

Supporting Information

for

Effect of uridine protecting groups on the diastereoselectivity of uridine-derived aldehyde 5'-alkynylation

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CNRS, Université Paris Descartes, Sorbonne Paris Cité (USPC), Centre Interdisciplinaire Chimie
Biologie-Paris (CICB-Paris), 45 rue des Saints Pères, 75270 Paris 06, France.

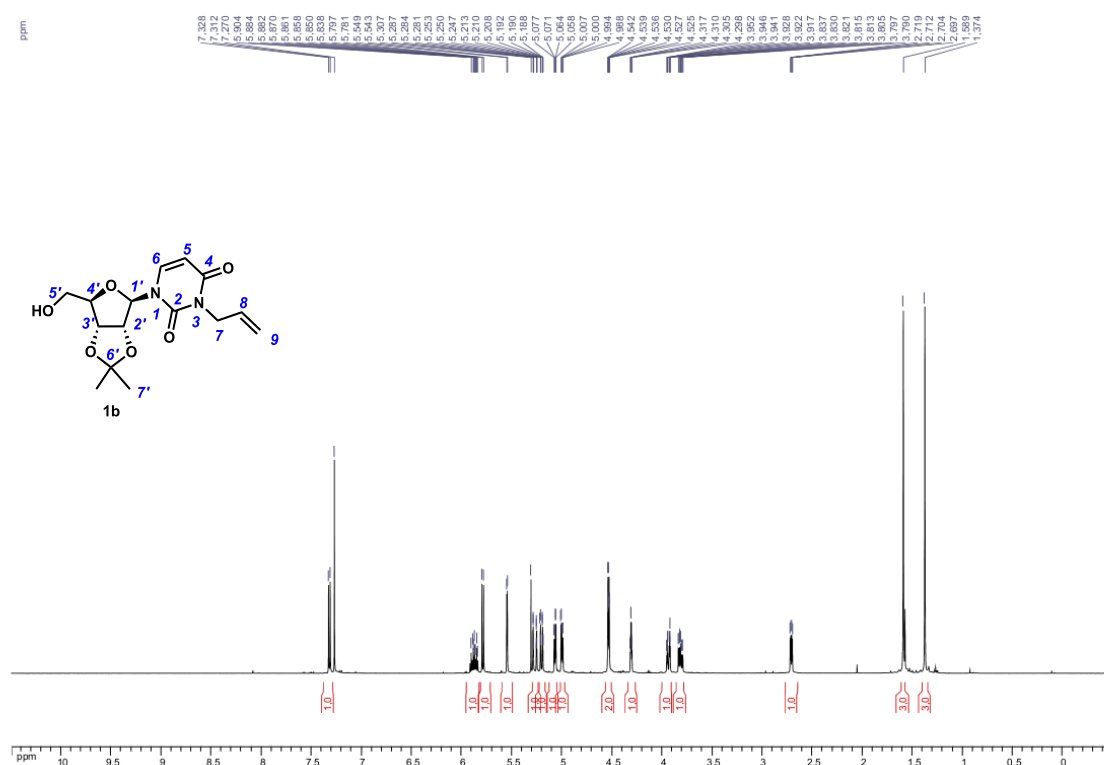
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- christine.gravier-pelletier@parisdescartes.fr

*Corresponding author

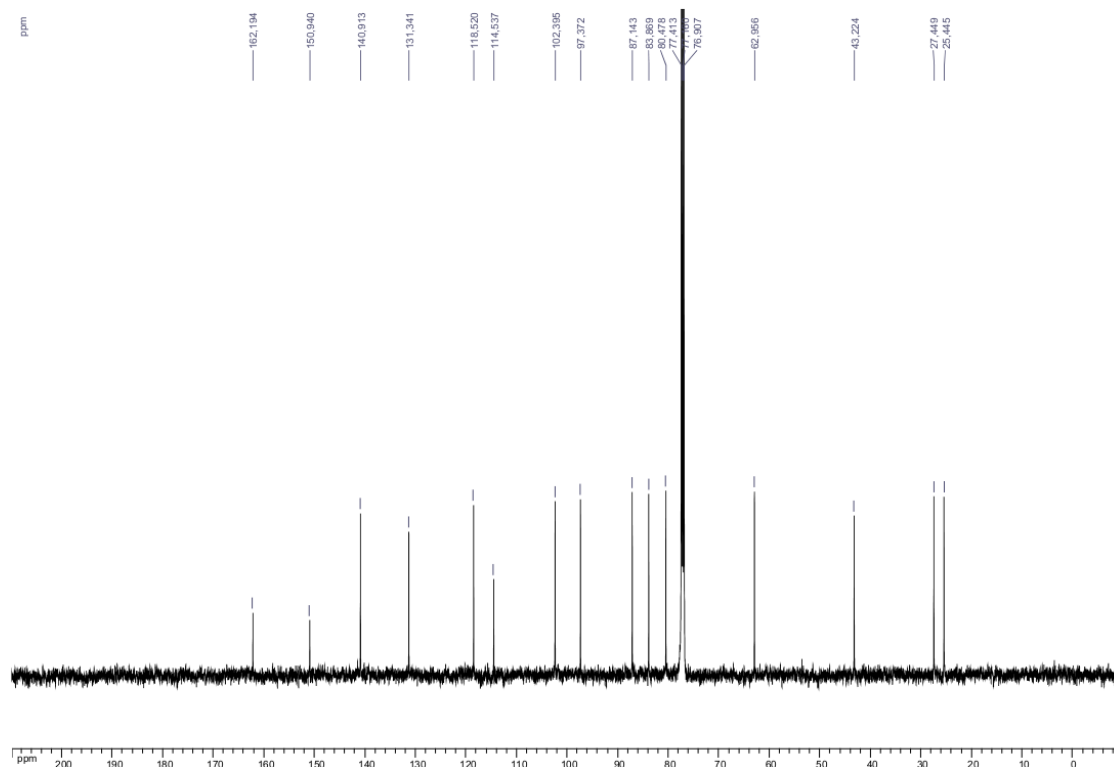
[‡]Equal contributors

Spectral data for new compounds

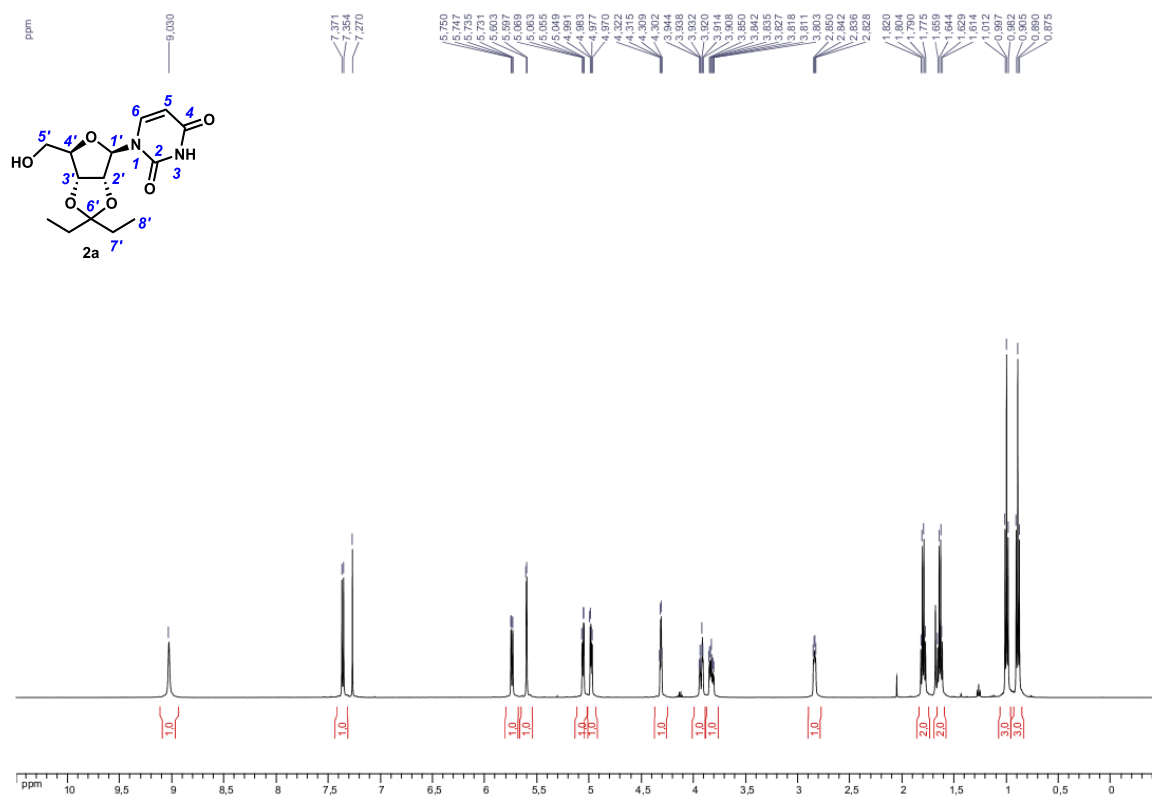
¹H NMR, compound **1b**



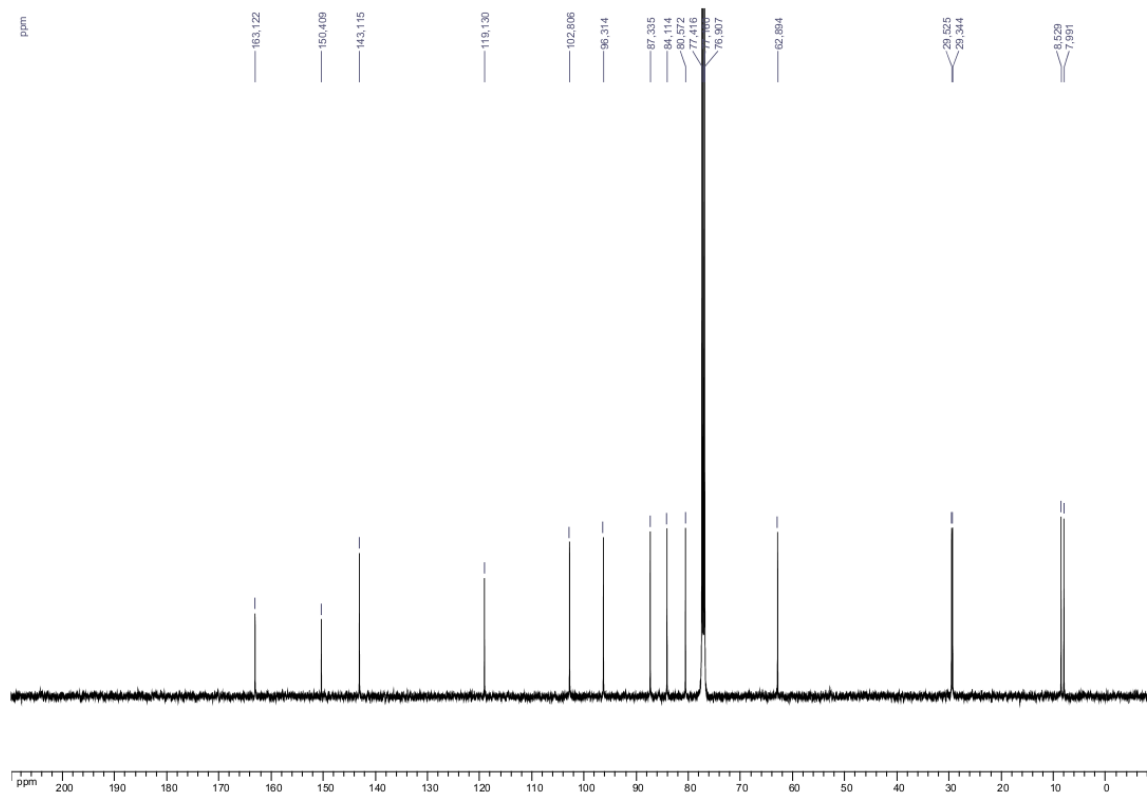
¹³C NMR



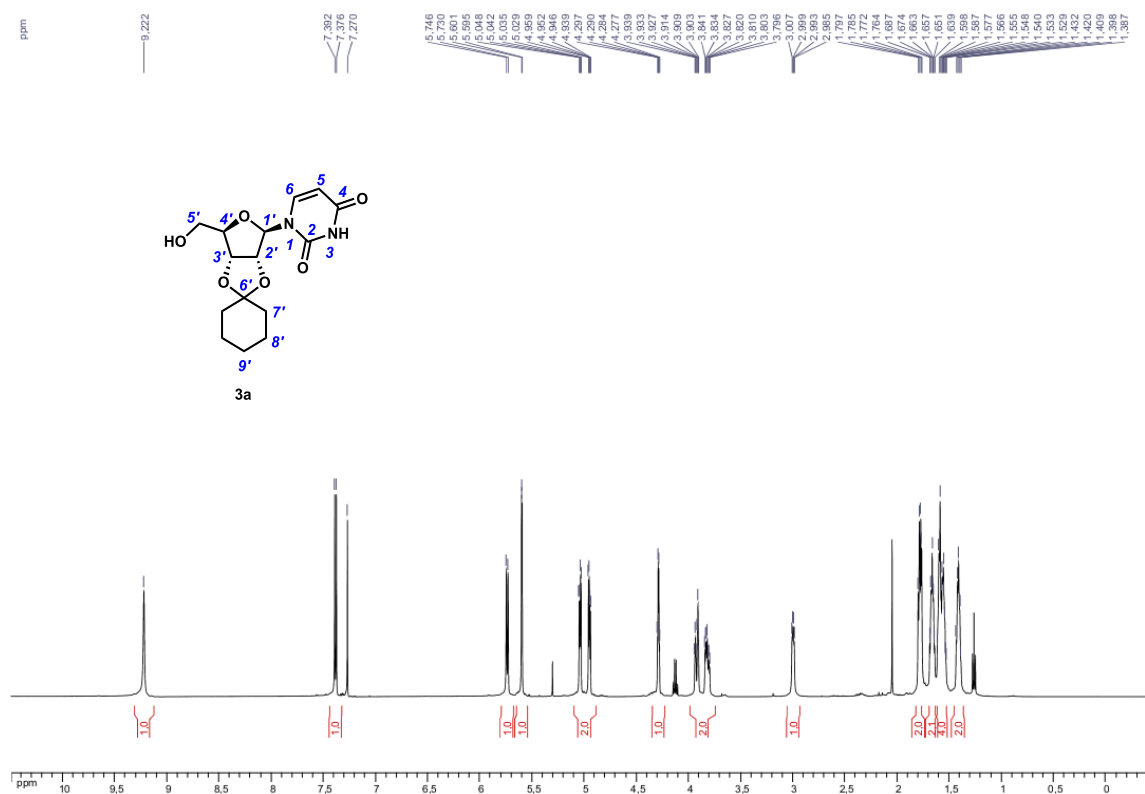
¹H NMR, compound 2a



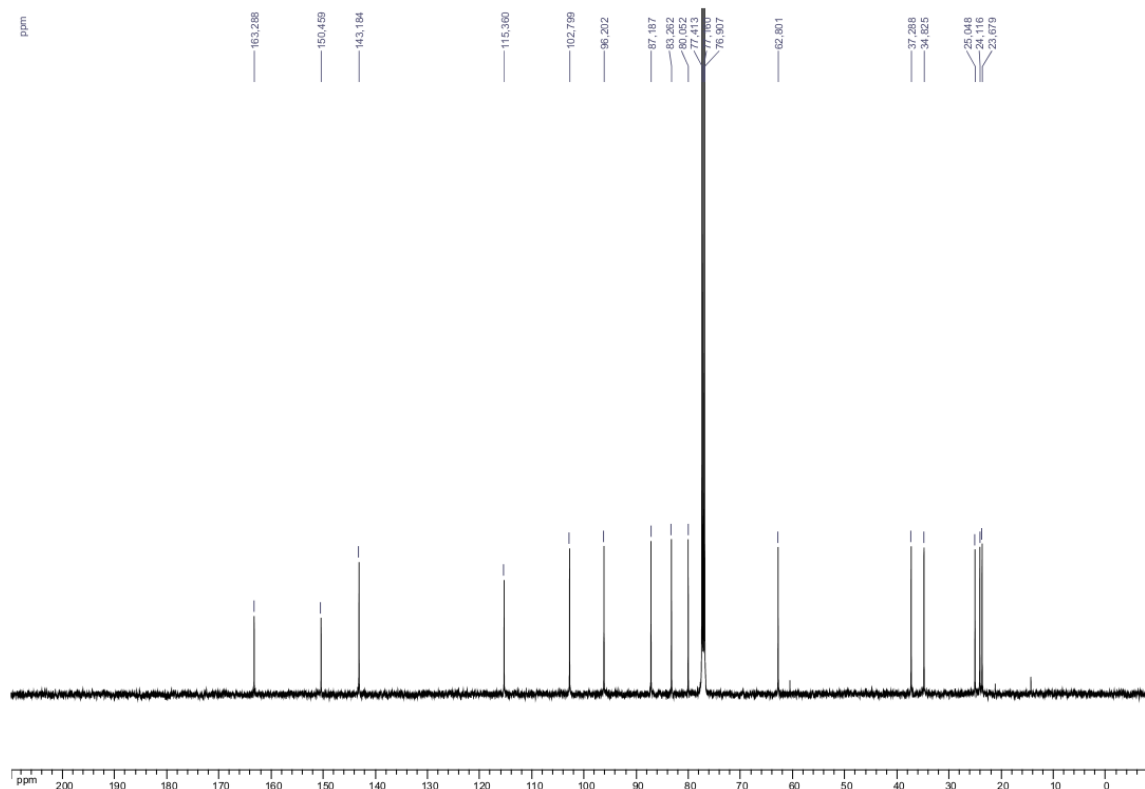
¹³C NMR

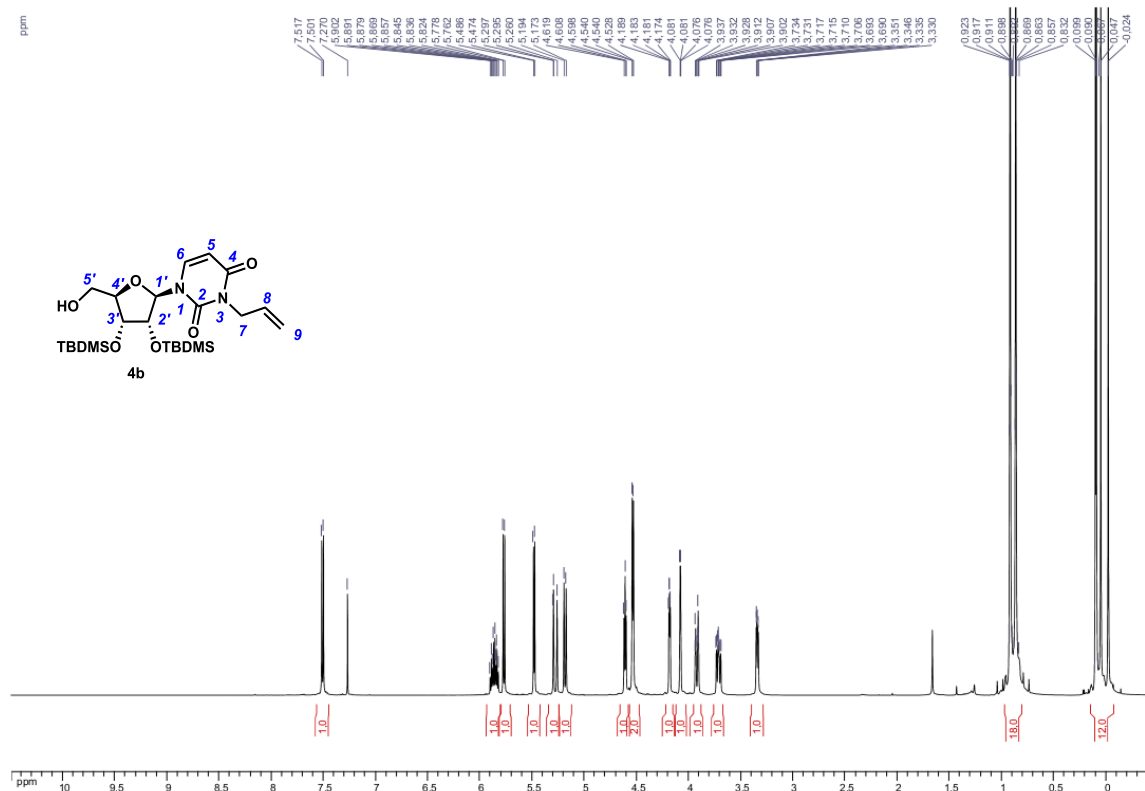
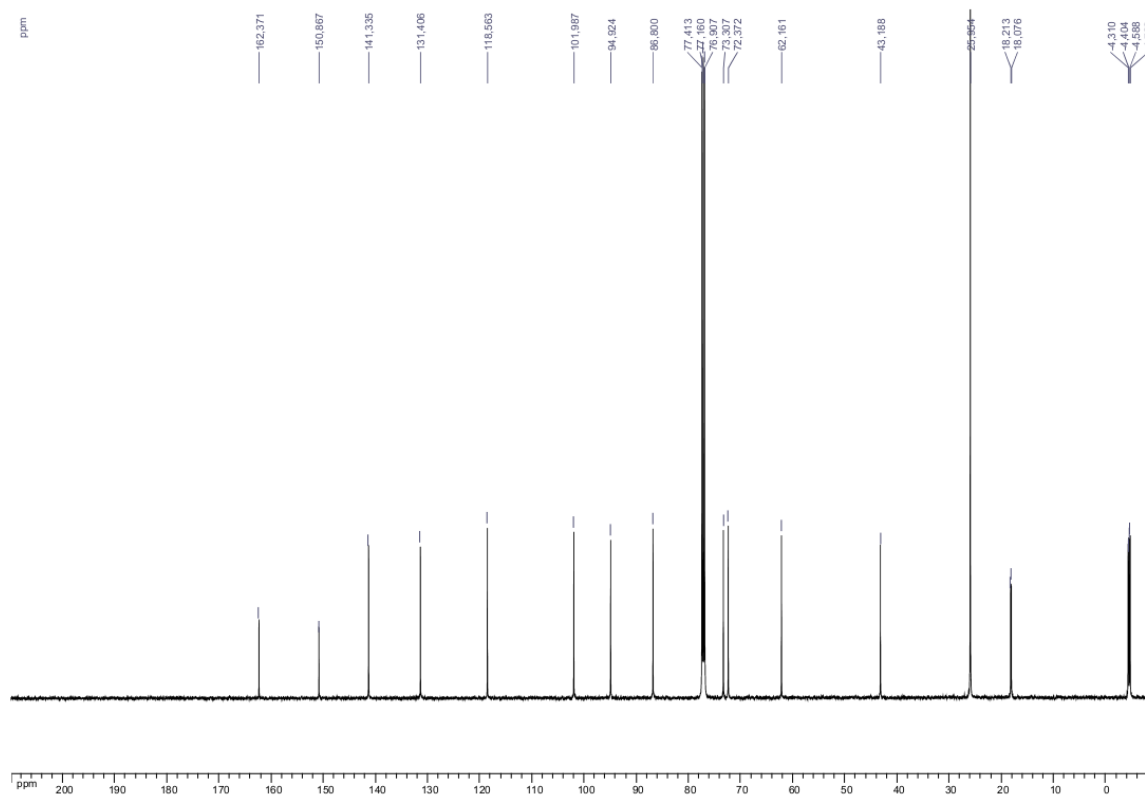


