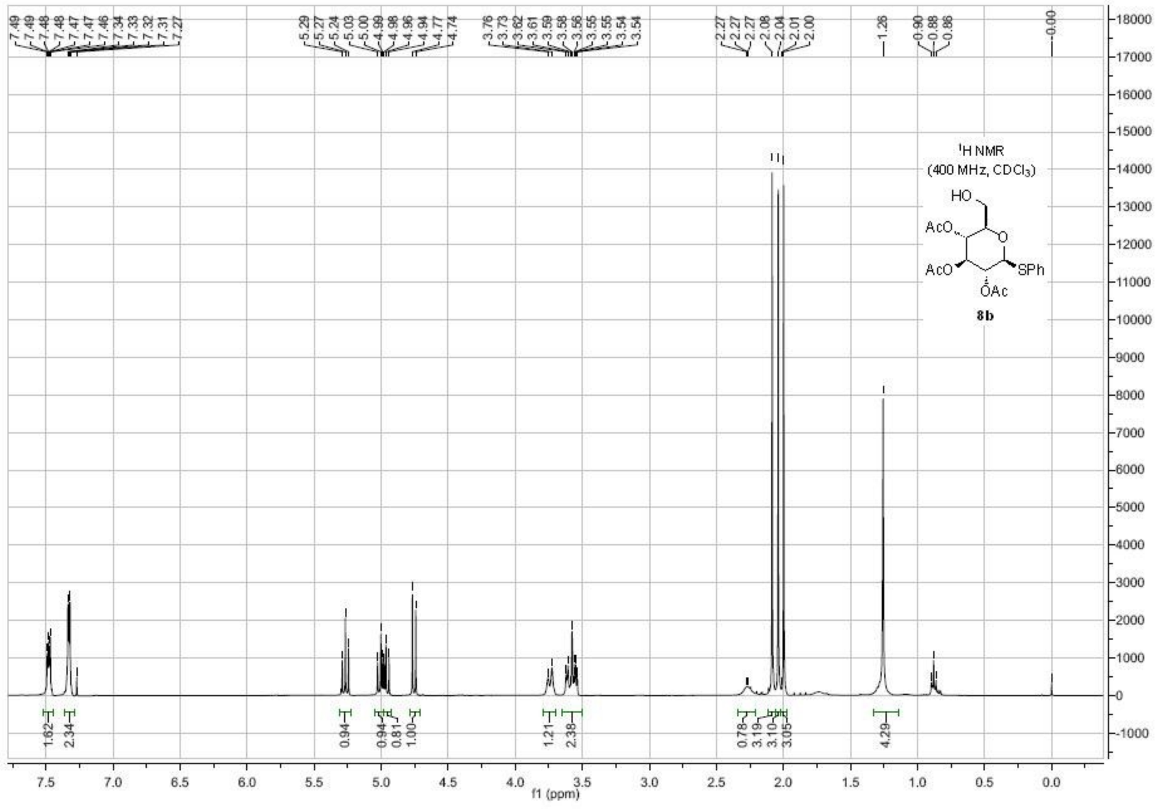

180.19
154.91
148.43
148.13
120.21
87.77
83.01
70.54
61.52
40.15
39.94
39.74
39.52
39.31
39.10
38.89
34.81
18.89
¹³C NMR
(100 MHz, DMSO-d6)
HO
O
N
N
O
NH
HO
N
HN
O
6b
H3C
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
-3000

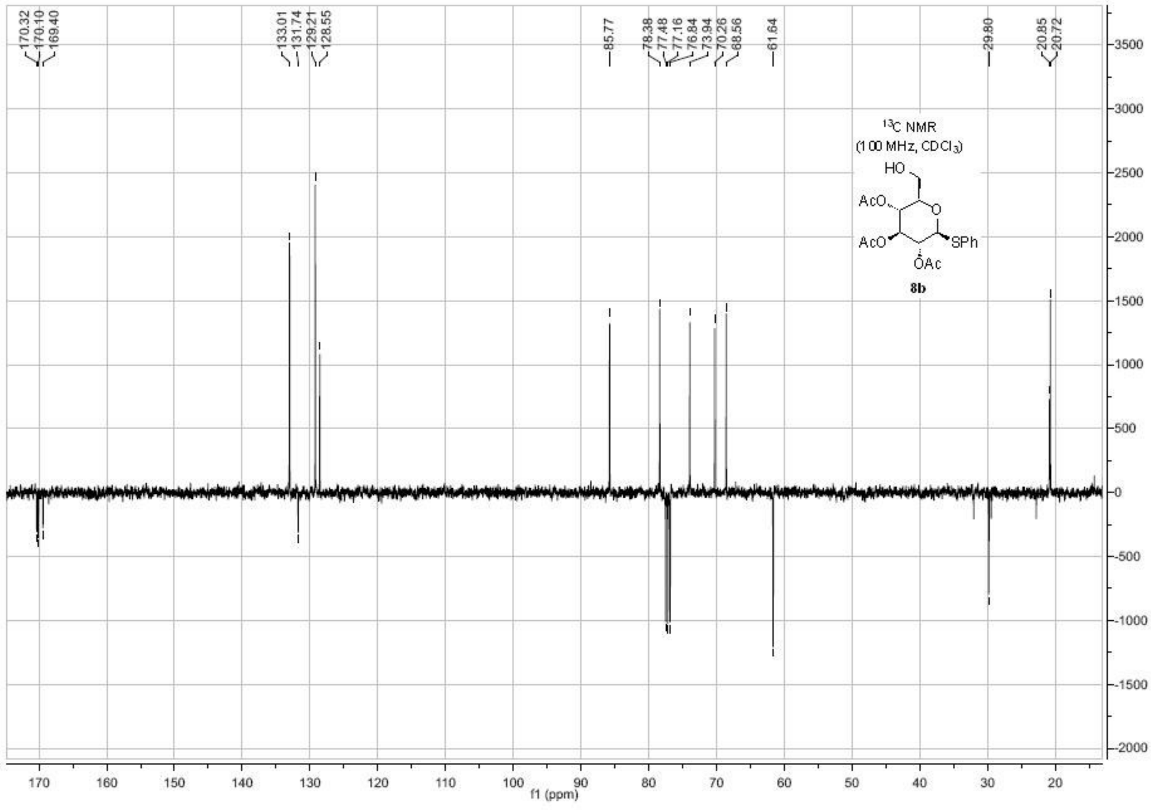

7.65
7.64
6.17
6.15
6.14
4.70
4.40
4.22
4.21
4.21
4.20
4.19
3.68
3.67
3.66
3.64
3.18
2.74
2.73
2.73
2.52
2.52
2.51
2.14
2.12
2.08
2.07
2.06
2.06
1.80
1.80
1.23
1.19
0.00 TMS
¹H NMR
(400 MHz, DMSO-d6)
CH3
O
H2N
N
O
NH
HO
O
7b
0.92
0.91
3.58
1.51
1.00
0.11
1.96
0.29
0.99
1.04
2.88
0.53
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

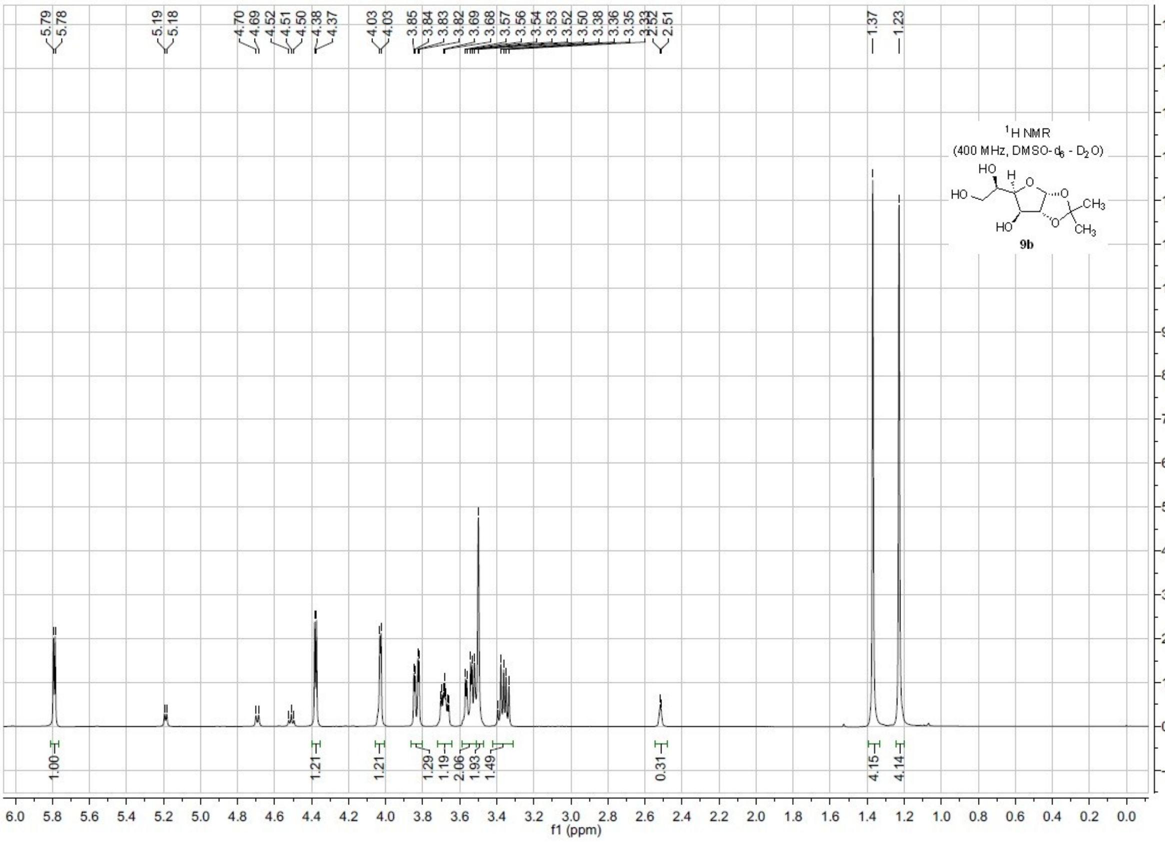

163.97
150.66
136.27
109.64
87.80
83.45
70.80
43.68
40.14
39.94
39.73
39.52
39.31
39.10
38.98
12.23
¹³C NMR
(100 MHz, DMSO-d6)
CH3
O
H2N
N
O
NH
HO
O
7b
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500

