Supporting Information I

Low-temperature, photoinduced thiol-ene click reaction: a mild and efficient method for the synthesis of sugar-modified nucleosides

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General method A for the photoinduced addition of thiols to alkenes at room temperature in the presence of DPAP

To a solution of the starting alkene (1.00 mmol) in the specified solvent (5-10 ml) thiol (1.5-6.0 equiv) and 2,2-dimethoxy-2-phenylacetophenone (DPAP, 25 mg, 0.10 mmol) were added. The solution was irradiated with UV light at room temperature for 15 min. The addition of DPAP and irradiation were repeated twice more.[a] Then the solution was concentrated and the residue was purified by flash column chromatography.

[a]It has been found that two or three short irradiation cycles with the freshly added DPAP were more efficient than a longer (45-60 min) irradiation with a higher amount of DPAP (0.3 equiv), because the reaction did not go forward upon prolonged exposure to UV-light without addition of a new portion of the initiator. Generally, the conversion significantly increased after the second and third irradiation cycles, but further irradiation did not result in noticeable improvement.

General method B for the Et_3B-catechol-mediated addition of thiols to alkenes

The starting alkene (0.20-0.50 mmol) and thiol (3 equiv. of 1-propanethiol or 1.5 equiv. of **4**) were dissolved in abs. dichloromethane (5 ml) and catechol (1.2 equiv.) and Et_3B (1 M solution in hexane, 1.2 equiv.) were added. The reaction mixture was stirred for 3-4 hours, then the solvent was evaporated in vacuum and the residue was purified by flash column chromatography.

General method C for the photoinduced addition of thiols to alkenes at –80 °C

The set-up consisted from the reaction vessel and the cooling medium (acetone–liquid nitrogen mixture) in a Dewar flask and a UV-lamp placed next to the mixture (Figure S1). To a solution of the starting alkene and thiol (1.2-2.0 equiv. thiol/alkene) in the given solvent (3-7 ml/1 mmol alkene) 2,2-dimethoxy-2-phenylacetophenone (DPAP) (0.10 equiv./alkene) was added. The reaction mixture was cooled to –80 °C- –85 °C, and irradiated with UV light for 15 min. Before irradiation, the entire set-up was covered by an aluminium foil tent. After 15 min DPAP (0.1 equiv.) dissolved in toluene (~0.3 ml/10 mg) was added, and the mixture was cooled to –80 °C- –85 °C and irradiated for another 15 min. The addition of DPAP and irradiation at this temperature was repeated once more. In some cases, the reaction mixture was frozen at –80 °C- –85 °C. In such cases the frozen mixture was thawn before adding the next portion of DPAP.

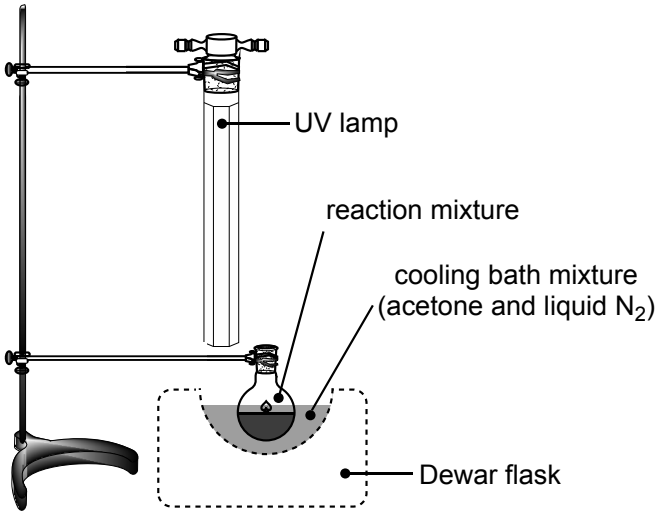
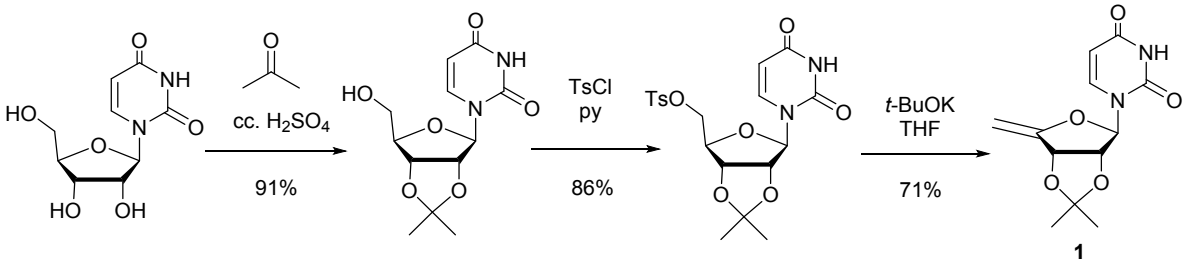


Figure S1. The experimental setup for irradiation at low temperature. Before irradiation, the entire set-up is covered by an aluminium foil tent in order to protect the laboratory personnel against UV light.

1-(2',3'-*O*-Isopropylidene-β-D-*erythro*-pent-4'-enofuranosyl)-uracil (1)



2',3'-*O*-Isopropylidene-uridine.[1] Uridine (10 g, 40.9 mmol) was suspended in acetone (300 ml) and 3.0 ml of cc. H_2SO_4 was added. The reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC (CH_2Cl_2/acetone 1/1 R_f = 0.42). The reaction mixture was neutralized with Et_3N and concentrated in *vacuo*. The residue was purified by flash column chromatography (gradient elution CH_2Cl_2/acetone 7/3→6/4) to yield 2',3'-*O*-isopropylidene-uridine (10.6 g, 91%) as a white solid.

$[\alpha]_D$= −20.91 (*c* = 0.22, MeOH); Mp 165-168 °C; MALDI-TOF MS: *m/z* calcd for $C_{12}H_{16}N_2NaO_6$ $[M+Na]^+$ 307.09, found 307.22.

2',3'-*O*-Isopropylidene-5'-*O*-tosyl-uridine. 2',3'-*O*-Isopropylidene-uridine (2.49 g, 8.78 mmol) was dissolved in dry pyridine, TsCl (3.35 g, 17.6 mmol, 2 equiv.) was added and the reaction mixture was stirred overnight. The reaction was monitored by TLC (CH_2Cl_2/acetone 6/4 R_f = 0.75). H_2O was added to the reaction mixture and stirred for 2 hours. The reaction mixture was concentrated in *vacuo*, the residue was dissolved in EtOAc and extracted with

H_2O. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give 2',3'-*O*-isopropylidene-5'-*O*-tosyl-uridine (3.32 g, 86%) as a white solid.
MALDI-TOF MS: *m/z* calcd for $C_{19}H_{22}N_2NaO_8S$ $[M+Na]^+$ 461.10, found 461.49.

1-(2',3'-*O*-Isopropylidene-β-D-*erythro*-pent-4'-enofuranosyl)-uracil (1).[1] 2',3'-*O*-isopropylidene-5'-*O*-tosyl-uridine (1.89 g, 4.3 mmol) was dissolved in 10 ml of dry THF. *t*-BuOK (1.23 g, 11.18 mmol, 2.6 equiv.) was added and the reaction mixture was stirred at room temperature for half an hour. The reaction was monitored by TLC (CH_2Cl_2/acetone 6/4 R_f = 0.66). The reaction mixture was diluted with H_2O (30 ml), neutralized with AcOH, and extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated in *vacuo*. The residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1) to give compound **1** (0.81g, 71%) as a pale yellowish solid.
$[\alpha]_D$= +126.2 (*c* = 0.21, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.99 (s, 1H, N*H*), 7.22 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.75 (d, *J* = 8.0 Hz, 1H, H-5 uracil), 5.68 (s, 1H, H-1'), 5.32 (d, *J* = 6.2 Hz, 1H, H-2'), 5.04 (d, *J* = 6.2 Hz, 1H, H-3'), 4.58 (dd, *J* = 2.4, 0.8 Hz, 1H, H-5'a), 4.39 (d, *J* = 2.3 Hz, 1H, H-5'b), 1.51 (s, 3H, *i*-propylidene CH_3), 1.39 (s, 3H, *i*-propylidene CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.8 (1C, C-4'), 163.7, 150.2 (2C, 2 x *C*O), 142.8 (1C, C-6 uracil), 113.9 (1C, *i*-propylidene C_q), 102.7 (1C, C-5 uracil), 87.1 (1C, C-5'), 96.6 (1C, C-1'), 83.0, 79.6 (2C, C-2', C-3'), 26.6, 25.4 (2C, 2 x *i*-propylidene *C*H_3), MALDI-TOF MS: *m/z* calcd for $C_{12}H_{14}N_2NaO_5$ $[M+Na]^+$ 289.08, found 289.19.

2',3'-*O*-Isopropylidene-5'-*S*-*n*-propyl-5'-thiouridine (3a) and 1-(2',3'-*O*-isopropylidene-5'-*S*-*n*-propyl-5'-thio-α-L-lyxofuranosyl)-uracil (3b)

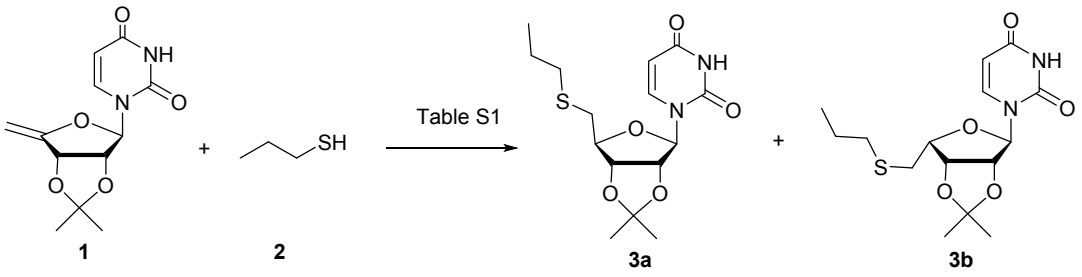


Table S1. Free radical addition of propanethiol to **1** upon various initiation methods

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : L-*lyxo*[a]	Yield (%)[b]
1 [c,d]	3 equiv.	DPAP, hν	toluene	rt.	1×15 min	2:1	53
2 [c]	3 equiv.	DPAP, hν	toluene	rt.	3×15 min	2:1	60
3 [c]	6 equiv.	DPAP, hν	toluene	rt.	3×15 min	2:1	69
4	8 equiv.	AIBN	toluene	120 °C	6 h	1.5:1	54
5	3 equiv.	Et_3B	CH_2Cl_2	rt.	2 days	2:1	38
6	3 equiv.	Et_3B, catechol	CH_2Cl_2	rt.	4 h	2:1	59
7 [e]	4 equiv.	TiO_2, hν	CH_3CN	rt.	2 days	-	0
8 [e]	4 equiv.	TiO_2, hν	CH_2Cl_2	rt.	2 days	2:1	7
9 [c]	2 equiv.	DPAP, hν	toluene	−30 °C	3×15 min	4:1	88
10 [c]	2 equiv.	DPAP, hν	toluene	−80 °C	3×15 min	5:1	89
11 [c]	2 equiv.	DPAP, hν	toluene:MeOH 1:1	−80 °C	3×15 min	6.3:1	88
12 [f]	2 equiv.	Et_3B, catechol	CH_2Cl_2:MeOH 1:1	−80 °C - −20 °C	24 h	2.5:1	64

[a] Ratio determined by ^{1}H NMR; [b]overall yield of products isolated by flash column chromatography; [c] irradiation by UV light (λ_{max}= 365 nm); [d] the same yield was achieved after 45 min irradiation in the presence of 0.3 equiv. of DPAP; [e] irradiation by visible light using a 100 W domestic lightbulb; [f]kept in refrigerator overnight

Photoinduced addition of thiol 2 to alkene 1 in the presence of DPAP (Entries 1, 2, 3 and 8-10, Table S1)

Method I (Entries 1, 2 and 3). Exomethylene derivative **1** (133 mg, 0.5 mmol) and 1-propanethiol **2** (3 equiv., 0.11 ml or 6 equiv., 0.22 ml) dissolved in toluene (5 ml) were reacted at rt according to **General method A** using one or three irradiation cycles. The reaction was monitored by TLC (hexane/acetone 6/4, R_f = 0.50). The crude product was purified by flash column chromatography (gradient elution hexane/acetone 8/2→75/25→7/3) to give a mixture of **3a** and **3b** with a 2:1 ratio (90 mg, 53% for Entry 1; 102 mg, 60% for Entry 2; 118 mg, 69% for Entry 3). A second flash column chromatography (CH_2Cl_2/acetone 95/5) of the diastereomeric mixture gave pure **3a** (hexane/acetone 7/3, R_f = 0.31) as a colourless syrup and pure **3b** (hexane/acetone 7/3, R_f = 0.30) as a colourless syrup.

Method II (Entry 9). Exomethylene derivative **1** (90 mg, 0.3 mmol) and 1-propanethiol **2** (0.6 mmol, 2 equiv., 60 µl) dissolved in toluene (1 ml) were reacted at −30 °C according to **General method C** using three irradiation cycles. The crude product was purified by flash column chromatography (gradient elution hexane/acetone 8/2→75/25→7/3) to give a 4:1 mixture of **3a** and **3b** (102 mg, 88%).

Method III (Entries 10 and 11). Exomethylene derivative **1** (90 mg, 0.3 mmol) and 1-propanethiol **2** (0.6 mmol, 2 equiv., 60 µl) dissolved in the given solvent (1 ml) were reacted at −80 °C according to **General method C** using three irradiation cycles. The crude product was purified by flash column chromatography (hexane/acetone 8/2→75/25→7/3). The yields and ratio of products are given in Table S1.

Addition reaction between 1 and 2 by thermoactivation in the presence of AIBN (Entry 3, Table S1)

Exomethylene derivative **1** (133 mg, 0.5 mmol) and 1-propanethiol **2** (2.0 mmol, 4 equiv., 0.18 ml) were dissolved in abs. toluene (5 ml) and AIBN (0.05 mmol, 0.1 equiv., 8.2 mg) was added. Argon gas was bubbled through the solution for 10 minutes and the reaction mixture was kept in a closed vessel at 120 °C for 3 hours. After 3 hours the conversion of the reaction was monitored by TLC. As the conversion of **1** was not complete, 0.1 equiv. of AIBN and 4 equiv. of 1-propanethiol were added, argon gas was bubbled through the solution and the reaction mixture was heated again for 3 hours. After completion of the reaction the solvent was evaporated in vacuum and the residue was purified by flash column chromatography (gradient elution hexane/acetone 8/2→75/25→7/3) to give a mixture of **3a** and **3b** with a 1.5:1 ratio (92 mg, 54%).

Et_3B-mediated addition of thiol 2 to alkene 1 (Entry 5, Table S1)

Exomethylene derivative **1** (50 mg, 0.188 mmol) and 1-propanethiol **2** (0.563 mmol, 3 equiv., 51 µl) were dissolved in CH_2Cl_2 (3 ml) and Et_3B (0.2068 mmol, 1.1 equiv., 0.207 ml, 1 M solution in hexane) was added. After 24 hours the conversion of the reaction was monitored by TLC. As the conversion of **1** was not complete, Et_3B (0.2 equiv., 40 µl, 1 M solution in hexane) was added and the stirring was continued. The addition of Et_3B was repeated twice more. The overall reaction time was 2 days, then the solvent was evaporated in vacuum and the residue was purified by flash column chromatography (hexane/acetone 7/3)to give a 2:1 mixture of **3a** and **3b** (23 mg, 38%).

Et_3B-catechol-mediated addition of thiol 2 to alkene 1 (Entries 6 and 12, Table S1)

Method I (Entry 6). Exomethylene derivative **1** (133 mg, 0.5 mmol) and 1-propanethiol **2** (1.5 mmol, 3 equiv., 0.11 ml) dissolved in CH_2Cl_2 (5 ml) were reacted according to **General method B**. The residue was purified by flash column chromatography (hexane/acetone 6/4, R_f = 0.40) to give a 2:1 mixture of **3a** and **3b** as a white solid (200 mg, 59%).

Method II (Entry 12). Exomethylene derivative **1** (266 mg, 1.0 mmol) and 1-propanethiol **2** (2.0 mmol, 2 equiv., 205 µl) were dissolved in a 1:1 mixture of CH_2Cl_2 and MeOH (2.0 ml) and catechol (132 mg, 1.2 mmol, 1.2 equiv.) and Et_3B (1 M solution in hexane, 1.2 mmol, 1.2 equiv., 785 µl) were added. The reaction mixture was cooled to −80 °C and monitored by TLC. As the conversion of **1** was not complete, Et_3B was added to the mixture every two hours (3 x 100 µl), then the recation mixture was kept in refrigerator overnight. The solvent

was evaporated in vacuum and the residue was purified by flash column chromatography (gradient elution hexane/acetone 8/2→75/25→7/3) to give a 2.5:1 mixture of **3a** and **3b** (218 mg, 64%).

Visible lighte promoted thiol-ene reaction between 1 and 2 using titanum dioxide (Entries 7 and 8, Table S1)

Exomethylene derivative **1** (100 mg, 0.376 mmol) was dissolved in abs. CH_2Cl_2 (2 ml) and TiO_2 (30 mg, 0.376 mmol, 1.0 equiv.) and 1-propanethiol (136 µl, 1.5 mmol, 4.0 equiv.) were added. The reaction mixture was irradiated with a domestic 100 W light bulb and stirred for 2 days, then the solvent was evaporated in vacuum and the residue was purified by flash column chromatography (eluent: hexane/acetone 85/15→8/2) to yield the mixture of **3a** and **3b** (9 mg, 7%) in a 2:1 ratio.

When CH_3CN was used as the solvent (Entry 7), no reaction was observed after 2 days.

Data for **3a** (D-*ribo* product)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.89 (s, 1H, N*H*), 7.37 (d, J = 8.1 Hz, 1H, H-6 uracil), 5.75 (d, J = 8.1 Hz, 1H, H-5 uracil), 5.69 (d, $J_{1',2'}$ = 2.2 Hz, 1H, H-1'), 4.99 (dd, $J_{2',3'}$ = 6.6 Hz, $J_{1',2'}$ = 2.2 Hz, 1H, H-2'), 4.82 (dd, $J_{2',3'}$ = 6.6 Hz, $J_{3',4'}$ = 4.2 Hz, 1H, H-3'), 4.27 (td, $J_{4',5'}$ = 6.1 Hz, $J_{3',4'}$ = 4.3 Hz, 1H, H-4'), 2.92-2.80 (m, 2H, H-5'a,b), 2.55 (t, J = 7.5 Hz, 2H, $CH_3CH_2CH_2$), 1.63 (dt, J = 14.7 Hz, J = 7.4 Hz, 2H, $CH_3CH_2CH_2$), 1.57 (s, 3H, *i*-propylidene CH_3), 1.36 (s, 3H, *i*-propylidene CH_3), 0.98 (t, J = 7.3 Hz, 3H, $CH_3CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.8, 150.1 (2C, 2 x *C*O uracil), 142.5 (1C, C-6 uracil), 114.7 (1C, *i*-propylidene C_q), 102.7 (1C, C-5 uracil), 94.2 (1C, C-1'), 86.7 (1C, C-4'), 84.5 (1C, C-2'), 83.2 (1C, C-3'), 35.1 (1C, $CH_3CH_2CH_2$), 34.5 (1C, C-5'), 27.2, 25.4 (2C, 2 x *i*-propylidene *C*H$_3$), 23.0 (1C, $CH_3CH_2CH_2$), 13.5 (1C, $CH_3CH_2CH_2$); ESI-TOF MS: MS: *m/z* calcd for $C_{15}H_{22}N_2NaO_5S$ $[M+Na]^+$ 365.114, found 365.119.

Data for **3b** (L-*lyxo* product)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.31 (s, 1H, N*H*), 7.22 (d, J = 8.0 Hz, 1H, H-6 uracil), 5.73 (dd, J = 8.1 Hz, J = 1.8 Hz, 1H, H-5 uracil), 5.36 (s, 1H, H-1'), 5.24 (d, $J_{2',3'}$ = 6.0 Hz, 1H, H-2'), 4.99 (dd, $J_{2',3'}$ = 5.9 Hz, $J_{3',4'}$ = 3.9 Hz, 1H, H-3'), 4.59 (td, $J_{4',5'}$ = 6.8 Hz, $J_{3',4'}$ = 3.9 Hz, 1H, H-4'), 2.88-2.76 (m, 2H, H-5'a,b), 2.57 (td, J = 7.2 Hz, J = 0.8 Hz, 2H, $CH_3CH_2CH_2$), 1.65-1.57 (m, 2H, $CH_3CH_2CH_2$), 1.52 (s, 3H, *i*-propylidene CH_3), 1.36 (s, 3H, *i*-propylidene CH_3), 0.99 (t, J = 7.3 Hz, 3H, $CH_3CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.7, 150.8 (2C, 2 x *C*O uracil), 143.7 (1C, C-6 uracil), 113.3 (1C, *i*-propylidene C_q),

102.5 (1C, C-5 uracil), 97.4 (1C, C-1'), 85.8 (1C, C-4'), 85.5 (1C, C-2'), 81.6 (1C, C-3'), 35.1 (1C, $CH_3CH_2CH_2$), 31.1 (1C, C-5'), 26.4, 24.9 (2C, 2 x *i*-propylidene CH_3), 23.1 (1C, $CH_3CH_2CH_2$), 13.6 (1C, $CH_3CH_2CH_2$); ESI-TOF MS: *m/z* calcd for $C_{15}H_{22}N_2NaO_5S$ $[M+Na]^+$ 365.114, found 365.122.

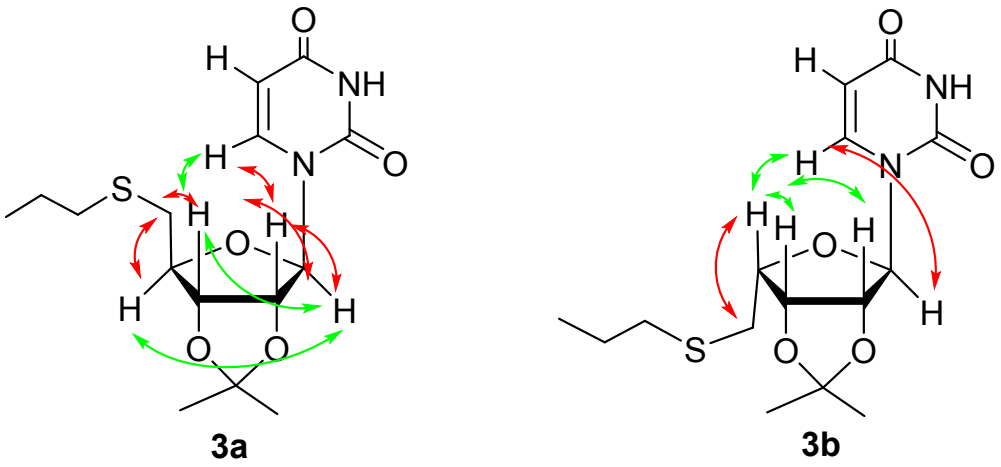


Figure S1. ROESY through-space connectivities observed in the ROESY spectra of **3a** and **3b**. Red arrows: strong RO effects, green arrows: weak RO effects.

2',3'-*O*-Isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thiouridine (15a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (15b)

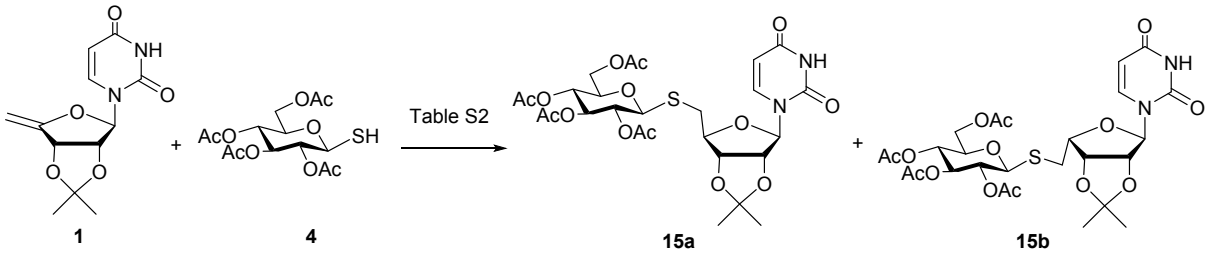


Table S2 Free radical addition of 1-thioglucose peracetate to **1** upon various initiation methods

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : L-*lyxo*[a]	Yield (%)[b]
1	1.5 equiv.	DPAP, hν	toluene	rt.	3×15 min	1.1:1	87
2	1.5 equiv.	AIBN	toluene	120 °C	6 h	1:1	5
3	1.5 equiv.	Et_3B	CH_2Cl_2	rt.	overnight	1:1	18
4	1.5 equiv.	Et_3B	MeOH	rt.	overnight	1:1	58
5	1.5 equiv.	Et_3B, catechol	CH_2Cl_2	rt.	4 h	1.1:1	80
6	1.2 equiv.	DPAP, hν	toluene	−80 °C	3×15 min	1:1	85
7	1.2 equiv.	DPAP, hν	toluene:MeOH 1:2	−80 °C	3×15 min	1:3	88
8	1.2 equiv.	DPAP, hν	MeOH	−80 °C	3×15 min	1:2	78

[a] Ratio determined by ^{1}H NMR; [b]overall yield of products isolated by column chromatography.

Photoinduced addition of thiol 4 to alkene 1 in the presence of DPAP (Entries 1, 6, 7 and 8, Table S2)

Methdod I (Entry 1): Exomethylene derivative **1** (133 mg, 0.50 mmol) and thiol **4** (1.5 equiv., 273 mg, 0.75 mmol) dissolved in toluene (5 ml) were reacted according to **General method A**. The residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1 R_f = 0.20) to give an inseparable 1:1 mixture of **15a** and **15b** (274 mg, 87%).

Methdod II (Entries 6-8): Exomethylene derivative **1** (88 mg, 0.33 mmol) and thiol **4** (1.2 equiv., 146 mg, 0.396 mmol) dissolved in the given solvent (1.0 ml) were reacted at −80 °C according to **General method C**. The yields and ratio of products are given in Table 2.

Addition reaction between 1 and 4 by thermoactivation in the presence of AIBN (Entry 2, Table S2)

Exomethylene derivative **1** (50 mg, 0.188 mmol) and thiol **4** (0.282 mmol, 1.5 equiv., 46.3 mg) were dissolved in abs. toluene and (5 ml) AIBN (0.1 equiv., 3.1 mg) was added. Argon gas was bubbled through the solution for 10 minutes and the reaction mixture was kept in a closed vessel at 120 °C for 3 hours. After 3 hours the conversion of the reaction was checked by TLC. As the reaction was not complete, AIBN (0.1 equiv., 3.1 mg) was added, argon gas was bubbled through the solution and the reaction mixture was heated again for subsequent 3 hours. The solvent was evaporated in vacuum and the residue was purified by flash column chromatography (gradient elution hexane/acetone 9/1→95/15→8/2) to give an inseparable 1:1 mixture of **15a** and **15b** (12 mg, 5%).

Et_3B-mediated addition of thiol 4 to alkene 1 (Entries 3 and 4, Table S2)

Exomethylene derivative **1** (50 mg, 0.188 mmol) and thiol **4** (0.282 mmol, 1.5 equiv., 46.3 mg) were dissolved in CH_2Cl_2 (3 ml) and Et_3B (0.2068 mmol, 1.1 equiv., 0.207 ml, 1 M solution in hexane) was added. After 24 hours the conversion of the reaction was monitored by TLC. As the conversion of **1** was not complete, Et_3B (0.2 equiv., 40 μl, 1 M solution in hexane) was added and the stirring was continued. The addition of Et_3B was repeated twice more and the mixrure was stirred overnight. The solvent was evaporated in vacuum and the residue was purified by flash column chromatography to give a 1:1 mixture of **15a** and **15b** (44 mg, 18%). The reaction was repeated in MeOH to give 125 mg of **15ab** (58%, 1:1 mixture).

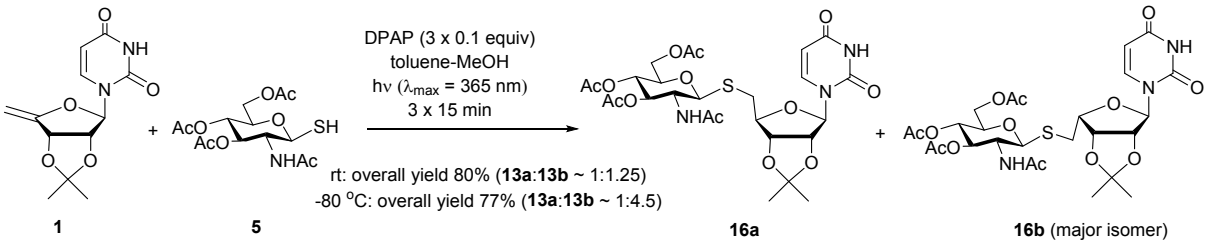
Et_3B-catechol-mediated addition of thiol 2 to alkene 1 (Entry 5, Table S2)

Exomethylene derivative **1** (81 mg, 0.3 mmol) and thiol **4** (0.45 mmol, 1.5 equiv., 164 mg,) dissolved in CH_2Cl_2 (4 ml) were reacted according to **General method B**. After 4 h, the solvents were evaporated and the residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1, R_f = 0.20) to give an inseparable 1.1:1 mixture of **15a** and **15b** (151 mg, 80%).

NMR data for **15a** (from the spectra of the 3:1 mixture of **15a** and **15b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.66 (s, 1H, N*H*), 7.24 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.71 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, H-5 uracil), 5.36 (s, 1H), 5.24-5.20 (m, 2H), 5.10 (d, *J* = 2.8 Hz, 1H), 5.08 (d, *J* = 3.1 Hz, 1H), 5.00 (dd, *J* = 9.7 Hz, *J* = 4.0 Hz, 1H), 4.67 (td, *J* = 6.8 Hz, *J* = 4.0 Hz, 1H), 4.6-4.56 (m, 1H), 4.20 (t, *J* = 3.8 Hz, 1H), 4.16 (d, *J* = 1.9 Hz, 1H), 3.73-3.66 (m, 1H), 3.07 (dd, *J* = 13.9 Hz, *J* = 7.3 Hz, 1H, H-5'a), 2.83 (dd, *J* = 13.9 Hz, *J* = 6.5 Hz, 1H, H-5'b), 2.06 (s, 3H, Ac C*H*$_3$), 2.04 (s, 3H, Ac C*H*$_3$), 2.01 (s, 3H, Ac C*H*$_3$), 1.99 (s, 3H, Ac C*H*$_3$), 1.51 (s, 3H, *i*-propylidene C*H*$_3$), 1.36 (s, 3H, *i*-propylidene C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.2, 169.4 (4C, 4 x Ac*C*O), 163.7, 150.8 (2C, 2 x *C*O uracil), 143.6 (1C, C-6 uracil), 113.2 (1C, *i*-propylidene C_q), 102.4 (1C, C-5 uracil), 97.0 (1, C-1'), 85.7, 85.4, 83.6, 81.2, 75.8, 73.9, 69.8, 68.2 (8C, skeleton carbons), 62.0 (1C, C-6_{Glcp}), 28.9 (1C, C-5'), 26.3, 24.8 (2C, 2 x *i*-propylidene *C*H$_3$), 20.8, 20.7, 20.6 (4C, 4 x Ac*C*H$_3$); MALDI-TOF MS: *m/z* calcd for $C_{26}H_{34}N_2NaO_{14}S$ $[M+Na]^+$: 653.16, found: 653.21.

2',3'-*O*-Isopropylidene-5'-*S*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-5'-thiouridine (16a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (16b)



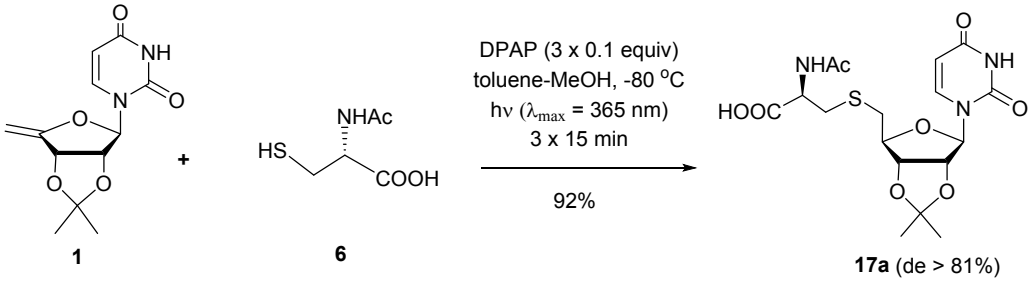
Exomethylene derivative **1** (133 mg, 0.50 mmol,) and thiol **5** (218 mg, 0.6 mmol, 1.2 equiv.) dissolved in a mixture of toluene/MeOH 1:2 (2 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography

(CH_2/Cl_2 7/3 R_f= 0.13) to give an inseparable 1:4.5 mixture of **16a** and **16b** as a yellow syrup (242 mg, 77%). The reaction was repeated at room temperature to give 252 mg of **16ab** (80%, 1:1.25 mixture).

NMR data for **16b** (from the spectra of the 1:4.5 mixture of **16a** and **16b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.21 (s, 1H, N*H* uracil), 7.40 (d, J = 7.9 Hz, 1H, H-6 uracil), 6.89 (d, J = 8.8 Hz, 1H, N*H*Ac), 5.76 (d, J = 8.0 Hz, 1H, H-5 uracil), 5.47 (s, 1H, H-1'), 5.24 (d, J = 6.3 Hz, 2H), 5.10 (t, J = 9.5 Hz, 1H), 5.03 (d, J = 4.1 Hz, 1H), 4.86 – 4.79 (m, 1H), 4.70 (d, J = 3.0 Hz, 1H), 4.24 (d, J = 8.5 Hz, 1H), 4.16 (d, J = 9.0 Hz, 2H), 3.77 (d, J = 9.0 Hz, 1H), 3.14 (dd, J = 12.9, 5.8 Hz, 1H, H-5'a), 2.85 (dd, J = 12.7, 4.6 Hz, 1H, H-5'b), 2.08, 2.03, 2.03, 1.93 (4xs, 4x3H, 4xAcCH_3), 1.52 (s, 3H, *i*-propylideneCH_3), 1.37 (s, 3H, *i*-propylideneCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.7, 170.5, 169.3 (4C, 4xAc*C*O), 164.0, 151.0 (2C, 2x uracil*C*O), 143.7 (1C, C-6 uracil), 112.9 (1C, *i*-propylideneC_q, 102.0 (1C, C-5 uracil), 96.4 (1C, C-1'), 85.47, 85.3, 83.9, 81.0, 75.4, 73.7, 68.5 (7C, skeletal carbons), 62.2 (1C, C-6''), 52.9 (1C, C-2''), 28.6 (1C, C-5'), 26.2, 24.7 (2C, 2x*i*-propylidene*C*H_3), 23.0, 20.6, 20.5, 20.5 (4C, 4xAc*C*H_3). MALDI-TOF MS: *m/z* calcd for $C_{26}H_{35}N_3NaO_{13}S$ $[M+Na]^+$ 652.18, found 652.13.

_N_-Acetyl-_S_-(5'-deoxy-2',3'-_O_-isopropylidene-uridine-5'-yl)-L-cystein (17)

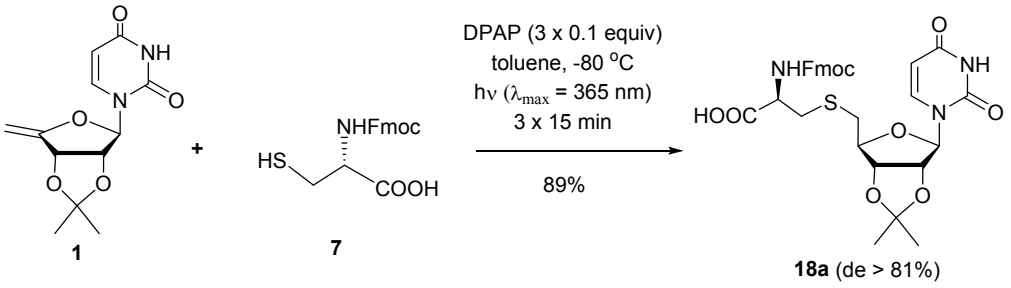


Exomethylene derivative **1** (1.0 mmol, 266 mg) and thiol **6** (1.2 equiv., 1.2 mmol, 195 mg) dissolved in a 1: 1 mixture of toluene and MeOH (10 ml) were reacted at −80 °C according to **General Method C.** The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 7/3 R_f = 0.22) to give **17** (392 mg, 92%, >81% diastereomeric purity) as a white powder.

$[\alpha]_D$: +5.0 (*c* = 0.50, MeOH); R_f = 0.22 (7:3 CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, MeOD) δ (ppm) 7.69 (d, *J* = 8.1 Hz, 1H, C-6 uracil), 5.78 (d, $J_{1',2'}$ = 2.3 Hz, 1H, H-1'), 5.74 (d, *J* = 8.0

Hz, 1H, C-5 uracil), 5.05 (dd, *J*= 6.5 Hz, 2.4 Hz, 1H, cys C*H*), 4.82 (dd, *J* = 6.5, 3.9 Hz, 1H), 4.47 (dt, *J* = 12.1, 6.0 Hz, 1H, H-3'), 4.24 (td, *J* = 6.5, 4.0 Hz, 1H, H-4'), 3.19-3.11 (m, 1H), 2.97-2.84 (m, 3H), 2.04 (d, *J* = 3.9 Hz, 3H, acetyl CH_3), 1.55 (s, 3H, *i*-propylidene CH_3), 1.36 (s, 3H, *i*-propylidene CH_3); ^{13}C NMR (100 MHz, MeOD) δ (ppm) 171.7 (1C, cys *C*O), 164.8, 150.6 (2C, 2 x *C*O uracil), 143.2 101.6 (2C, C-6 uracil, C-5 uracil), 114.0 (1C, *i*-propylidene C_q), 93.53 (1C, C-1'), 86.44, 84.08, 83.26 (3 C, C-2', C-3', C- 4'), 54.2 (1 C, cys *C*H), 34.6, 34.1 (2 C, C-5', cys *C*H_2), 26.1, 24.2 (2 C, 2 x *i*-propylidene *C*H_3), 21.5 (1 C, acetyl *C*H_3); ESI-TOF MS: *m/z* calcd for $C_{17}H_{23}N_3NaO_8S$ $[M+Na]^+$ 452.110, found 452.111.

_N_-(9-Fluorenylmethoxycarbonyl)-_S_-(5'-deoxy-2',3'-_O_-isopropylidene-uridine-5'-yl)-L-cystein (18)

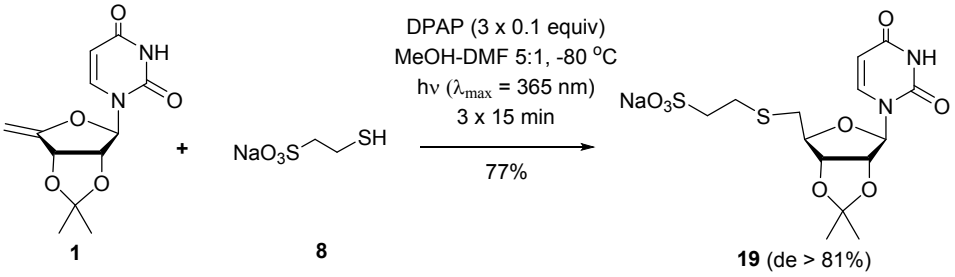


Exomethylene derivative **1** (1.0 mmol, 266 mg) and thiol **7** (1.2 equiv., 1.2 mmol, 413 mg) dissolved in a 2:3 mixture of toluene and MeOH (10 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 85/15 R_f = 0.21) to give **18** (548 mg, 89%, >81% diastereomeric purity) as a pale yellowish powder.

$[\alpha]_D$: +0.22 (*c* = 0.45, MeOH); R_f = 0.21 (85:15 CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, DMSO) δ (ppm) 7.88 (d, *J* = 7.5 Hz, 2H), 7.70 (t, *J* = 6.8 Hz, 3H), 7.43-7.36 (m, 2H), 7.35-7.28 (m, 2H), 6.92 (d, *J* = 7.1 Hz, 1H), 5.77 (d, $J_{1,2}$ = 2.1 Hz, 1H, H-1'), 5.64 (d, *J* = 8.0 Hz, 1H, H-5 uracil), 4.99 (dd, *J* = 6.5, 2.3 Hz, 1H, cys C*H*), 4.72 (dd, *J* = 6.0, 3.9 Hz, 1H), 4.36-4.27 (m, 1H), 4.26-4.15 (m, 2H), 4.08 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.98 (d, *J* = 3.7 Hz, 1H), 3.41 (ddd, *J* = 26.6 Hz, *J* = 14.0 Hz, *J* = 7.0 Hz, 3H), 3.06 (dd, *J* = 16.8 Hz, *J* = 7.2 Hz, 1H), 2.88-2.74 (m, 3H), 2.54-2.48 (m, 1H), 1.45 (s, 3H, *i*-propylidene CH_3), 1.25 (s, 3H, *i*-propylidene CH_3); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 163.7, 150.7 (2C, 2 x *C*O uracil), 156.1 (1C, Fmoc *C*O), 144.4, 141.2 (4C, 4 x C_q Fmoc), 143.1, 102.4 (2C, C-6 uracil, C-5 uracil), 128.0, 127.5, 125.8, 120.5 (8C, arom.), 113.7 (1C, *i*-propylidene C_q), 92.3 (1C, C-1'), 85.8, 83.9, 83.3 (3C, C-2', C-3', C-4'), 66.0 (1C, Fmoc *C*H_2), 55.9 (1C, Cys *C*H), 47.2 (1C,

C-9 fluorene), 35.5, 34.4 (2C, C-5', cys *C*H_2), 27.4, 25.6 (2C, 2 x *i*-propylidene *C*H_3); ESI-TOF MS: *m/z* calcd for $C_{30}H_{31}N_3NaO_9S$ $[M+Na]^+$ 632.167, found 632.169.

2-[*S*-(5'-deoxy-2',3'-isopropylidene-uridine-5'-yl)]-mercaptoethanesulfonate Na salt (19)

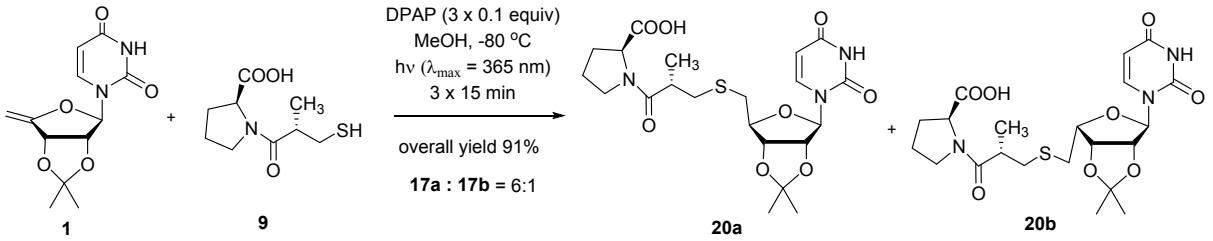


Exomethylene derivative **1** (0.5 mmol, 133 mg) and thiol **8** (1.2 equiv., 0.6 mmol, 98.5 mg) dissolved in MeOH/DMF 5:1 (2 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 8/2 R_f = 0.19) to give **19** (164 mg, 77%, >81% diastereomeric purity) as a white solid.

The same reaction in MeOH gave **19** in a 64% yield (de >81%).

$[\alpha]_D$: +1.90 (*c* = 0.21, MeOH); R_f = 0.19 (8:2 CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, MeOD) δ (ppm) 7.69 (d, *J* = 8.0 Hz, 1H, H-6 uracil), 5.78 (d, *J* = 2.2 Hz, 1H, H-1'), 5.74 (d, *J* = 8.0 Hz, 1H, H-5 uracil), 5.06 (dd, *J* = 6.5 Hz, *J* = 2.2 Hz, 1H, H-2'), 4.89-4.81 (m, 4H), 4.25 (td, *J* = 6.5 Hz, *J* = 4.3 Hz, 1H, H-3'), 3.34-3.30 (m, 1H), 3.13-3.05 (m, 3H), 3.01-2.88 (m, 5H), 1.56 (s, 3H, *i*-propylidene C*H*$_3$), 1.37 (s, 3H, *i*-propylidene C*H*$_3$); ^{13}C NMR (100 MHz, MeOD) δ (ppm) 143.2 (1C, C-6 uracil), 114.1 (1C, *i*-propylidene C_q), 101.6 (1C, C-5 uracil), 93.7 (1C, C-1'), 86.6, 84.1, 83.3 (3C, C-2', C-3', C-4'), 51.6 (1C, *C*H_2SO_3Na), 33.7 (1C, C-5'), 26.8 (1C, S*C*H_2MeSNa), 26.1, 24.1 (2 C, 2 x *i*-propylidene *C*H_3); ESI-TOF MS: *m/z* calcd for $C_{14}H_{19}N_2Na_2O_8S_2$ $[M+Na]^+$ 453.037, found 453.035.

***S*-(5'-Deoxy-2',3'-*O*-isopropylidene-uridine-5'-yl]-captopril (20a) and *S*-[1-(5'-Deoxy-2',3'-*O*-isopropylidene-α-L-lyxofuranose-5'-yl)-uracil]-captopril (20b)**

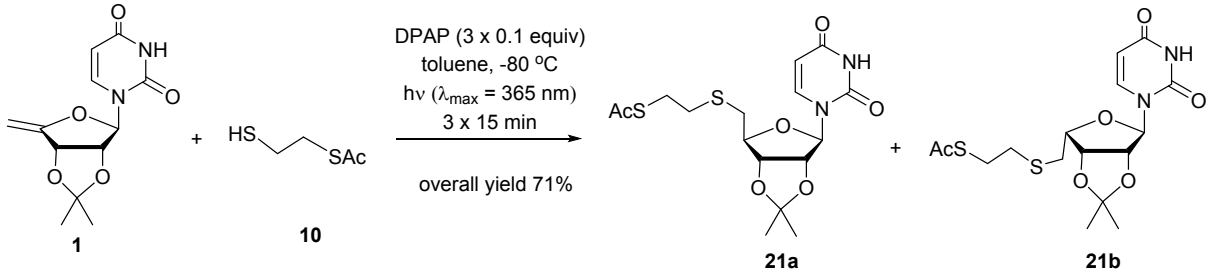


Exomethylene derivative **1** (0.5 mmol, 133 mg) and thiol **9** (1.2 equiv., 0.6 mmol, 130 mg) dissolved MeOH (1 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH 8/2, R_f = 0.25) to give an inseparable 6:1 mixture of **20a** and **20b** (220 mg, 91%) as a white solid.

NMR data of **20a** (from the spectra of the 6:1 mixture of **20a** and **20b**)

^{1}H NMR (400 MHz, MeOD) δ (ppm) 7.63 (d, J = 8.1 Hz, 1H, H-6 uracil), 5.75-5.70 (m, 2H, H-5 uracil, H-1'), 5.06 (dd, J = 1.9 Hz, 1H), 4.81 (dd, J = 7.9 Hz, J = 3.8 Hz, 3H), 4.40-4.34 (m, 1H), 4.21 (dt, J = 10.2 Hz, J = 5.0 Hz, 1H), 3.70 (s, 2H), 2.90-2.83 (m, 4H), 2.16-2.03 (m, 4H), 1.55 (s, 3H, *i*-propylideneCH_3), 1.36 (s, 3H, *i*-propylidene CH_3), 1.17 (t, J = 6.6 Hz, 5H); ^{13}C NMR (100 MHz, MeOD) δ (ppm) 178.9, 174.7 (2C, 2 x *C*O captopril), 164.7, 150.5 (2C, 2 x *C*O uracil), 143.5 (1C, C-6 uracil), 114.2 (1C, *i*-propylidene C_q), 101.9 (1C, C-5 uracil), 94.2 (1C, C-1'), 87.2, 84.1, 83.4 (3C, C-2', C-3', C-4'), 61.2, 38.6 (2C, 2 x *C*H captopril), 35.9, 34.4 (2C, 2 x S*C*H$_2$), 29.1, 24.6 (2C, 2 x *C*H$_2$ captopril), 26.4, 24.5 (2C, 2 x *i*-propylidene *C*H$_3$), 16.4 (1C, captopril *C*H$_3$); ESI-TOF MS: *m/z* calcd for $C_{21}H_{29}N_3NaO_8S$ $[M+Na]^+$ 506.157, found 506.155.

2',3'-*O*-Isopropylidene-5'-*S*-(acetylthioethyl)-5'-thiouridine (21a) and 1-[2',3'-O-isopropylidene-5'-*S*-(acetylthioethyl)-5'-thio-α-L-lyxofuranosyl]-uracil (21b)



Exomethylene derivative **1** (91 mg, 0.34 mmol,) and thiol **10** (0.093 ml, 2 equiv) dissolved in toluene (1 ml) were reacted at−80 °C according to **General method C**. The crude product was purified by flash column chromatography (hexane : acetone 7:3) to give an inseparable 6:1 mixture of **21a** and **21b** as a yellow syrup (98 mg, 71%). The reaction was also carried out in

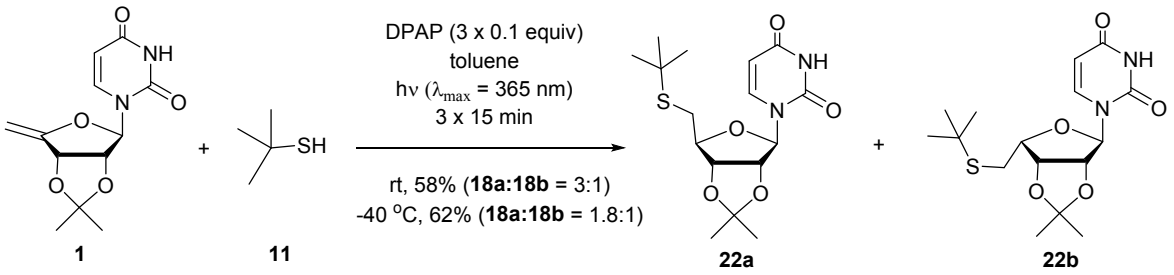
a toluene:MeOH 2:1 mixture to give **21a** and **21b** with the same 6:1 diastereosomeric ratio in 70% yield.

NMR data for **21a** (from the spectra of the 5.5:1 mixture of **21a** and **21b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.95 (s, 1H, N*H*), 7.32 (d, J = 8.1 Hz, 1H, H-6), 5.74 (dd, J = 8.1, 1.3 Hz, 1H, H-5), 5.65 (d, J = 2.1 Hz, 1H, H-1'), 5.00 (dd, J = 6.5, 2.1 Hz, 1H, H-2'), 4.81 (dd, J = 6.5, 4.3 Hz, 1H, H-3'), 4.27 (td, J = 6.2, 4.4 Hz, 1H, H-4'), 3.06 (ddd, J = 8.5, 5.9, 2.1 Hz, 2H), 2.94 (d, J = 6.3 Hz, 2H), 2.78 – 2.65 (m, 2H), 2.32 (s, 3H, AcCH_3), 1.55 (s, 3H, *i*-propylideneCH_3), 1.34 (s, 3H, *i*-propylidene CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.4 (1C, Ac*C*O), 163.8, 150.1 (2C, 2x*C*O uracil), 142.7 (1C, C-6 uracil), 114.7 (1C, *i*-propylideneC_q), 102.7 (1C, C-6 uracil), 94.6 (1C, C-1'), 87.0, 84.4, 83.2 (3C, C-2', C-3', C-4'), 34.2, 32.4, 29.1 (3C, 3x*C*H$_2$), 30.6 (1C, Ac*C*H$_3$), 27.1, 25.3 (2C, 2x *i*-propylidene *C*H$_3$).

ESI-ToF MS: *m/z* calcd for $C_{16}H_{22}N_2NaO_6S_2^+$ $[M+Na]^+$ 425.081, found 425.085.

2',3'-*O*-Isopropylidene-5'-*S*-(2-methylprop-2-yl)-5'-thiouridine (22a) and 1-(2',3'-*O*-isopropylidene-5'-*S*-(2-methylpprop-2-yl)-5'-thio-α-L-lyxofuranosyl)-uracil (22b)



Exomethylene derivative **1** (133 mg, 0.5 mmol) and 2-methylpropane-2-thiol **11** (6 equiv., 3 mmol, 190 μl) dissolved in toluene (3 ml) were reacted at rt according to **General method A** using three irradiation cycles. The reaction was monitored by TLC (hexane/acetone 7/4, R_f = 0.30). The crude product was purified by flash column chromatography (gradient elution hexane/acetone 8/2→7/3) to give an unseparable mixture of **22a** and **22b** with a 3:1 ratio (104 mg, 58%).

The reaction was also attempted at −80 °C according to **General method C**. After the first irradiation cycle at −80 °C, very low conversion was observed by TLC. Then, the reaction mixture was allowed to warm up to −40 °C and three irradiation cycles were carried out at −40 °C. After column chromatographic purification a 1.8:1 mixture of **22a** and **22b** was isolated with 62% yield.

NMR data for **22a** (from the spectra of the 3:1 mixture of **22a** and **22b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.70 (s, 1H, ,N*H*), 7.38 (d, J = 8.1 Hz, 1H, H-6 uracil), 5.75 (d, J = 8.1 Hz, 1H, H-5 uracil), 5.69 (d, $J_{1',2'}$ = 2.2 Hz, 1H, H-1'), 4.96 (dd, $J_{2',3'}$ = 6.6

Hz, $J_{1',2'}$ = 2.2 Hz, 1H, H-2'), 4.81 (dd, $J_{2',3'}$ = 6.6 Hz, $J_{3',4'}$ = 4.2 Hz, 1H, H-3'), 4.28 (td, $J_{4',5'}$ = 6.1 Hz, $J_{3',4'}$ = 4.3 Hz, 1H, H-4'), 2.92-2.80 (m, 2H, H-5'a,b), 2.93 (dd, 1H, J_{gem} = 12.6, $J_{4',5'}$ = 6.3 Hz, 1H, H-5'a), 2.85 (dd, 1H, J_{gem} = 12.6, $J_{4',5'}$ = 6.3 Hz, 1H, H-5'b), 1.57 (s, 3H, , *i*-propylidene CH_3), 1.36 (s, 3H, *i*-propylidene CH_3), 1.34 (s, 9H, SC(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.6, 150.0 (2C, 2 x *C*O uracil), 142.4 (1C, C-6 uracil), 114.7 (1C, *i*-propylidene C_q), 102.6 (1C, C-5 uracil), 94.2 (1C, C-1'), 86.5 (1C, C-4'), 84.5 (1C, C-2'), 83.1 (1C, C-3'), 42.7, (1C, C_q), 30.9 (1C, C-5'), 30.8 (3C, SC(*C*H_3)$_3$), 27.1, 25.3 (2C, 2 x *i*-propylidene *C*H_3). Elemental analysis: calcd (%) for $C_{16}H_{24}N_2O_5S$: C 53.92, H 6.79, N 7.86, S 8.99, found C 53.83, H 6.82, N 7.90, S 8.93.

2',3'-*O*-Isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-5'-thiouridine (23a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (23b)

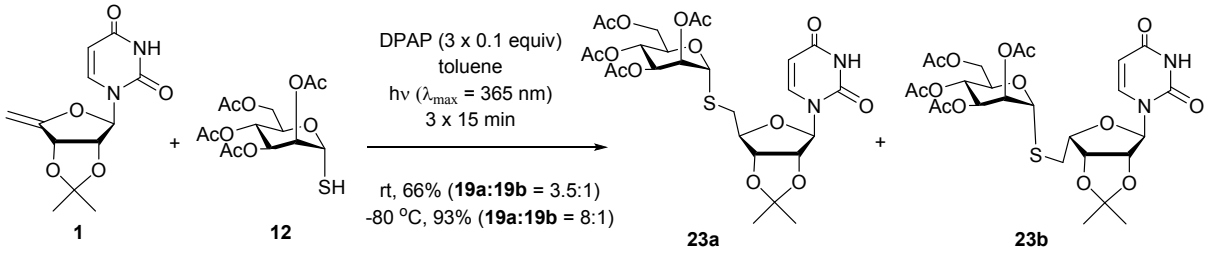


Table S3.

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : L-*lyxo*[a]	Yield (%)[b]
1	1.2 equiv.	DPAP, hν	toluene	rt.	3×15 min	4.6:1	60
2	1.2 equiv.	DPAP, hν	toluene/MeOH 1/2	-80 °C	3×15 min	4.6:1	78
3	1.2 equiv.	DPAP, hν	toluene	-80 °C	3×15 min	8:1	89

Method I (entry 1)**:** Exomethylene derivative **1** (133 mg, 0.50 mmol) and thiol **12** (273 mg, 0.75 mmol, 1.2 equiv.) dissolved in toluene (2 ml) were reacted at room temperature according to **General method A**. The residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1 R_f = 0.18) to give an inseparable 4.6:1 mixture of **23a** and **23b** (189 mg, 60%) as a colourless syrup.

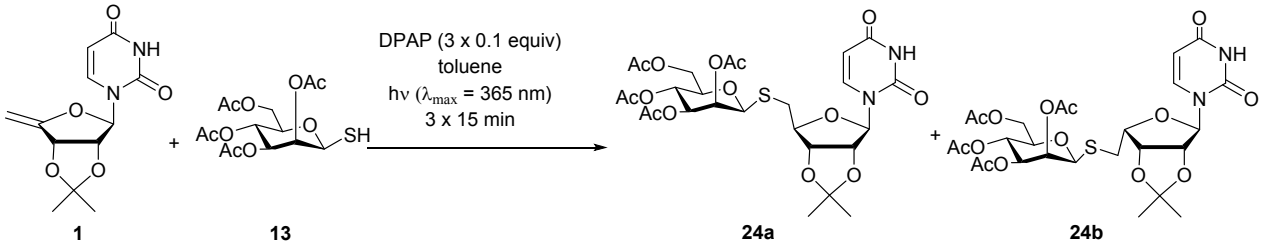
Method II (entry 2)**:**): Exomethylene derivative **1** (133 mg, 0.50 mmol) and thiol **12** (273 mg, 0.75 mmol, 1.2 equiv.) dissolved in a mixture of toluene/MeOH 1/2 (2 ml) were reacted at -80 °C according to **General method C**. The residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1 R_f = 0.18) to give an inseparable 4.6:1 mixture of **23a** and **23b** (246 mg, 78%).

Method III (entry 3)**:**): Exomethylene derivative **1** (133 mg, 0.50 mmol) and thiol **12** (273 mg, 0.75 mmol, 1.2 equiv.) dissolved in toluene (2 ml) were reacted at -80 °C according to **General method C**. The residue was purified by flash column chromatography (CH_2Cl_2/acetone 9/1 R_f = 0.18) to give an inseparable 8:1 mixture of **23a** and **23b** (279 mg, 89%).

NMR data for **23a** (from the spectra of the 8:1 mixture of **23a** and 2**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.20 (s, 1H, N*H*), 7.32 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.76 (dd, *J* = 7.9, 1.6 Hz, 1H, H-5 uracil), 5.62 (d, *J* = 1.7 Hz, 1H, H-1'), 5.39 – 5.33 (m, 3H, 3x Manp skeleton H), 5.26 (d, *J* = 3.3 Hz, 1H, Manp skeleton H), 5.08 (dd, *J* = 6.6, 1.8 Hz, 1H, H-2'), 4.86 (dd, *J* = 6.6, 4.1 Hz, 1H, H-3'), 4.39 (dd, *J* = 9.9, 2.0 Hz, 1H, H-6''a), 4.31 (d, *J* = 4.3 Hz, 1H, H-4'), 4.11 (dd, *J* = 12.3, 1.9 Hz, 1H, H-6''b), 3.10 (dd, *J* = 13.9, 7.1 Hz, 1H, H-5'a), 2.92 (dd, *J* = 14.0, 5.6 Hz, 1H, H-5'b), 2.16 (s, 3H, AcC*H*$_3$), 2.11 (s, 3H, AcC*H*$_3$), 2.06 (s, 3H, AcC*H*$_3$), 1.99 (s, 3H, AcC*H*$_3$), 1.55 (s, 3H, *i*-propylideneC*H*$_3$), 1.36 (s, 3H, *i*-propylideneC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.5, 169.7, 169.6, 169.5 (4C, 4x Ac*C*O), 163.7, 150.0 (2C, 2x *C*O uracil), 142.9 (1C, C-6 uracil), 114.4 (1C, *i*-propylideneC_q), 102.6 (1C, C-5 uracil), 94.9 (1C, C-1'), 86.3, 84.2, 83.3, 82.9, 77.5, 77.2, 76.8, 70.6, 69.2, 68.9, 65.9 (8C, skeletal carbons), 62.0 (1C, C-6''), 33.3 (1C, C-5'), 26.8, 25.0 (2C, 2x *i*-propylidene*C*H$_3$), 20.7, 20.6, 20.5, 20.4 (4C, 4xAc*C*H$_3$). MALDI-TOF MS: *m/z* calcd for $C_{26}H_{34}N_2NaO_{14}S$ $[M+Na]^+$ 653.16, found 653.13. Elemental analysis: calcd (%) for $C_{26}H_{34}N_2O_{14}S$: C 49.52, H 5.43, N 4.44, S 5.08, found C 49.38, H 5.41, N 4.45, S 5.05

2',3'-*O*-Isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-5'-thiouridine (24a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (24b)



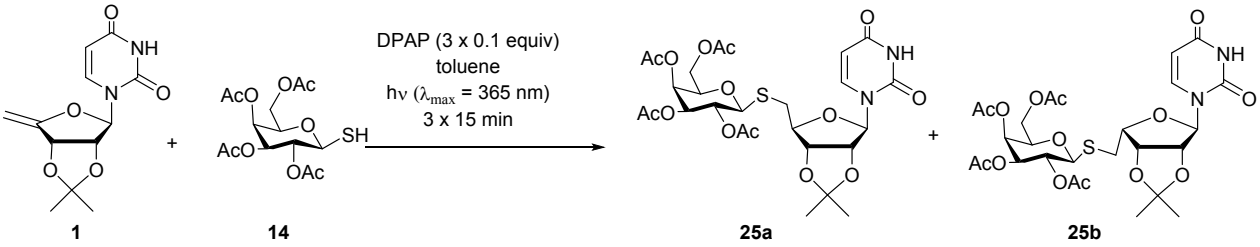
Method I: Exomethylene derivative **1** (133 mg, 0.5 mmol) and thiol **13** (218 mg, 0.6 mmol, 1.2 equiv.) dissolved in toluene (5 ml) and were reacted at room temperature according to **general method A**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.24) to give an inseparable 1.2:1 mixture of **24a** and **24b** (176 mg, 56%).

Method II: Exomethylene derivative **1** (133 mg, 0.5 mmol) and thiol **13** (218 mg, 0.6 mmol, 1.2 equiv.) dissolved in toluene (5 ml) and were reacted at -80 °C according to **general method C**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.24) to give an inseparable 1:1 mixture of **24a** and **24b** (226 mg, 72%).

Method III: Exomethylene derivative **1** (66 mg, 0.25 mmol) and thiol **13** (109 mg, 0.3 mmol, 1.2 equiv.) dissolved in toluene/MeOH 1:2 (3 ml) and were reacted at -80 °C according to **general method C**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.24) to give an inseparable 1:1 mixture of **24a** and **24b** (103 mg, 66%).

MALDI-TOF MS: *m/z* calcd for $C_{26}H_{34}N_2NaO_{14}S$ $[M+Na]^+$ 653.16, found 653.21.

2',3'-*O*-Isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-5'-thiouridine (25a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (25b)



Method I: Exomethylene derivative **1** (133 mg, 0.5 mmol) and thiol **14** (218 mg, 0.6 mmol, 1.2 equiv.) dissolved in toluene (3 ml) and were reacted at room temperature according to **general method A**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.22) to give an inseparable 1:1.6 mixture of **25a** and **25b** (213 mg, 68%).

Method II: Exomethylene derivative **1** (133 mg, 0.5 mmol) and thiol **13** (218 mg, 0.6 mmol, 1.2 equiv.) dissolved in toluene (5 ml) and were reacted at -80 °C according to **general method C**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.22) to give an inseparable 1:1.6 mixture of **25a** and **25b** (253 mg, 80%).

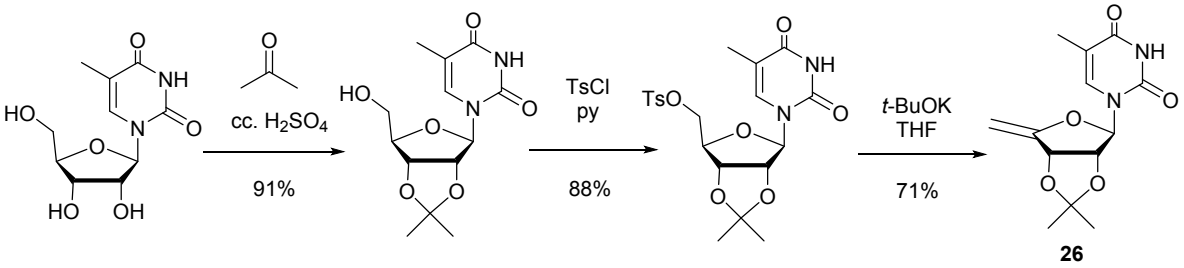
Method III: Exomethylene derivative **1** (66 mg, 0.25 mmol) and thiol **13** (109 mg, 0.3 mmol, 1.2 equiv.) dissolved in toluene/MeOH 1:2 (3 ml) and were reacted at -80 °C according to **general method C**. The residue was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.22) to give an inseparable 1:3 mixture of **25a** and **25b** (123 mg, 78%).