¹H NMR, compound **3a**

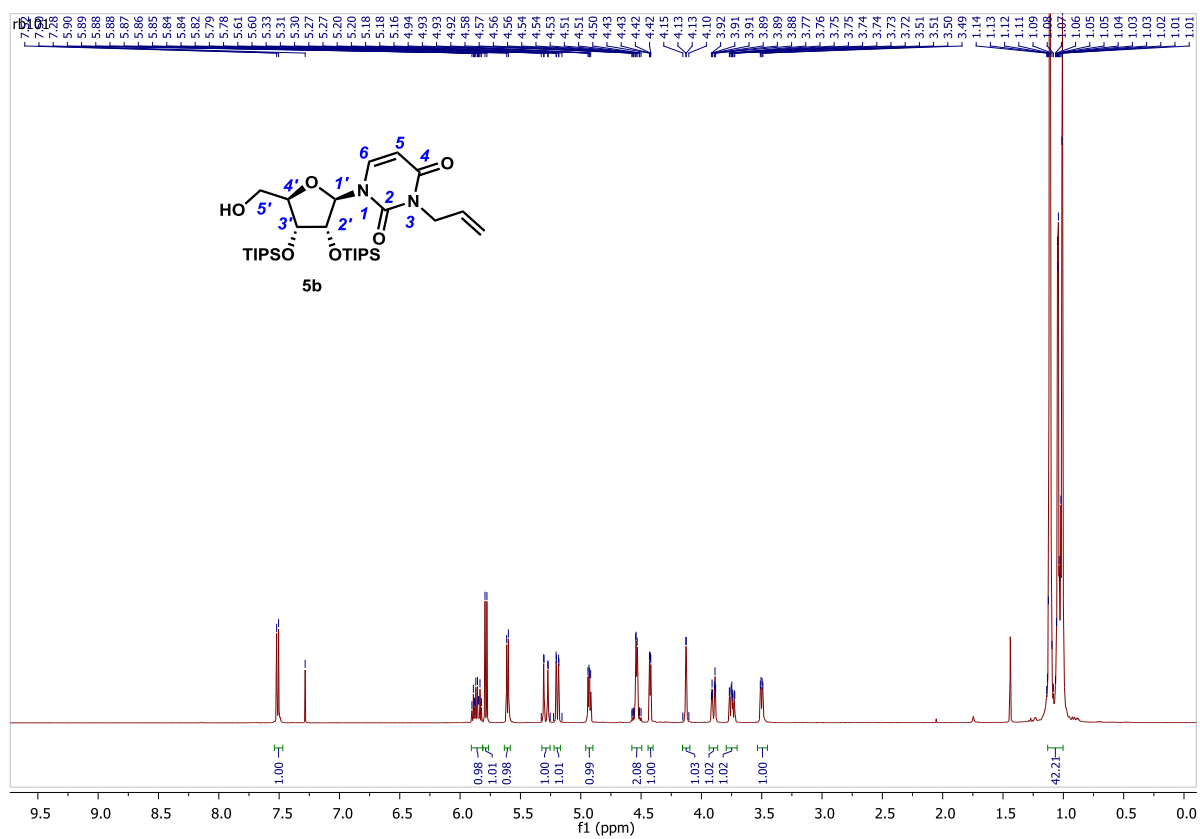


¹³C NMR

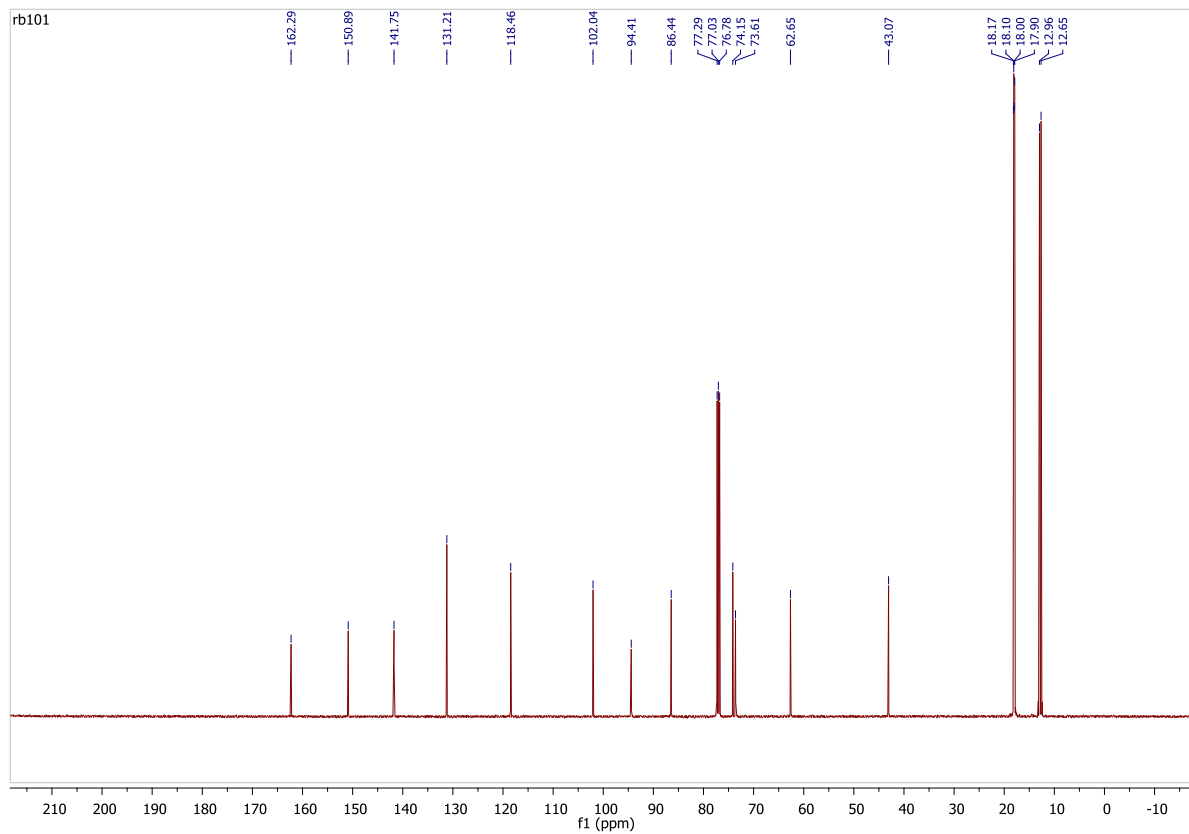


¹H NMR, compound **4b**¹³C NMR

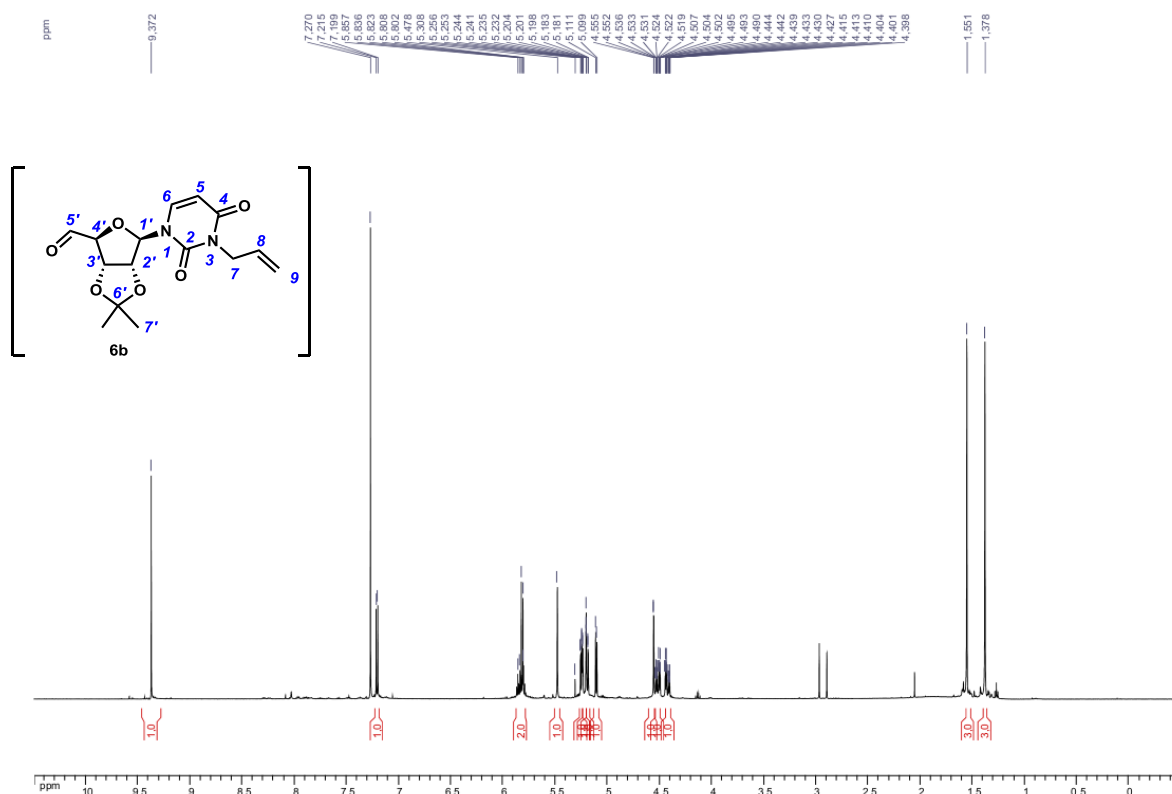
¹H NMR, compound **5b**



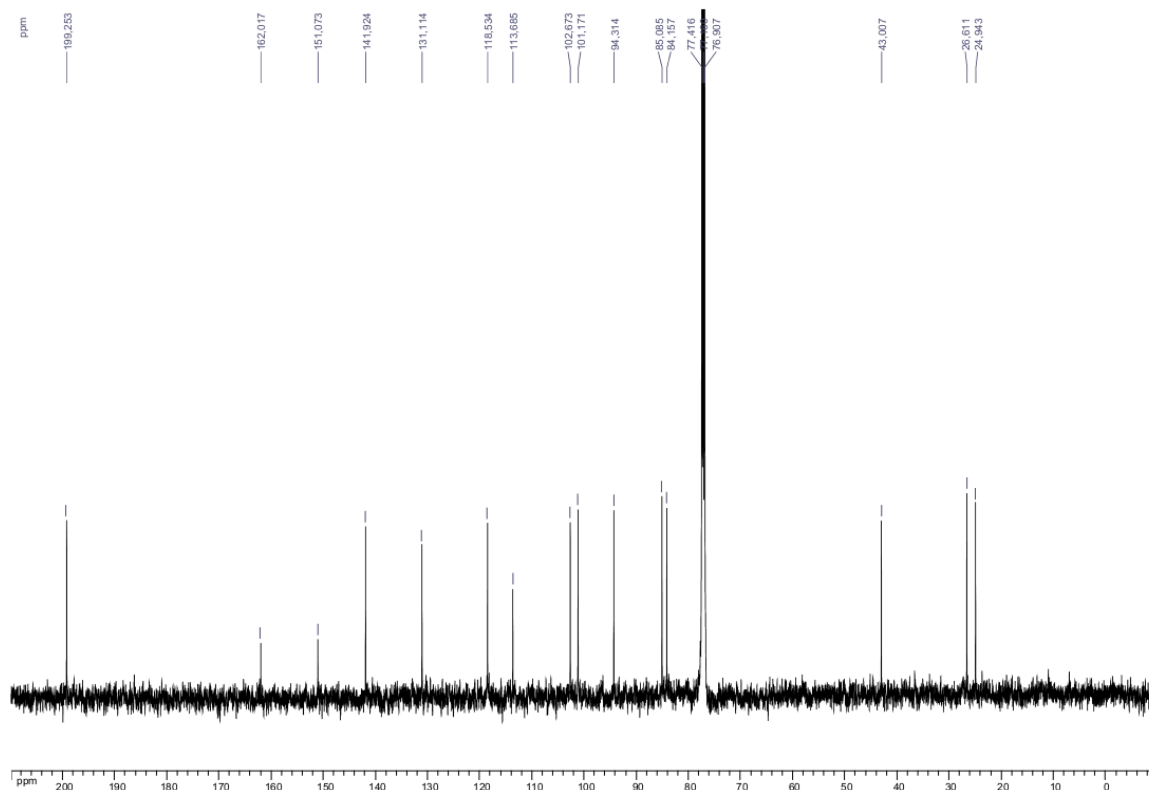
¹³C NMR

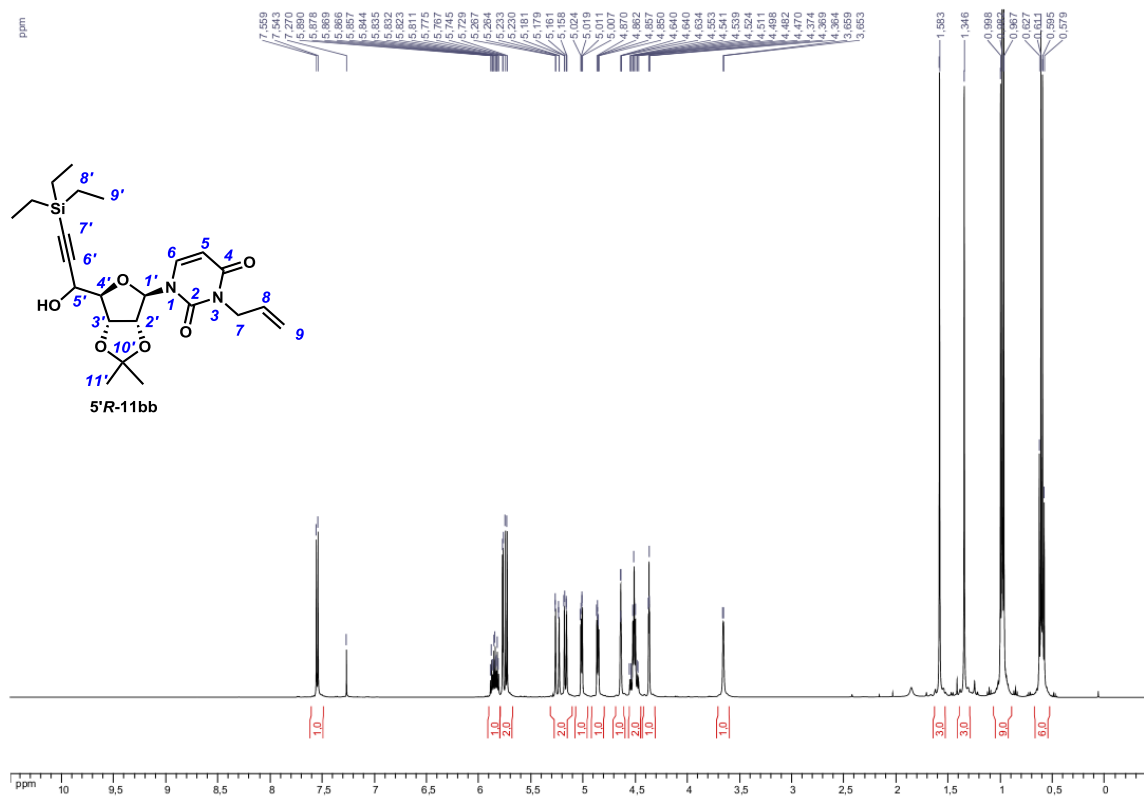
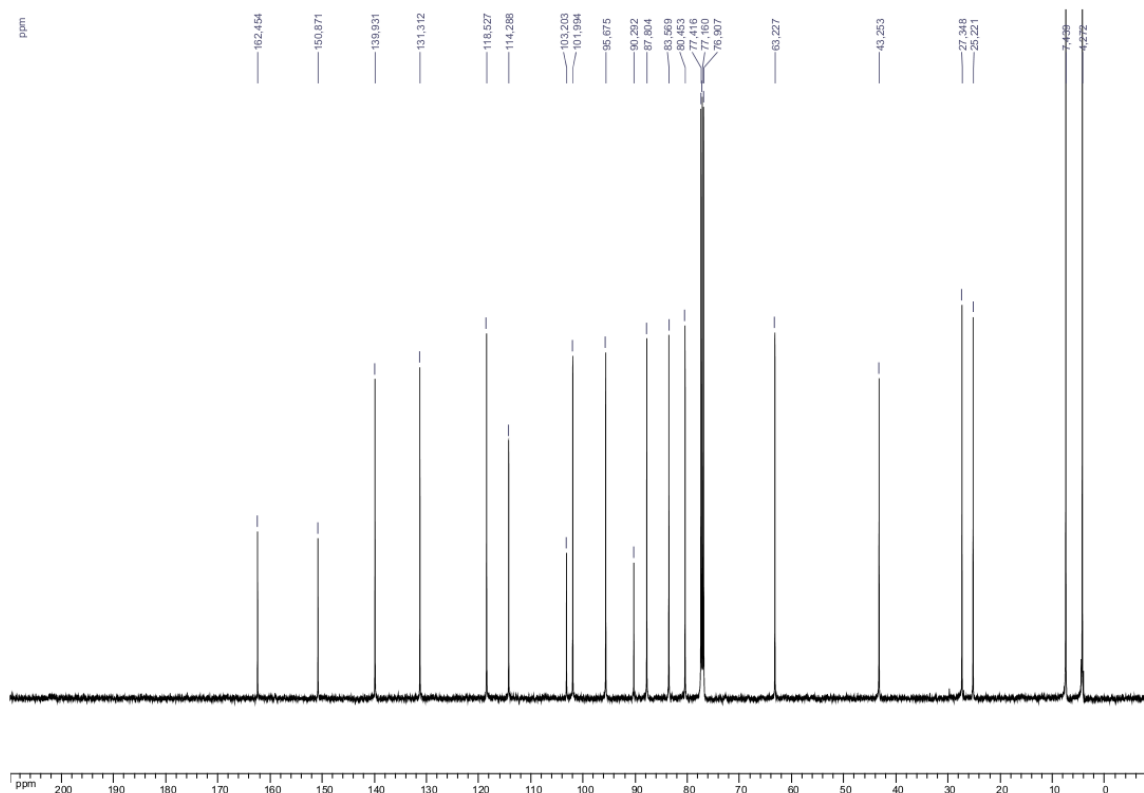