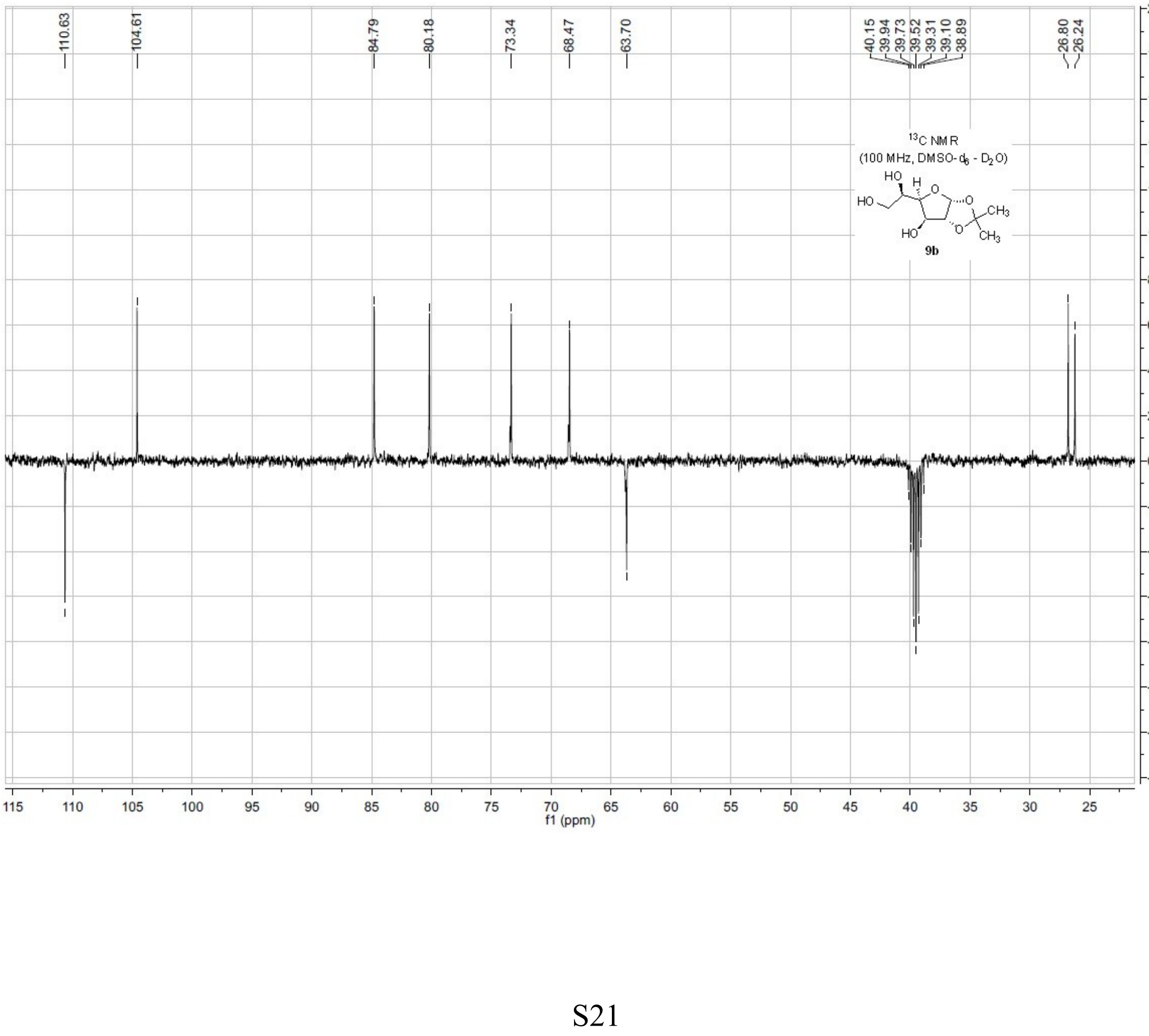

7.64 7.64 7.62 7.46 7.45 7.43 7.36 7.34 7.32 7.31 7.30 7.30 7.29 7.27 7.26 7.24 7.24 7.23 7.22 7.21 7.20 7.18 7.16 7.14 5.18 5.16 5.13 5.10 5.08 5.06 5.05 5.03 5.01 4.74 4.72 3.60 3.59 3.58 3.58 3.57 3.56 3.56 3.28 3.27 3.25 3.24 3.16 3.14 3.13 3.12 2.10 2.09 1.96 1.70 1.62 1.61 1.26 0.97 0.95 0.90 0.88 0.87 0.86 0.85 0.85 0.83
1H NMR
(400 MHz, CDCl3)
TrO
AcO
AcO
O
SPh
OAc
8a
1.77 5.98 12.92 0.92 0.85 0.88 1.00 1.05 1.05 1.09 2.98 2.83 2.93 1.19 0.12 1.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

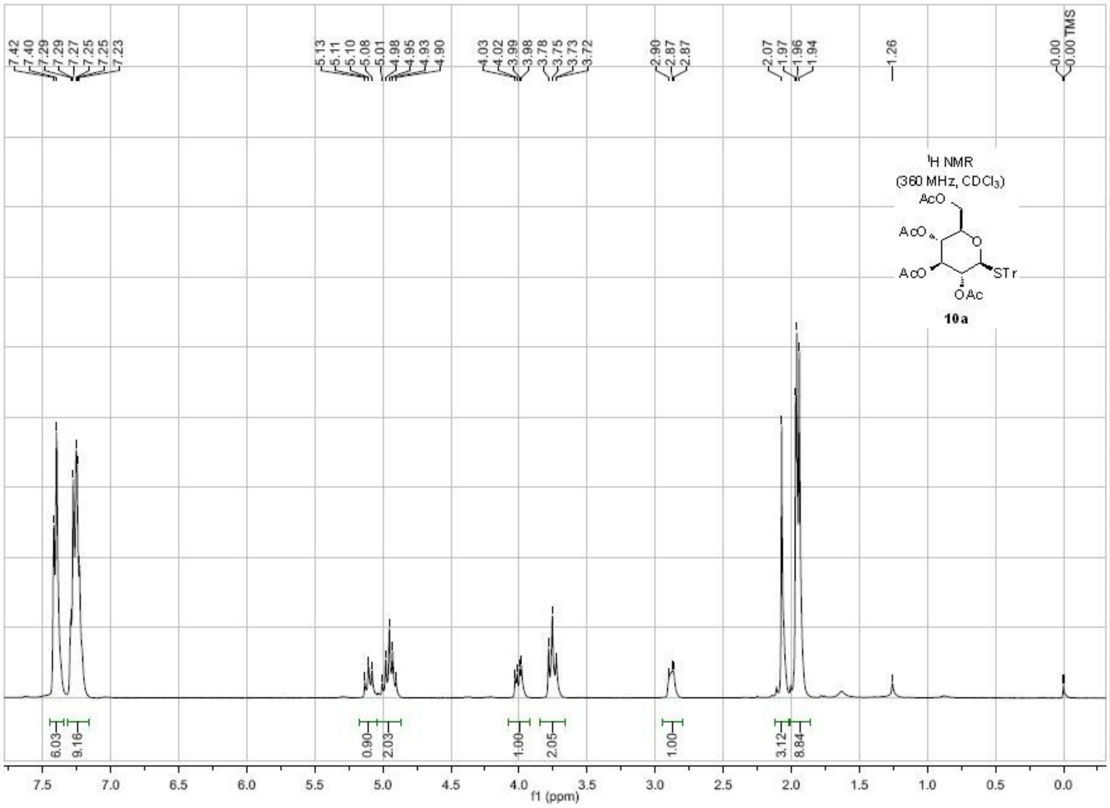

170.39 169.44 169.04 143.68 133.33 131.91 129.12 128.80 128.41 128.17 127.93 127.14 86.79 85.69 77.68 77.48 77.16 76.84 74.46 70.20 68.47 62.10 20.89 20.74 20.47
13C NMR
(100 MHz, CDCl3)
TrO
AcO
AcO
O
SPh
OAc
8a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)
3500 3000 2500 2000 1500 1000 500 0 -500 -1000 -1500 -2000

