

Supporting Information for

Participation of an additional 4'-hydroxymethyl group in the cleavage and isomerization of ribonucleoside 3'-
phosphodiester

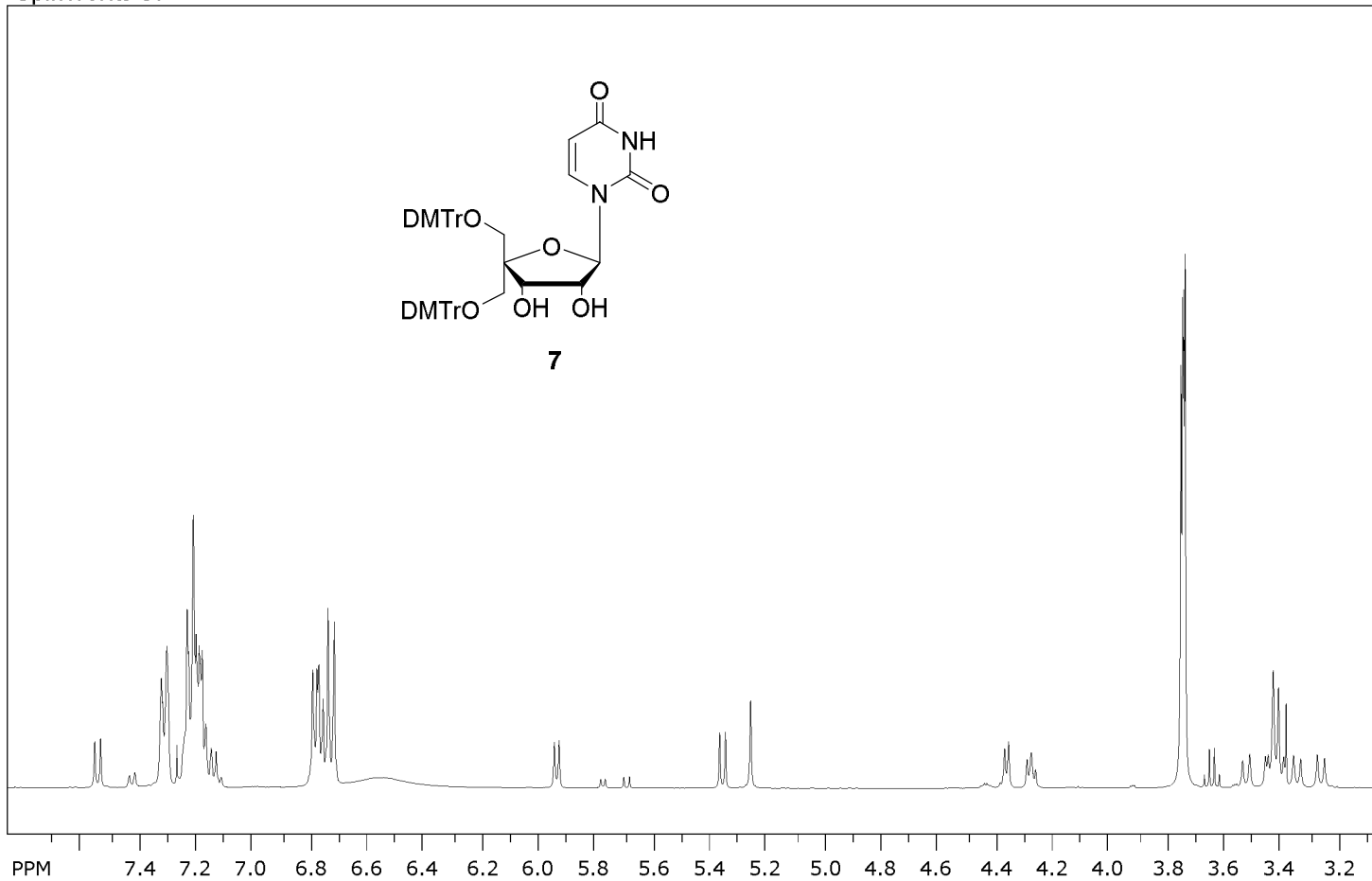
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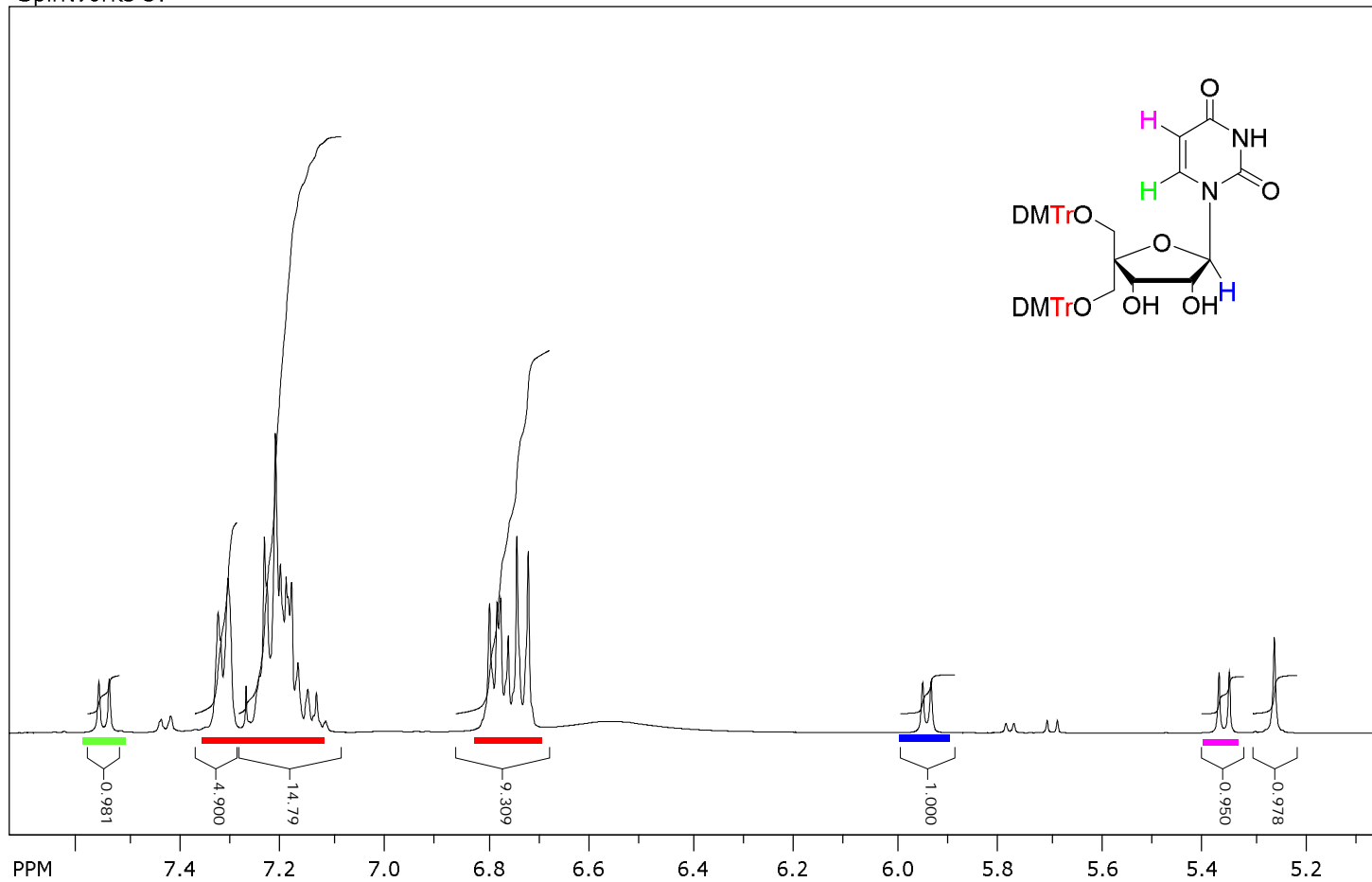
SpinWorks 3:



file: ... TBDMS (impure)\LL384-311013\1\fid exp: <zg30>
transmitter freq.: 399.753198 MHz
time domain size: 65536 points
width: 7183.91 Hz = 17.9709 ppm = 0.109618 Hz/pt
number of scans: 32

freq. of 0 ppm: 399.750000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 77.358 ppm/cm: 0.19351

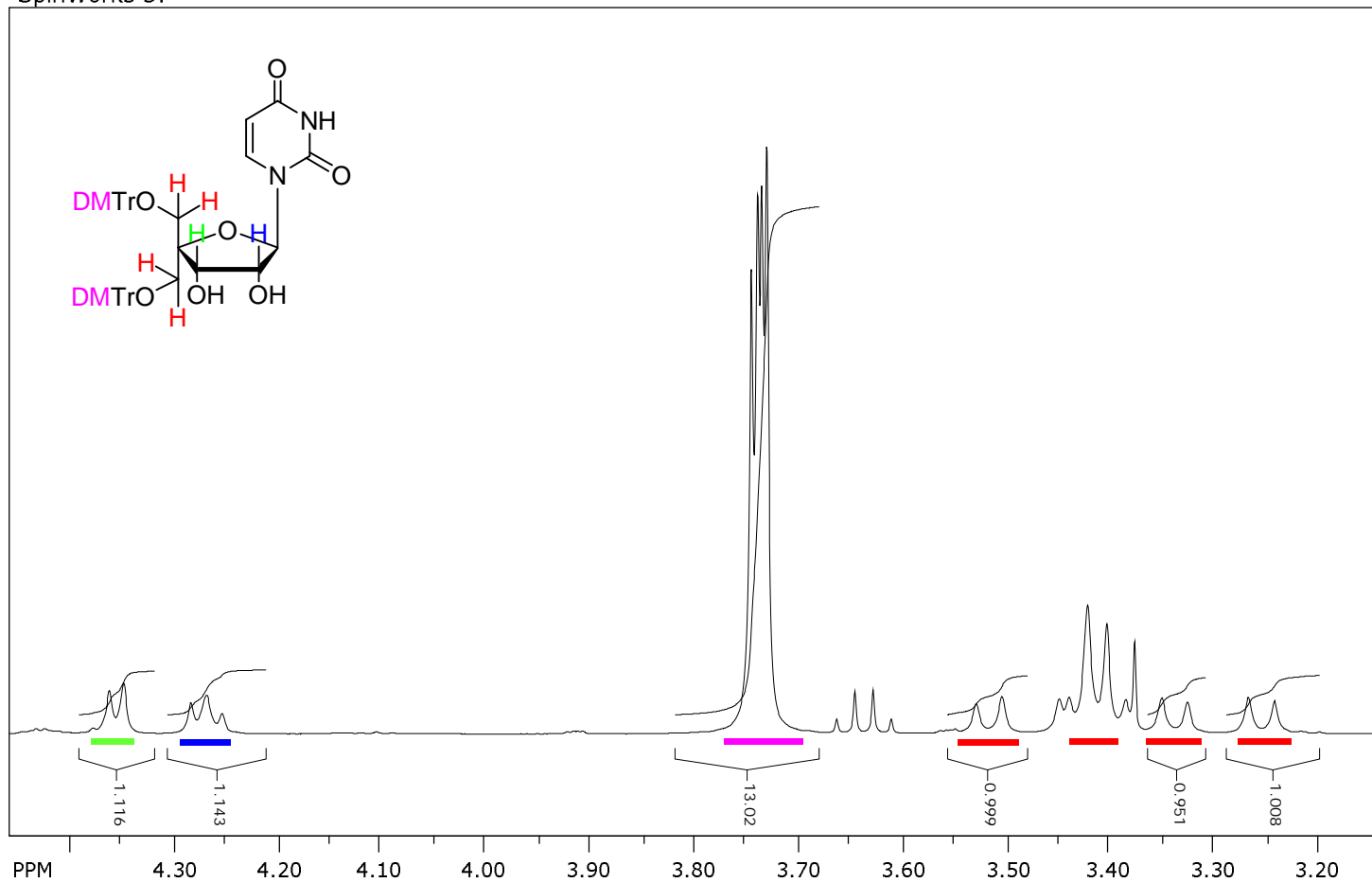
SpinWorks 3:



file: ... TBDMS (impure)\LL384-311013\1\fid exp: <zg30>
transmitter freq.: 399.753198 MHz
time domain size: 65536 points
width: 7183.91 Hz = 17.9709 ppm = 0.109618 Hz/pt
number of scans: 32

freq. of 0 ppm: 399.750000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 43.109 ppm/cm: 0.10784

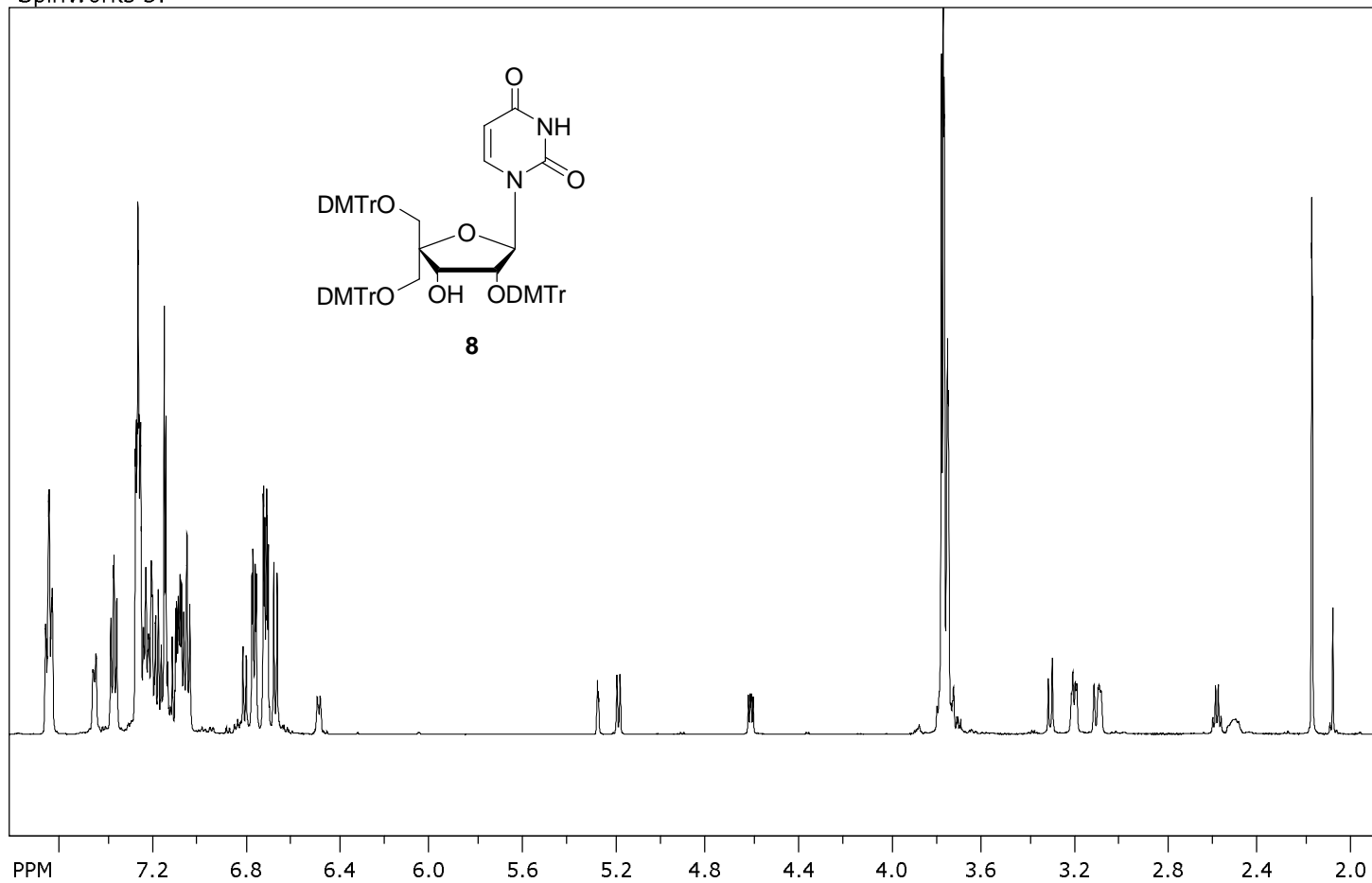
SpinWorks 3:



file: ... TBDMS (impure)\LL384-311013\1\fid expt: <zg30>
transmitter freq.: 399.753198 MHz
time domain size: 65536 points
width: 7183.91 Hz = 17.9709 ppm = 0.109618 Hz/pt
number of scans: 32

freq. of 0 ppm: 399.750000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 21.212 ppm/cm: 0.05306

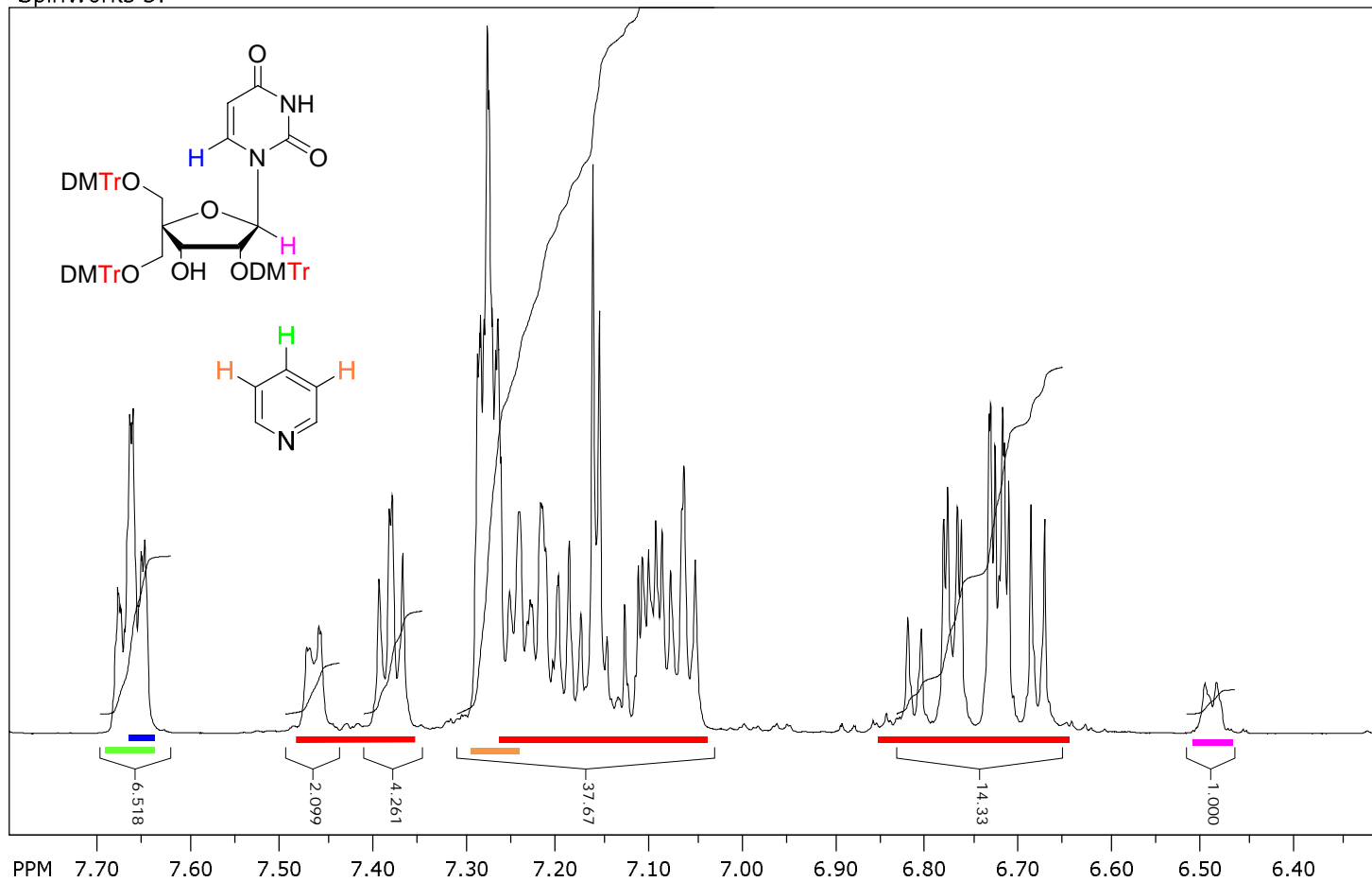
SpinWorks 3:



file: ...-5'' tris DMTr\LL366-250713\1\fid expt: <zg30>
transmitter freq.: 600.133706 MHz
time domain size: 65536 points
width: 9615.38 Hz = 16.0221 ppm = 0.146719 Hz/pt
number of scans: 32

freq. of 0 ppm: 600.130000 MHz
processed size: 32768 complex points
LB: 0.100 GF: 0.0000
Hz/cm: 143.834 ppm/cm: 0.23967