NMR data of **25b** from the 1:3 mixture of **25a** and **25b:**

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.70 (s, 1H, N*H*), 7.25 (d, J = 8.1 Hz, 1H, H-6), 5.72 (d, J = 8.0 Hz, 1H, H-5), 5.44 (d, J = 3.1 Hz, 1H), 5.36 (s, 1H), 5.27 (d, J = 5.9 Hz, 1H), 5.23 (d,

J = 9.9 Hz, 1H), 5.08 (d, *J* = 3.2 Hz, 1H), 5.02 – 4.98 (m, 1H), 4.76 (td, *J* = 6.8, 3.9 Hz, 1H, H-4'), 4.61 (d, *J* = 10.0 Hz, 1H), 4.19 – 4.06 (m, 3H), 3.95 (d, *J* = 6.7 Hz, 1H), 3.11 (dd, *J* = 13.9, 6.7 Hz, 1H, H-5'a), 2.87 (dd, *J* = 13.9, 7.1 Hz, 1H, H-5'b), 2.17 (s, 3H, AcCH_3), 2.07 (s, 3H, AcCH_3), 2.03 (s, 3H, AcCH_3), 1.99 (s, 3H, AcCH_3), 1.51 (s, 3H, *i*-propylideneCH_3), 1.36 (s, 3H, *i*-propylideneCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.6, 170.3, 170.1, 169.6 (4C, 4xAc*C*O), 163.7, 150.9 (2C, 2x uracil*C*O), 143.9 (1C, C-6), 113.1 (1C, *i*-propylideneC_q), 102.4 (1C, C-5), 97.4, 85.4, 84.3, 81.4, 74.3, 71.8, 67.2 (9C, skeletal carbons), 61.1 (1C, C-6''), 29.5 (1C, C-5'), 26.3, 24.8 (2C, 2x*i*-propylidene*C*H_3), 20.8, 20.7, 20.6 (4C, 4xAc*C*H_3). ESI-TOF MS: *m/z* calcd for $C_{26}H_{34}N_2NaO_{14}S$ $[M+Na]^+$ 653.162, found 653.190.

1-(2',3'-*O*-Isopropylidene-β-D-*erythro*-pent-4'-enofuranosyl)-thymine (26)



26

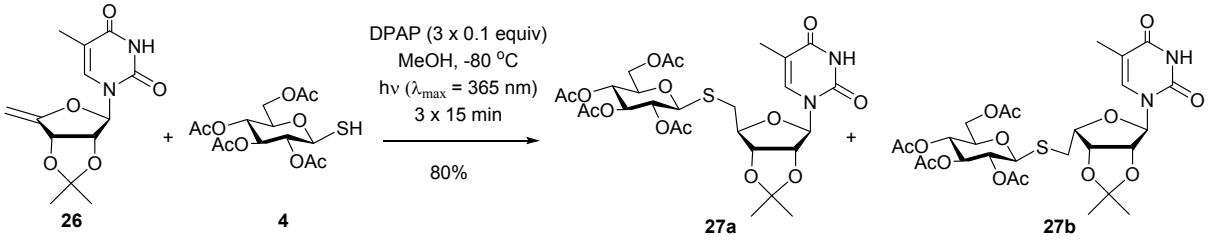
2',3'-*O*-Isopropylidene-5-methyluridine. 5-Methyluridine (2.0 g, 7.75 mmol) was suspended in acetone (50 ml), cooled to 0 °C, and cc. H_2SO_4 (0.5 ml) was added. The reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC (CH_2Cl_2/acetone 1/1, R_f = 0.57). The reaction mixture was neutralized with Et_3N and concentrated in *vacuo*. The residue was purified by flash column chromatography (gradient elution CH_2Cl_2/acetone 7/3→6/4) to yield 2',3'-*O*-isopropylidene-5-methyluridine (2.08 g, 91%) as a white foam.

$[\alpha]_D$= −9.33 (*c* = 0.15, MeOH); R_f = 0.57 (1:1 CH_2Cl_2/acetone); ^{1}H NMR (400 MHz, DMSO) δ (ppm) 11.36 (s, 1H, N*H*), 7.65 (s, 1H, H-6 thymine), 5.84 (d, *J* = 2.8 Hz, 1H, H-1'), 5.09 (t, *J* = 5.2 Hz, 1H, O*H*), 4.88 (dd, *J* = 6.4, 2.9 Hz, 1H, H-2'), 4.76 (dd, *J* = 6.4, 3.7 Hz, 1H, H-3'), 4.04 (q, *J* = 4.2 Hz, 1H, H-4'), 3.65-3.52 (m, 2H, H-5'a and H-5'b), 1.77 (s, 3H, thymine CH_3), 1.48 (s, 3H, *i*-propylidene CH_3), 1.29 (s, 3H, *i*-propylidene CH_3); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 163.8, 150.4 (2C, 2 x *C*O thymine), 137.5 (1C, C-6 thymine), 113.1 (1C, *i*-propylidene C_q), 109.5 (1C, C-5), 90.5 (1C, C-1'), 86.1, 83.5, 80.4 (3C, C-2', C-3', C-4'), 61.3 (1C, C-5'), 27.1, 25.2 (2C, 2 x *i*-propylidene *C*H_3), 12.1 (1C, thymine *C*H_3); MALDI-TOF MS: *m/z* calcd for $C_{13}H_{18}N_2NaO_6$ $[M+Na]^+$ 321.11, found 321.29.

2',3'-*O*-Isopropylidene-5-methyl-5'-*O*-tosyl-uridine. 2',3'-*O*-Isopropylidene-5-methyl-uridine (1.89 g, 2.98 mmol) was dissolved in dry pyridine (10 ml), TsCl (1.13 g, 5.95 mmol, 2 equiv.) was added and the reaction mixture was stirred overnight. The reaction was monitored by TLC (CH_2Cl_2/acetone 7/3, R_f = 0.75). H_2O (4 ml) was added to the reaction mixture and stirred for half an hour. The reaction mixture was concentrated in *vacuo*, the residue was dissolved in EtOAc (200 ml) and extracted with H_2O (3 x 50 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give 2',3'-*O*-isopropylidene-5-methyl-5'-*O*-tosyl-uridine (1.18 g, 88%) as a white solid.
MALDI-TOF MS: *m/z* calcd for $C_{20}H_{24}N_2NaO_8S$ $[M+Na]^+$ 475.12, found 475.49.

1-(2',3'-*O*-Isopropylidene-β-D-*erythro*-pent-4'-enofuranosyl)-thymine (26)[2] 2',3'-*O*-Isopropylidene-5-methyl-5'-*O*-tosyl-uridine (1.18 g, 2.61 mmol) was dissolved in dry THF (9 ml). *t*-BuOK (0.76 g, 6.78 mmol, 2.5 equiv.) was added and the reaction mixture was stirred at room temperature for half an hour. The reaction was monitored by TLC (hexane/acetone 75/25 R_f = 0.27). The reaction mixture was diluted with H_2O (30 ml), neutralized with AcOH, and extracted with CH_2Cl_2 (3 x 90 ml). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated in *vacuo*. The residue was purified by flash column chromatography (hexane/acetone 7/3) to give compound **26**[2] (671 mg, 92%) as a pale white foam.
$[\alpha]_D$= +0.95 (*c* = 0.12, $CHCl_3$); R_f = 0.27 (75:25 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.85 (s, 1H, N*H*), 7.02 (d, *J* = 1.0 Hz, 1H, H-6 thymine), 5.63 (s, 1H, H-1'), 5.34 (d, *J* = 6.2 Hz, 1H, H-2'), 5.06 (d, *J* = 6.2 Hz, 1H, H-3'), 4.56 (d, *J* = 1.7 Hz, 1H, H-5'a), 4.38 (d, *J* = 2.4 Hz, 1H, H-5'b), 1.92 (d, *J* = 0.8 Hz, 3H, thymine C*H*$_3$), 1.52 (s, 3H, *i*-propylidene C*H*$_3$), 1.39 (s, 3H, *i*-propylidene C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.4 (1C, *C*O thymine), 163.0 (1C, C-4'), 150.4 (1C, *C*O thymine), 138.8 (1C, H-6 thymine), 113.9 (1C, *i*-propylidene C_q), 111.3 (1C, C-5 thymine), 86.7 (1C, C-5'), 96.8 (1C, C-1'), 83.1, 79.9 (2C, C-2', C-3'), 26.7, 25.5 (2C, 2 x *i*-propylidene *C*H$_3$), 12.4 (1C, thymine *C*H$_3$); MALDI-TOF MS: *m/z* calcd for $C_{13}H_{16}N_2NaO_5$ $[M+Na]^+$ 303.10, found 303.14.

2',3'-*O*-Isopropylidene-5-methyl-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thio-5-methyluridine (27a) and 1-[2',3'-*O*-isopropylidene-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thio-α-L-lyxofuranosyl]-thymine (27b)

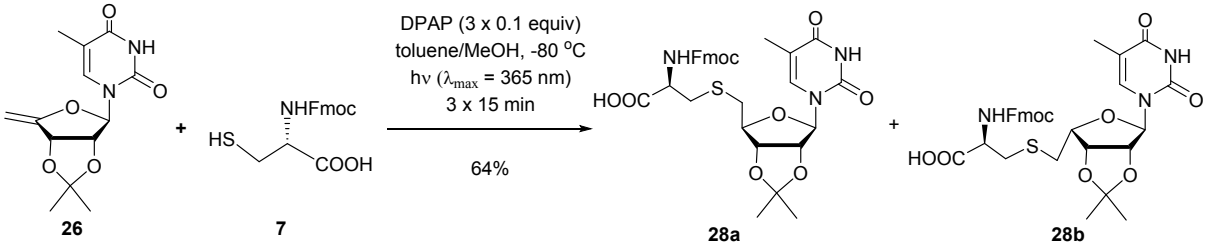


Exomethylene derivative **26** (0.5 mmol, 140 mg) and thiol **4** (273 mg, 0.75 mmol, 1.5 equiv.) dissolved MeOH (4 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (hexane/acetone 7/3 → 6/4) to give an inseparable 1:2.5 mixture of **27a** and **27b** (257 mg, 80%) as a white foam.

NMR data of **27b** (from the spectra of the 1:2.5 mixture of **27a** and **27b**)

R_f = 0.12 (7:3 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.55 (s, 1H, N*H*), 7.05 (s, 1H, H-6 thymine), 5.31 (s, 1H), 5.30 (s, 1H), 5.12-5.06 (m, 1H), 5.26 (t, *J* = 5.6 Hz, 1H), 5.20 (dd, *J* = 9.3, 4.5 Hz, 1H), 5.15-4.99 (m, 3H), 4.70 (td, *J* = 6.8, 3.8 Hz, 1H, H-4'), 4.59 (d, *J* = 10.1 Hz, 1H, H-1"), 4.22 (ddd, *J* = 11.2 Hz, *J* = 6.6 Hz, *J* = 4.4 Hz, 1H, H-6"a), 4.14 (dt, *J* = 12.4 Hz, *J* = 2.5 Hz, 1H, H-6"b), 3.70 (ddd, *J* = 9.9 Hz, *J* = 4.4 Hz, *J* = 2.6 Hz, 1H, H-5"), 3.06 (dd, *J* = 13.9 Hz, *J* = 7.4 Hz, 1H, H-5'a), 2.83 (dd, *J* = 13.8 Hz, *J* = 6.5 Hz, 1H, H-5'b), 2.07 (s, 3H, C*H*$_3$ acetyl), 2.04 (s, 3H, C*H*$_3$ acetyl), 2.01 (s, 3H, C*H*$_3$ acetyl), 1.99 (s, 3H, C*H*$_3$ acetyl), 1.90 (s, 3H, C*H*$_3$ thymine), 1.51 (s, 3H, C*H*$_3$ *i*-propylidene), 1.36 (s, 3H, C*H*$_3$ *i*-propylidene); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.3, 169.5, 169.4 (4C, 4 x CO acetyl), 164.4, 150.9 (2C, 2 x CO thymine), 139.9 (1C, C-6 thymine), 113.1, 110.9 (2C, C_q *i*-propylidene, C-5 thymine), 97.1 (1C, C-1'), 85.6, 85.4, 83.6, 81.4, 75.8, 73.9, 70.0, 68.3 (9C, C-1",2",3",4",5", C-2',3',4'), 62.1 (1C, C-6"), 29.1 (1C, C-5'), 26.4, 24.9 (2C, 2 x *C*H$_3$ *i*-propylidene), 20.8, 20.7, 20.6, 12.3 (4C, 4 x *C*H$_3$ acetyl); ESI-TOF MS for **27ab**: *m/z* calcd for $C_{27}H_{36}N_2NaO_{14}S$ $[M+Na]^+$: 667.178, found: 667.210.

_N_-(9-Fluorenylmethoxycarbonyl)-_S_-[(5'-deoxy-2',3'-_O_-isopropylidene)-5-methyluridine-5'-yl]-cysteine (28a) and 1-[5'-deoxy-2',3'-_O_-isopropylidene-5'(_N_-9-fluorenylmethoxy-carbonyl-_S_-cysteinyl)-α-L-lyxofuranosyl]-thymine (28b)



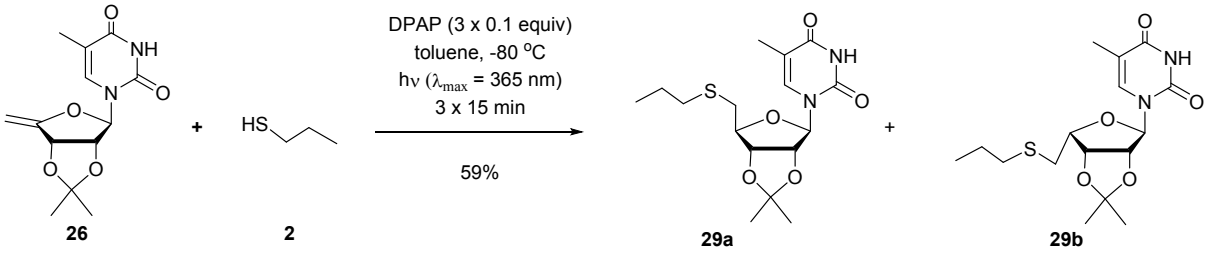
Exomethylene derivative **26** (280 mg, 1.0 mmol,) and thiol **7** (412 mg, 1.2 mmol, 1.2 equiv.) dissolved in MeOH/toluene 6/4 (10 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (gradient elution CH_2Cl_2/MeOH/AcOH 12/0.5/0.05 → 10/0.5/0.05→95/5/0.05) to give an inseparable 5:1 mixture of **28a** and **28b** (399 mg, 64%) as a white solid.

R_f = 0.29 (10:0.5:0.05 CH_2Cl_2/MeOH/AcOH);

NMR data of **28a** (from the spectra of the 5:1 mixture of **28a** and **28b**)

^{1}H NMR (400 MHz, DMSO) δ (ppm) 11.42 (s, 1H), 7.89 (d, J = 7.5 Hz, 2H), 7.78-7.70 (m, 3H), 7.55 (s, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 5.79 (d, J = 1.8 Hz, 1H, H-1'), 5.00 (dd, J = 6.3, 1.8 Hz, 1H, H-2'), 4.79-4.70 (m, 1H), 4.37-4.07 (m, 6H), 3.05 (dd, J = 13.5, 3.9 Hz, 1H), 2.93-2.67 (m, 4H), 2.51 (s, 1H), 2.29 (s, 1H), 1.78 (s, 3H, thymine CH_3), 1.48 (s, 3H, *i*-propylidene CH_3), 1.28 (s, 3H, *i*-propylidene CH_3); ^{13}C NMR (100 MHz, DMSO) δ (ppm) 172.3 (1C, *C*OOH), 156.1 (1C, *C*O Fmoc), 163.9, 150.3 (2C, 2 x *C*O thymine), 143.8, 140.8 (4C, 4 x Fmoc C_q), 138.1 (1C, C-6 thymine), 128.9, 128.2, 127.7, 127.1, 125.3, 120.1 (8C, arom.), 113.5 (1C, *i*-propylidene C_q), 109.8 (1C, C-5), 91.3 (1C, C-1'), 85.5, 83.3, 82.8 (3C, C-2', C-3', C-4'), 65.8 (1C, Fmoc *C*H$_2$), 53.9 (1C, *C*H cys), 46.7 (1C, 9*C*H fluorene), 33.6, 33.3 (2C, 2 x S*C*H$_2$), 27.0, 25.2 (2C, *i*-propylidene *C*H$_3$), 12.0 (1C, thymine *C*H$_3$); MALDI-TOF MS: *m/z* calcd for $C_{31}H_{33}N_3NaO_9$ $[M+Na]^+$ 646.18, found 646.17. Elemental analysis: calcd (%) for $C_{31}H_{33}N_3O_9$: C 59.70, H 5.33, N 6.74, S 5.14, found C 59.60, H 5.31, N 6.70, S 5.12.

2',3'-*O*-Isopropylidene-5-methyl-5'-*S*-*n*-propyl-5'-thio-5-methyluridine (29a) and 1-(2',3'-*O*-isopropylidene-5'-*S*-*n*-propyl-5'-thio-α-L-lyxofuranosyl)-thymine (29b)



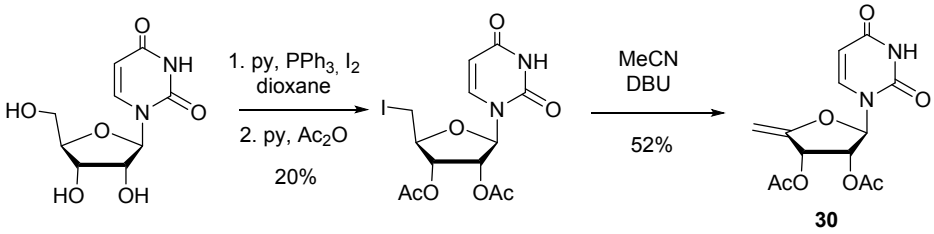
Exomethylene derivative **26** (0.28 mmol, 80 mg) and thiol **2** (1.5 equiv., 0.43 mmol, 38 μl) dissolved toluene (4 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (hexane/acetone 7/3 → 6/4) to give an

inseparable 5:1 mixture of **29a** and **29b** (60 mg, 59%) as a colourless syrup. The reaction was repeated using 3 equiv. of thiol **2** to give **29a** and **29b** (5:1 mixture) in 78% yield.

NMR data of **29a** (from the spectra of the 5:1 mixture of **29a** and **29b**)

R_f = 0.23 (7:3 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.31 (s, 1H, N*H*), 7.17 (d, *J* = 0.6 Hz, 1H, H-6), 5.68 (d, *J* = 2.1 Hz, 1H, H-1'), 4.98 (dd, *J* = 6.6 Hz, *J* = 2.2 Hz, 1H, H-2'), 4.81 (dd, *J* = 6.5 Hz, *J* = 4.2 Hz, 1H, H-3'), 4.25 (dd, *J* = 10.2 Hz, *J* = 5.9 Hz, 1H, H-4'), 2.89-2.84 (m, 2H, H-5'a and H-5'b), 2.56 (t, *J* = 7.3 Hz, 2H, $CH_3CH_2CH_2$), 1.93 (s, 3H, thymine C*H*$_3$), 1.62 (dd, *J* = 14.7 Hz, *J* = 7.3 Hz, 2H, $CH_3CH_2CH_2$), 1.57 (s, 3H, *i*-propylidene C*H*$_3$), 1.35 (s, 3H, *i*-propylidene C*H*$_3$), 0.98 (t, *J* = 7.3 Hz, 3H, PrC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.1, 150.2 (2C, 2 x thymine *C*O), 138.3 (1C, thymine C-6), 114.8 (1C, *i*-propylidene C_q), 111.3 (1C, thymine C-5), 93.9 (1C, C-1'), 86.4, 84.4, 83.2 (3C, C-2', C-3', C-4'), 35.2 (1C, $CH_3CH_2CH_2$), 34.6 (1C, C-5'), 27.3, 25.4 (2C, 2 x *i*-propylidene *C*H$_3$), 23.1 (1C, $CH_3CH_2CH_2$), 13.5 (1C, Pr*C*H$_3$), 12.5 (1C, thymine *C*H$_3$); MALDI-TOF MS for **21ab**: *m/z* calcd for $C_{16}H_{24}N_2NaO_5S$ $[M+Na]^+$ 379.13, found 379.23. Elemental analysis: calcd (%) for $C_{16}H_{24}N_2O_5S$: C 53.92, H 6.79, N 7.86, S 8.99, found : C 53.71, H 6.81, N 7.82, S 8.97.

1-(2',3'-Di-*O*-acetyl-β-D-*erythro*-pent-4'-enofuranosyl)-uracil (30)



2',3'-Di-*O*-acetyl-5'-deoxy-5'-iodouridine. Uridine (5.00 g, 20.5 mmol) was dissolved in dioxane (150 ml). Pyridine (3.32 ml, 41 mmol, 2 equiv.), PPh_3 (8.07 g, 30.75 mmol, 1.5 equiv.) and I_2 (7.8 g, 30.75 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at room temperature overnight. The next day, MeOH (8 ml) and saturated aq. $Na_2S_2O_3$ solution (4.77 ml) were added and the reaction mixture was evaporated under reduced pressure. The crude product was dissolved in dry pyridine (50 ml), Ac_2O (9.67 ml, 102.3 mmol, 5 equiv.) was added and the reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC ($CHCl_3$/MeOH 12/0.5) Th next day, the reaction mixture was evaporated in *vacuo*. The residue was dissolved in $CHCl_3$ (100 ml) and

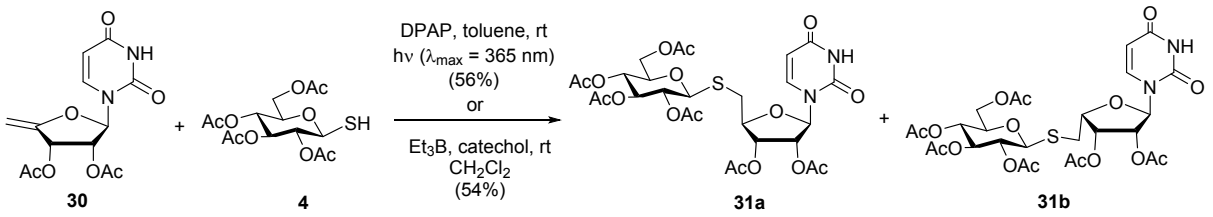
extracted with 0.5 M HCl solution (50 ml). The inorganic phase was extracted with $CHCl_3$ (100 ml). The combined organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography ($CHCl_3$/MeOH 25/1) to give 2',3'-di-*O*-acetyl-5'-deoxy-5'-iodouridine (1.79 g, 20%).

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 7.57 (d, J = 8.2 Hz, 1H, H-6 uracil), 6.08 (d, J = 6.2 Hz, 1H, H-1'), 5.85 (dd, J = 8.1 Hz, J = 1.7 Hz, 1H, H-5 uracil), 5.38 (t, J = 6.4 Hz, 1H), 5.22 (dd, J = 6.5 Hz, J = 4.4 Hz, 1H), 4.08 (q, J = 4.3 Hz, 1H), 3.52 (d, J = 4.3 Hz, 2H), 2.12 (2s, 2 x 3H, 2 x Ac CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 169.6, 169.5 (2C, 2 x Ac *C*O), 162.9, 150.3 (2C, 2 x uracil *C*O), 140.2 (1C, C-6 uracil), 103.6 (1C, C-5 uracil), 87.0 (1 C, C-1'), 80.5, 73.1, 72.2 (3C, C-2', C-3', C-4'), 20.5, 20.3 (2C, 2 x Ac *C*H$_3$), 5.6 (1C, C-5').

1-(2',3'-Di-*O*-acetyl-β-D-*erythro*-pent-4'-enofuranosyl)-uracil (30).[3] 2',3'-Di-*O*-acetyl-5'-deoxy-5'-iodouridine (1.9 g, 3.3 mmol) was dissolved in MeCN (15 ml), cooled to 0 °C and DBU (1.34 ml, 10.8 mmol, 2.5 equiv.) was added. The reaction mixture was stirred under an Ar atmosphere overnight. The reaction was monitored by TLC ($CHCl_3$/MeOH 12/0.5 R_f =0.22). Next day the reaction mixture was neutralized with AcOH and concentrated in *vacuo*. The residue was dissolved in $CHCl_3$ (150 ml) and extracted with saturated aq. $NaHCO_3$ solution (3 x 50 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash column chromatography ($CHCl_3$/MeOH 12/0.1) to give 1-(2',3'-di-*O*-acetyl-β-D-*erythro*-pent-4'-enofuranosyl)-uracil **22**[3] (699 mg, 52%).

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 9.68 (s, 1H, NH), 7.22 (d, J = 8.1 Hz, 1H, H-6 uracil), 6.27 (d, J = 5.7 Hz, 1H), 5.86 (d, J = 5.4 Hz, 1H), 5.84 (d, J = 7.9 Hz, 1H, H-5 uracil), 5.40 (t, J = 5.7 Hz, 1H,), 4.71 (d, J = 2.6 Hz, 1H), 4.48 (d, J = 2.7 Hz, 1H), 2.16 (s, 3H, Ac CH_3), 2.11 (s, 3H, Ac CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 169.8, 169.6 (2C, 2 x Ac *C*O), 163.0, 150.4 (2C, 2 x uracil *C*O), 156.2 (1C, C-4'), 139.2 (1C, C-6 uracil), 104.0 (1C, C-5 uracil), 90.1 (1C, C-5'), 88.1, 72.6 (1C, C-1'), 69.4 (2C, C- 2', C-3'), 20.7, 20.5 (2C, 2x Ac *C*H$_3$).

2',3'-Di-*O*-acetyl-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thiouridine (31a) and [1-(2',3'-di-*O*-acetyl-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (31b)



Methdod I (UV-light initiated reaction): Exomethylene derivative **30** (0.29 mmol, 90 mg) and thiol **4** (1.5 equiv., 158 mg, 0.43 mmol) dissolved in toluene (5 ml) were reacted according to **General method A**. The residue was purified by flash column chromatography ($CHCl_3$/MeOH 98/2, R_f = 0.15) to give a 1.1:1 mixture of **31a** and **31b** (109 mg, 56%).

Methdod II (Et_3B-catechol mediated reaction): Exomethylene derivative **30** (0.24 mmol, 75 mg) and thiol **4** (1.5 equiv., 131 mg, 0.36 mmol) dissolved in CH_2Cl_2 (5.0 ml) were reacted at rt according to **General method B**. The crude product was purified by flash column chromatography (hexane/acetone 6/4 R_f = 0.15) to give a 1.1:1 mixture of **31a** and **31b** (87 mg, 54%). Further flash column chromatographic separation ($CHCl_3$/MeOH 99/1) provided pure **31a** (R_f = 0.12) and **31b** (R_f = 0.11).

Data for **31a**

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.84 (s, 1H, N*H*), 7.45 (d, J = 8.2 Hz, 1H, H-6 uracil), 6.02 (d, $J_{1',2'}$ = 5.9 Hz, 1H, H-1'), 5.82 (dd, J = 8.1 Hz, J = 2.0 Hz, 1H, H-5 uracil), 5.39-5.34 (m, 2H, H-2', H-3'), 5.24 (t, $J_{2'',3'';3'',4''}$ = 9.4 Hz, 1H, H-3''), 5.09 (t, $J_{3'',4'';4'',5''}$ = 9.8 Hz, 1H, H-4''), 5.04 (t, $J_{1'',2'';2'',3''}$ = 9.6 Hz, 1H, H-2''), 4.53 (d, J = 9.9 Hz, 1H, H-1''), 4.33 (q, J = 4.4 Hz, 1H, H-4'), 4.24 (dd, J = 12.4 Hz, J = 4.9 Hz, 1H, H-6''a), 4.14 (dd, J = 12.4 Hz, J = 2.1 Hz, 1H, H-6''b), 3.76 (ddd, J = 10.0 Hz, J = 4.8 Hz, J = 2.2 Hz, 1H, H-5''), 3.06 (qd, J = 14.2 Hz, J = 4.6 Hz, 2H, H-5'a,b), 2.12, 2.08, 2.03, 2.02 (4 x s, 18H, 6 x Ac *C*H$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.2, 169.7, 169.6, 169.5 (6C, 6 x Ac *C*O), 162.7, 150.3 (2C, 2 x *C*O uracil), 139.4 (1C, C-6 uracil), 103.7 (1C, C-5 uracil), 86.9 (1C, C-1'), 82.1 (1C, C-1''), 81.8 (1C, C-4'), 76.4 (1C, C-5''), 73.7 (1C, C-3''), 72.4, 72.1 (2C, C-2', C-3'), 69.6 (1C, C-2''), 68.3 (1C, C-4''), 62.2 (1C, C-6''), 30.9 (1C, C-5'), 20.8, 20.7, 20.6, 20.5 (6C, 6 x Ac *C*H$_3$); MALDI-TOF MS: *m/z* calcd for $C_{27}H_{34}N_2NaO_{16}S$ $[M+Na]^+$ 697.15, found 697.32.

Elemental analysis: calcd (%) for $C_{27}H_{34}N_2O_{16}S$: C 48.07, H 5.08, N 4.15, S 4.75, found : C 48.23, H 5.06, N 4.16, S 4.77

Data for **31b**

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63 (s, 1H, N*H*), 7.41 (d, J = 8.1 Hz, 1H, H-6 uracil), 5.98 (d, $J_{1',2'}$ = 6.9 Hz, 1H, H-1'), 5.79 (dd, J = 8.1 Hz, J = 1.8 Hz, 1H, H-5 uracil), 5.73 (dd, $J_{1',2'}$ = 6.9 Hz, $J_{2',3'}$ = 4.6 Hz, 1H, H-2'), 5.62-5.60 (m, 1H, H-3), 5.21 (t, $J_{2'',3'';3'',4''}$ = 9.3 Hz, 1H, H-3''), 5.11 (t, $J_{3'',4'';4'',5''}$ = 9.8 Hz, 1H, H-4''), 4.99 (t, $J_{1'',2'';2'',3''}$ = 9.6 Hz, 1H, H-2''), 4.89 (td, J = 7.2 Hz, J = 3.1 Hz, 1H, H-4'), 4.53 (d, $J_{1'',2''}$ = 10.0 Hz, 1H, H-1''), 4.41 (dd, J = 12.5 Hz, J = 2.1 Hz, 1H, H-6''a), 4.12 (dd, J = 12.5 Hz, J = 3.8 Hz, 1H, H-6''b), 3.72-3.68 (m, 1H, H-5''), 2.95-2.81 (m, 2H, H-5'a,b), 2.18, 2.13, 2.05, 2.01 (4 x s, 18H, 6 x Ac CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.3, 169.7, 169.6, 169.5 (6C, 6 x Ac *C*O), 162.7, 150.4 (2C, 2 x *C*O uracil), 140.7 (1C, C-6 uracil), 103.5 (1C, C-5 uracil), 88.6 (1C, C-1'), 83.8 (1C, C-1''), 80.7 (1C, C-4'), 76.2 (1C, C-5''), 74.0 (1C, C-2'), 73.7 (1C, C-3''), 71.8 (1C, C-3'), 69.8 (1C, C-2''), 68.1 (1C, C-4''), 61.3 (1C, C-6''), 29.1 (1C, C-5'), 20.9, 20.8, 20.7, 20.6, 20.5 (6C, 6 x Ac *C*H_3). Elemental analysis: calcd (%) for $C_{27}H_{34}N_2O_{16}S$: C 48.07, H 5.08, N 4.15, S 4.75, found : C 47.33, H 5.05, N 4.17, S 4.71

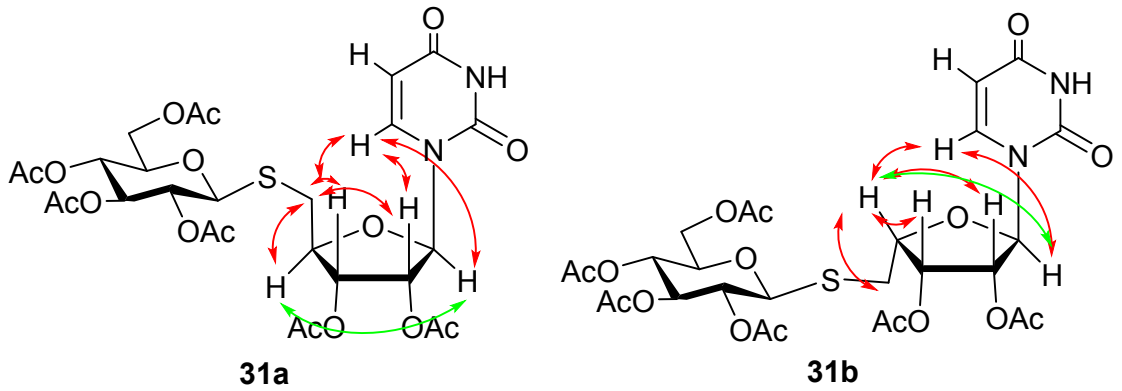
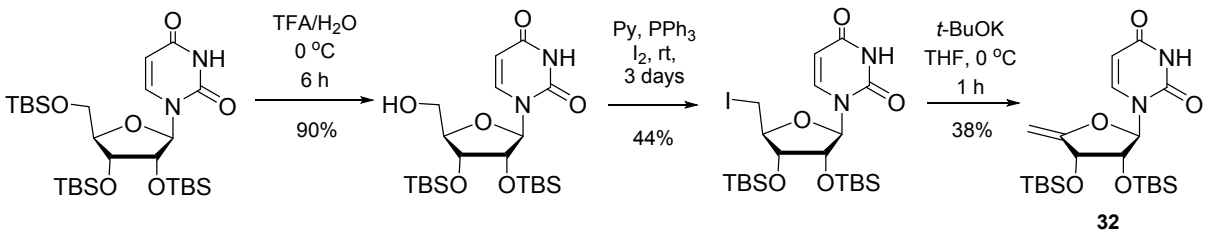


Figure S2. ROESY through-space connectivities observed in the ROESY spectra of **31a** and **31b**. Red arrows: strong RO effects, green arrows: weak RO effects.

1-[2',3'-Di-*O*-(*tert*-butyldimethylsilyl)-β-D-*erythro*-pent-4'-enofuranosyl]-uracil (26)



2',3'-Di-*O*-(*tert*-butyldimethylsilyl)uridine. 2',3',5'-tris-*O*-(*tert*-butyldimethylsilyl)uridine[4](4.4 g, 7.5 mmol) was dissolved in THF (80 ml). A mixture of

TFA (20 ml) and H_2O (20 ml) was added and the reaction mixture was stirred under an Ar athmosphere at 0 °C for 6h. The reaction was monitored by TLC (hexane/acetone 8/2 R_f =0.22). The reaction mixture was diluted with aq. saturated $NaHCO_3$ solution (300 ml) and extracted with EtOAc (2 x 150 ml). The combined organic phase was extracted with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/acetone 8/2) to yield 2',3'-di-*O*-(*tert*-butyldimethylsilyl)uridine (3.2 g, 90%).

$[\alpha]_D$: −27.56 (*c* = 0.08, $CHCl_3$); R_f = 0.22 (8:2 hexane/acetone); ^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 8.74 (s, 1H, N*H*), 7.73 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.84 (d, *J* = 8.0, 1H, H-5 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-5'a), 3.86-3.81 (m, 1H, H-5'b), 3.12 (d, *J* = 4.7 Hz, 1H, O*H*), 1.03, 0.99 (2 x s, 18H, 2 x *t*-Bu-CH_3), 0.21, 0.20, 0.18, 0.15 (4 x s, 12H, 4 x SiCH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 163.9, 150.6 (2C, 2 x uracil CO), 143.1 (1C, C-6 uracil), 102.1 (1C, C-5 uracil), 93.6 (1C, C-1'), 86.0, 74.0, 71.6 (3C, C-2', C-3', C-4'), 61.5 (1C, C-5'), 26.0, 25.9 (6C, 2 x SiC(CH_3)$_3$), 18.2, 18.1 (2C, 2 x *t*-BuC_q); MALDI-TOF-MS: *m/z* calcd for $C_{21}H_{40}N_2NaO_6Si_2$ [M+Na]+ 495.23, found 495.33.

5'-Deoxy-5'-iodo-2',3'-di-*O*-(*tert*-butyldimethylsilyl)uridine. 2',3'-di-*O*-(*tert*-butyldimethylsilyl)uridine (2.84 g, 6 mmol) and PPh_3 (2.3 g, 9 mmol, 1.5 equiv.) were dissolved in a mixture of pyridine (0.96 ml, 12 mmol, 2 equiv.) and 1,4-dioxane (70 ml). I_2 (2.3 g, 9 mmol, 1.5 equiv.) was added and the reaction mixture was stirred under an Ar atmosphere at room temperature. The reaction was monitored by TLC (hexane/acetone 8/2 R_f = 0.30). Since the conversion was not complete further I_2 (0.76 g, 3 mmol, 0.5 equiv.) and PPh_3 (0.76 g, 3 mmol, 0.5 equiv.) were added the next day. On the third day, MeOH (3.2 ml) was added and the solids were filtered off. 10% aq. $Na_2S_2O_3$ solution (480 ml) was added to the filtrate, and extracted with EtOAc (3 x 250 ml). The combined organic phase was extracted with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/acetone 85/15) to give 5'-deoxy-5'-iodo-2',3'-di-*O*-(*tert*-butyldimethylsilyl)uridine (1.54 g, 44%)

$[\alpha]_D$: +4.47 (*c* = 0.09, $CHCl_3$); R_f = 0.30 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.78 (s, 1H, N*H*), 7.72 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.92 (dd, *J* = 8.0, 1.0 Hz, 1H, H-5 uracil), 5.79 (d, *J* = 4.5 Hz, 1H, H-1'), 4.60 (t, *J* = 4.5 Hz, 1H, H-2'), 4.14 (q, *J* = 4.8 Hz, 1H, H-4'), 4.08 (t, *J* = 4.4 Hz, 1H, H-3'), 3.67 (dd, *J* = 11.1 Hz, *J* = 5.3 Hz, 1H, H-5'a), 3.49 (dd, *J* = 11.1 Hz, *J* = 4.8 Hz, 1H, H-5'b), 1.06 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu), 0.29 (s, 3H,

SiCH_3), 0.26 (s, 3H, SiCH_3), 0.21 (2 x s, 2x 3H, 2 x SiCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.0, 150.7 (2C, 2 x uracil *C*O), 142.2 (1C, C-6 uracil), 102.9 (1C, C-5 uracil), 92.4 (1C, C-1'), 83.3, 75.4, 74.6 (3C, C-2', C-3', C-4'), 26.4, 26.3 (6C, 2 x SiC(CH_3)$_3$), 18.6 (2C, 2 x *t*-BuC_q), 6.8 (1C, C-5'), −3.6, −3.7, −4.0, −4.2 (4C, 4 x SiCH_3).

1-[2',3'-Di-*O*-(*tert*-butyldimethylsilyl)-β-D-*erythro*-pent-4'-enofuranosyl]-uracil (32).[5]

5'-Deoxy-5'-iodo-2',3'-di-*O*-(*tert*-buthyldimethylsilyl)uridine (750 mg, 1.29 mmol) was dissolved in dry THF (10 ml). The reaction mixture was cooled to 0 °C and *t*-BuOK (375.5 mg, 3.35 mmol, 2.5 equiv.) was added. The reaction was monitored by TLC (hexane/acetone 7/3 R_f = 0.44). After 1 hour, the reaction mixture was diluted with H_2O (30 ml), neutralized with AcOH and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated in *vacuo*. The crude product was purified by flash column chromatography (hexane/acetone 8/2) to give 1-[2',3'-di-*O*-(*tert*-butyldimethylsilyl)-ß-D-*erythro*-pent-4'-enofuranosyl]-uracil (224 mg, 38%).

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) 9.26 (s, 1H, N*H*), 7.26 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 6.14 (d, *J* = 5.2 Hz, 1H, H-1'), 5.87 (dd, *J* = 8.1, 2.1 Hz, 1H, H-5 uracil), 4.62 (d, *J* = 2.3 Hz, 1H, H-5'a), 4.42 (d, *J* = 4.2 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H, H-5'b), 4.31-4.23 (m, 1H), 1.00 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu), 0.19 (2 x s, 6H, 2 x SiCH_3), 0.13 (s, 3H, SiCH_3), 0.11 (s, 3H, SiCH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) 160.5, 150.0 (2C, 2 x uracil *C*O), 139.4 (1C, C-6 uracil), 103.1 (1C, C-5 uracil), 87.0 (1C, C-5'), 90.0 (1C, C-1'), 75.2, 71.9 (2C, C-2', C-3'), 25.8, 25.7 (6C, 2 x SiC(CH_3)$_3$), 18.2, 18.0 (2C, 2 x *t*-BuC_q), −4.5, −4.4, −4.6, −4.9 (4C, 4 x SiCH_3).

2',3'-Di-*O*-*tert*-butyldimethylsilyl-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thiouridine (33a) and 1-[2',3'-di-*O*-*tert*-butyldimethylsylil-5'-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-5'-thio-α-L-lyxofuranosyl]-uracil (33b)

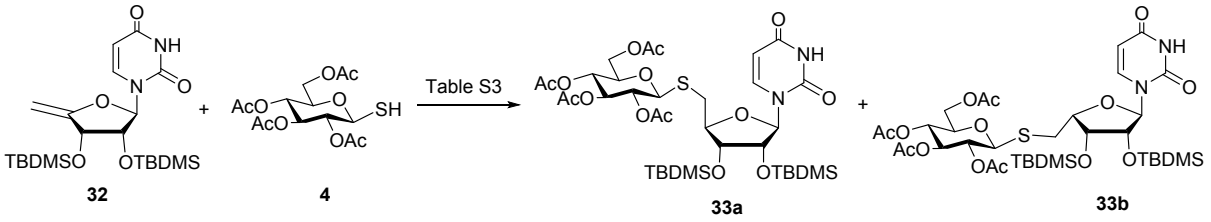


Table S3. Free radical addition of 1-thioglucose peracetate to **26** upon various initiation methods

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : L-*lyxo*[a]	Yield (%)[b]
1	1.5 equiv.	DPAP, hν	toluene	rt.	3×15 min	1:3.7	77
2	1.5 equiv.	Et_3B, catechol	CH_2Cl_2	rt.	4 h	1:3.5	82
3	1.2 equiv.	DPAP, hν	toluene	−80 °C	3×15 min	1:6	98

[a] Ratio determined by ^{1}H NMR; [b]overall yield of products isolated by flash column chromatography.

UV-light initiated reactions:

Entry 1: Exomethylene derivative **32** (0.25 mmol, 113 mg) and thiol **4** (1.5 equiv., 137 mg, 0.375 mmol) dissolved in toluene (5 ml) were reacted at rt according to **General method A**. The residue was purified by flash column chromatography (hexane/acetone 8/2 R_f = 0.20) to give a ~1:3.7 mixture of **33a** and **33b** (158 mg, 77%). Pure compound **33b** was isolated by give a ~1:3.7 mixture of **33a** and **33b** (158 mg, 77%). Pure compound **33b** was isolated by a second flash column chromatographc purification in a hexane/acetone 9/1 eluent.

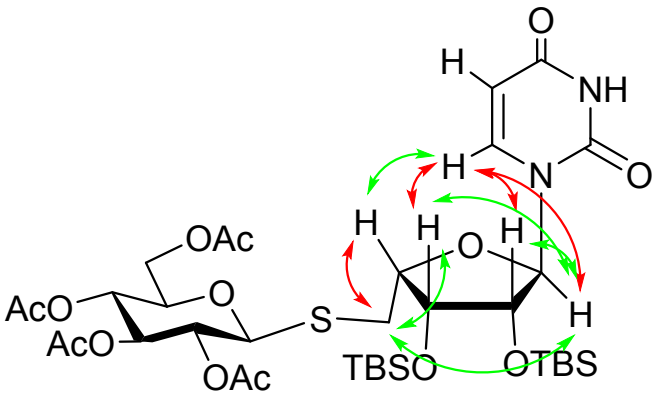
Entry 3: Exomethylene derivative **32** (0.25 mmol, 113 mg) and thiol **4** (1.2 equiv., 110 mg, 0.3 mmol) dissolved in toluene (5 ml) were reacted at rt according to **General method C**. The residue was purified by flash column chromatography (hexane/acetone 8/2 R_f = 0.20) to give a 1:6 mixture of **33a** and **33b** (201 mg, 98%).

Et_3B-catechol mediated reaction (Entry 2): Exomethylene derivative **32** (0.25 mmol, 113 mg) and thiol **4** (1.5 equiv., 137 mg, 0.375 mmol) dissolved in abs. CH_2Cl_2 (5.0 ml) were reacted at rt according to **General method B**. The crude product was purified by flash column chromatography to give a ~1:3.5 mixture of **33a** and **33b** (168 mg, 82%)

Data of **33b (**L-lyxo derivative)

$[\alpha]_D$ = −29.5 (*c* = 0.17; $CHCl_3$); R_f = 0.20 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.32 (s, 1H, N*H*), 7.34 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.74 (dd, *J* = 8.1 Hz, *J* = 2.1 Hz, 1H, H-5 uracil), 5.62 (d, *J* = 5.8 Hz, 1H, H-1'), 5.21 (t, *J* = 9.3 Hz, 1H, H-3"), 5.11 (t, *J* = 9.7 Hz, 1H, H-4"), 5.02 (t, *J* = 9.6 Hz, 1H, H-2"), 4.67-4.61 (m, 1H, H-2'), 4.60-4.57 (m, 1H, H-4'), 4.54 (d, *J* = 10.1 Hz, 1H, H-1"), 4.31 (dd, *J* = 12.5 Hz, *J* = 2.2 Hz, 1H, H-6"a), 4.20-4.16 (m, 2H, H-3, H-6"b), 3.69 (ddd, *J* = 10.0 Hz, *J* = 3.7 Hz, *J* = 2.5 Hz, 1H, H-5"), 3.01 (dd, *J* = 14.0 Hz, *J* = 6.5 Hz, 1H, H-5'a), 2.82 (dd, *J* = 14.0 Hz, *J* = 7.0 Hz, 1H, H-5'b), 2.09, 2.05, 2.04, 2.01 (4 x s, 12H, 4 x Ac C*H*$_3$), 0.94, 0.86 (2 x s, 18H, 6 x *t*-Bu C*H*$_3$), 0.15, 0.12, 0.06, 0.01 (4 x s, 12H, 4 x C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.3, 169.6, 169.5 (4C, 4 x Ac *C*O), 162.9, 150. 0 (2C, 2 x *C*O uracil), 142.1 (1C, C-6 uracil), 102.5 (1C, C-5

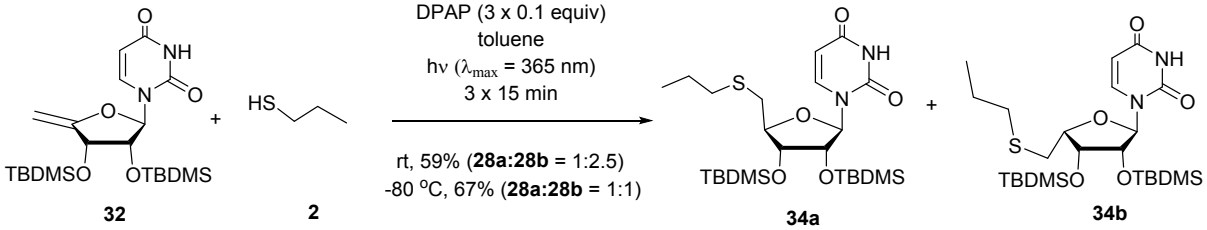
uracil), 92.7 (1C, C-1'), 84.3 (1C, C-1"), 81.9 (1C, C-4'), 76.2 (1C, C-5"), 75.8 (1C, C-2'), 74.0 (1C, C-3"), 73.3 (1C, C-3'), 70.0 (1C, C-2"), 68.3 (1C, C-4"), 61.6 (1C, C-6"), 30.4 (1C, C-5'), 26.1, 26.0 (6C, 6 x *t*-Bu CH_3), 21.0, 20.8, 20.7 (4C, 4 x Ac CH_3), 18.5, 18.2 (2C, 2 x *t*-Bu C_q), −3.9, −4.3, −4.8 (4C, 4 x CH_3); ESI-TOF MS: *m/z* calcd for $C_{35}H_{58}N_2NaO_{14}SSi_2$ $[M+Na]^+$ 841,304, found 841.303.



33b

Figure S3. ROESY through-space connectivities observed in the ROESY spectra of **33b**. Red arrows: strong RO effects, green arrows: weak RO effects.

2',3'-Di-*O*-*tert*-butyldimethylsilyl-5'-*S*-*n*-propyl-5'-thiouridine (34a) and 1-(2',3'-di-*O*-*tert*-butyldimethylsylil-5'-*S*-*n*-propyl-5'-thio-α-L-lyxofuranosyl)-uracil (34b)



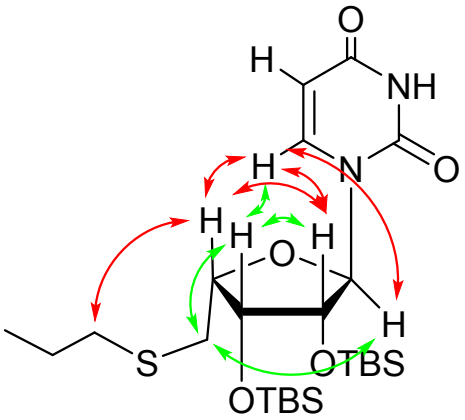
Method I. Exomethylene derivative **32** (91 mg, 0.2 mmol) and 1-propanethiol **2** (3 equiv., 0.6 mmol, 55 µl) dissolved in toluene (5 ml) were reacted at rt according to **General method A** using three irradiation cycles. The reaction was monitored by TLC (hexane/acetone 6/4, R_f = 0.50). The crude product was purified by flash column chromatography (hexane/acetone 85/15) to give a mixture of **34a** and **34b** with a 1:2.5 ratio (62 mg, 59%). Pure **34b** was obtained by a second flash column chromatography (gradient elution hexane/acetone 95/5→9/1→85/15).

Method II. Exomethylene derivative **32** (50 mg, 0.11 mmol) and 1-propanethiol **2** (2 equiv., 0.22 mmol, 21 µl) dissolved in toluene (0.5 ml) were reacted at rt according to **General method C** using three irradiation cycles. The reaction was monitored by TLC

(hexane/acetone 6/4, R_f = 0.50). The crude product was purified by flash column chromatography (hexane/acetone acetone 8/2) to give a mixture of **34a** and **34b** with a 1:1 ratio (40 mg, 67%)

Data of **34b**

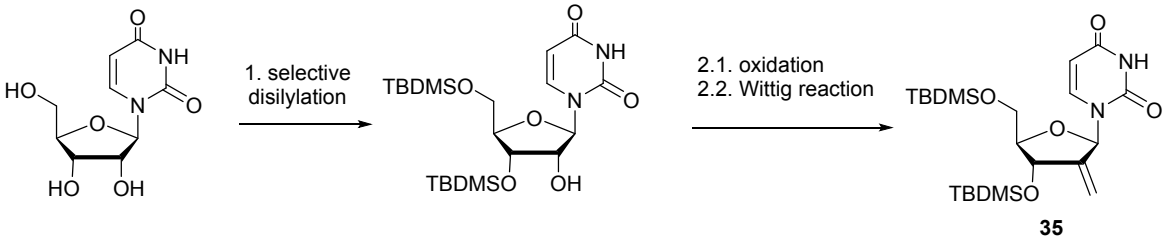
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.93 (s, 1H, N*H*), 7.20 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.74 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H, H-5 uracil), 5.50 (d, *J* = 5.3 Hz, 1H, H-1'), 4.66 (dd, *J* = 5.3 Hz, *J* = 3.8 Hz, 1H, H-2'), 4.45 (td, *J* = 6.7 Hz, *J* = 3.6 Hz, 1H, H-4'), 4.18 (t, *J* = 3.7 Hz, 1H, H-3'), 2.79 (d, *J* = 6.7 Hz, 2H, H-5'a,b), 2.55 (ddd, *J* = 8.1 Hz, *J* = 7.1 Hz, *J* = 2.2 Hz, 2H, SCH_2 propyl), 1.62 (ddd, *J* = 14.6 Hz, *J* = 7.2 Hz, *J* = 2.1 Hz, 2H, CH_2 propyl), 0.99 (t, *J* = 7.3 Hz, *J* = 6.5 Hz, 3H, CH_3 propyl), 0.93, 0.89 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.14, 0.11, 0.06, 0.02 (4 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.4, 150. 0 (2C, 2 x *C*O uracil), 142.2 (1C, C-6 uracil), 102.3 (1C, C-5 uracil), 94.1 (1C, C-1'), 82.4 (1C, C-4'), 75.4 (1C, C-2'), 73.3 (1C, C-3'), 34.9 (1C, SCH_2 propyl), 31.7 (1C, C-5'), 26.1, 26.0 (6C, 6 x *t*-Bu *C*H_3), 23.1 (1C, *C*H_2 propyl), 18.5, 18.2 (2C, 2 x *t*-Bu C_q), 13.6 (1C, *C*H_3 propyl), −4.0, −4.3, −4.4, −4.8 (4C, 4 x *C*H_3); ESI-TOF MS: *m/z* calcd for $C_{24}H_{46}N_2NaO_5SSi_2$ $[M+Na]^+$ 553.256, found 553.255.



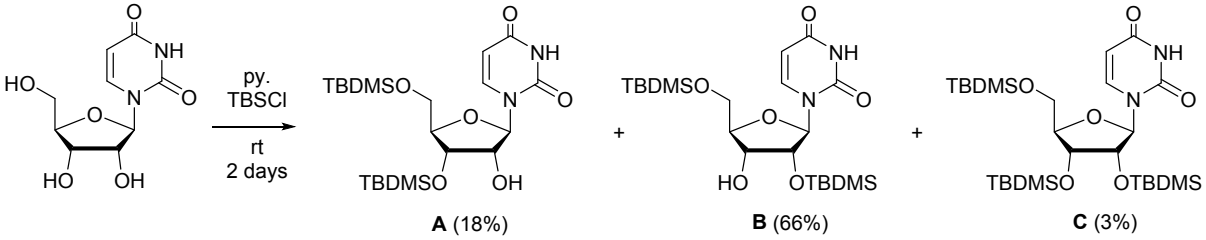
34b

Figure S4. ROESY through-space connectivities observed in the ROESY spectra of **34b**. Red arrows: strong RO effects, green arrows: weak RO effects.

2'-Deoxy-2'-methylene-3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (35)



1. Selective disilylation of uridine[6]



Uridine (6.0 g, 24.6 mmol) was dissolved in dry pyridine (50 ml), and TBDMSCl (11.1 g, 73.6 mmol, 3 equiv.) was added. The reaction mixture was stirred at room temperature for 2 days. The reaction was monitored by TLC (hexane/EtOAc 7/3, R_{fA} = 0.12, R_{fB} = 0.36, R_{fC} = 0.57) The solvent was evaporated in *vacuo*, the residue was dissolved in CH_2Cl_2 (500 ml) and extracted with 10% aq. $NaHSO_4$ solution (2 x 200 ml) and saturated aq. $NaHCO_3$ solution (1 x 100 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The resuidue was purified by flash column cromatography (gradient elution, hexane/acetone: 8/2→75/25→7/3→1/1) to give white foams of 2',3',5'-tri-*O*-(*tert*-butyldimethylsilyl)uridine (410 mg, 2.8%), 2',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (7.70 g, 66.4%) and 3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (2.07 g, 17.8%).

3',5'-Di-*O*-(*tert*-butyldimethylsilyl)uridine (A)

$[\alpha]_D$: −1.58 (*c* = 0.19, $CHCl_3$,); R_{fA} = 0.12 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.75 (s, 1H, N*H*), 7.79 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.94 (d, *J* = 4.4 Hz, 1H, H-1'), 5.66 (d, *J* = 8.1 Hz, 1H, H-5 uracil), 4.24 (t, *J* = 4.9 Hz, 1H, H-2'), 4.04 (dt, *J* = 8.6 Hz, *J* = 3.7 Hz, 2H, H-3', H-4'), 3.93 (dd, *J* = 11.6 Hz, *J* = 2.3 Hz, 1H, H-5'a), 3.72 (dd, *J* = 11.6 Hz, *J* = 1.9 Hz, 1H, H-5'b), 3.18 (d, *J* = 6.9 Hz, 1H), 0.90 (s, 18H, 2 x *t*-Bu), 0.12, 0.11 (2 x s, 2 x 3H, 2 x SiCH_3), 0.08 (s, 6H, 2 x SiCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.5, 150.7 (2C, 2 x uracil *C*O), 140.0 (1C, C-6 uracil), 102.5 (1C, C-5 uracil), 89.2 (1C, C-1'), 84.9, 75.4, 70.9 (3C, C-2', C-3', C-4'), 62.1 (1C, C-5'), 25.9, 25.7 (6C, 2 x SiC(CH_3)$_3$), 18.4, 18.1 (2C, 2 x *t*-BuC_q), −4.7, −5.5 (4C, 4 x SiCH_3); MALDI-TOF MS: *m/z* calcd for $C_{21}H_{40}N_2NaO_6Si_2$ $[M+Na]^+$ 495.23, found 495.26.

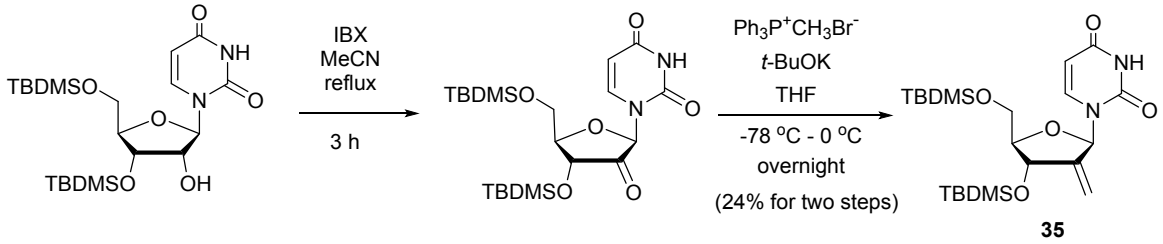
2',5'-Di-*O*-(*tert*-butyldimethylsilyl)uridine (B)

$[\alpha]_D$: +13.57 (*c* = 0.14, $CHCl_3$); R_{fB} = 0.36 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.80 (s, 1H, N*H*), 7.99 (d, *J* = 8.2 Hz, 1H, H-6 uracil), 5.97 (d, *J* = 4.0 Hz, 1H, H-1'), 5.70 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 1H, H-5 uracil), 4.20 (t, *J* = 4.3 Hz, 1H, H-2'), 4.13 (dd, *J* = 6.2 Hz, *J* = 3.5 Hz, 1H), 4.10 (t, *J* = 3.4 Hz, 1H,), 4.00 (dd, *J* = 11.7 Hz, *J* = 1.7 Hz, 1H, H-5'a), 3.82 (dd, *J* = 11.7 Hz, *J* = 1.4 Hz, 1H, H-5'b), 2.67 (d, *J* = 5.4 Hz, 1H, O*H*), 0.93 (s, 9H, *t*-Bu), 0.90 (s, 9H, *t*-Bu), 0.14 (s, 3H, SiCH_3), 0.12 (s, 6H, 2 x SiCH_3), 0.09 (s, 3H, SiCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.6, 150.5 (2C, 2 x uracil *C*O), 140.1 (1C, C-6 uracil), 102.3 (1C, C-5 uracil), 88.5 (1C, C-1'), 84.7, 76.5, 70.3 (3C, C-2', C-3', C-4'), 62.5 (1C, C-5'), 25.9, 25.7 (6C, 2 x SiC(CH_3)$_3$), 18.4, 18.0 (2C, 2 x *t*-BuC_q), −4.8, −5.3, −5.6, −5.6 (4C, 4 x SiCH_3); MALDI-TOF MS: *m/z* calcd for $C_{21}H_{40}N_2NaO_6Si_2$ $[M+Na]^+$ 495.23, found 495.35.

2',3',5'-Tri-*O*-(*tert*-butyldimethylsilyl)uridine (C)

$[\alpha]_D$: +23.57 (*c* = 0.28, $CHCl_3$); R_{fC} = 0.57 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.61 (s, 1H, NH), 6.80 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 4.59 (d, *J* = 2.8 Hz, 1H, H-1'), 4.44 (d, *J* = 8.0 Hz, 1H, H-5 uracil), 2.86-2.80 (m, 3H, H-2', H-3', H-4'), 2.75 (d, *J* = 11.6 Hz, 1H, H-5'a), 2.51 (d, *J* = 11.6 Hz, 1H, H-5'b), −0.31 (s, 9H, *t*-Bu), −0.35 (s, 9H, *t*-Bu), −0.36 (s, 9H, *t*-Bu), −1.12 (s, 3H, SiCH_3), −1.14 (s, 6H, 2 x SiCH_3), −1.17 (s, 3H, SiCH_3), −1.18 (s, 6H, 2 x SiCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.9, 150.6 (2C, 2 x uracil *C*O), 140.5 (1C, C-6 uracil), 101.9 (1C, C-5 uracil), 89.2 (1C, C-1'), 84.4, 76.3, 70.6 (3C, C-2', C-3', C-4'), 61.7 (1C, C-5'), 26.1, 25.9, 25.9 (9C, 3 x SiC(CH_3)$_3$), 18.6, 18.2, 18.1 (3C, 3 x *t*-BuC_q), −4.1, −4.4, −4.7, −4.8, −5.3, −5.5 (6C, 6 x SiCH_3); MALDI-TOF MS: *m/z* calcd for $C_{27}H_{54}N_2NaO_6Si_3$ $[M+Na]^+$ 609.32, found 609.36.

2. Oxidation and Wittig olefination of 3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine[6]



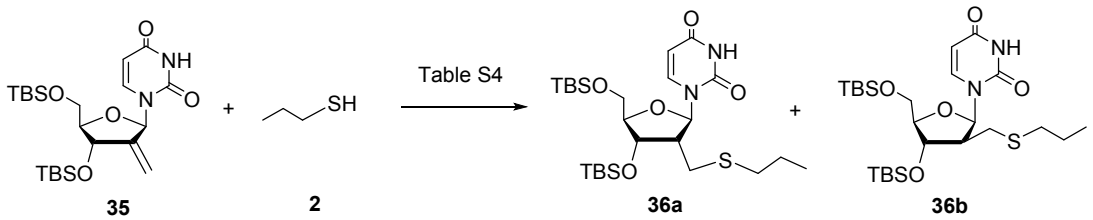
3',5'-Di-*O*-(*tert*-butyldimethylsilyl)-2'-ketouridine. 3',5'-bis-*O*-(*tert*-butyldimethylsilyl)-uridine (1.5 g, 3.17 mmol) and IBX (2.67 g, 9.52 mmol, 3 equiv.) was suspended in dry MeCN (20 ml). The reaction mixture was stirred at 100 °C (reflux) for 3h. The reaction was

monitored by TLC (CH_2Cl_2/acetone 95/5 R_f = 0.43). The suspension was diluted with EtOAc, filtered and washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude product was used in the next step without purification.

2'-Deoxy-2'-methylene-3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (35).[6] Methyl-triphenylphosphonium-bromide (3.39 g, 9.49 mmol, 3 equiv.) was suspended in dry THF (20 ml) under an Ar atmosphere and *t*-BuOK (1.07 g, 9.49 mmol, 3 equiv.) was added. The yellow suspension was stirred at room temperature for 2 h and cooled to −78 °C. To this suspension was added the 3',5'-di-*O*-(*tert*-butyldimethylsilyl)-2'-ketouridine and the reaction mixture was allowed to warm to −10 °C over 1 h and stored at 0−4 °C overnight. The reaction was monitored by TLC (hexane/acetone 8/2 R_f = 0.29). The reaction mixture was diluted with CH_2Cl_2 (200 ml) and washed with saturated aq. NH_4Cl solution (3 x 50 ml). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (gradient elution hexane/acetone 9/1→85/15) to yield 2'-deoxy-2'-methylene-3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (330 mg, 24%) as a yellow solid.

$[\alpha]_D$: +6.90 (*c* = 0.42, $CHCl_3$); R_f = 0.29 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.51 (s, 1H, N*H*), 7.59 (d, *J* = 8.0 Hz, 1H, H-6 uracil), 6.67 (s, 1H, H-1'), 5.71 (d, *J* = 7.2 Hz, 1H, H-5 uracil), 5.41 (d, *J* = 14.9 Hz, 2H, exomethylene CH_2), 4.79 (d, *J* = 1.2 Hz, 1H, H-3'), 3.98 (d, *J* = 10.6 Hz, 1H, H-5'a), 3.79 (dd, *J* = 13.0, 9.5 Hz, 2H, H-5'b, H-4'), 0.91, 0.93 (2 x s, 18H, 2 x *t*-Bu), 0.16, 0.15 (2 x s, 6H, 2 x SiCH_3) 0.12, 0.11 (2 x s, 6H, 2 x SiCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.4, 150.8 (2C, 2 x uracil *C*O), 148.8 (1C, C-2'), 140.7 (1C, C-6 uracil), 113.3 (1C, exomethylene *C*H_2), 102.7 (1C, C-5), 84.7 (1C, C-1'), 84.0, 69.7 (2C, 3'*C*H, 4'*C*H), 60.8 (1C, C-5'), 25.9, 25.7 (6C, 2 x SiC(CH_3)$_3$), 18.3, 18.0 (2C, *t*-BuC_q), −4.3, −4.6, −5.5, −5.4 (4C, 4 x SiCH_3); MALDI-TOF MS: *m/z* calcd for $C_{22}H_{40}N_2NaO_5Si_2$ $[M+Na]^+$ 491.24, found 491.29.

2'-Deoxy-2'-*C*-(*n*-propylsulfanylmethyl)-3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (36a) and 1-[2'-Deoxy-2'-*C*-(*n*-propylsulfanylmethyl)-3',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-arabinofuranosyl]-uracil (36b)



35 **2** **36a** **36b**

Table S5. Free radical addition of 1-propanethiol **2** to **29** upon various initiation methods

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : D-*arabino*[a]	Yield (%)[b]
1	3 equiv.	DPAP, hν	toluene	rt.	3×15 min	~1:4	39
2	3 equiv.	Et_3B, catechol	CH_2Cl_2	rt.	4 h	desilylated products	
3	3 equiv.	DPAP, hν	toluene	−80 °C	3×15 min	1:12.5	68

[a] Ratio determined by ^{1}H NMR; [b]overall yield of products isolated by flash column chromatography.