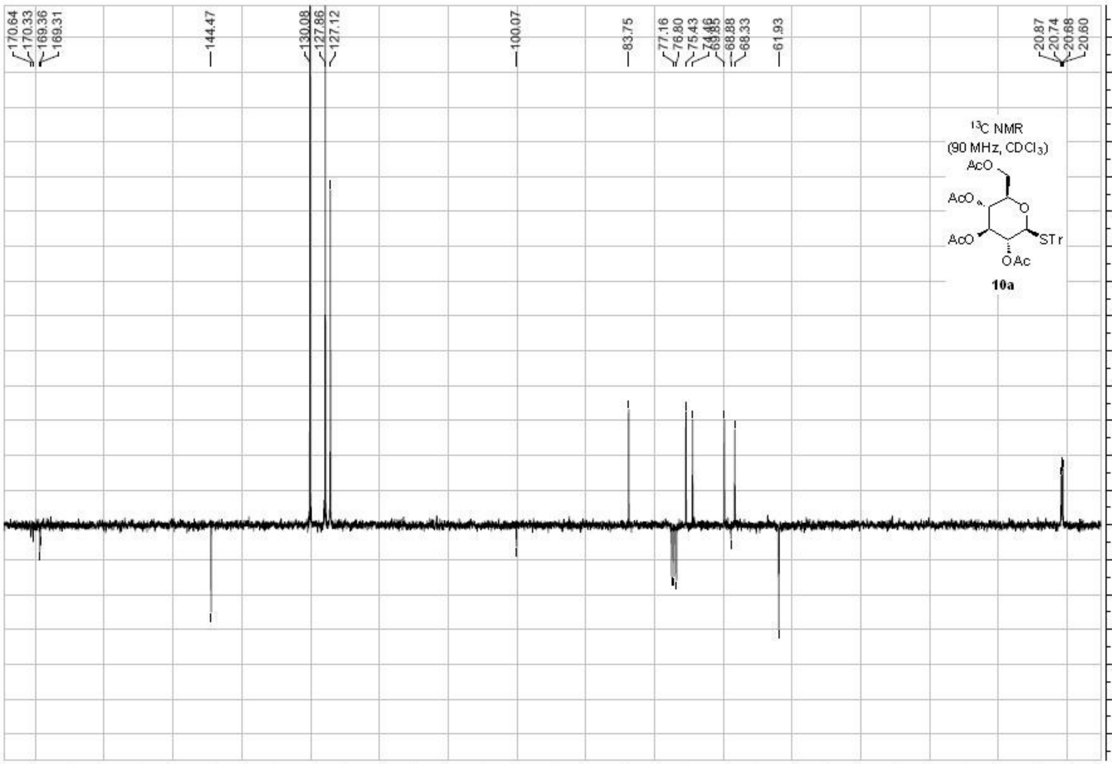

7.49
7.49
7.48
7.47
7.47
7.46
7.34
7.33
7.32
7.31
7.27
5.29
5.27
5.24
5.03
5.00
4.99
4.98
4.96
4.94
4.77
4.74
3.76
3.73
3.62
3.61
3.59
3.58
3.56
3.55
3.55
3.54
3.54
2.27
2.27
2.27
2.08
2.04
2.01
2.00
1.26
0.90
0.88
0.86
0.00
1H NMR
(400 MHz, CDCl3)
HO
AcO
AcO
O
SPh
OAc
8b
1.62
2.34
0.94
0.94
0.81
1.00
1.21
2.38
0.78
3.19
3.10
3.05
4.29
f1 (ppm)

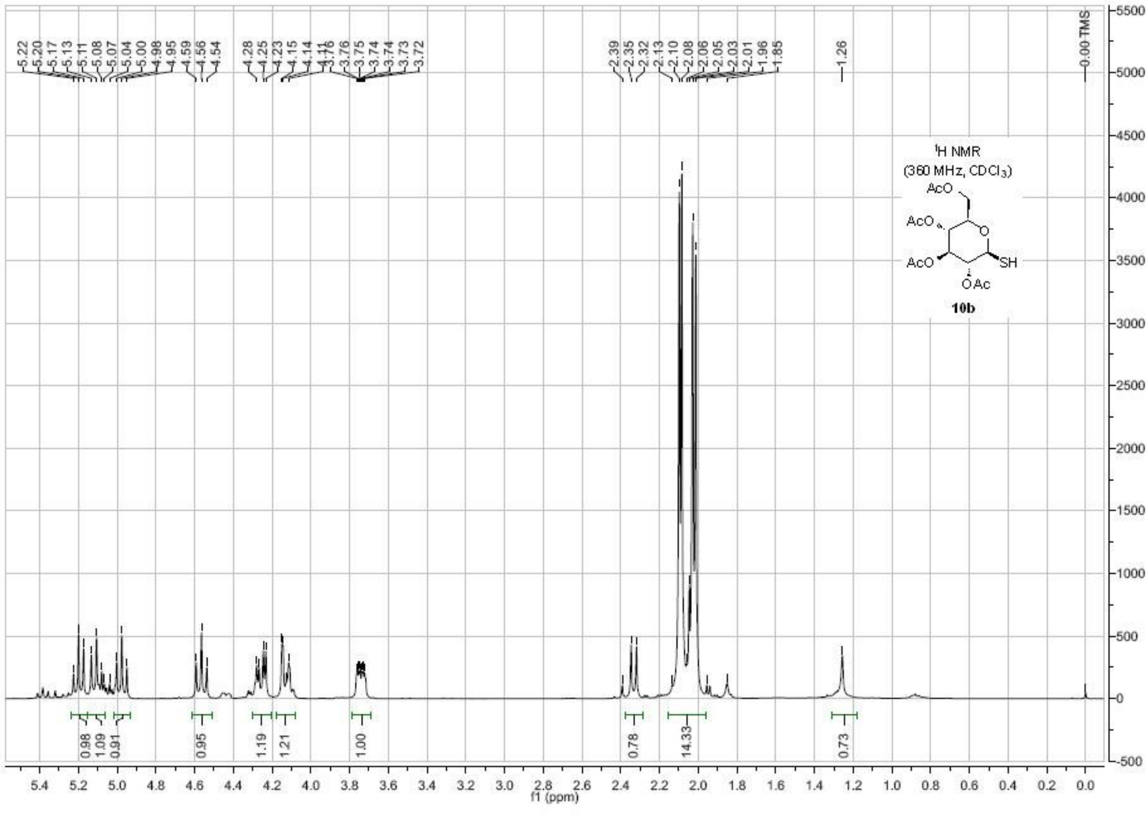

170.32
170.10
169.40
133.01
131.74
129.21
128.55
85.77
78.38
77.48
77.16
76.84
73.94
70.26
68.56
61.64
29.80
20.85
20.72
13C NMR
(100 MHz, CDCl3)
HO
AcO
AcO
O
SPh
OAc
8b
f1 (ppm)