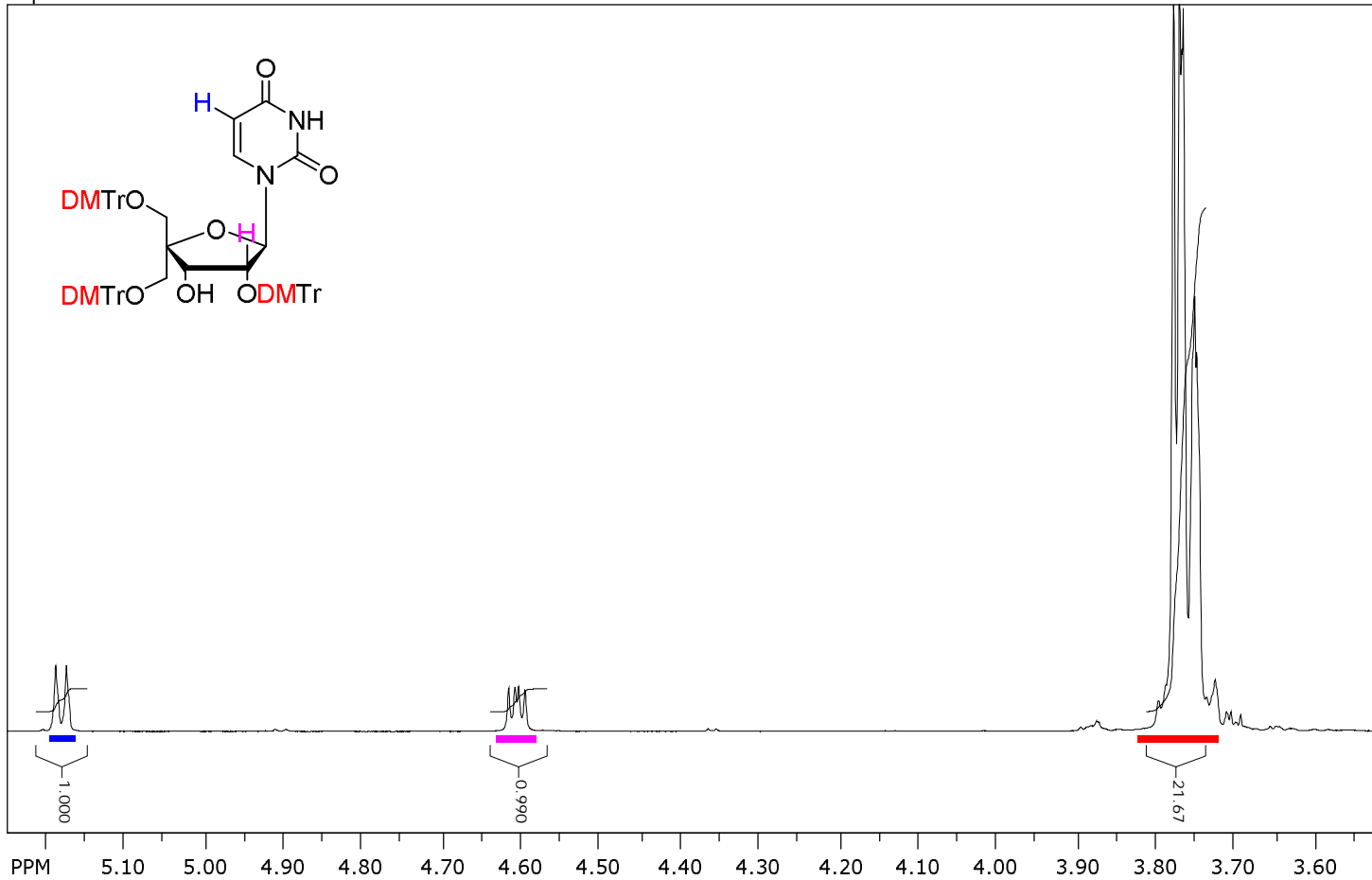
SpinWorks 3:



file: ...'-5'' tris DMTr\LL366-250713\1\fid exp: <zg30>
transmitter freq.: 600.133706 MHz
time domain size: 65536 points
width: 9615.38 Hz = 16.0221 ppm = 0.146719 Hz/pt
number of scans: 32

freq. of 0 ppm: 600.130000 MHz
processed size: 32768 complex points
LB: 0.100 GF: 0.0000
Hz/cm: 35.897 ppm/cm: 0.05982

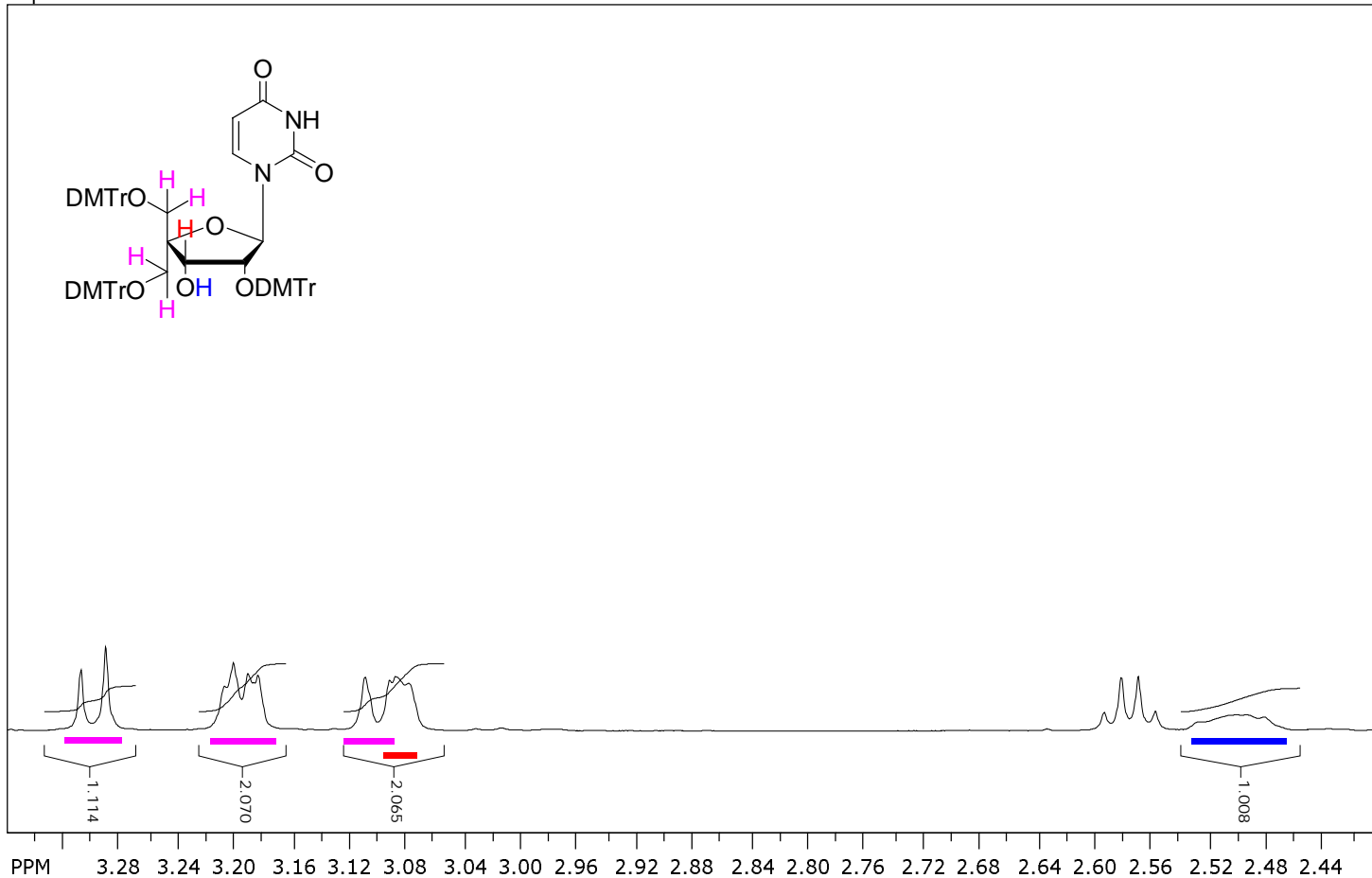
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\1\fid expt: <zg30>
transmitter freq.: 600.133706 MHz
time domain size: 65536 points
width: 9615.38 Hz = 16.0221 ppm = 0.146719 Hz/pt
number of scans: 32

freq. of 0 ppm: 600.130000 MHz
processed size: 32768 complex points
LB: 0.100 GF: 0.0000
Hz/cm: 41.758 ppm/cm: 0.06958