¹H NMR, compound **6b**

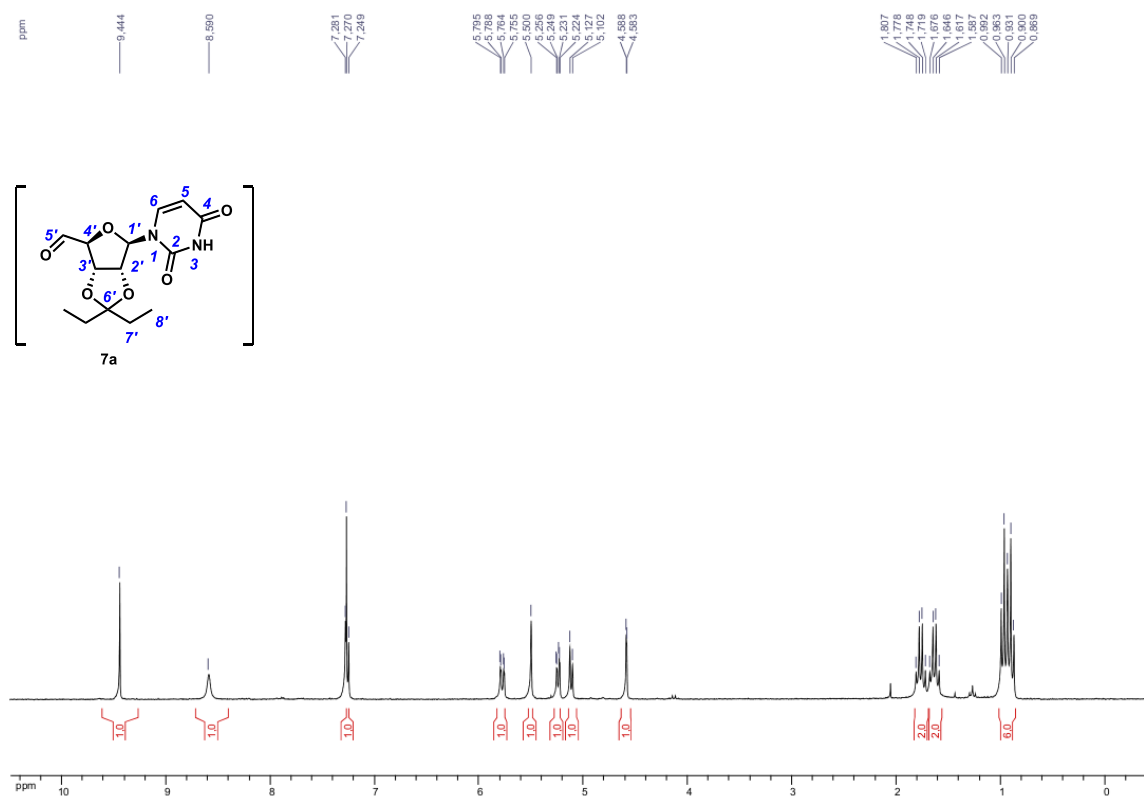


¹³C NMR

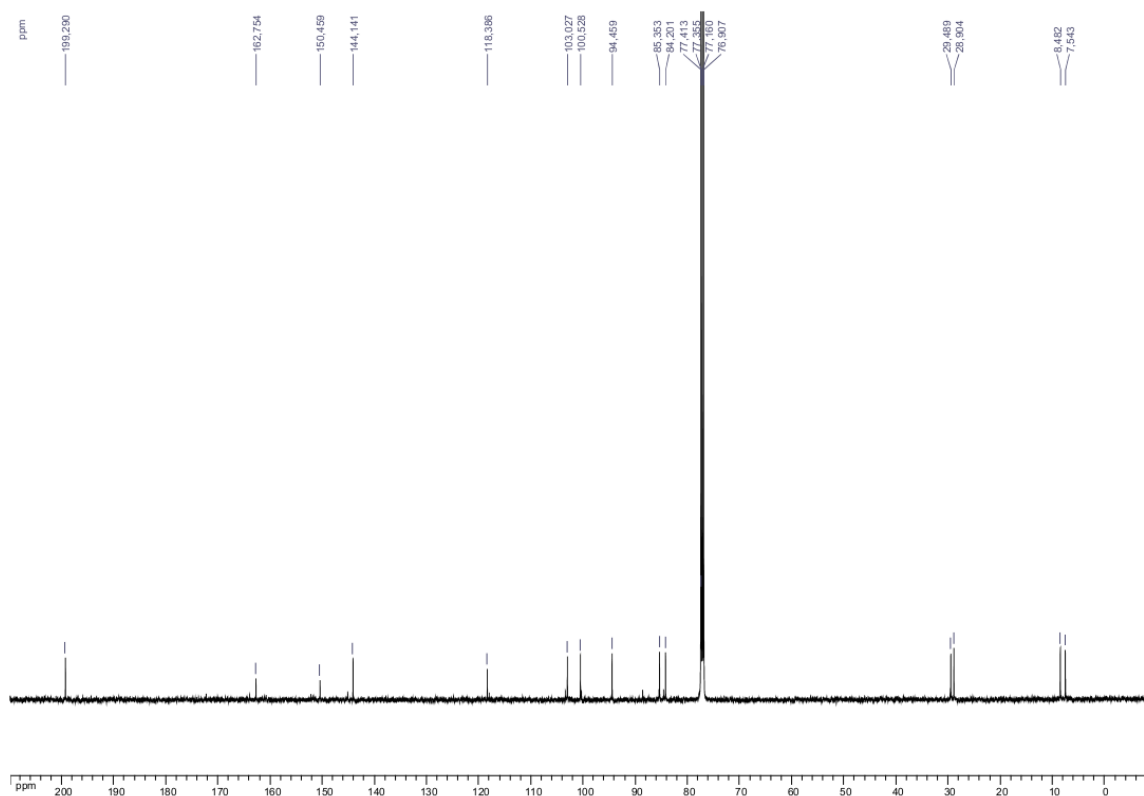


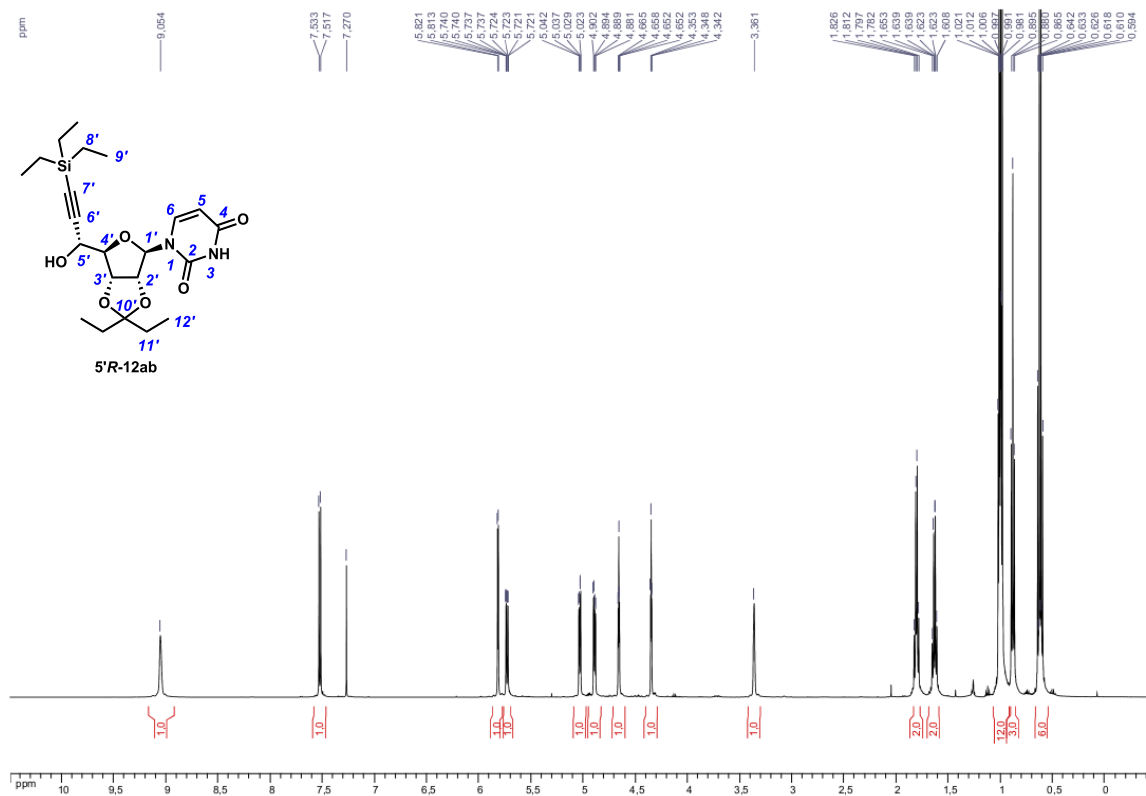
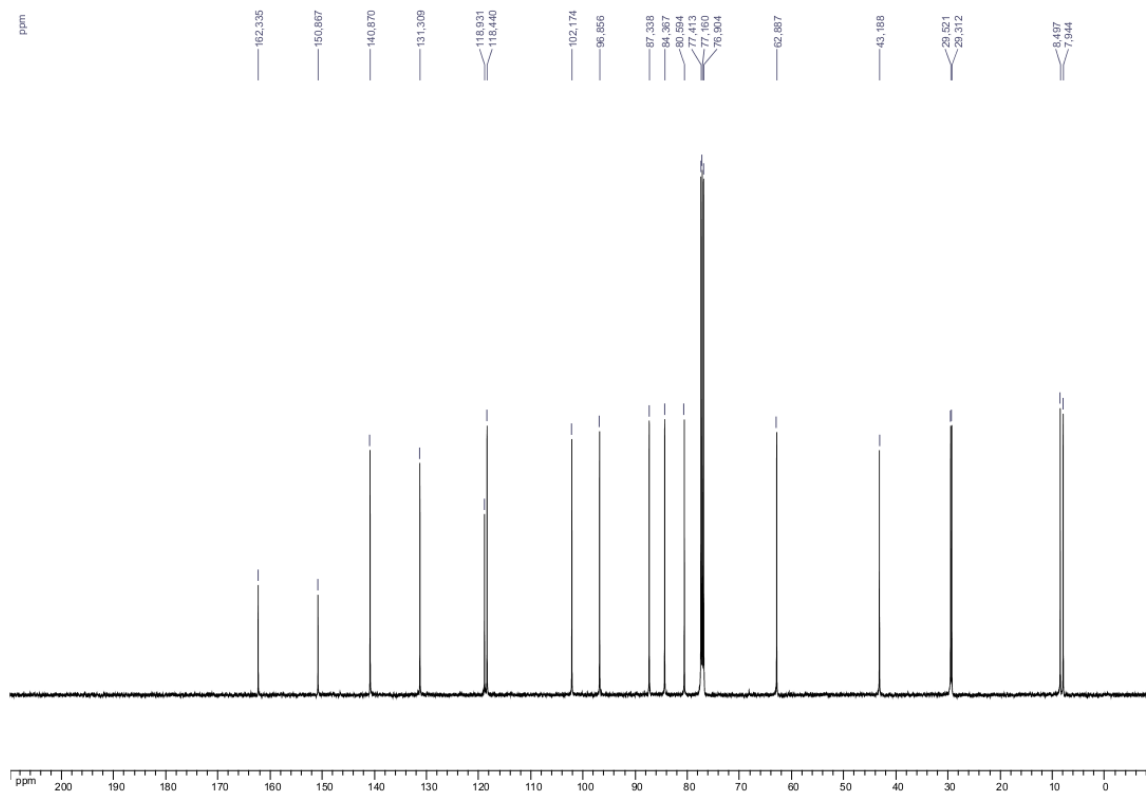
¹H NMR, compound (5'*R*)-11bb¹³C NMR

¹H NMR, compound 7a

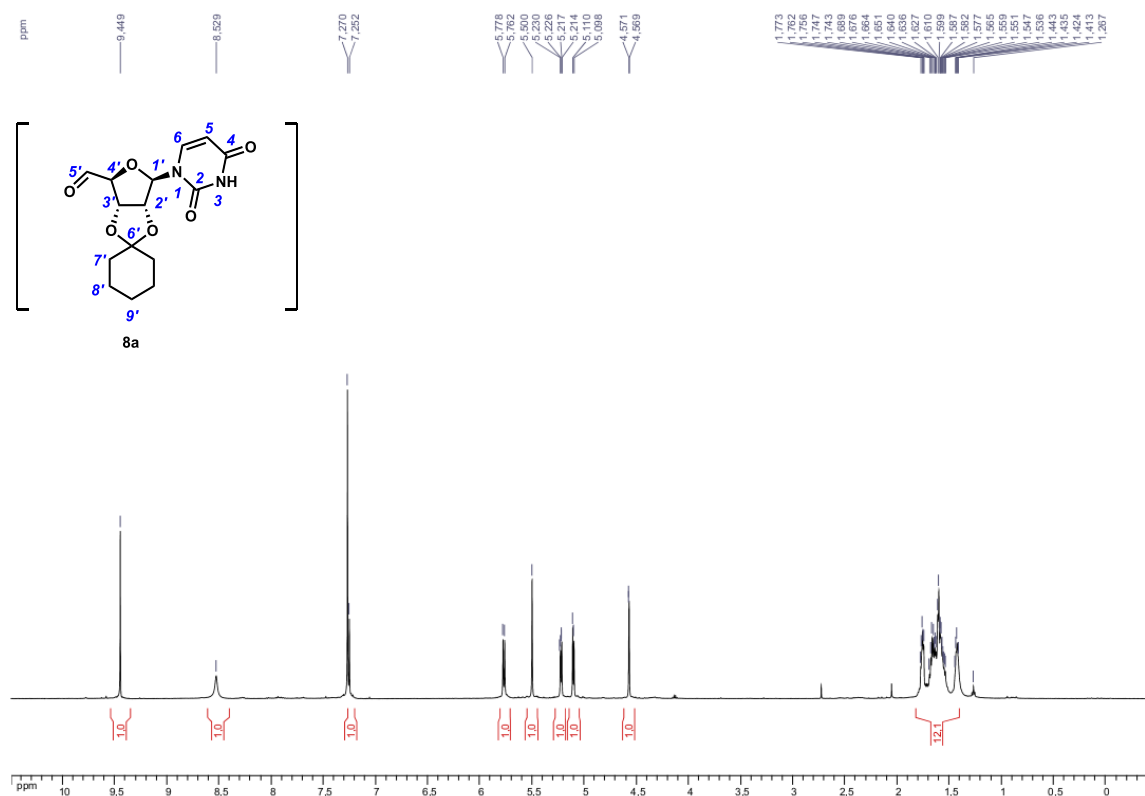


¹³C NMR

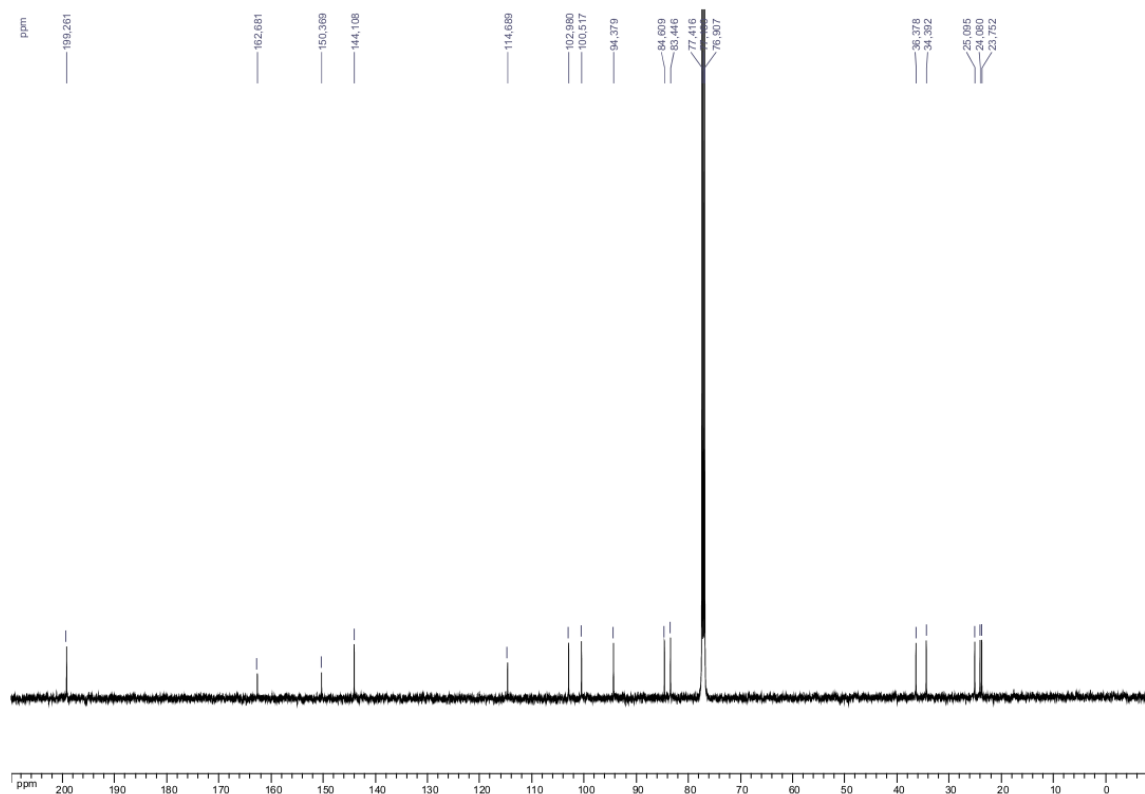


¹H NMR, compound **5'R-12ab**¹³C NMR

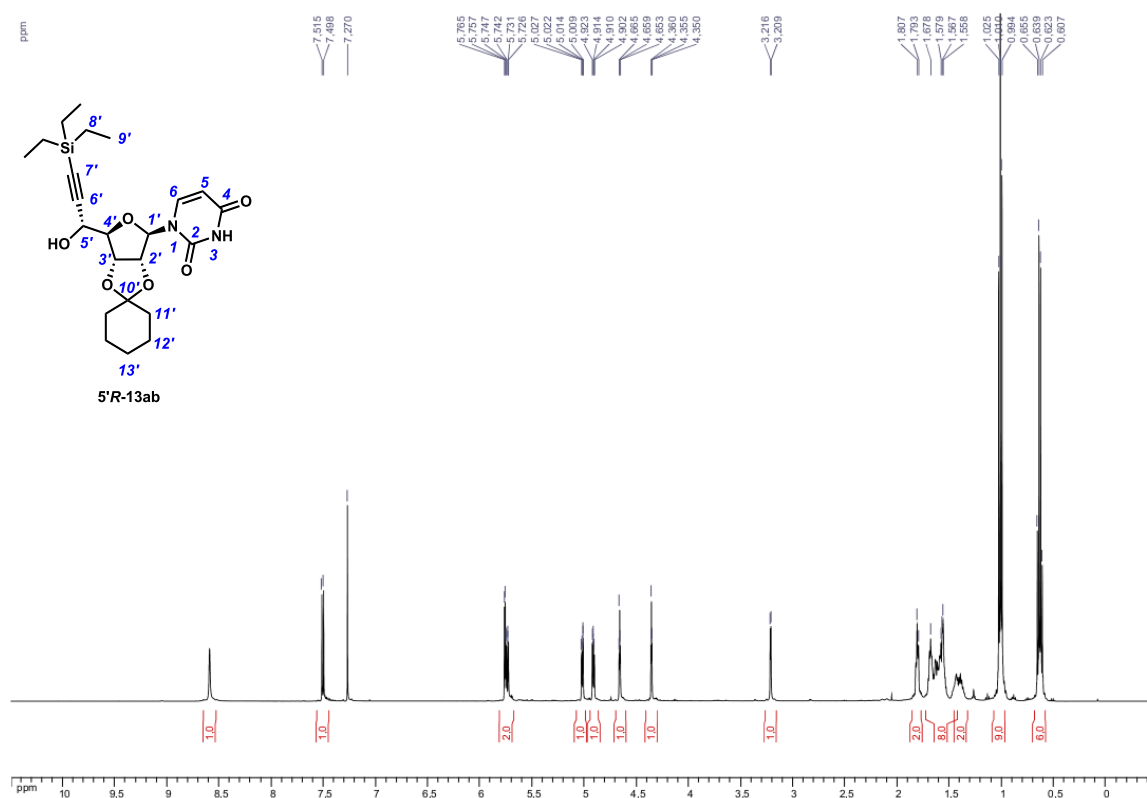
¹H NMR, compound **8a**



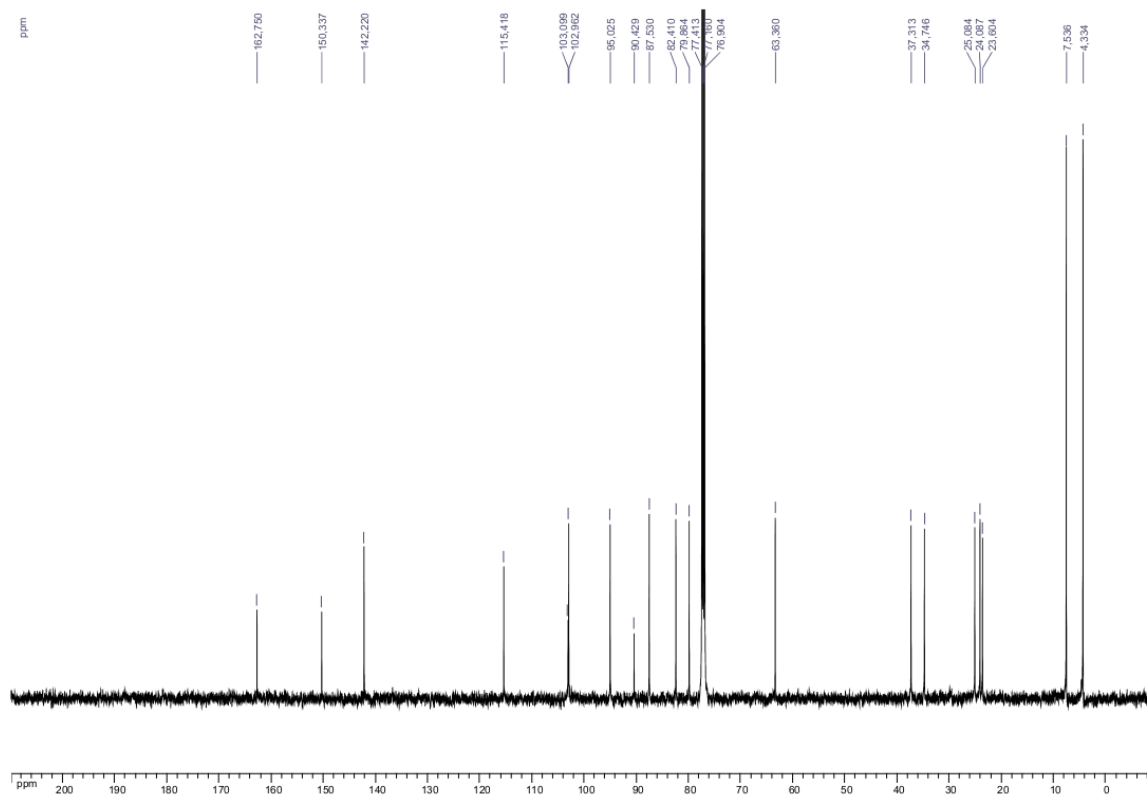
¹³C NMR

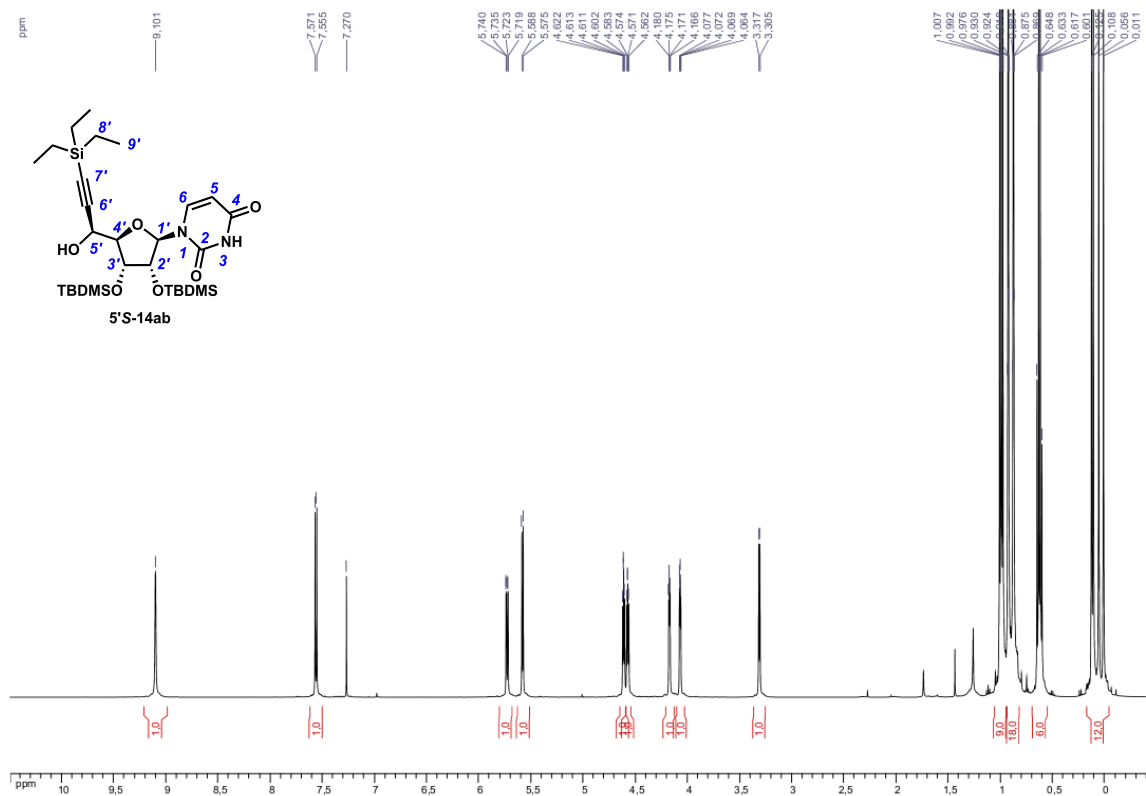
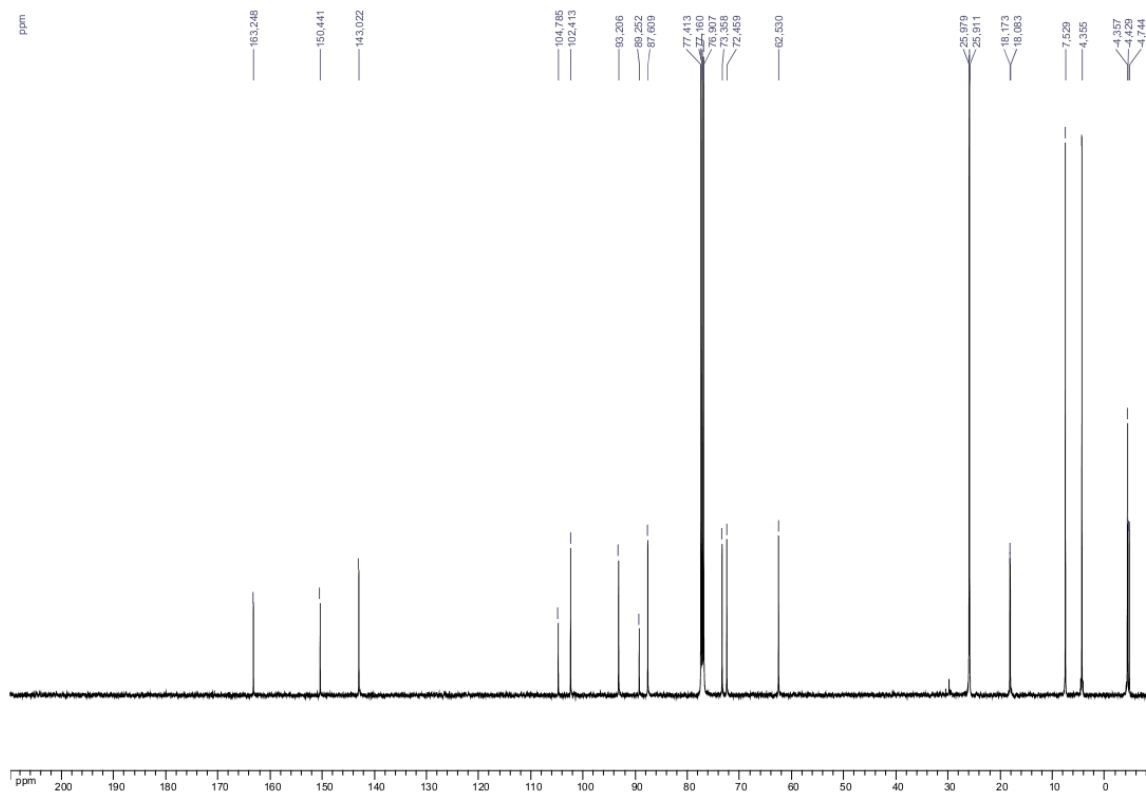