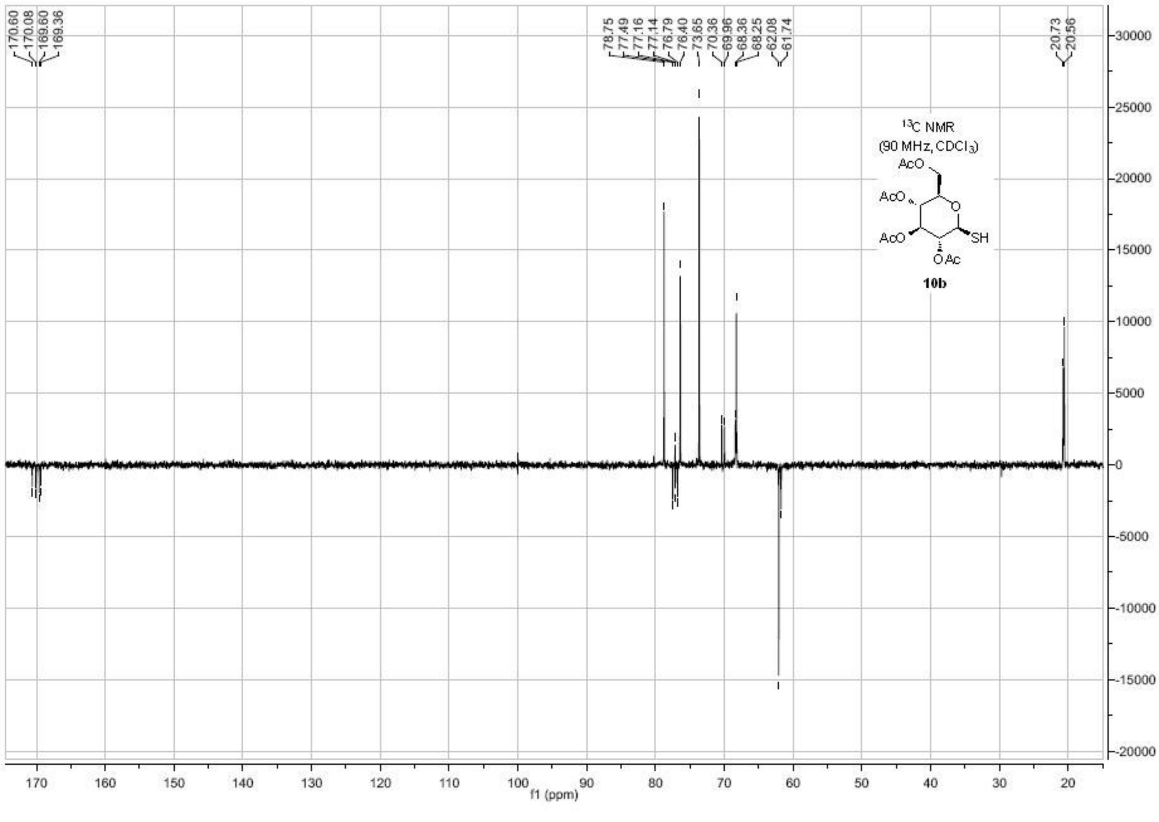

5.79
5.78
5.19
5.18
4.70
4.69
4.52
4.51
4.50
4.38
4.37
4.03
4.03
3.85
3.84
3.83
3.82
3.69
3.68
3.57
3.56
3.54
3.53
3.52
3.50
3.38
3.36
3.35
3.33
2.52
2.51
1.37
1.23
¹H NMR
(400 MHz, DMSO-d6 - D2O)
HO
H
HO
O
O
CH3
HO
O
CH3
9b
1.00
1.21
1.21
1.29
1.19
2.06
1.93
1.49
0.31
4.15
4.14
f1 (ppm)

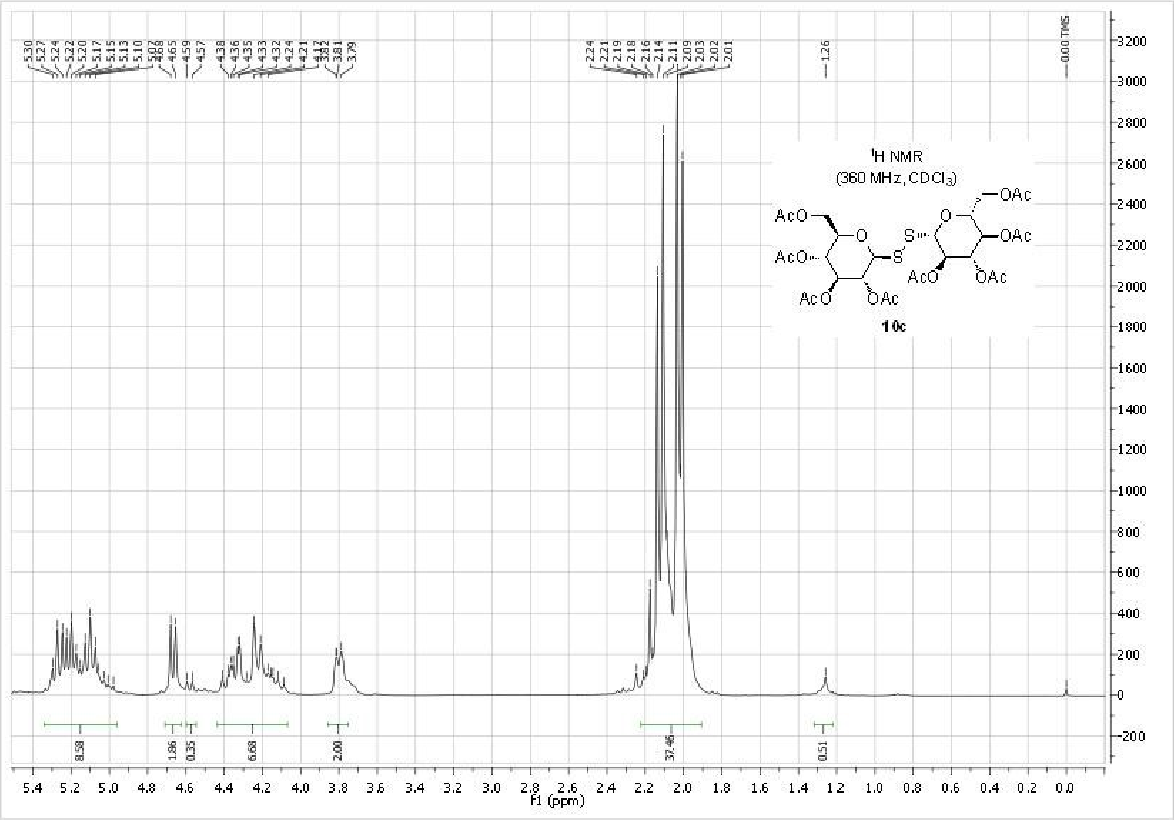

110.63
104.61
84.79
80.18
73.34
68.47
63.70
40.15
39.94
39.73
39.52
39.31
39.10
38.89
26.80
26.24
¹³C NMR
(100 MHz, DMSO-d6 - D2O)
HO
H
HO
O
O
CH3
HO
O
CH3
9b
f1 (ppm)

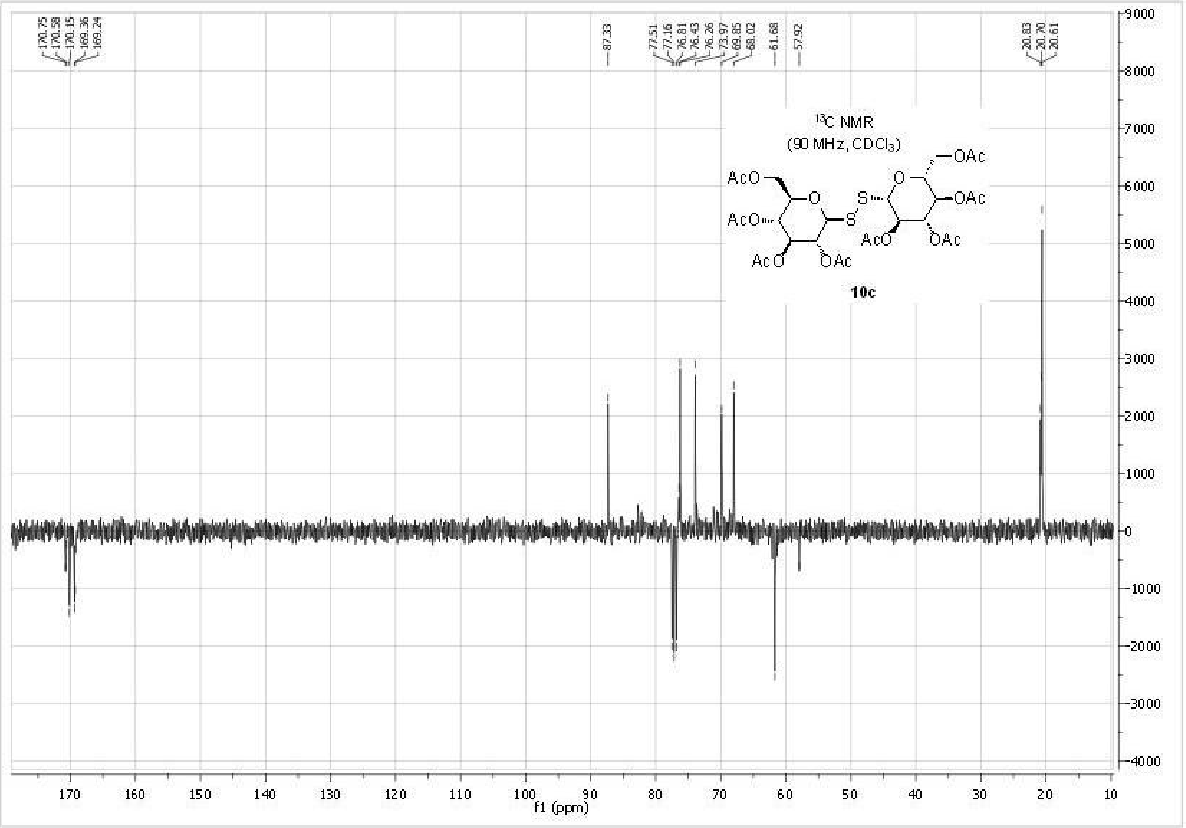

7.42
7.40
7.29
7.29
7.27
7.25
7.25
7.23
5.13
5.11
5.10
5.08
5.01
4.98
4.95
4.93
4.90
4.03
4.02
3.99
3.98
3.78
3.75
3.73
3.72
2.90
2.87
2.87
2.07
1.97
1.96
1.94
1.26
0.00
0.00 TMS
^{1}H NMR
(360 MHz, CDCl$_3$)
AcO
AcO
AcO
O
STr
OAc
10a
6.03
9.16
0.90
2.03
1.00
2.05
1.00
3.12
8.84
4500
4000
3500
3000
2500
2000
1500
1000
500
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