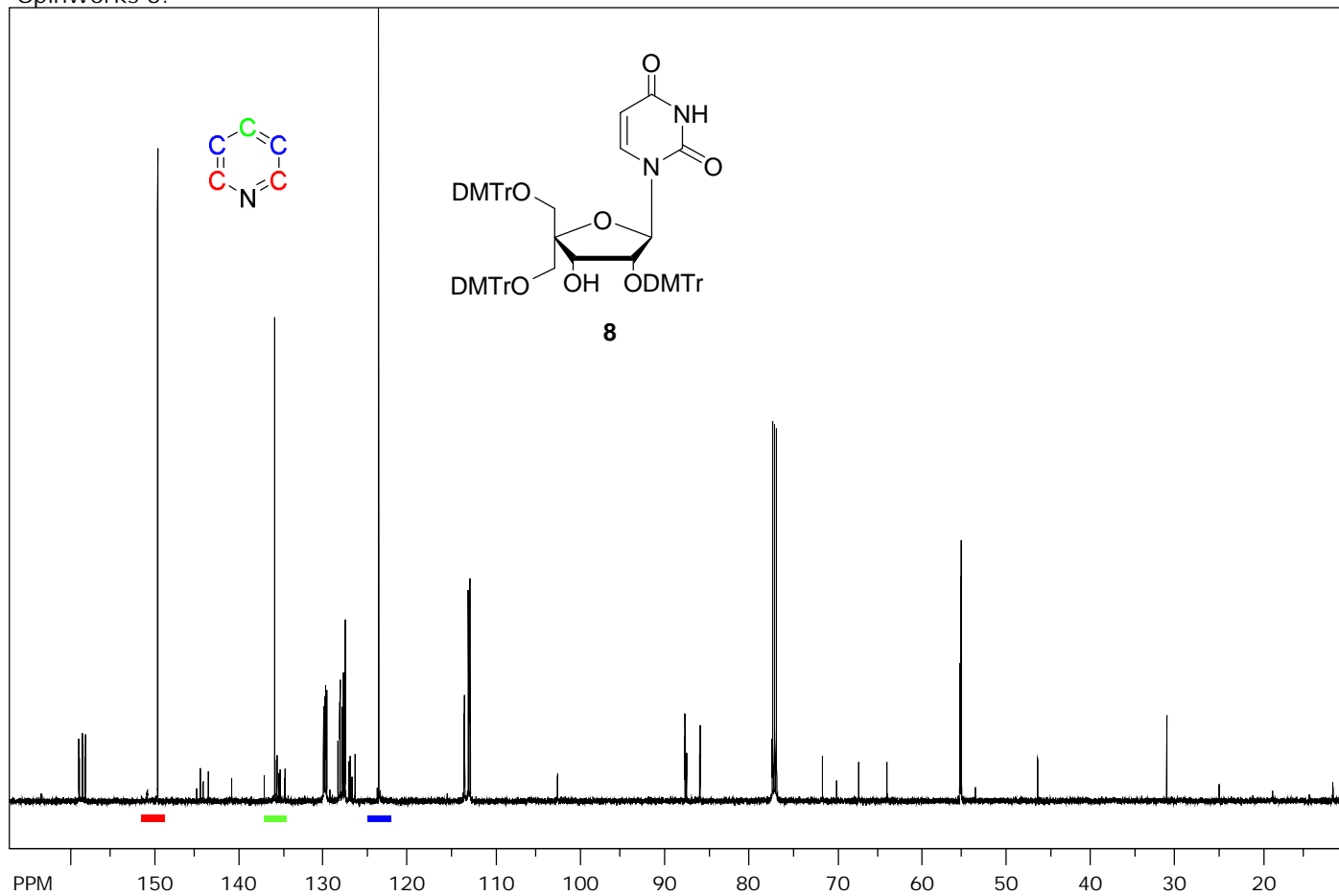
SpinWorks 3:



file: ...-5'' tris DMTr\LL366-250713\1\fid expt: <zg30>
transmitter freq.: 600.133706 MHz
time domain size: 65536 points
width: 9615.38 Hz = 16.0221 ppm = 0.146719 Hz/pt
number of scans: 32

freq. of 0 ppm: 600.130000 MHz
processed size: 32768 complex points
LB: 0.100 GF: 0.0000
Hz/cm: 23.119 ppm/cm: 0.03852

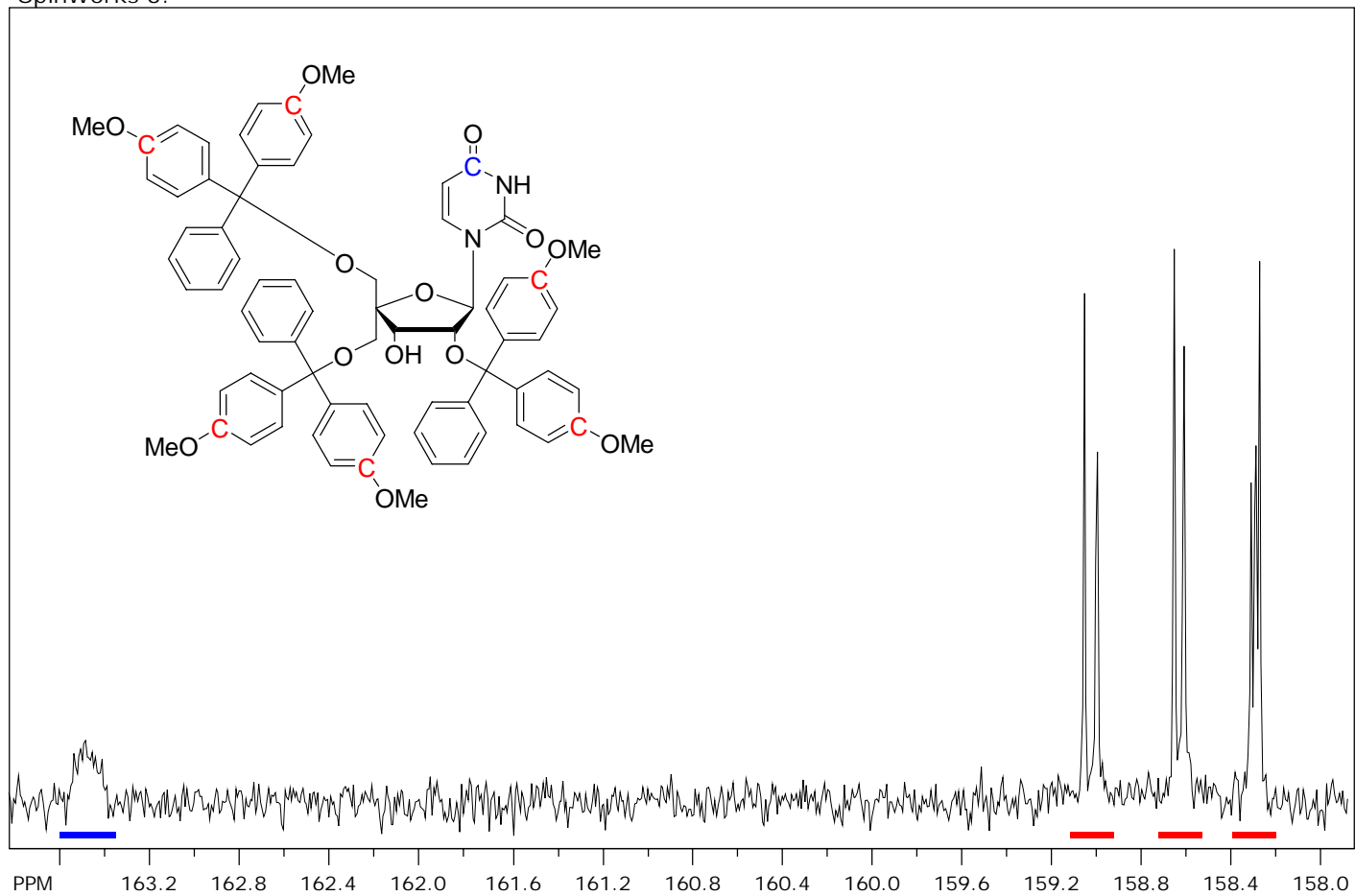
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 991.588 ppm/cm: 6.57038

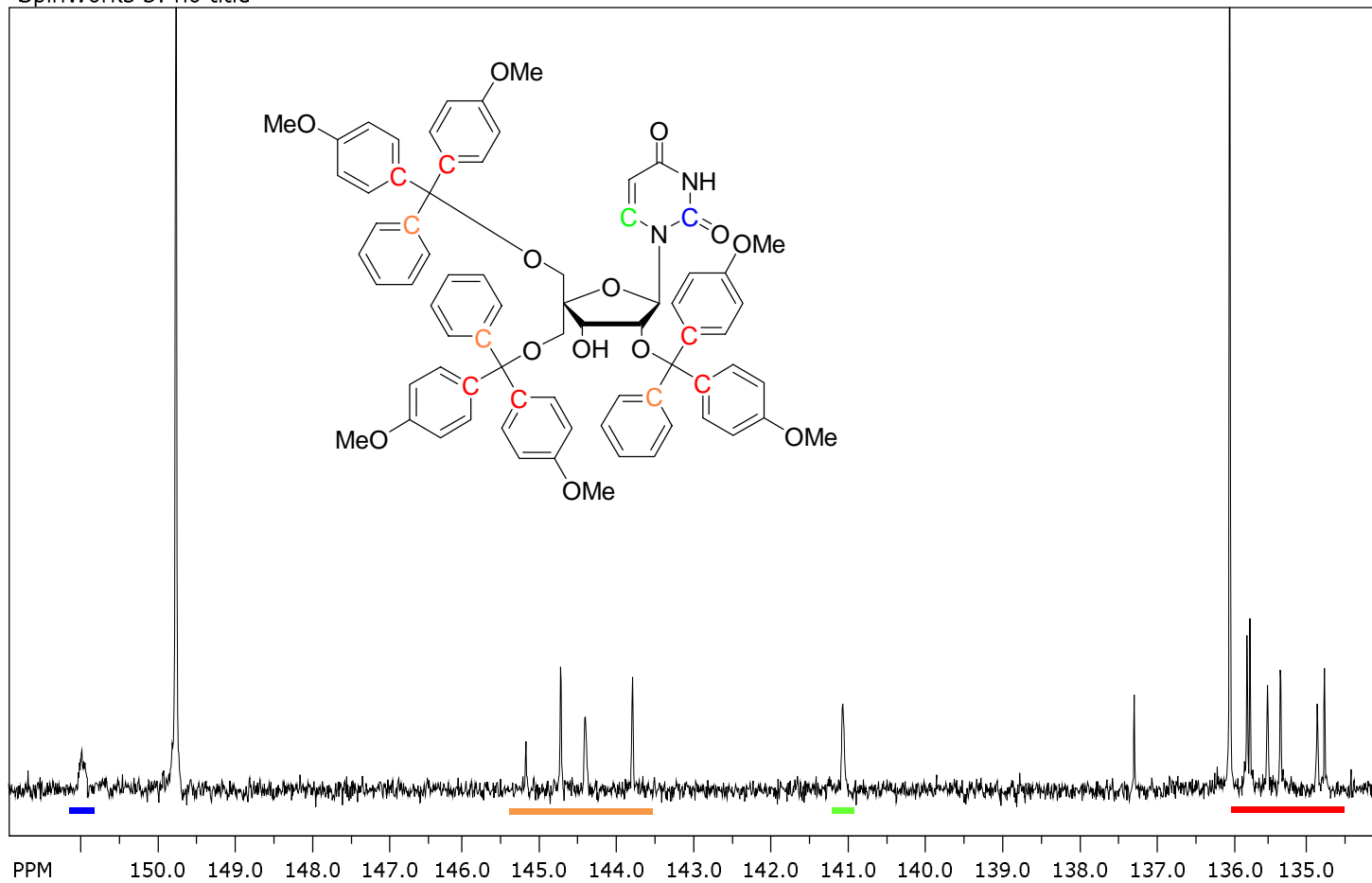
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 37.473 ppm/cm: 0.24830