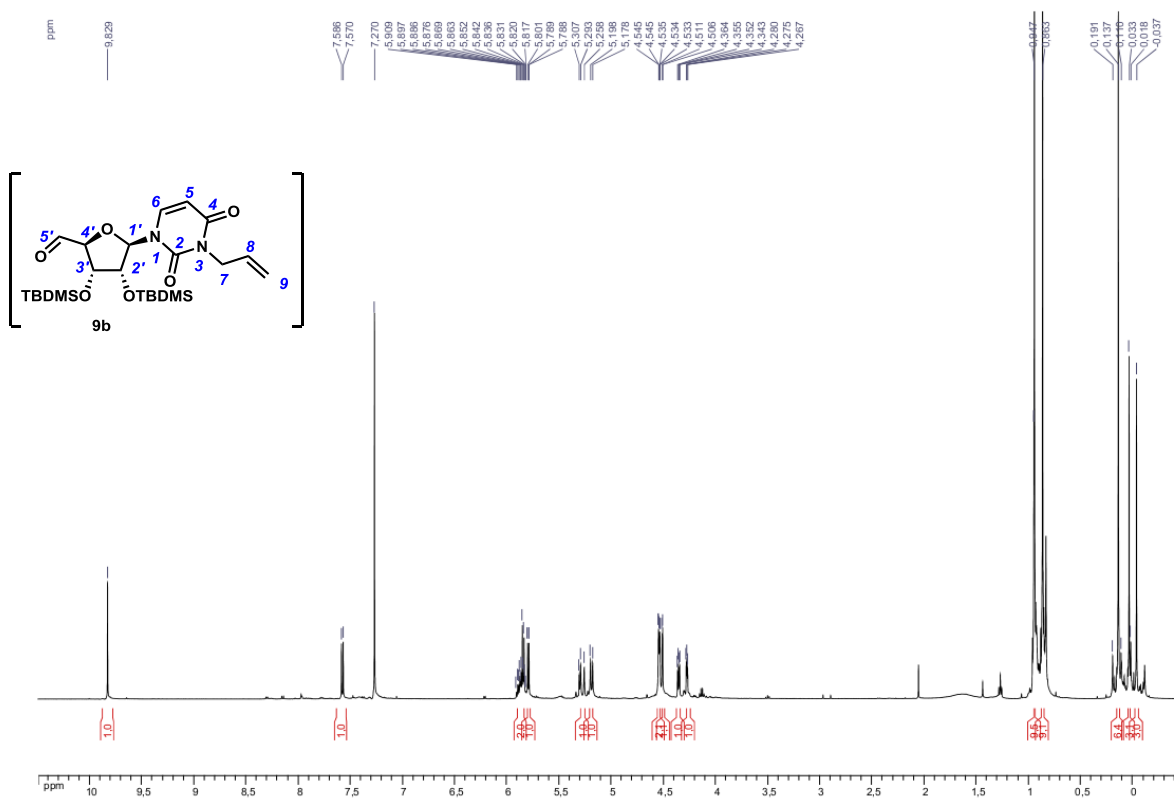
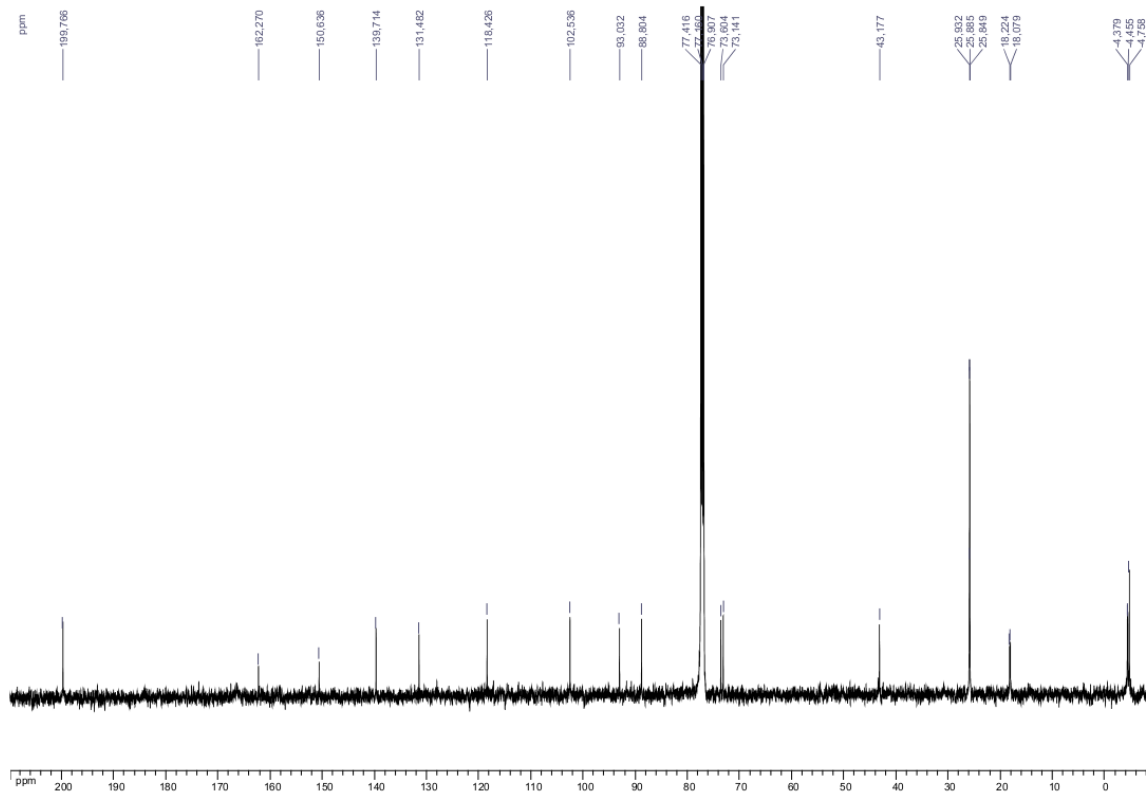
¹H NMR, compound **5'R-13ab**