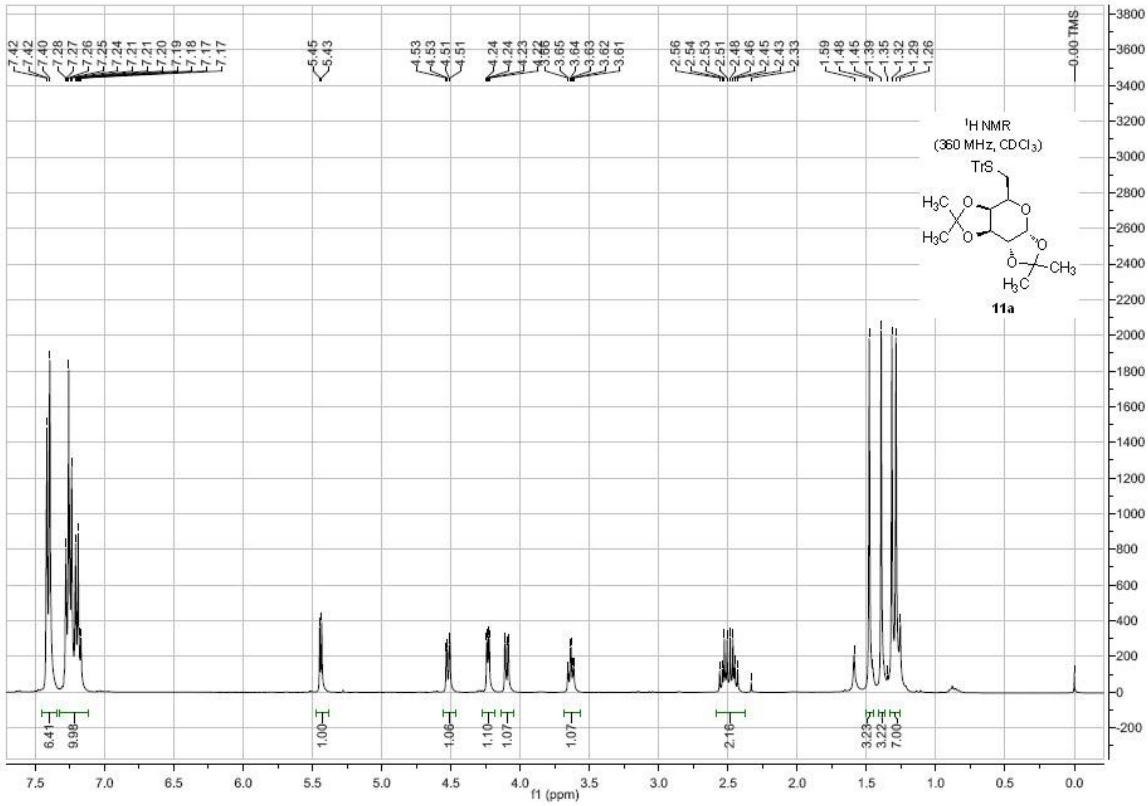

170.64
170.33
169.36
169.31
144.47
130.08
127.86
127.12
100.07
83.75
77.16
76.80
75.43
74.46
69.85
68.88
68.33
61.93
20.87
20.74
20.68
20.60
^{13}C NMR
(90 MHz, CDCl$_3$)
AcO
AcO
AcO
O
STr
OAc
10a
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
-6000
-8000
-10000
-12000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

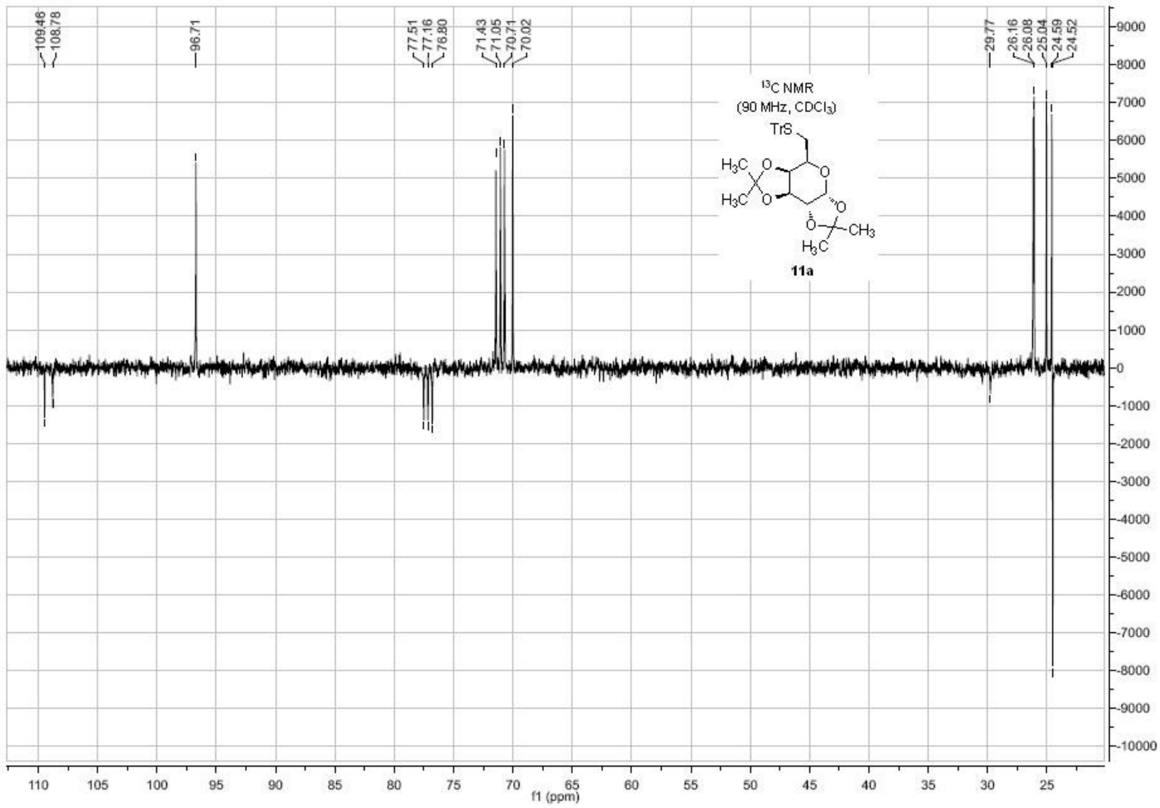

5.22
5.20
5.17
5.13
5.11
5.08
5.07
5.04
5.00
4.98
4.95
4.59
4.56
4.54
4.28
4.25
4.23
4.15
4.14
4.11
3.76
3.75
3.74
3.74
3.73
3.72
2.39
2.35
2.32
2.13
2.10
2.08
2.06
2.05
2.03
2.01
1.96
1.85
1.26
0.00 TMS
^{1}H NMR
(360 MHz, CDCl$_3$)
AcO
AcO
AcO
O
SH
OAc
10b
0.98
1.09
0.91
0.95
1.19
1.21
1.00
0.78
14.33
0.73
f1 (ppm)

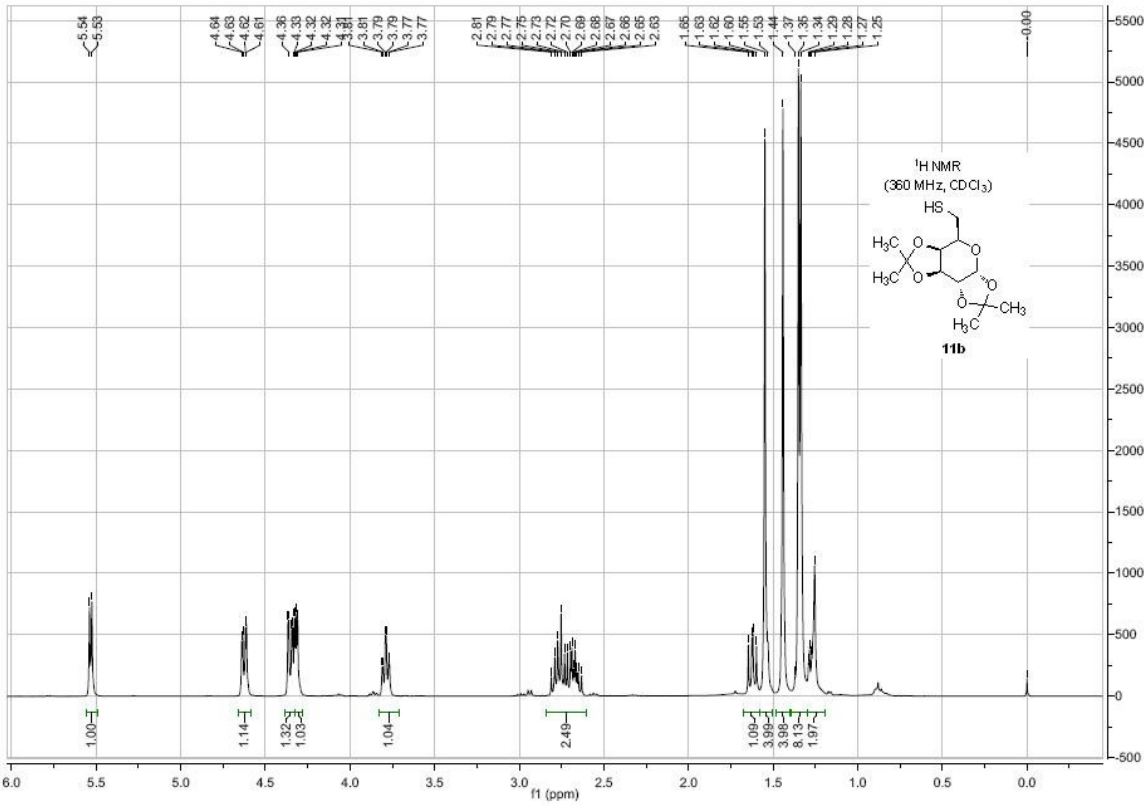

170.60
170.08
169.60
169.36
78.75
77.49
77.16
77.14
76.79
76.40
73.65
70.36
69.96
68.36
68.25
62.08
61.74
20.73
20.56
^{13}C NMR
(90 MHz, CDCl$_3$)
AcO
AcO
AcO
O
SH
OAc
10b
f1 (ppm)