UV-light initiated reactions:

Entry 1: Exomethylene derivative **35** (50 mg, 0.107 mmol) and 1-propanethiol **2** (0.320 mmol, 3 equiv., 29 µl) dissolved in toluene (5 ml) were reacted according to **General method A** using three irradiation cycles. The reaction was monitored by TLC (CH_2Cl_2/acetone 95/5, R_f = 0.45). The crude product was purified by flash column chromatography (gradient elution hexane/acetone 95/5→9/1→85/15→8/2). A second flash column chromatography (CH_2Cl_2/acetone 99/1) gave a mixture of **36a** and **36b** (22.5 mg, 39%) with a ~1:4 ratio**.**

Entry 3 Exomethylene derivative **35** (0.11 mmol, 50 mg) and thiol **2** (3.0 equiv, 0.33 mmol, 34 µl) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (hexane/acetone 9/1) to give **36b** (40 mg, 68%, >85% diastereomeric purity) as a white solid, containing a ~8% impurity of the corresponding D-*ribo* isomer by the ^{1}H-NMR spectrum.

Data of **36b**

$[\alpha]_D$: +49.50 (*c* = 0.20, $CHCl_3$); R_f = 0.45 (95:5 CH_2Cl_2/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.26 (s, 1H, N*H*), 7.71 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 6.28 (d, *J* = 7.0 Hz, 1H, H-1'), 5.69 (dd, *J* = 8.1 Hz, *J* = 1.9 Hz, 1H, H-5 uracil), 4.33 (t, *J* = 6.3 Hz, 1H, H-3'), 3.97-3.94 (m, 1H, H-5'a), 3.82-3.79 (m, 2H, H-4', H-5'b), 2.75 (dd, *J* = 14.0 Hz, *J* = 6.8 Hz, 1H, H-2'), 2.67 (dd, *J* = 12.8 Hz, *J* = 6.0 Hz, 1H, SCH_2a), 2.42 (t, *J* = 7.3 Hz, 2H, SCH_2 propyl), 2.35 (dd, *J* = 12.8 Hz, *J* = 7.9 Hz, 1H, SCH_2b), 1.54 (dd, *J* = 14.6 Hz, *J* = 7.3 Hz, 2H, CH_2 propyl), 0.99-0.87 (m, 21H, 6 x *t*-Bu-CH_3, CH_3 propyl), 0.15, 0.13, 0.12, 0.11 (4 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.6, 150.6 (2C, 2 x *C*O uracil), 141.2 (1C, C-6 uracil), 101.7 (1C, C-5 uracil), 85.7 (2C, C-1', C-4'), 73.1 (1C, C-3'), 61.2 (1C, C-5'), 50.5 (1C, C-2'), 35.0 (1C, S*C*H$_2$ propyl), 29.0 (1C, S*C*H$_2$), 26.1, 25.8 (6C, 6 x *t*-Bu-*C*H$_3$), 22.8 (1C, *C*H$_2$ propyl), 18.5, 18.0 (2C, 2 x *t*-Bu-C$_q$), 13.5 (1C, *C*H$_3$ propyl), −4.1, −4.3, −5.2, −5.3 (4C, 4 x *C*H$_3$); MALDI-TOF MS: m/z calcd for $C_{25}H_{48}N_2NaO_5SSi_2$ $[M+Na]^+$ 567.271, found 567.290.

2'-Deoxy-2'-*C*-[(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl]-3',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (37a) and 1-[2'-Deoxy-2'-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl-3',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-arabinofuranosyl]-uracil (37b)

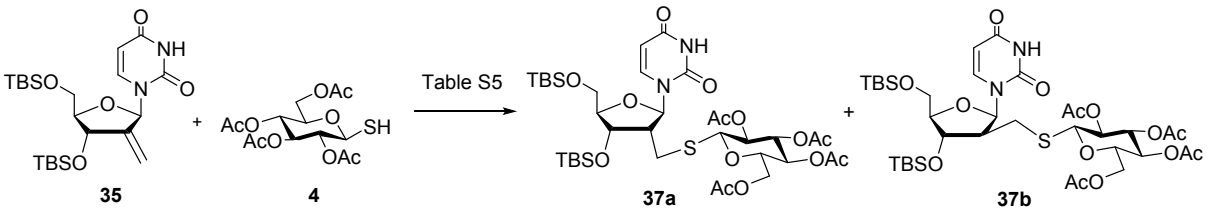


Table S6. Free radical addition of 1-thioglucose peracetate to **29** upon various initiation methods

Entry	Thiol	Initiation	Solvent	Temperature	Time	D-*ribo* : D-*arabino*[a]	Yield (%)[b]
1	1.5 equiv.	DPAP, hν	toluene	rt.	3×15 min	1:5	68
2	1.5 equiv.	Et_3B, catechol	CH_2Cl_2	rt.	4 h	1:5	67
3	1.2 equiv.	DPAP, hν	toluene	−80 °C	3×15 min	1:10	89

[a] Ratio determined by ^{1}H NMR; [b]overall yield of products isolated by flash column chromatography.

UV-light initiated reactions:

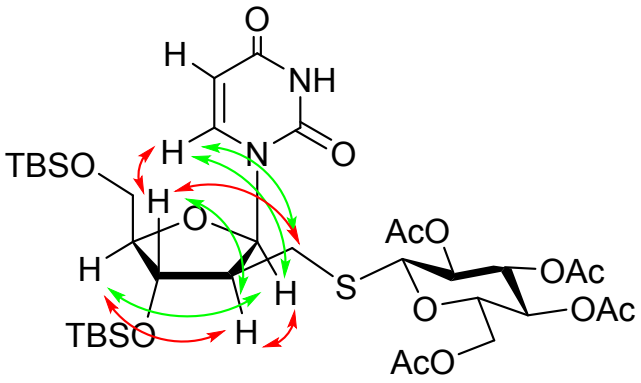
Entry 1: Exomethylene derivative **35** (50 mg, 0.1067 mmol) and thiol **4** (0.16 mmol, 1.5 equiv., 58.3 mg) dissolved in toluene (6 ml) were reacted according to **General method A** using three irradiation cycles. The reaction was monitored by TLC (hexane/acetone 7/3, R_f = 0.28). The crude product was purified by flash column chromatography (gradient elution hexane/acetone 9/1→85/15) to give a mixture of **37a** and **37b** (60 mg, 68%) with a ~1:5 ratio.

Entry 3: Exomethylene derivative **35** (0.14 mmol, 38 mg) and thiol **4** (1.2 equiv., 0.17 mmol, 63 mg) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (hexane/acetone 8/2) to give **37b** (56 mg, 89%) as a white solid, containing a ~9% impurity of the corresponding D-*ribo* isomer by the ^{1}H-NMR spectrum.

Et_3B-catechol mediated reaction (Entry 2): To the solution of exomethylene derivative **35** (0.2 mmol, 94 mg) and thiol **4** (1.5 equiv., 109 mg, 0.3 mmol) in abs. CH_2Cl_2 (5.0 ml) Et_3B (1 M in hexane, 240 μl) and catechol (26.4 mg) were added at rt according to **General method B**. The crude product was purified by flash column chromatography (hexane/acetone 8/2) to give a ~1:5 mixture of **31a** and **37b** (111 mg, 67%). Pure compound **37b** was isolated by a second flash chromatography (toluene/MeOH 95/5).

Data of **37b.**

$[\alpha]_D$: −1.94 (*c* = 0.15, $CHCl_3$); R_f = 0.28 (7:3 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (s, 1H, N*H*), 7.64 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 6.31 (d, *J* = 7.5 Hz, 1H, H-1'), 5.69 (dd, *J* = 8.1 Hz, *J* = 2.1 Hz, 1H, H-5 uracil), 5.21 (t, *J* = 9.4 Hz, 1H, H-3"), 5.03 (t, *J* = 9.9 Hz, 1H, H-4"), 4.97 (t, *J* = 9.6 Hz, 1H, H-2"), 4.42 (d, *J* = 10.0 Hz, 1H, H-1"), 4.26 (dd, *J* = 12.4 Hz, *J* = 4.8 Hz, 1H, H-6"a), 4.22 (t, *J* = 7.7 Hz, 1H, H-3'), 4.11 (dd, *J* = 12.4 Hz, *J* = 1.9 Hz, 1H, H-6"b), 3.95 (dd, *J* = 11.8 Hz, *J* = 1.7 Hz, 1H, H-5'a), 3.79 (dd, *J* = 11.8 Hz, *J* = 2.0 Hz, 1H, H-5'b), 3.75-3.70 (m, 2H, H-4, H-5"), 3.01 (dd, *J* = 12.9 Hz, *J* = 4.5 Hz, 1H, SCH_2a), 2.88 (ddd, *J* = 17.0 Hz, *J* = 8.4 Hz, *J* = 4.6 Hz, 1H, H-2'), 2.46 (dd, *J* = 12.8 Hz, *J* = 9.6 Hz, 1H, SCH_2b), 2.10, 2.04, 2.02, 1.99 (4 x s, 12H, 4 x Ac CH_3), 0.95, 0.91 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.16, 0.12, 0.11, 0.10 (4 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 170.2, 169.6, 169.5 (4C, 4 x Ac *C*O), 163.2, 150.3 (2C, 2 x *C*O uracil), 141.2 (1C, C-6 uracil), 102.4 (1C, C-5 uracil), 85.1 (1C, C-4'), 84.9 (1C, C-1'), 82.8 (1C, C-1"), 76.3 (1C, C-5"), 76.0 (1C, C-3"), 73.8 (1C, C-3'), 72.6 (1C, C-2"), 68.3 (1C, C-4"), 62.2 (1C, C-6"), 60.7 (1C, C-5'), 51.3 (1C, C-2'), 26.1, 25.8 (6C, 6 x *t*-Bu *C*H_3), 25.7 (1C, S*C*H_2), 20.9, 20.7, 20.6 (4C, 4 x Ac *C*H_3), 18.6, 17.9 (2C, 2 x *t*-Bu C_q), −4.0, −4.2, −5.3 (4C, 4 x *C*H_3); ESI-TOF MS: *m/z* calcd for $C_{36}H_{60}N_2NaO_{14}SSi_2$ $[M+Na]^+$ 855.320, found 855.322.

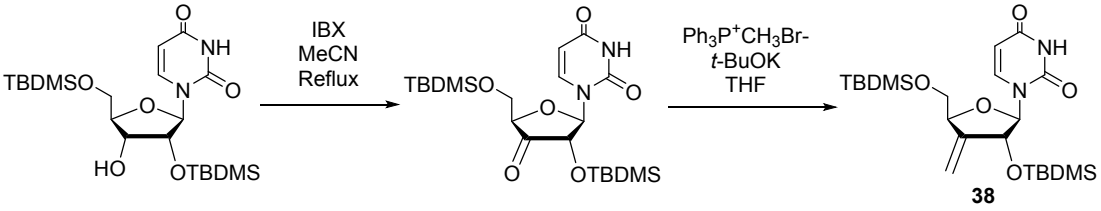


37b (major product)

Figure S5. ROESY through-space connectivities observed in the ROESY spectra of **37b**.

Red arrows: strong RO effects, green arrows: weak RO effects.

3'-Deoxy-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (38)



2',5'-Di-*O*-(*tert*-butyldimethylsilyl)-3'-ketouridine.

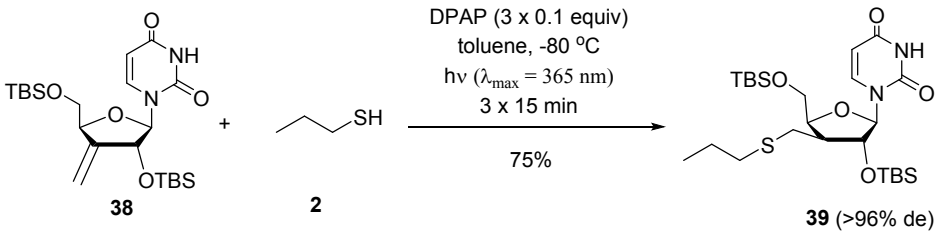
2',5'-Di-*O*-(*tert*-butyldimethylsilyl)-uridine (1.418 g, 3 mmol) and IBX (2.5 g, 9 mmol, 3 equiv.) were suspended in dry MeCN (20 ml). The reaction mixture was stirred at 100 °C (reflux) for 135 minutes. The reaction was monitored by TLC (CH_2Cl_2/acetone 95/5 R_f = 0.42). The suspension was diluted with EtOAc, the solids were filtered off and washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude product was used in the next step without purification.

3'-Deoxy-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (38).[6]

Methyl-triphenylphosphonium-bromide (3.21 g, 9 mmol, 3 equiv.) was suspended in dry THF (20 ml) under Ar and *t*-BuOK (1.01 g, 9 mmol, 3 equiv.) was added. The yellow suspension was stirred at room temperature for 2 h and cooled to −78 °C. To this suspension was added the 2',5'-di-*O*-(*tert*-butyldimethylsilyl)-3'-ketouridine and the reaction mixture was allowed to warm to −10 °C over 1 h and stored at 0−4 °C for 4 h. The reaction was monitored by TLC (hexane/acetone 8/2 R_f = 0.33). The reaction mixture was diluted with CH_2Cl_2 (200 ml) and washed with saturated aq. NH_4Cl solution (3 x 50 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography (gradient elution hexane/acetone 9/1→85/15) to yield 3'-deoxy-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (781 mg, 57%) as a yellow foam. $[\alpha]_D$: +65.59 (*c* = 0.34, $CHCl_3$); R_f = 0.33 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.69 (s, 1H, N*H*), 7.94 (d, *J* = 8.2 Hz, 1H, H-6 uracil), 5.95 (d, *J* = 6.6 Hz, 1H, H-1'), 5.74 (dd, *J* = 8.1 Hz, *J* = 2.0 Hz, 1H, H-5 uracil), 5.24 (t, *J* = 2.1 Hz, 1H, exomethylene CH_a), 5.12 (dd, *J* = 2.4 Hz, *J* = 1.7 Hz, 1H, exomethylene CH_b), 4.64 (d, *J* = 1.6 Hz, 1H), 4.56-4.51 (m, 1H), 3.97 (dd, *J* = 11.1 Hz, *J* = 2.2 Hz, 1H, H-5'a), 3.70 (dd, *J* = 11.1 Hz, *J* = 1.9 Hz, 1H, H-5'b), 0.91, 0.88 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.08, 0.07, 0.03, −0.04 (4 x s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.4, 150.7 (2C, 2 x uracil *C*O), 147.0 (1C, C-3'), 140.3 (1C, C-6 uracil), 108.4 (1C, exomethylene *C*H_2), 102.9 (1C, C-5 uracil), 87.6, 81.1, 76.6 (3C, C-1', C-2', C-4'), 66.1 (1C, C-5'), 25.8, 25.5 (6C, 6 x *t*-Bu *C*H_3), 18.4, 17.9 (2C, 2 x *t*-Bu C_q),

−4.9, −5.0, −5.5, −5.6 (4C, 4 x CH_3); MALDI-TOF MS: m/z calcd for $C_{22}H_{40}N_2NaO_5Si_2$ $[M+Na]^+$ 491.24; found 491.36.

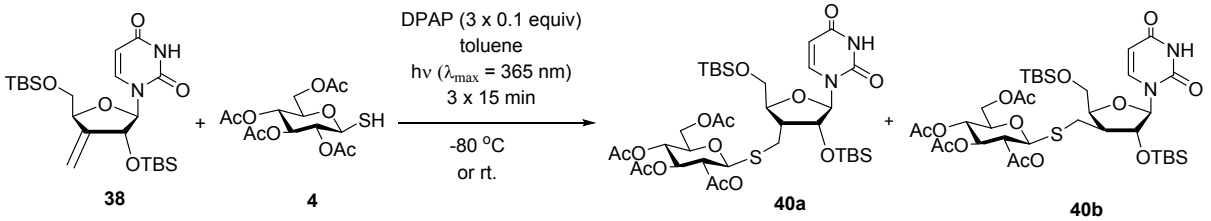
1-[3'-Deoxy-3'-*C*-(*n*-propylsulfanylmethyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-xylofuranosyl]-uracil (39)



Exomethylene derivative **38** (0.21 mmol, 100 mg) and thiol **2** (2.0 equiv, 0.42 mmol, 40 µl) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The crude product was purified by flash column chromatography (hexane/acetone 9/1 R_f = 0.22) to give **38** (85 mg, 75%, >96% diastereomeric purity) as a white solid. Attempted reactions between **38** and **2** at room temperature using either UV-light or Et_3B-catechol initiations were unsucsessful. (No reaction was observed in either case.)

$[\alpha]_D$: +67.62 (*c* = 0.21, $CHCl_3$); R_f = 0.22 (9:1 hexane/acetone); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.55 (s, 1H, N*H*), 7.98 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.96 (d, *J* = 6.6 Hz, 1H, H-1'), 5.72 (dd, *J* = 8.1 Hz, *J* = 2.1 Hz, 1H, H-5 uracil), 4.31 (d, *J* = 7.6 Hz, 1H, H-4'), 4.12 (dd, *J* = 8.7 Hz, *J* = 6.7 Hz, 1H, H-2'), 4.00-3.94 (m, 1H, H-5'a), 3.88 (dd, *J* = 11.8 Hz, *J* = 2.3 Hz, 1H, H-5'b), 2.79-2.62 (m, 3H, SCH_2, H-3'), 2.57-2.44 (m, 2H, SCH_2), 1.69-1.54 (m, 2H, CH_2 propyl), 1.02-0.97 (m, 3H, CH_3 propyl), 0.95, 0.85 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.14, −0.01, −0.11 (3 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.3, 150.8 (2C, 2 x uracil *C*O), 140.5 (1C, C-6 uracil), 102.8 (1C, C-5 uracil), 87.6, 79.3, 77.3 (3C, C-1', C-2', C-3'), 63.6 (1C, C-5'), 46.7 (1C, C-3'), 34.3 (1C, SCH_2), 28.7 (1C, SCH_2), 25.9, 25.5 (6C, 6 x *t*-Bu CH_3), 22.7 (1C, CH_2 propyl), 18.2, 17.7 (2C, 2 x *t*-Bu C_q), 13.4 (1C, CH_3 propyl), −4.6, −4.7, −5.5, −5.7 (4C, 4 x CH_3); MALDI-TOF MS: *m/z* calcd for $C_{25}H_{48}N_2NaO_5SSi_2$ $[M+Na]^+$ 567.27; found 567.33. Elemental analysis: calcd (%) for $C_{25}H_{48}N_2NaO_5SSi_2$: C 55.11, H 8.88, N 5.14, S 5.88, found: C 55.47, H 8.83, N 5.13, S 5.84,

1-[3'-Deoxy-3'-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl]-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl]-uracil (40a) and 1-[3'-Deoxy-3'-*C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-xylofuranosyl]-uracil (40b)



-80 °C: **34a**:**34b** ~ 1:17, overall yield 49% (33% of **32** and 30% of **4** were recovered)
rt: **34a**:**34b** ~ 1:3, overall yield 26% (30% of **32** was recovered)

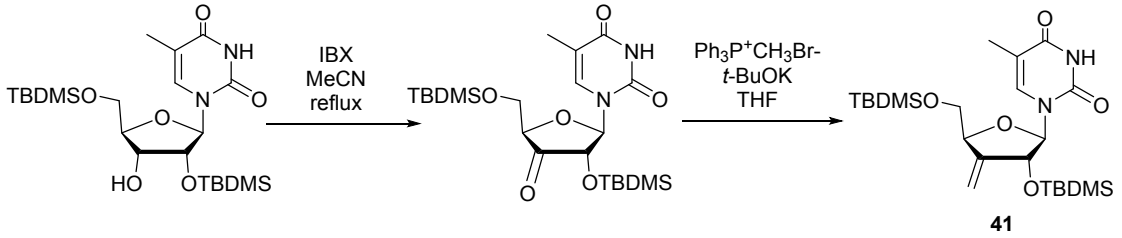
Exomethylene derivative **38** (0.50 mmol, 234 mg) and thiol **4** (1.2 equiv, 0.6 mmol, 219 mg) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The reaction was monitored by TLC (hexane/acetone 8/2 R_f =0.24) The crude product was purified by flash column chromatography (hexane/acetone 9/1→85/15→8/2) to give **40b** (199 mg, 49%, ~89% diastereomeric purity) as a white solid.

The same reaction was also carried out at rt to yield an unseparable 1:3 mixture of **40a** and **40b**. with 26% yield.

Data of **40b**:

$[\alpha]_D$: +33.04 (*c* = 0.23, $CHCl_3$); R_f = 0.24 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.80 (s, 1H, N*H*), 7.95 (d, *J* = 8.1 Hz, 1H, H-6 uracil), 5.95 (d, *J* = 6.6 Hz, 1H, H-1'), 5.73 (d, *J* = 8.0 Hz, 1H, H-5 uracil), 5.27 (t, *J* = 9.3 Hz, 1H, H-3"), 5.05-4.96 (m, 2H, H-2", H-4"), 4.53 (d, *J* = 10.1 Hz, 1H, H-1"), 4.36 (d, *J* = 7.9 Hz, 1H, H-4'), 4.18 (d, *J* = 3.8 Hz, 2H, H-6"a,b), 4.12 (dd, *J* = 8.8 Hz, *J* = 7.1 Hz, 1H, H-2'), 3.91 (s, 2H, H-5'a,b), 3.79-3.74 (m, 1H, H-5"), 2.96-2.90 (m, 2H, S*CH*$_2$), 2.87-2.80 (m, 1H, H-3'), 2.15, 2.07, 2.05, 2.02 (4 x s, 12H, 4 x Ac-*CH*$_3$), 0.96, 0.89 (2 x s, 18H, 6 x *t*-Bu *CH*$_3$), 0.15, 0.04, −0.08 (3 x s, 12H, 4 x *CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.7, 170.1, 169.4, 169.2 (4C, 4 x Ac-*C*O), 163.3, 150.8 (2C, 2 x *C*O uracil), 140.3 (1C, C-6 uracil), 102.8 (1C, C-5 uracil), 87.5 (1C, C-1'), 85.2 (1C, C-1"), 79.0 (1C, C-4'), 77.4 (1C C-2'), 76.2 (1C, C-5"), 73.6 (1C, C-3"), 69.7 (1C, C-2"), 68.3 (1C, C-4"), 63.7 (1C, C-5'), 62.4 (1C, C-6"), 47.5 (1C, C-3'), 28.9 (1C, S*C*H$_2$), 25.9, 25.5 (6C, 6 x *t*-Bu *C*H$_3$), 20.7, 20.6, 20.5 (4C, 4 x Ac *C*H$_3$), 18.1, 17.7 (2C, 2 x *t*-Bu C_q), −4.6, −4.7, −5.5, −5.7 (4C, 4 x *C*H$_3$); MALDI-TOF MS: *m/z* calcd for $C_{36}H_{60}N_2NaO_{14}SSi_2$ $[M+Na]^+$ 855.32; found 855.36. Elemental analysis: calcd (%) for $C_{25}H_{48}N_2NaO_5SSi_2$: C 55.11, H 8.88, N 5.14, S 5.88, found: C 55.04, H 8.90, N 5.17, S 5.83,

3'-Deoxy-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-5-methyluridine (41)



41

3'-Keto-5-methyl-2',5'-di-*O-tert*-butyldimethylsylil-uridine.

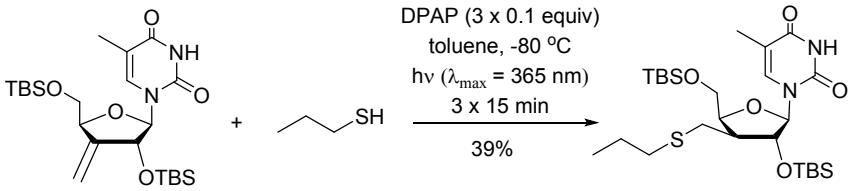
5-Methyl-2',5'-bis-*O*-(*tert*-butyldimethylsilyl)-uridine[7] (1.49 g, 3.06 mmol) and IBX (2.57 g, 9.18 mmol, 3 equiv.) were suspended in dry MeCN (20 ml) and stirred at 100 °C for 3 h. The rection was monitored by TLC (CH_2Cl_2/acetone 95/5 R_f =0.67). The reaction mixture was diluted with EtOAc (100 ml), filtered and evaporated under reduced pressure. The crude 5-methyl-3'-ketouridine was used in the next Wittig reaction without purification.

3'-Deoxy-5-methyl-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)uridine (41).

Methyl-triphenylphosphonium-bromide (3.28 g, 9.18 mmol, 3 equiv.) was suspended in dry THF (20 ml) under Ar and *t*-BuOK (1.03 g, 9.18 mmol, 3 equiv.) was added. The yellow suspension was stirred at room temperature for 2 h and cooled to −78 °C. To this suspension was added the ketouridine and the reaction mixture was allowed to warm to −10 °C over 1 h and stored at 0−4 °C overnight. The reaction was monitored by TLC (hexane/acetone 8/2 R_f = 0.33). The reaction mixture was diluted with CH_2Cl_2 (200 ml) and washed with saturated aq. NH_4Cl solution (3 x 50 ml). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (gradient ellution hexane/acetone 9/1→85/15) to yield 3'-deoxy-5-methyl-3'-methylene-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-uridine (985 mg, 67%) as a yellow solid. $[\alpha]_D$: +32.86 (*c* = 0.14, $CHCl_3$); R_f = 0.33 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.42 (s, 1H, N*H*), 7.56 (d, *J* = 0.9 Hz, 1H, H-6 thymine), 5.93 (d, *J* = 7.3 Hz, 1H, H-1'), 5.24 (t, *J* = 2.0 Hz, 1H, exomethylene CH_a), 5.12 (dd, *J* = 2.3 Hz, *J* = 1.6 Hz, 1H, exomethylene CH_b), 4.62 (d, *J* = 1.6 Hz, 1H), 4.57-4.51 (m, 1H), 3.96 (dd, *J* = 11.1 Hz, *J* = 2.0 Hz, 1H, H-5'a), 3.70 (dd, *J* = 11.1 Hz, *J* = 2.1 Hz, 1H, H-5'b), 1.95 (d, *J* = 0.5 Hz, 3H, CH_3 thymine), 0.93, 0.88 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.10, 0.09, 0.02, −0.07 (4 x s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.8, 150.8 (2C, 2 x thymine *C*O), 147.4 (1C, C-3'), 135.4 (1C, C-6 thymine), 111.5, 108.0 (2C, exomethylene *C*H_2, C-5 thymine), 86.9, 80.8, 75.9 (3C, C-1', C-

2', C-4'), 66.2 (1C, C-5'), 25.9, 25.5 (6C, 6 x *t*-Bu CH_3), 18.5, 17.9 (2C, *t*-Bu C_q), 12.3 (1C, CH_3 thymine), −4.9, −5.0, −5.4 (4C, 4 x CH_3); MALDI-TOF MS: *m/z* calcd for $C_{23}H_{42}N_2NaO_5Si_2$ $[M+Na]^+$ 505.25; found 505.33.

1-[3'-Deoxy-3'-*C*-(*n*-propylsulfanylmethyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-xylofuranosyl]-thymine (42)



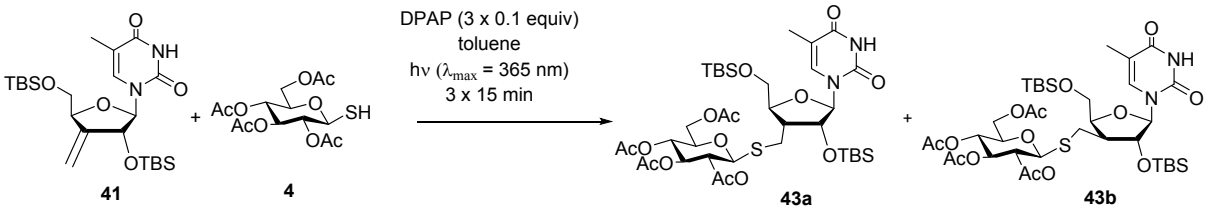
Exomethylene derivative **41** (0.21 mmol, 101 mg) and thiol **2** (2 equiv., 0.42 mmol, 40 µl) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The reaction was monitored by TLC (hexane/acetone 85/15 R_f =0.42) The crude product was purified by flash column chromatography (hexane/acetone 9/1→85/15→8/2) to give **42** (46 mg, 39%, >85% diastereomeric purity) as a white solid. (The D-*xylo*:D-*ribo* ratio was ~ 12.5:1 by the ^{1}H-NMR spectrum). Unreacted **41** (45 mg, 44%) was recovered from the reaction mixture.

Attempted reactions between **41** and **2** at room temperature using either UV-light or Et_3B-catechol initiations were unsucsessful. (No reaction was observed in either case.)

$[\alpha]_D$: +72.94 (*c* = 0.17, $CHCl_3$); R_f = 0.42 (85:15 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.95 (s, 1H, N*H*), 7.54 (s, 1H, H-6 thymine), 5.94 (d, *J* = 6.9 Hz, 1H, H-1'), 4.31 (d, *J* = 8.2 Hz, 1H, H-4'), 4.13 (dd, *J* = 9.1 Hz, *J* = 7.0 Hz, 1H, H-2'), 4.00 (d, *J* = 11.7 Hz, 1H, H-5'a), 3.89 (dd, *J* = 11.8 Hz, *J* = 2.1 Hz, 1H, H-5'b), 2.85-2.74 (m, 2H, SCH_2), 2.73-2.63 (m, 1H, H-3'), 2.52 (ddd, *J* = 12.2 Hz, *J* = 8.0 Hz, *J* = 4.4 Hz, 2H, SCH_2), 1.96 (s, 3H, CH_3 thymine), 1.68-1.56 (m, 2H, CH_2 propyl), 1.02 (t, *J* = 7.4 Hz, 3H, CH_3 propyl), 0.99, 0.86 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.18, 0.01, −0.11 (3 x s, 12H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.6, 150.8 (2C, 2 x thymine *C*O), 135.4 (1C, C-6 thymine), 111.2 (1C, C-5 thymine), 87.3, 78.8, 76.5 (3C, C-1', C-2', C-4'), 63.4 (1C, C-5'), 46.5 (1C, C-3'), 34.3 (1C, SCH_2), 28.6 (1C, S*C*H_2), 26.1, 25.5 (6C, 2 x *t*-Bu *C*H_3), 22.8 (1C, *C*H_2 propyl), 18.3, 17.7 (2C, 2 x *t*-Bu C_q), 13.4 (1C, *C*H_3 propyl), 12.3 (1C, *C*H_3 thymine), −4.6, −4.7, −5.3, −5.4 (4C, 4 x *C*H_3); MALDI-TOF MS: *m/z* calcd for $C_{26}H_{50}N_2NaO_5SSi_2$ $[M+Na]^+$ 581.29, found

581.34. Elemental analysis: calcd (%) for $C_{26}H_{50}N_2O_5SSi_2$: C 55.87, H 9.02, N 5.01, S 5.74, found: C 55.39, H 9.01, N 5.01, S 5.75,

1-[3'-Deoxy-3'-*C*-((2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl]-5-methyluracil (43a) and 1-[3'-Deoxy-3'-*C*-((2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylthio)methyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-xylofuranosyl]-5-methyluracil (43b)



-80 °C: **37a**:**37b** ~ 1:50, overall yield 30% (42% of **35** and 43% of **4** were recovered)
rt: **37a**:**37b** ~ 1:2, overall yield 27% (40% of **35** was recovered)

Exomethylene derivative **41** (0.5 mmol, 241 mg) and thiol **4** (1.2 equiv., 0.6 mmol, 219 mg) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The reaction was monitored by TLC (hexane/acetone 8/2 R_f =0.19) The crude product was purified by flash column chromatography (hexane/acetone 85/15→7/3) to give **43b** (125 mg, 30%, >96% diastereomeric purity) as a white solid.

The same reaction was also carried out at rt to yield a 1:2 mixture of **43a** and **43b** with 27% yield. Pure **43a** and **43b** were obtained by a second flash column chromatography (hexane/acetone 9/1→85/15).

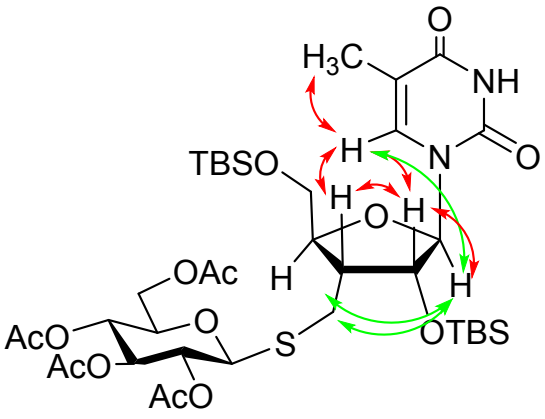
Data of **43a**:

$[\alpha]_D$: + 5,399 (*c* = 1.67, $CHCl_3$); R_f = 0.19 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.64 (s, 1H, N*H*), 7.73 (d, *J* = 1.1 Hz, 1H, H-6 thymine), 5.81 (d, *J* = 1.9 Hz, 1H, H-1'), 5.31 (t, *J* = 9.4 Hz, 1H, H-3"), 5.19 (t, *J* = 9.7 Hz, 1H, H-4"), 5.12 (t, *J* = 9.5 Hz, 1H, H-2"), 4.56 (d, *J* = 10.0 Hz, 1H, H-1"), 4.42 (dd, *J* = 4.9 Hz, *J* = 1.9 Hz, 1H, H-2'), 4.35 (dd, *J* = 12.4 Hz, *J* = 4.7 Hz, 1H, H-6"a), 4.22-4.17 (m, 3H, H-4', H-5'a, H-6"b), 3.86 (dd, *J* = 11.7 Hz, *J* = 2.3 Hz, 1H, H-5'b), 3.82-3.78 (m, 1H, H-5"), 3.00-2.85 (m, 2H, SCH_2), 2.45-2.38 (m, 1H, H-3'), 2.18, 2.14, 2.11 (3 x s, 12H, 4 x Ac CH_3), 2.02 (d, *J* = 0.8 Hz, 3H, CH_3 thymine), 1.06, 1.02 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.29, 0.27, 0.25, 0.24 (4 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.6, 170.3, 169.5, 169.3 (4C, 4 x Ac *C*O), 163.7, 150.4 (2C, 2 x *C*O thymine), 135.6 (1C, C-6 thymine), 110.1 (1C, C-5 thymine), 90.7 (1C, C-1'), 84.3 (1C, C-4'), 83.3 (1C, C-1"), 77.4 (1C C-2'), 76.2 (1C, C-5"), 73.9 (1C, C-3"), 70.0 (1C, C-2"), 68.3 (1C, C-4"), 63.0 (1C, C-5'), 62.1 (1C, C-6"), 41.6 (1C, C-3'), 26.2, 26.0 (6C, 6 x *t*-Bu

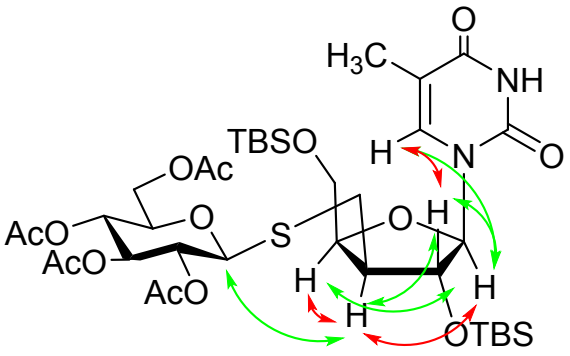
CH_3), 25.3 (1C, SCH_2), 20.8, 20.7 (4C, 4 x Ac CH_3), 18.8, 18.2 (2C, 2 x *t*-Bu C_q), 12.8 (1C, CH_3 thymine), −4.3, −5.0, −5.2 (4C, 4 x CH_3); MALDI-TOF: *m/z* calcd for $C_{37}H_{62}N_2NaO_{14}SSi_2$ $[M+Na]^+$: 869.34; found 869.40. Elemental analysis: calcd (%) for $C_{37}H_{62}N_2O_{14}SSi_2$: C 52.46, H 7.38, N 3.31, S 3.78, found: C 51.77, H 7.31, N 3.30, S 3.79,

Data for **43b:**

$[\alpha]_D$: +16,21 (*c* = 2.84, $CHCl_3$); R_f = 0.19 (8:2 hexane/acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.29 (s, 1H, N*H*), 7.51 (s, 1H, H-6 thymine), 5.92 (d, *J* = 6.9 Hz, 1H, H-1'), 5.25 (t, *J* = 9.4 Hz, 1H, H-3"), 5.04-4.95 (m, 2H, H-2", H-4"), 4.52 (d, *J* = 10.1 Hz, 1H, H-1"), 4.33 (d, *J* = 8.2 Hz, 1H, H-4'), 4.17 (d, *J* = 3.9 Hz, 2H, H-6"a,b), 4.10 (dd, *J* = 9.1 Hz, *J* = 7.0 Hz, 1H, H-2'), 3.91 (q, *J* = 11.4 Hz, 2H, H-5'a,b), 3.77-3.72 (m, 1H, H-5"), 2.96-2.91 (m, 2H, SCH_2), 2.80-2.76 (m, 1H, H-3'), 2.15, 2.06, 2.04, 2.02 (4 x s, 12H, 4 x Ac CH_3), 1.95 (s, 3H, CH_3 thymine), 0.97, 0.88 (2 x s, 18H, 6 x *t*-Bu CH_3), 0.16, 0.03, −0.11 (3 x s, 12H, 4 x CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 170.2, 169.5, 169.3 (4C, 4 x Ac *C*O), 163.8, 151.0 (2C, 2 x *C*O thymine), 135.4 (1C, C-6 thymine), 111.4 (1C, C-5 thymine), 87.1 (1C, C-1'), 85.4 (1C, C-1"), 78.6 (1C, C-4'), 76.8 (1C, C-2'), 76.3 (1C, C-5"), 73.7 (1C, C-3"), 69.9 (1C, C-2"), 68.4 (1C, C-4"), 63.7 (1C, C-5'), 62.6 (1C, C-6"), 47.5 (1C, C-3'), 29.1 (1C, SCH_2), 26.2, 25.7 (6C, 6 x *t*-Bu CH_3), 20.8, 20.7, 20.6 (4C, 4 x Ac CH_3), 18.3, 17.8 (2C, 2 x *t*-Bu C_q), −4.5, −4.6, −5.3 (4C, 4 x CH_3); MALDI-TOF: *m/z* calcd for $C_{37}H_{62}N_2O_{14}SSi_2$ $[M+Na]^+$: 869.34; found 869.40. Elemental analysis: calcd (%) for $C_{37}H_{62}N_2O_{14}SSi_2$: C 52.46, H 7.38, N 3.31, S 3.78, found: C 52.13, H 7.31, N 3.32, S 3.77.



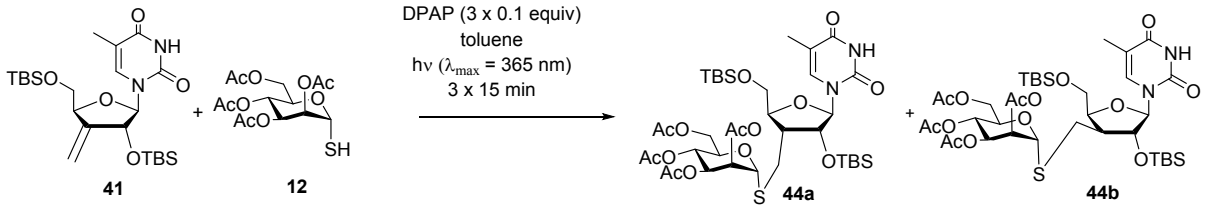
43a (minor product)



43b (major product)

Figure S6. ROESY through-space connectivities observed in the ROESY spectra of **43a** and **43b**. Red arrows: strong RO effects, green arrows: weak RO effects.

1-[3'-Deoxy-3'-*C*-((2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosylthio)methyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-ribofuranosyl]-5-methyluracil (44a) and 1-[3'-Deoxy-3'-*C*-((2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosylthio)methyl)-2',5'-di-*O*-(*tert*-butyldimethylsilyl)-β-D-xylofuranosyl]-5-methyluracil (44b)



Exomethylene derivative **41** (0.5 mmol, 241 mg) and thiol **12** (1.2 equiv., 0.6 mmol, 219 mg) dissolved in toluene (1 ml) were reacted at −80 °C according to **General method C.** The reaction was monitored by TLC (hexane/acetone 7/3 R_f =0.45) The crude product was purified by flash column chromatography (hexane/acetone 85/15→8/2) to give **44b** (254 mg, 60%, >96% diastereomeric purity) as a white foam.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 9.66 (s, 1H, N*H*), 7.41 (s, 1H, H-6), 5.86 (d, J = 7.0 Hz, 1H, H-1'), 5.31 (d, J = 9.9 Hz, 1H), 5.28 – 5.25 (m, 2H), 5.23 (d, J = 1.0 Hz, 1H), 5.15 (dd, J = 10.1, 3.4 Hz, 1H), 4.29 – 4.26 (m, 1H), 4.26 – 4.21 (m, 2H), 4.05 (dd, J = 9.1, 7.2 Hz, 1H), 3.99 (d, J = 10.3 Hz, 1H), 3.83 (s, 2H), 2.87 – 2.75 (m, 2H), 2.67 (ddd, J = 18.3, 9.3, 5.3 Hz, 1H, H-3'), 2.12 (s, 3H, AcCH_3), 2.03 (s, 3H, AcCH_3), 1.98 (s, 3H, AcCH_3), 1.92 (s, 3H, AcCH_3), 1.86 (s, 3H, ThymineCH_3), 0.91 (s, 9H, SiC(CH_3)$_3$), 0.77 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3), -0.08 (s, 3H, SiCH_3), -0.20 (s, 3H, SiCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.4, 169.9, 169.7, 169.5 (4C, 4xAc*C*O), 163.8, 150.8 (2C, 2xthymine *C*O), 135.1 (1C, C-6), 111.2 (1C,C-5), 86.9, 81.4, 78.1, 76.2, 70.7, 69.3, 69.2, 65.9, (8C, skeletal carbons)), 63.5, 62.2 (2C, C-5', C-6''), 46.2 (1C, C-3'), 26.9 (1C, S*C*H$_2$), 26.0 , 25.4 (6C, 6x*t*-Bu*C*H$_3$), 20.8, 20.6, 20.6, 20.5 (4C, 4x Ac*C*H$_3$), 18.2, 17.6 (2C, 2x *t*-Bu*C*$_q$), 12.2 (1C, thymine*C*H$_3$), -4.6, -4.8, -5.4, -5.5 (4C, 4xSi*C*H$_3$). ESI-TOF: *m/z* calcd for $C_{37}H_{62}N_2O_{14}SSi_2$ [M+Na]$^+$: 869.335; found 869.336.

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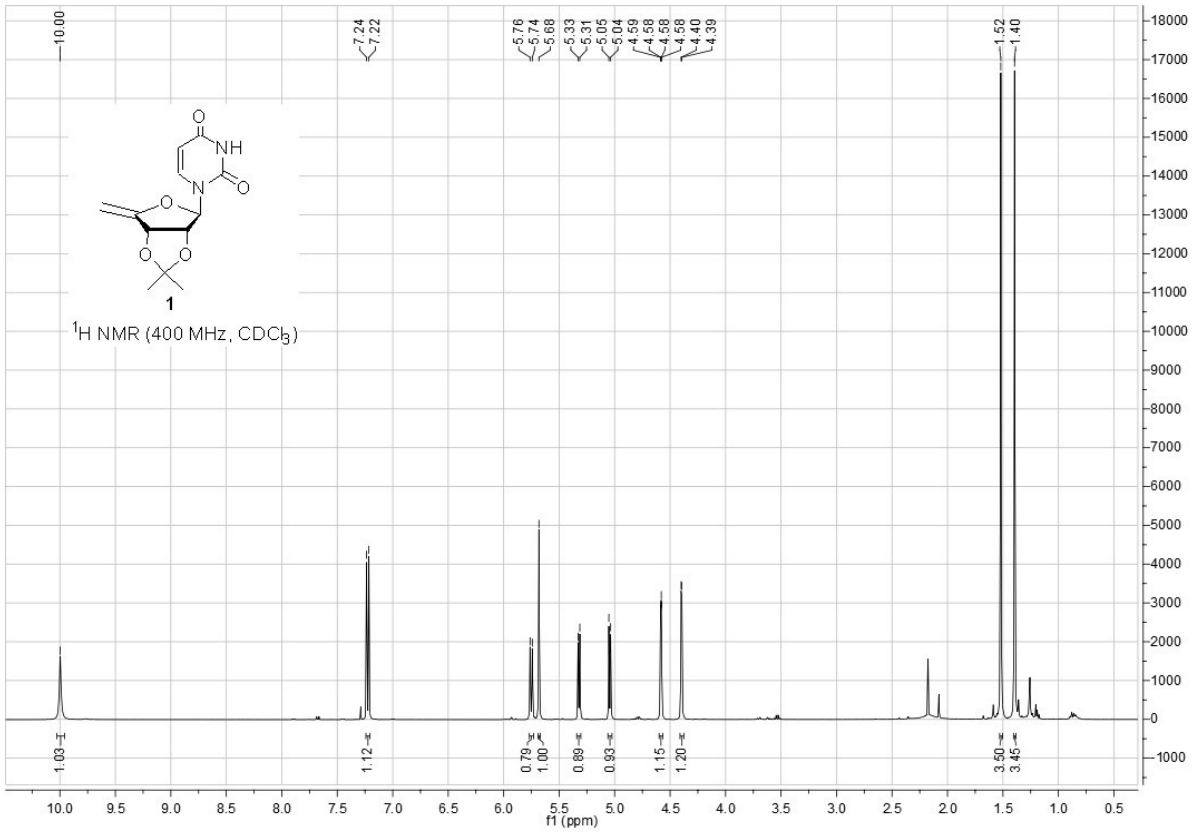
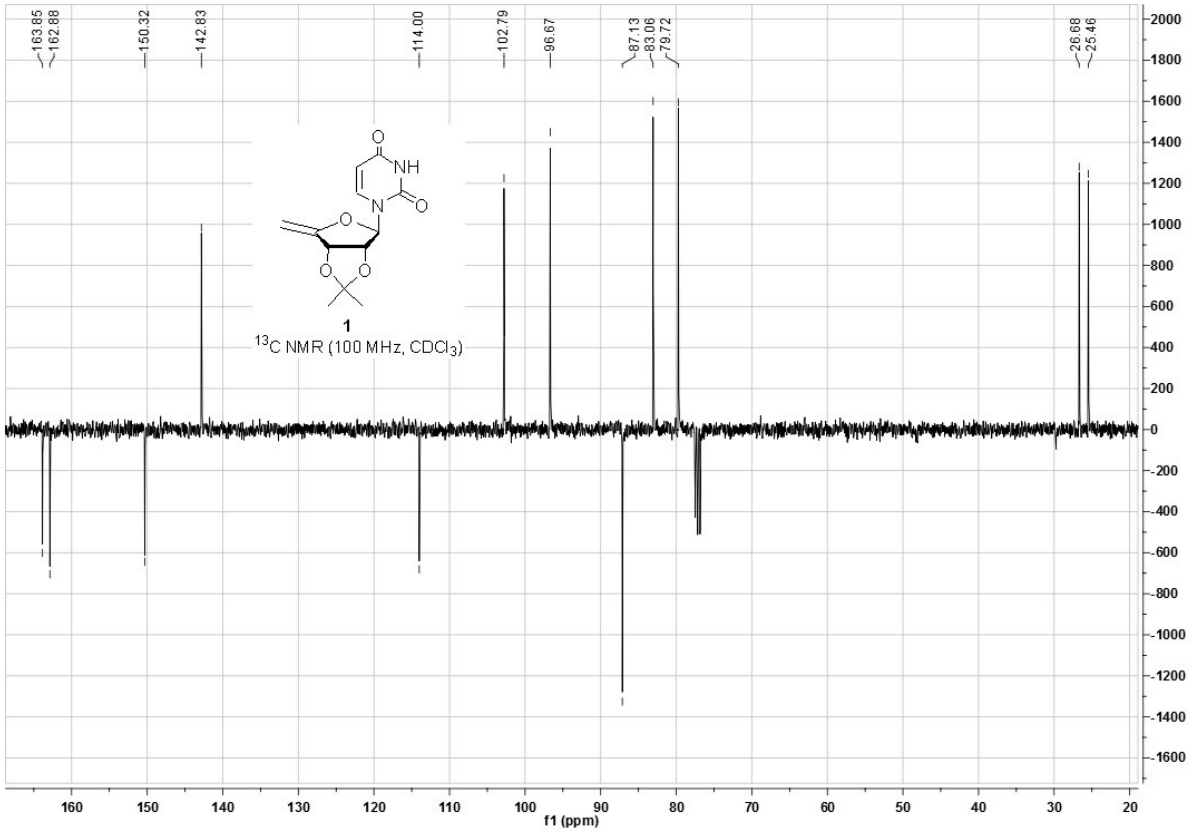
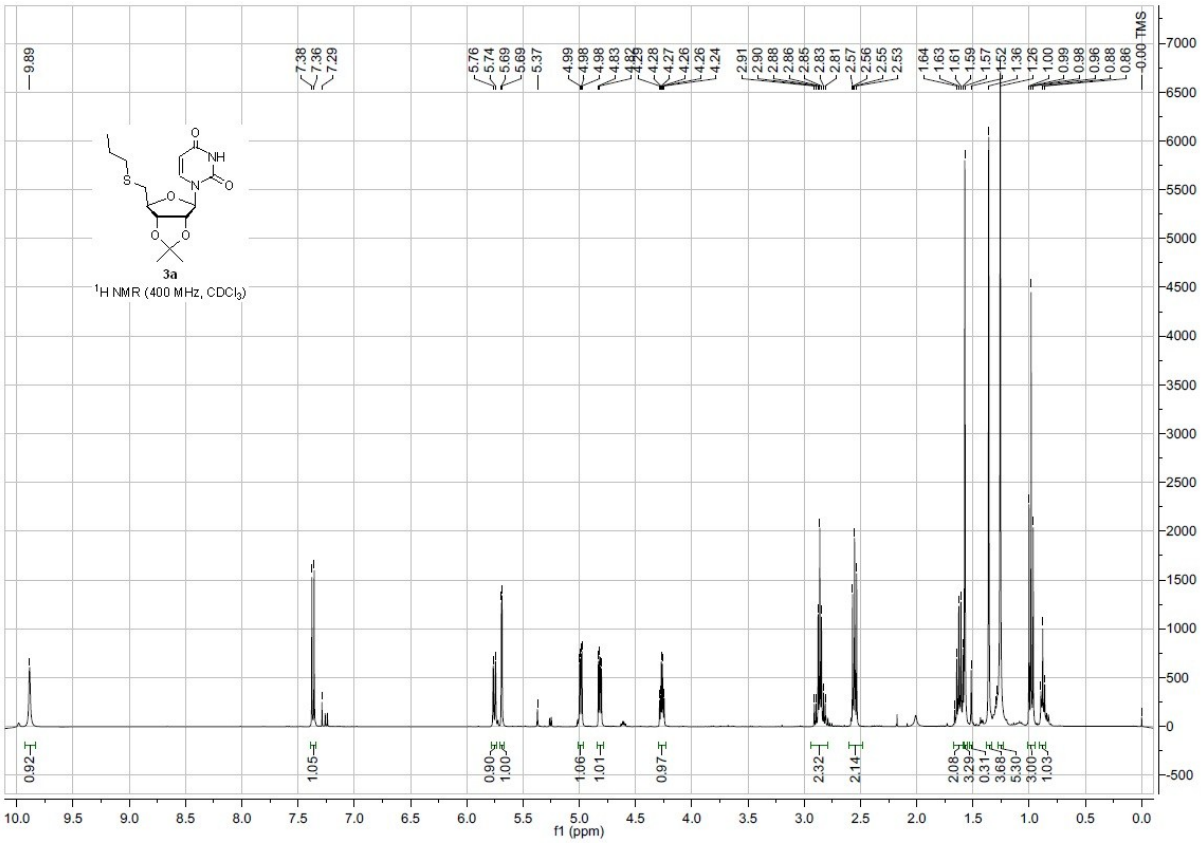
NMR spectra of compounds



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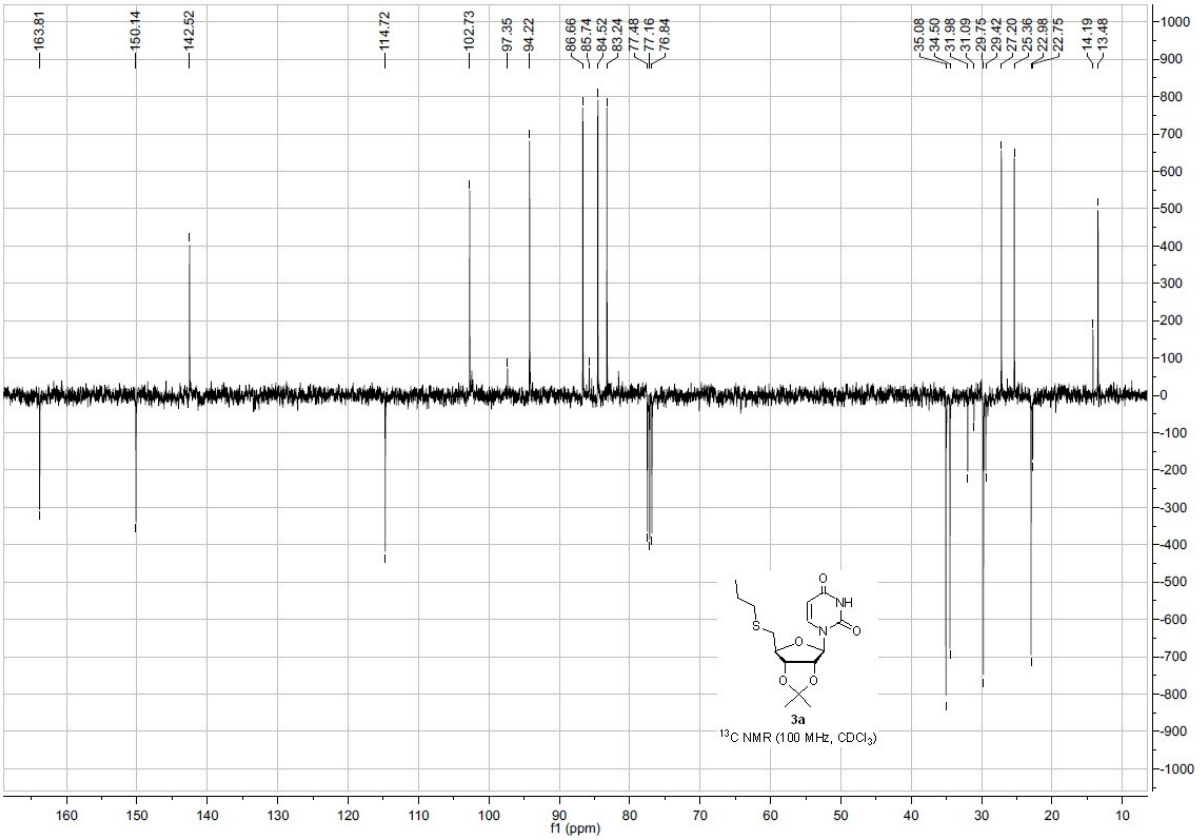
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


3a
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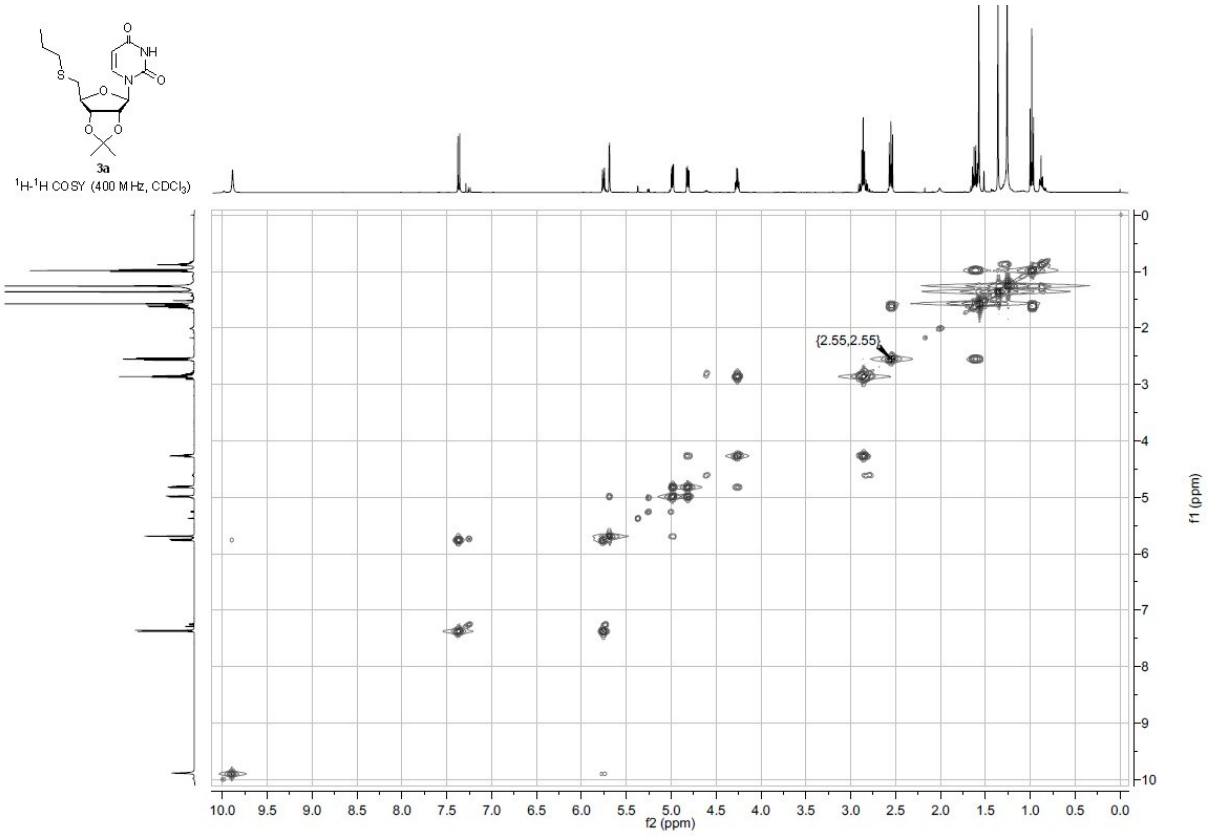
f1 (ppm)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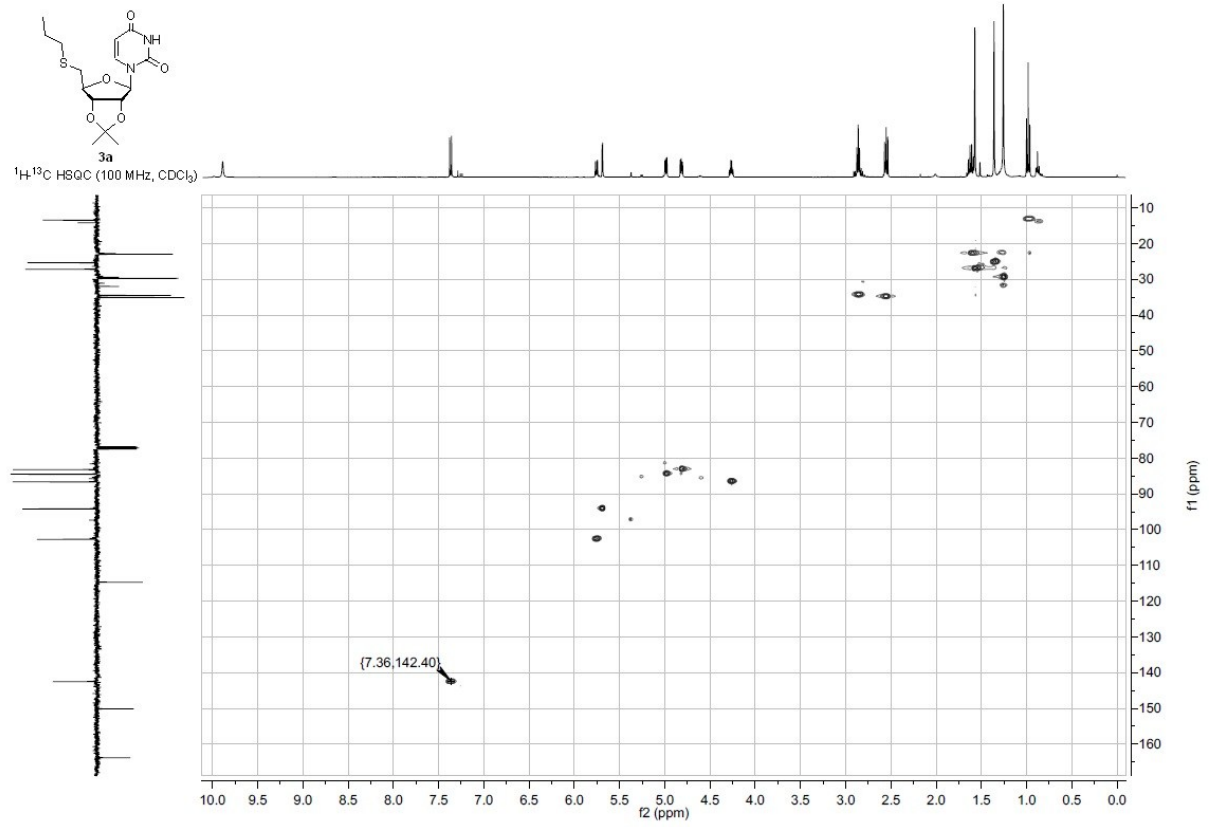
{2.55,2.55}
f2 (ppm)
f1 (ppm)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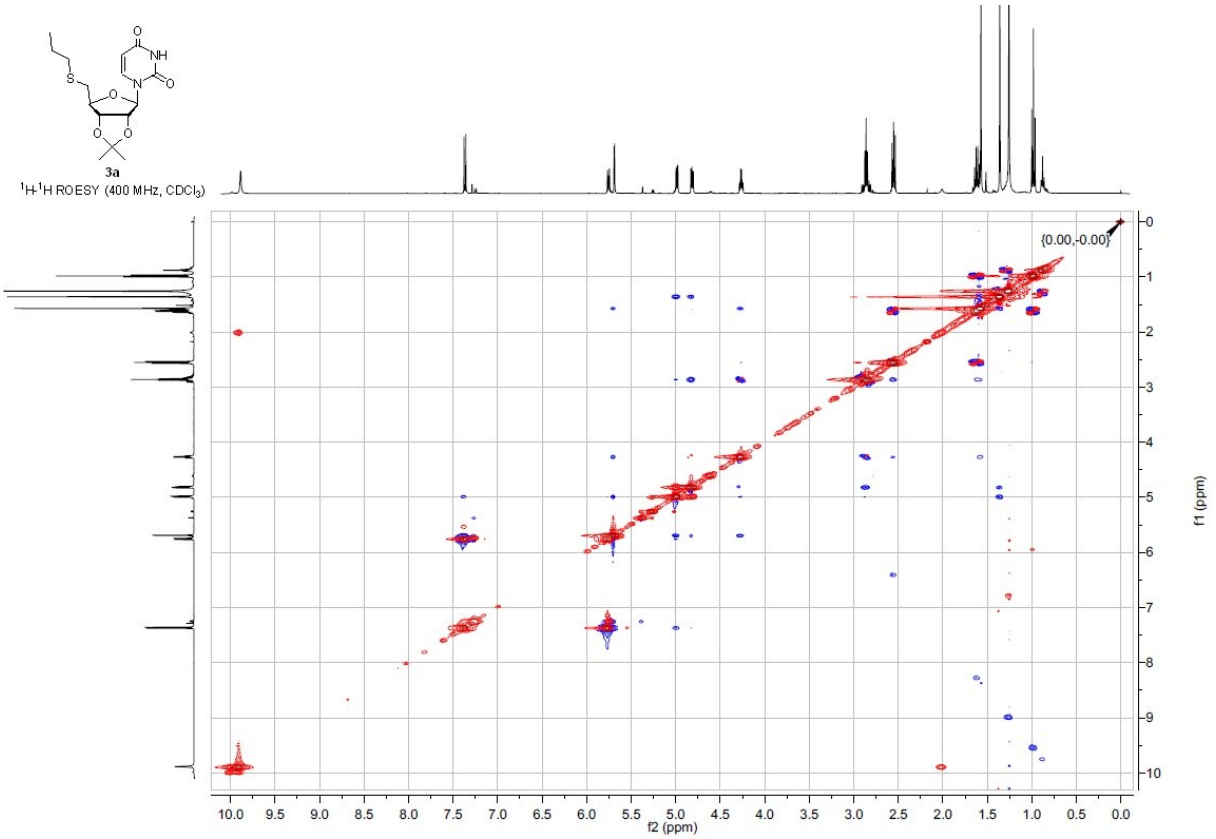
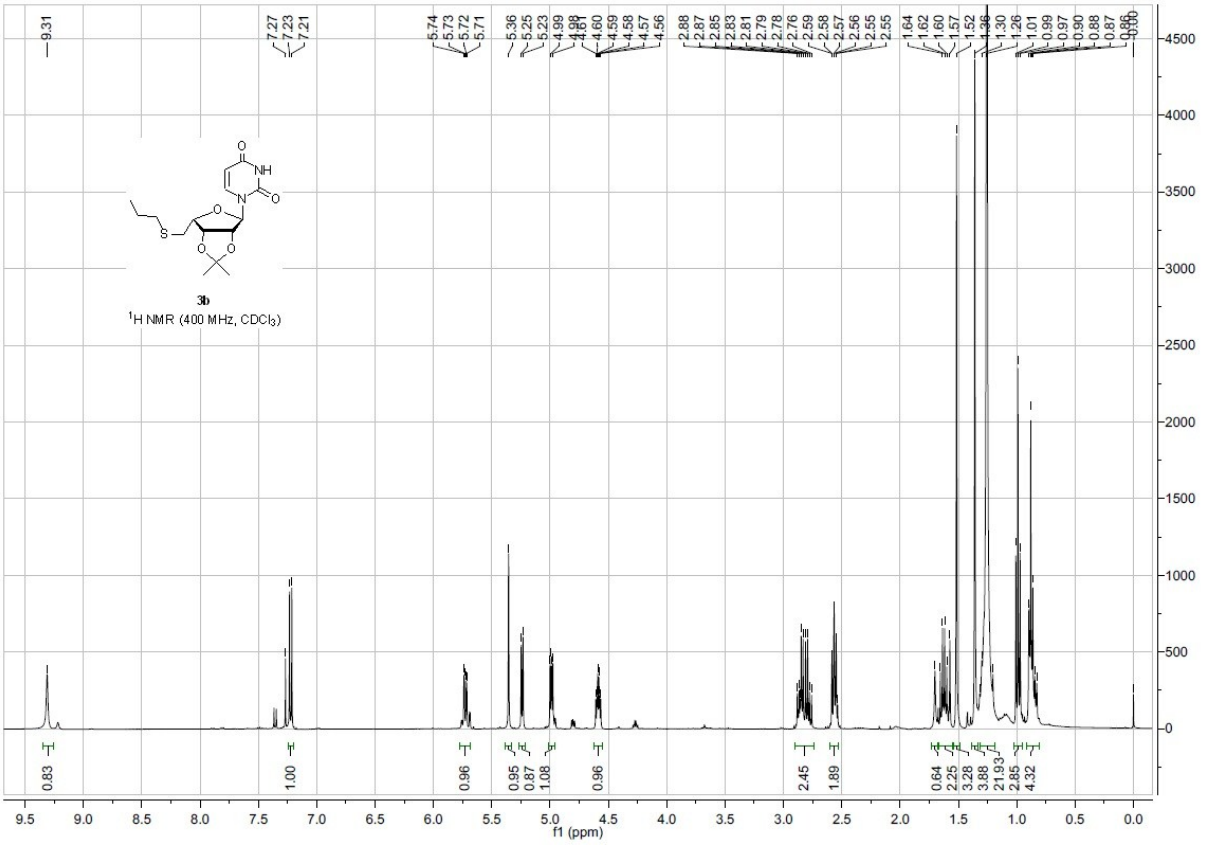
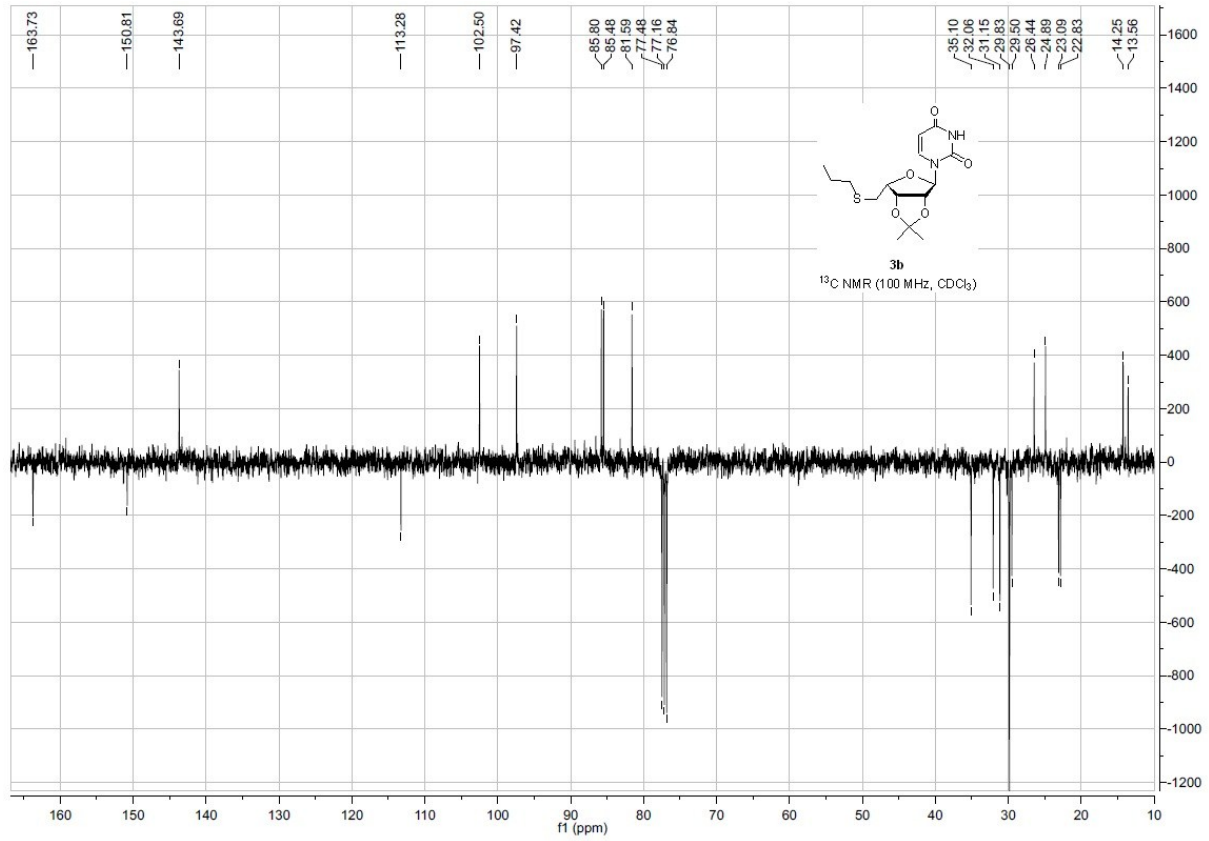
{7.36,142.40}
f2 (ppm)
f1 (ppm)