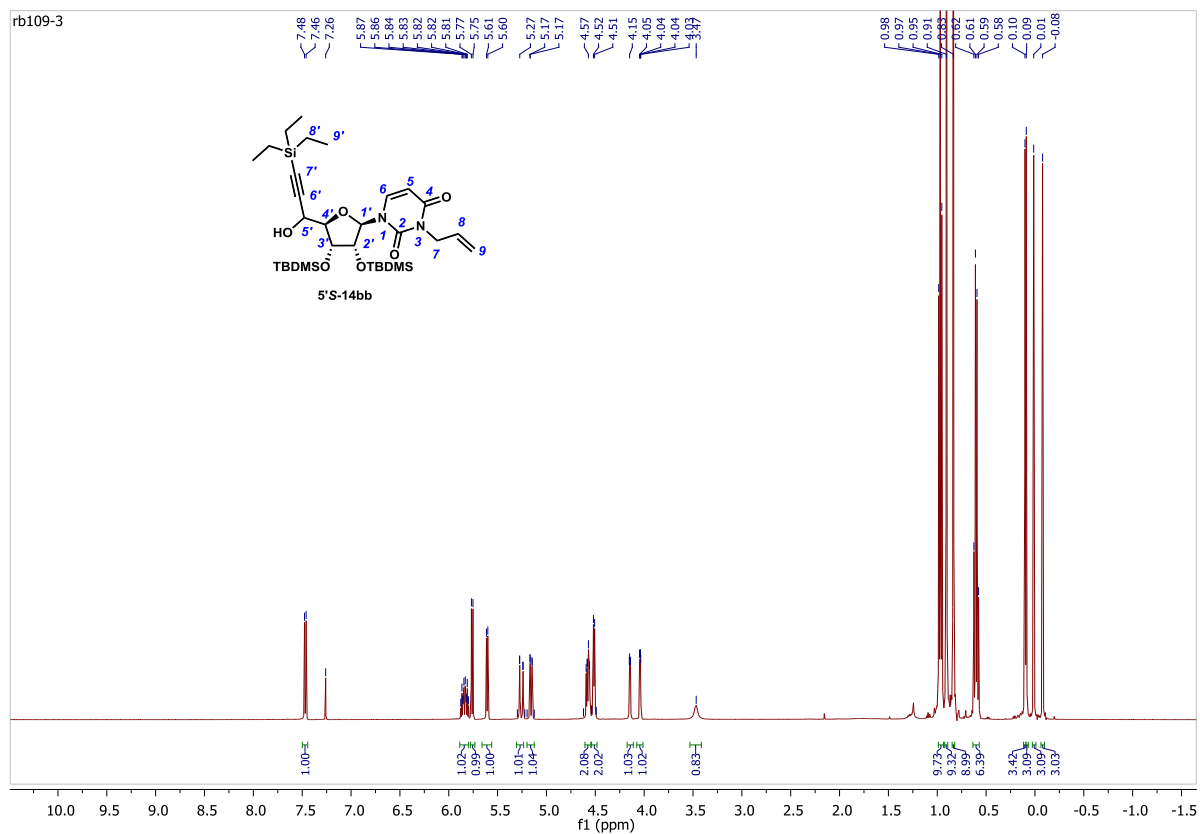
¹³C NMR



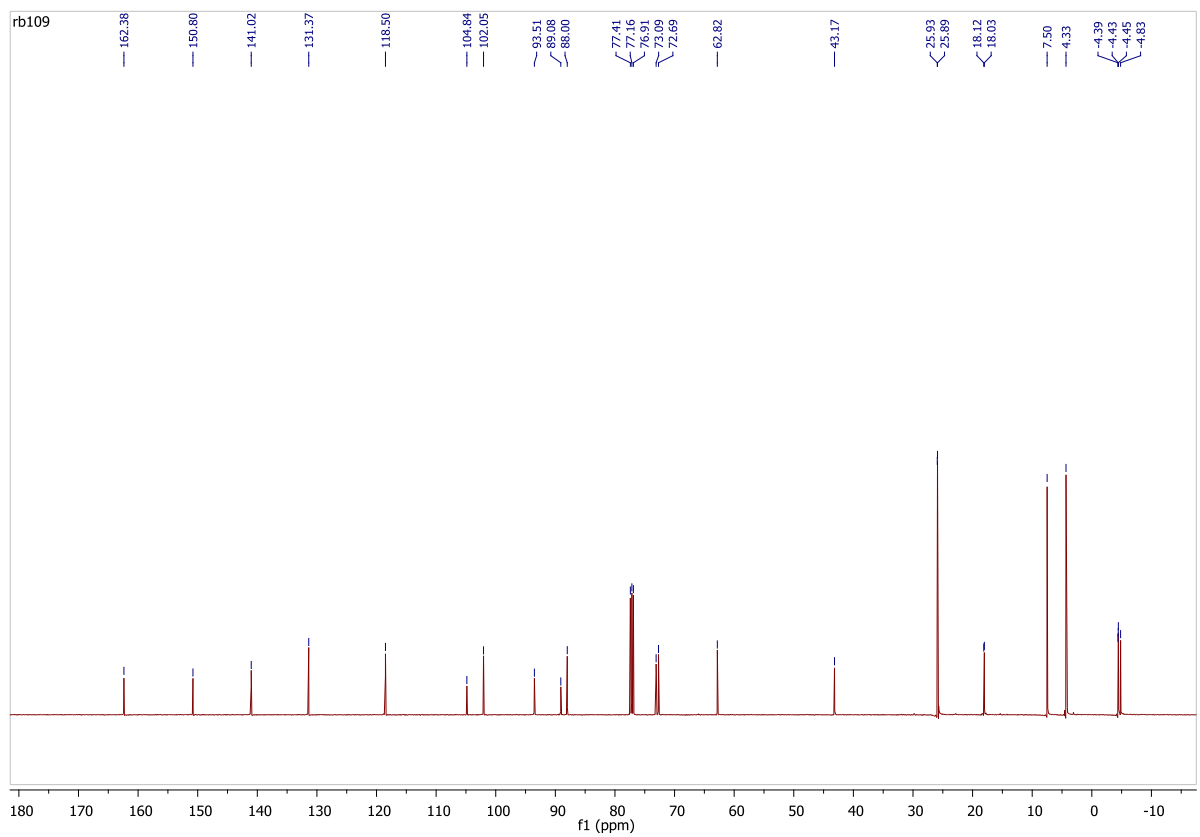
¹H NMR, compound **5'S-14ab**¹³C NMR

¹H NMR, compound **9b**¹³C NMR

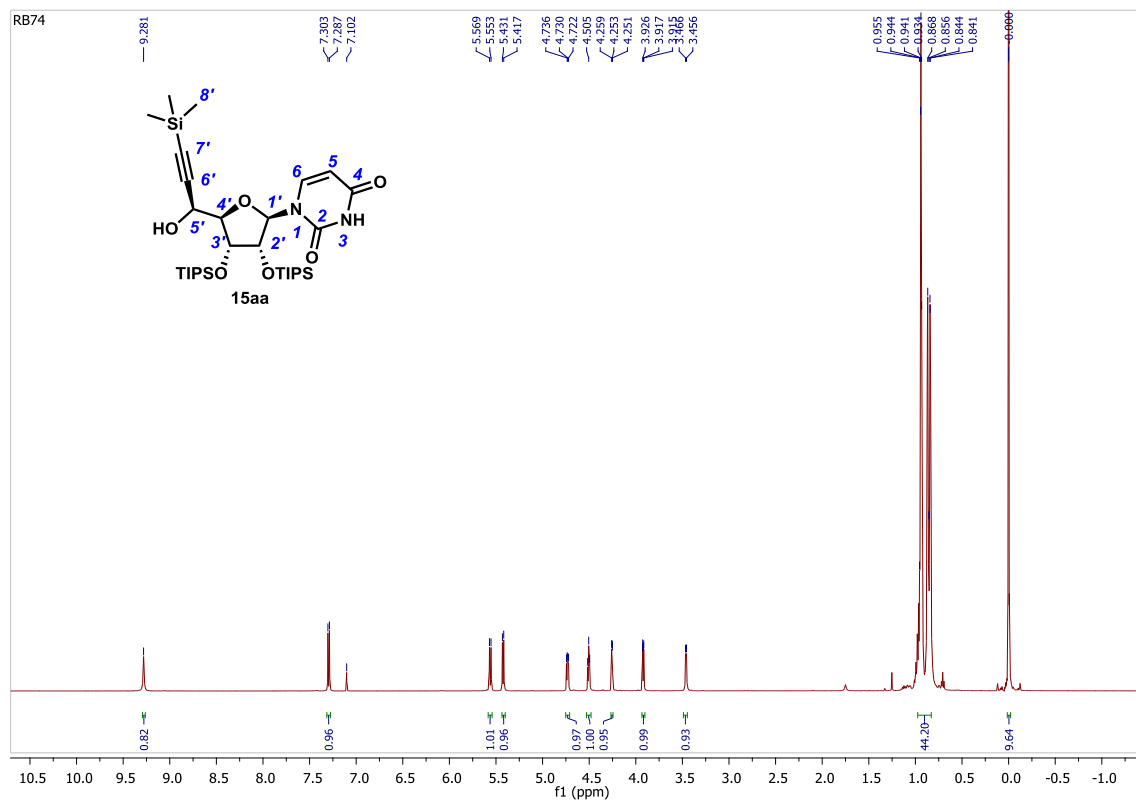
¹H NMR, compound **5'S-14bb**



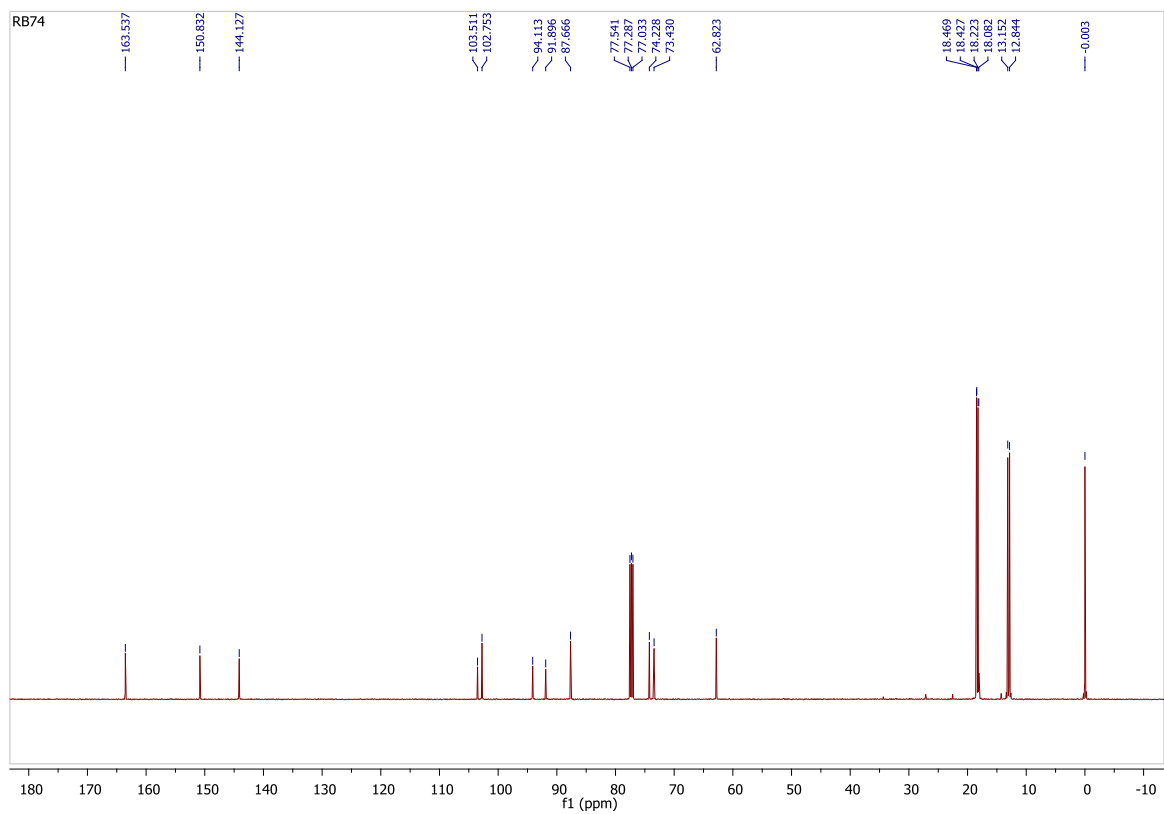
¹³C NMR



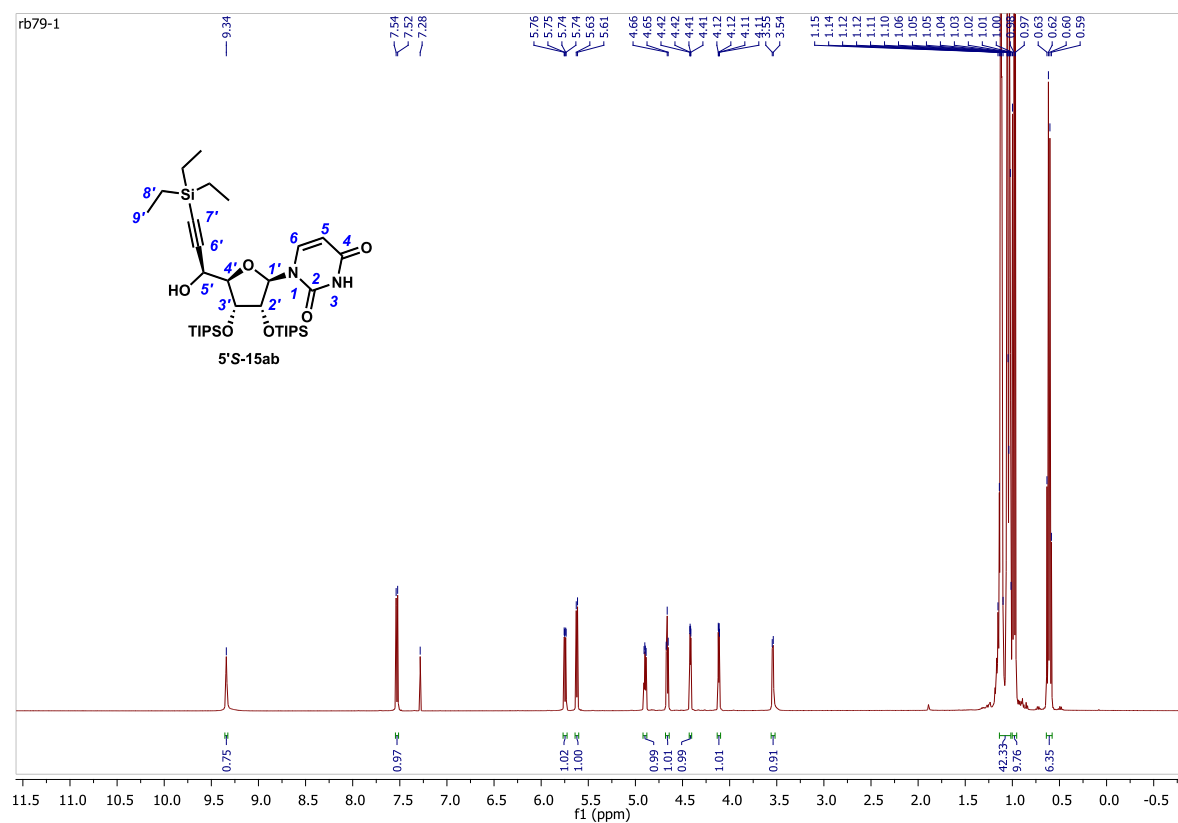
¹H NMR, compound **5'S-15aa**



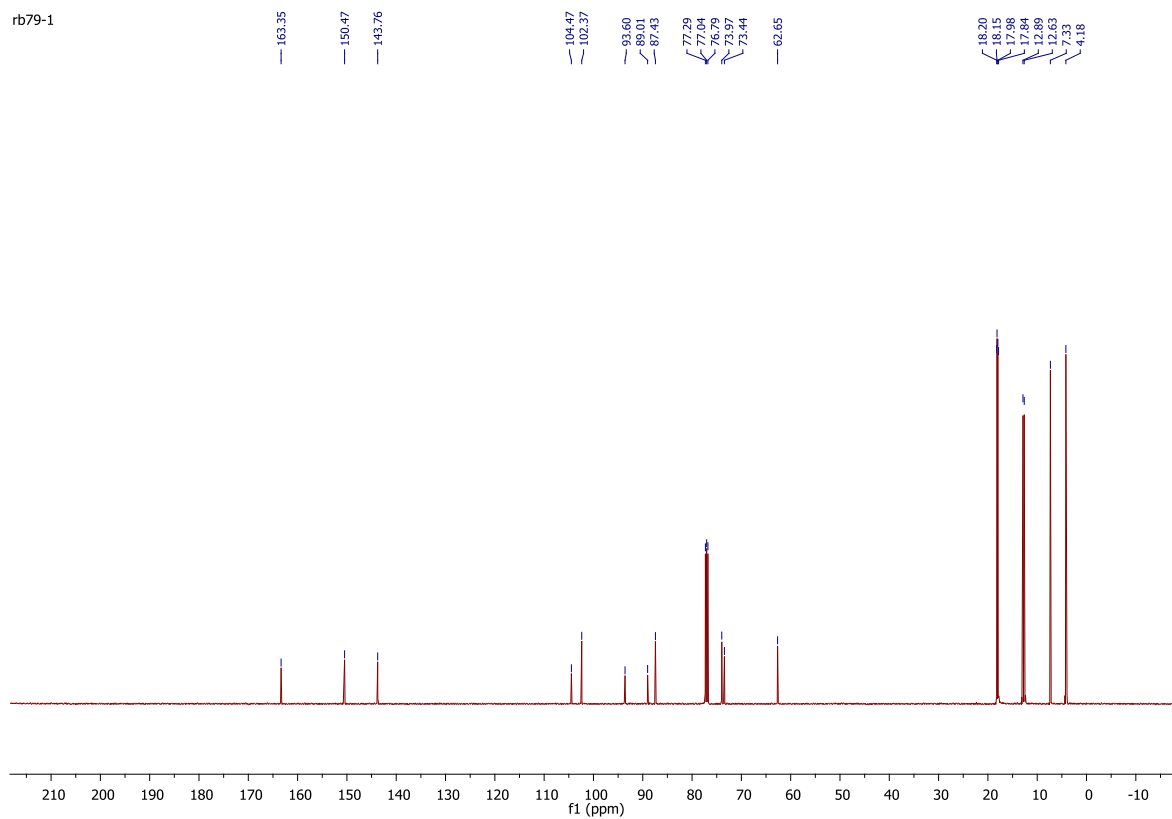
¹³C NMR



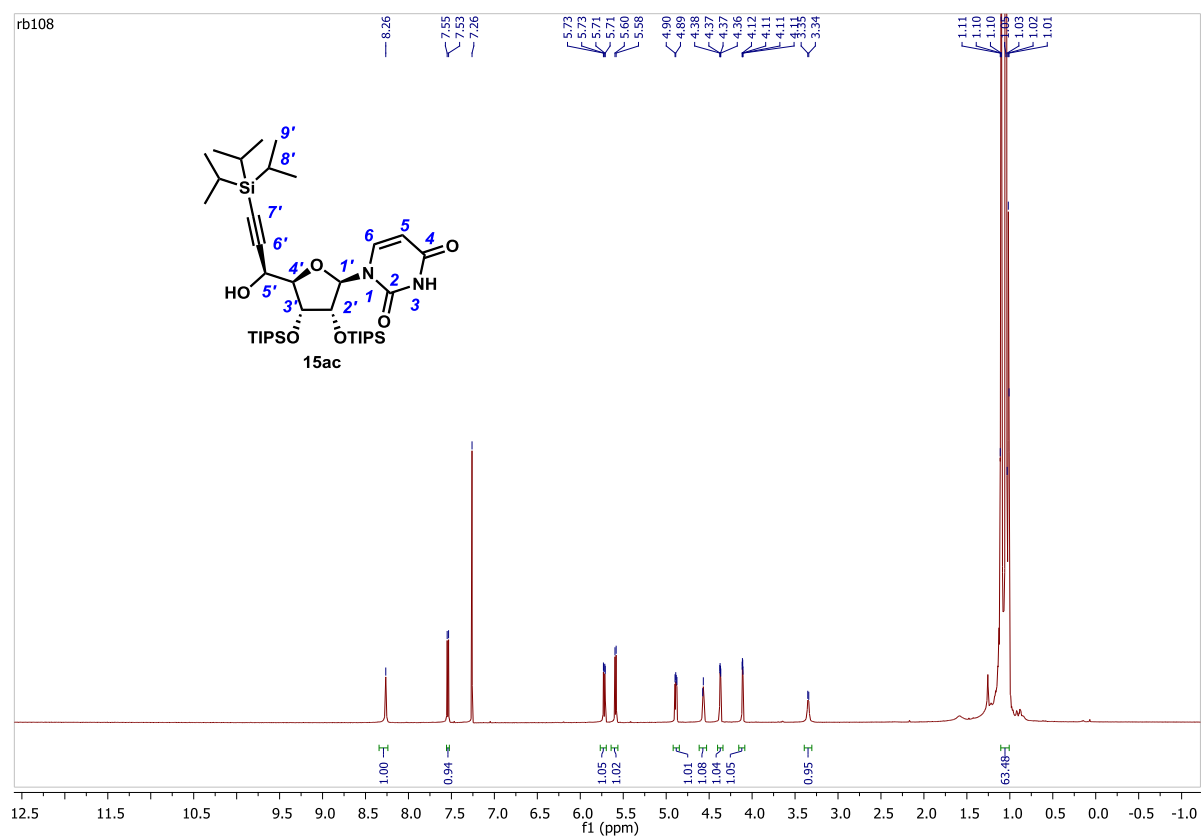
¹H NMR, compound **5'S-15ab**



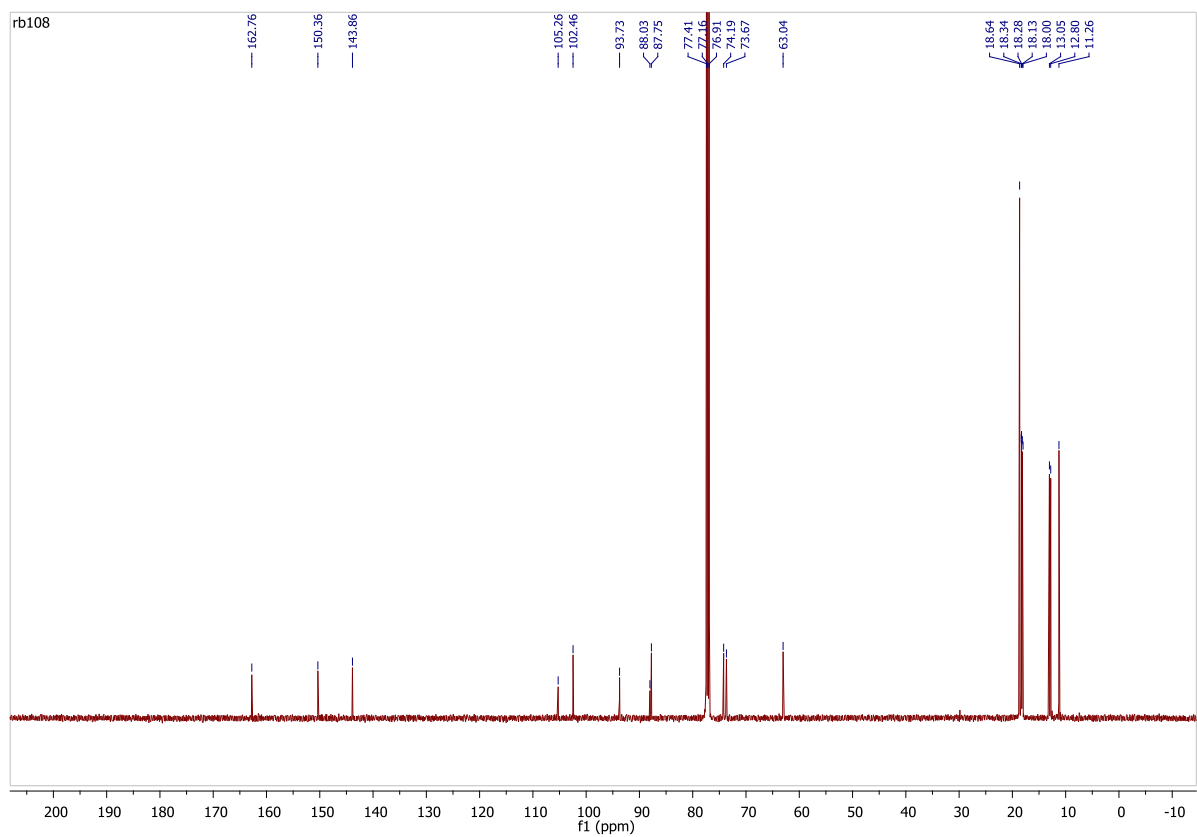
¹³C NMR



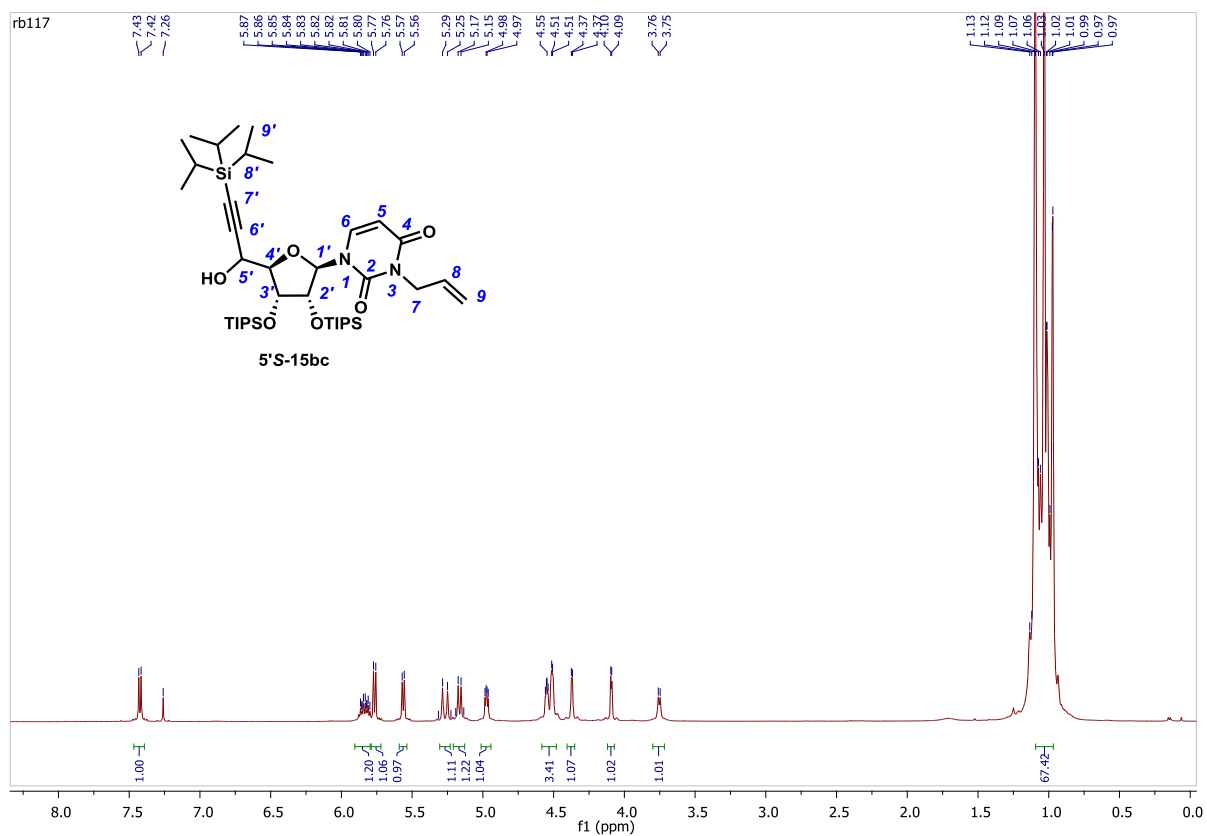
¹H NMR, compound **5'S-15ac**



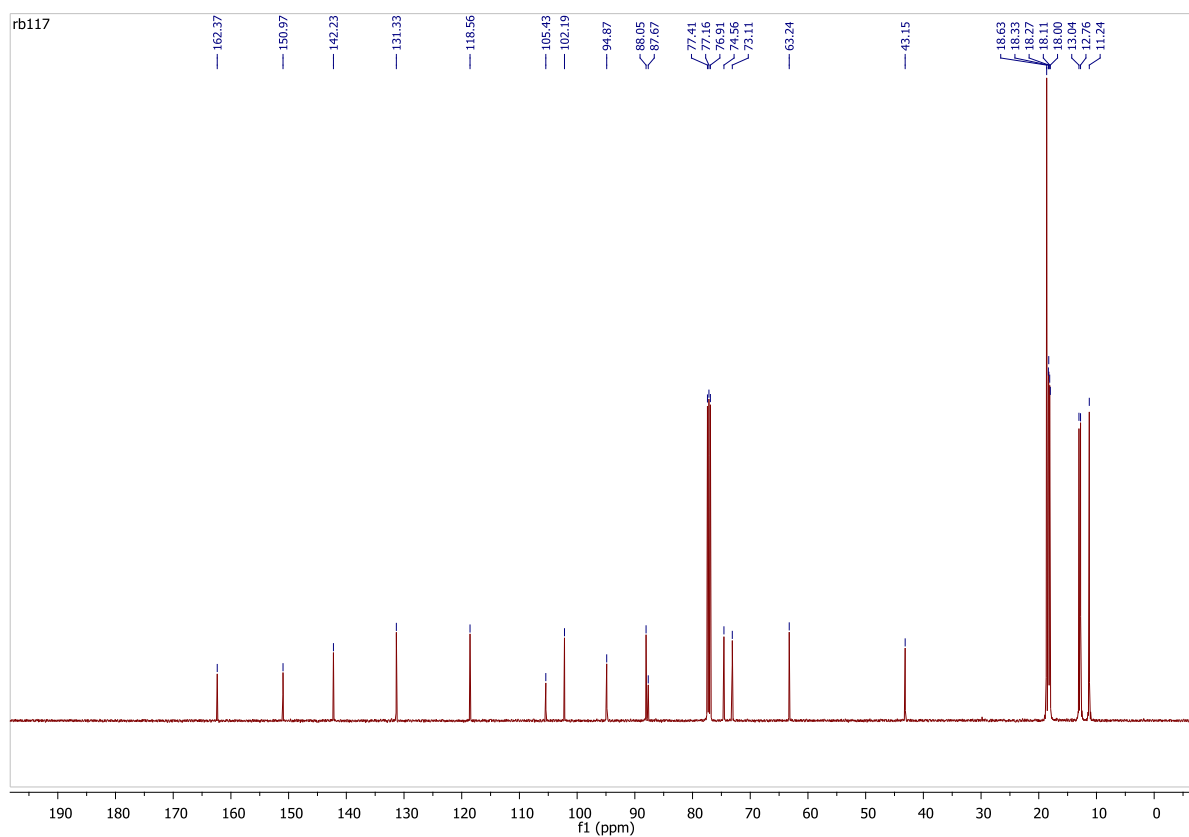
¹³C NMR



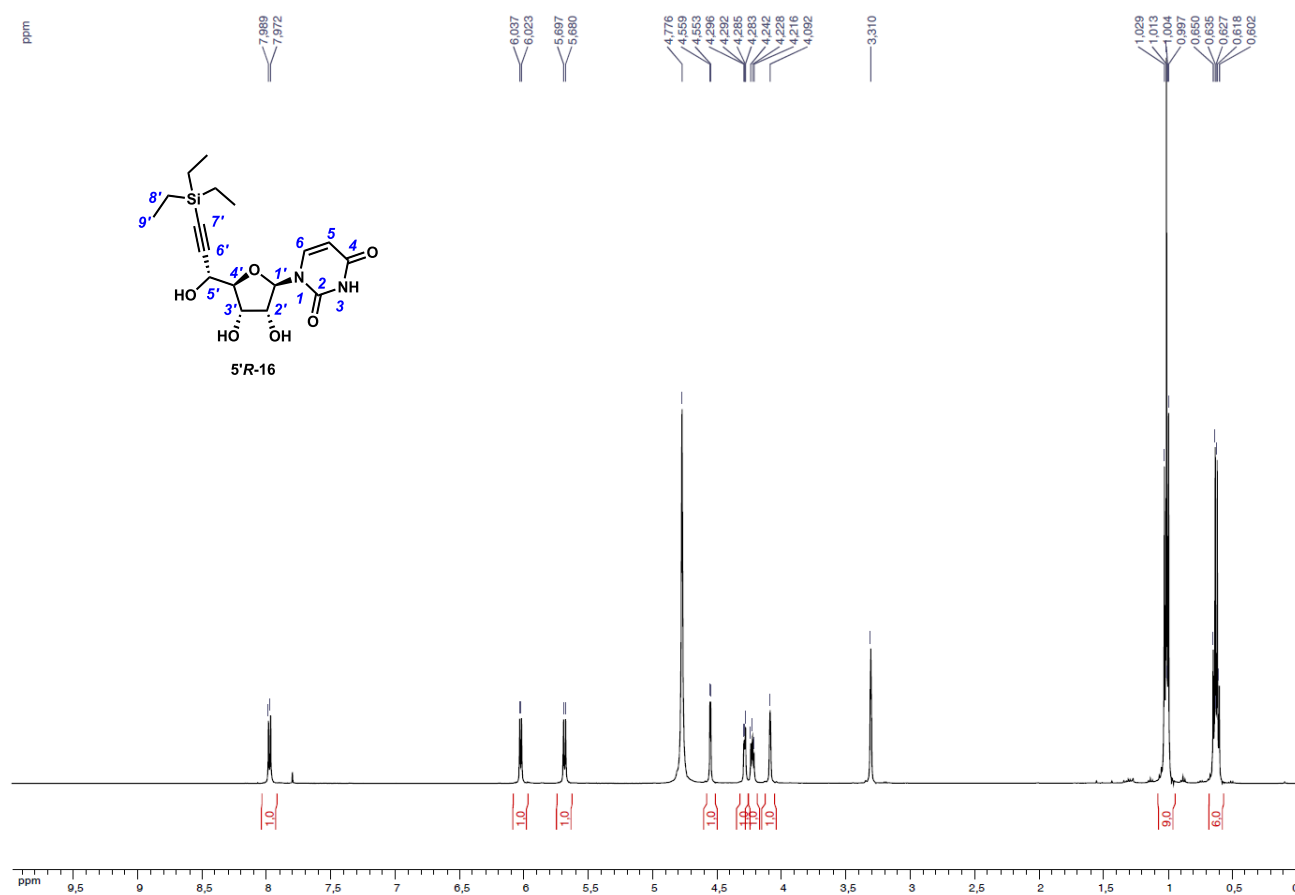
¹H NMR, compound **5'S-15bc**



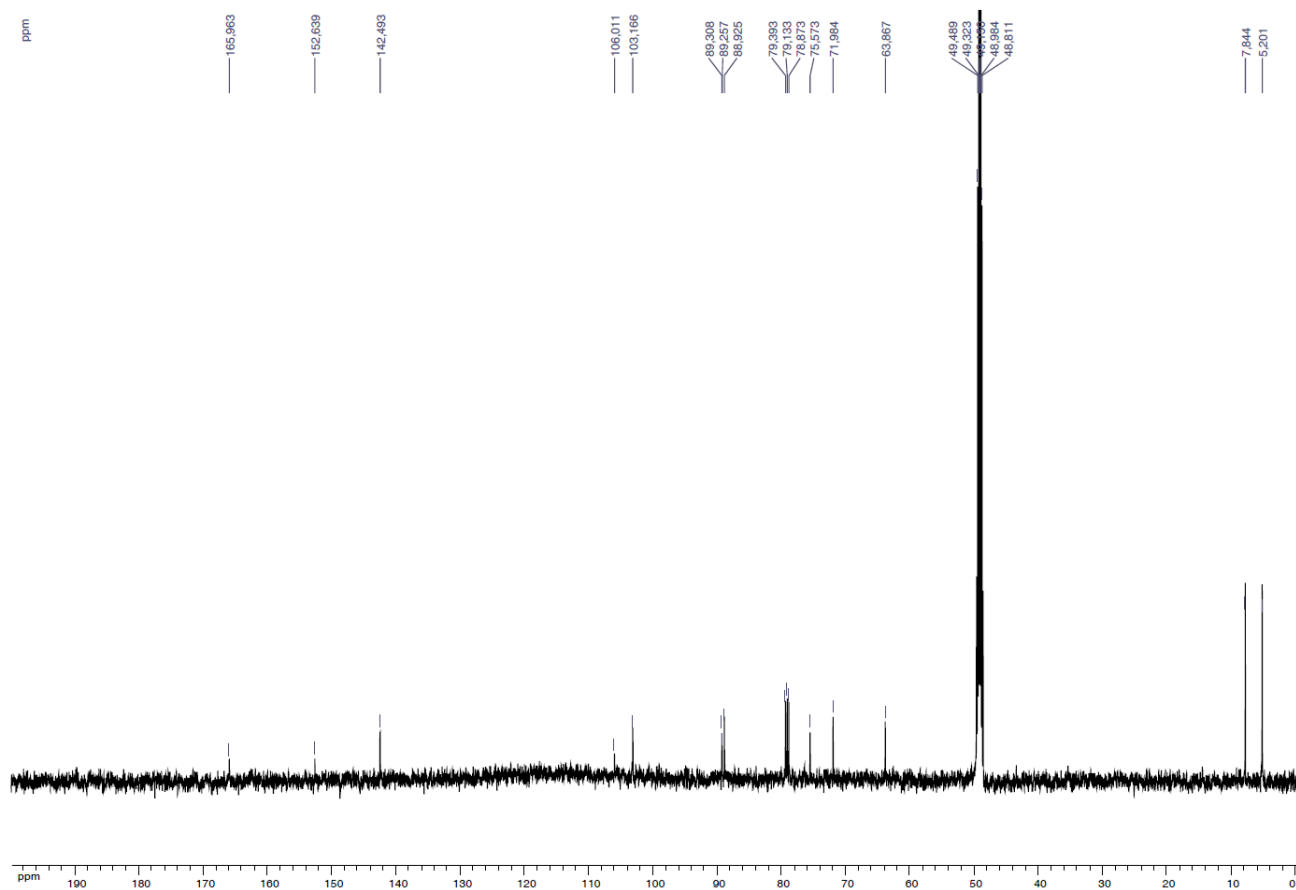
¹³C NMR



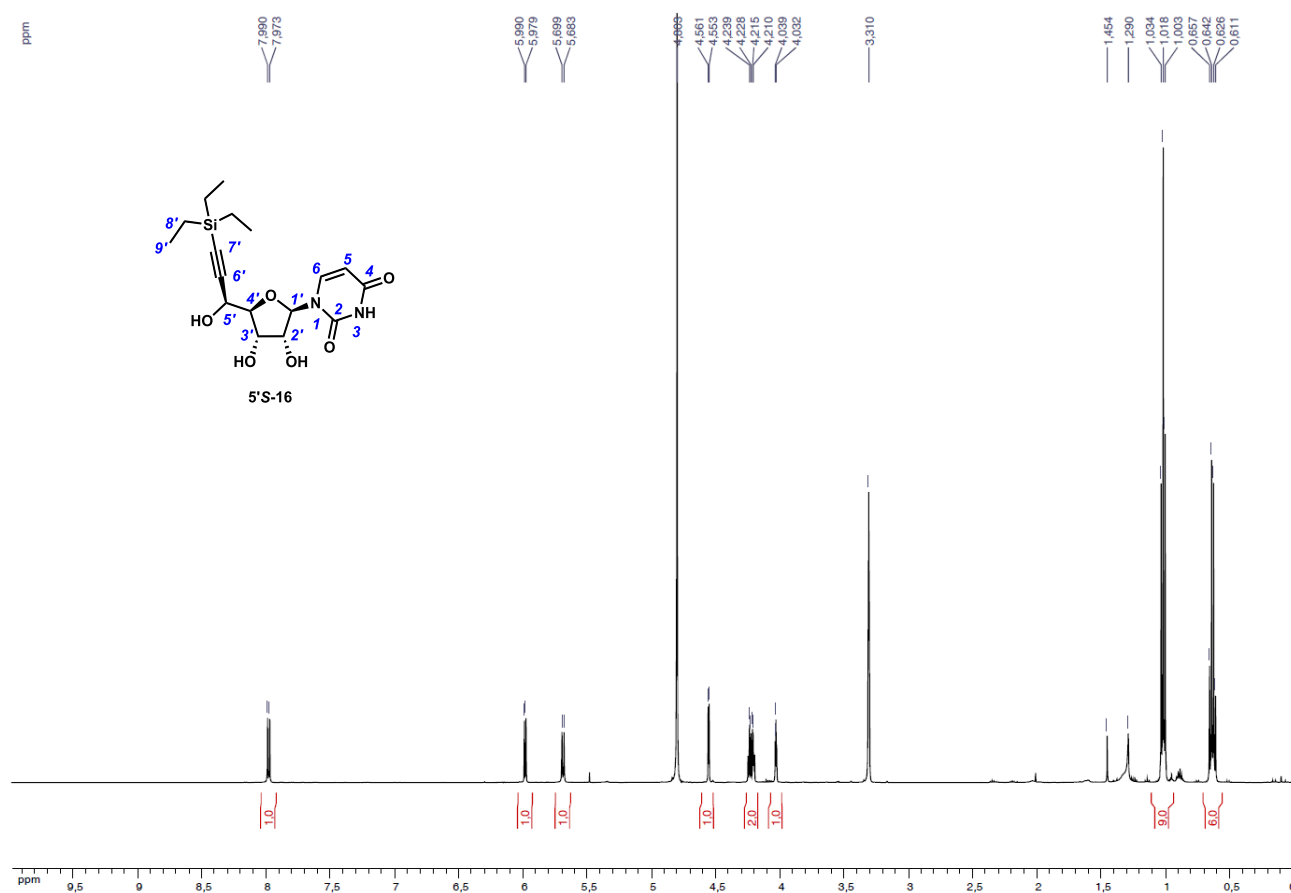
^1H NMR, 500 MHz (CD_3OD), compound **5'R-16**



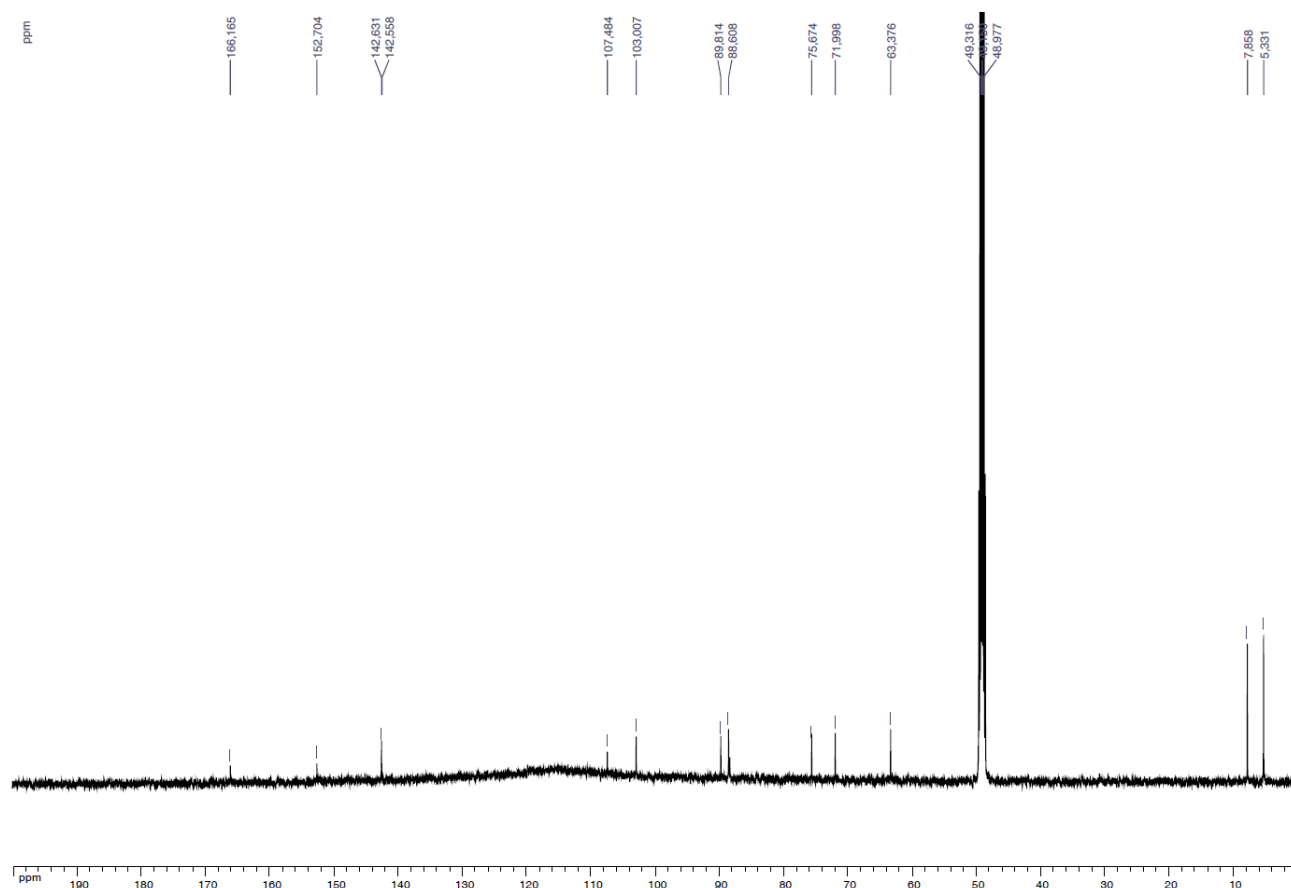
^{13}C NMR, 125 MHz (CD_3OD)