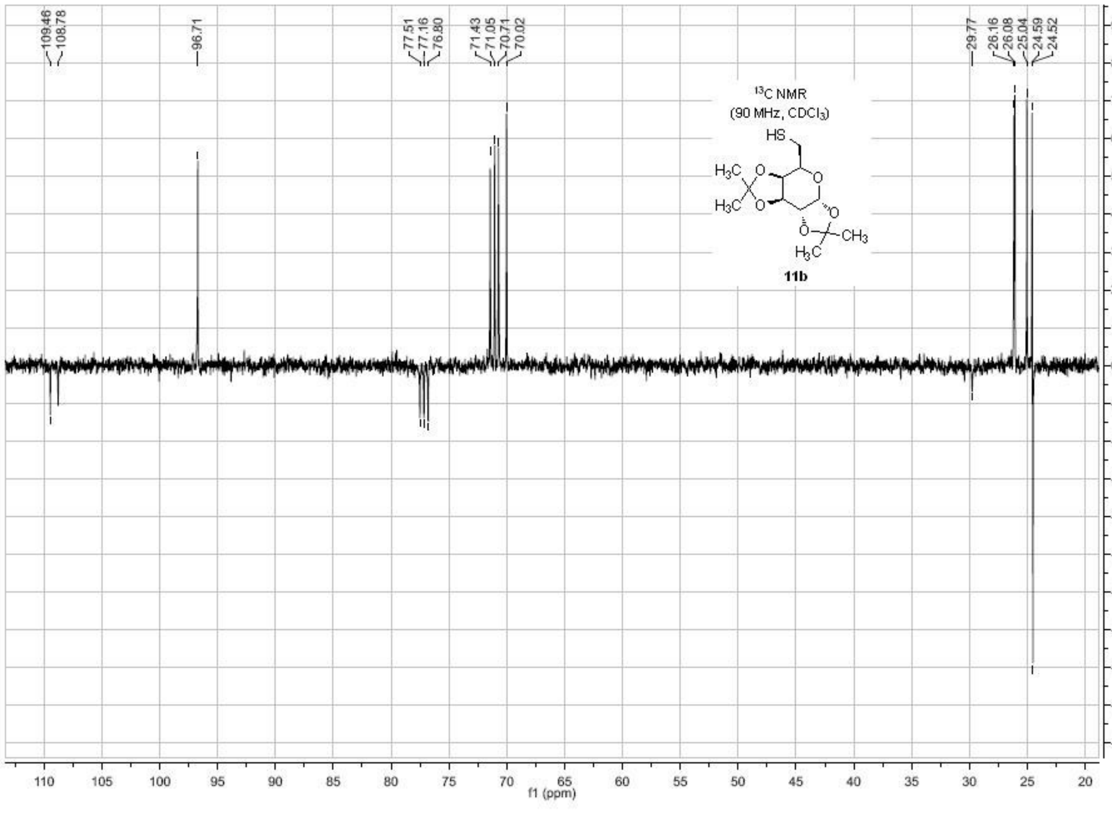

5.30
5.27
5.24
5.22
5.20
5.17
5.15
5.13
5.10
5.07
4.68
4.65
4.59
4.57
4.38
4.36
4.35
4.33
4.32
4.24
4.21
3.82
3.81
3.79
2.24
2.21
2.19
2.18
2.16
2.14
2.11
2.09
2.03
2.02
2.01
1.26
0.00 TMS
^{1}H NMR
(360 MHz, CDCl$_3$)
AcO
AcO
AcO
OAc
S
S
O
O
OAc
OAc
OAc
AcO
10c
8.58
1.86
0.35
6.68
2.00
37.46
0.51
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f1 (ppm)
3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

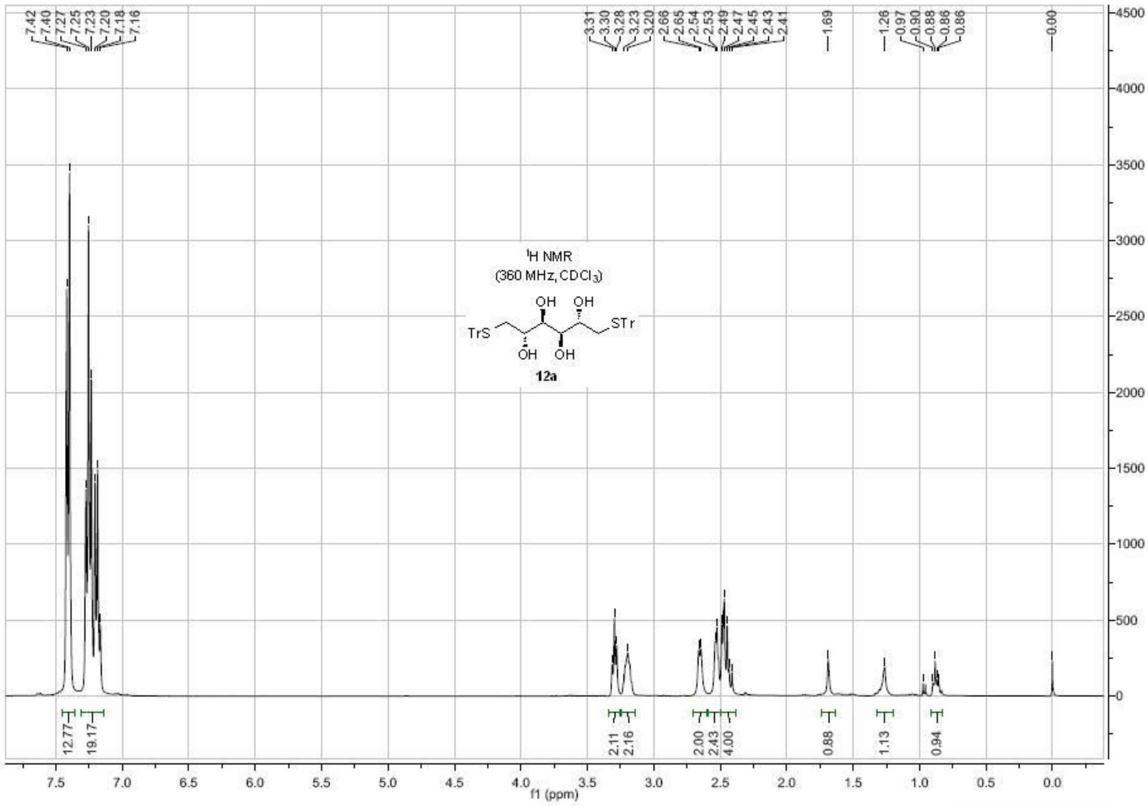

170.75
170.58
170.15
169.36
169.24
87.33
77.51
77.16
76.81
76.43
76.26
73.97
69.85
68.02
61.68
57.92
20.83
20.70
20.61
^{13}C NMR
(90 MHz, CDCl$_3$)
AcO
AcO
AcO
OAc
S
S
O
O
OAc
OAc
OAc
AcO
10c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000 -3000 -4000