3a
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
{0.00,-0.00}
f2 (ppm)
f1 (ppm)


3b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)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32.06
31.15
29.83
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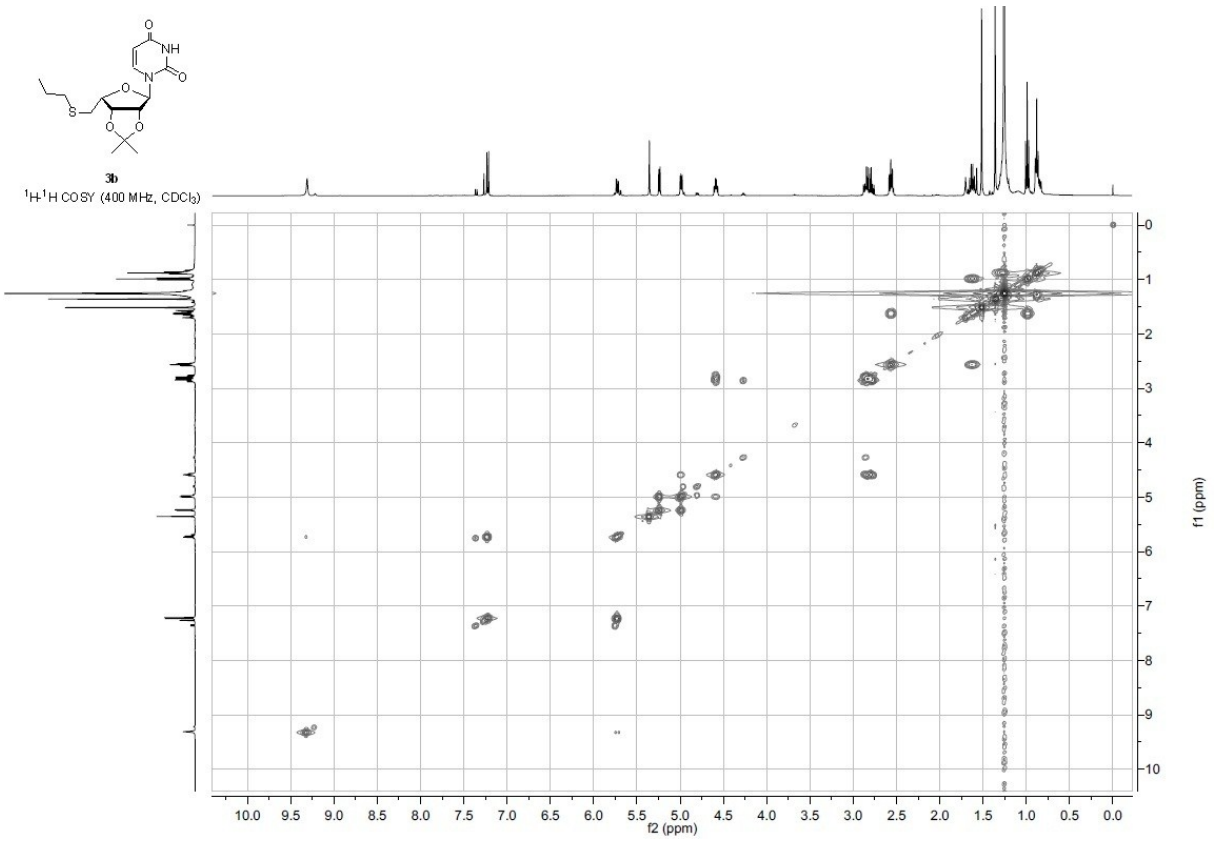
13.56
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)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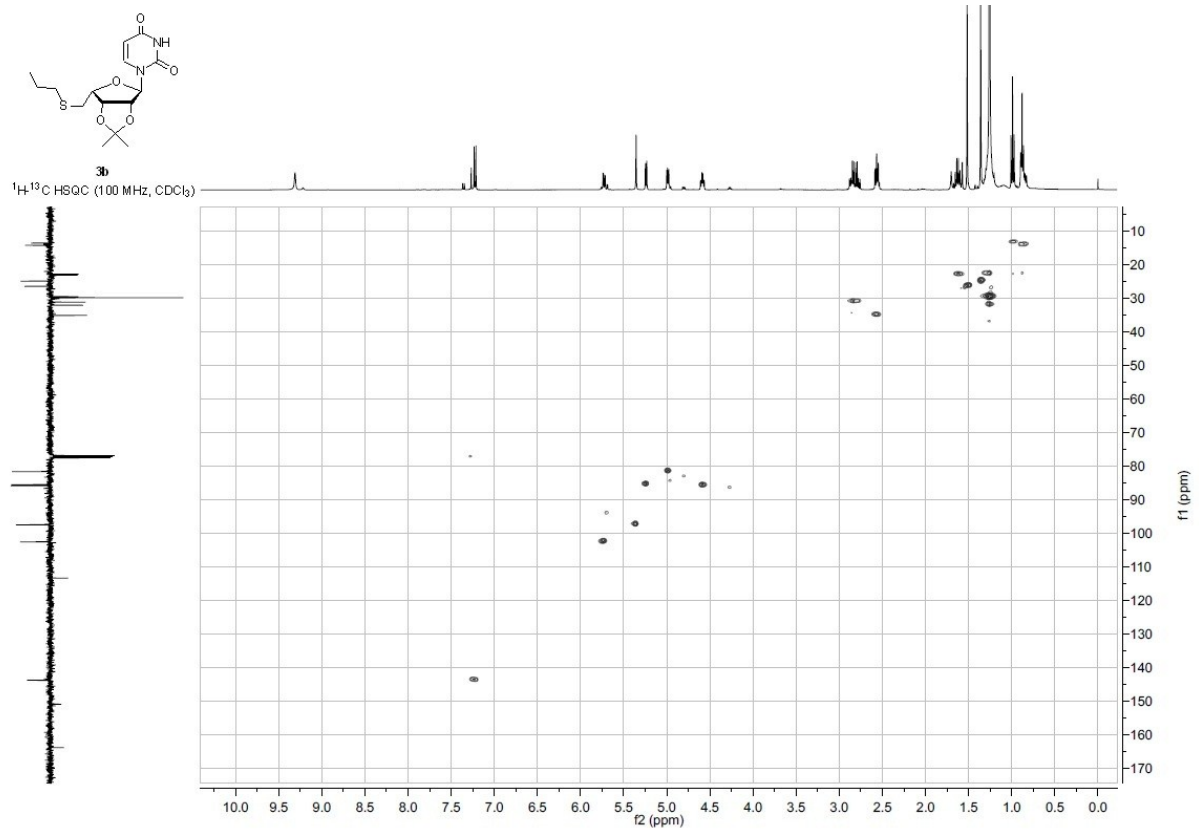
1H-1H COSY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)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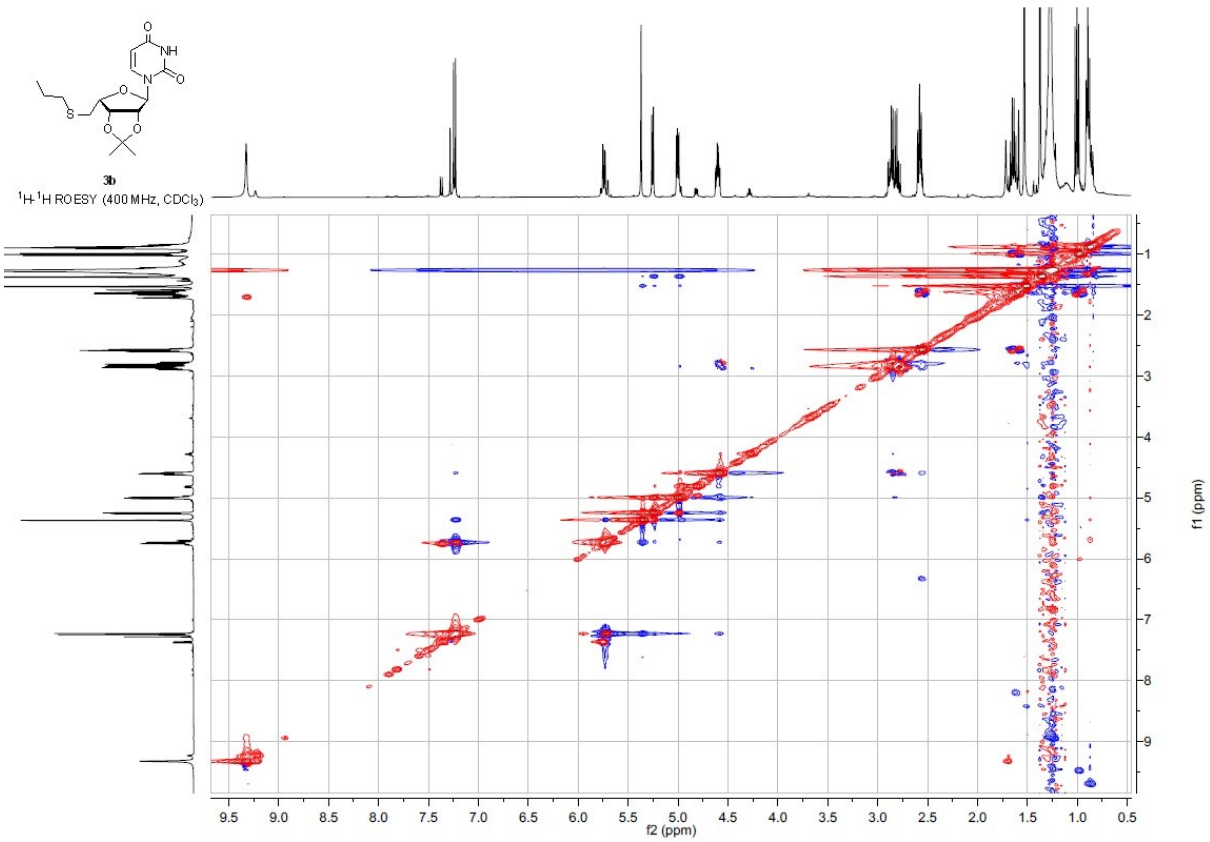
f2 (ppm)
f1 (ppm)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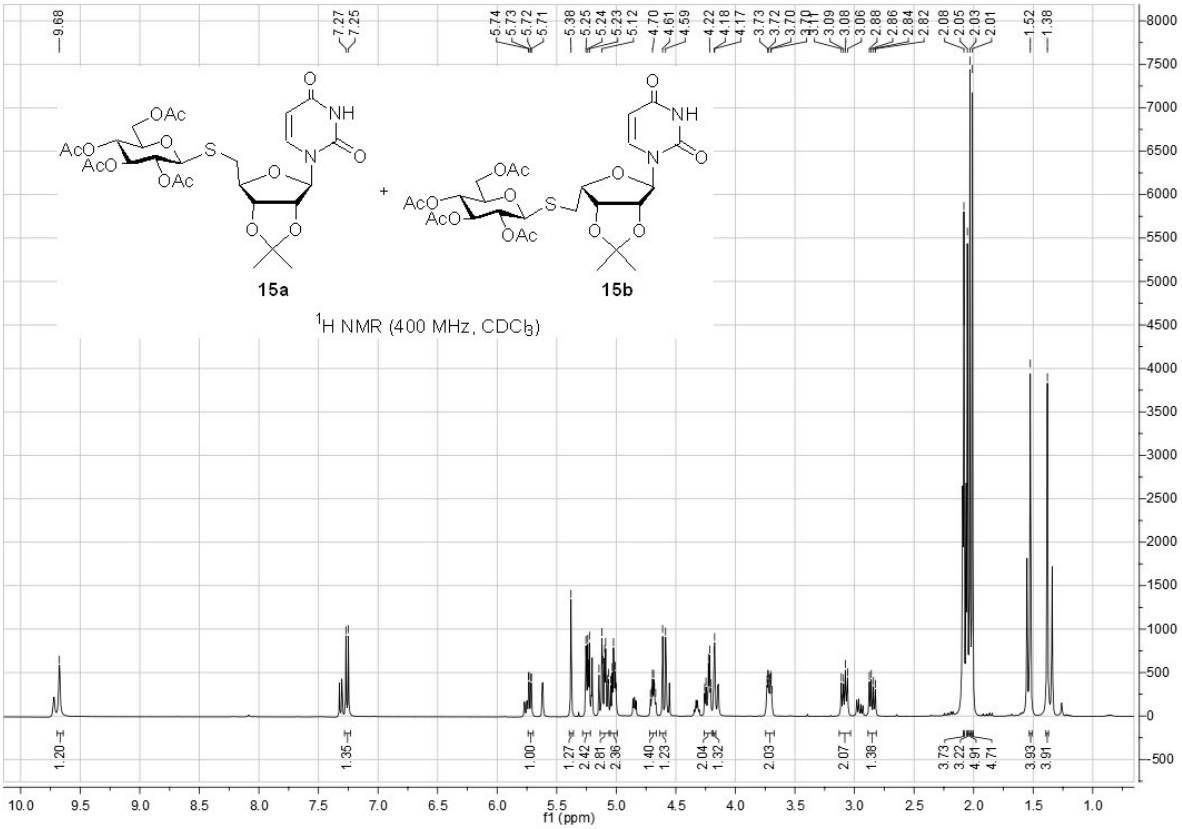
f2 (ppm)
f1 (ppm)


15a
15b
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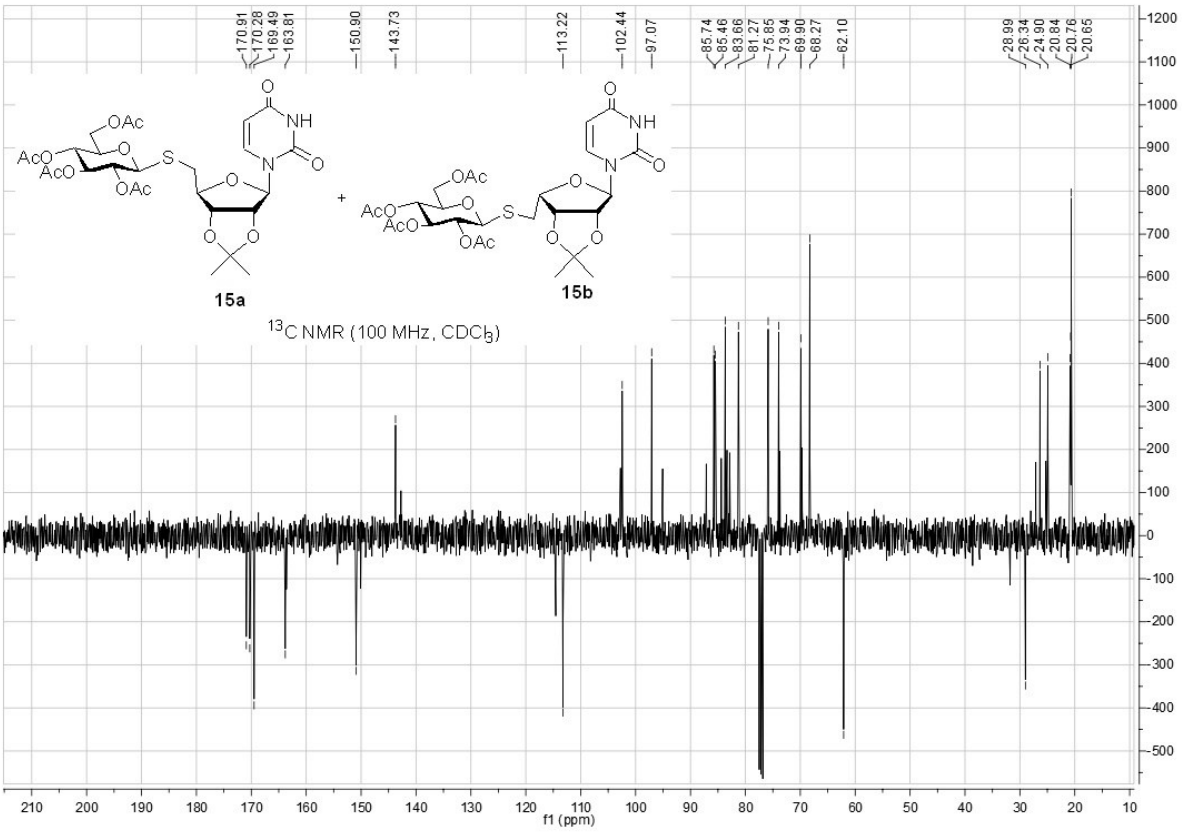
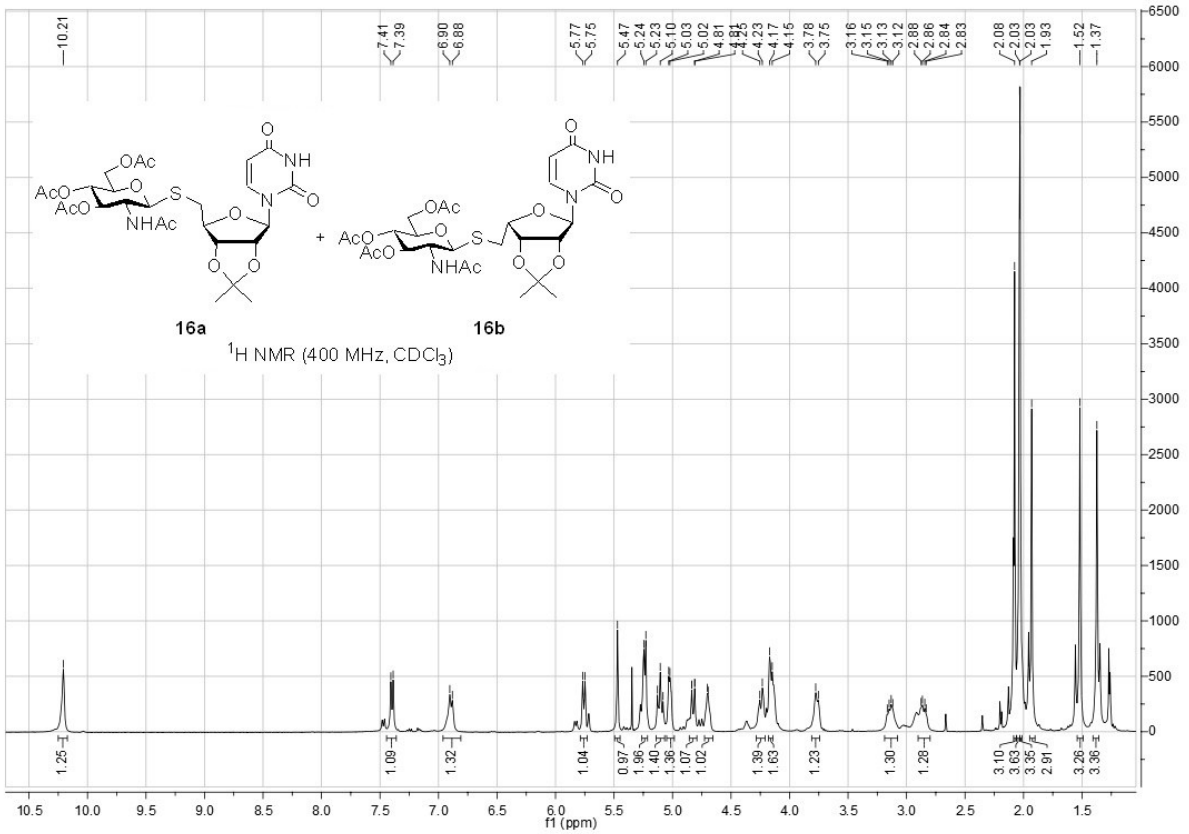
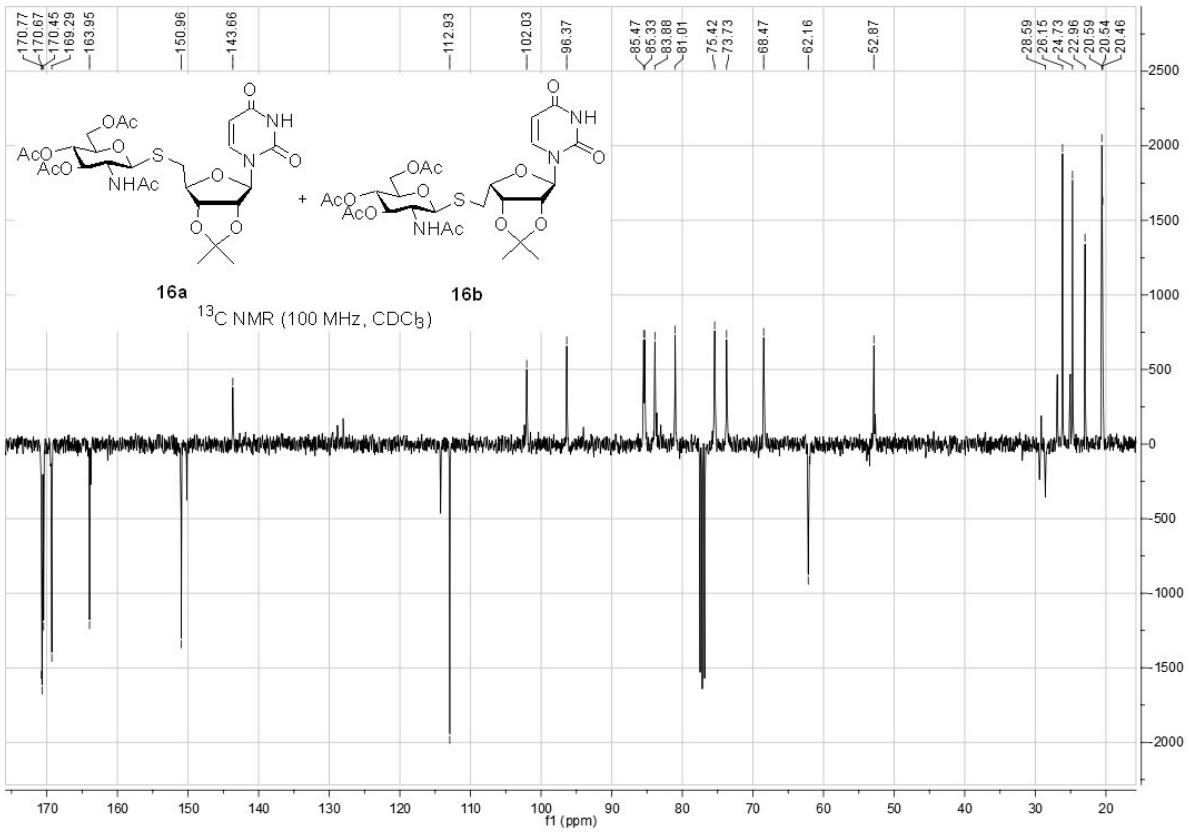
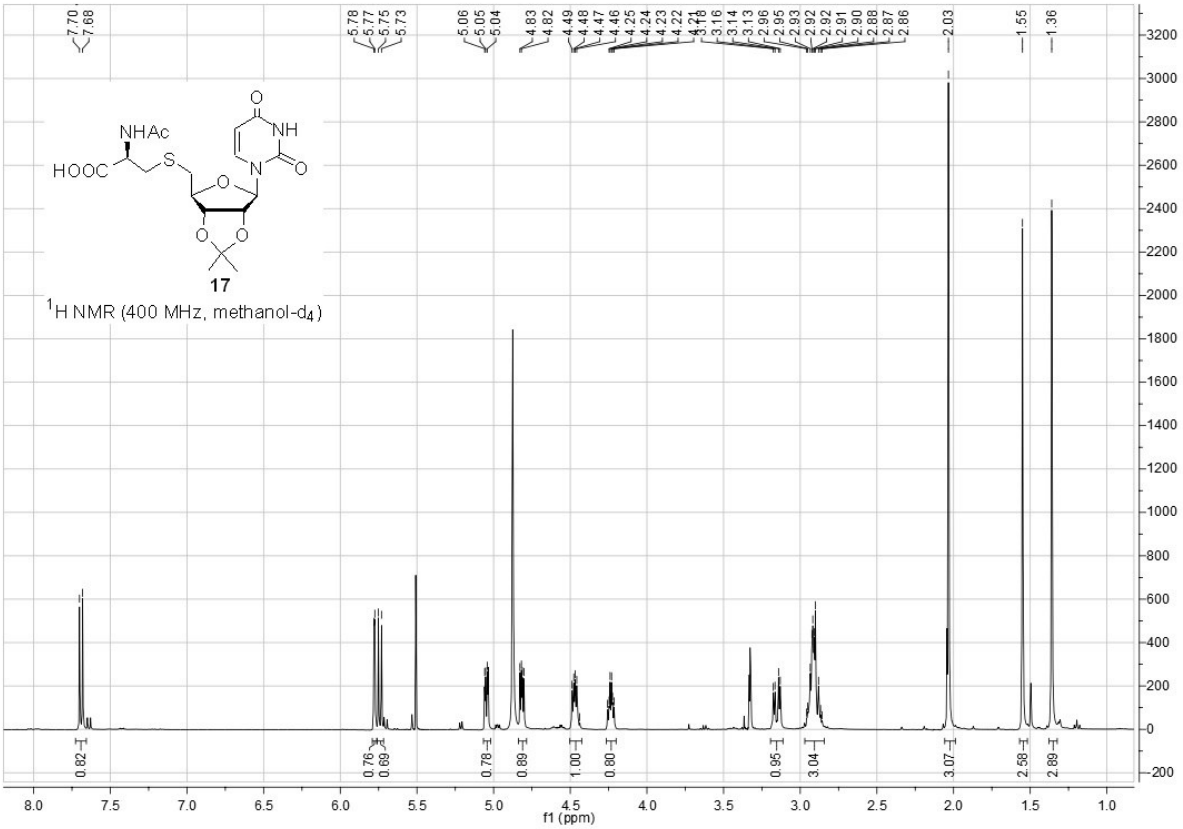
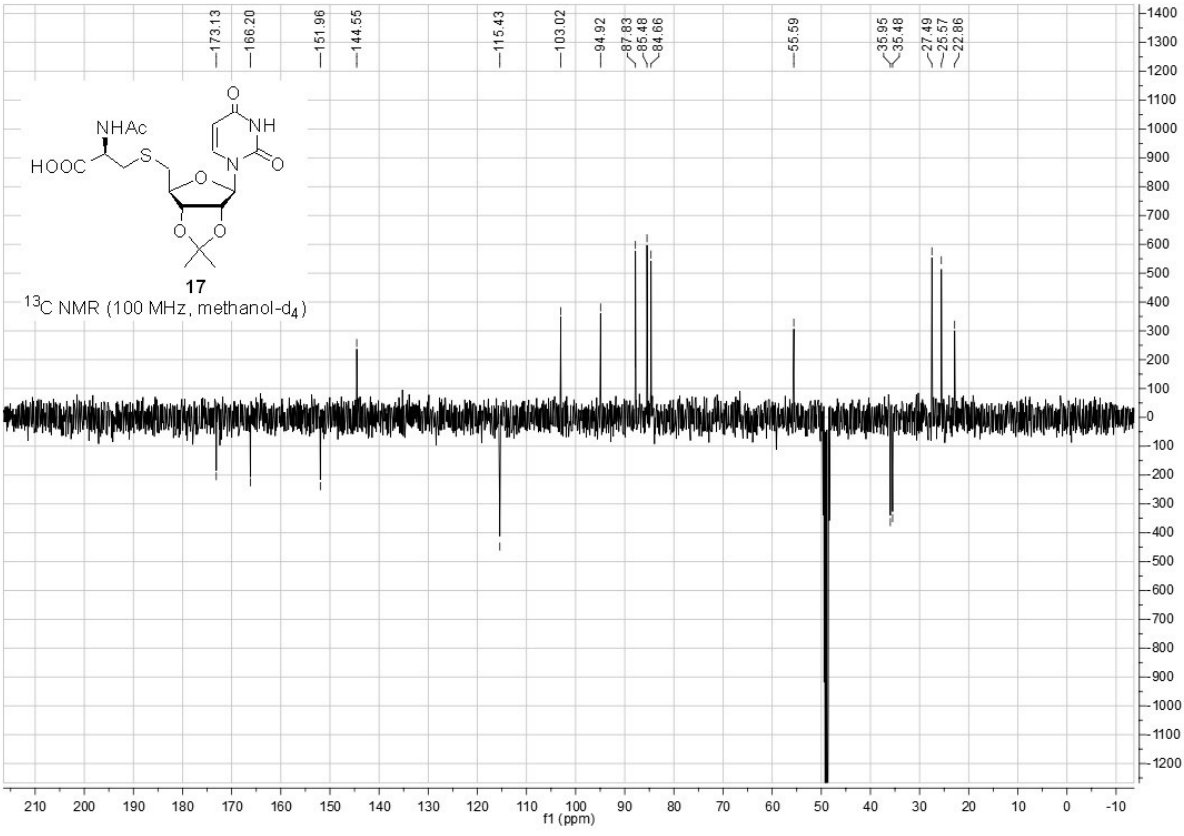
f1 (ppm)

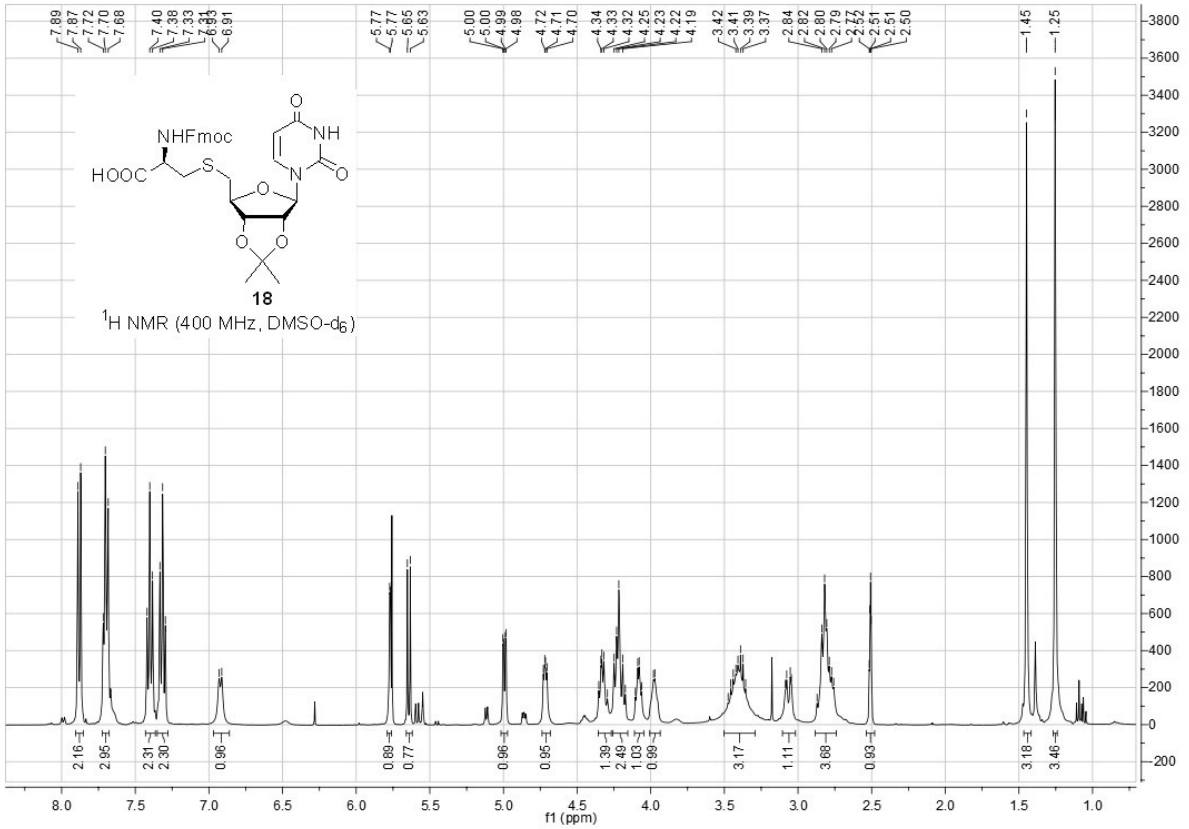

15a
15b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

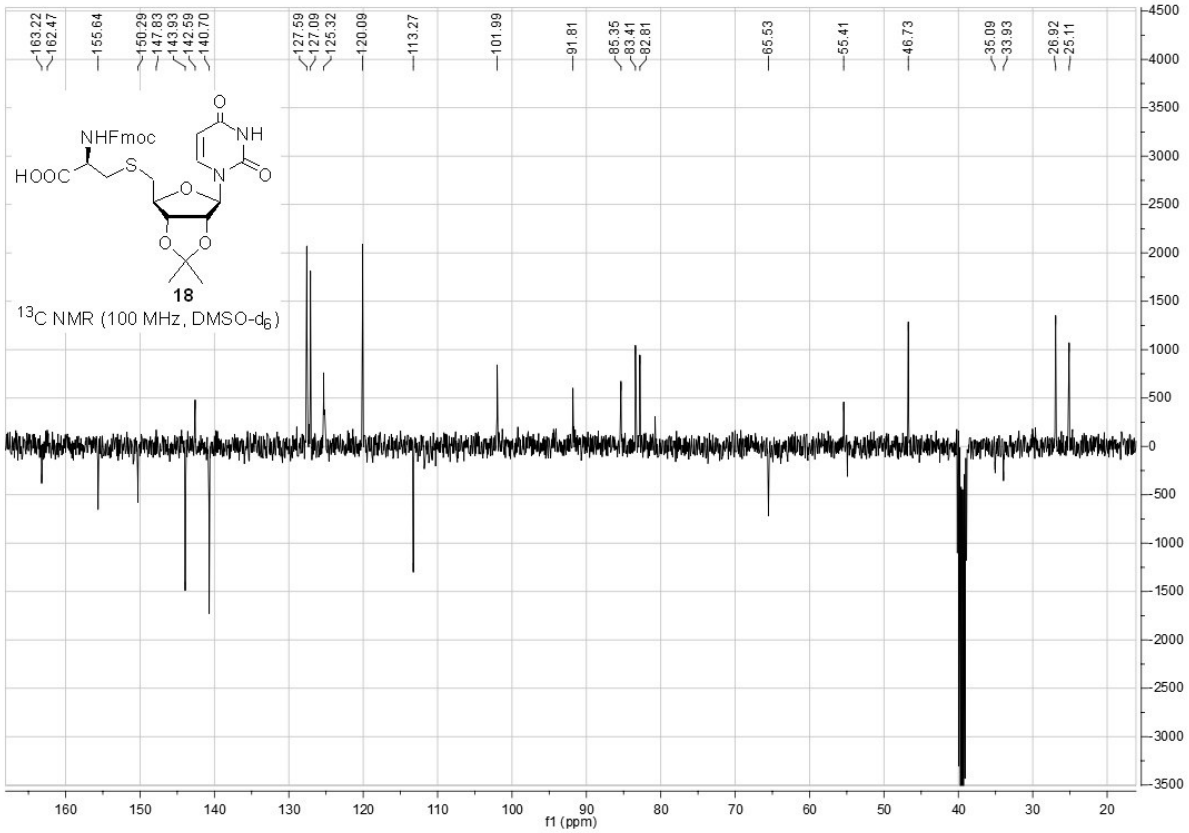

16a
16b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

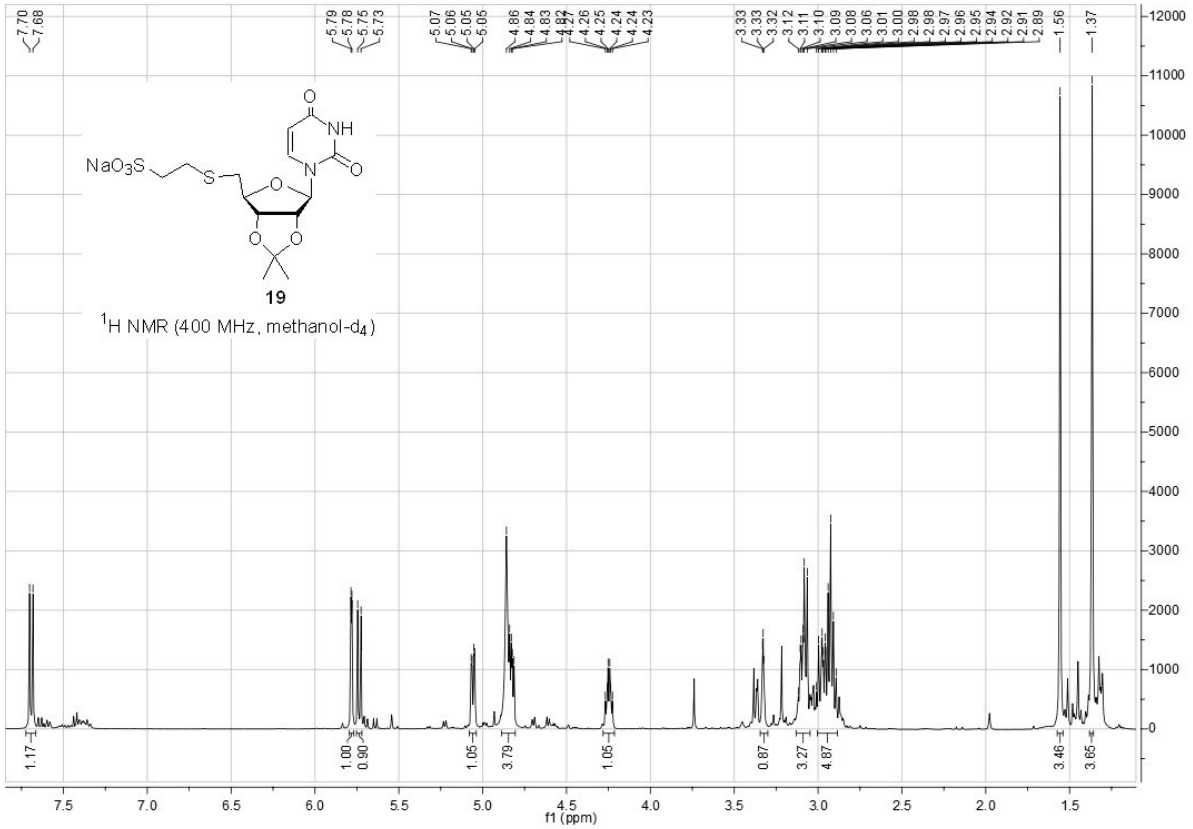

16a
16b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

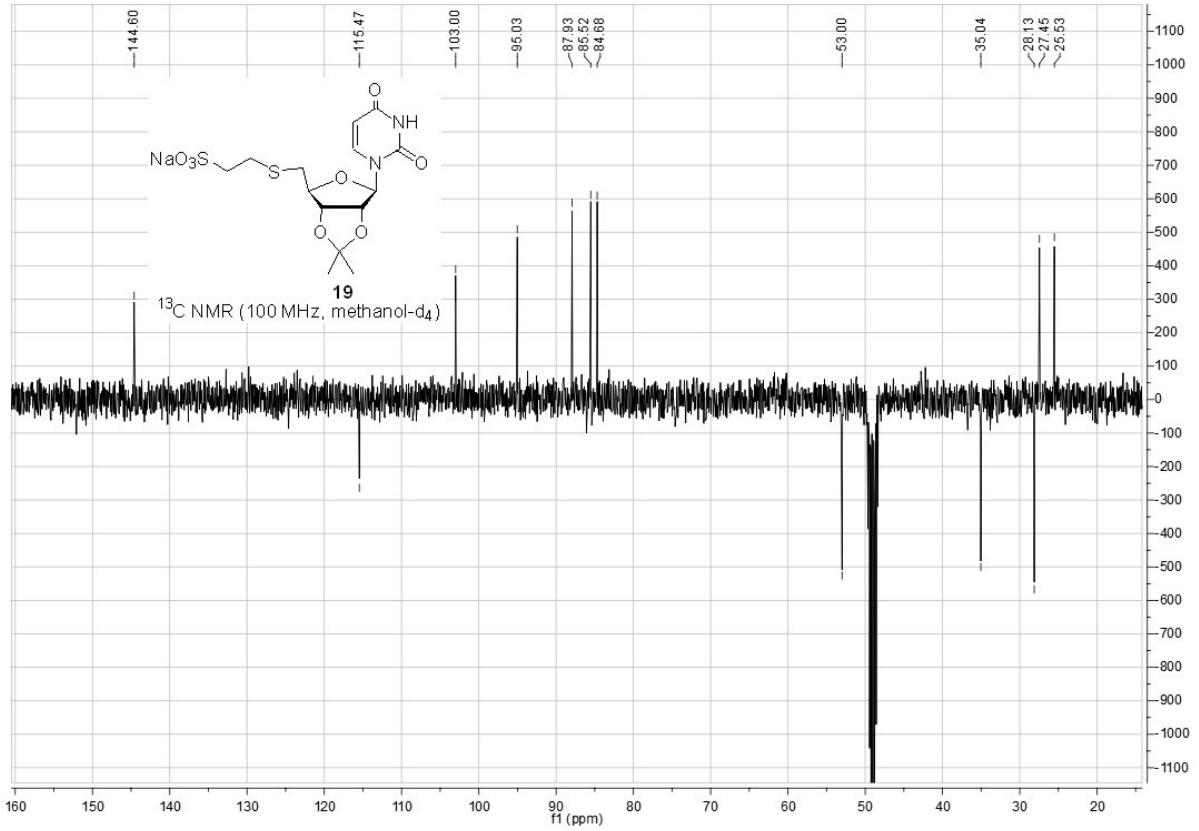

NHAc
HOOC
NH
O
S
O
N
O
O
O
17
^{1}H NMR (400 MHz, methanol-d$_4$)
f1 (ppm)

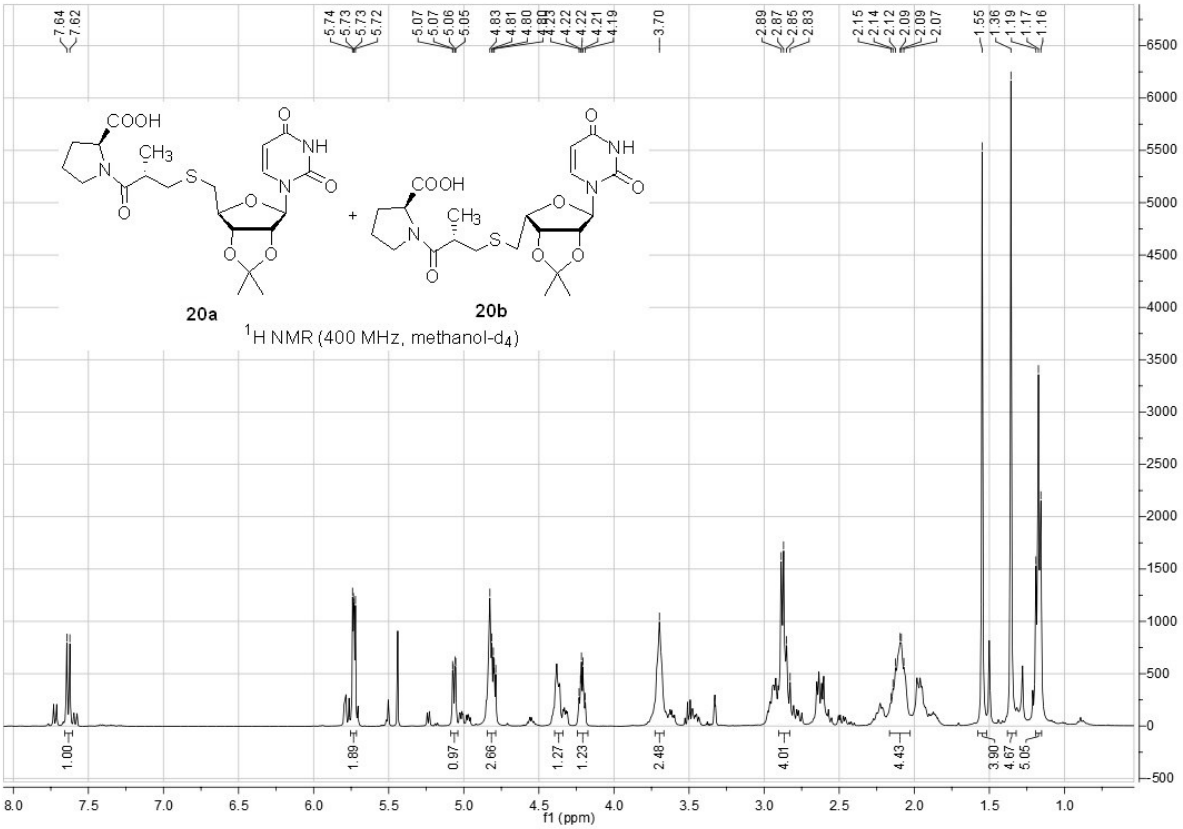

NHAc
HOOC
NH
O
S
O
N
O
O
O
17
^{13}C NMR (100 MHz, methanol-d$_4$)
f1 (ppm)

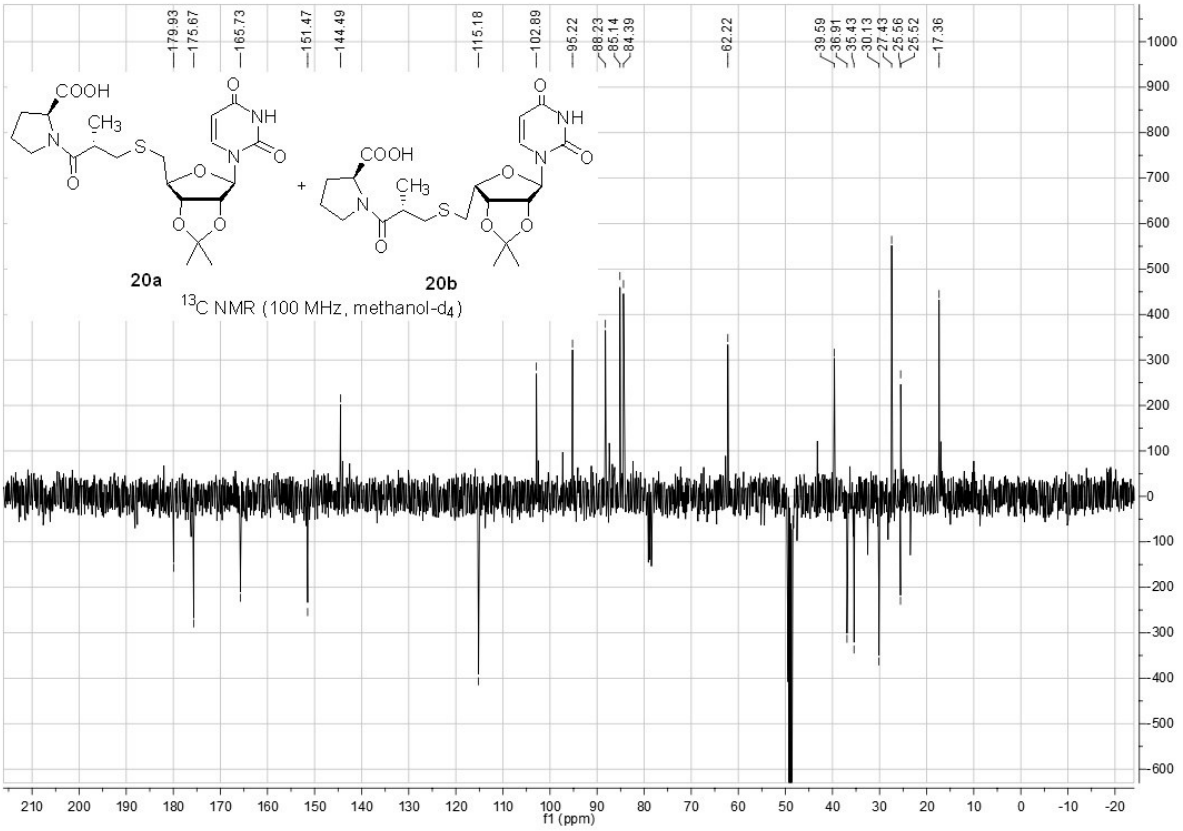

NHFmoc
HOOC
NH
O
O
18
^{1}H NMR (400 MHz, DMSO-d$_6$)

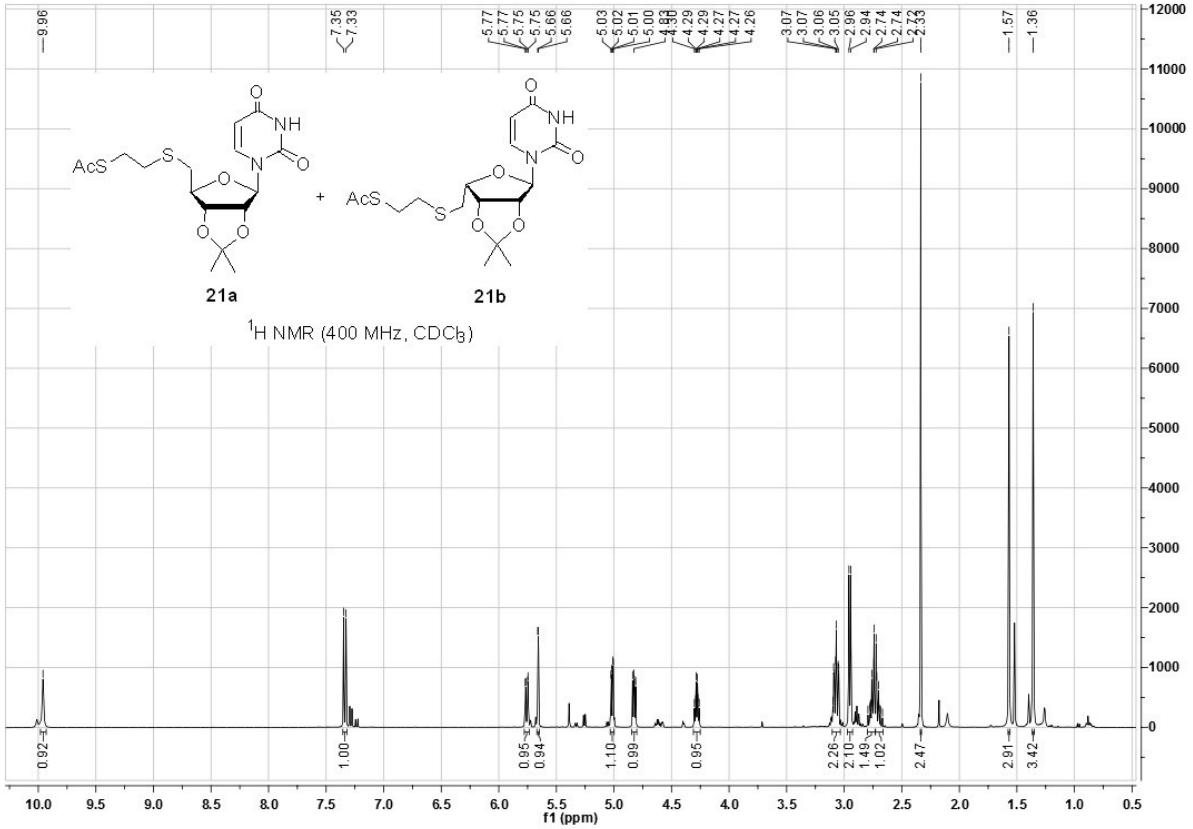

NHFmoc
HOOC
NH
O
O
18
^{13}C NMR (100 MHz, DMSO-d$_6$)

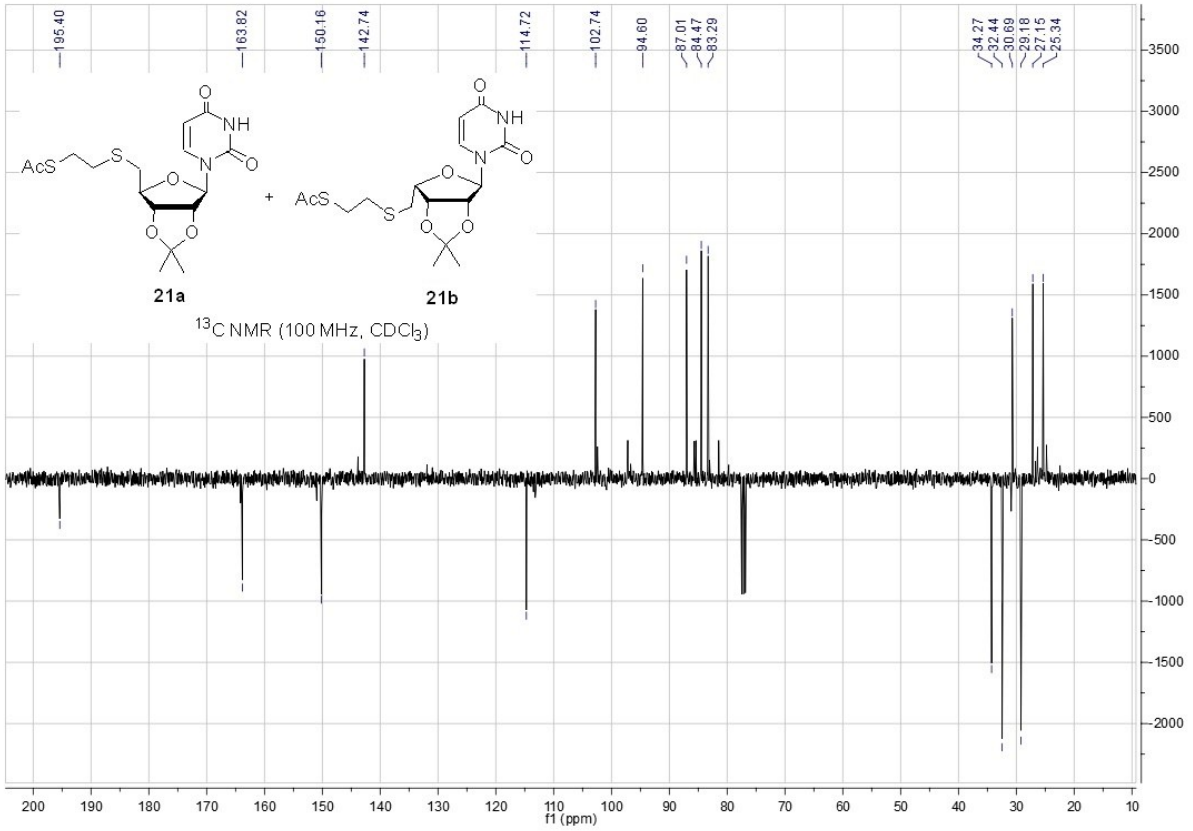

NaO3S
NH
19
1H NMR (400 MHz, methanol-d4)
f1 (ppm)

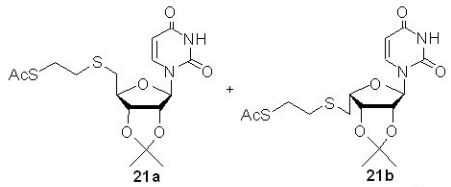

NaO3S
NH
19
13C NMR (100 MHz, methanol-d4)
f1 (ppm)


20a
20b
^{1}H NMR (400 MHz, methanol-d$_4$)
f1 (ppm)


20a
20b
^{13}C NMR (100 MHz, methanol-d$_4$)
f1 (ppm)

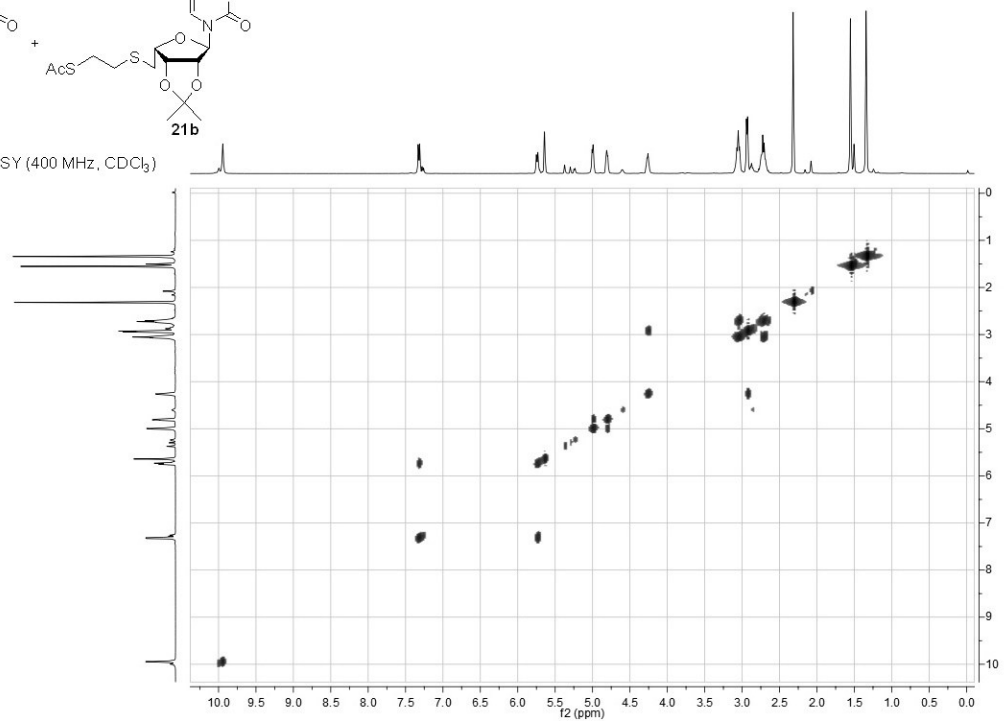

21a
21b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

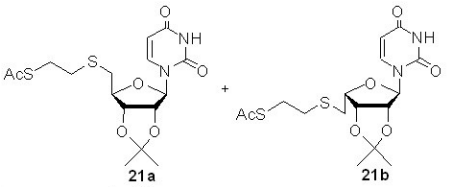

21a
21b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



21a **21b**

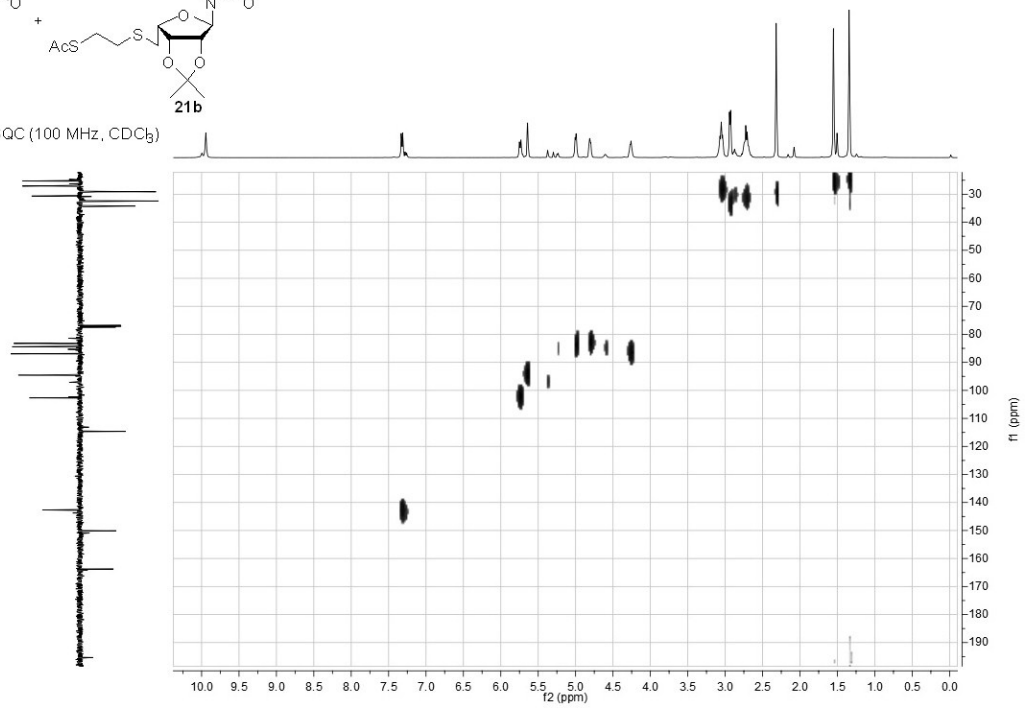
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)