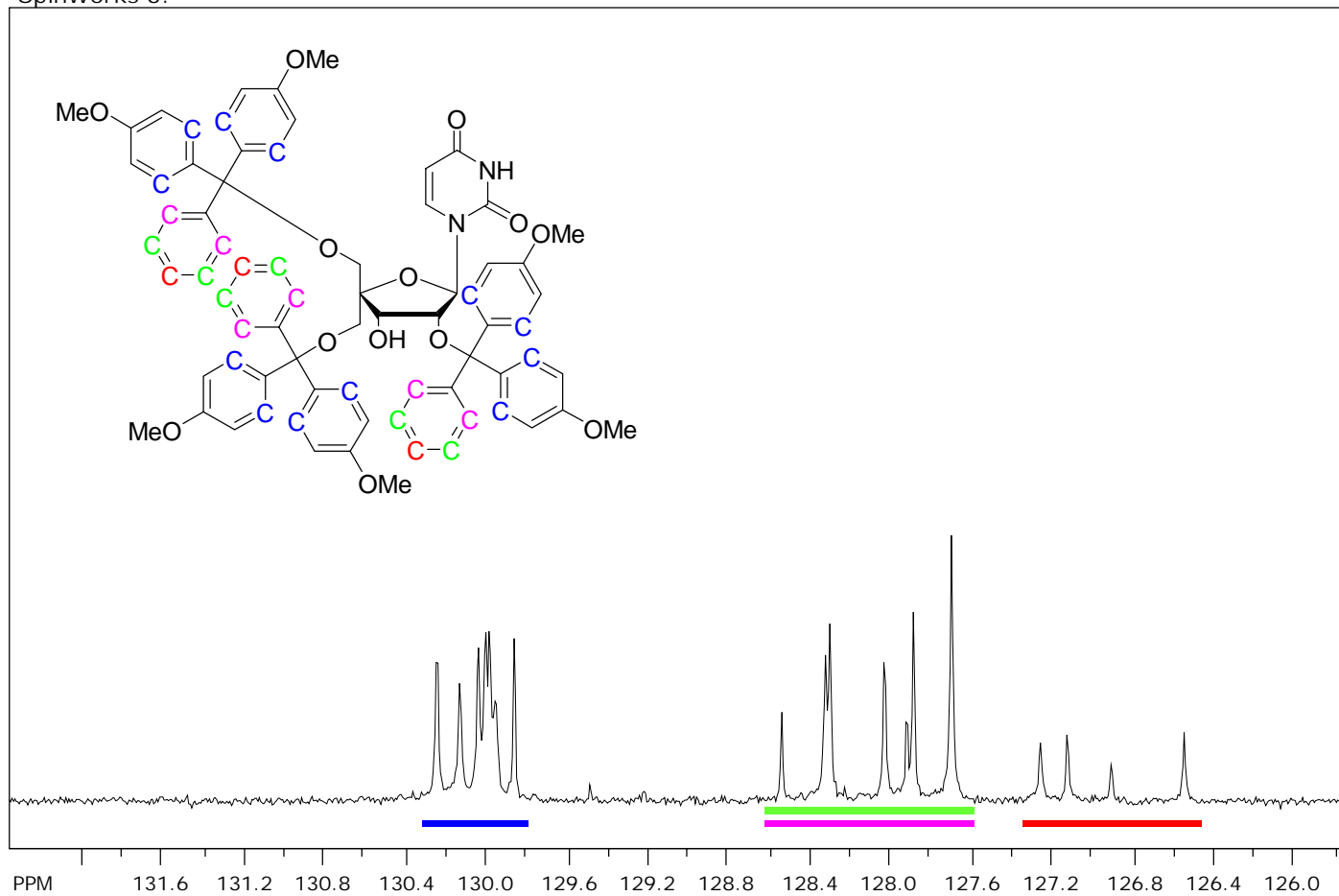
SpinWorks 3: no title



file: ...-5'' tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 108.534 ppm/cm: 0.71916

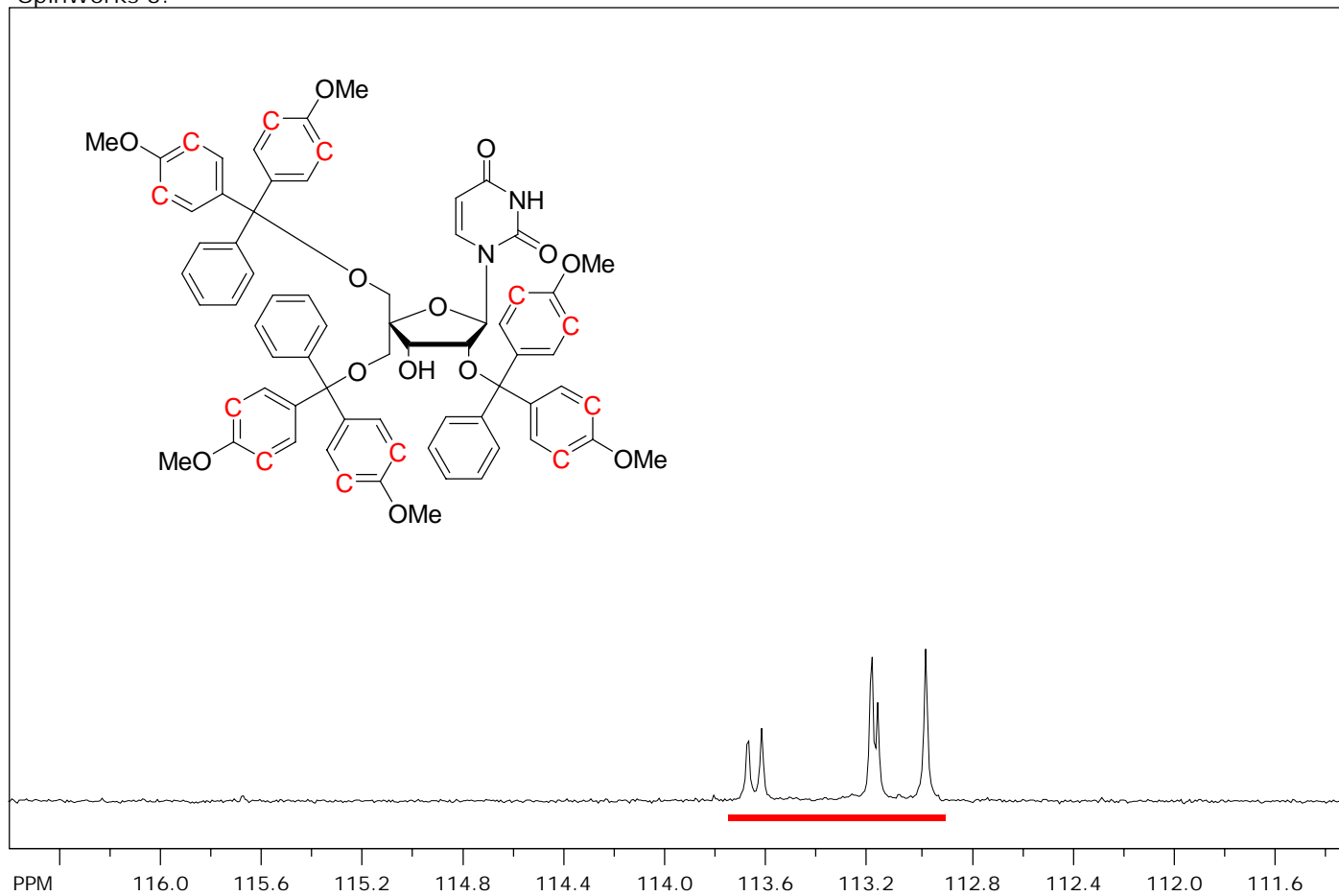
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\2\fid expt: <zgpg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 41.843 ppm/cm: 0.27725

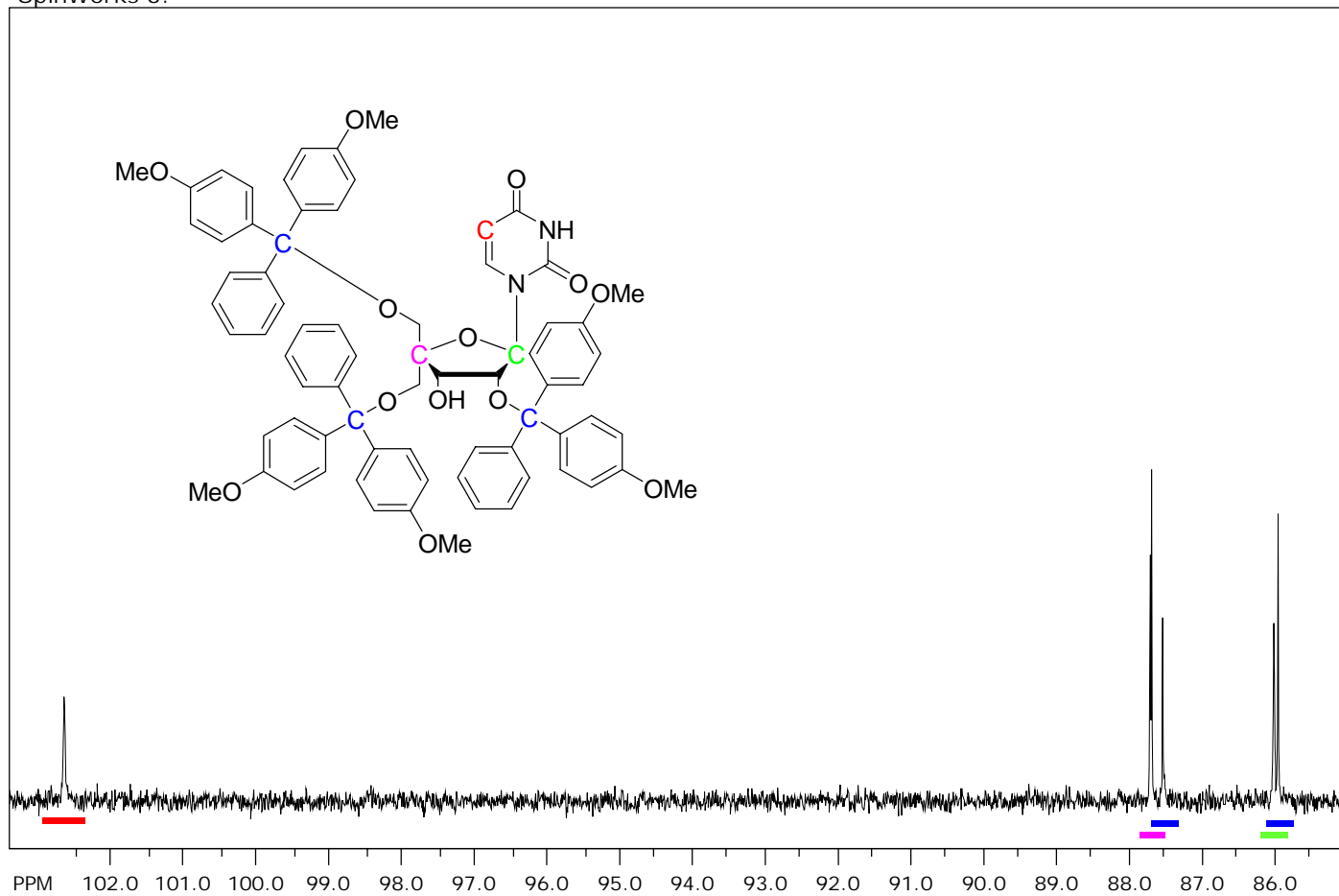
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\2\fid expt: <zpgp30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 33.322 ppm/cm: 0.22079