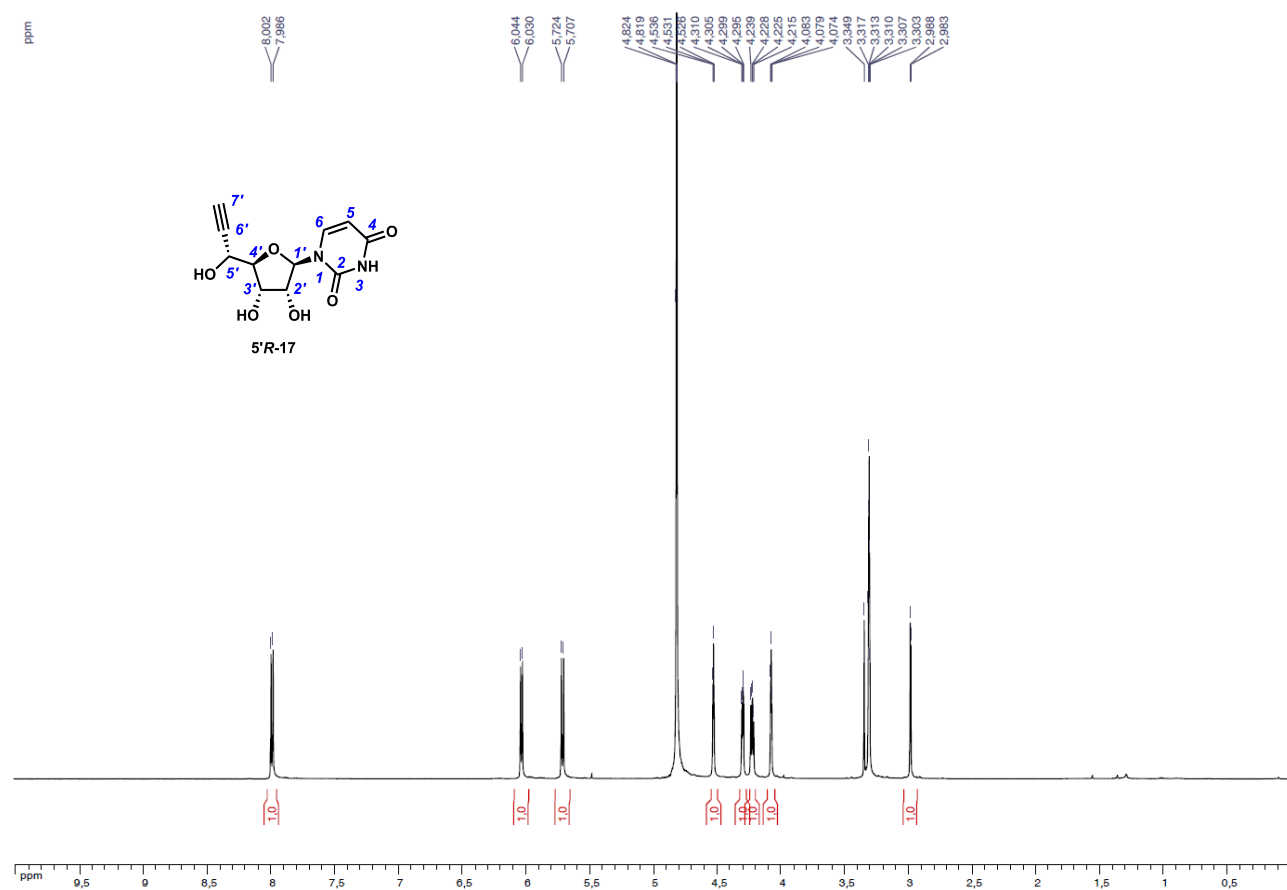
^1H NMR, 500 MHz (CD_3OD , compound **5'S-16**)



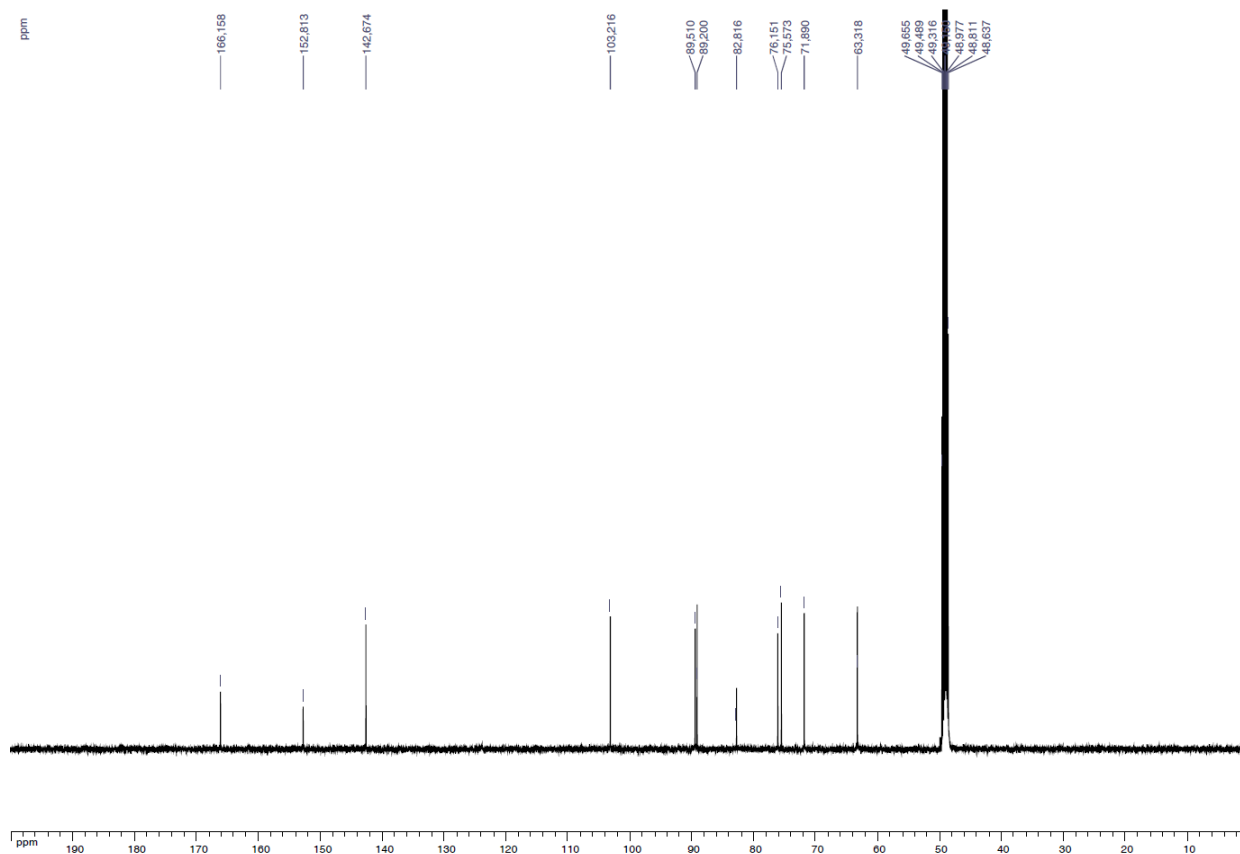
^{13}C NMR, 125 MHz (CD_3OD)



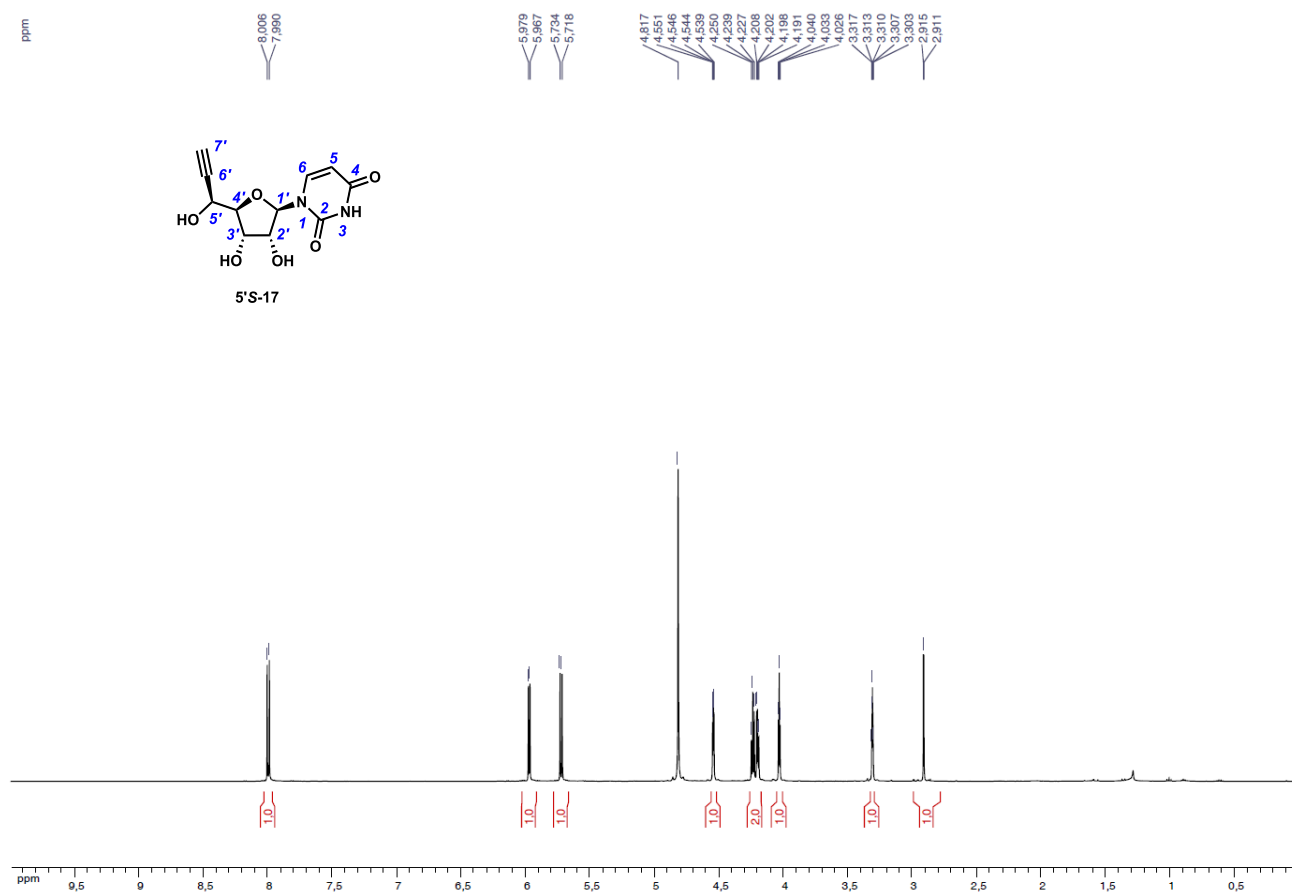
^1H NMR, 500 MHz (CD_3OD), compound **5'R-17**



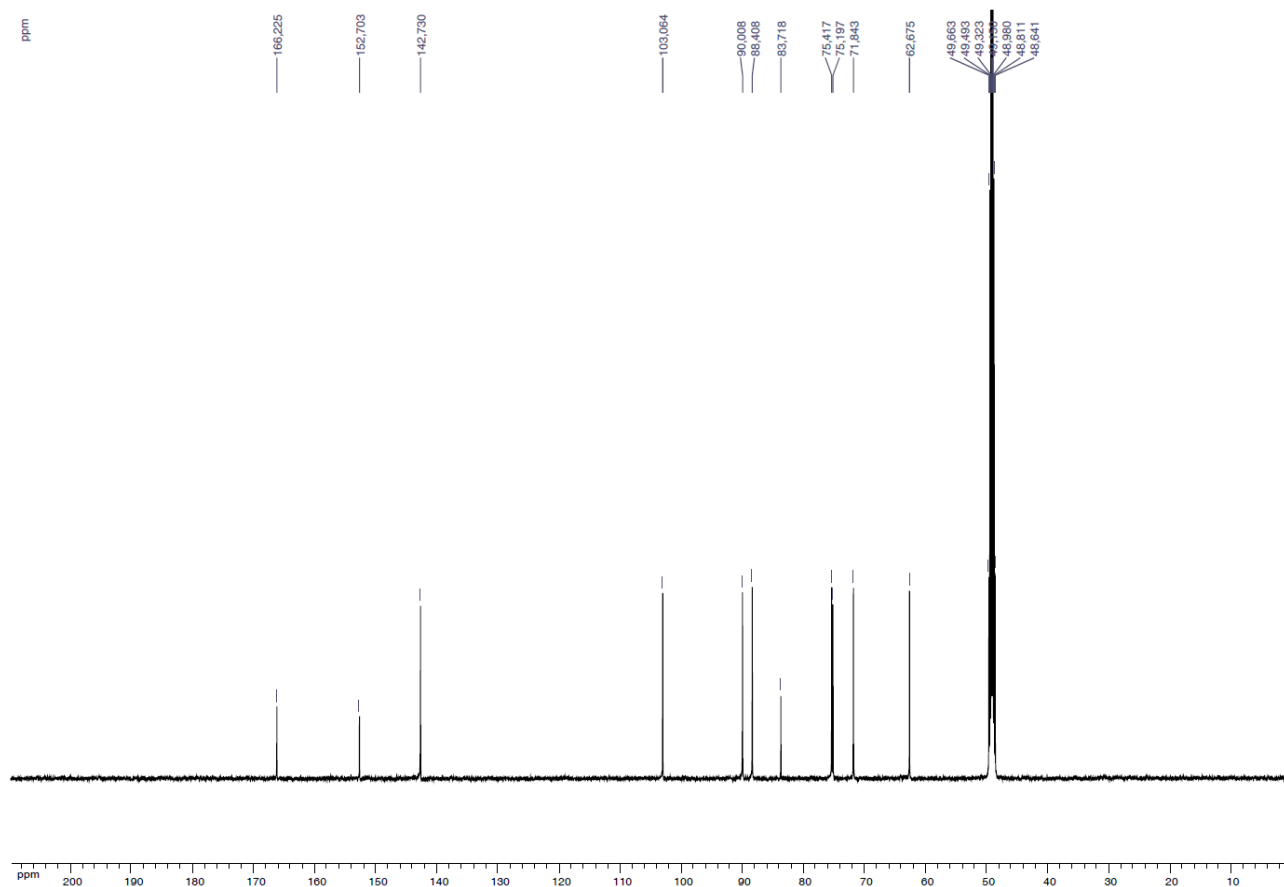
^{13}C NMR, 125 MHz (CD_3OD)



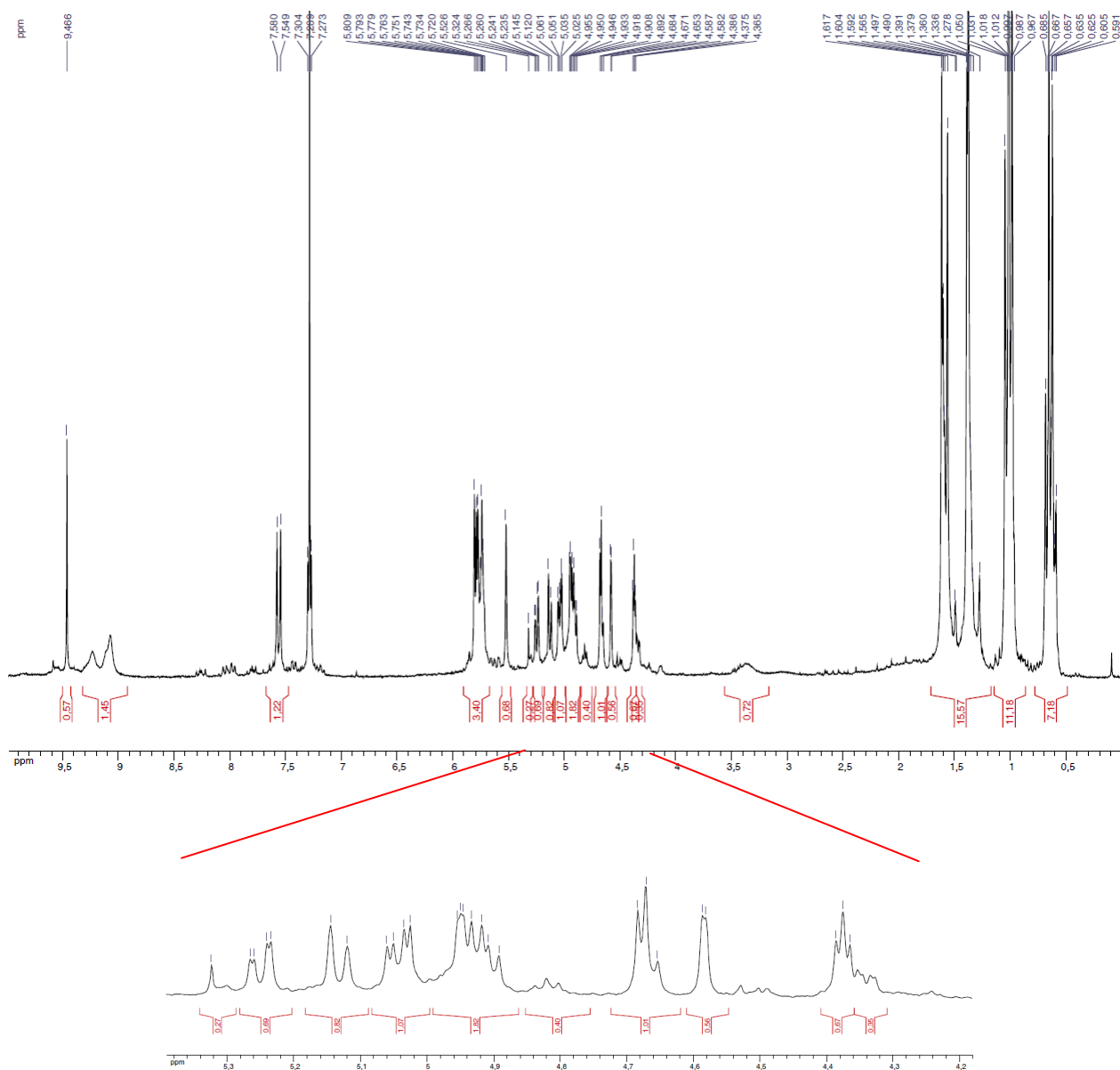
^1H NMR, 500 MHz (CD_3OD), compound **5'S-17**



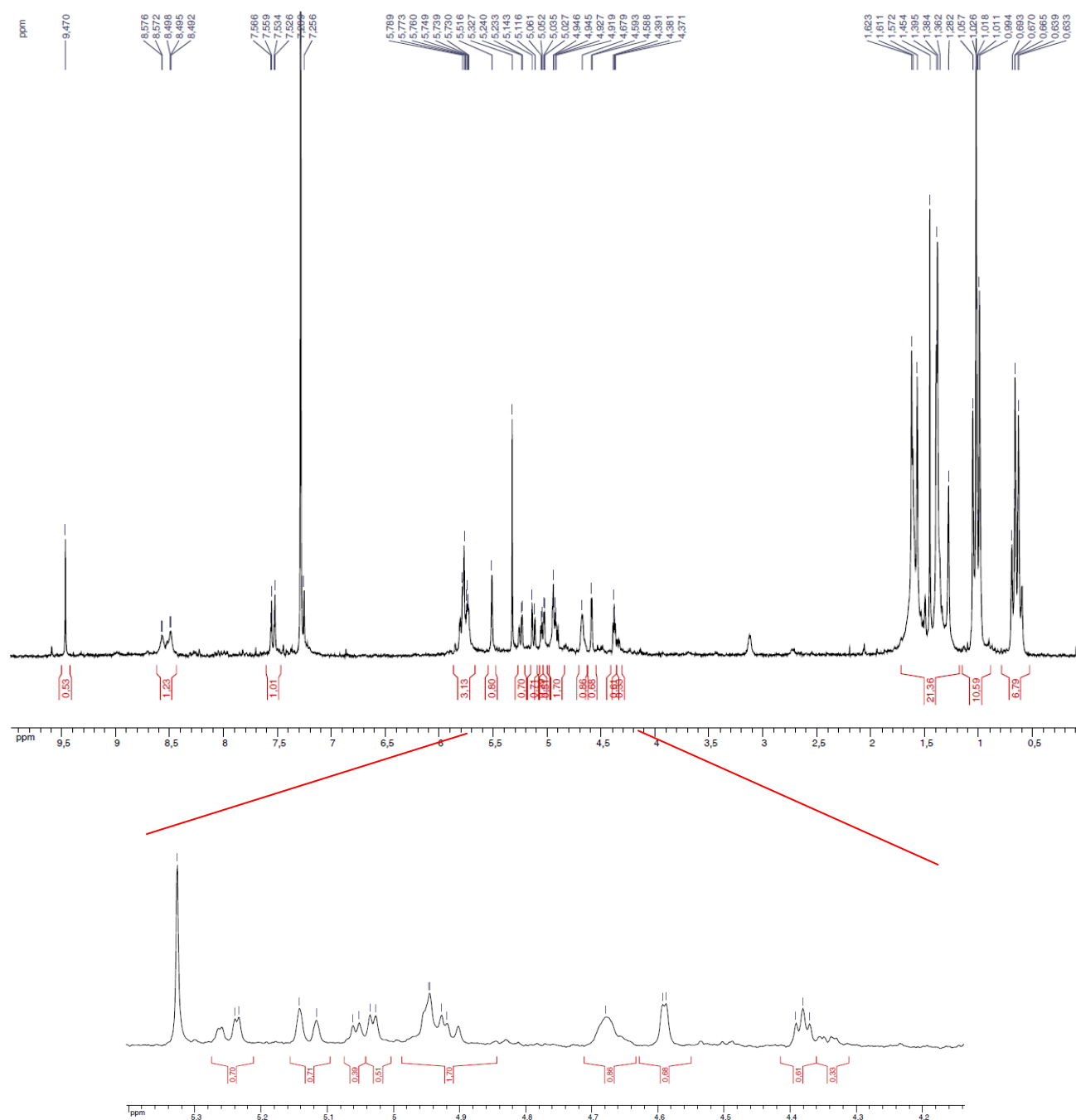
^{13}C NMR, 125 MHz (CD_3OD)