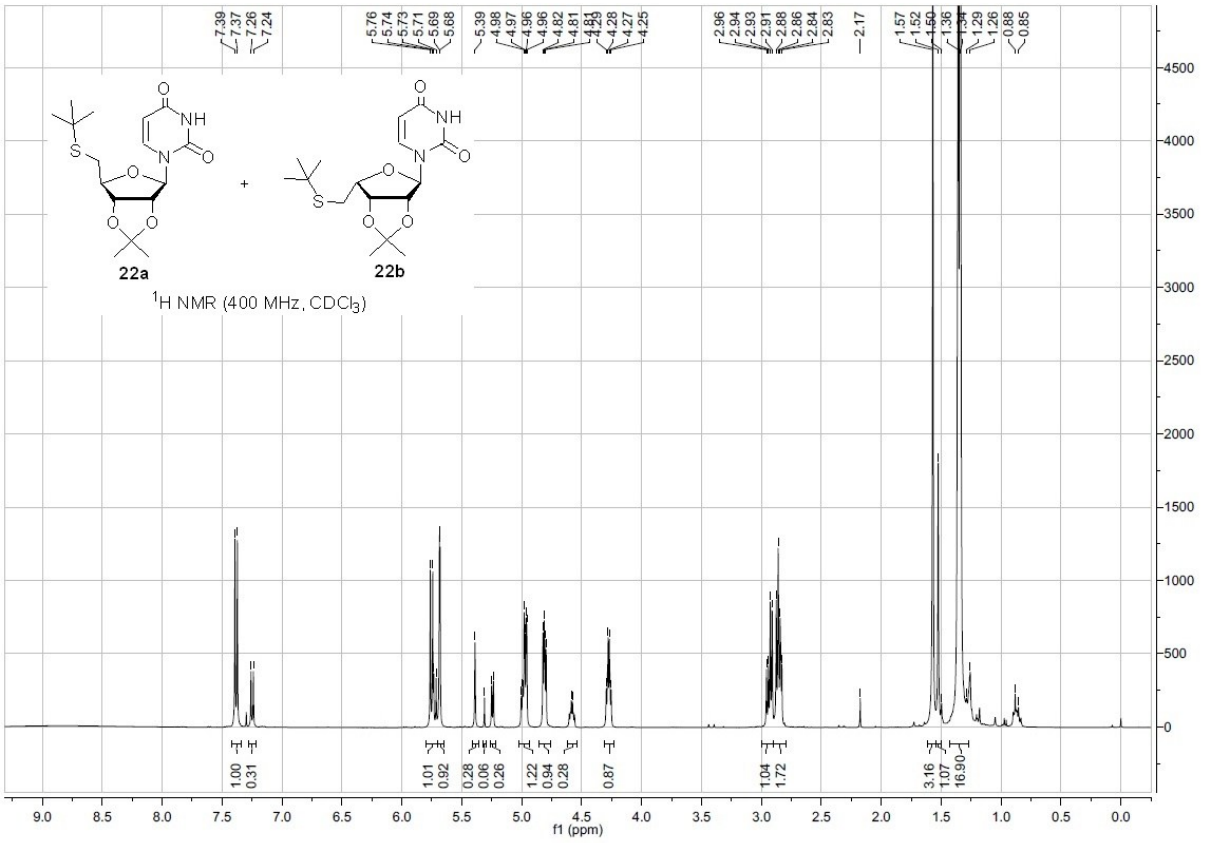


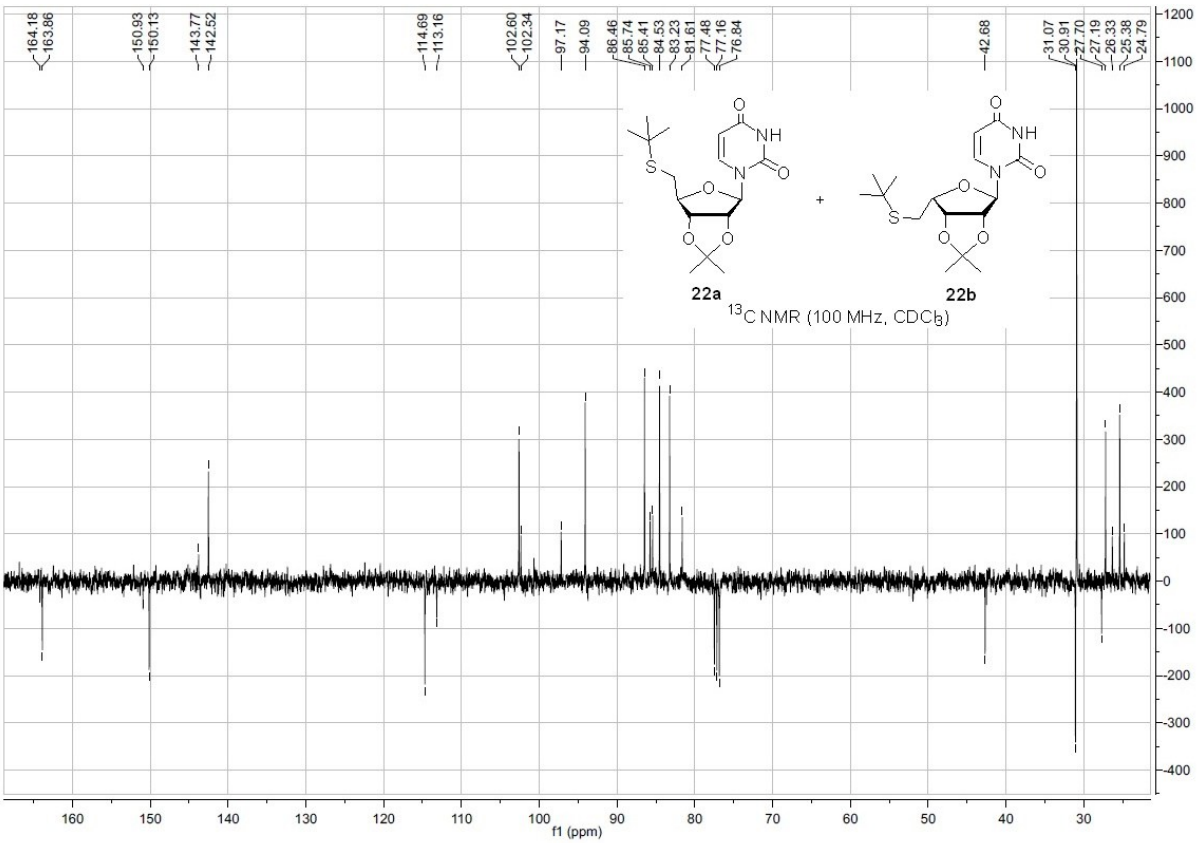


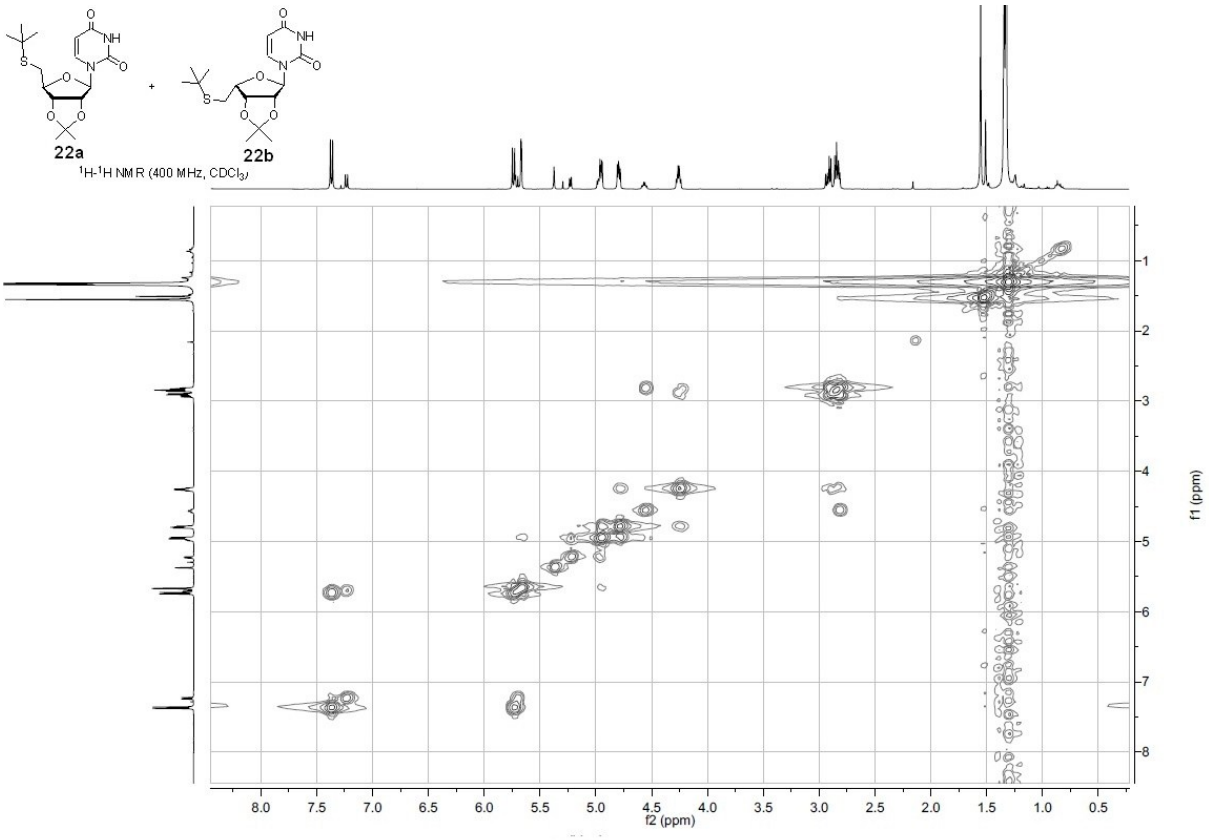
21a **21b**

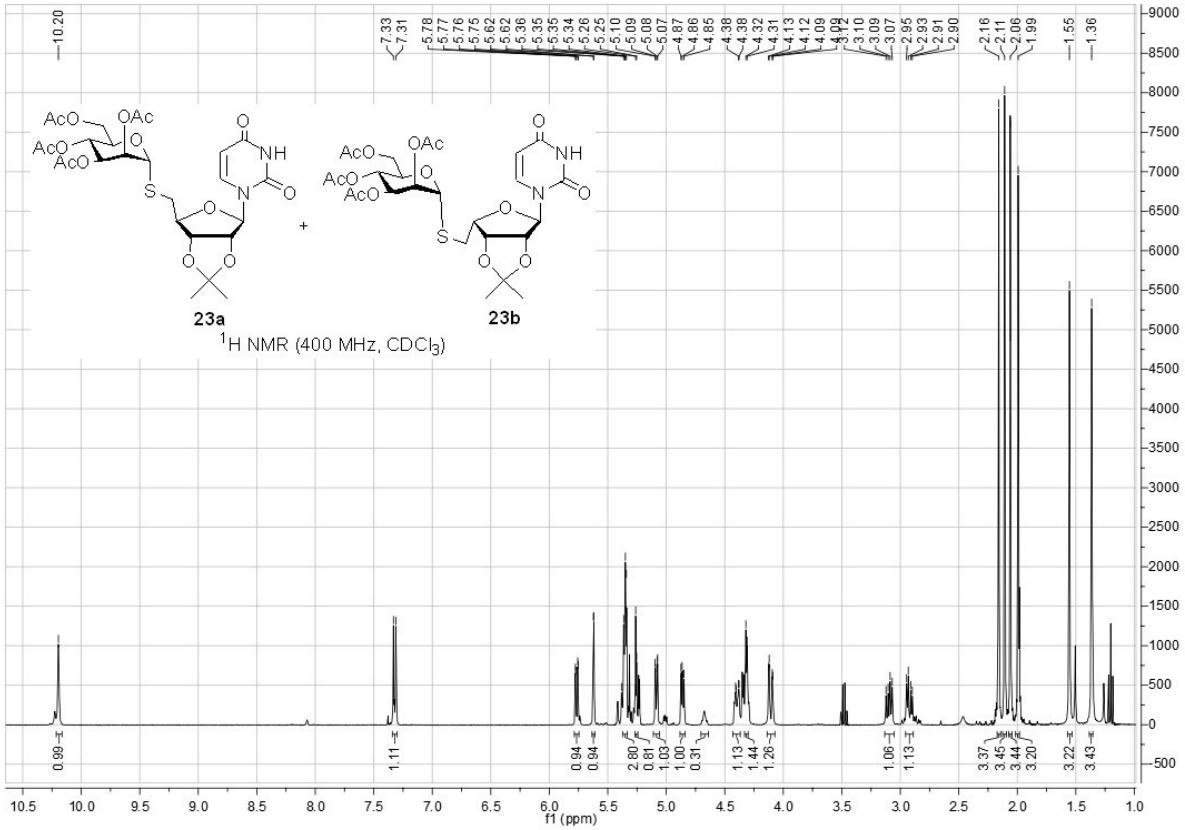
^{1}H-^{13}C HSQC (100 MHz, $CDCl_3$)

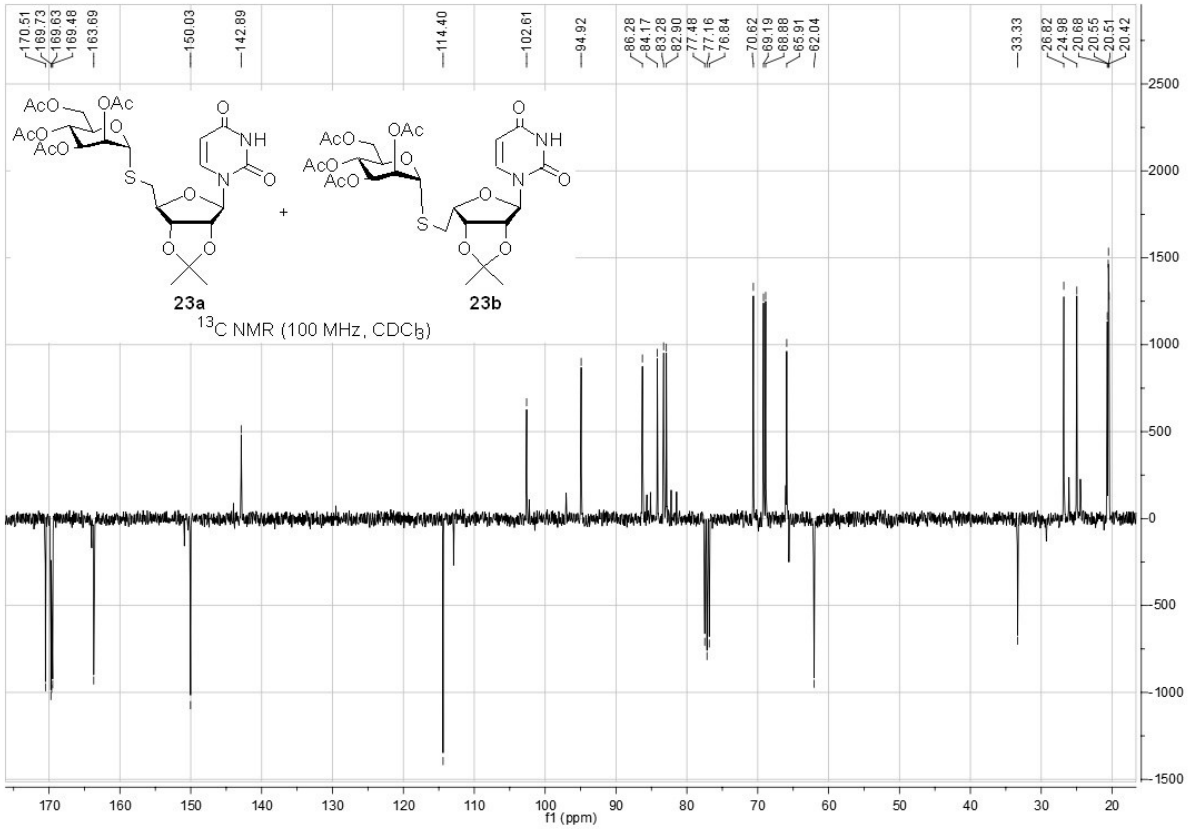


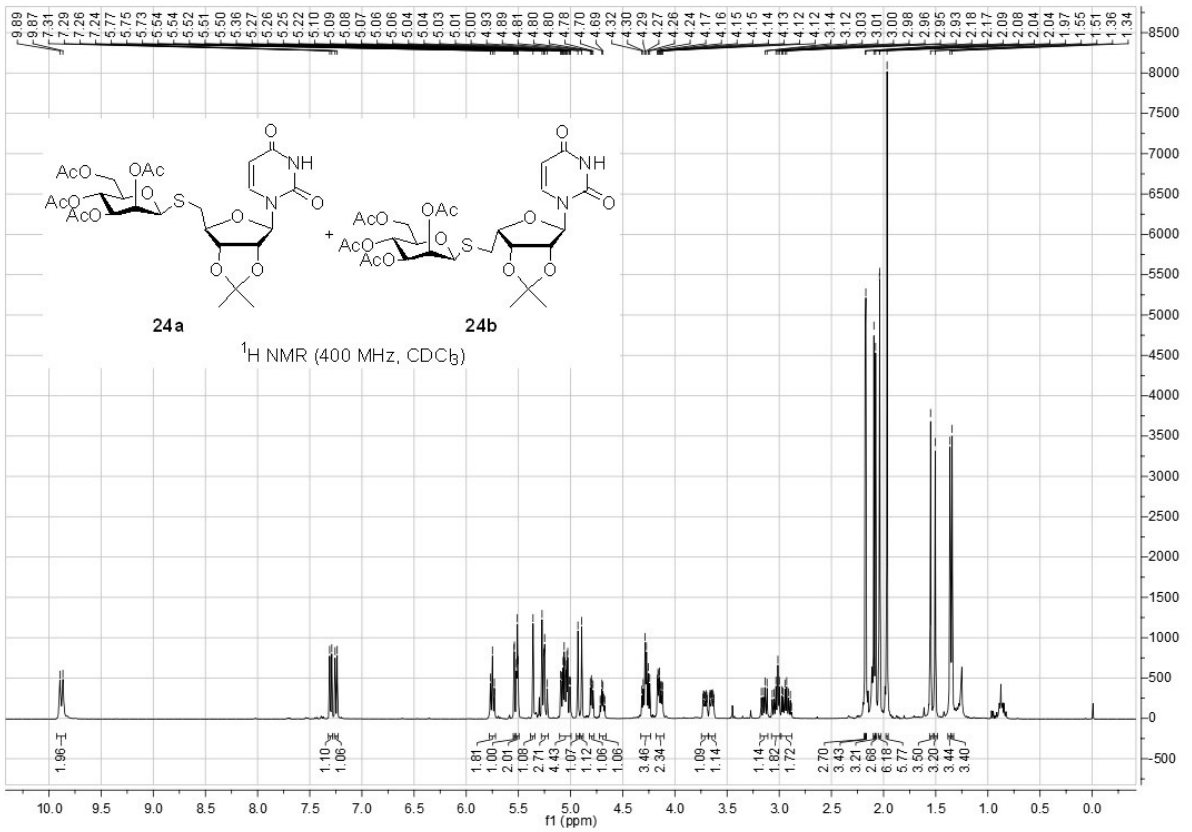

22a
22b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

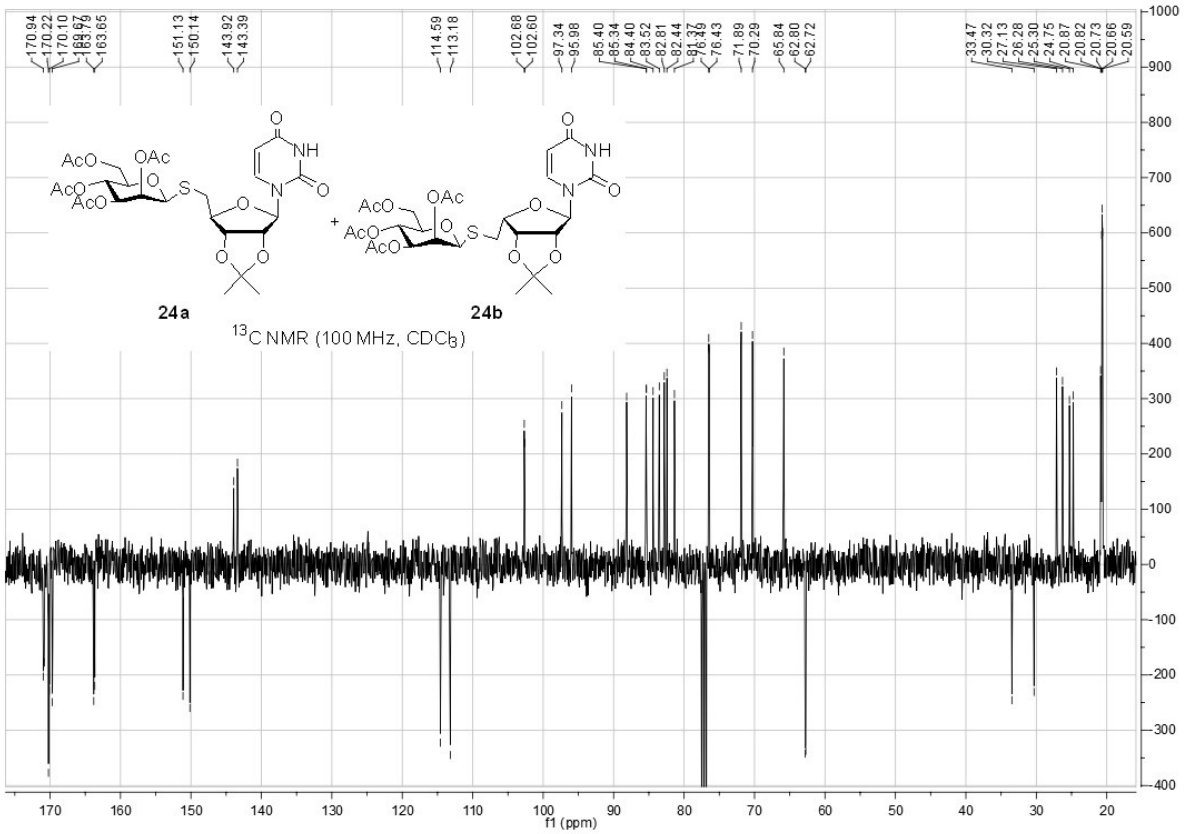

22a
22b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

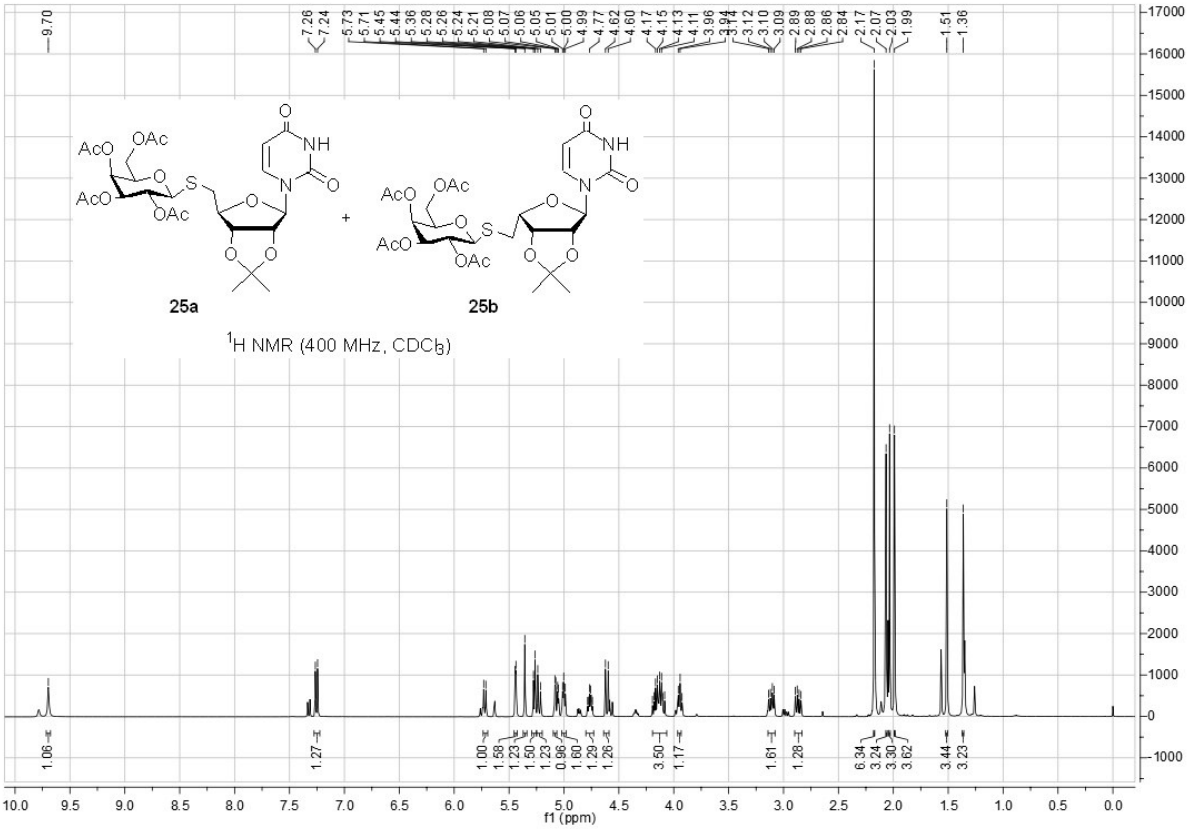

22a
22b
^{1}H-^{1}H NMR (400 MHz, $CDCl_3$)
f2 (ppm)
f1 (ppm)

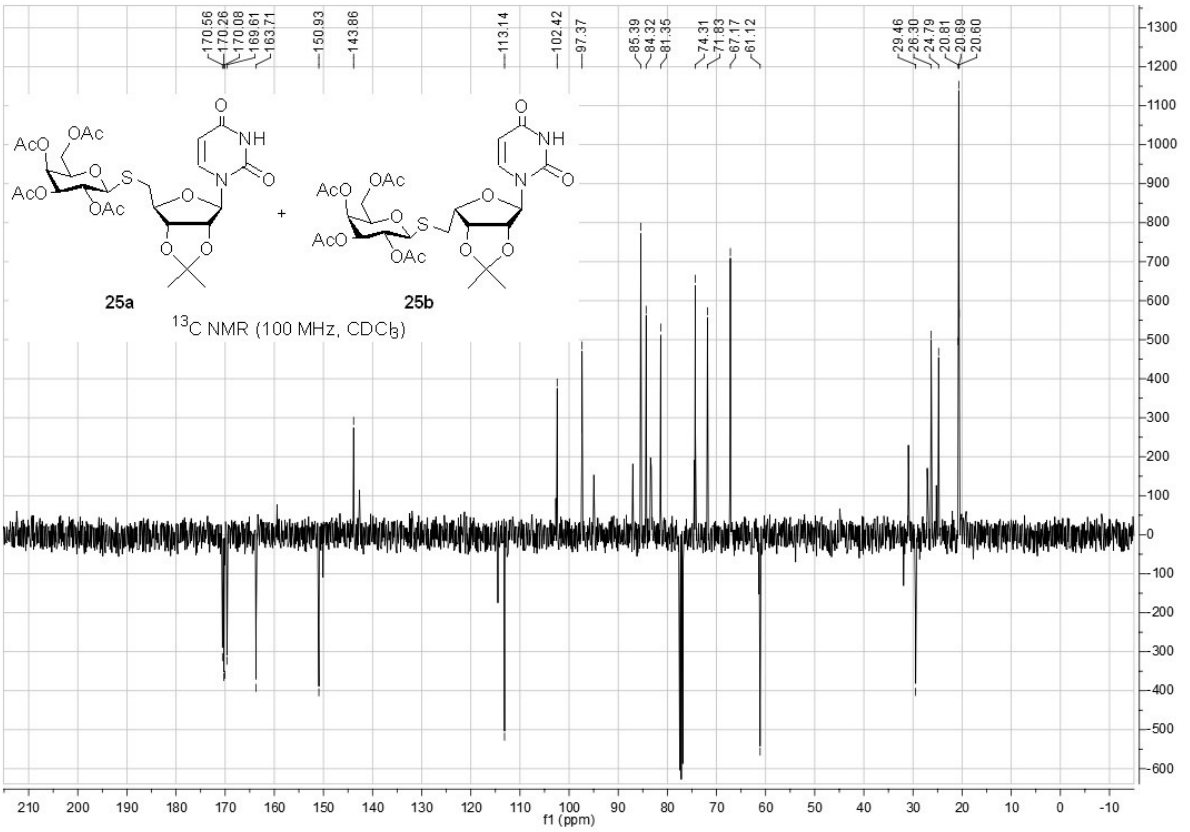

23a
23b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

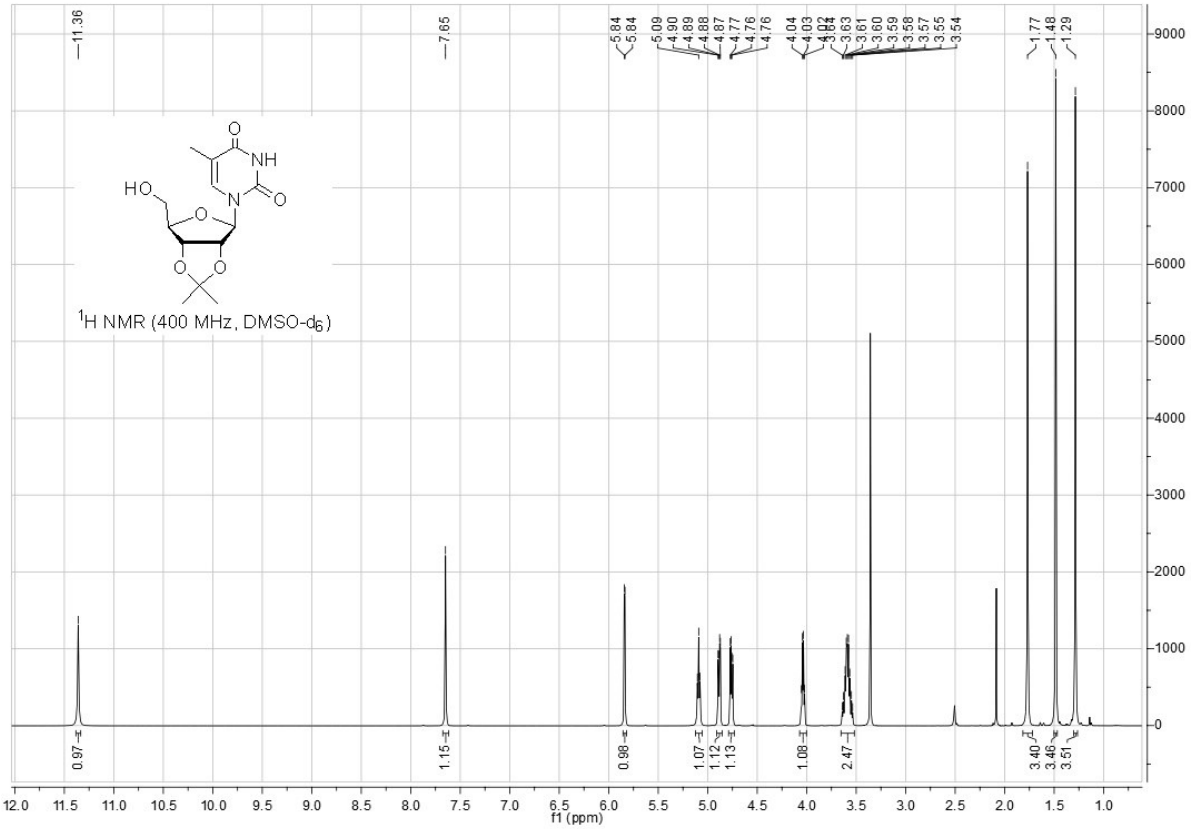

23a
23b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

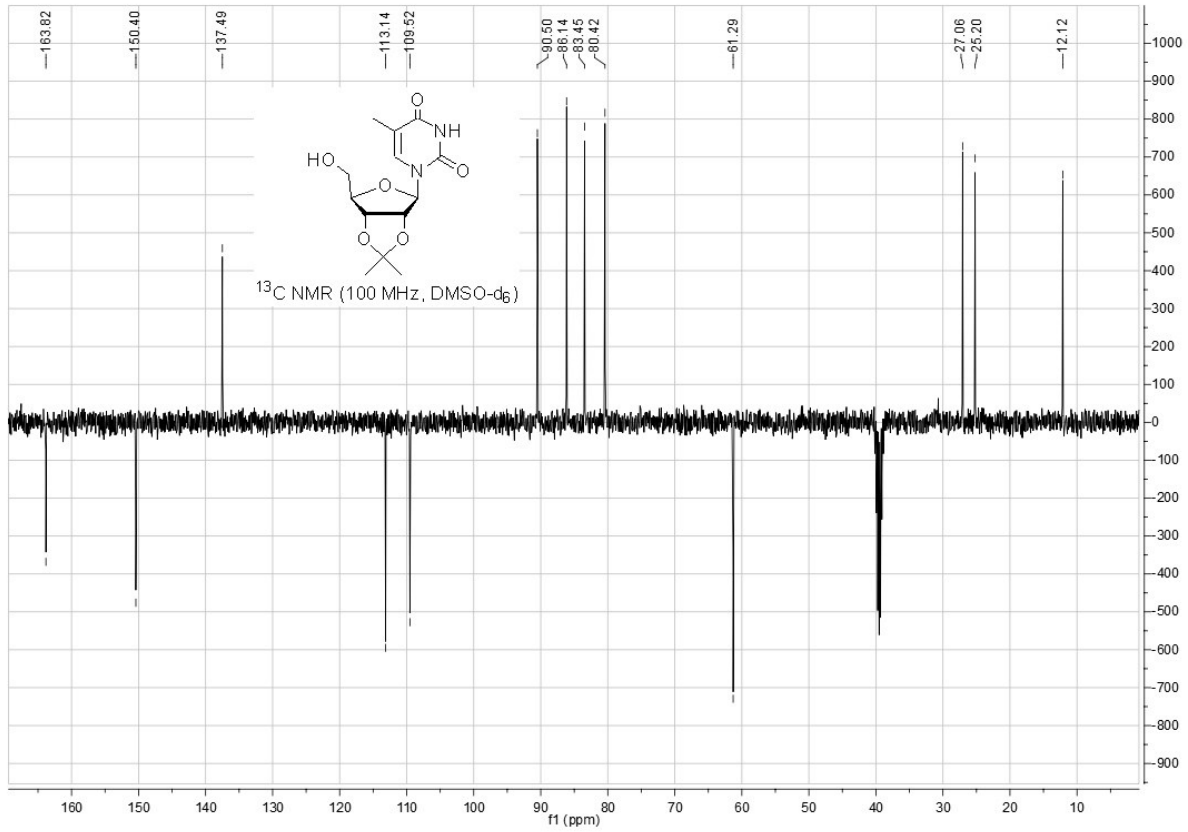

24a
24b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

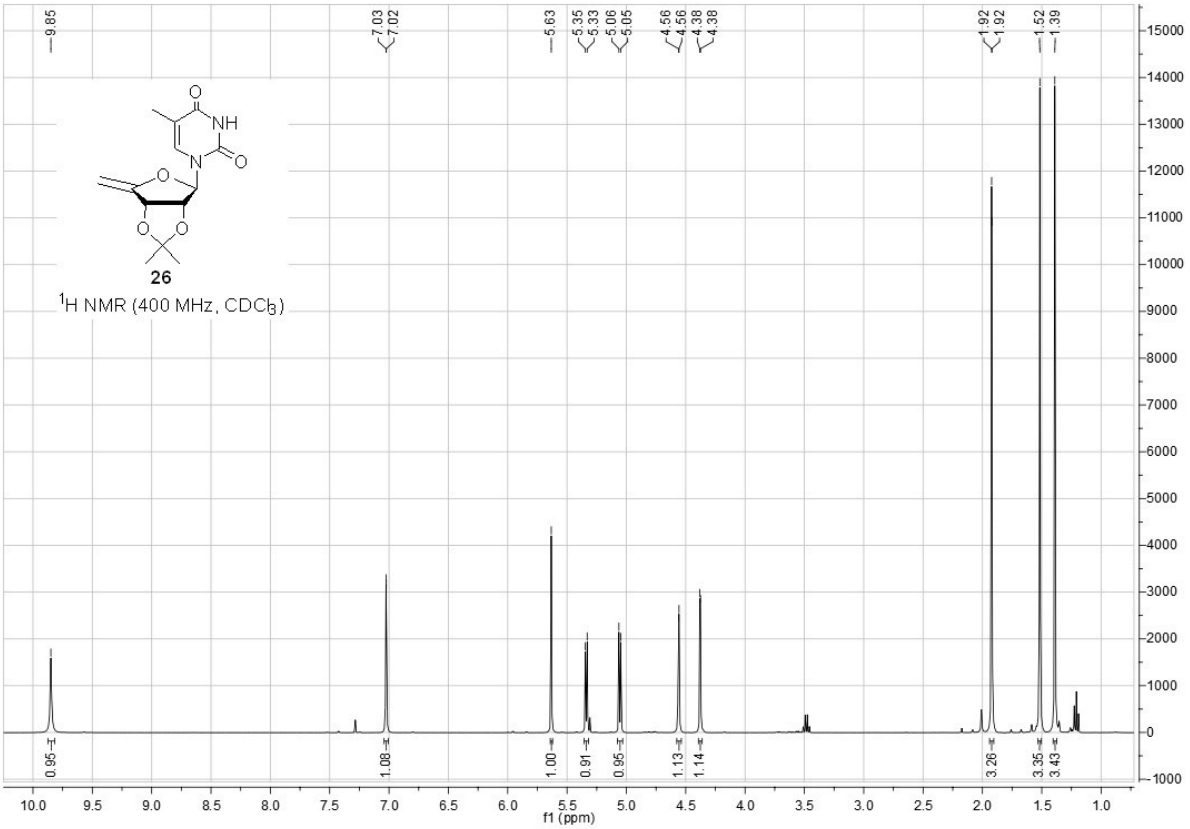

24a
24b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

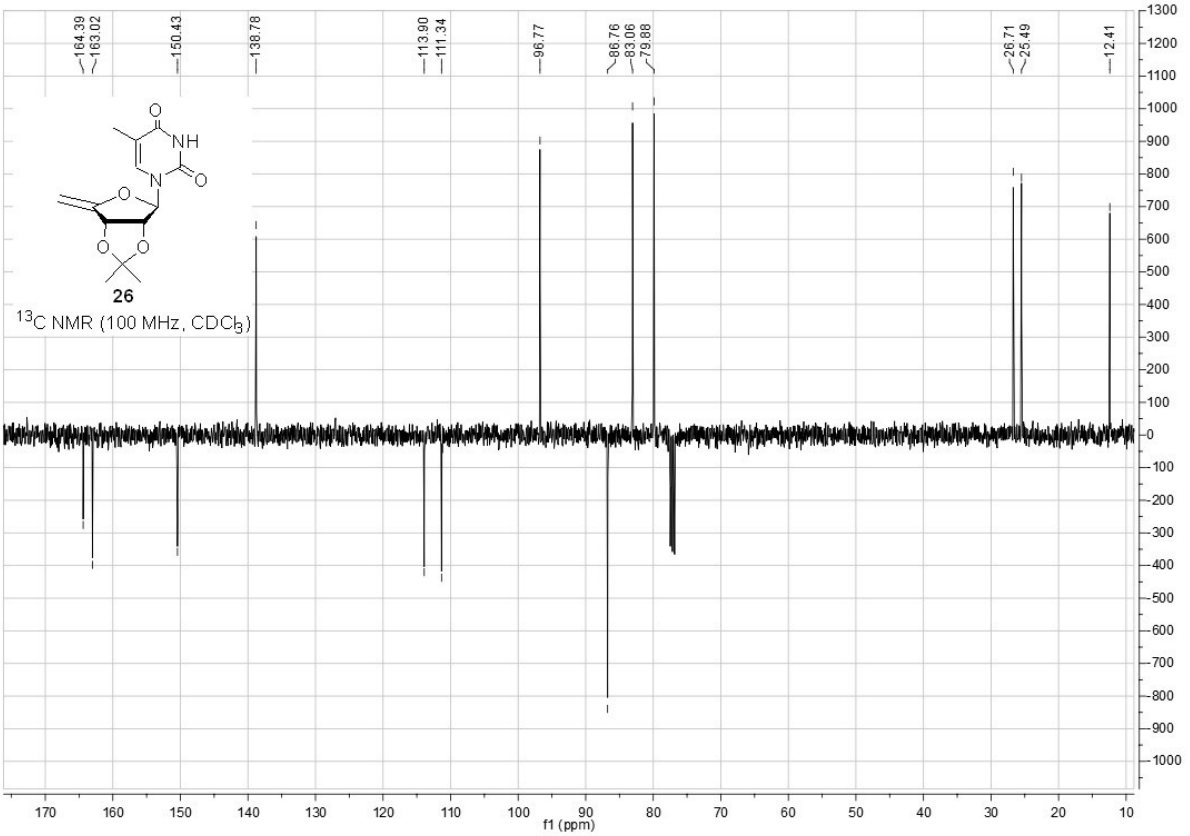

25a
25b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

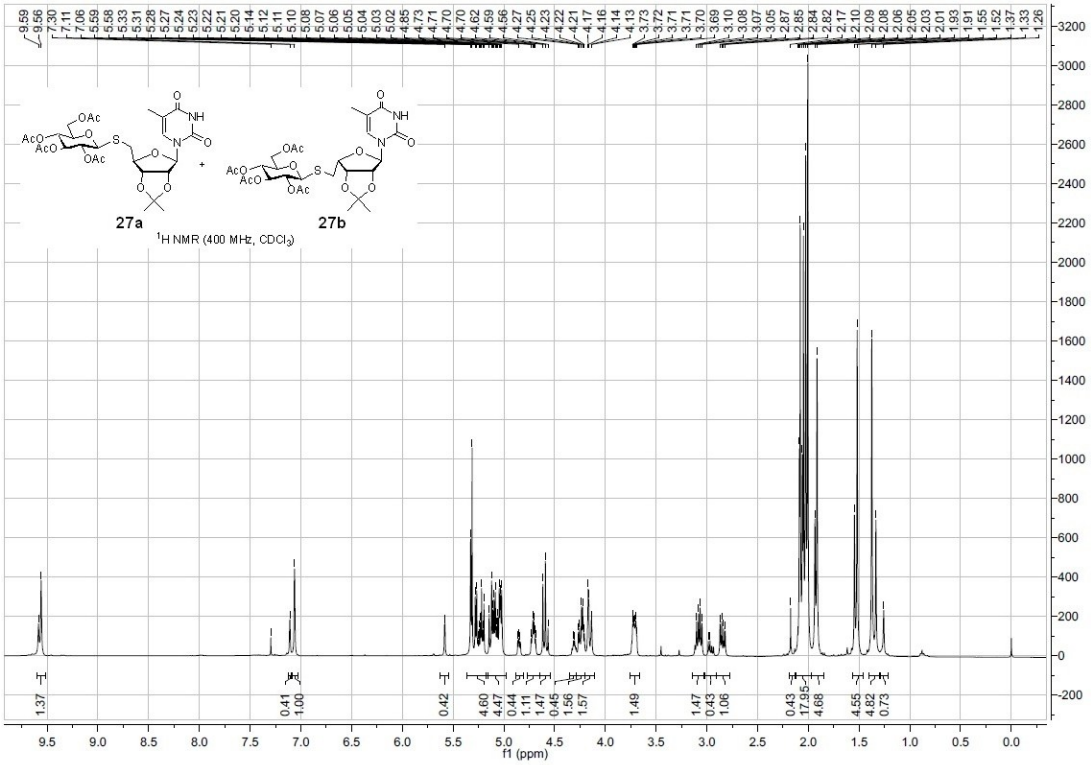

25a
25b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

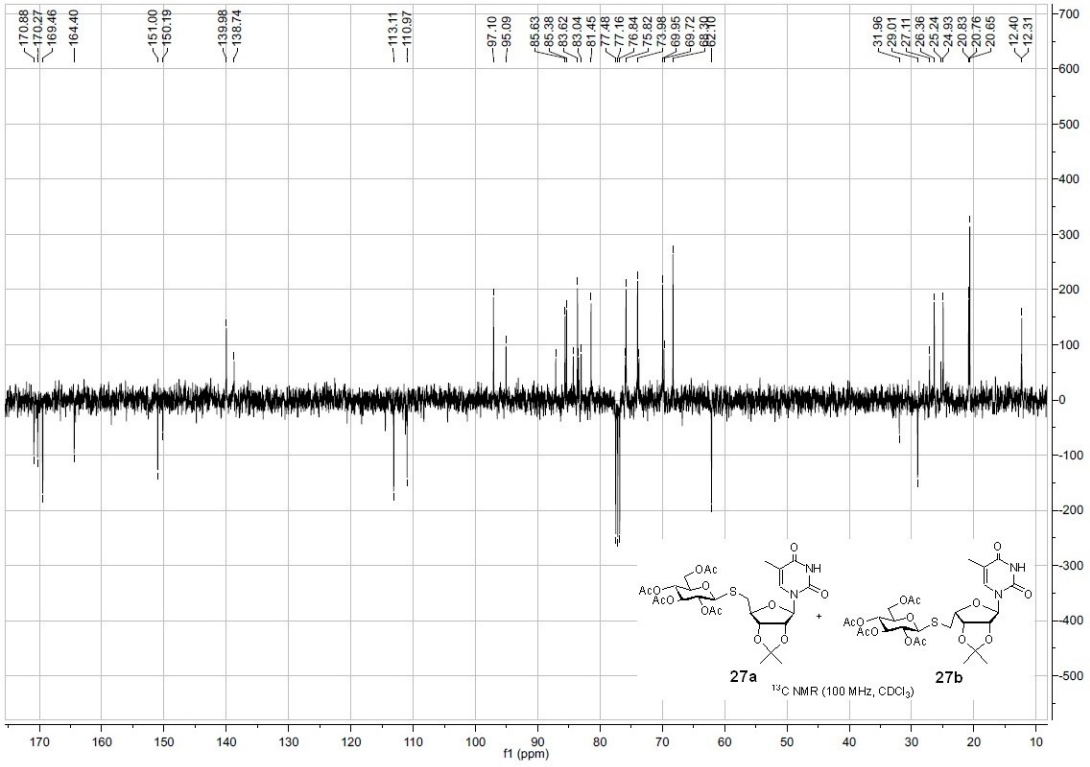

11.36
7.65
5.84
5.84
5.09
4.90
4.89
4.88
4.87
4.77
4.76
4.76
4.04
4.03
3.63
3.61
3.60
3.59
3.58
3.57
3.55
3.54
1.77
1.48
1.29
0.97
1.15
0.98
1.07
1.12
1.13
1.08
2.47
3.40
3.46
3.51
f1 (ppm)
HO
NH
O
N
O
O
O
O
^{1}H NMR (400 MHz, DMSO-d$_6$)

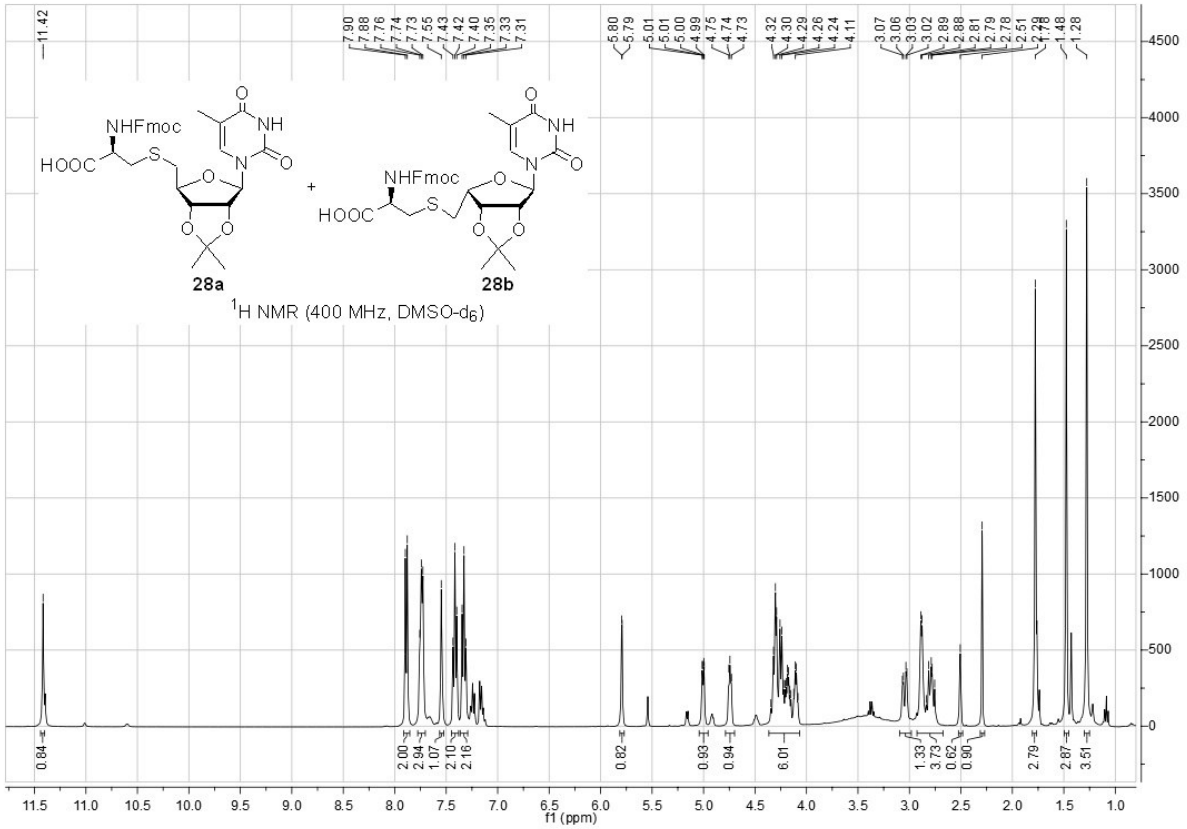

163.82
150.40
137.49
113.14
109.52
90.50
86.14
83.45
80.42
61.29
27.06
25.20
12.12
f1 (ppm)
HO
NH
O
N
O
O
O
O
^{13}C NMR (100 MHz, DMSO-d$_6$)

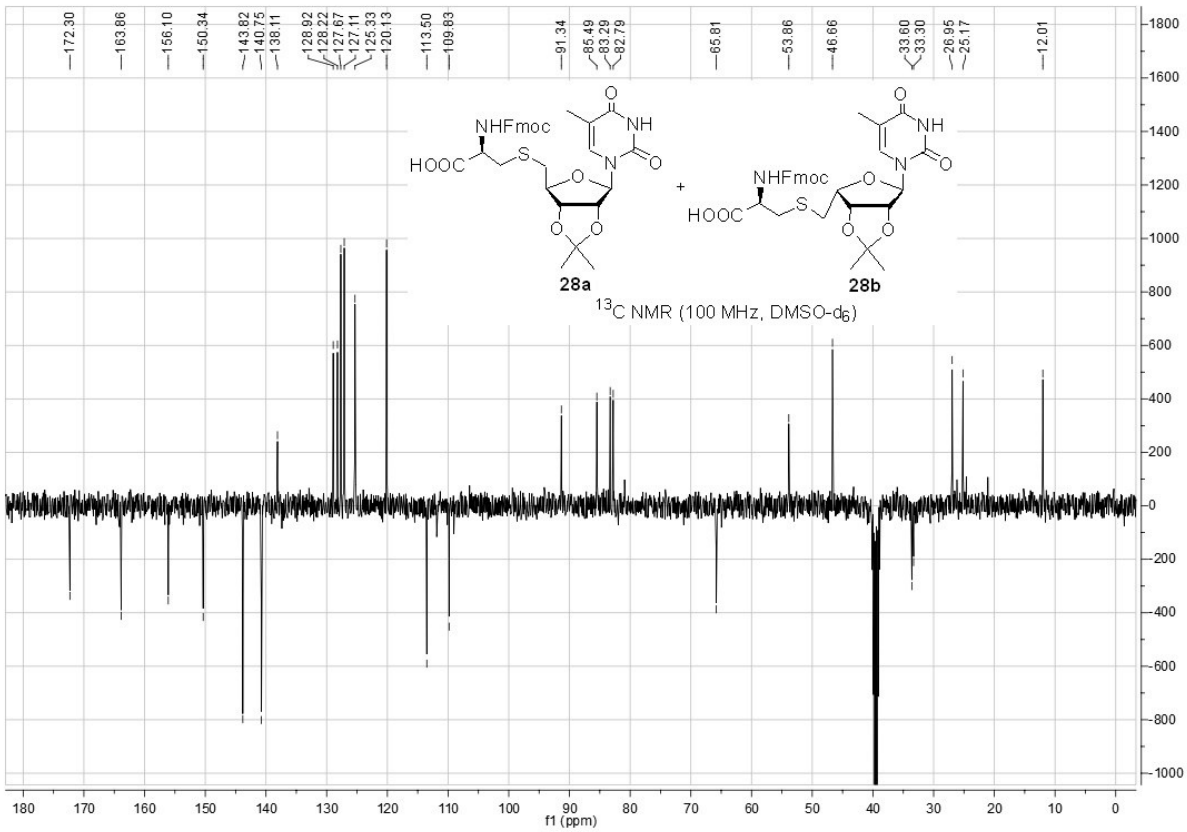

9.85
7.03
7.02
5.63
5.35
5.33
5.06
5.05
4.56
4.56
4.38
4.38
1.92
1.92
1.52
1.39
26
^{1}H NMR (400 MHz, $CDCl_3$)
0.95
1.08
1.00
0.91
0.95
1.13
1.14
3.26
3.35
3.43
f1 (ppm)

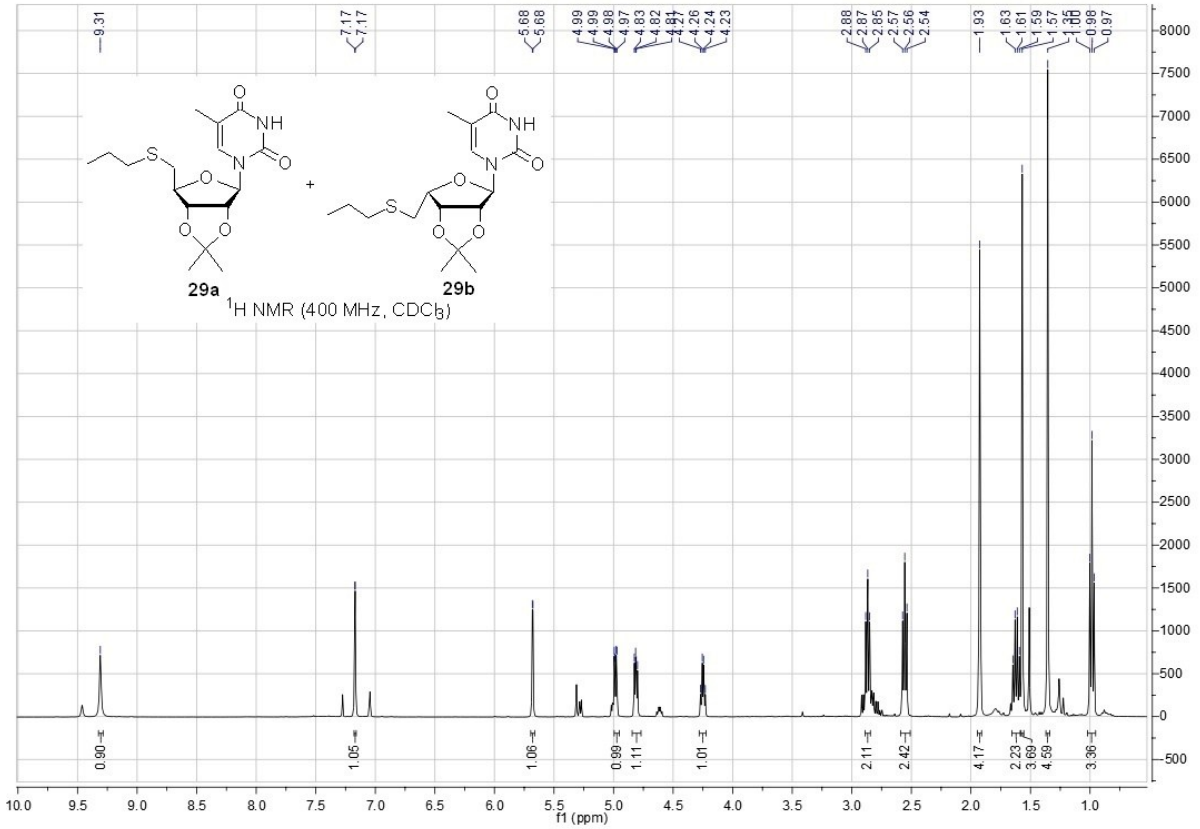

164.39
163.02
150.43
138.78
113.90
111.34
96.77
86.76
83.06
79.88
26.71
25.49
12.41
26
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

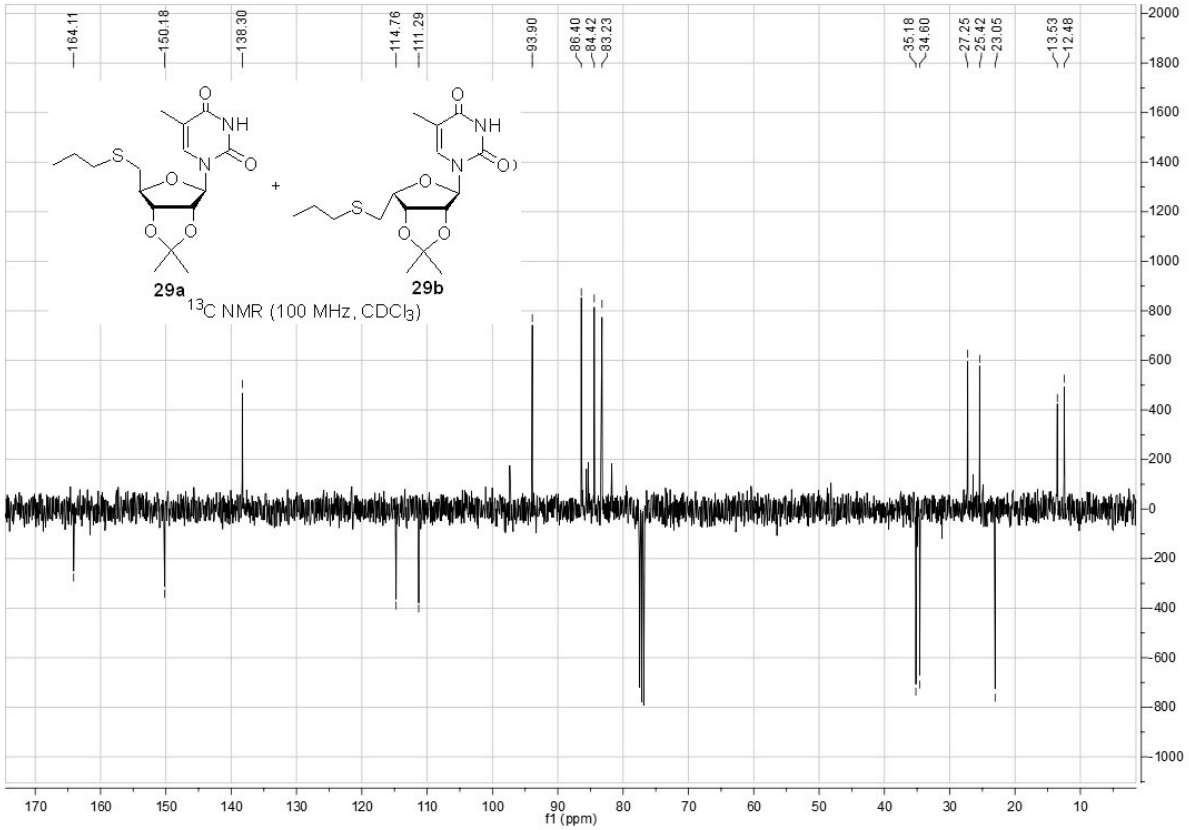

27a
27b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

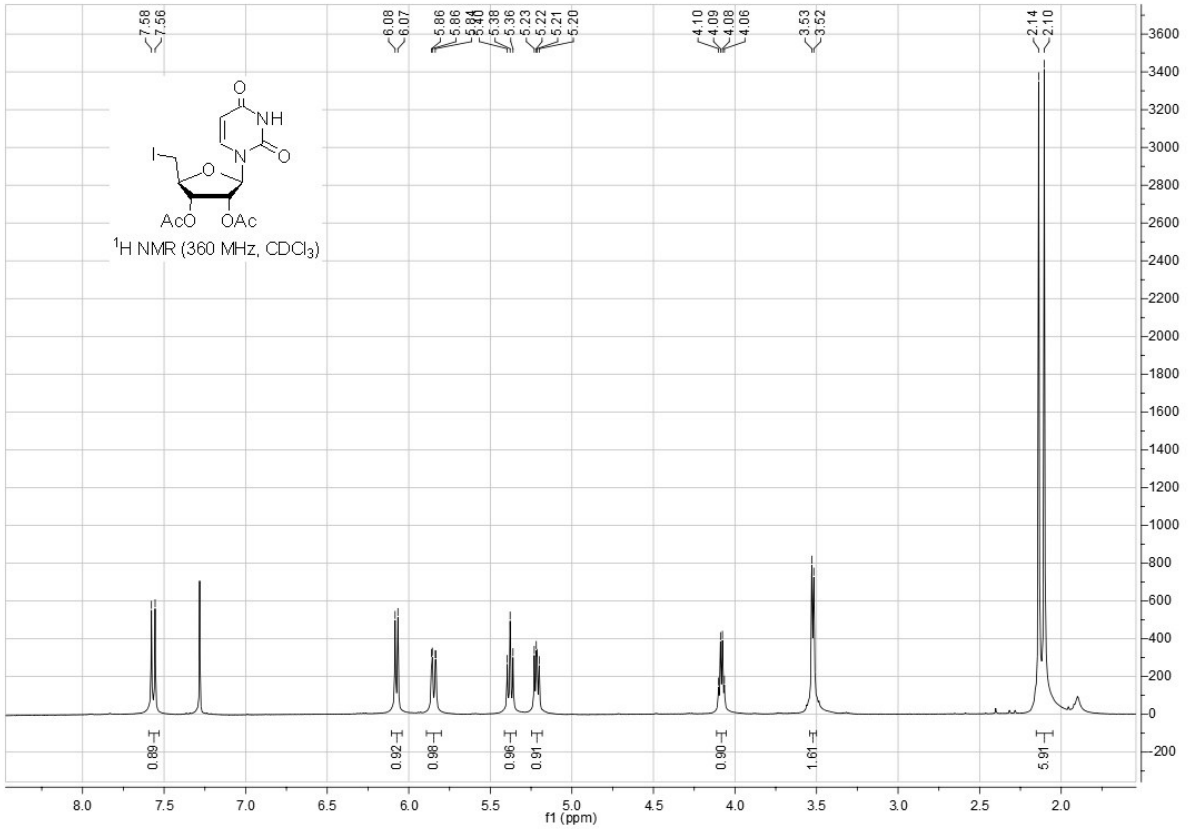

27a
27b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

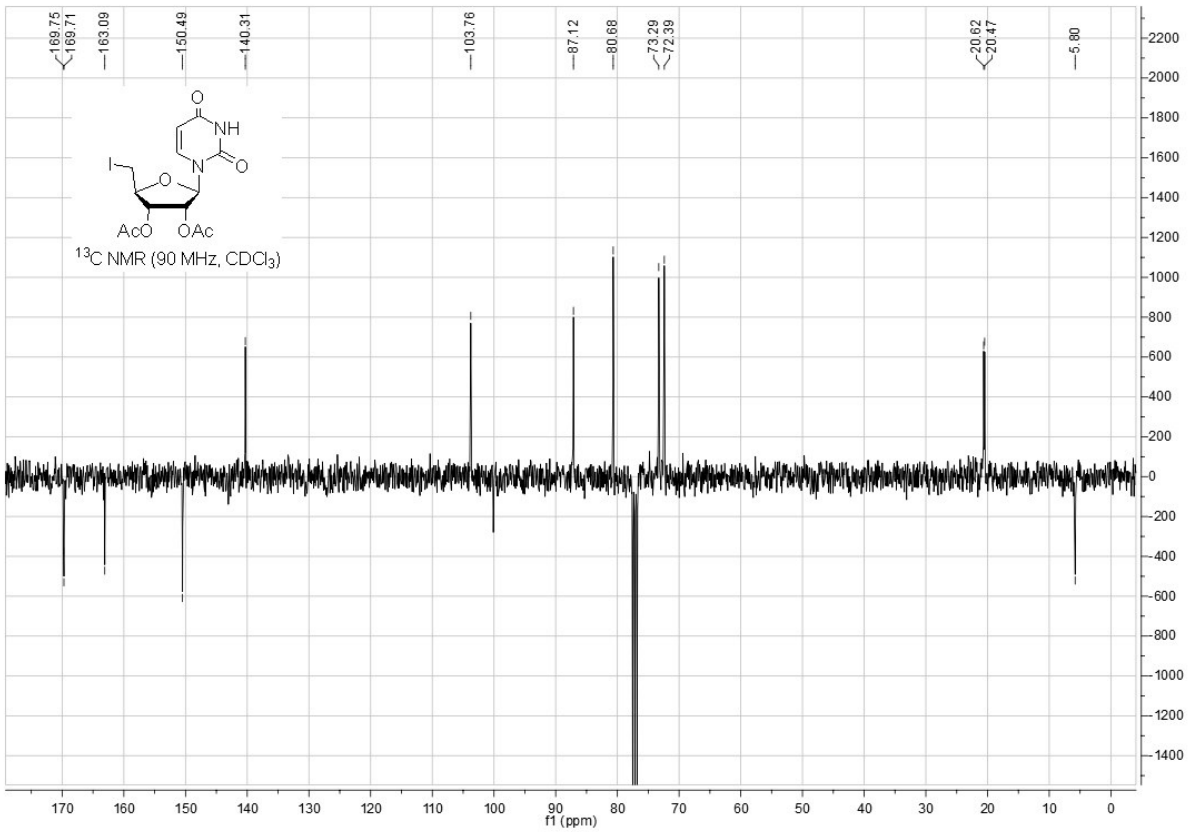

NHFmoc
HOOC
NH
O
N
S
28a
28b
^{1}H NMR (400 MHz, DMSO-d$_6$)
f1 (ppm)