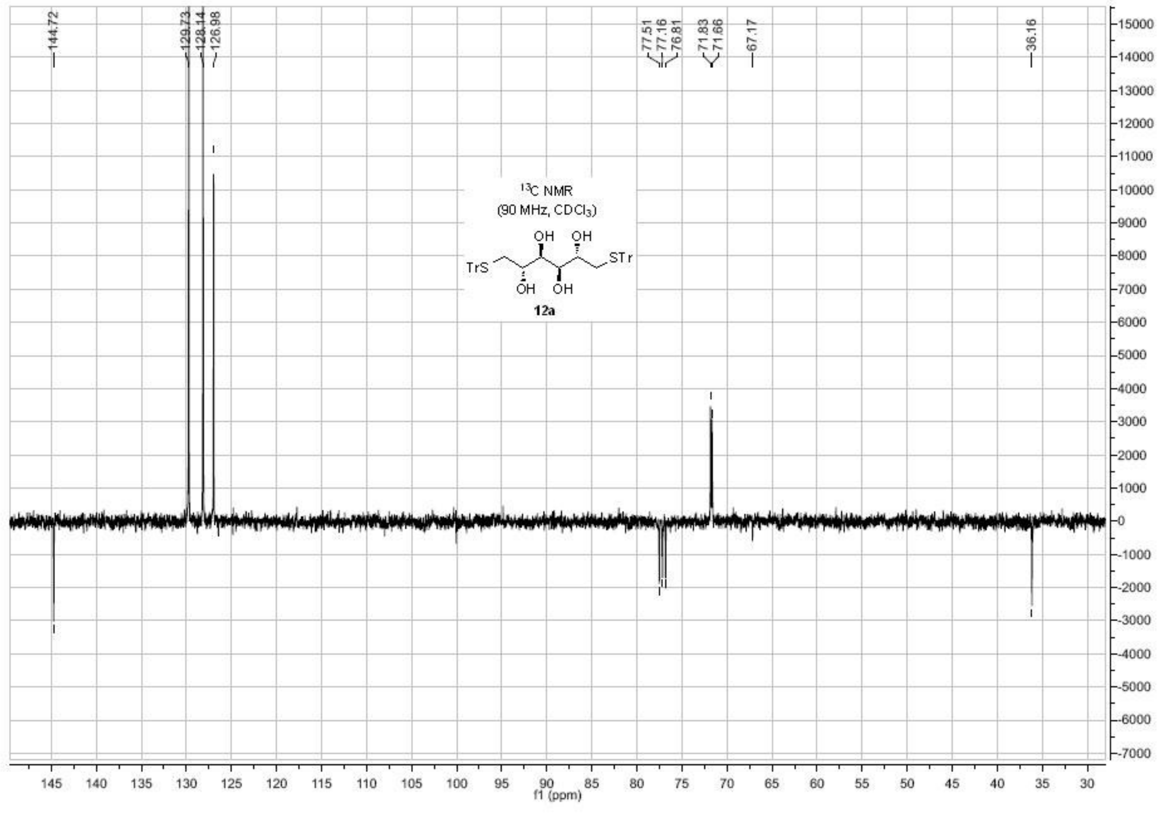

7.42
7.42
7.40
7.28
7.27
7.26
7.25
7.24
7.21
7.21
7.20
7.19
7.18
7.17
7.17
5.45
5.43
4.53
4.53
4.51
4.51
4.24
4.24
4.23
4.23
4.22
3.66
3.65
3.64
3.63
3.62
3.61
2.56
2.54
2.53
2.51
2.48
2.46
2.45
2.43
2.33
1.59
1.48
1.45
1.39
1.35
1.32
1.29
1.26
0.00 TMS
^{1}H NMR
(360 MHz, CDCl$_3$)
TrS
H$_3$C
H$_3$C
O
O
O
O
O
CH$_3$
H$_3$C
11a
6.41
9.98
1.00
1.06
1.10
1.07
1.07
2.16
3.23
3.22
7.00
f1 (ppm)

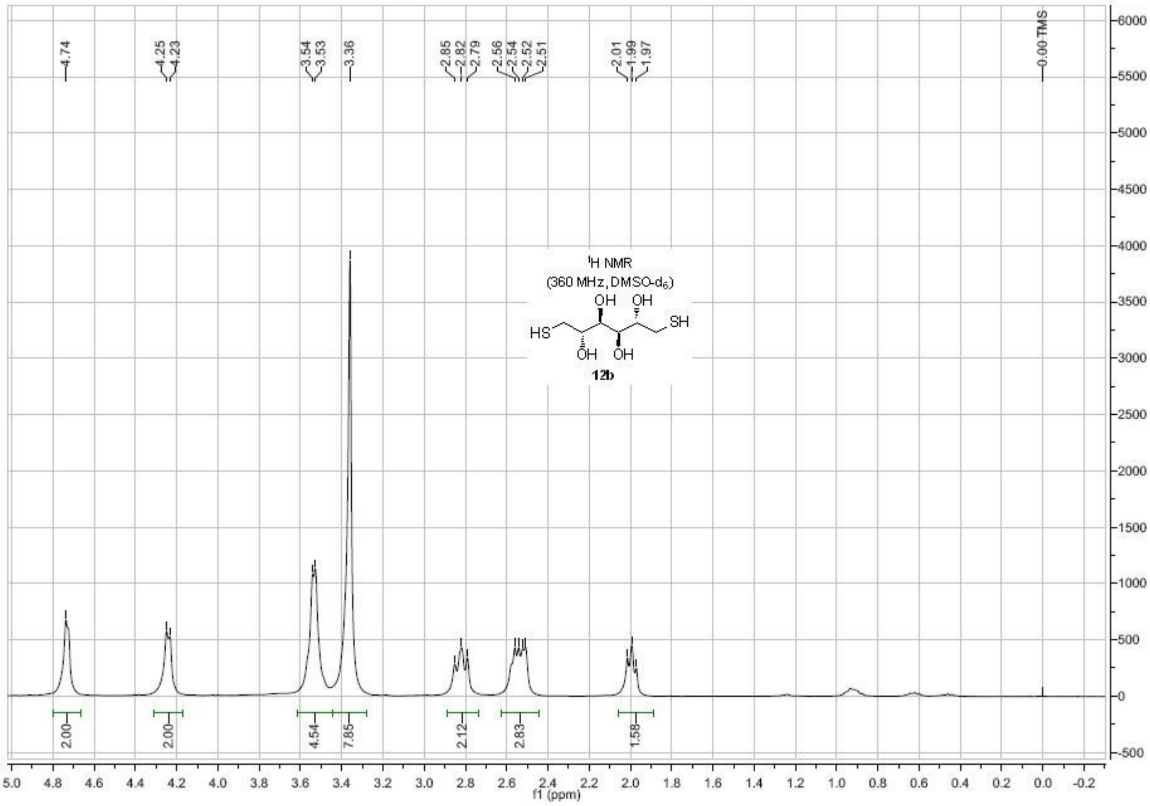

109.46
108.78
96.71
77.51
77.16
76.80
71.43
71.05
70.71
70.02
29.77
26.16
26.08
25.04
24.59
24.52
^{13}C NMR
(90 MHz, CDCl$_3$)
TrS
H$_3$C
H$_3$C
O
O
O
O
O
CH$_3$
H$_3$C
11a
f1 (ppm)

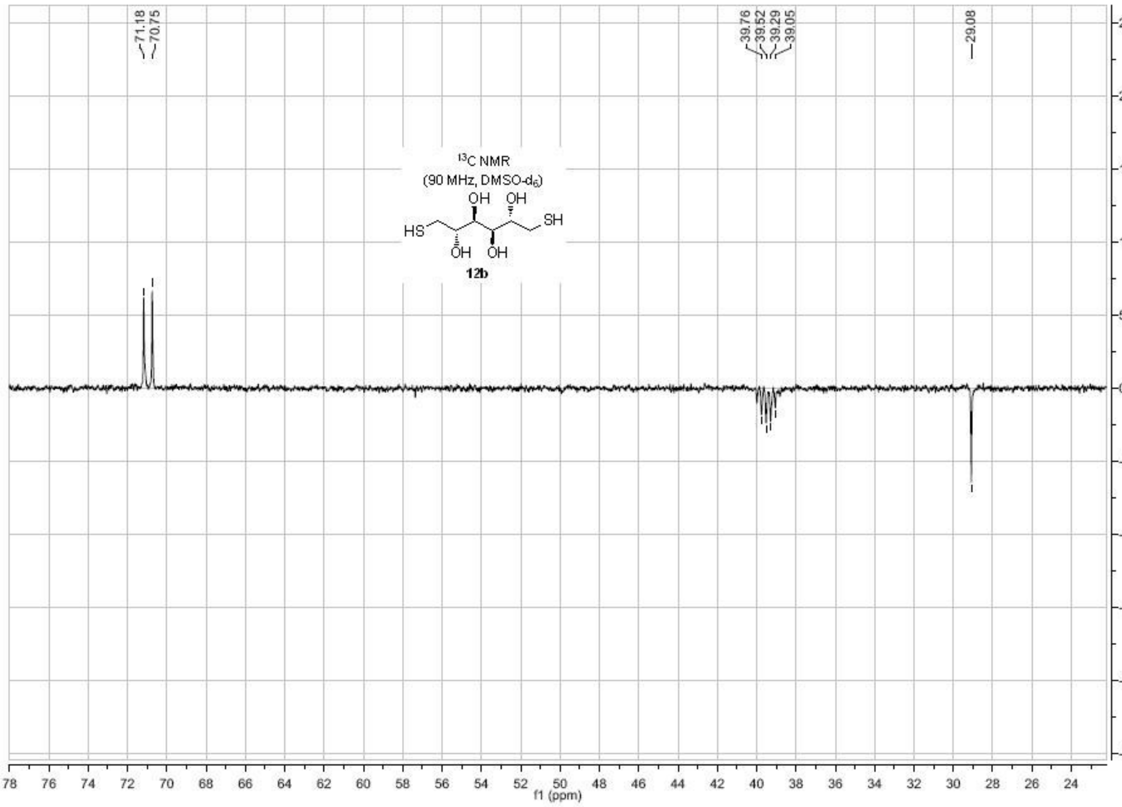

5.54
5.53
4.64
4.63
4.62
4.61
4.36
4.33
4.32
4.32
4.31
4.31
3.81
3.79
3.79
3.77
3.77
2.81
2.79
2.77
2.75
2.73
2.72
2.70
2.69
2.68
2.67
2.66
2.65
2.63
1.65
1.63
1.62
1.60
1.55
1.53
1.44
1.37
1.35
1.34
1.29
1.28
1.27
1.25
0.00
1.00
1.14
1.32
1.03
1.04
2.49
1.09
3.99
3.98
8.13
1.97
^{1}H NMR
(360 MHz, CDCl$_3$)
HS
H$_3$C
H$_3$C
O
O
O
O
O
CH$_3$
H$_3$C
11b
f1 (ppm)