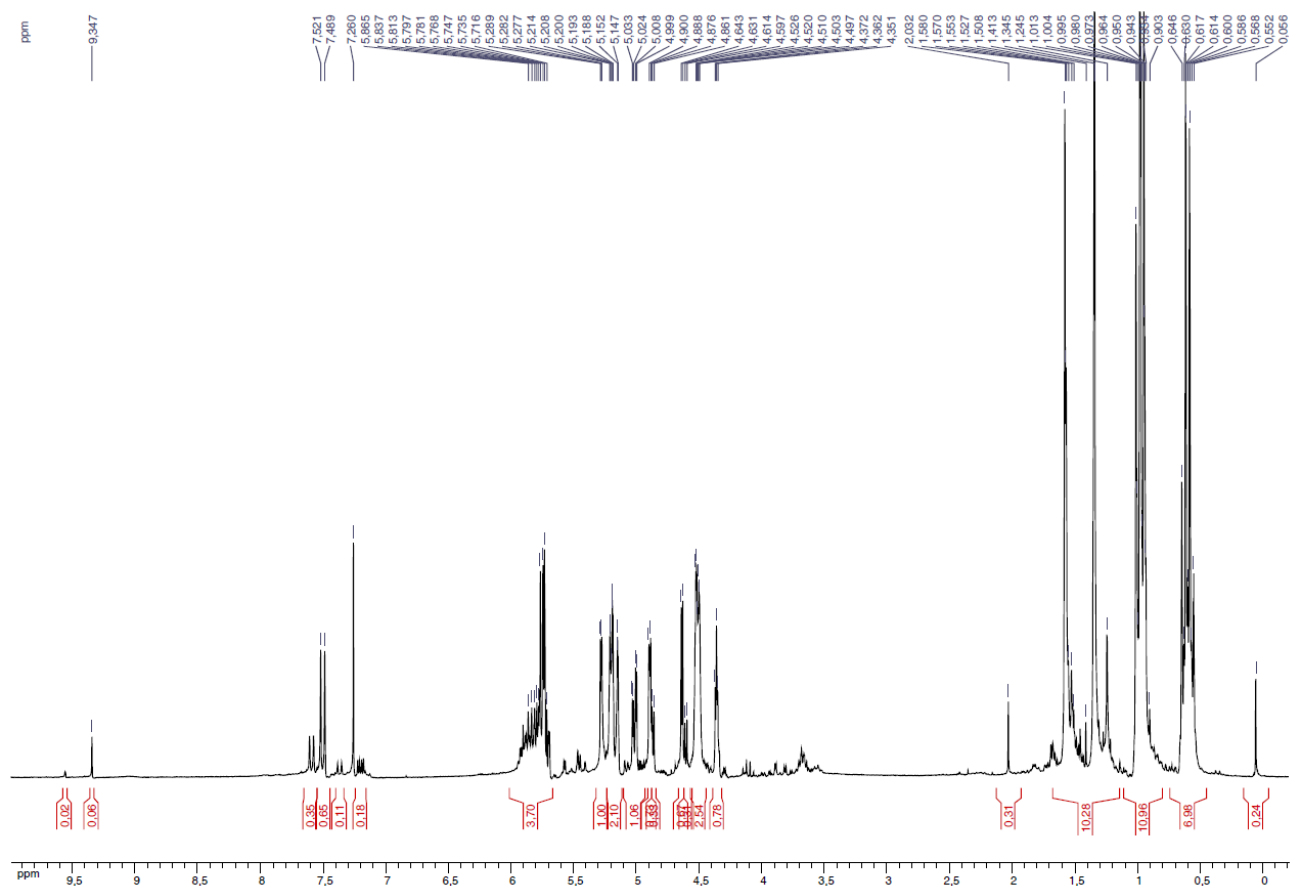
NMR spectrum of the crude for entry 1 (-50 °C)



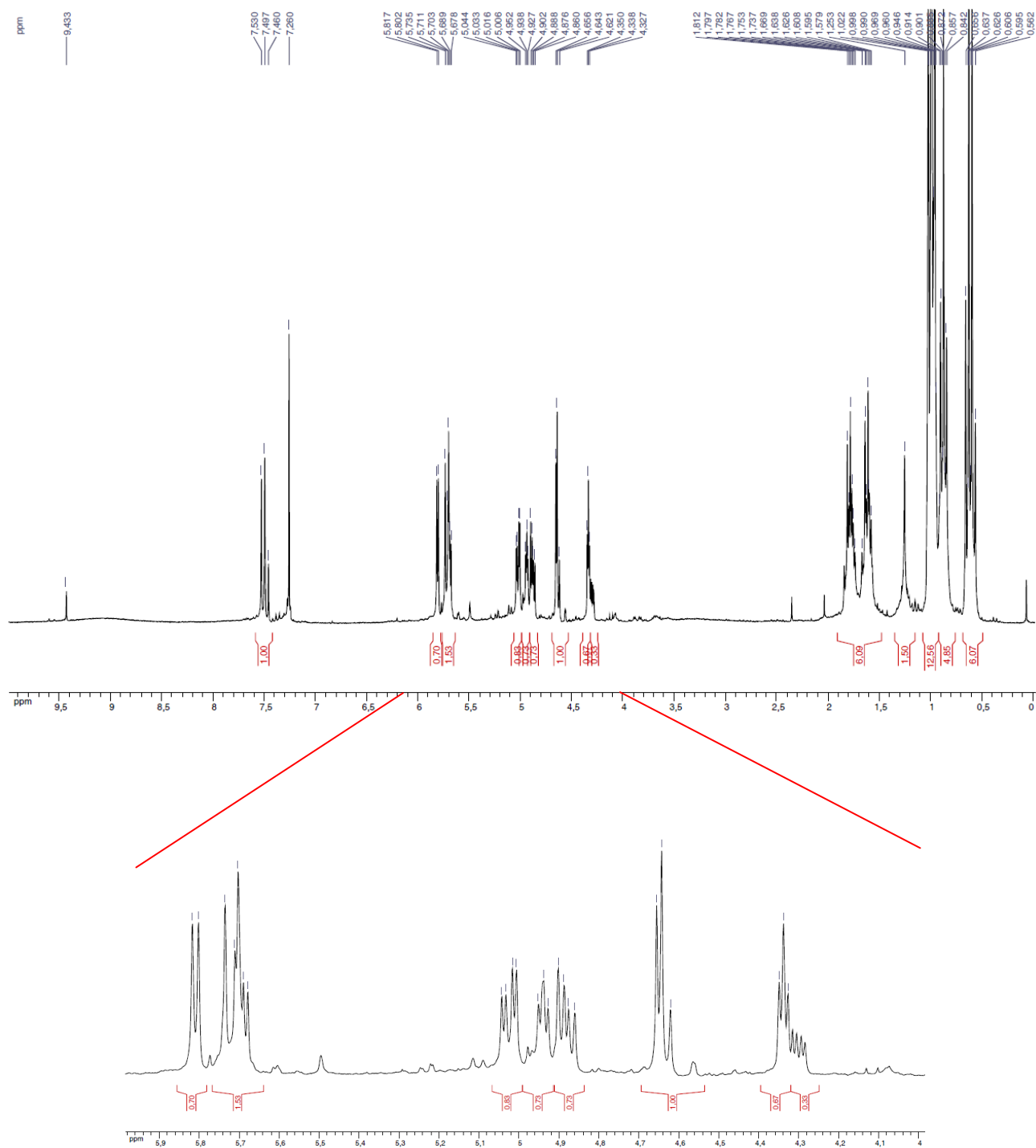
NMR spectrum of the crude for entry 2 (-78 °C)



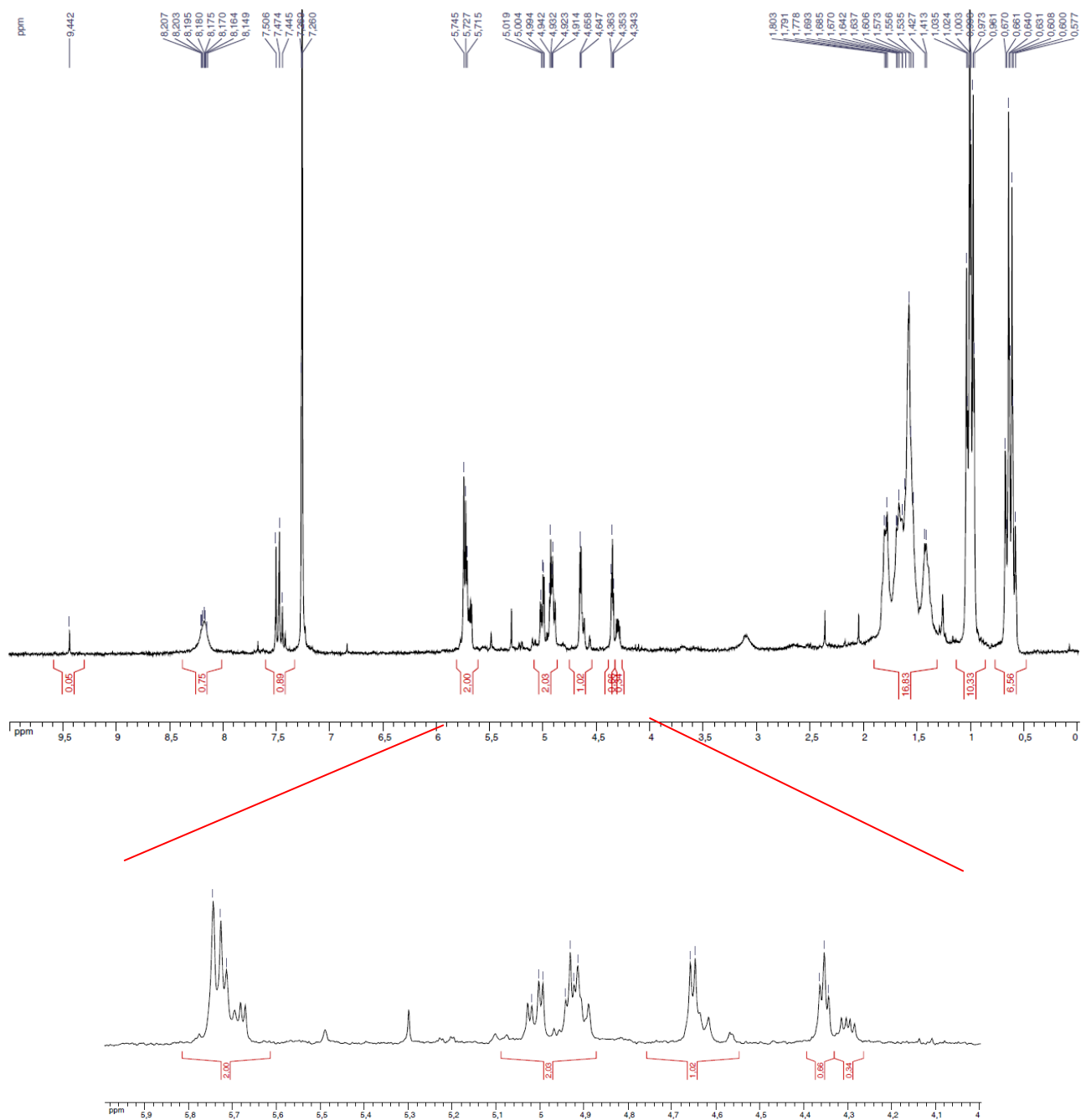
NMR spectrum of the crude for entry 3 (-15 °C)



NMR spectrum of the crude for entry 4 (-15 °C)



NMR spectrum of the crude for entry 5 (-15 °C)



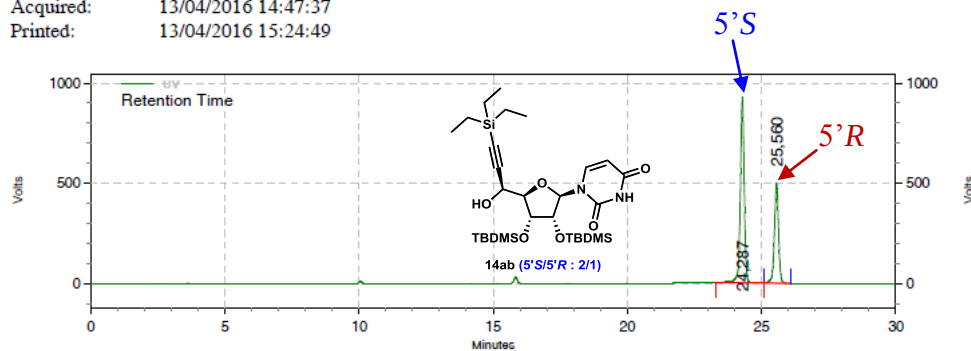
HPLC and ^1H NMR of the crude mixture for the 5'R/5'S determination

HPLC conditions were optimized on a 2/1 mixture 5'S/5'R of **14ab** (last fraction of a purification enriched in the minor diastereomer)

HPLC ($\text{CH}_3\text{CN} / \text{H}_2\text{O}$ 60 / 40 to 0 / 100, 1.0 mL min^{-1} , 254 nm) ; $t_R = 24.29 \text{ min}$, $t_R = 25.56 \text{ min}$

Area % Report

Data File: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Data\MF 652-5.dat
Method: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Method\RBO.met
Acquired: 13/04/2016 14:47:37
Printed: 13/04/2016 15:24:49



UV Results

Retention Time	Area	Area %	Height	Height %
24,287	36997826	63,44	3699455	64,98
25,560	21324477	36,56	1994042	35,02

HPLC (CH₃CN / H₂O 60 / 40 to 0 / 100, 1.0 mL min⁻¹, 254 nm) ; t_R= 29.60 min, t_R= 31.93 min

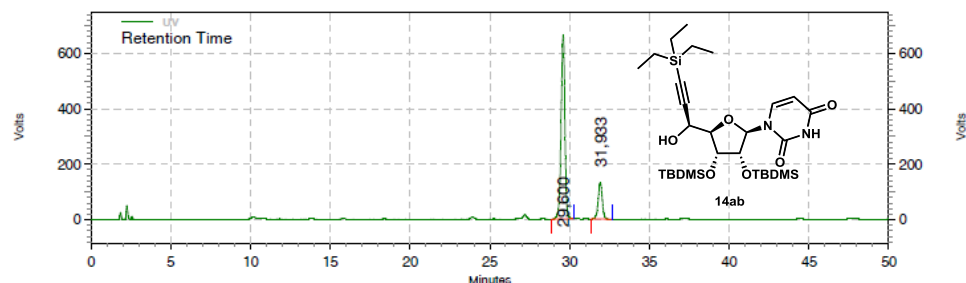
Area % Report

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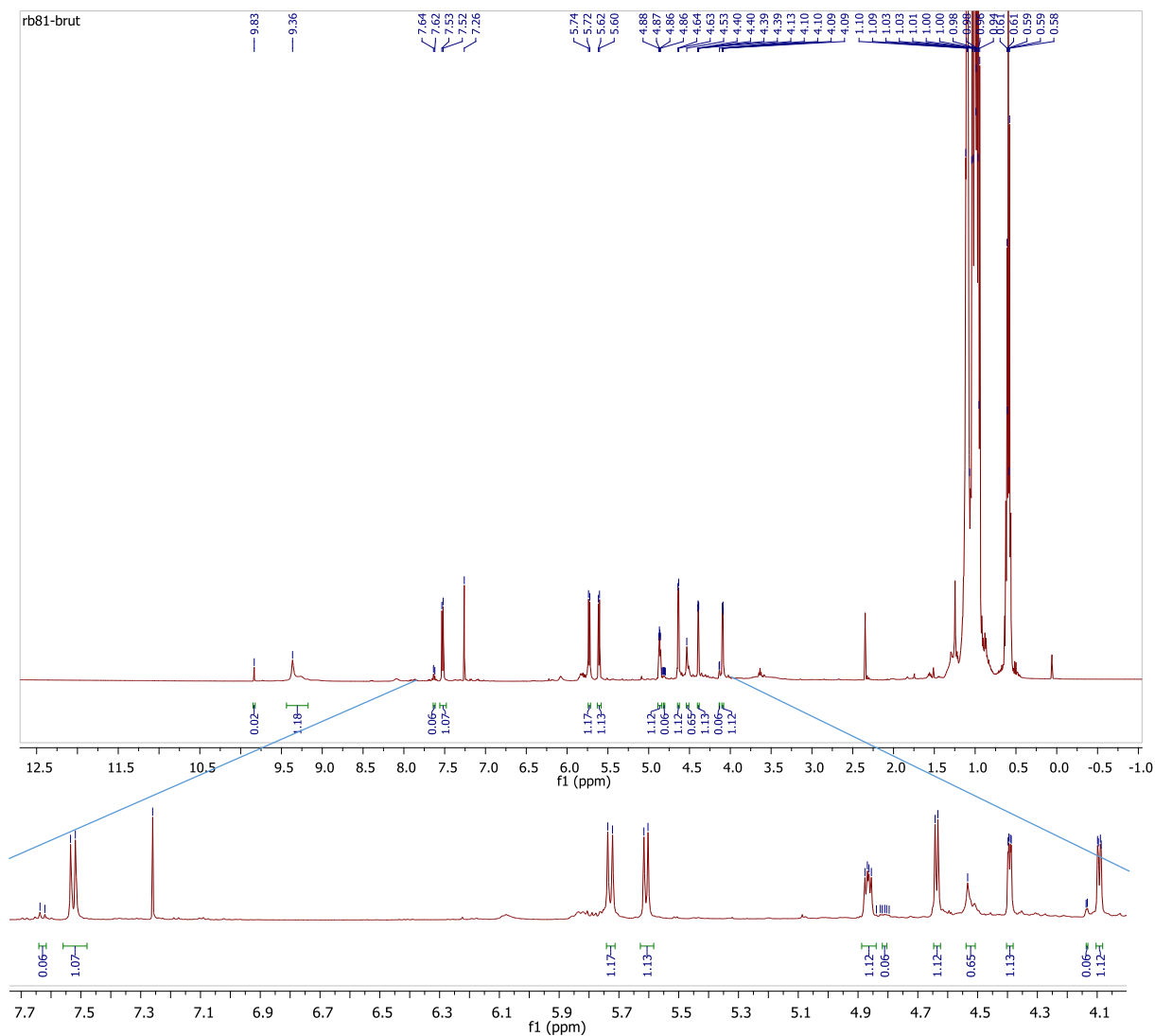
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UV Results

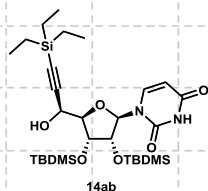
Retention Time	Area	Area %	Height	Height %
29,600	44083635	82,38	2658218	83,52
31,933	9428089	17,62	524335	16,48



HPLC (CH₃CN / H₂O 80 /20 to 0 /100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 20.04 min, t_R= 21.36 min

HPLC (CH₃CN / H₂O 80 /20 to 0 /100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 20.04 min, t_R= 21.36 min

Data File: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Data\rbo-tbs--78.dat
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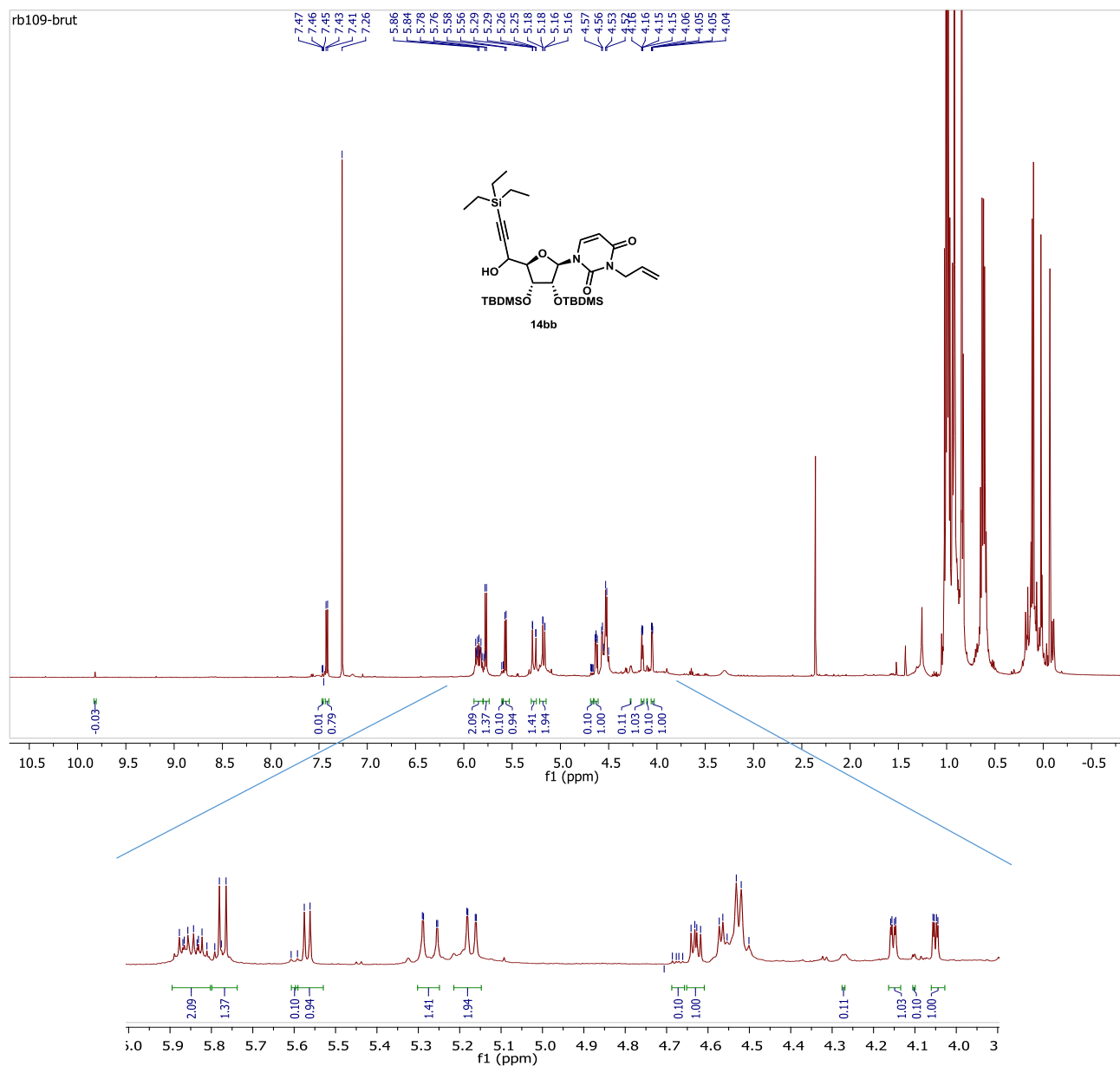


¹H NMR spectrum of compound 10b in CDCl₃.

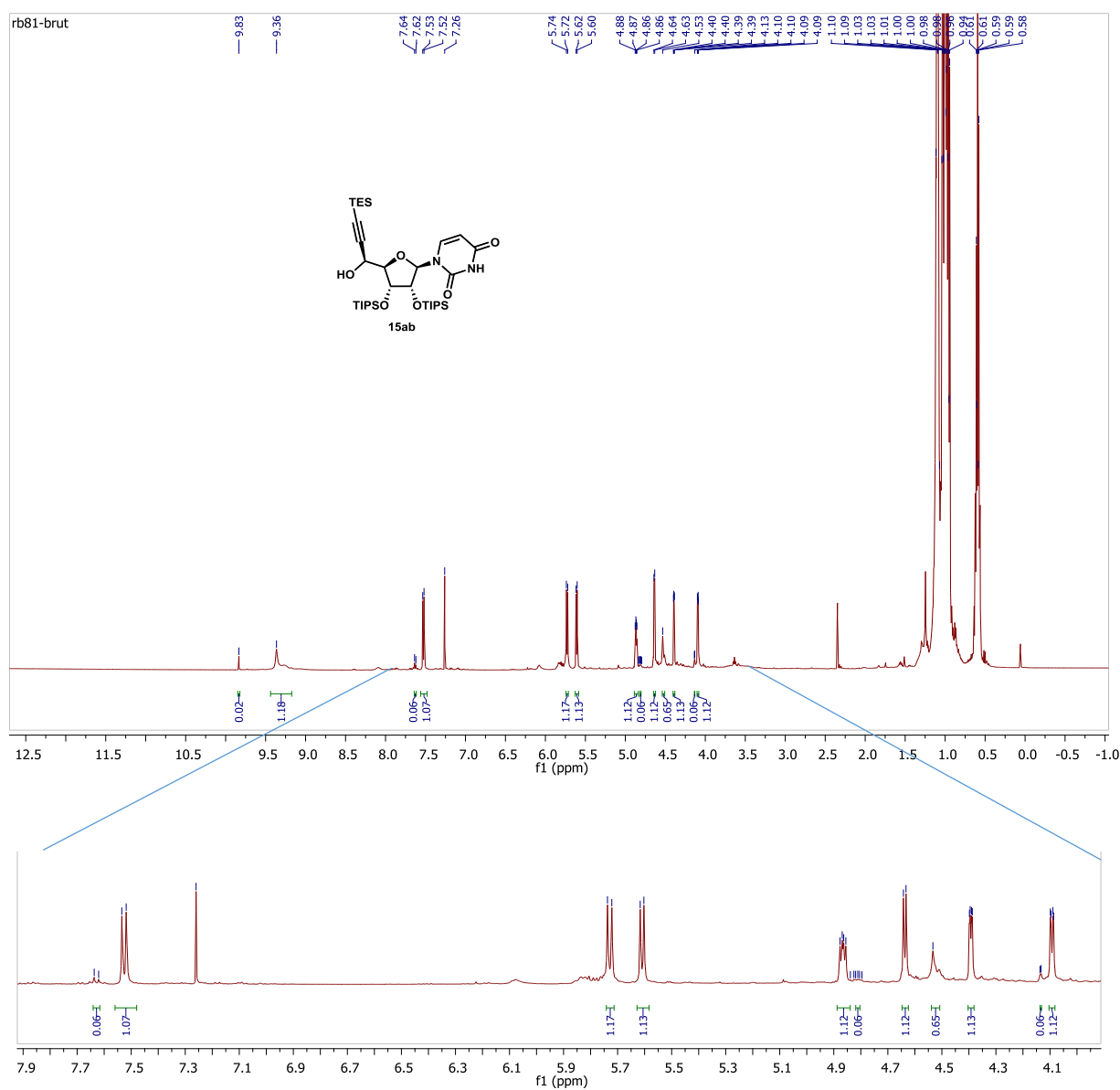
The main spectrum displays peaks from 0 to 10 ppm. The x-axis is labeled "f1 (ppm)". The y-axis represents intensity. The spectrum shows a complex pattern of peaks, with a prominent peak at approximately 7.5 ppm and a cluster of peaks between 0 and 2 ppm. Integration values are provided for several peaks: 0.03, 1.05, 0.13, 1.14, 0.22, 1.33, 1.35, 3.59, 1.14, 0.21, 1.13, 3.59, 1.14, 0.21, 1.13.