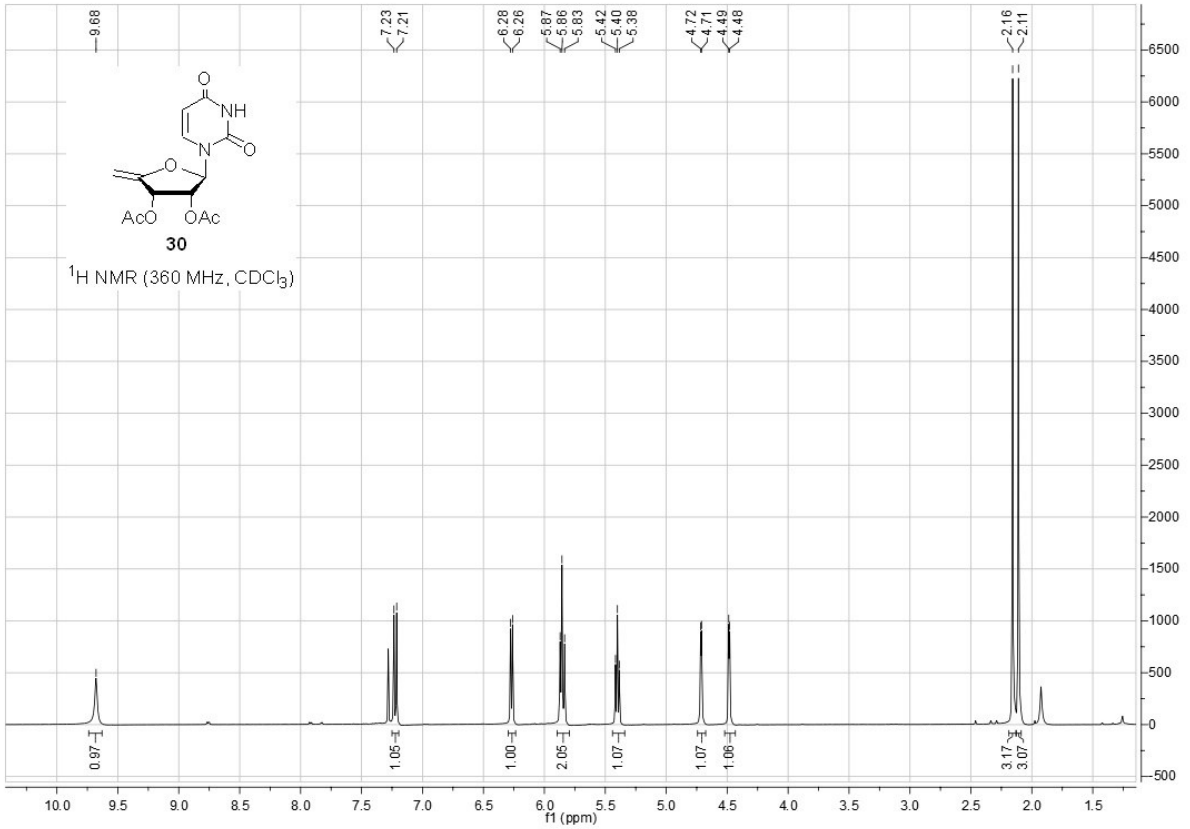

NHFmoc
HOOC
NH
O
N
S
28a
28b
^{13}C NMR (100 MHz, DMSO-d$_6$)
f1 (ppm)

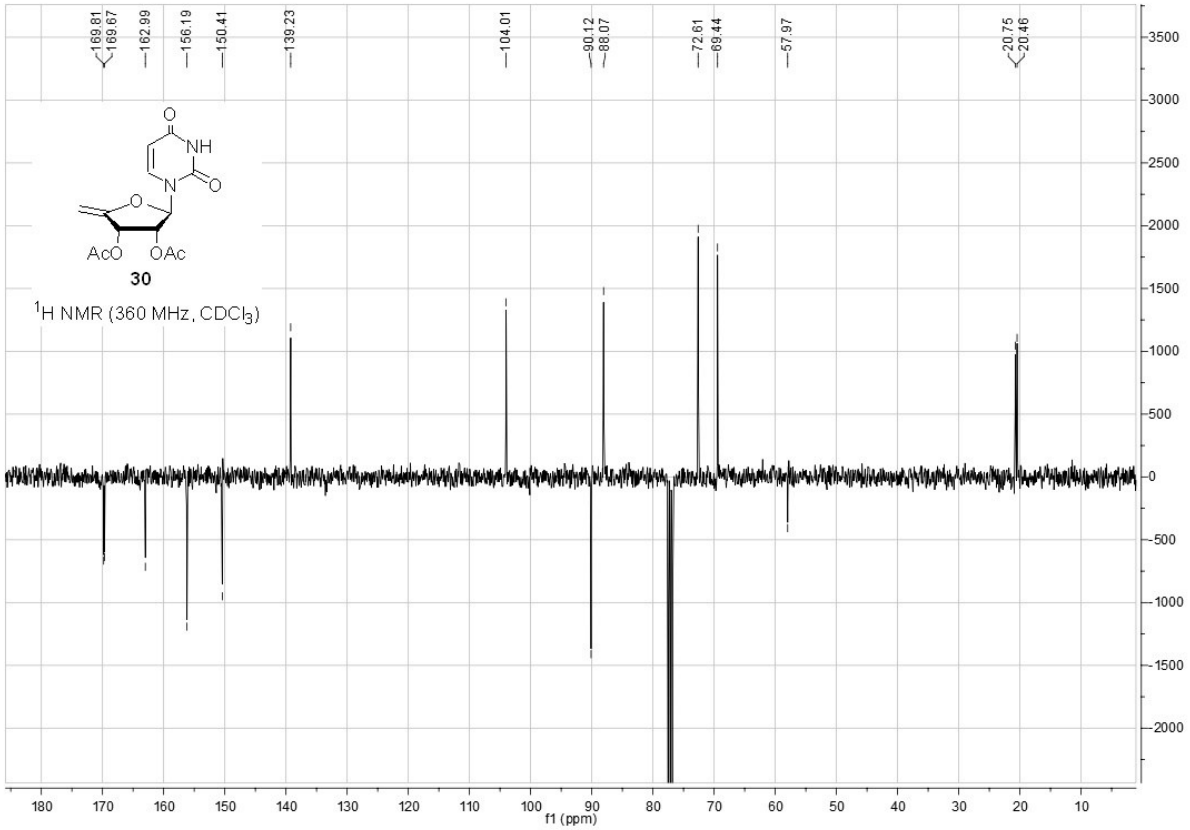

29a
29b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

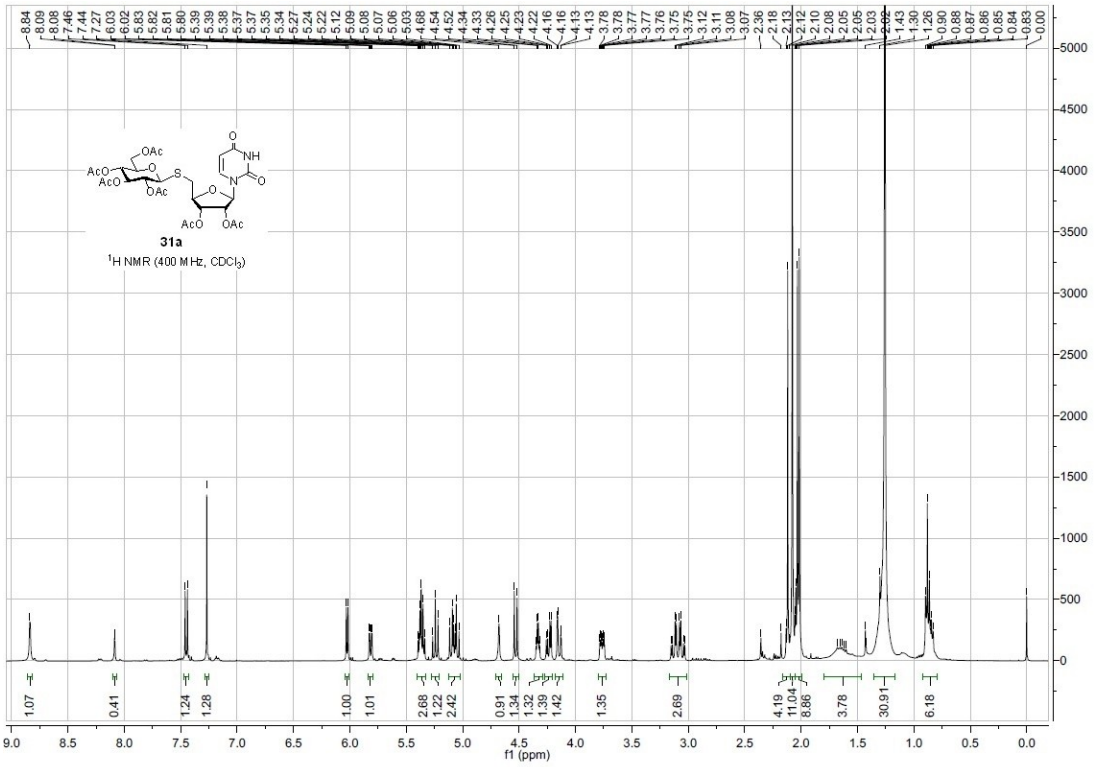

29a
29b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

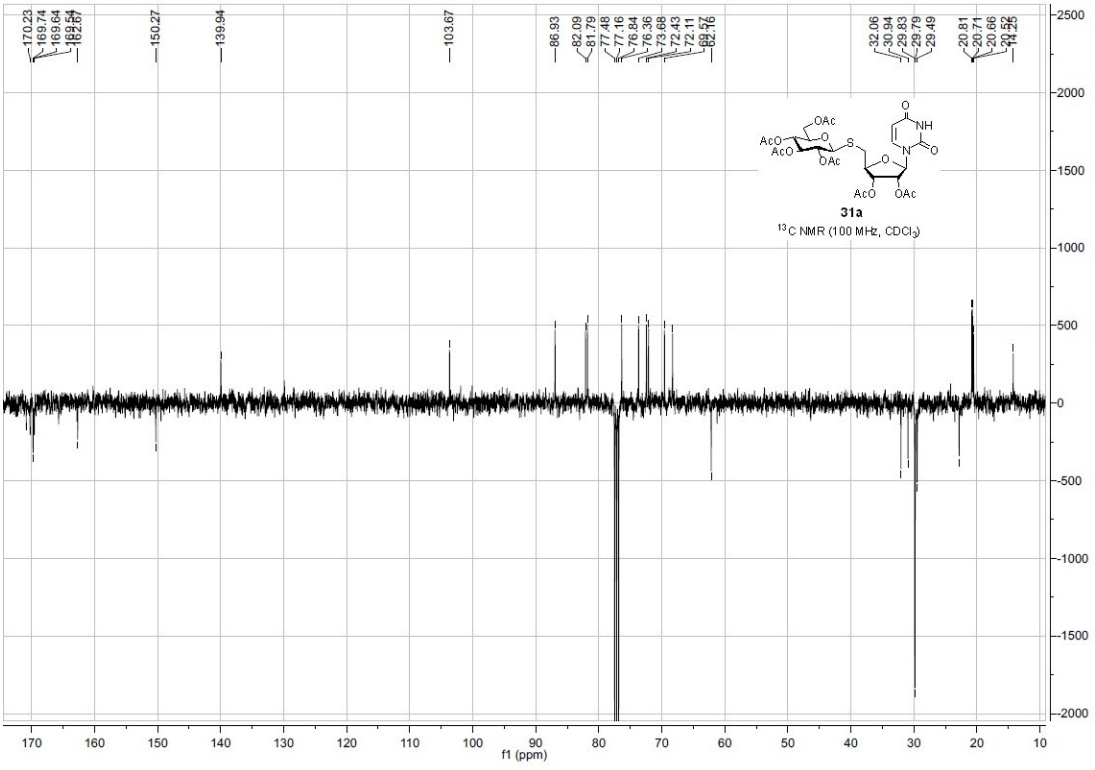

7.58
7.56
6.08
6.07
5.86
5.86
5.84
5.40
5.38
5.36
5.23
5.22
5.21
5.20
4.10
4.09
4.08
4.06
3.53
3.52
2.14
2.10
O
NH
O
N
I
O
AcO
OAc
^{1}H NMR (360 MHz, CDCl$_3$)
0.89
0.92
0.98
0.96
0.91
0.90
1.61
5.91
f1 (ppm)

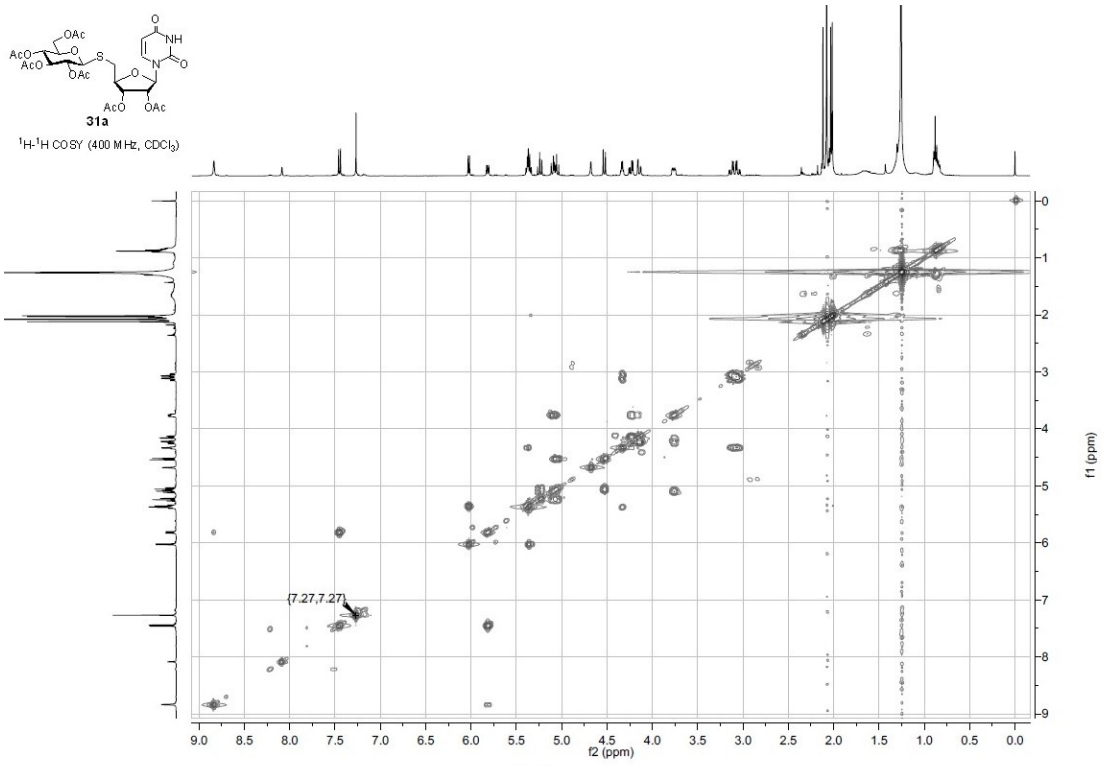

169.75
169.71
163.09
150.49
140.31
103.76
87.12
80.68
73.29
72.39
20.62
20.47
5.80
O
NH
O
N
I
O
AcO
OAc
^{13}C NMR (90 MHz, CDCl$_3$)
f1 (ppm)

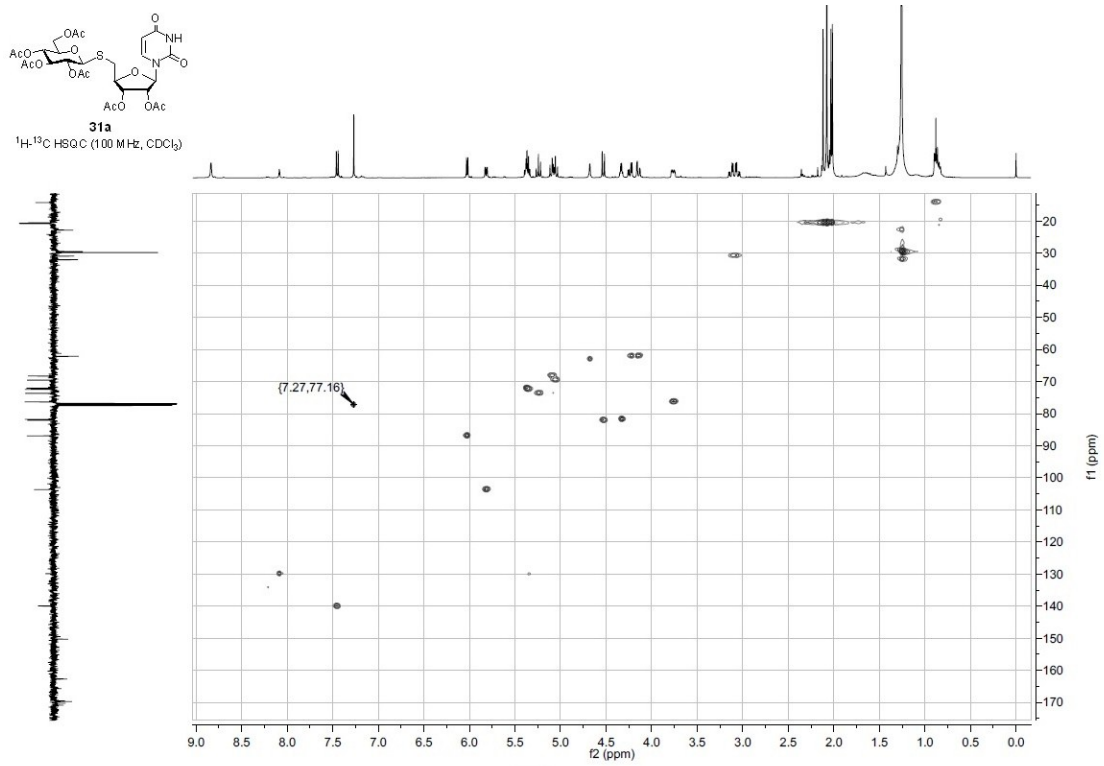

9.68
7.23
7.21
6.28
6.26
5.87
5.86
5.83
5.42
5.40
5.38
4.72
4.71
4.49
4.48
2.16
2.11
NH
O
N
O
O
AcO
OAc
30
1H NMR (360 MHz, CDCl3)
0.97
1.05
1.00
2.05
1.07
1.07
1.06
3.17
3.07
f1 (ppm)

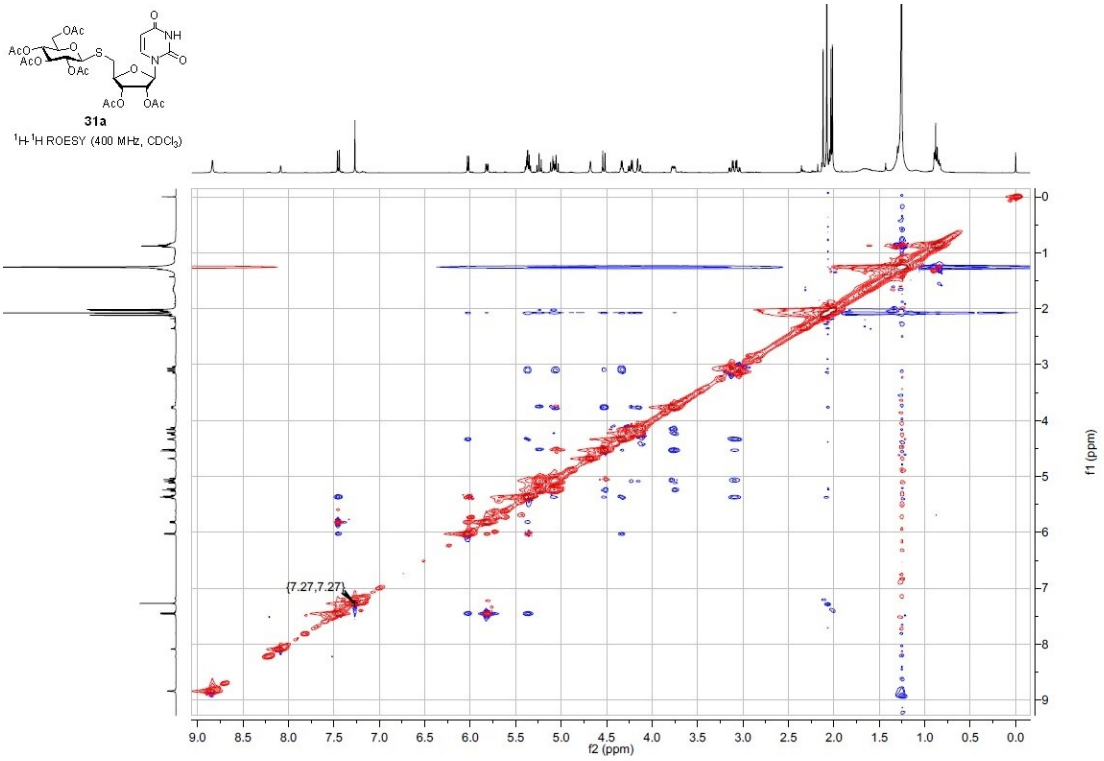

169.81
169.67
162.99
156.19
150.41
139.23
104.01
90.12
88.07
72.61
69.44
57.97
20.75
20.46
NH
O
N
O
O
AcO
OAc
30
1H NMR (360 MHz, CDCl3)
f1 (ppm)

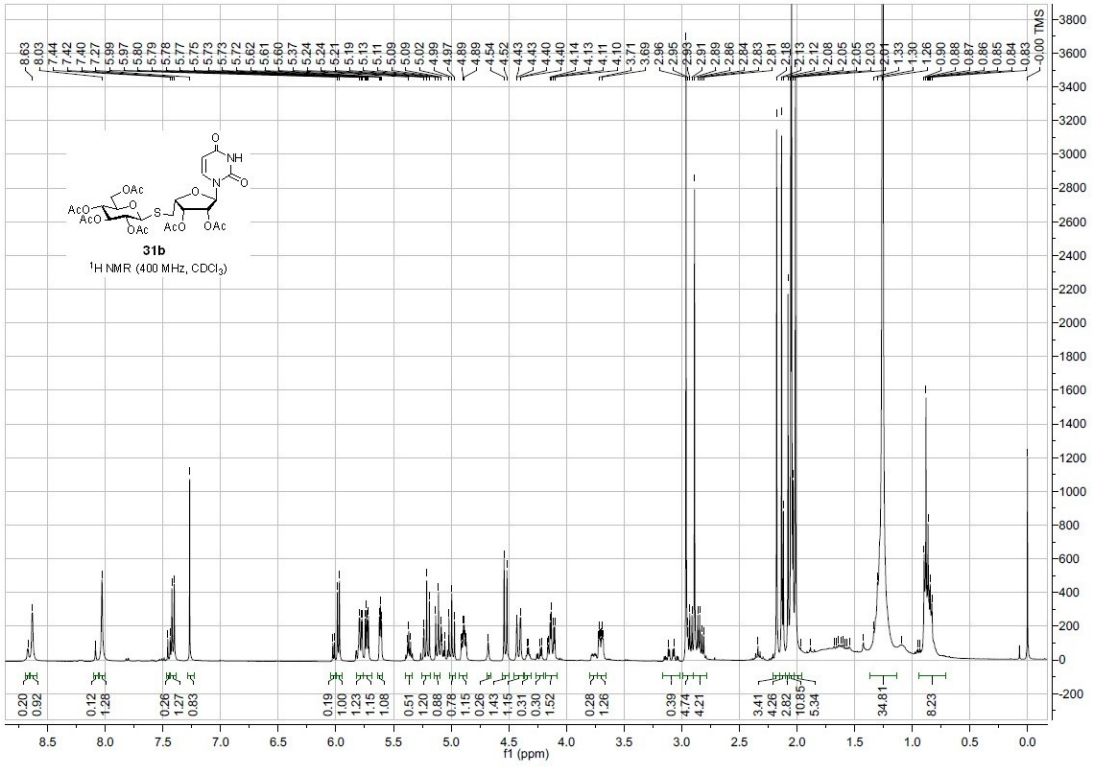

31a
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

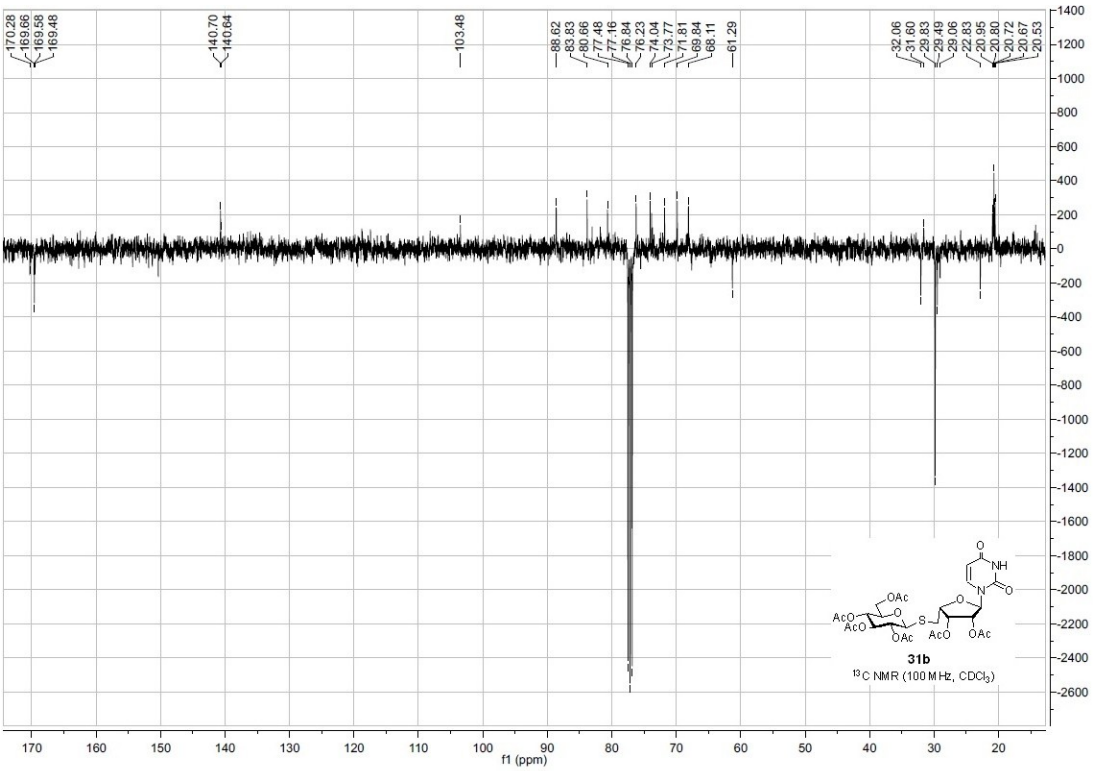

31a
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

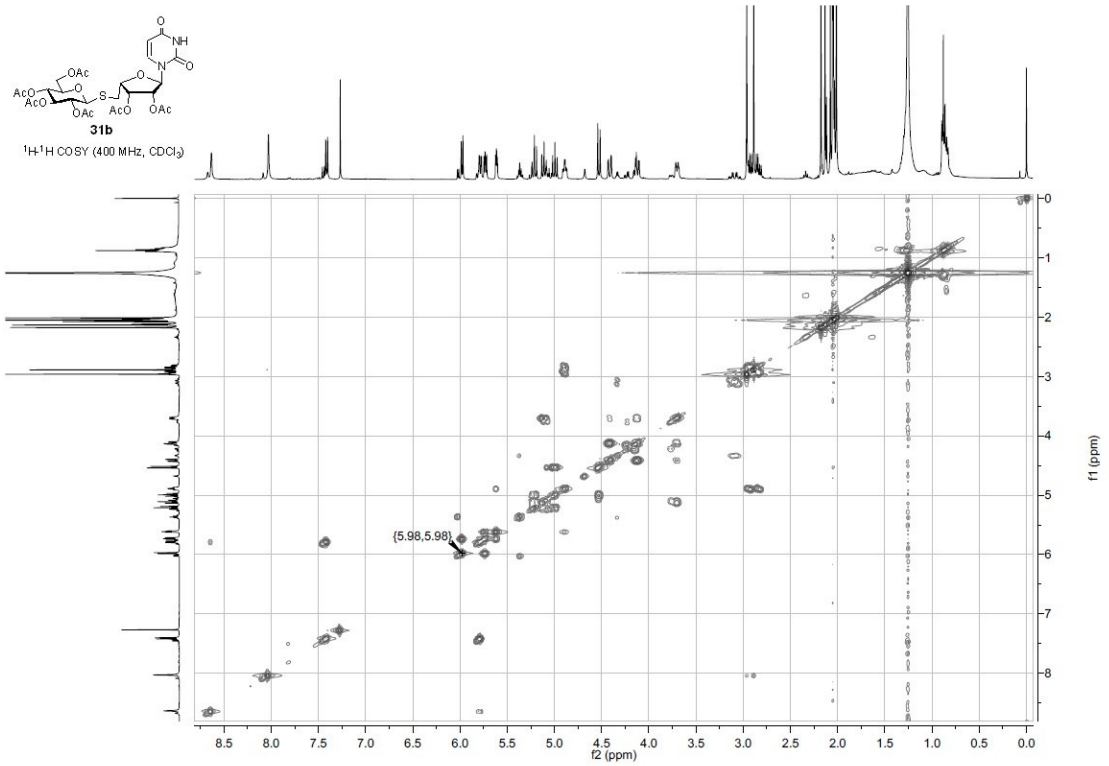

31a
^{1}H-^{1}H COSY (400 MHz, CDCl$_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

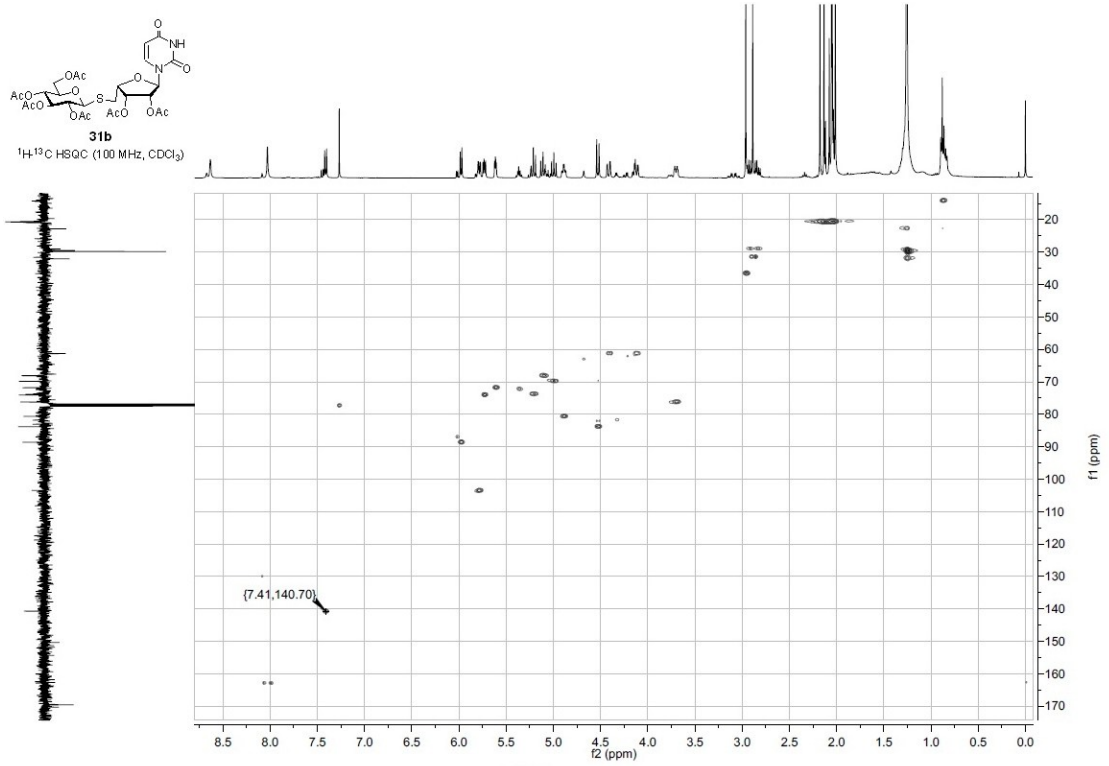

31a
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
(7.27,77.16)
f2 (ppm)
f1 (ppm)

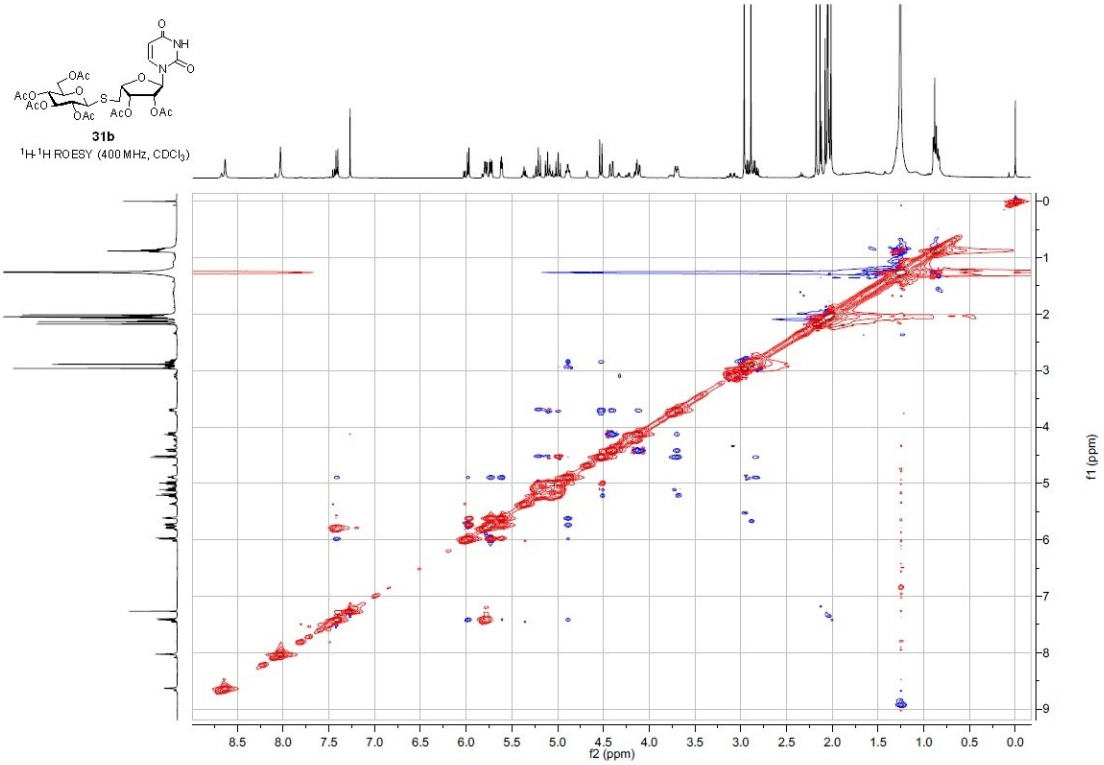

31a
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

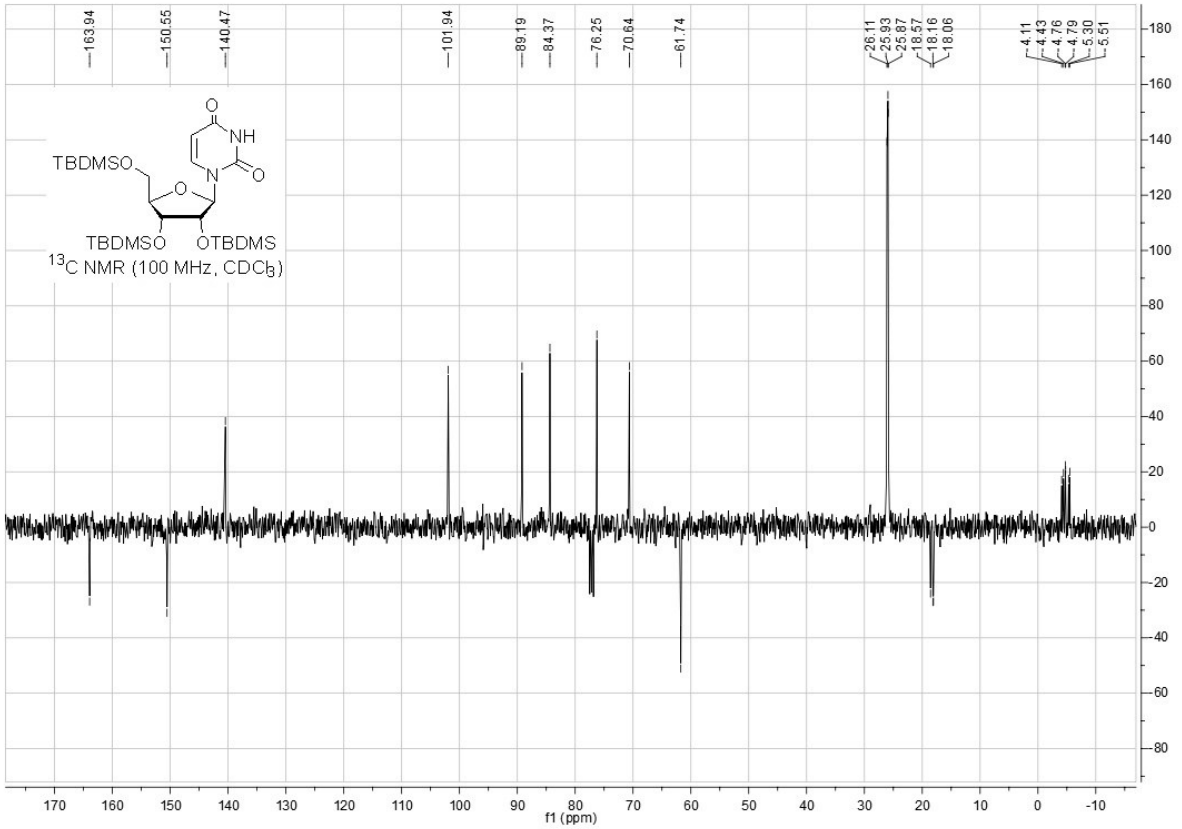

31b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

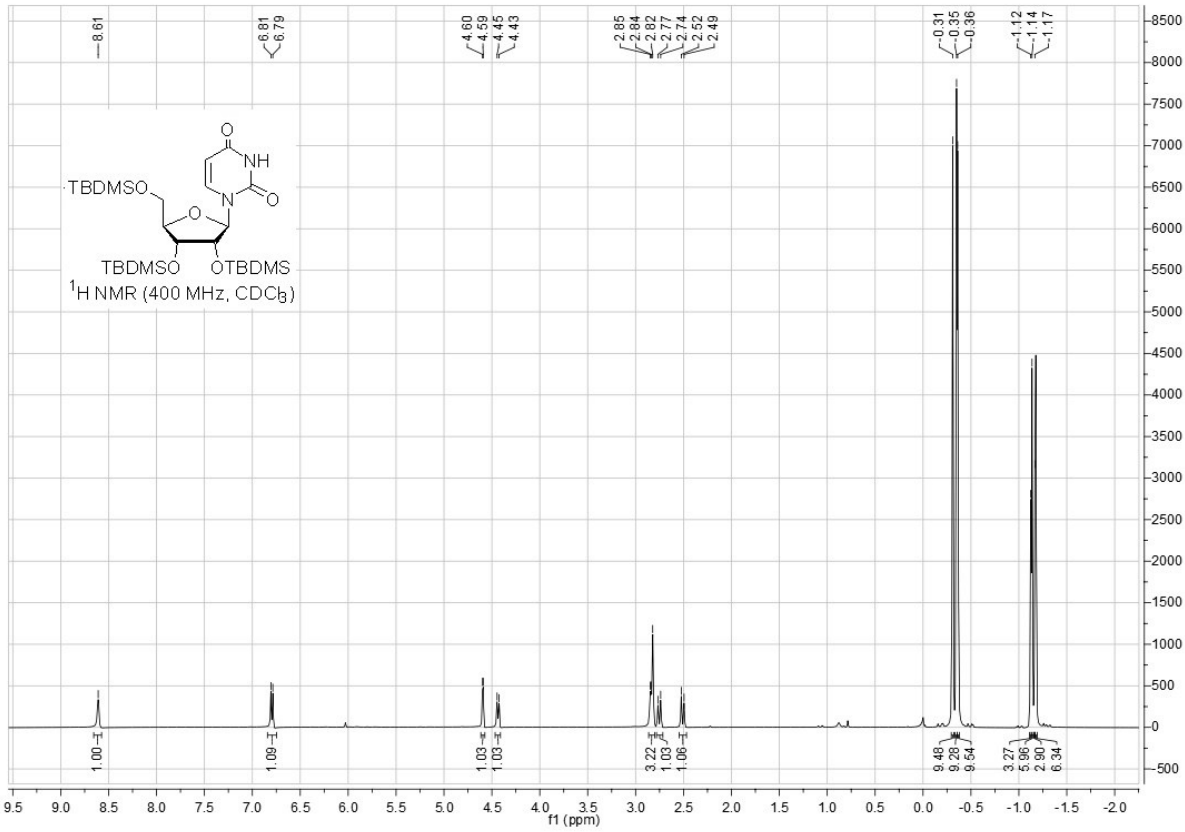

31b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

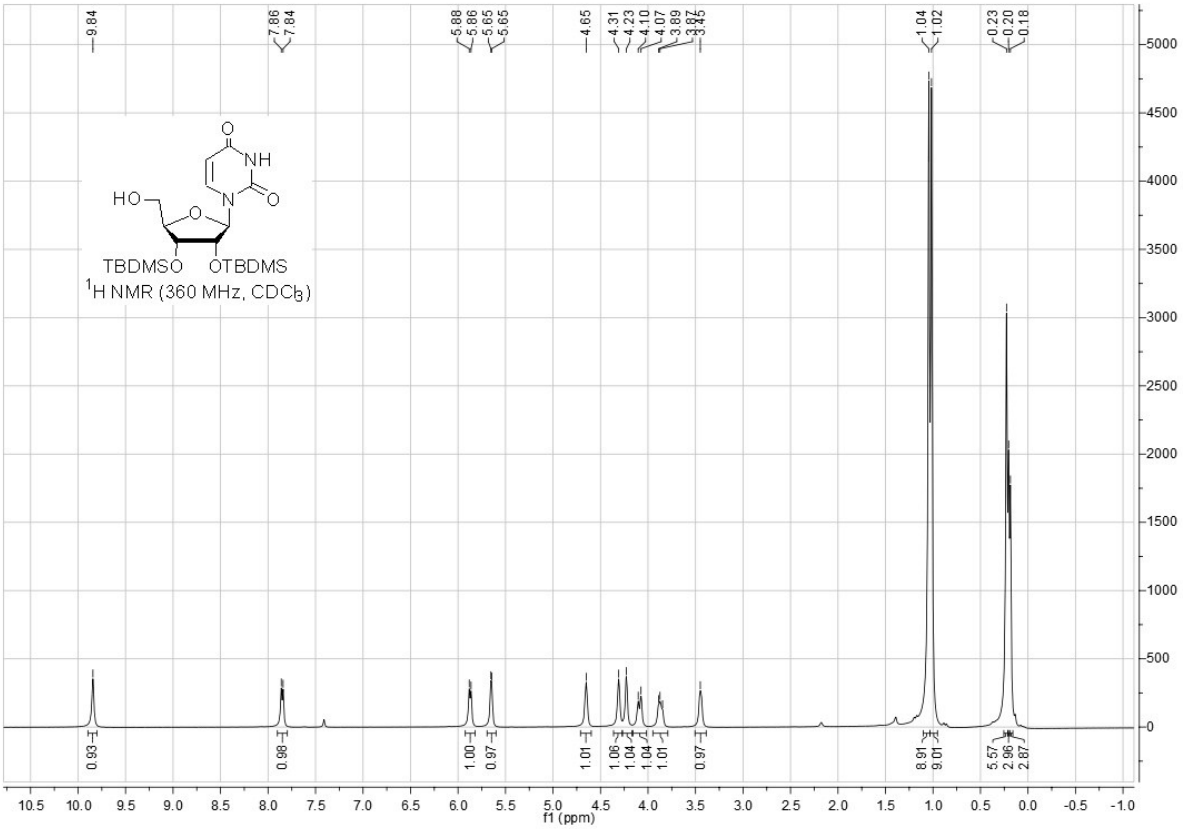

31b
^{1}H-^{1}H COSY (400 MHz, CDCl$_3$)
{5.98,5.98}
f2 (ppm)
f1 (ppm)

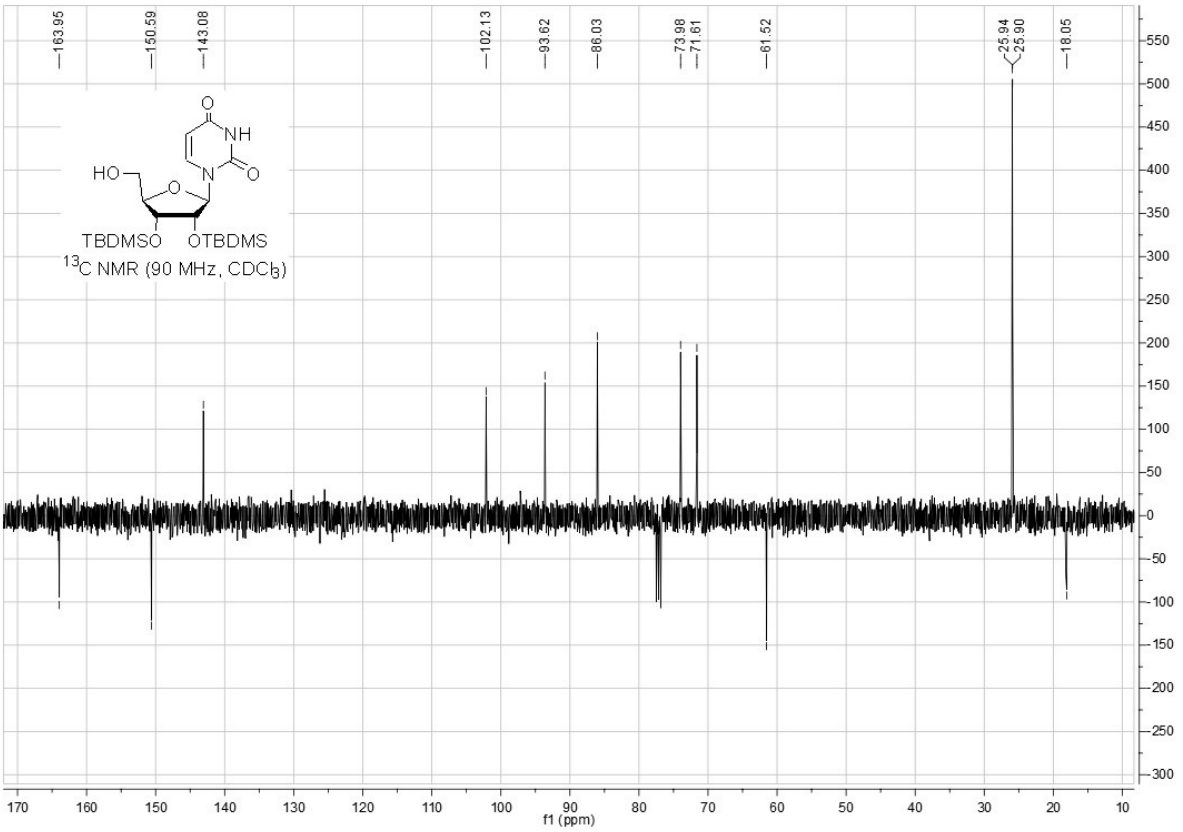

31b
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
{7.41,140.70}
f2 (ppm)
f1 (ppm)

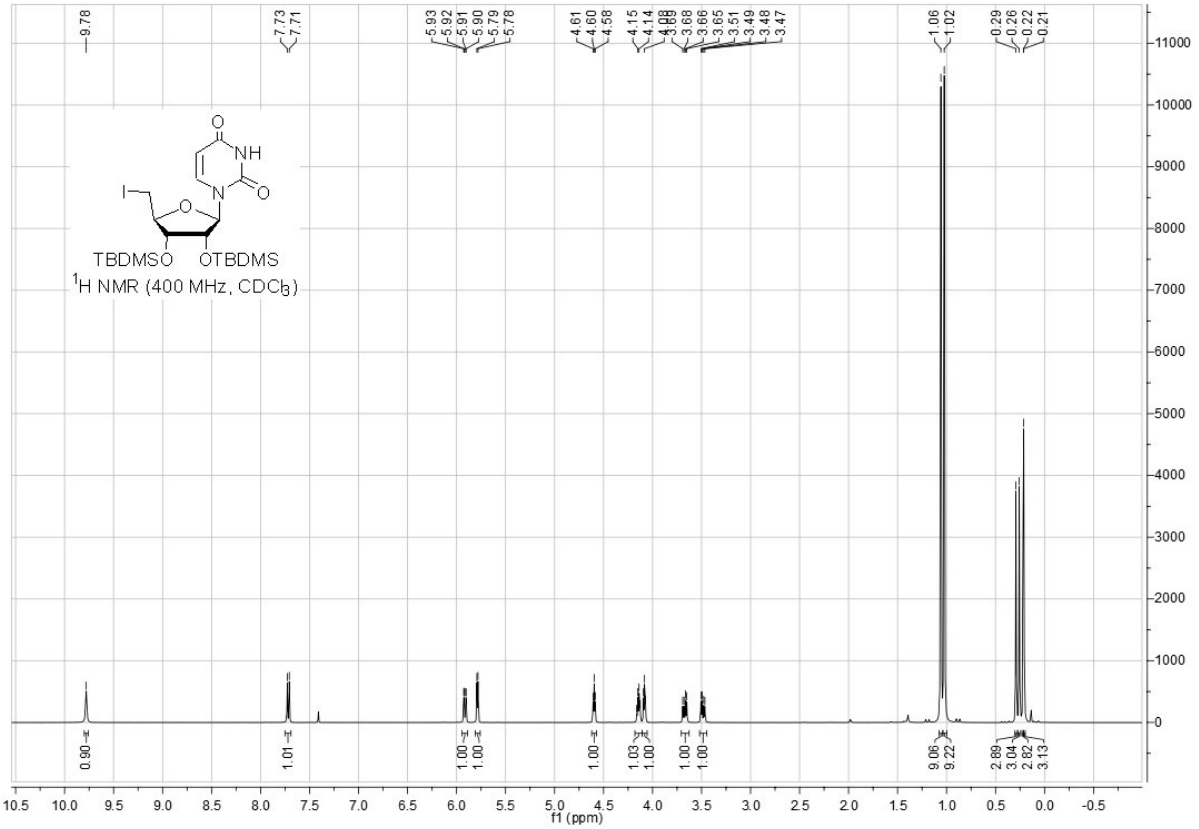

31b
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)

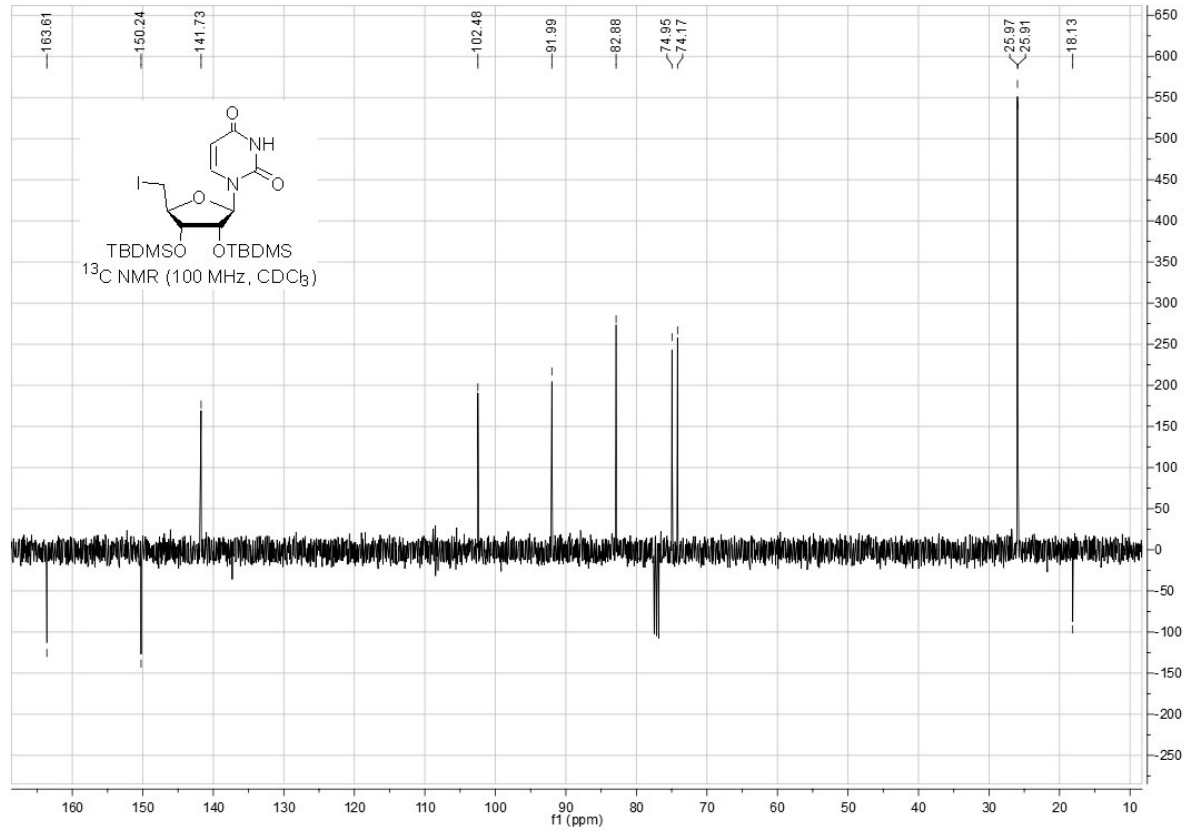

163.94
150.55
140.47
101.94
89.19
84.37
76.25
70.64
61.74
26.11
25.93
25.87
18.57
18.16
18.06
4.11
4.43
4.76
4.79
5.30
5.51
TBDMSO
TBDMSO
OTBDMS
13C NMR (100 MHz, CDCl3)
f1 (ppm)

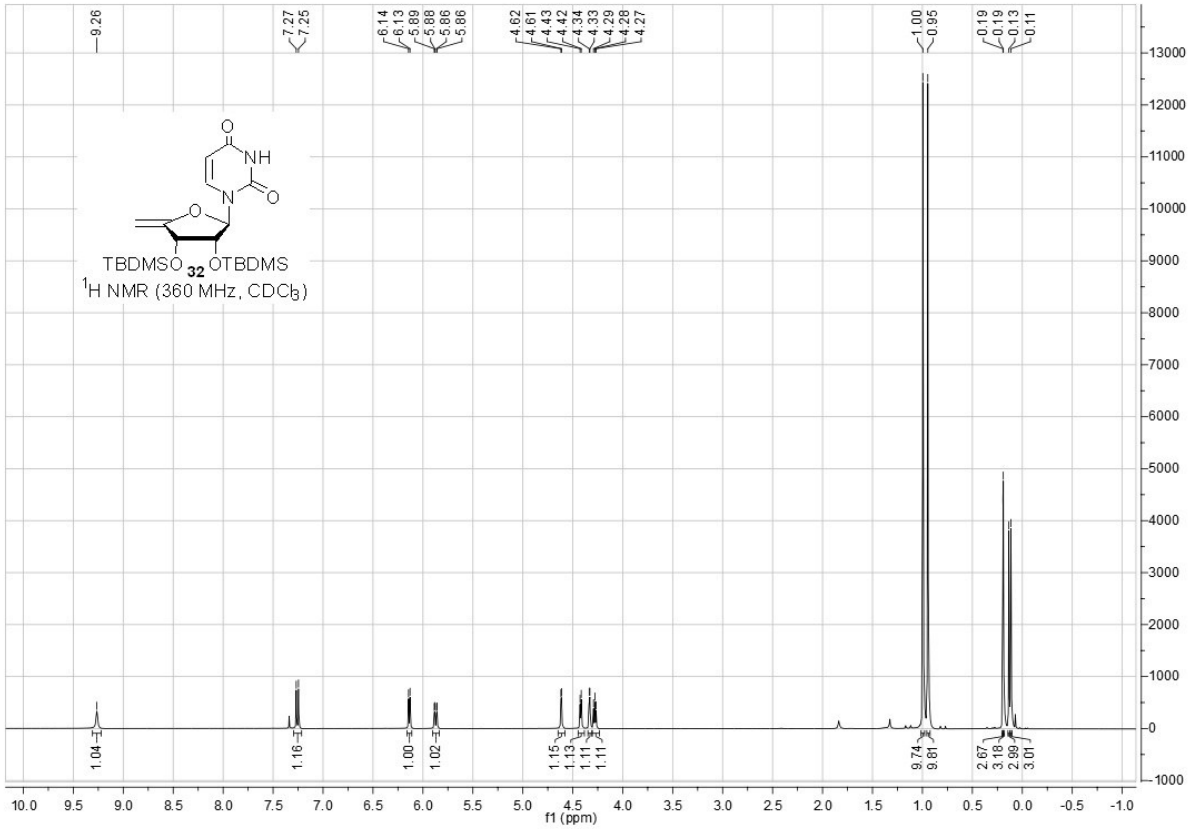

8.61
6.81
6.79
4.60
4.59
4.45
4.43
2.85
2.84
2.82
2.77
2.74
2.52
2.49
0.31
0.35
0.36
1.12
1.14
1.17
TBDMSO
TBDMSO
OTBDMS
1H NMR (400 MHz, CDCl3)
1.00
1.09
1.03
1.03
3.22
1.03
1.06
9.48
9.28
9.54
3.27
5.96
2.90
6.34
f1 (ppm)

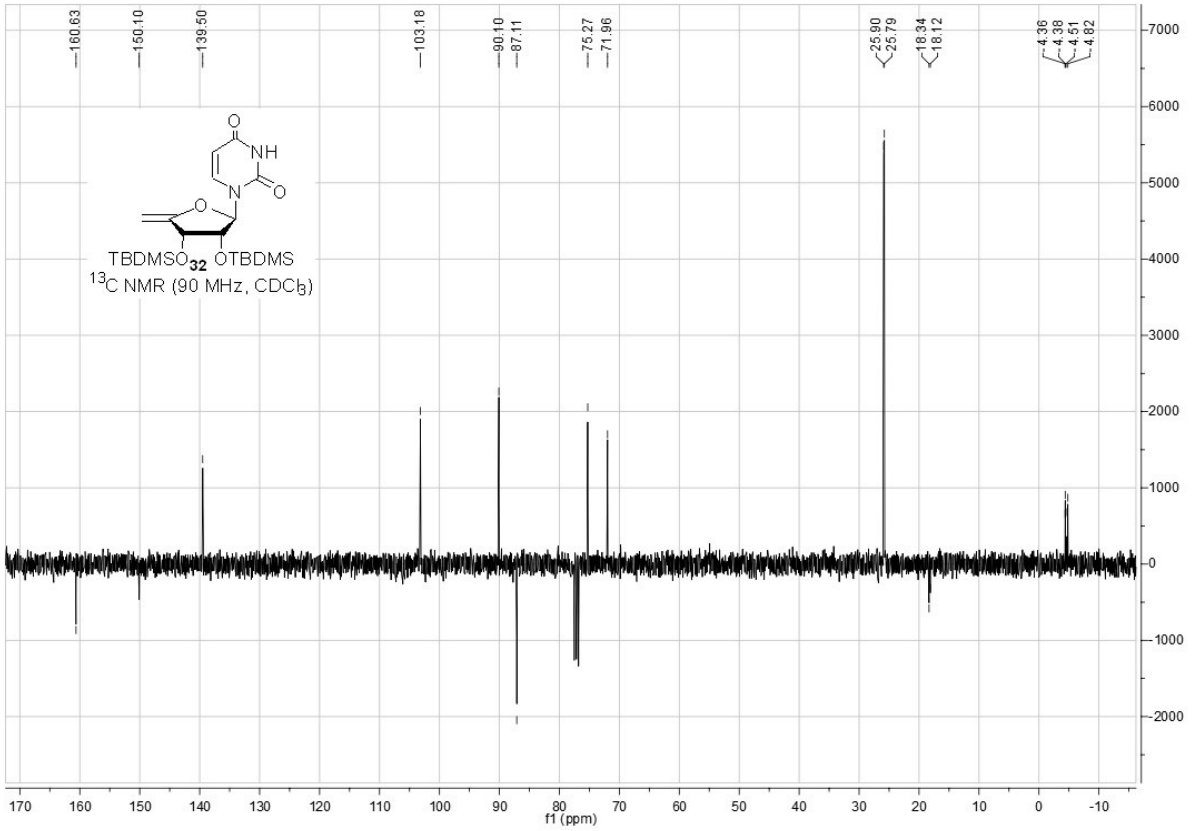

9.84
7.86
7.84
5.88
5.86
5.65
5.65
4.65
4.31
4.23
4.10
4.07
3.89
3.87
3.45
1.04
1.02
0.23
0.20
0.18
HO
NH
O
N
O
TBDMSO
OTBDMS
1H NMR (360 MHz, CDCl3)
0.93
0.98
1.00
0.97
1.01
1.06
1.04
1.04
1.01
0.97
8.91
9.01
5.57
2.96
2.87
f1 (ppm)

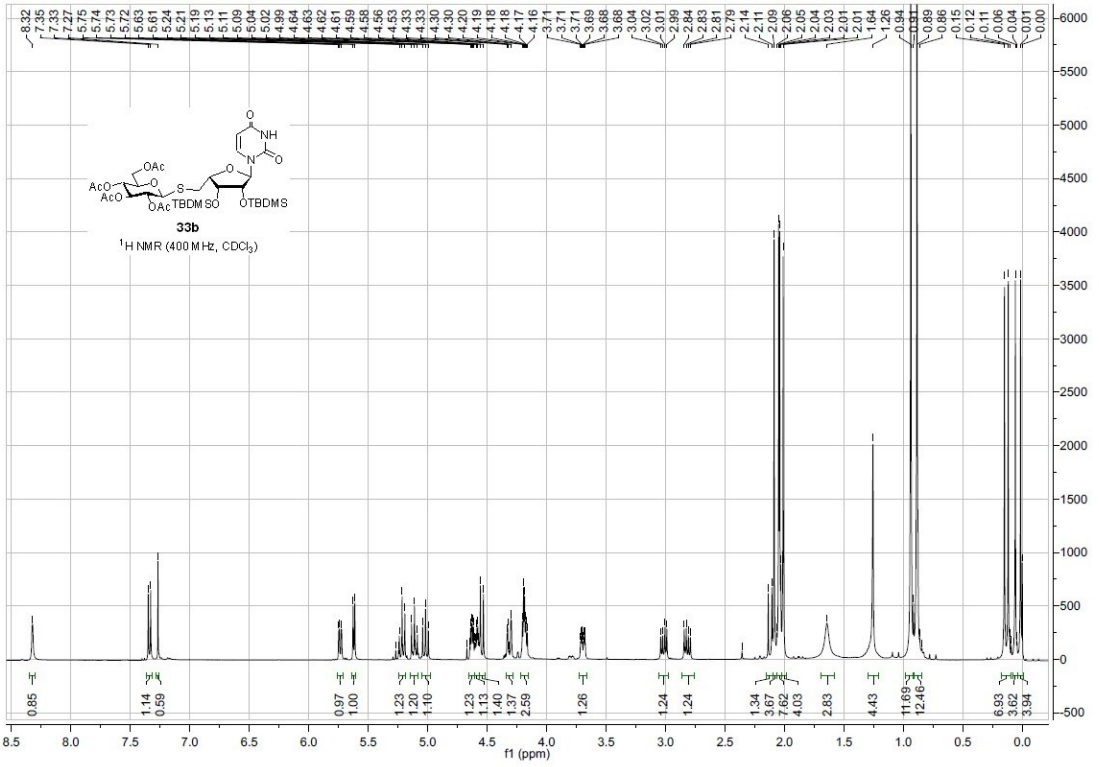

163.95
150.59
143.08
102.13
93.62
86.03
73.98
71.61
61.52
25.94
25.90
18.05
HO
NH
O
N
O
TBDMSO
OTBDMS
13C NMR (90 MHz, CDCl3)
f1 (ppm)