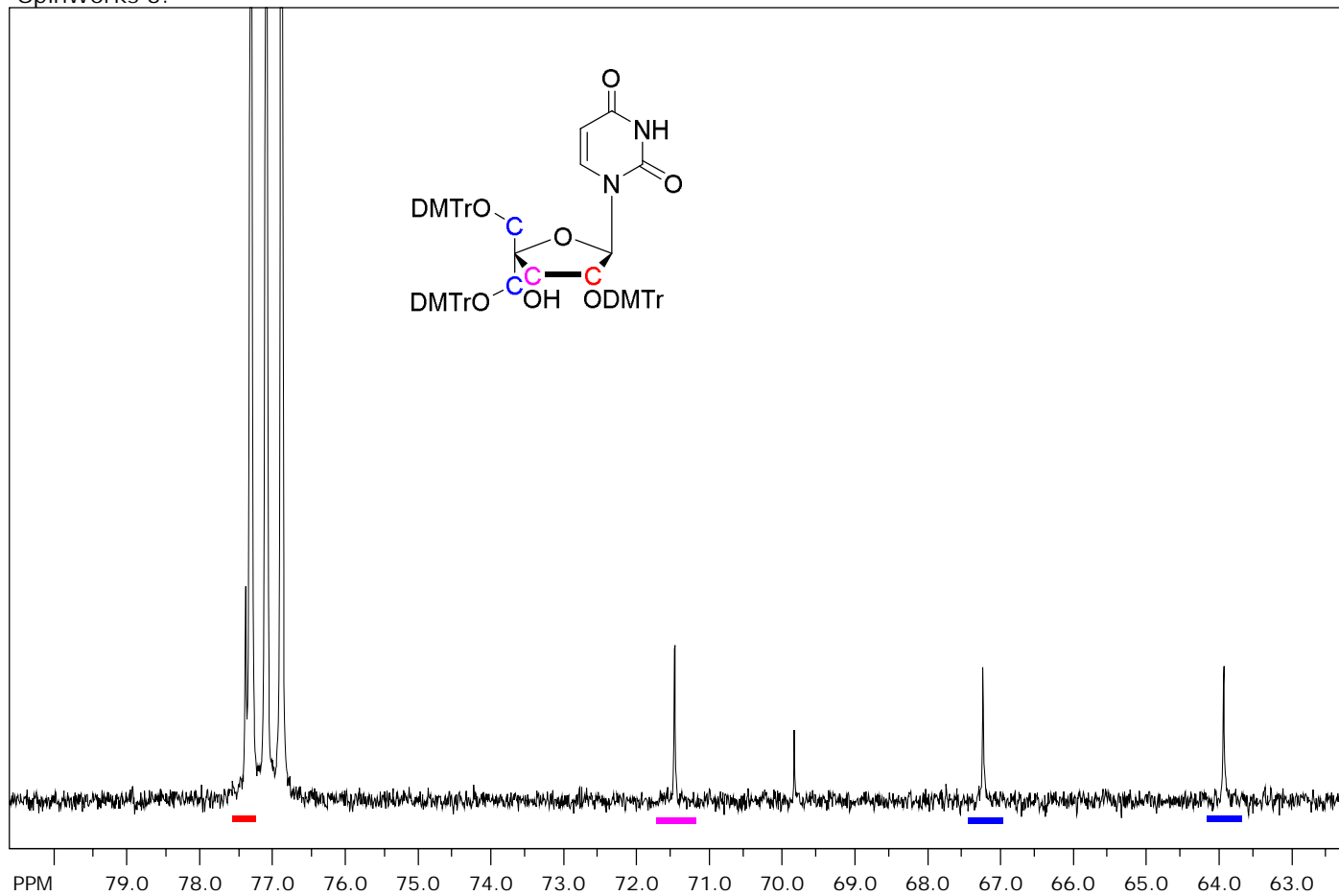
SpinWorks 3:



file: ...-5" tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 116.449 ppm/cm: 0.77161

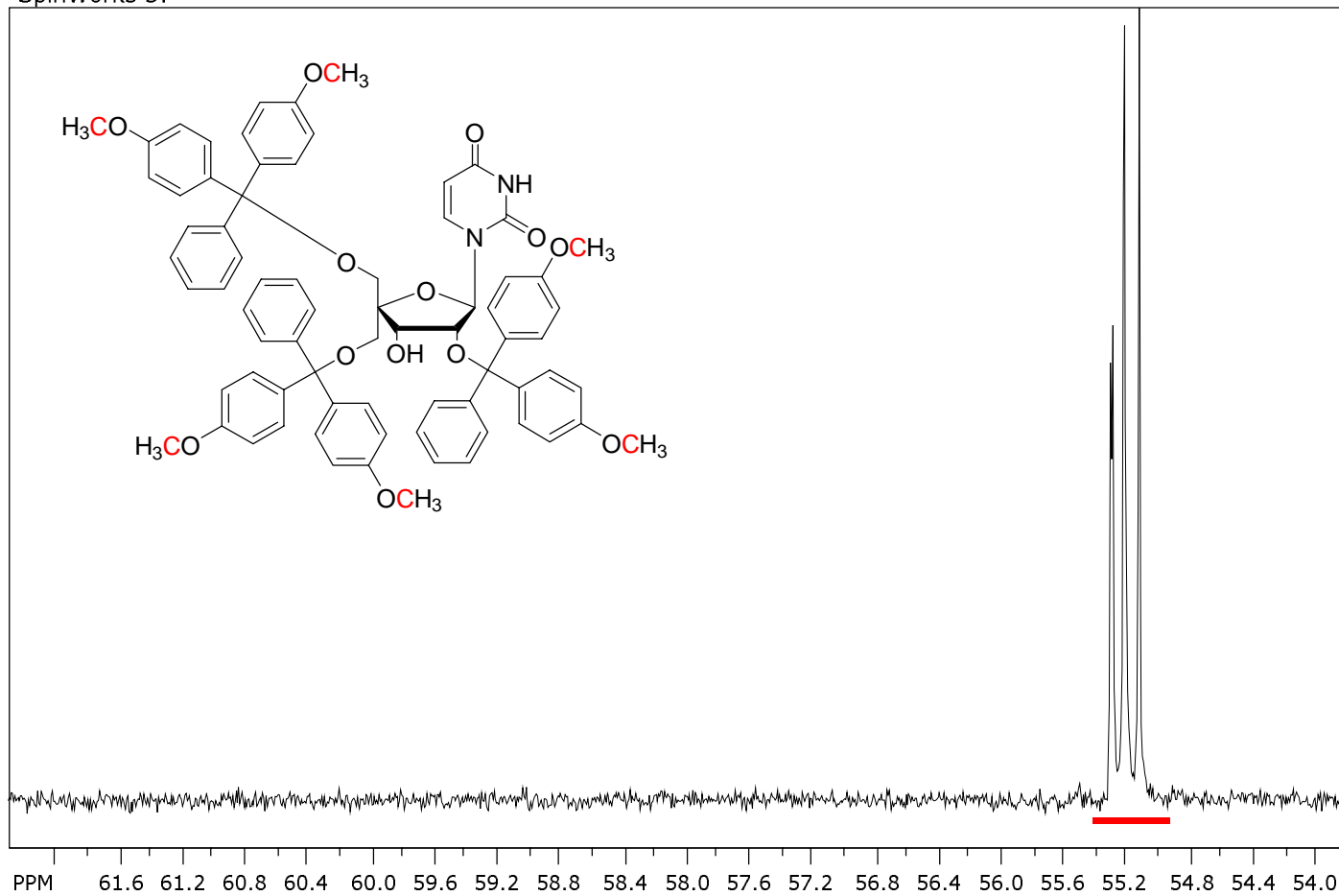
SpinWorks 3:



file: ...'-5" tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 116.449 ppm/cm: 0.77161