The inset spectrum shows a zoomed-in view of the aromatic region from 7.3 to 7.9 ppm. The x-axis is labeled "f1 (ppm)". The y-axis represents intensity. The inset shows a cluster of peaks, with a prominent peak at approximately 7.5 ppm. Integration values are provided for several peaks: 1.05, 0.13, 1.14.

NMR spectrum of the crude for entry 8



NMR spectrum of the crude for entry 9

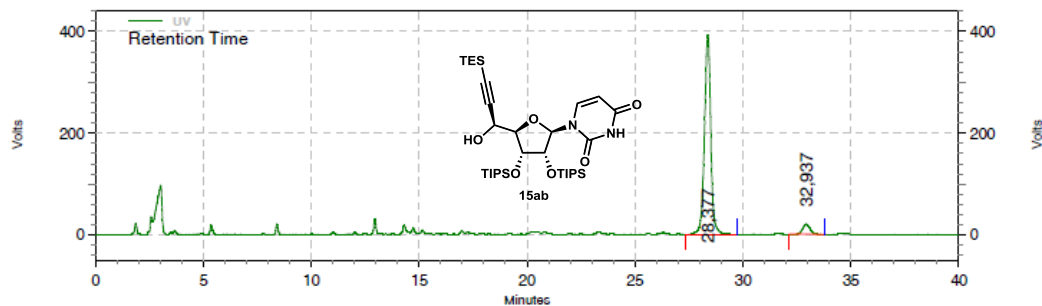


HPLC and NMR spectra of the crude for entry 10 (- 78 °C)

HPLC (CH₃CN / H₂O 60 /40 to 0 /100, 1.0 mL min⁻¹, 254 nm) ; t_R= 28.38 min, t_R= 32.94 min

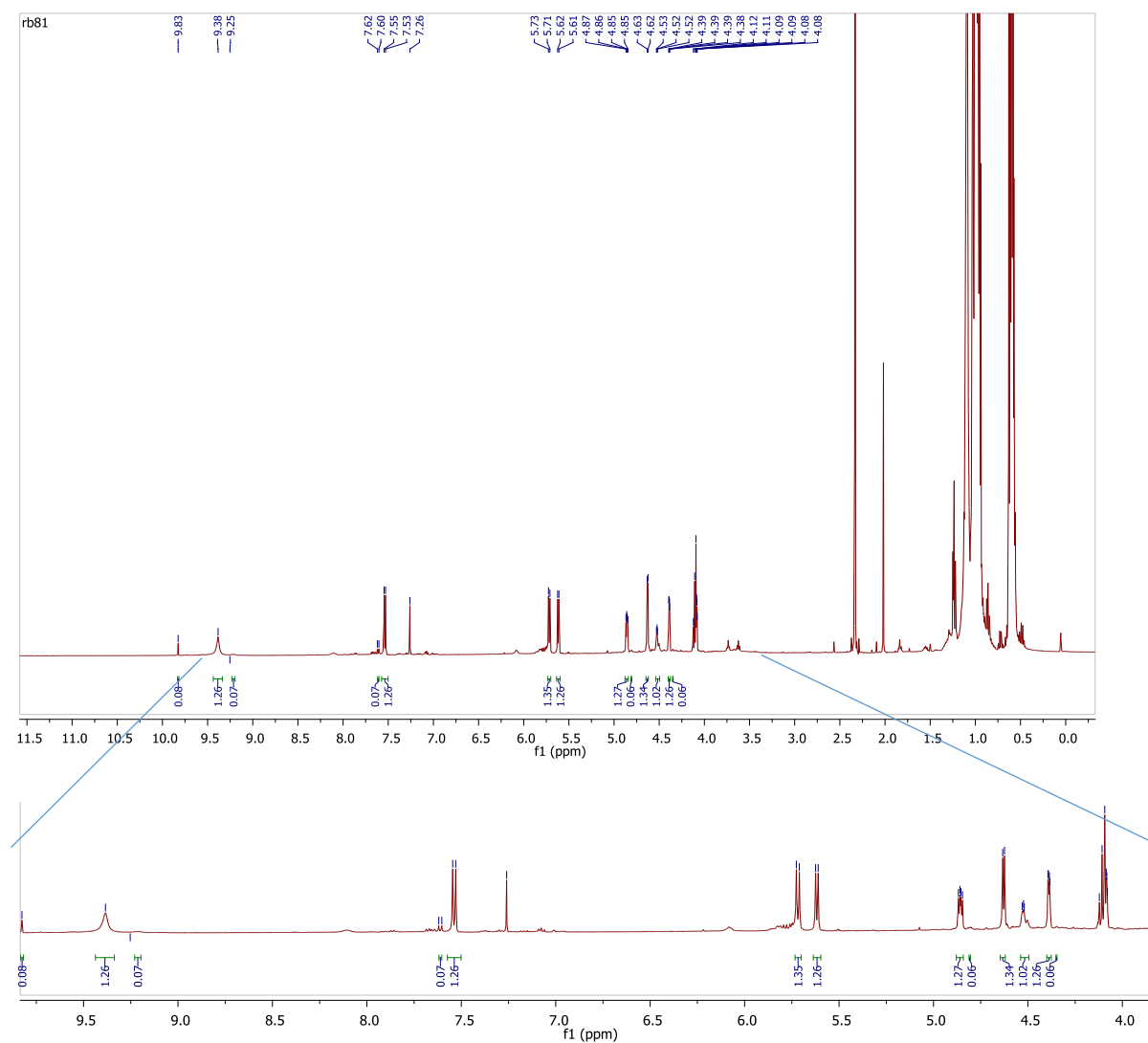
Area % Report

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 Printed: 14/04/2016 09:44:51



UV Results

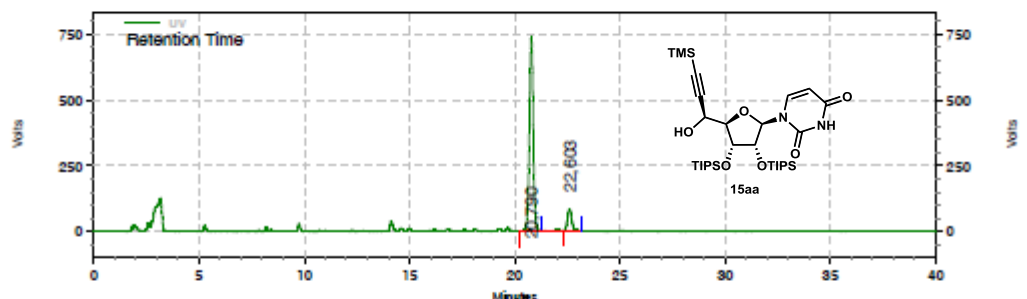
Retention Time	Area	Area %	Height	Height %
28,377	31792512	94,33	1568029	95,20
32,937	1909706	5,67	79026	4,80



HPLC (CH₃CN / H₂O 60 /40 to 0 /100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 20.79 min, t_R= 22.60 min

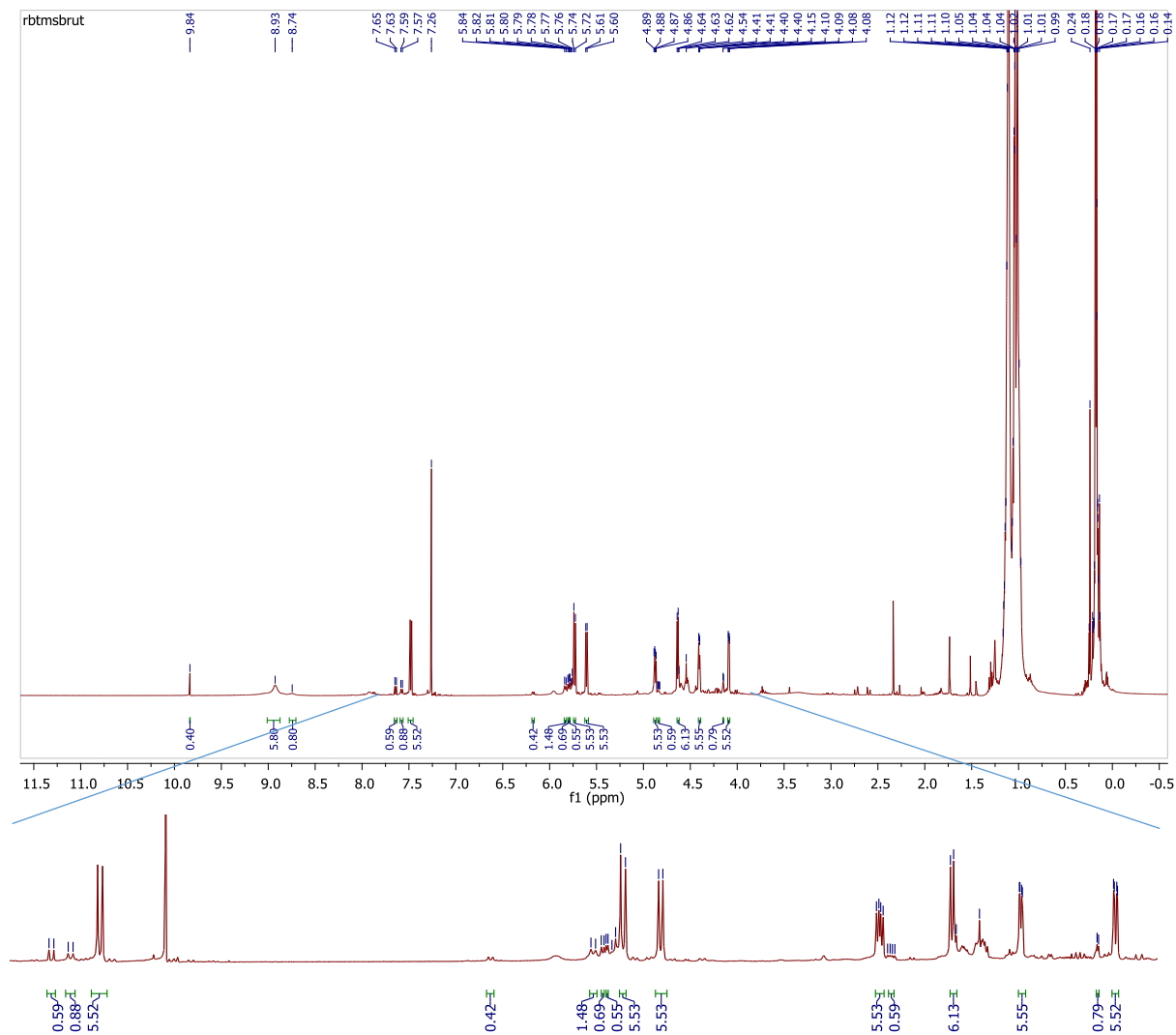
Area % Report

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UV Results

Retention Time	Area	Area %	Height	Height %
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22.603	5001014	11.85	336330	10.25

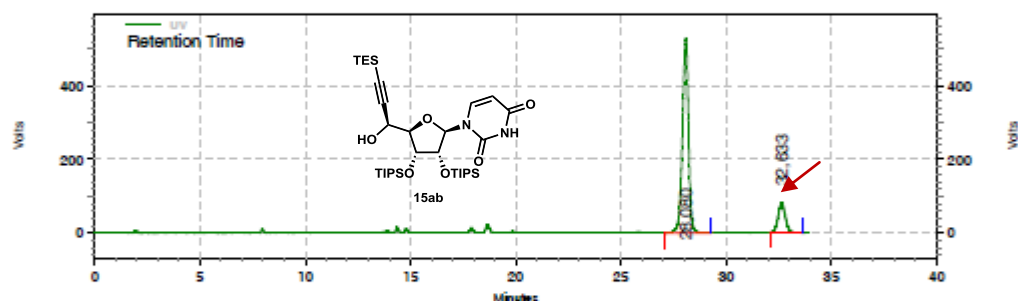


HPLC spectrum of a fraction enriched in the minor diastereomer

HPLC (CH₃CN / H₂O 60 / 40 to 0 / 100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 28.08 min, t_R= 32.63 min

Area % Report

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UV Results

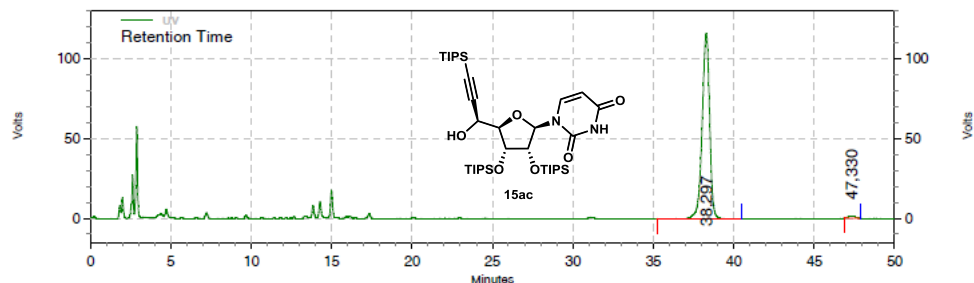
Retention Time	Area	Area %	Height	Height %
28,080	42432780	84,71	2107745	80,87
32,033	7601250	15,29	318070	13,13

HPLC and NMR spectra of the crude for entry 12 (- 78 °C, 5 equiv. of Grignard reagent)

HPLC (CH₃CN / H₂O 60 / 40 to 0 / 100, 1.0 mL.min⁻¹, 254 nm) ; t_R = 38.29 min, t_R = 47.33 min

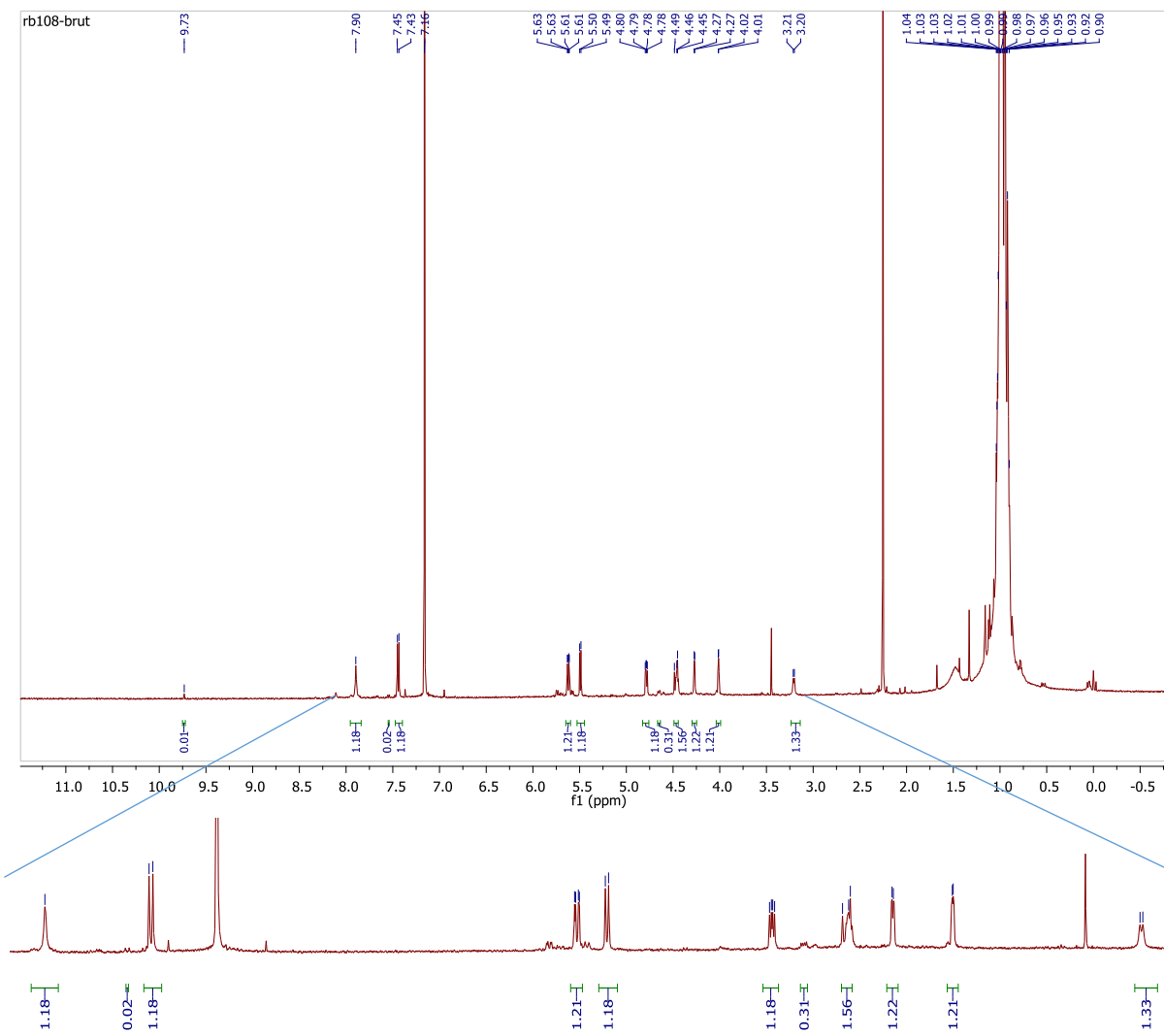
Area % Report

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UV Results

Retention Time	Area	Area %	Height	Height %
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47,330	181142	1,19	5672	1,20

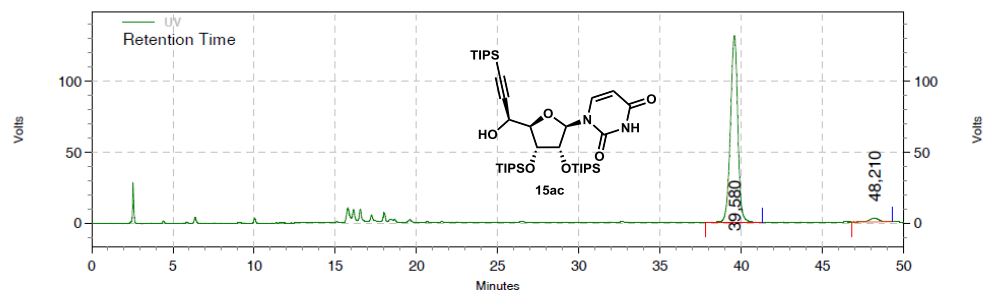


HPLC spectrum of the crude for entry 13 (- 15 °C, 5 equiv. of Grignard reagent)

HPLC (CH₃CN / H₂O 60 /40 to 0 /100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 39.58 min, t_R= 48.21 min

Area % Report

Data File: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Data\rbtips-tips-5eqi-15c.dat
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UV Results

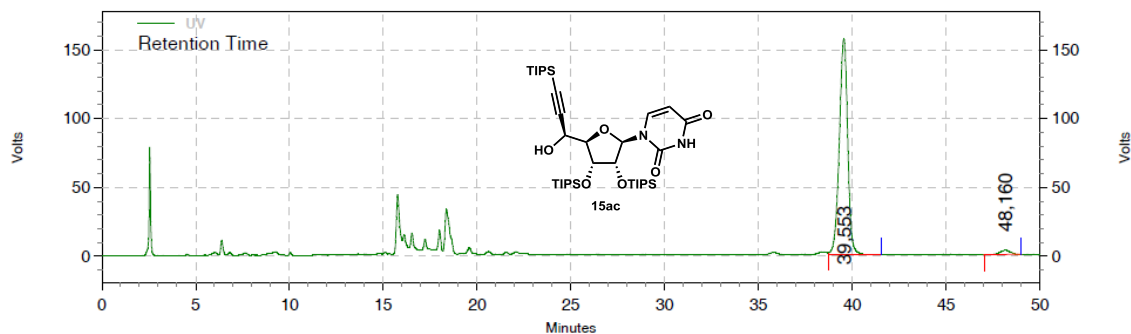
Retention Time	Area	Area %	Height	Height %
39,580	16486718	97,48	525181	98,05
48,210	425558	2,52	10441	1,95

HPLC spectrum of the crude for entry 14 (- 15 °C, 2.5 equiv. of Grignard reagent)

HPLC (CH₃CN / H₂O 60 /40 to 0 /100, 1.0 mL.min⁻¹, 254 nm) ; t_R= 39.55 min, t_R= 48.16 min

Area % Report

Data File: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Data\rbtips-tips-2.5eqi-15c.dat
 Method: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Method\RBO.met
 Acquired: 21/06/2016 15:42:36
 Printed: 21/06/2016 16:38:41



UV Results

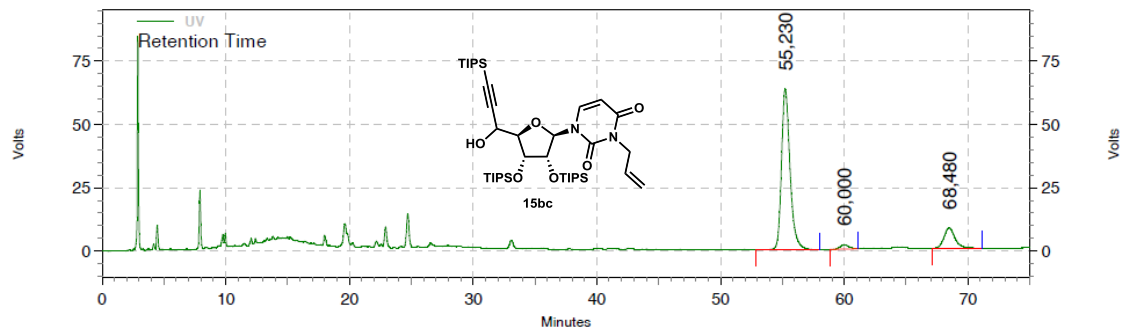
Retention Time	Area	Area %	Height	Height %
39,553	19496086	97,51	627274	98,06
48,160	496880	2,49	12381	1,94

HPLC spectrum of the crude for entry 15

HPLC (CH₃CN / H₂O 60 / 40 to 0 / 100, 1.0 mL min⁻¹, 254 nm) ; t_R = 55.23 min, t_R = 68.48 min

Area % Report

Data File: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Data\rbtips-tips-allyl -78-2.dat
 Method: D:\EZChrom Elite\Enterprise\Projects\Aur lie\Method\RBO.met
 Acquired: 29/06/2016 14:02:35
 Printed: 29/06/2016 15:41:33



UV Results

Retention Time	Area	Area %	Height	Height %	
55.230	12103261	83.97	253196	86.73	88.83%
60.000	366316	2.54	6909	2.37	
68.480	1944803	13.49	31827	10.90	11.16%