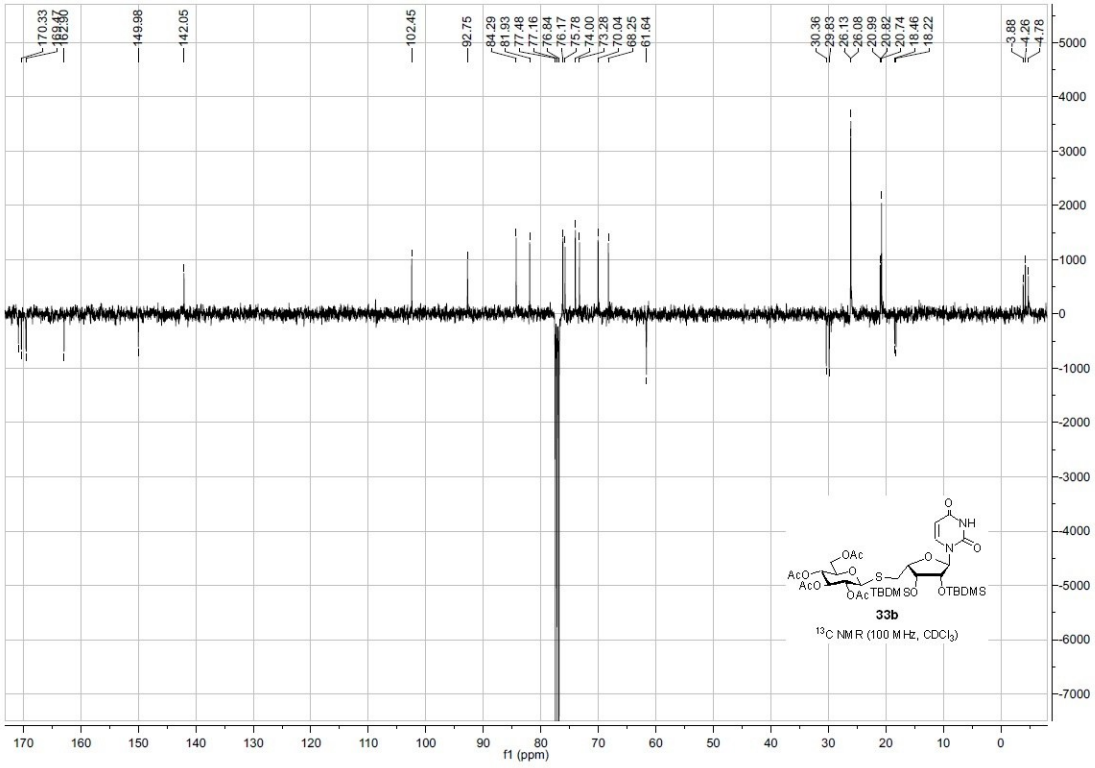

TBDMSO OTBDMS
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

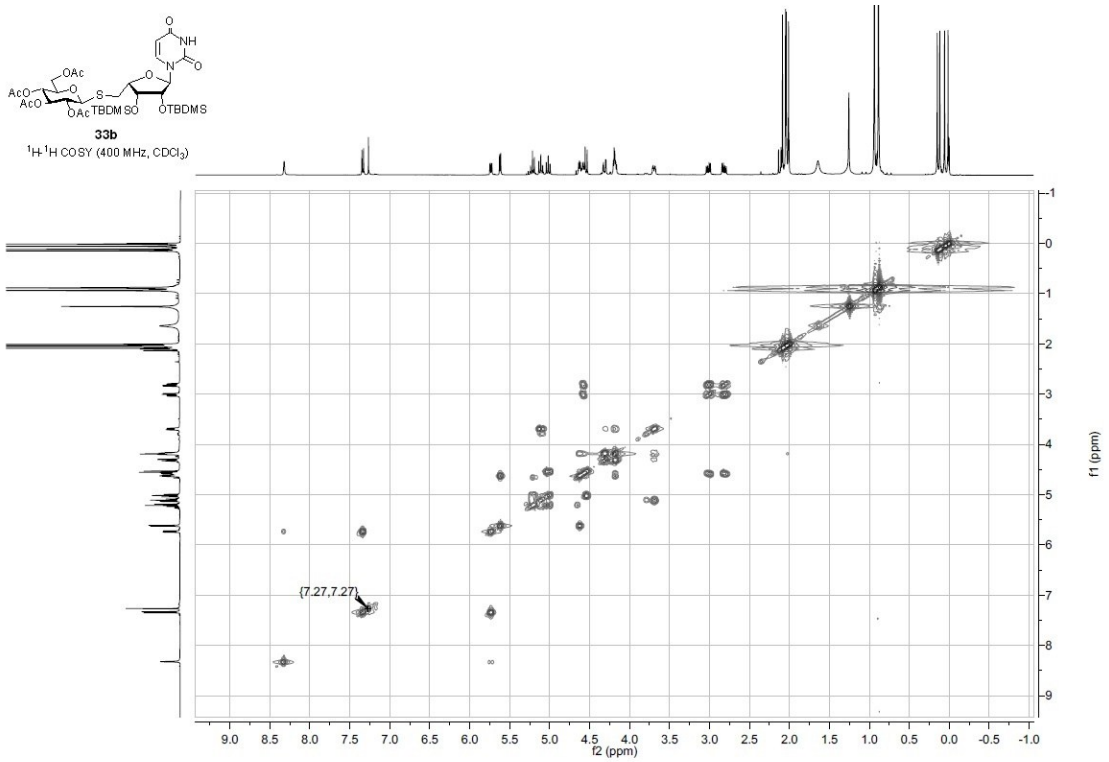

TBDMSO OTBDMS
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

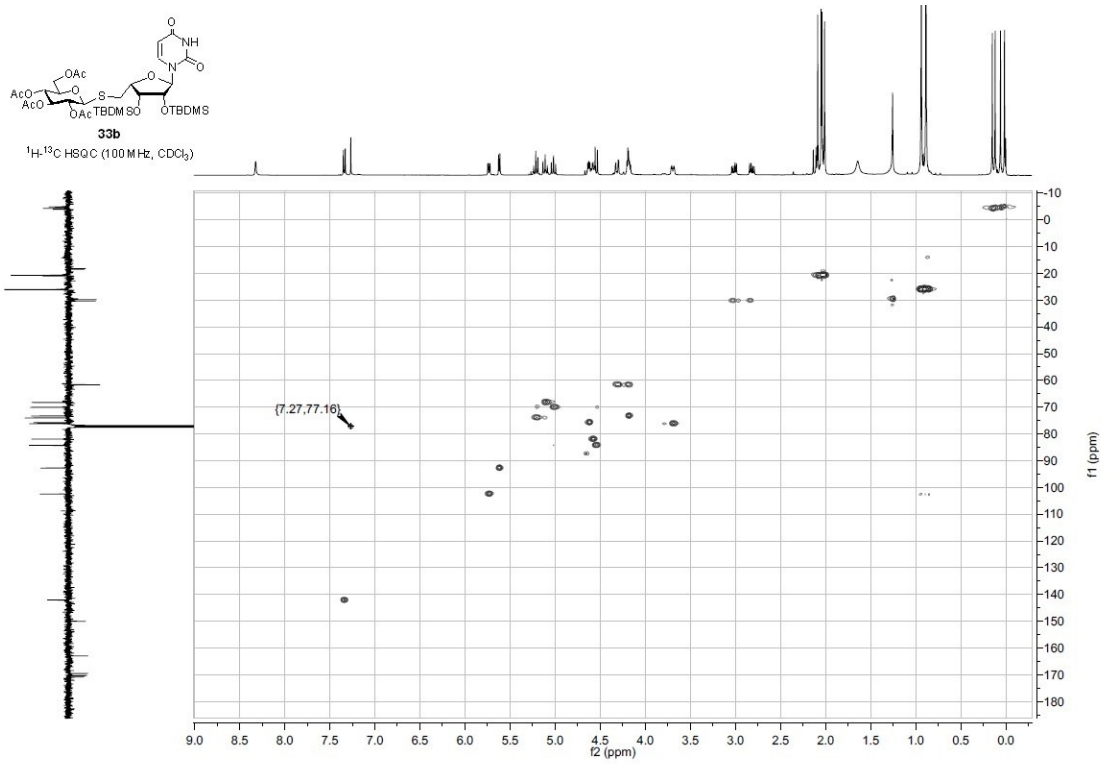

TBDMSO 32 OTBDMS
1H NMR (360 MHz, CDCl3)
f1 (ppm)

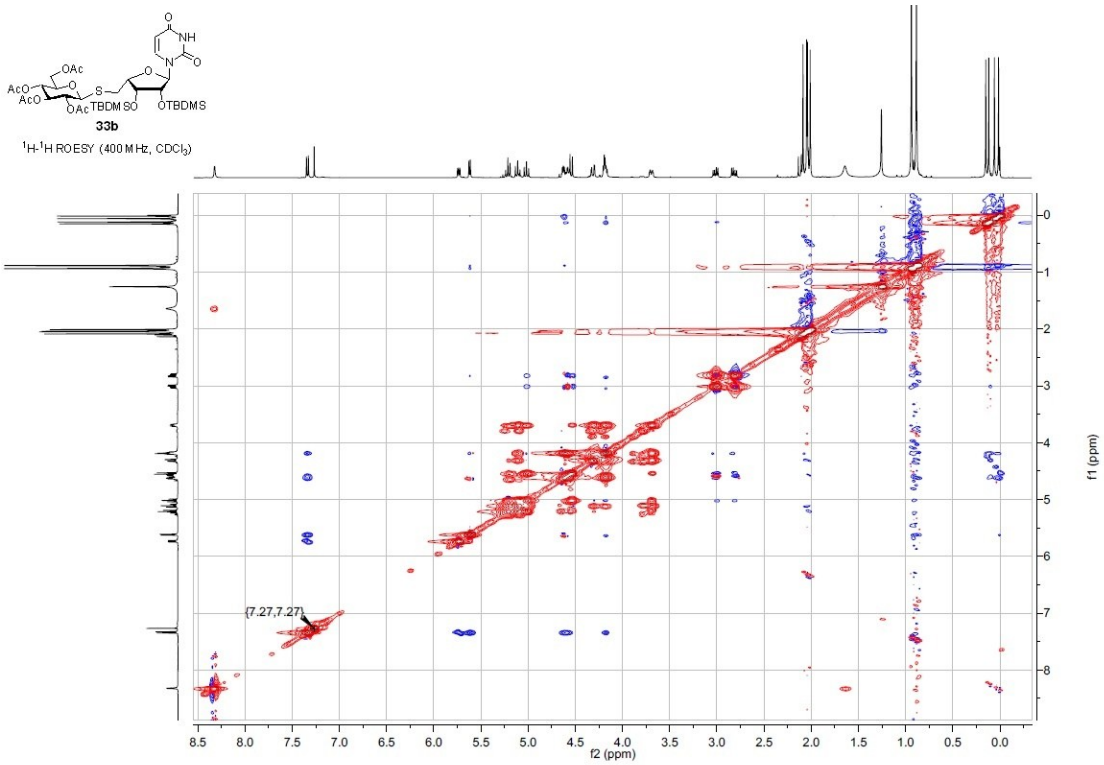

TBDMSO32 OTBDMS
13C NMR (90 MHz, CDCl3)
f1 (ppm)

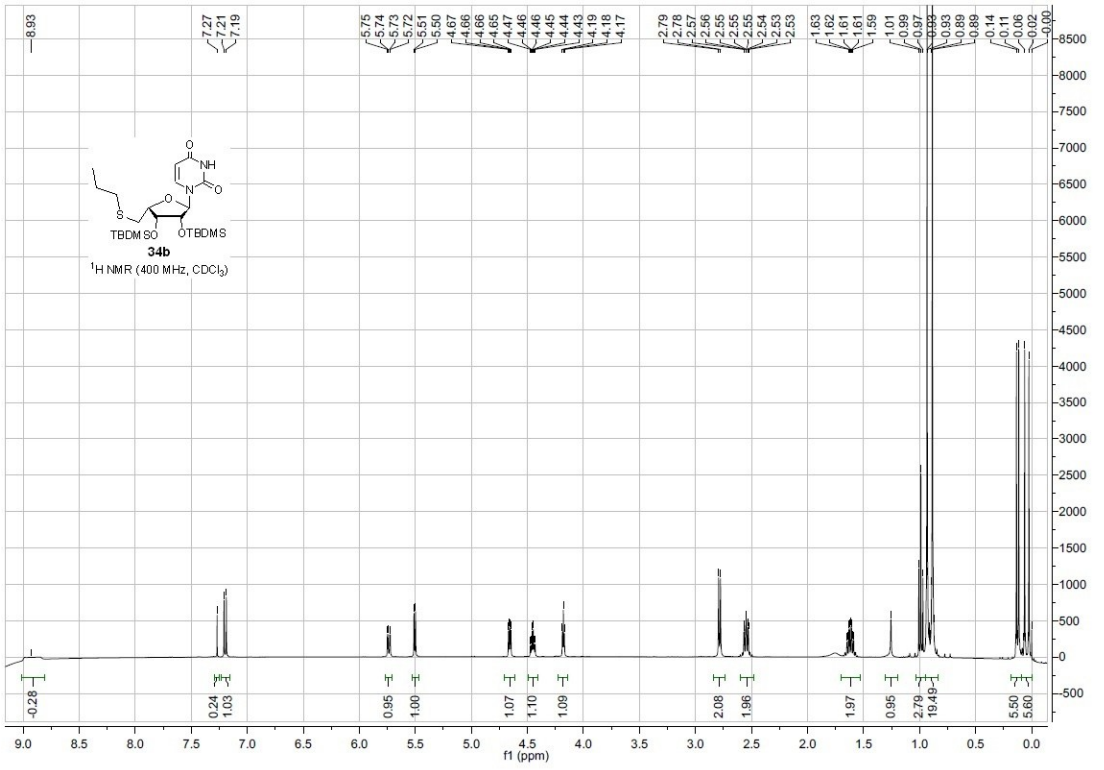

33b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

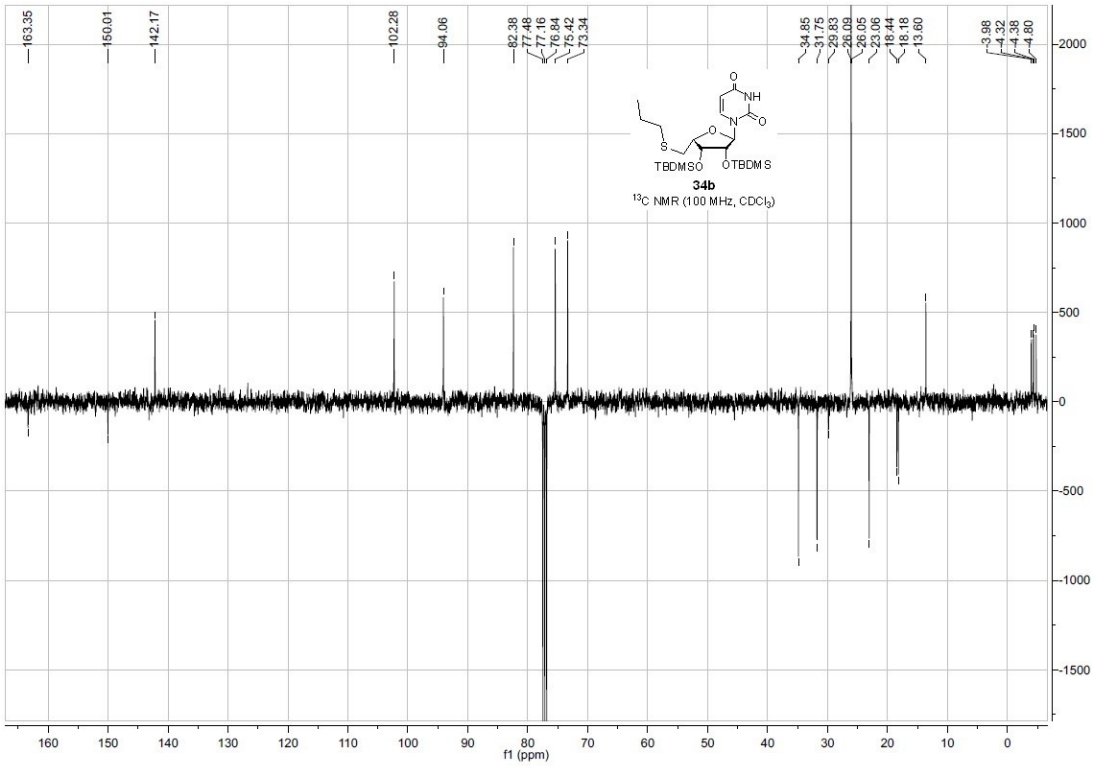

33b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

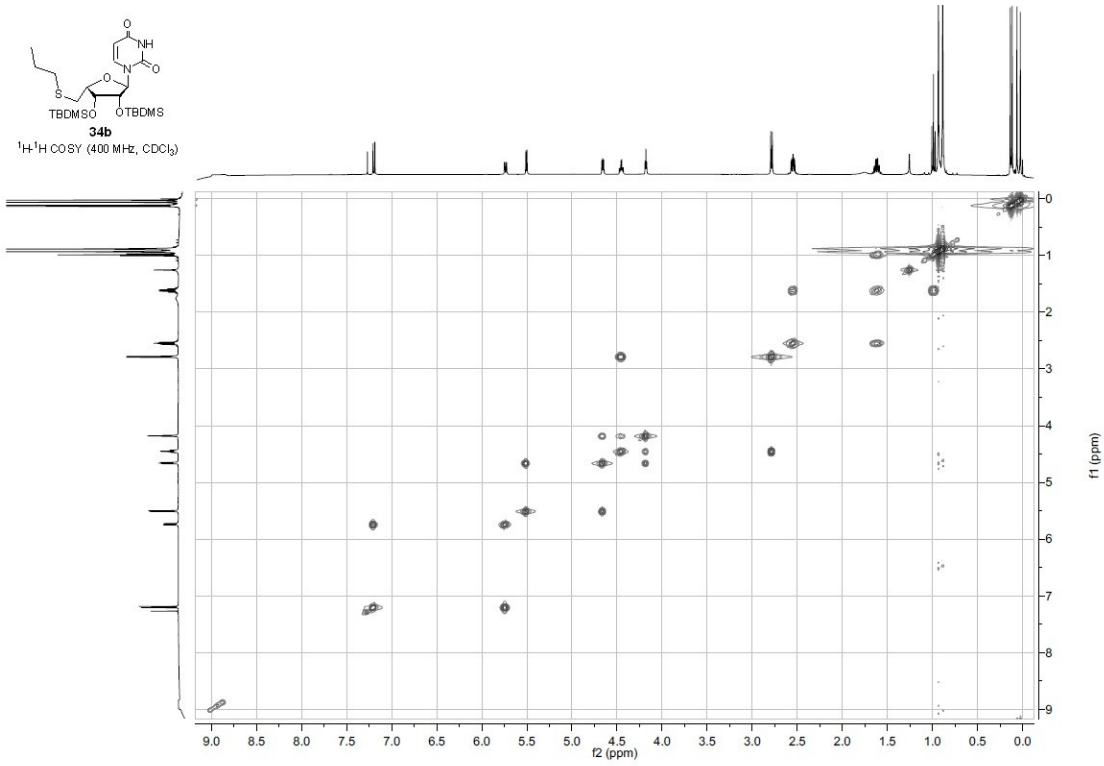

33b
^{1}H-^{1}H COSY (400 MHz, CDCl$_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

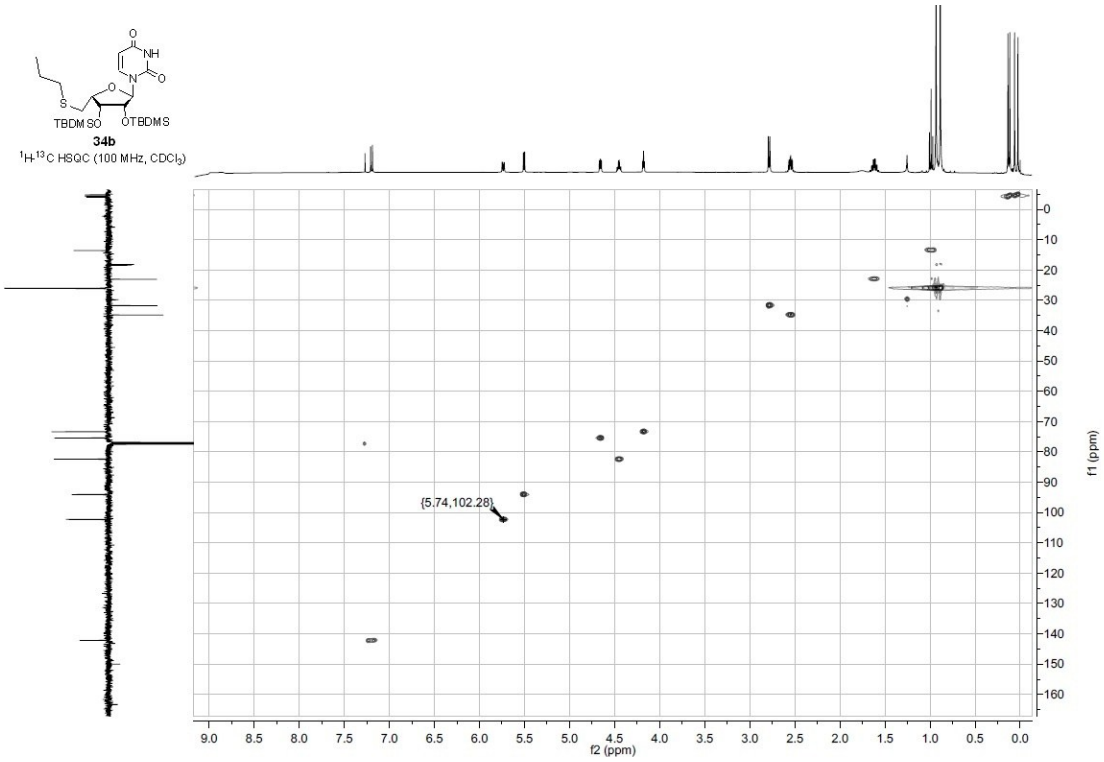

33b
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
(7.27,77.16)
f2 (ppm)
f1 (ppm)

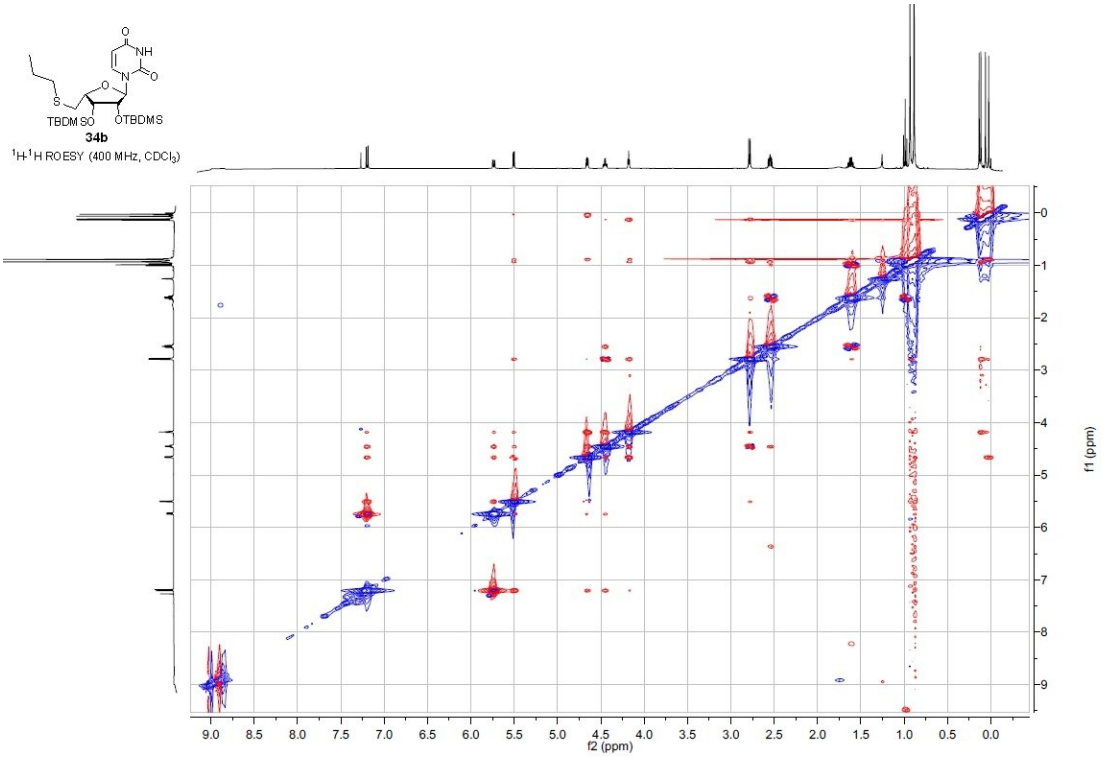

33b
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

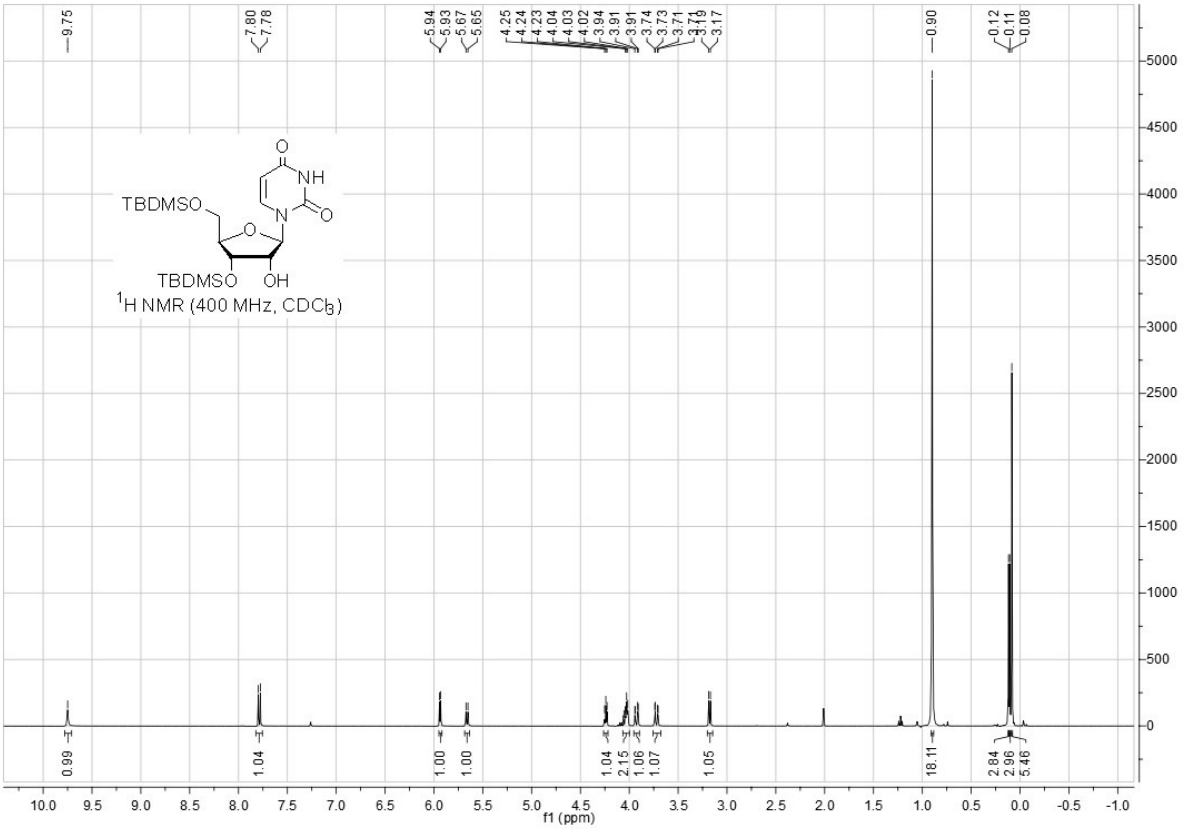

34b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

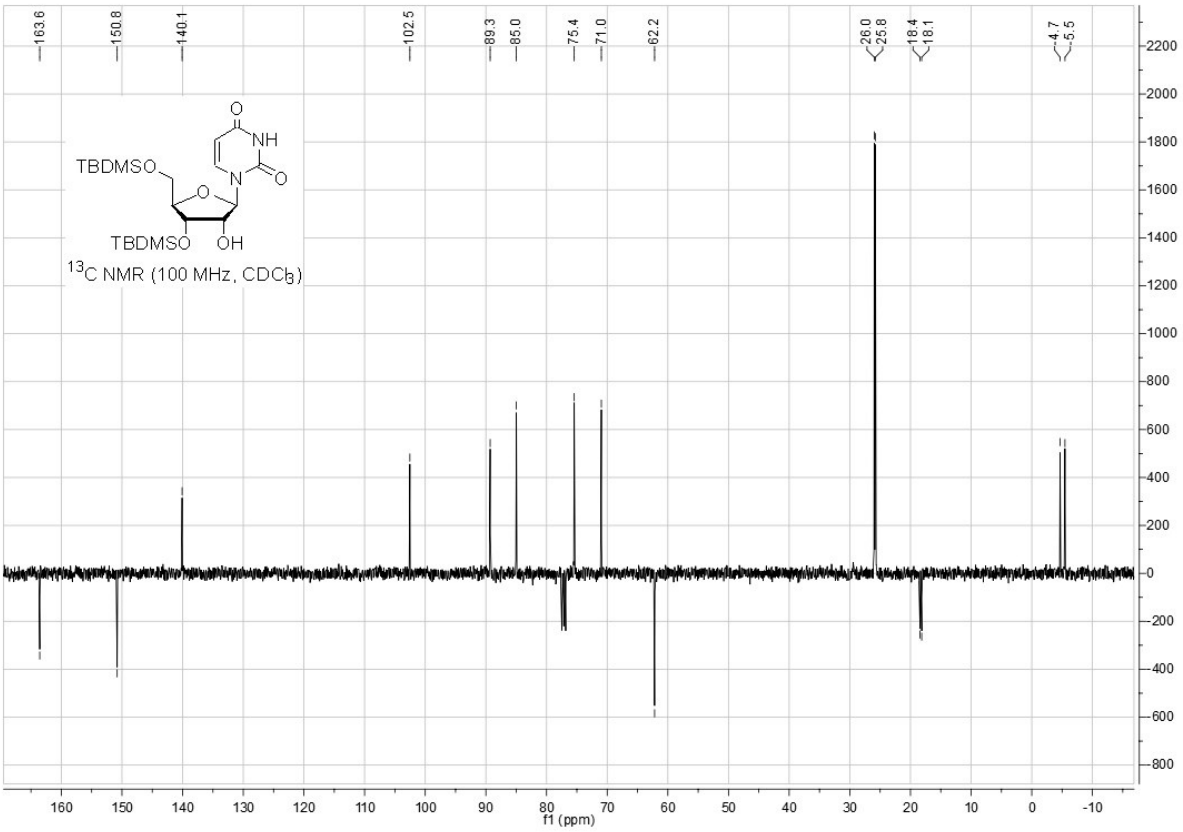

163.35
150.01
142.17
102.28
94.06
82.38
77.48
77.16
76.84
75.42
73.34
34.85
31.75
29.83
26.09
26.05
23.06
18.44
18.18
13.60
-3.98
-4.32
-4.38
-4.80
TBDMSO
OTBDMS
34b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

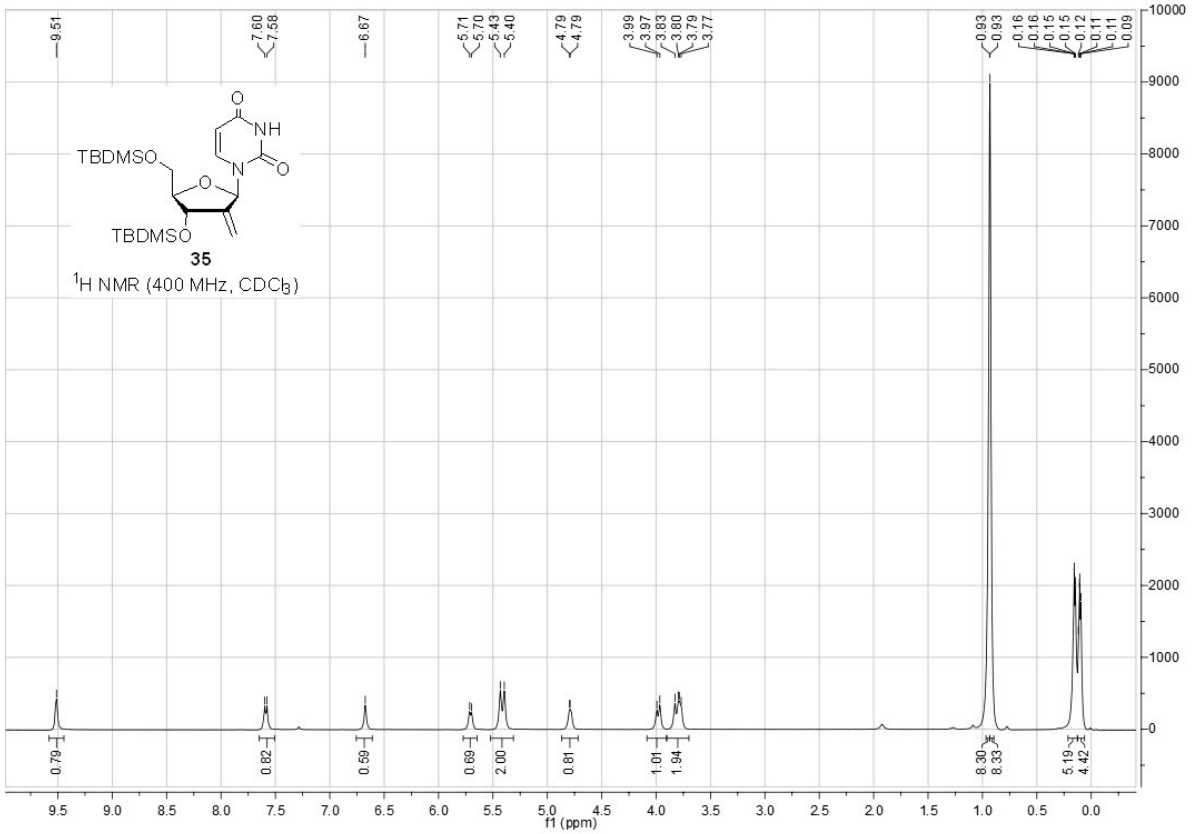

TBDMSO
OTBDMS
34b
1H-1H COSY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

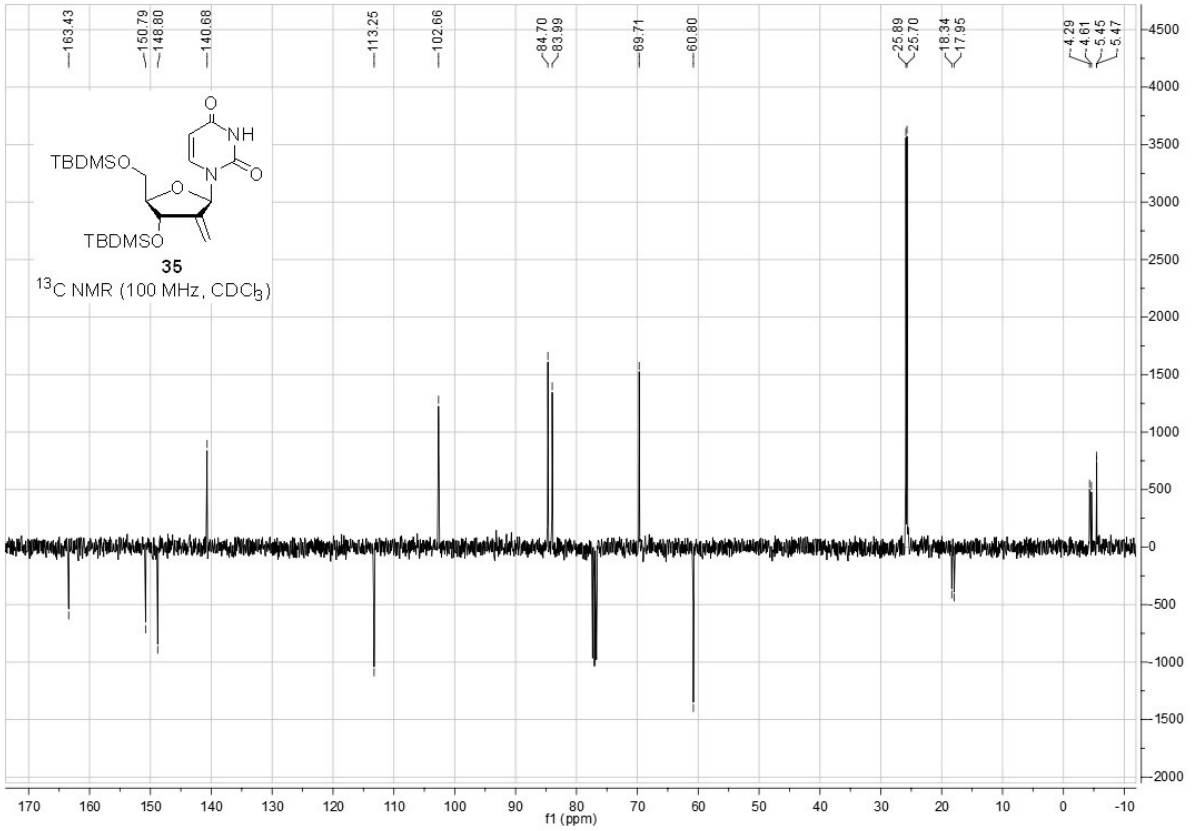

TBDMSO
OTBDMS
34b
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
(5.74,102.28)
f2 (ppm)
f1 (ppm)

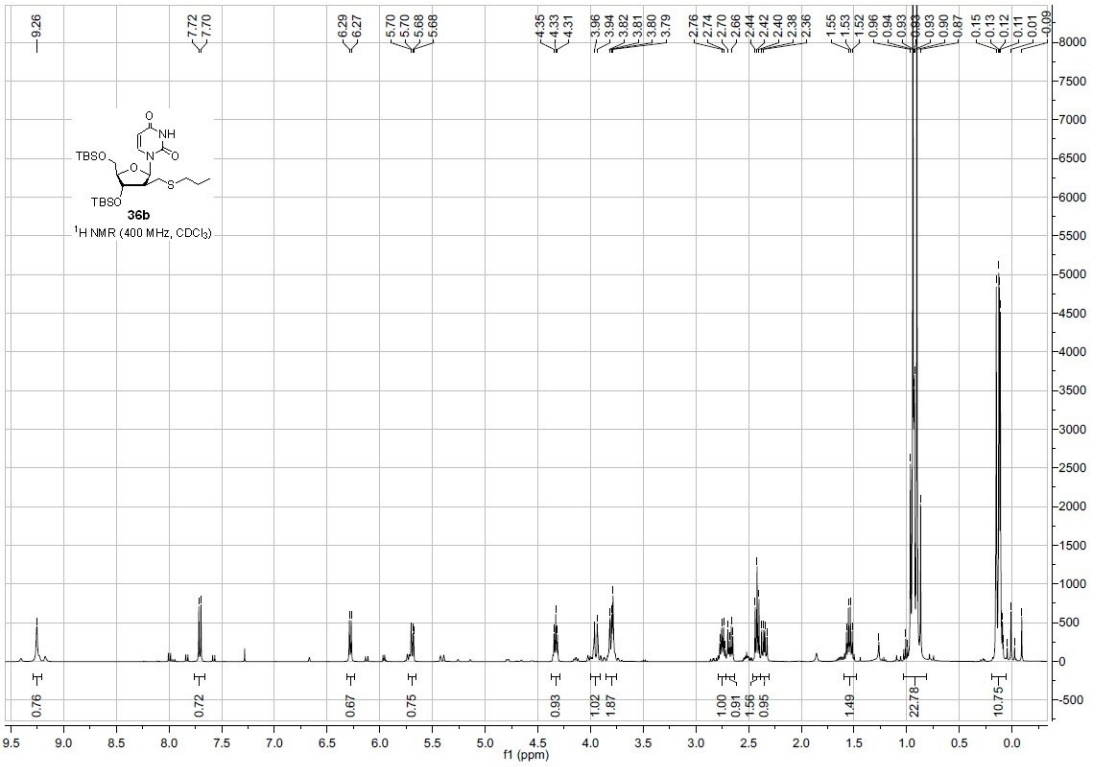

TBDMSO
OTBDMS
34b
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)

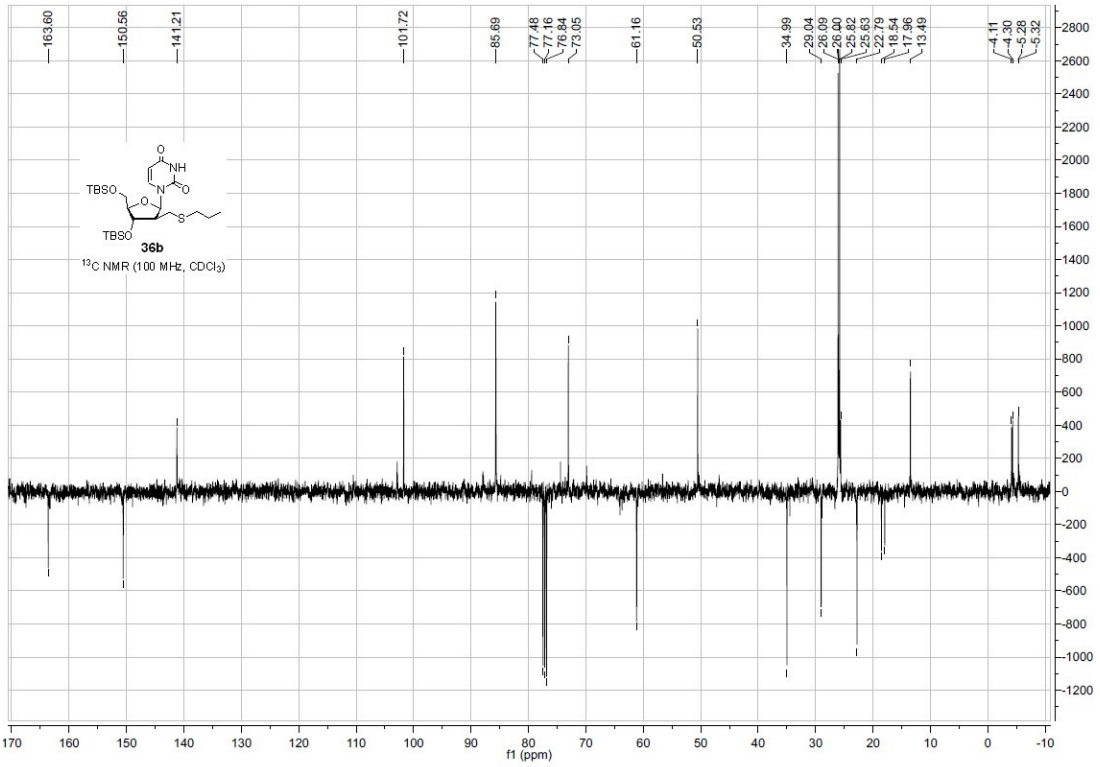

TBDMSO
TBDMSO
OH
NH
O
N
O
O
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

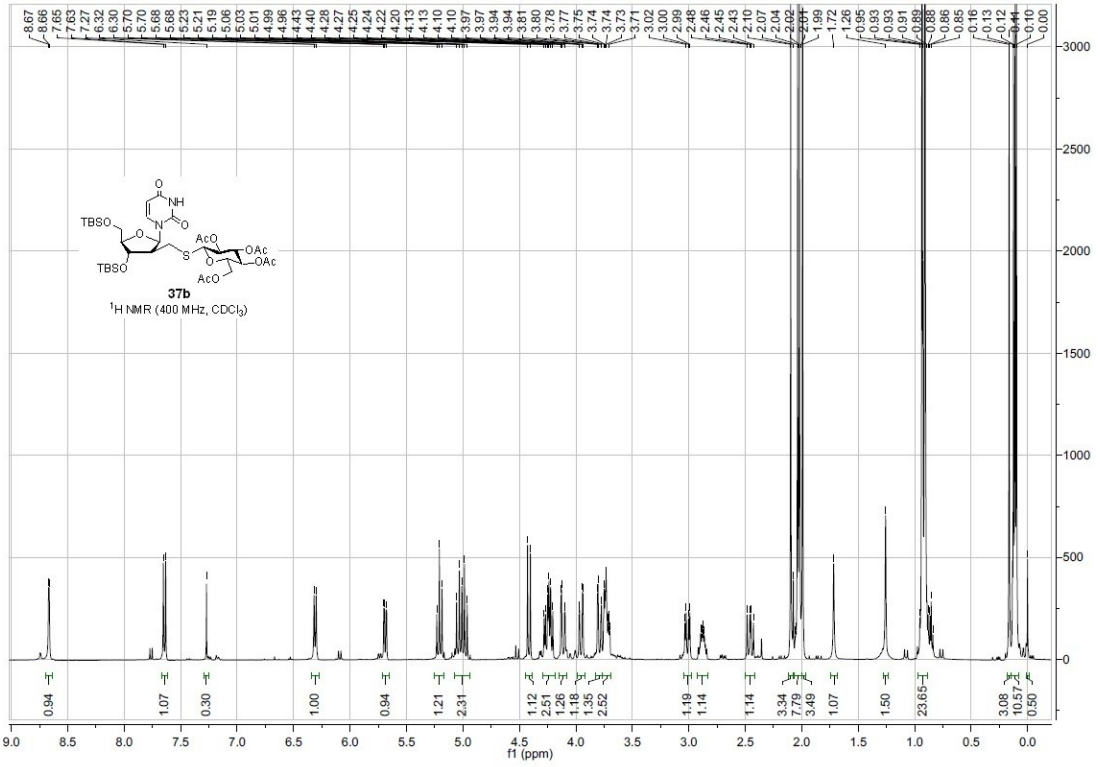

TBDMSO
TBDMSO
OH
NH
O
N
O
O
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

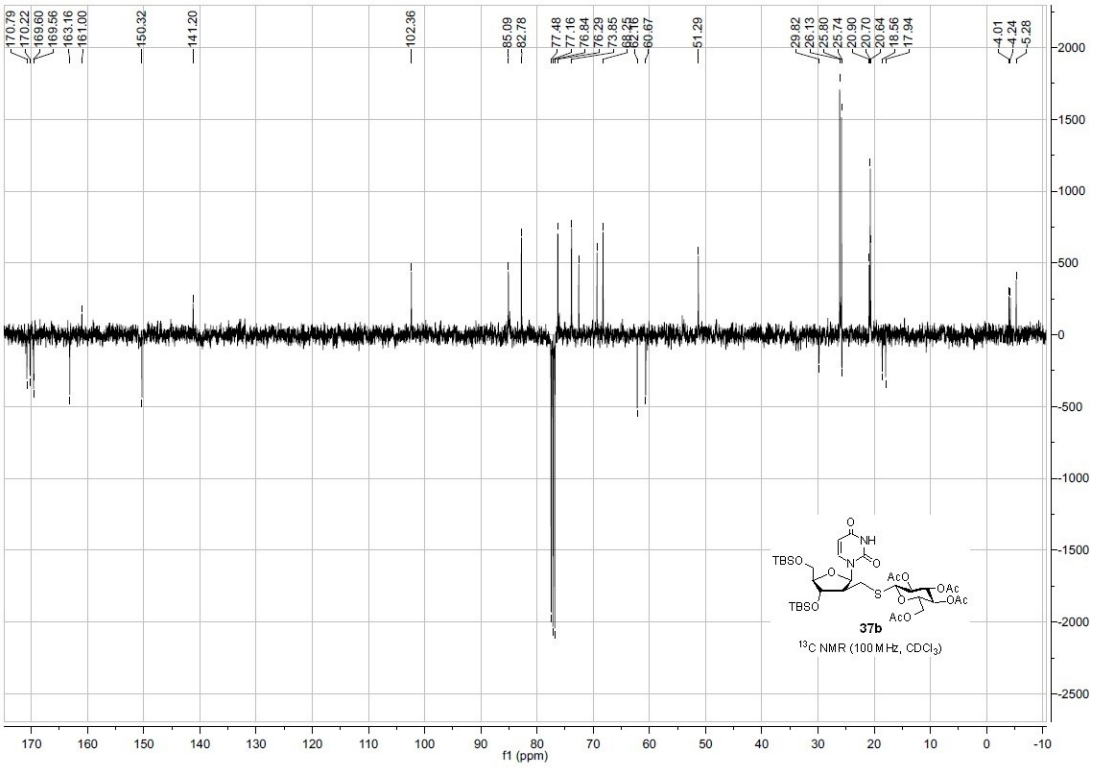

TBDMSO
TBDMSO
NH
O
N
O
O
35
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

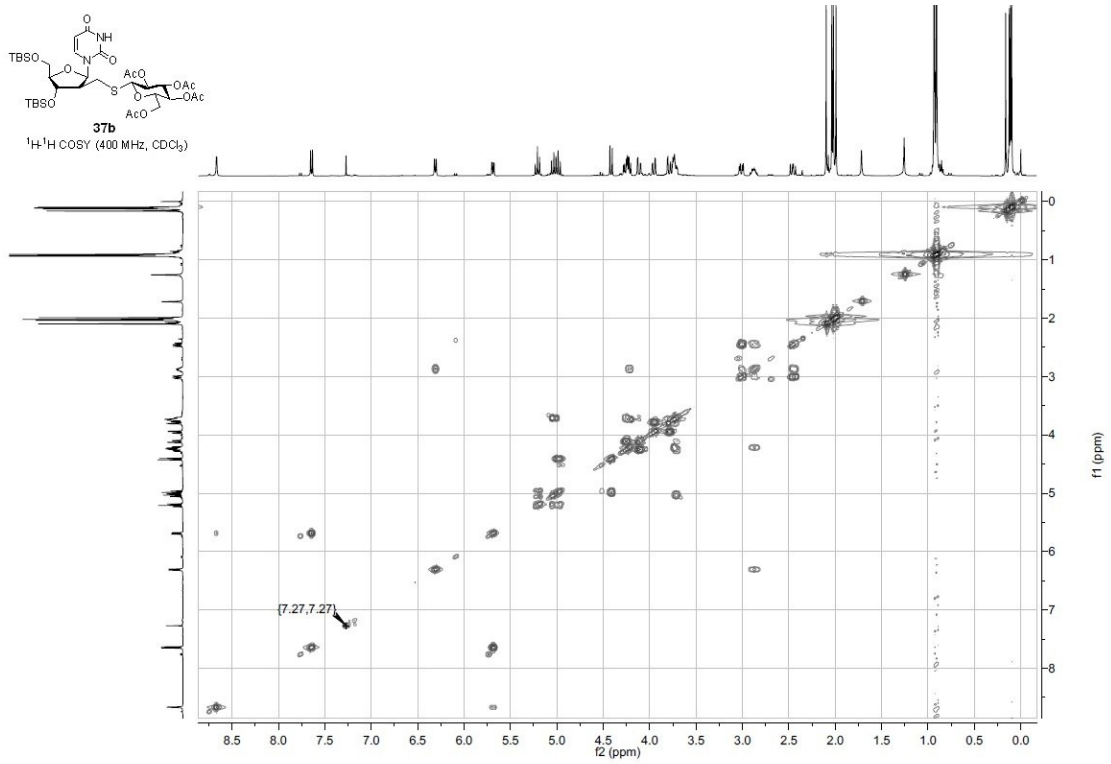

TBDMSO
TBDMSO
NH
O
N
O
O
35
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

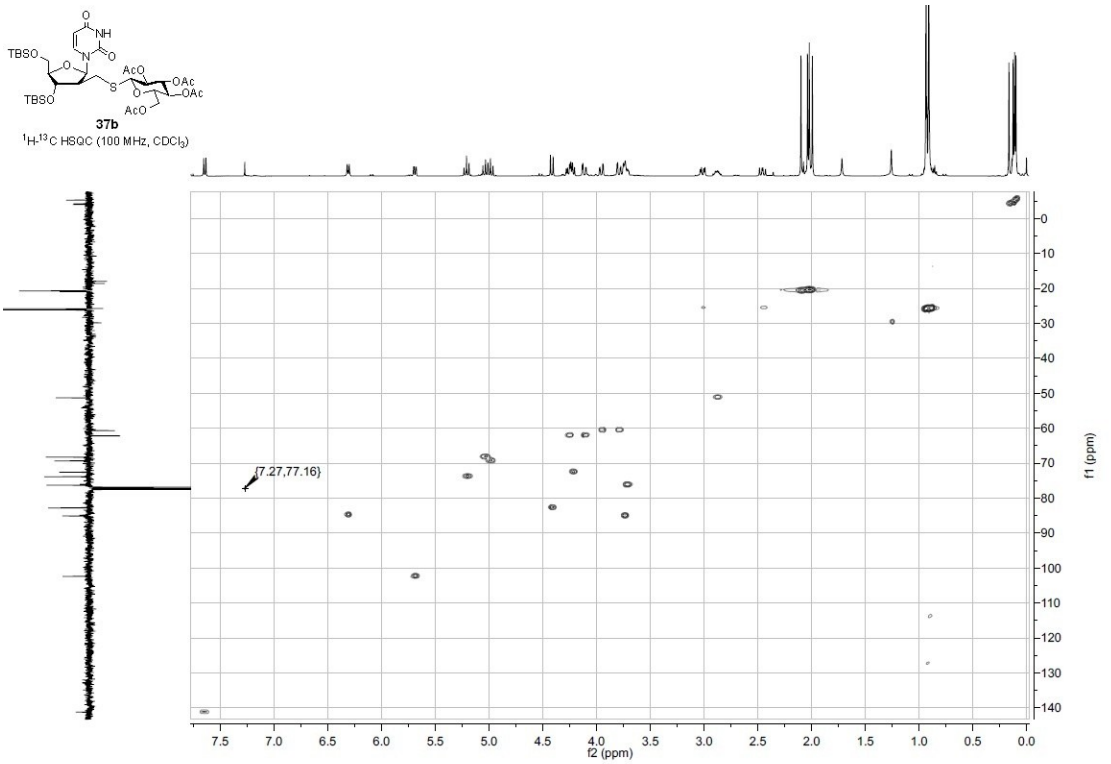

TBSO
TBSO
S
NH
O
O
N
O
36b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

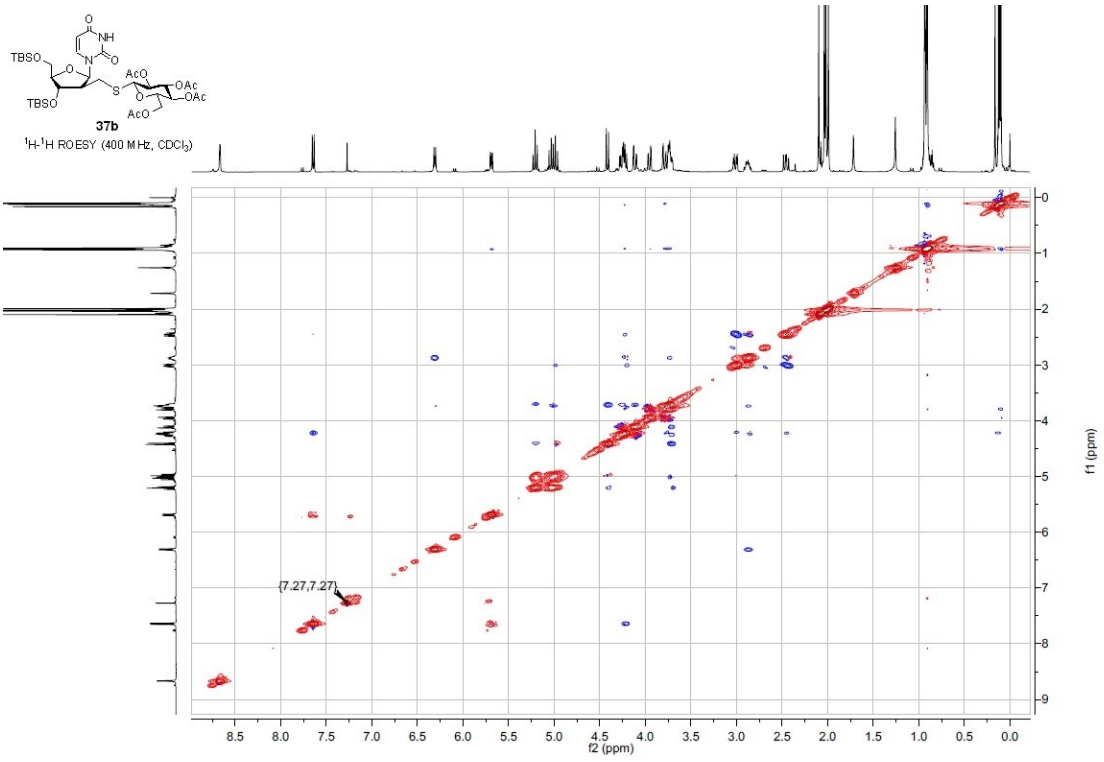

TBSO
TBSO
S
NH
O
O
N
O
36b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

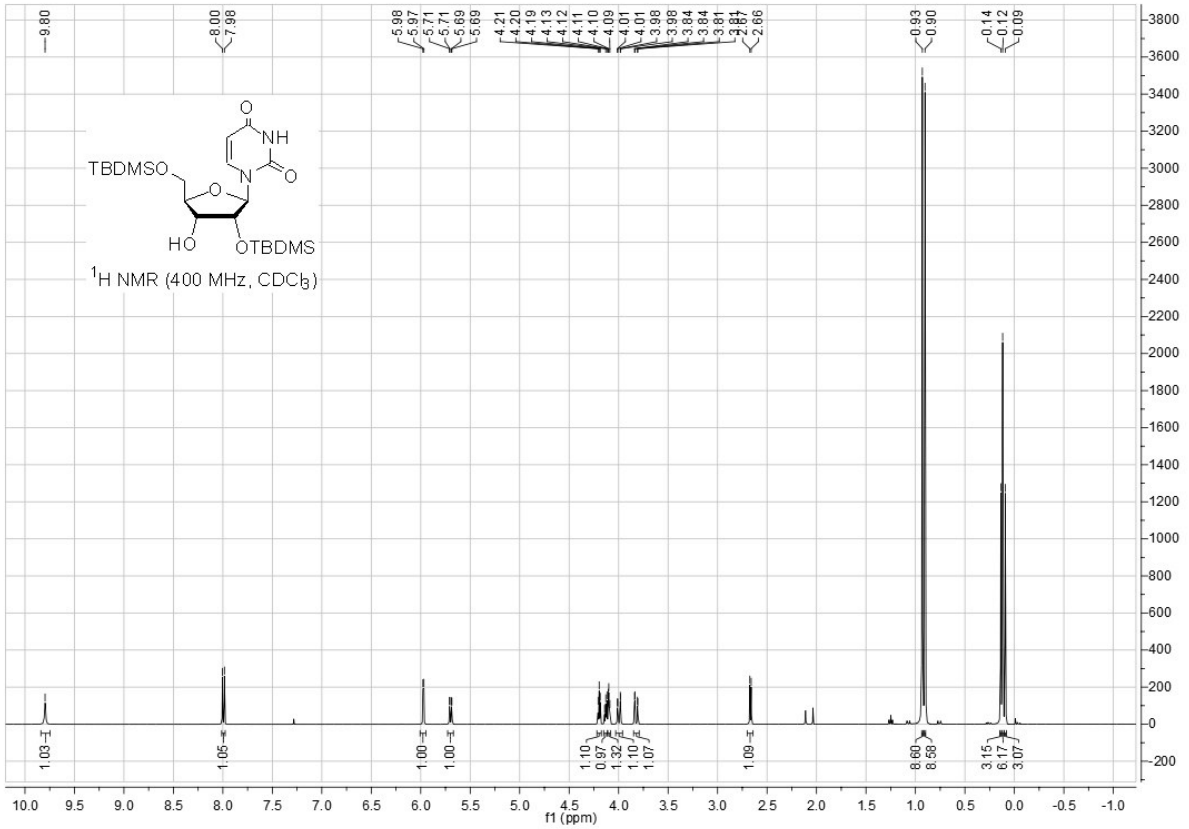

37b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

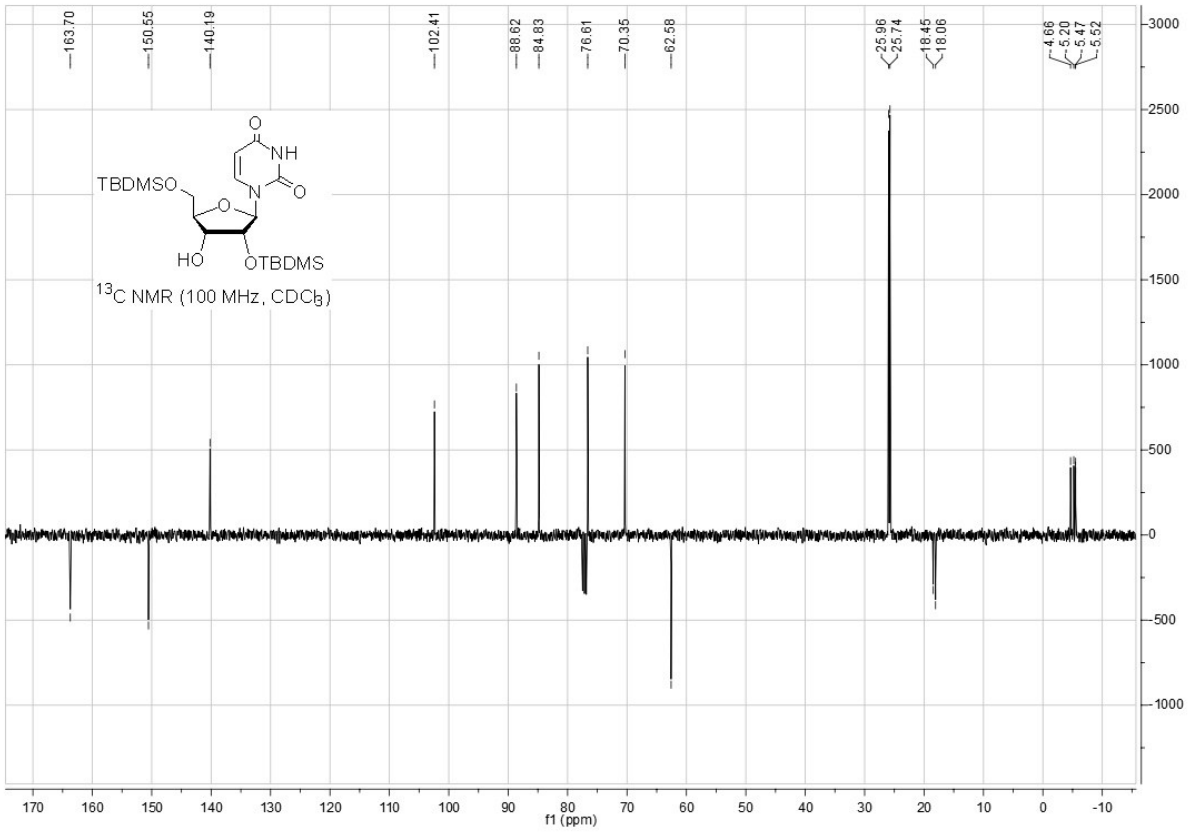

37b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

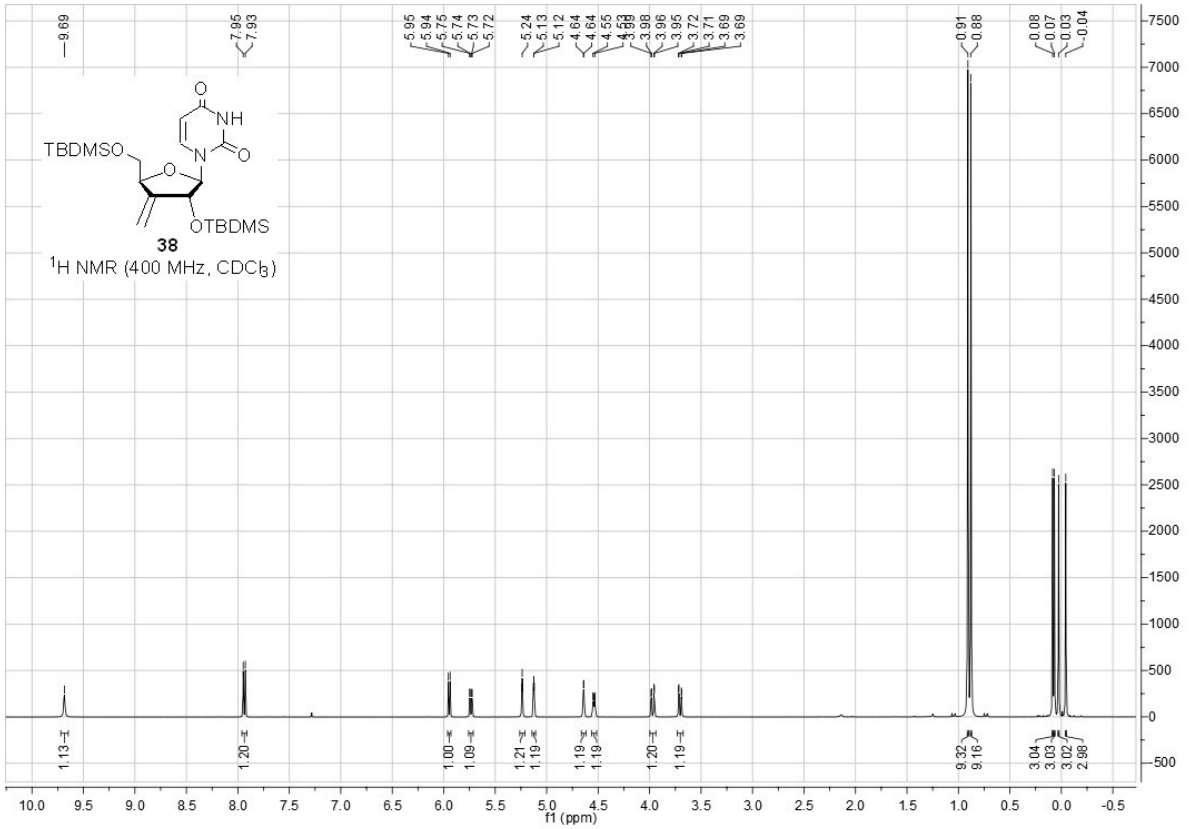

37b
^{1}H-^{1}H COSY (400 MHz, $CDCl_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