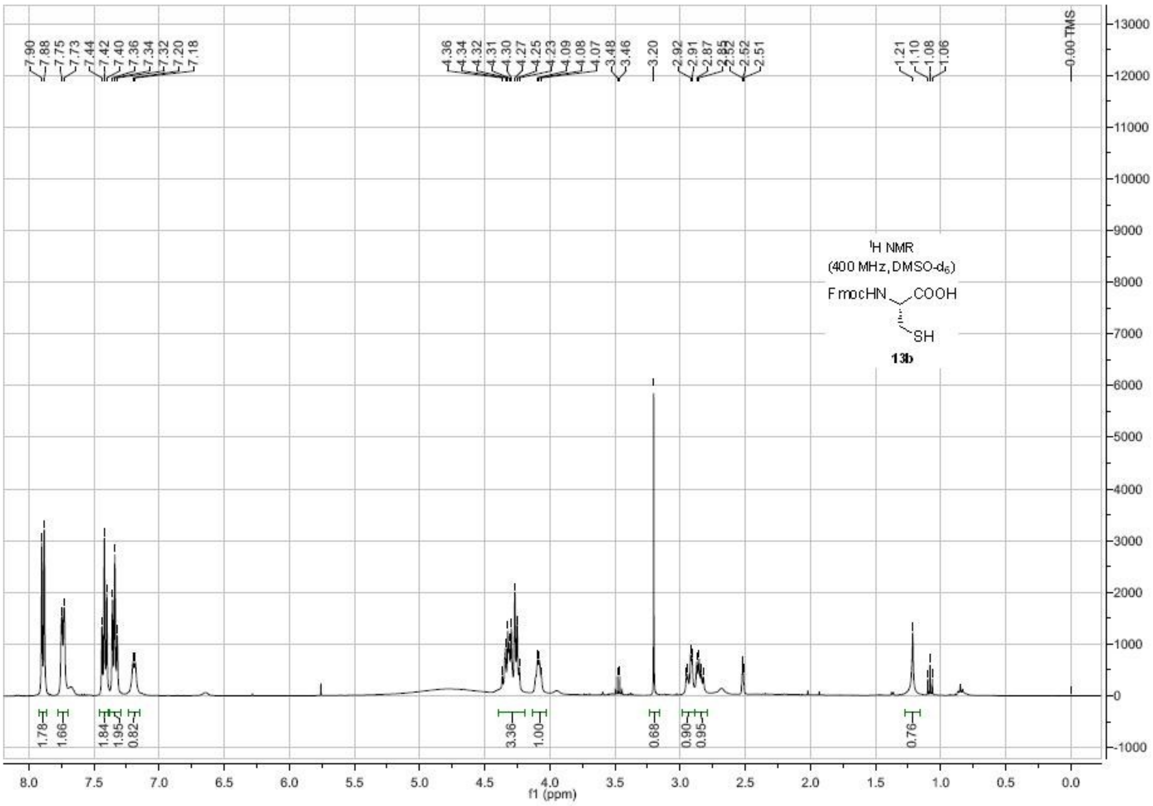

109.46
108.78
96.71
77.51
77.16
76.80
71.43
71.05
70.71
70.02
29.77
26.16
26.08
25.04
24.59
24.52
^{13}C NMR
(90 MHz, CDCl$_3$)
HS
H$_3$C
H$_3$C
O
O
O
O
O
CH$_3$
H$_3$C
11b
f1 (ppm)

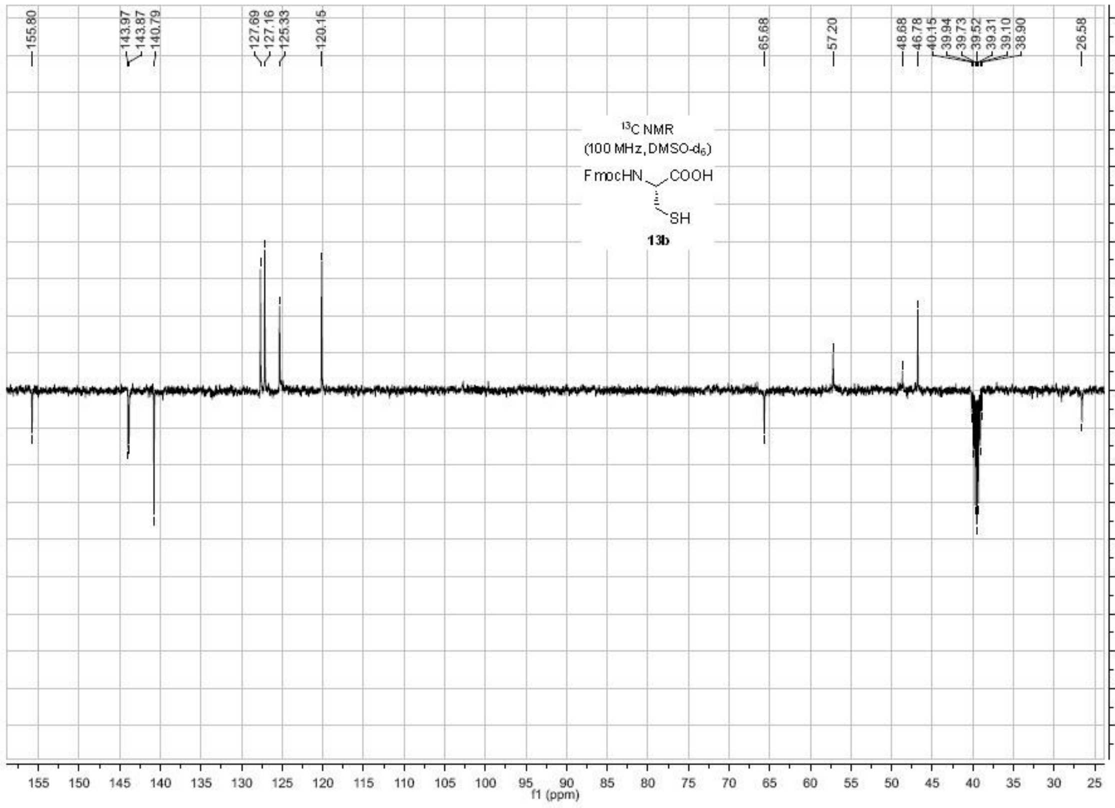

7.42
7.40
7.27
7.25
7.23
7.20
7.18
7.16
3.31
3.30
3.28
3.23
3.20
2.66
2.65
2.54
2.53
2.49
2.47
2.45
2.43
2.41
1.69
1.26
0.97
0.90
0.88
0.86
0.86
0.00
¹H NMR
(360 MHz, CDCl₃)
OH
OH
TrS
STr
OH
OH
12a
12.77
19.17
2.11
2.16
2.00
2.43
4.00
0.88
1.13
0.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0


144.72
129.73
128.14
126.98
77.51
77.16
76.81
71.83
71.66
67.17
36.16
¹³C NMR
(90 MHz, CDCl₃)
OH
OH
TrS
STr
OH
OH
12a
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000


4.74
4.25
4.23
3.54
3.53
3.36
2.85
2.82
2.79
2.56
2.54
2.52
2.51
2.01
1.99
1.97
0.00 TMS
¹H NMR
(360 MHz, DMSO-d₆)
OH
OH
HS
SH
OH
OH
12b
2.00
2.00
4.54
7.85
2.12
2.83
1.58
f1 (ppm)
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500


71.18
70.75
39.76
39.52
39.29
39.05
29.08
¹³C NMR
(90 MHz, DMSO-d₆)
OH
OH
HS
SH
OH
OH
12b
f1 (ppm)
78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24
25000 20000 15000 10000 5000 0 -5000 -10000 -15000 -20000 -25000


7.90
7.88
7.75
7.73
7.44
7.42
7.40
7.36
7.34
7.32
7.20
7.18
4.36
4.34
4.32
4.31
4.30
4.27
4.25
4.23
4.09
4.08
4.07
3.48
3.46
3.20
2.92
2.91
2.87
2.85
2.52
2.51
1.21
1.10
1.08
1.06
0.00 TMS
^{1}H NMR
(400 MHz, DMSO-d_6)
FmocHN
COOH
SH
13b
1.78
1.66
1.84
1.95
0.82
3.36
1.00
0.68
0.90
0.95
0.76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


155.80
143.97
143.87
140.79
127.69
127.16
125.33
120.15
65.68
57.20
48.68
46.78
40.15
39.94
39.73
39.52
39.31
39.10
38.90
26.58
^{13}C NMR
(100 MHz, DMSO-d_6)
FmocHN
COOH
SH
13b
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
-1200
-1400
-1600
-1800