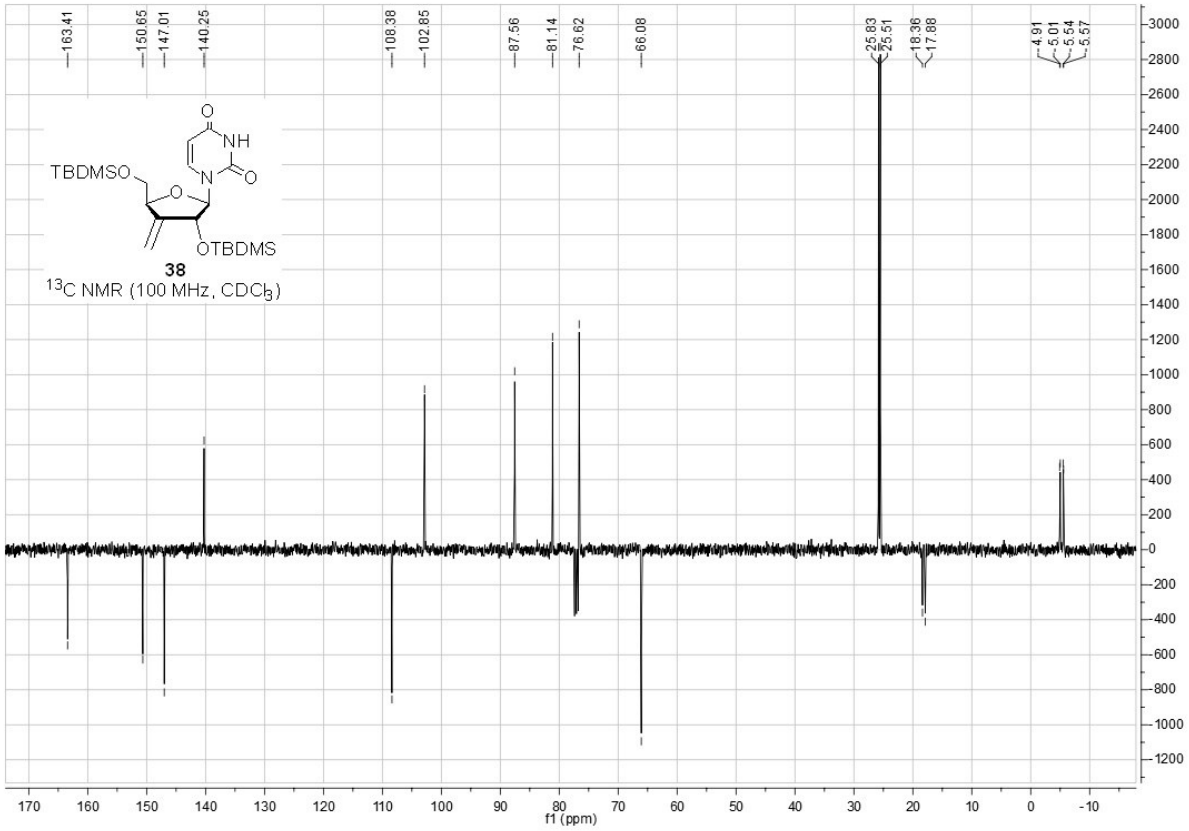

37b
^{1}H-^{13}C HSQC (100 MHz, $CDCl_3$)
(7.27,77.16)
f2 (ppm)
f1 (ppm)

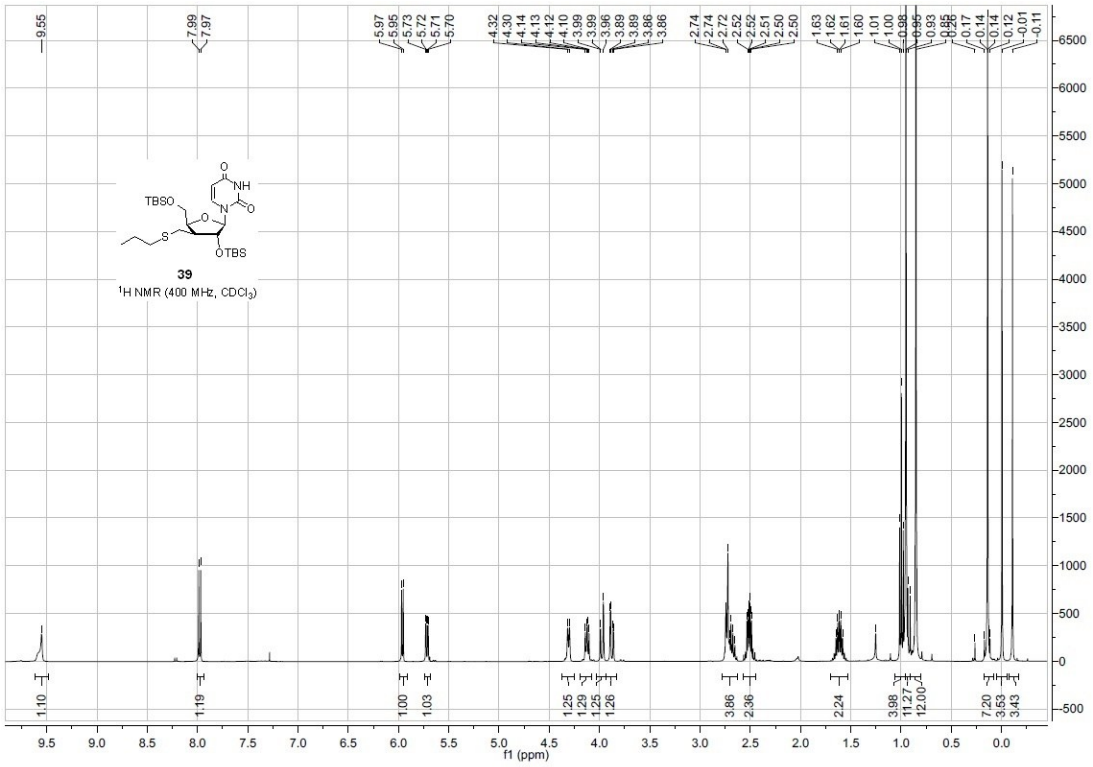

37b
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
(7.27,7.27)
f2 (ppm)
f1 (ppm)

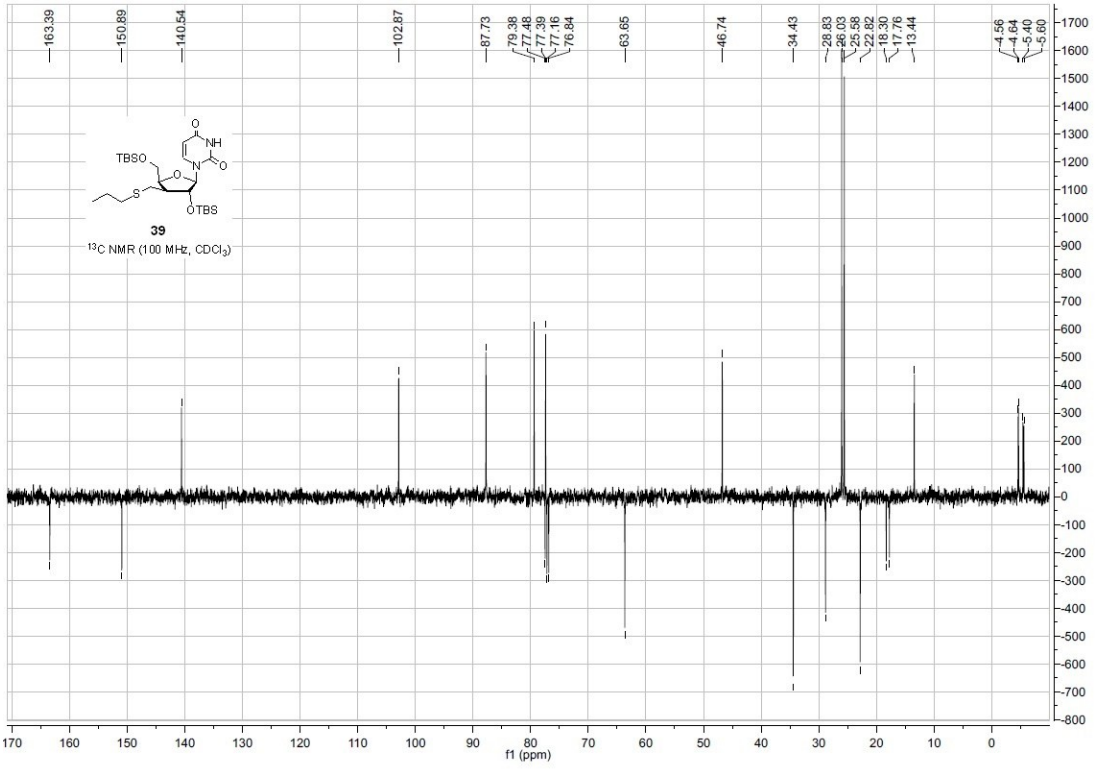

TBDMSO
HO
OTBDMS
NH
O
N
O
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

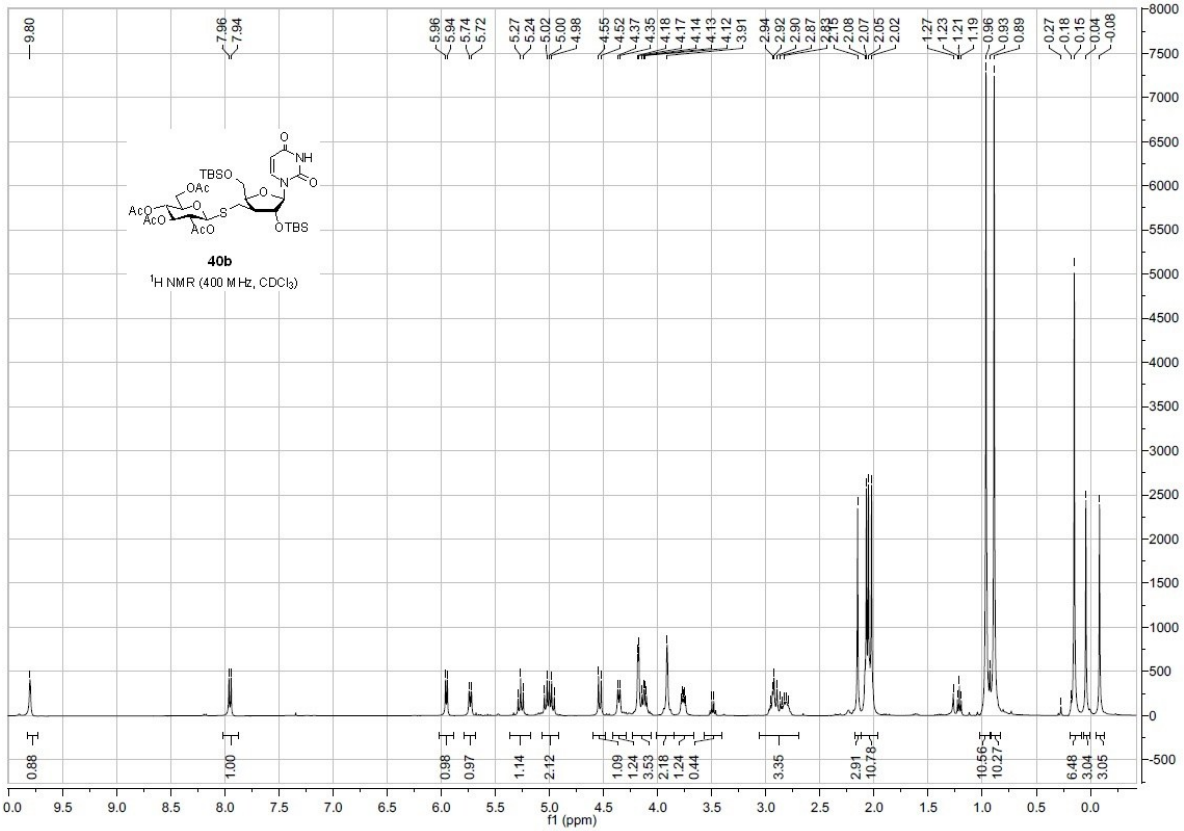

TBDMSO
HO
OTBDMS
NH
O
N
O
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

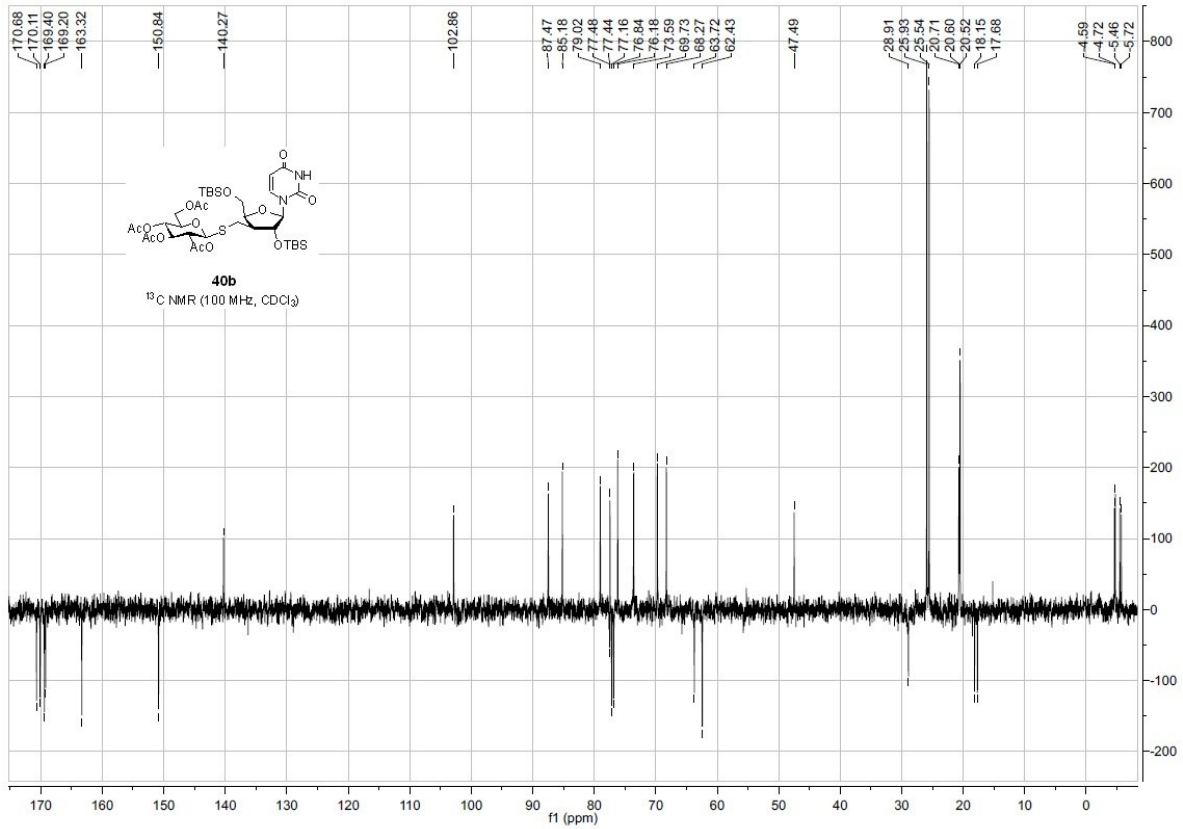

TBDMSO
NH
O
N
O
OTBDMS
38
^{1}H NMR (400 MHz, CDCl$_3$)

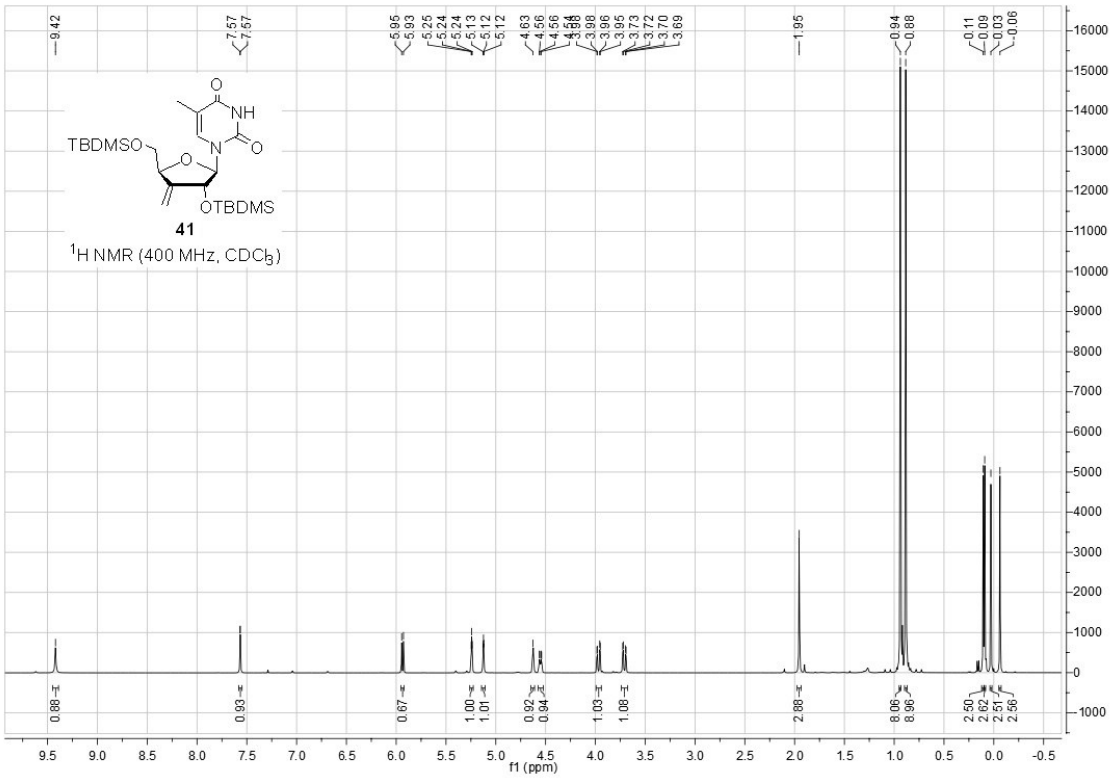

TBDMSO
NH
O
N
O
OTBDMS
38
^{13}C NMR (100 MHz, CDCl$_3$)

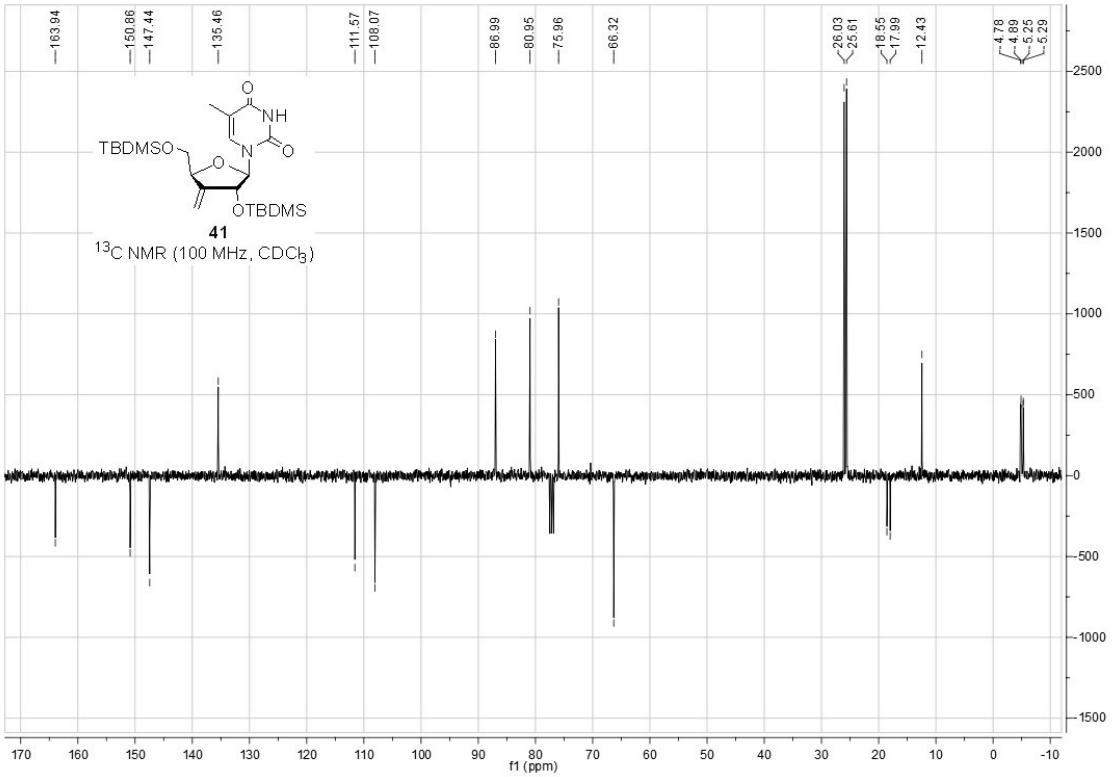

TBSO
NH
O
N
S
OTBS
39
1H NMR (400 MHz, CDCl3)
f1 (ppm)

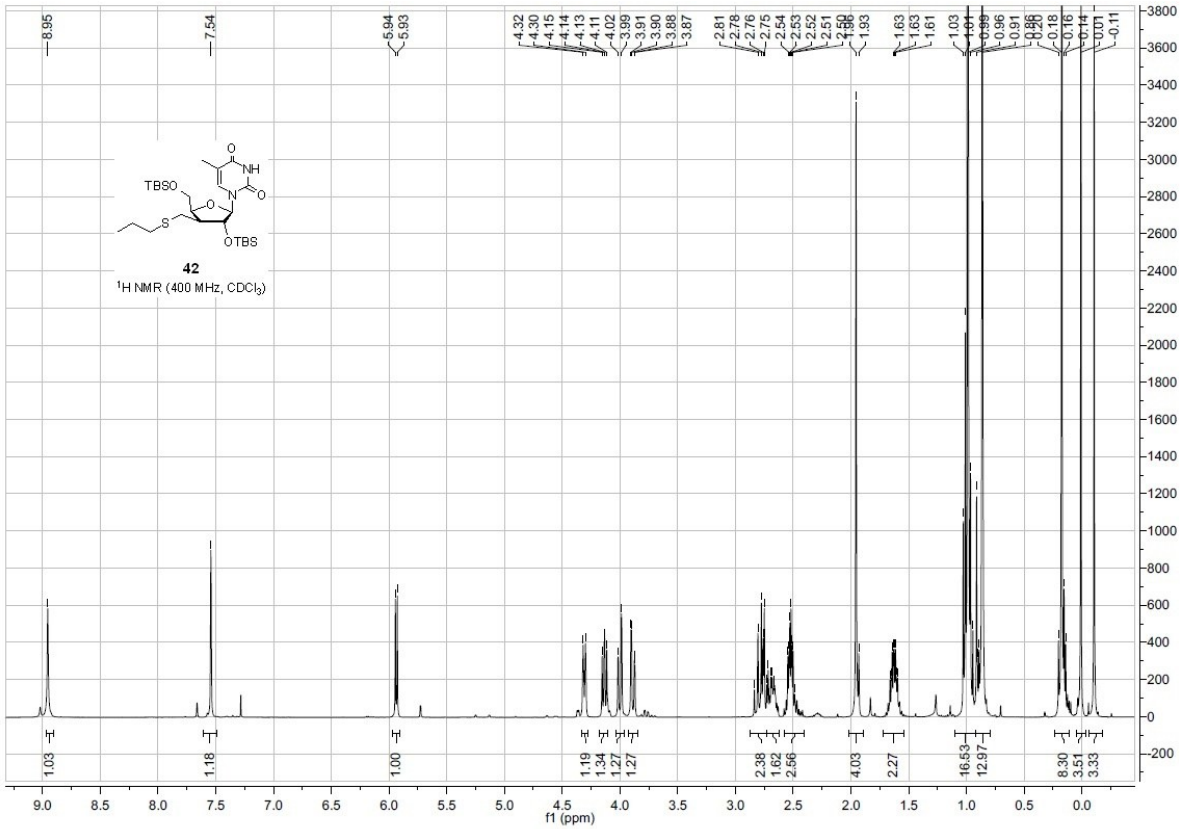

TBSO
NH
O
N
S
OTBS
39
13C NMR (100 MHz, CDCl3)
f1 (ppm)

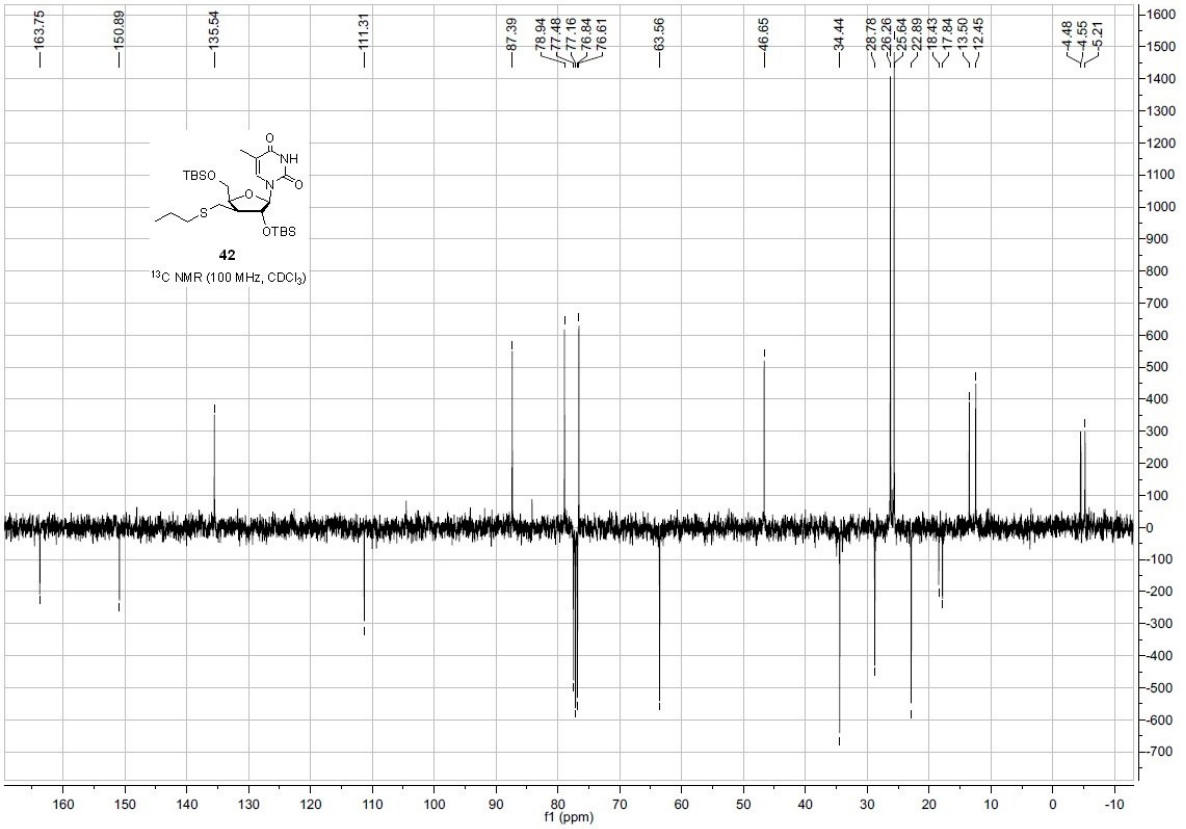

TBSO
OAc
AcO
AcO
AcO
S
O
NH
N
O
OTBS
40b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

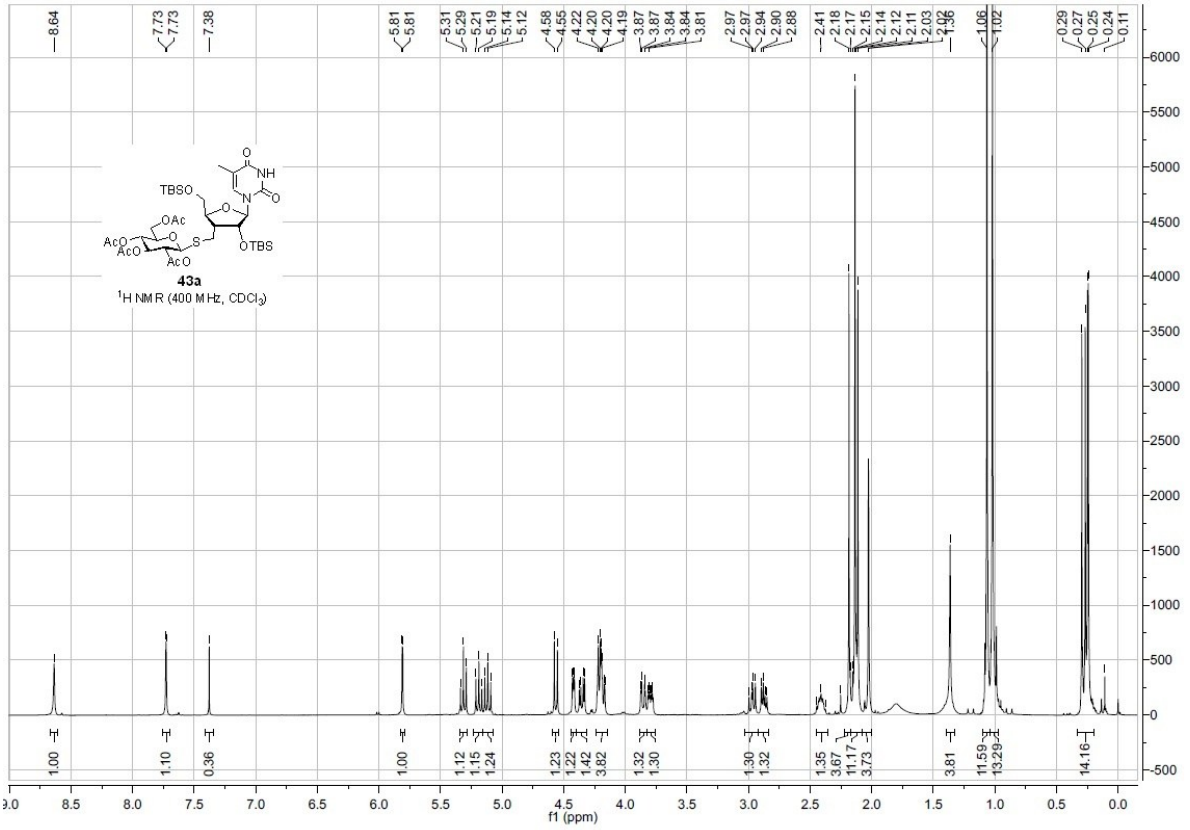

TBSO
OAc
AcO
AcO
AcO
S
O
NH
N
O
OTBS
40b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

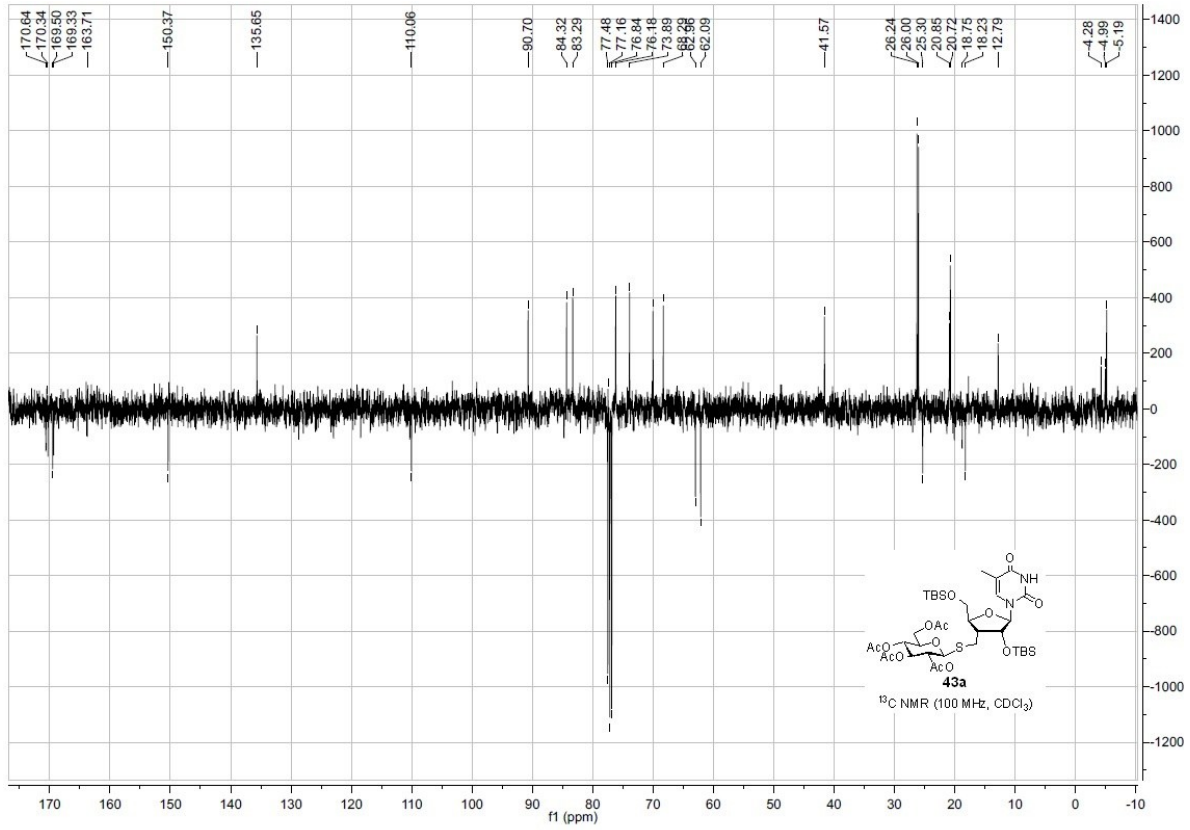

TBDMSO
OTBDMS
41
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

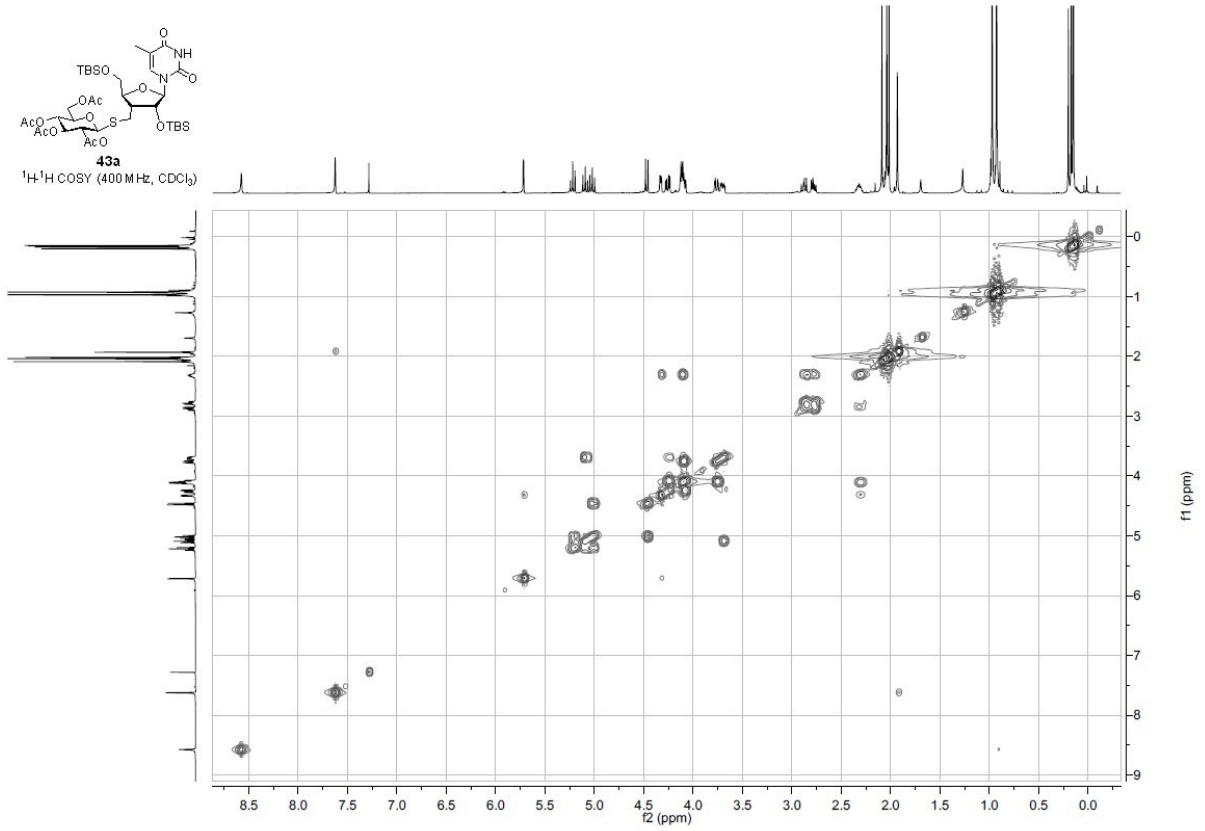

TBDMSO
OTBDMS
41
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

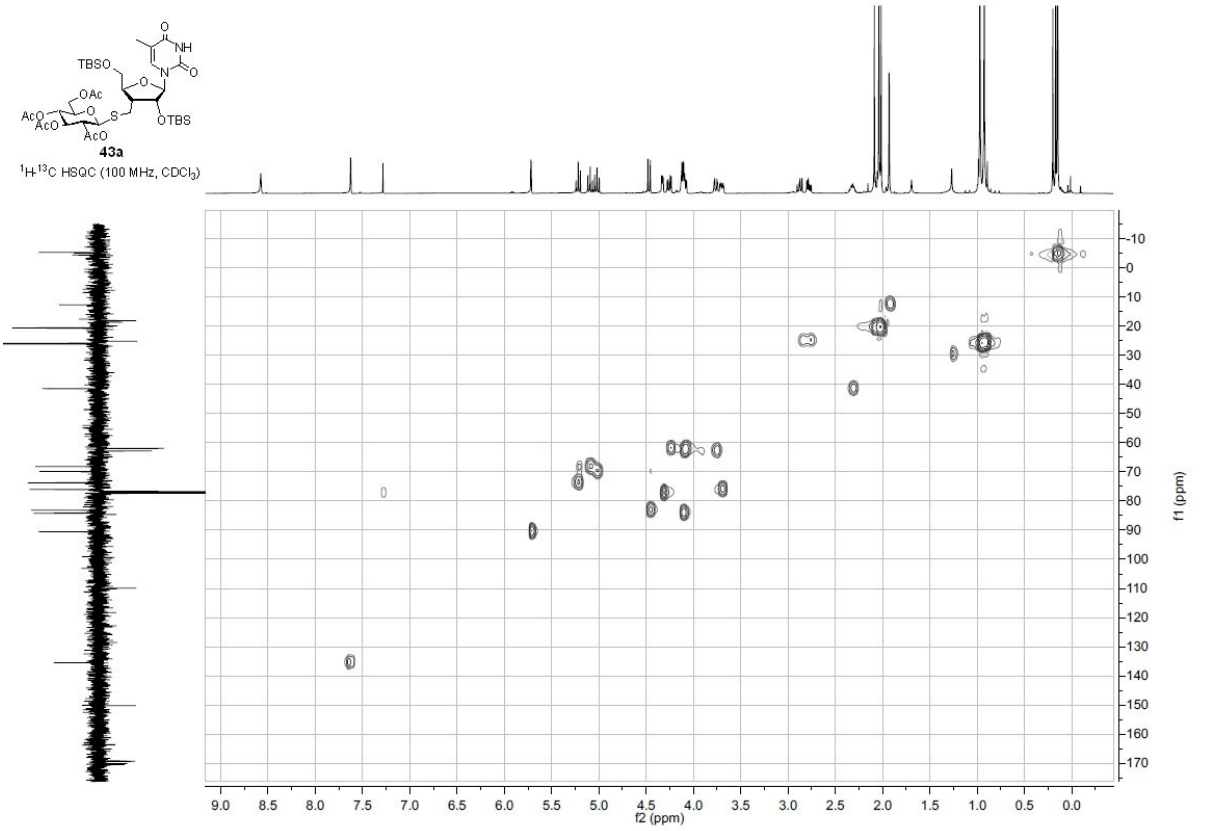

TBSO
NH
O
N
O
S
OTBS
42
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

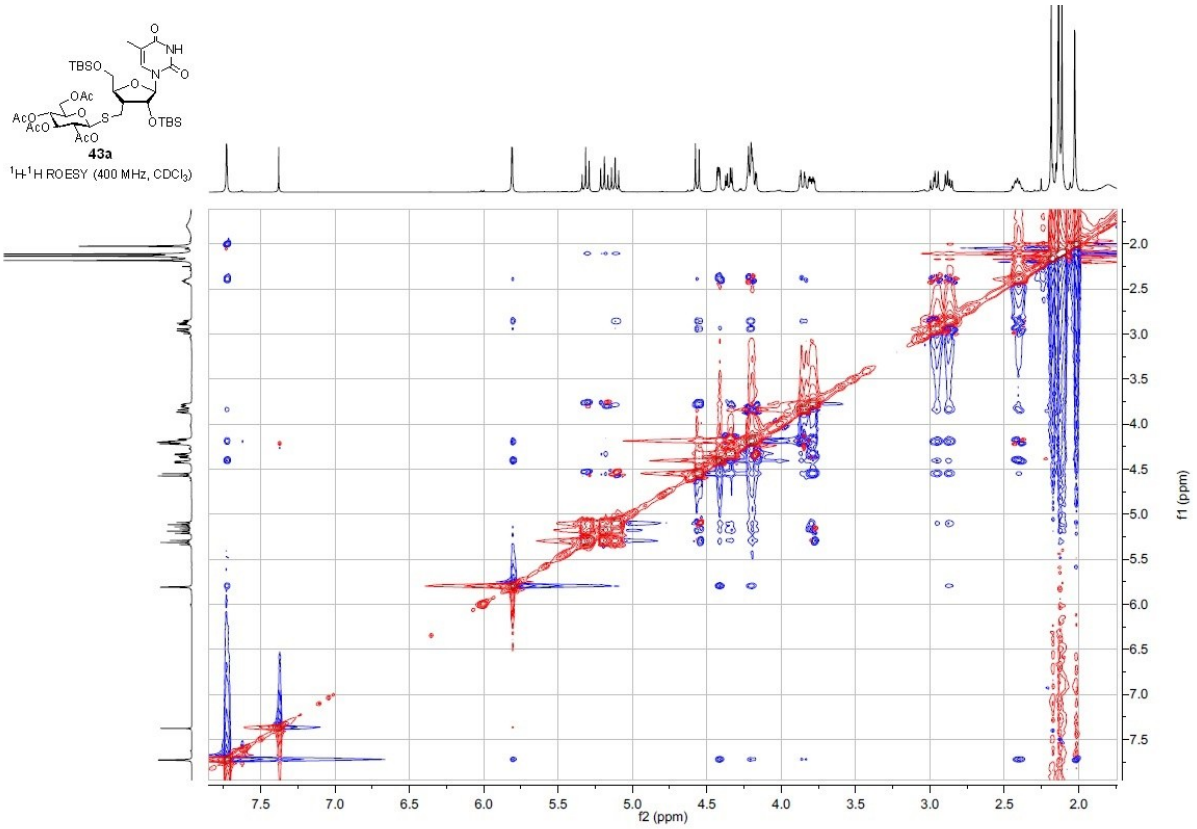

TBSO
NH
O
N
O
S
OTBS
42
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

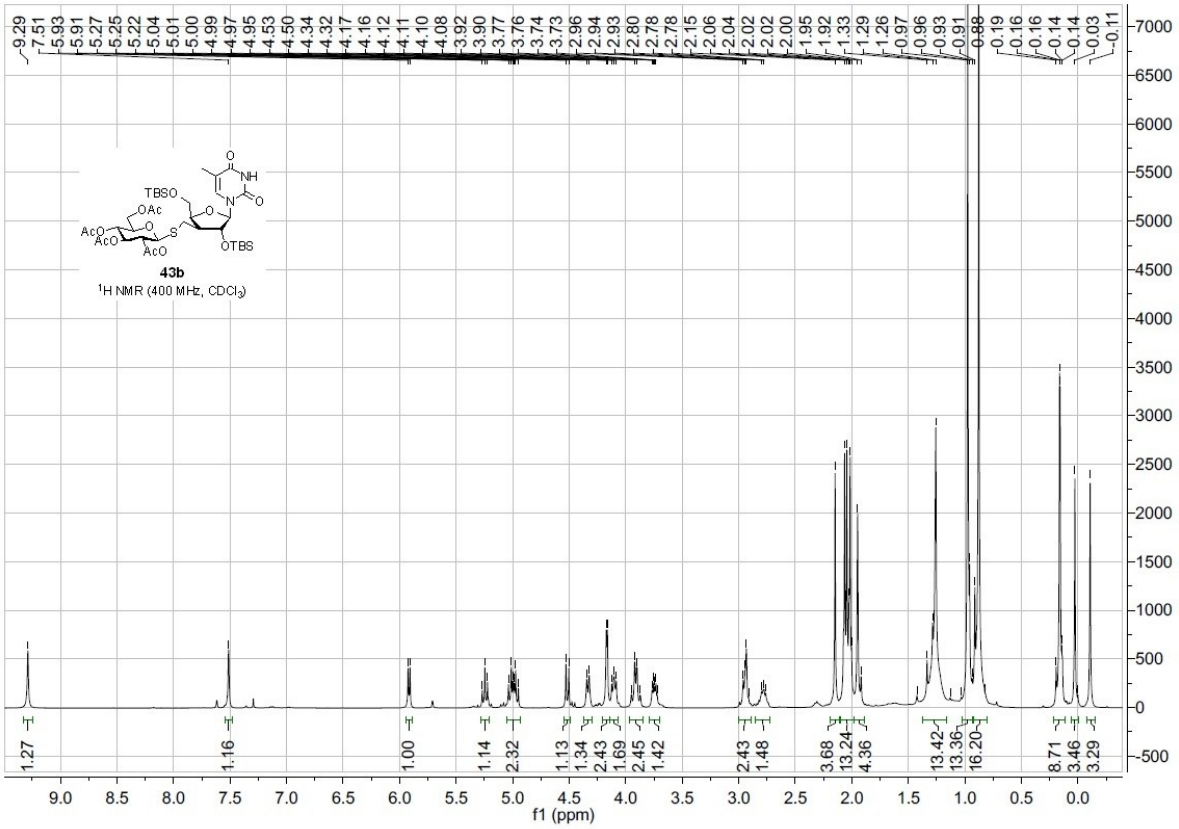

43a
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

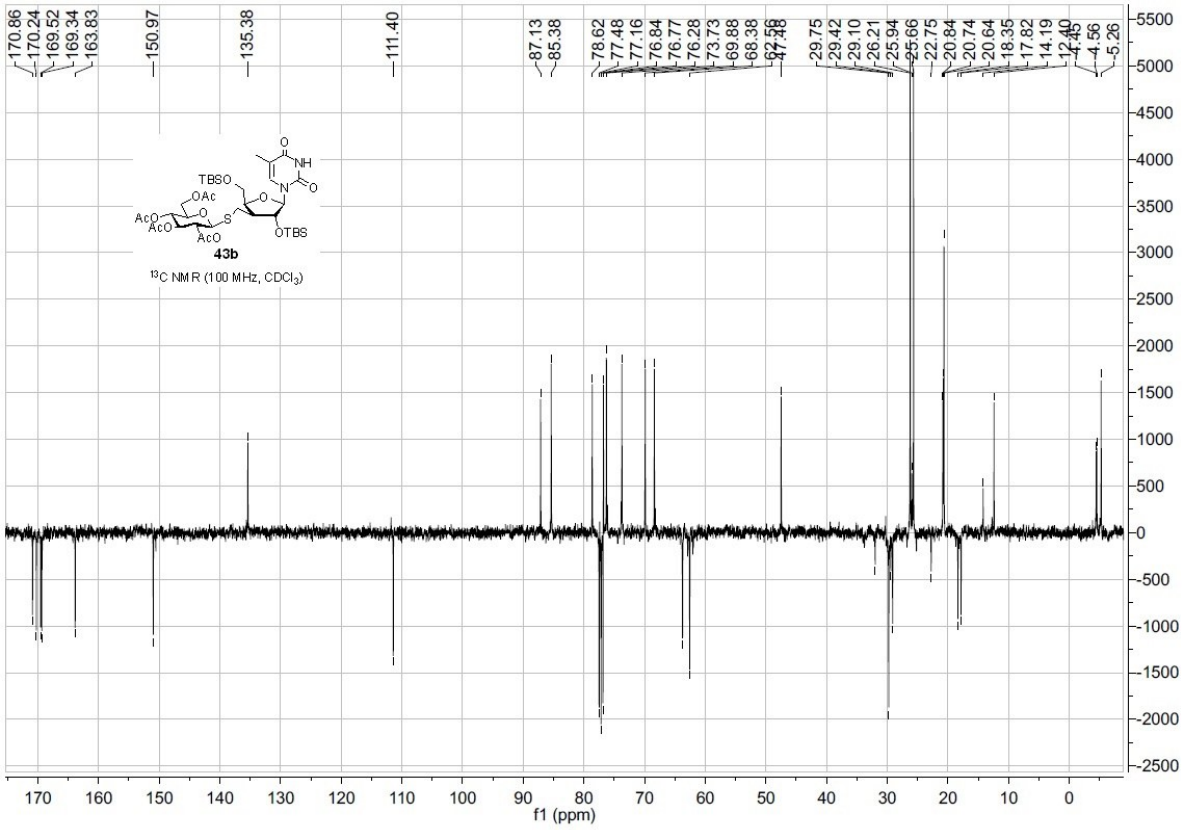

43a
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

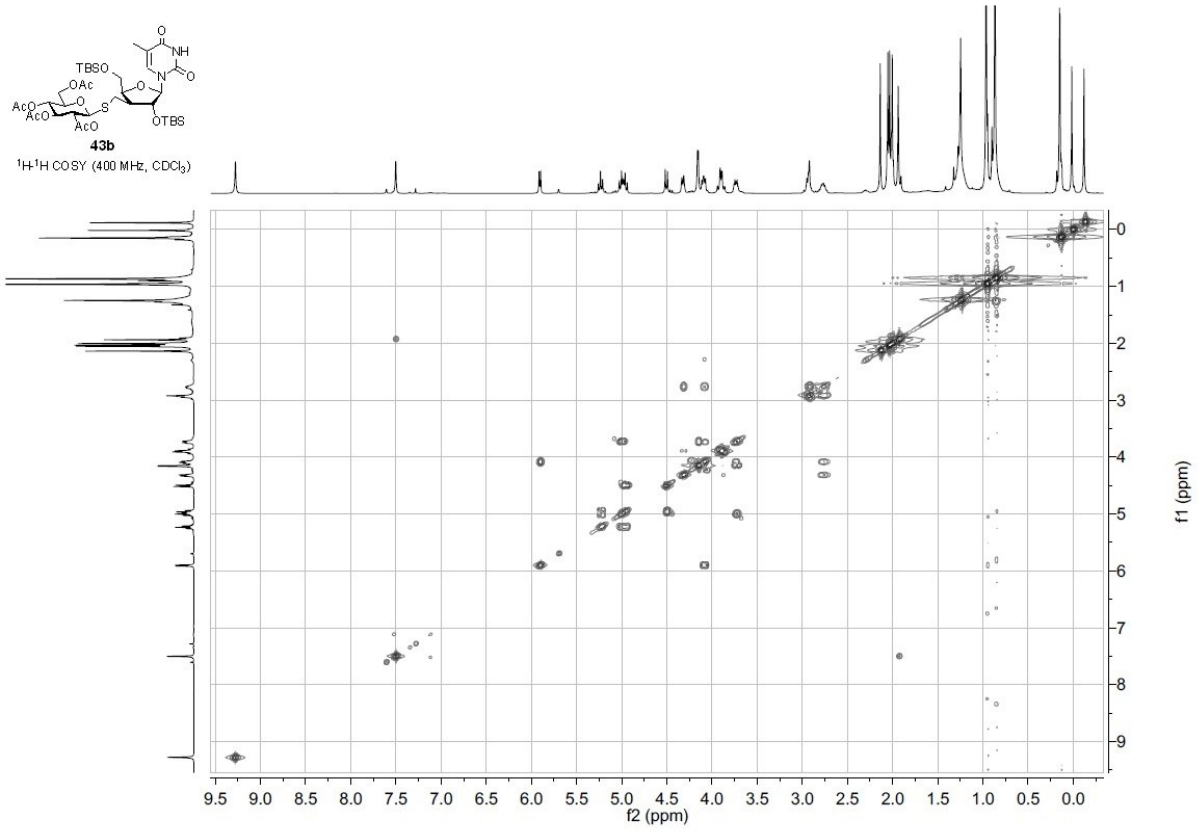

43a
^{1}H-^{1}H COSY (400 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)

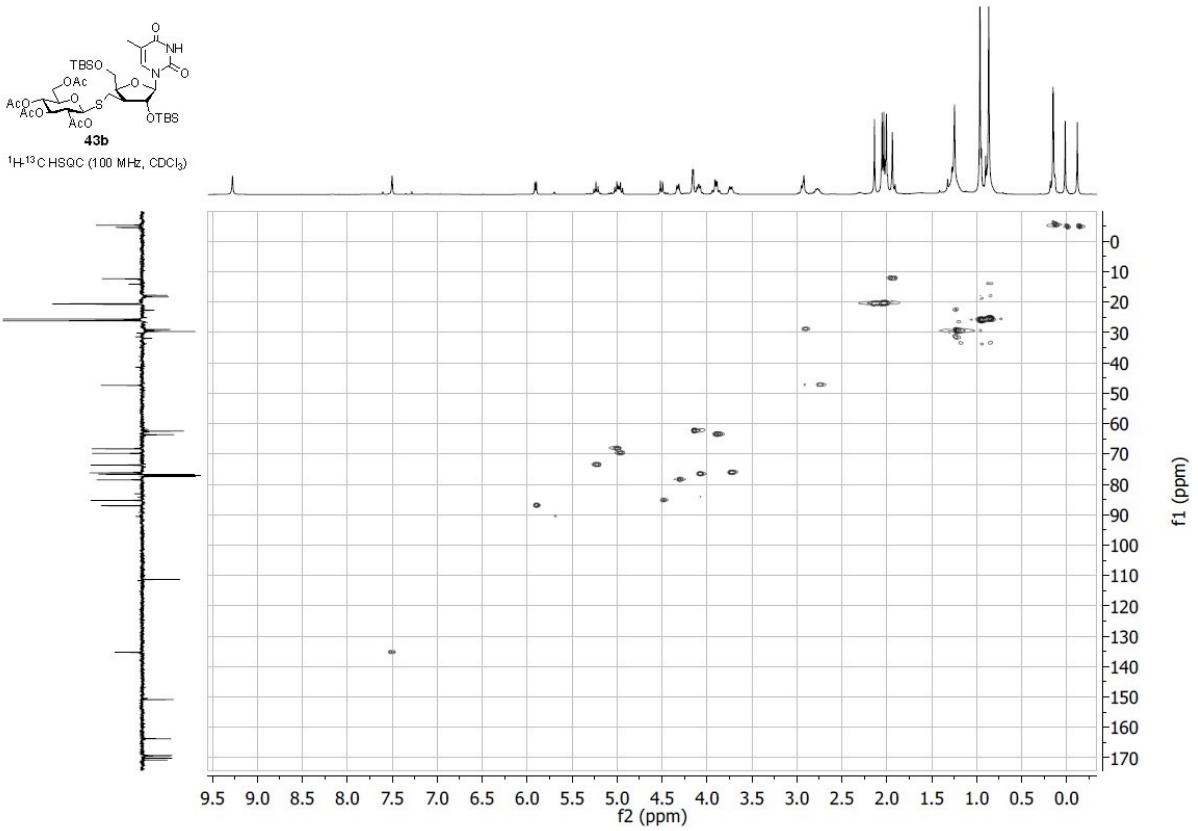

43a
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)

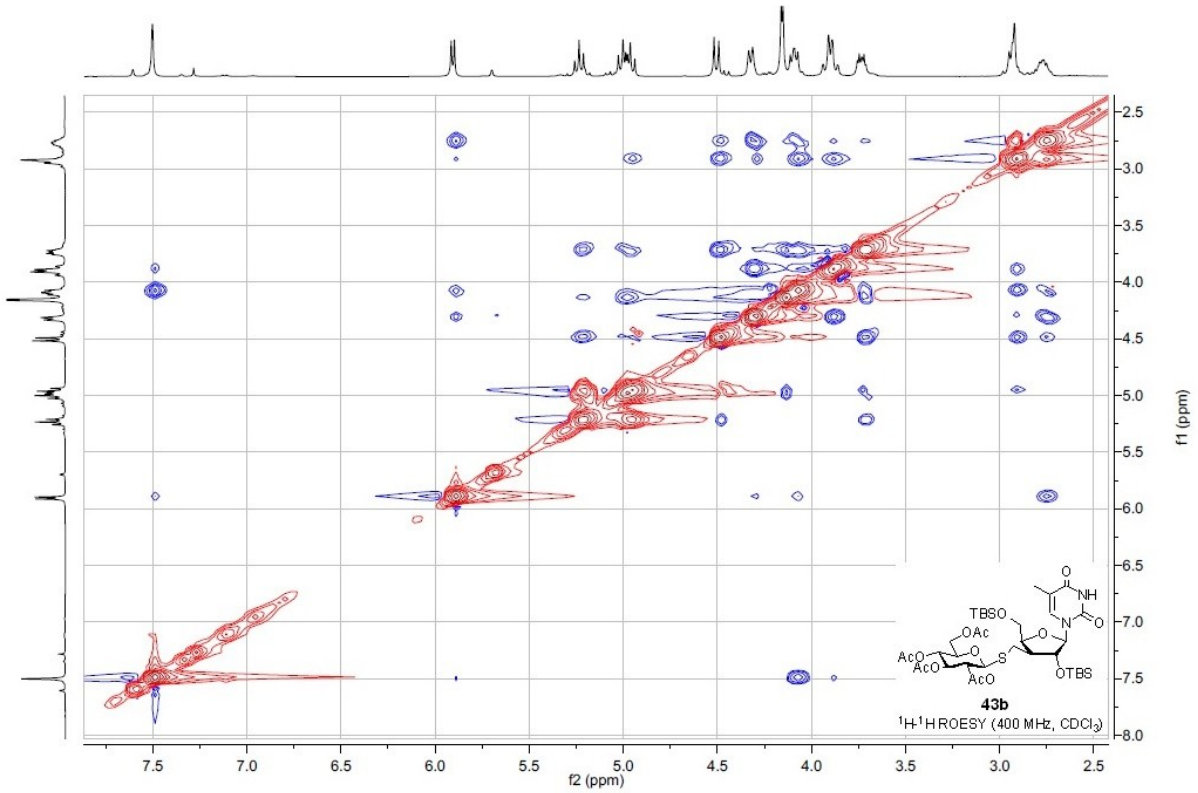

43a
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)

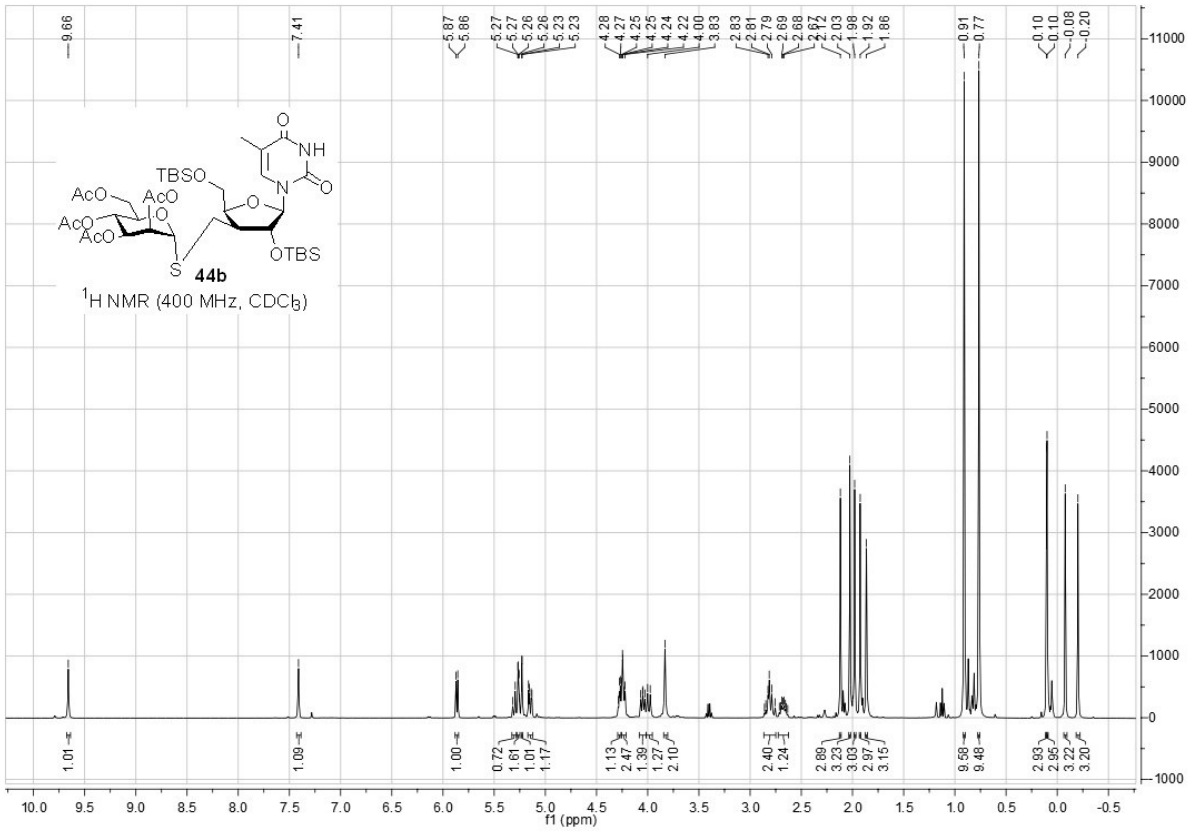

43b
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

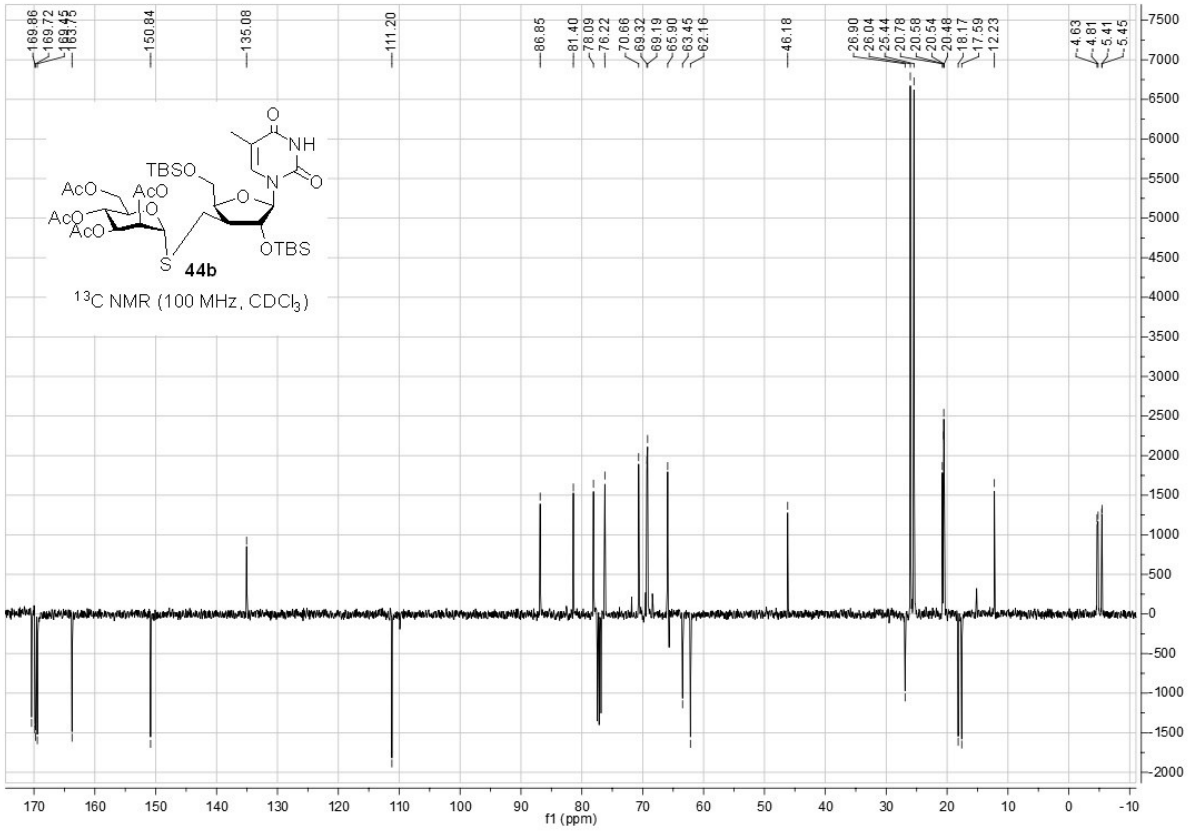

170.86
170.24
169.52
169.34
163.83
150.97
135.38
111.40
87.13
85.38
78.62
77.48
77.16
76.84
76.77
76.28
73.73
69.88
68.38
62.56
47.48
29.75
29.42
29.10
26.21
25.94
25.66
22.75
20.84
20.74
20.64
18.35
17.82
14.19
12.40
4.45
4.56
5.26
TBSO
OAc
AcO
AcO
AcO
O
S
NH
O
N
O
OTBS
43b
13C NMR (100 MHz, CDCl3)
f1 (ppm)


TBSO
OAc
AcO
AcO
AcO
O
S
NH
O
N
O
OTBS
43b
1H-1H COSY (400 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


43b
^{1}H-^{13}C HSQC (100 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)


43b
^{1}H-^{1}H ROESY (400 MHz, CDCl$_3$)
f2 (ppm)
f1 (ppm)


44b
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


44b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)