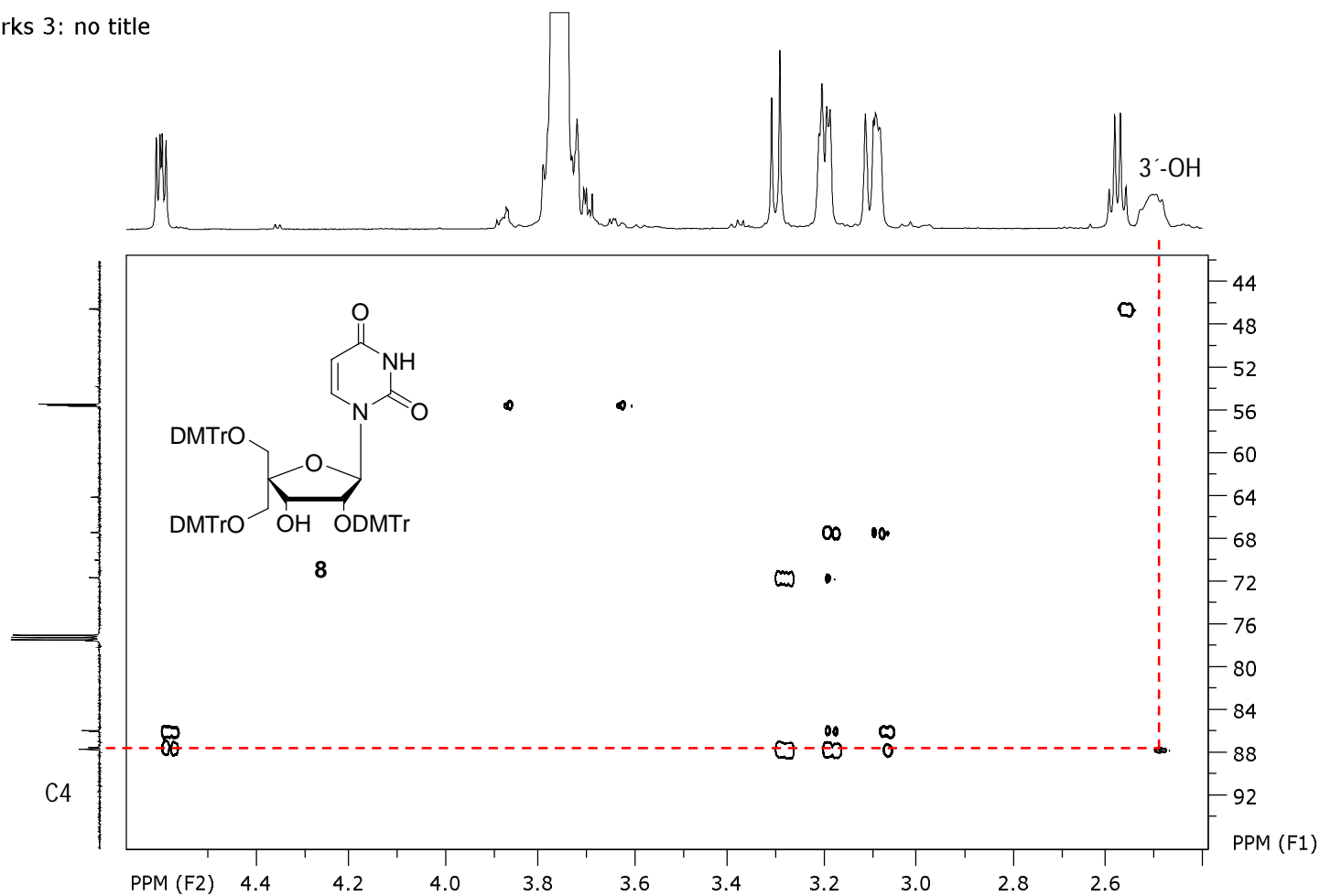
SpinWorks 3:



file: ...'-5'' tris DMTr\LL366-250713\2\fid expt: <zpgg30>
transmitter freq.: 150.917899 MHz
time domain size: 65536 points
width: 35971.22 Hz = 238.3496 ppm = 0.548877 Hz/pt
number of scans: 812

freq. of 0 ppm: 150.902808 MHz
processed size: 32768 complex points
LB: 0.500 GF: 0.0000
Hz/cm: 53.678 ppm/cm: 0.35567

SpinWorks 3: no title

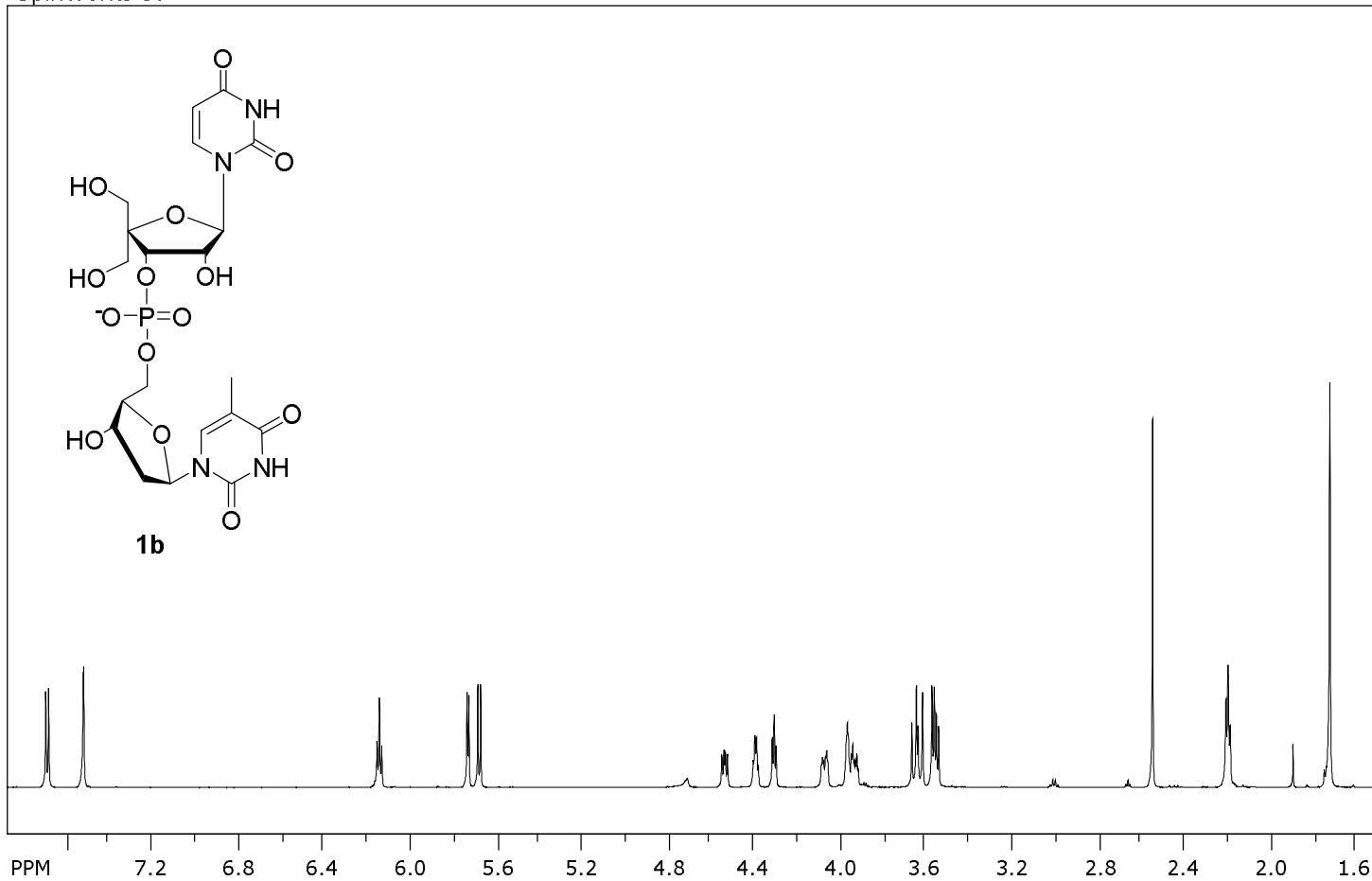


file: ...-5'' tris DMTr\LL366-250713\5\ser
expt: <hmbcgp1pndqf>
transmitter freq: 600.132581 MHz
time domain size: 4096 by 256 points
width (F2): 4807.69 Hz = 8.0111 ppm = 1.1738 Hz/pt
number of scans: 6

F2: freq. of 0 ppm: 600.1300106 MHz
processed size: 2048 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 68.598 ppm/cm: 0.11430

F1: freq. of 0 ppm: 150.9027969 MHz
processed size: 1024 complex points
window function: Sine
shift: 0.0 degrees
Hz/cm: 761.671 ppm/cm: 5.04697

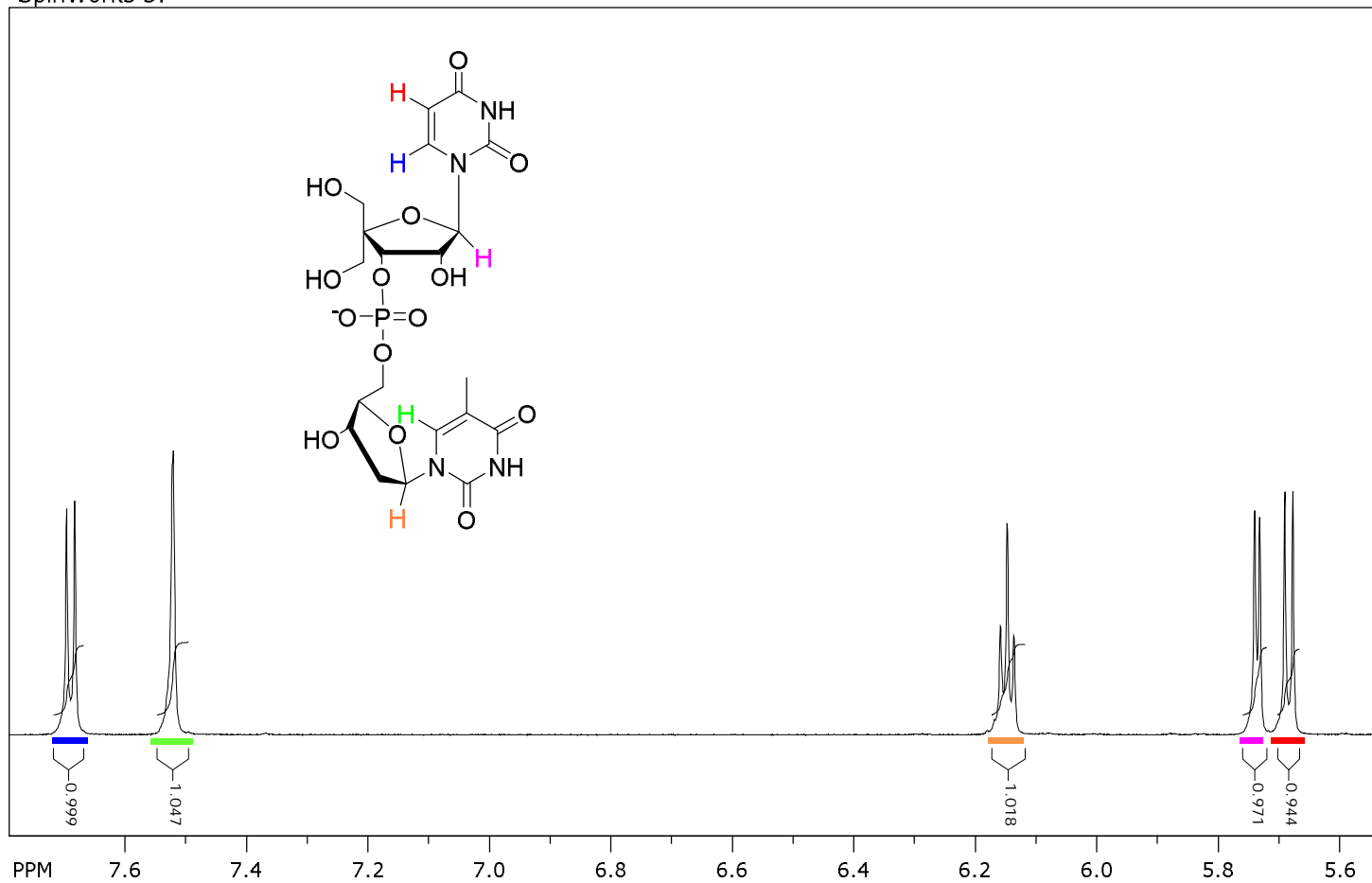
SpinWorks 3:



file: ...399-300614 (proton, cosy, P)\1\fid exp: <zgpr>
transmitter freq.: 600.132821 MHz
time domain size: 32768 points
width: 7309.94 Hz = 12.1805 ppm = 0.223082 Hz/pt
number of scans: 64

freq. of 0 ppm: 600.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 153.903 ppm/cm: 0.25645

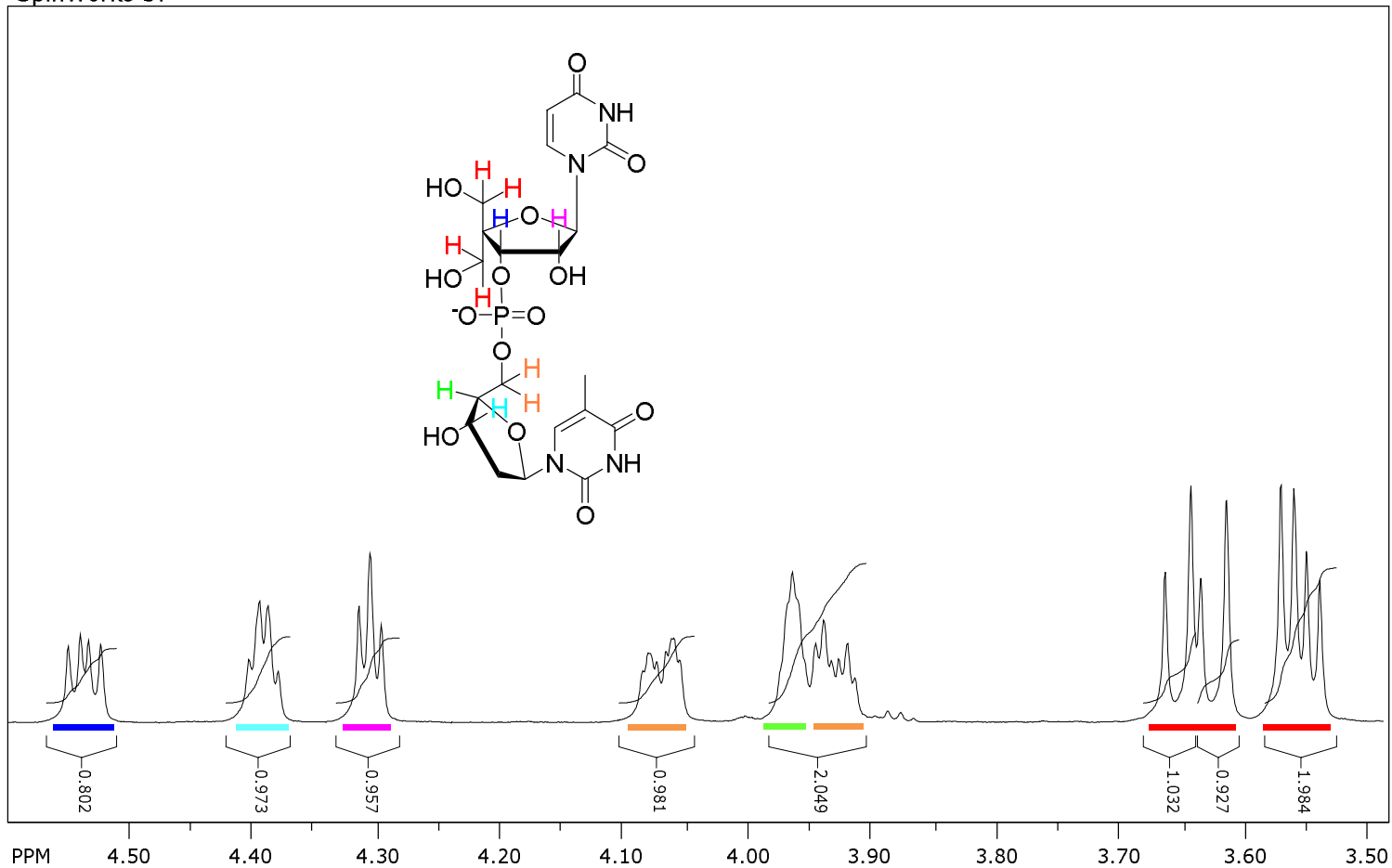
SpinWorks 3:



file: ...399-300614 (proton, cosy, P)\1\fid exp: <zgpr>
transmitter freq.: 600.132821 MHz
time domain size: 32768 points
width: 7309.94 Hz = 12.1805 ppm = 0.223082 Hz/pt
number of scans: 64

freq. of 0 ppm: 600.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 54.581 ppm/cm: 0.09095

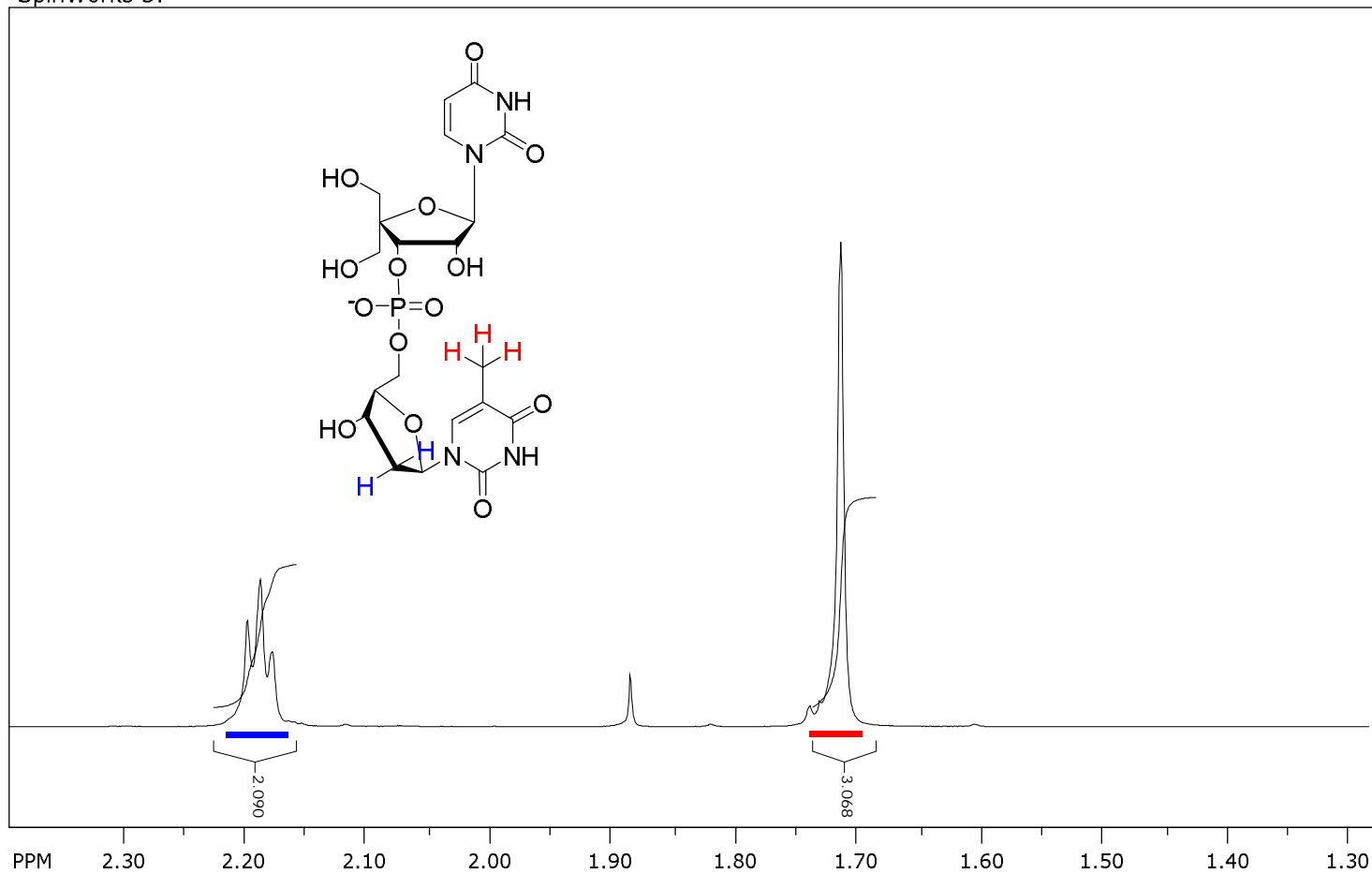
SpinWorks 3:



file: ...399-300614 (proton, cosy, P)\1\fid exp: <zgpr>
 transmitter freq.: 600.132821 MHz
 time domain size: 32768 points
 width: 7309.94 Hz = 12.1805 ppm = 0.223082 Hz/pt
 number of scans: 64

freq. of 0 ppm: 600.130000 MHz
 processed size: 16384 complex points
 LB: 0.000 GF: 0.0000
 Hz/cm: 26.684 ppm/cm: 0.04446

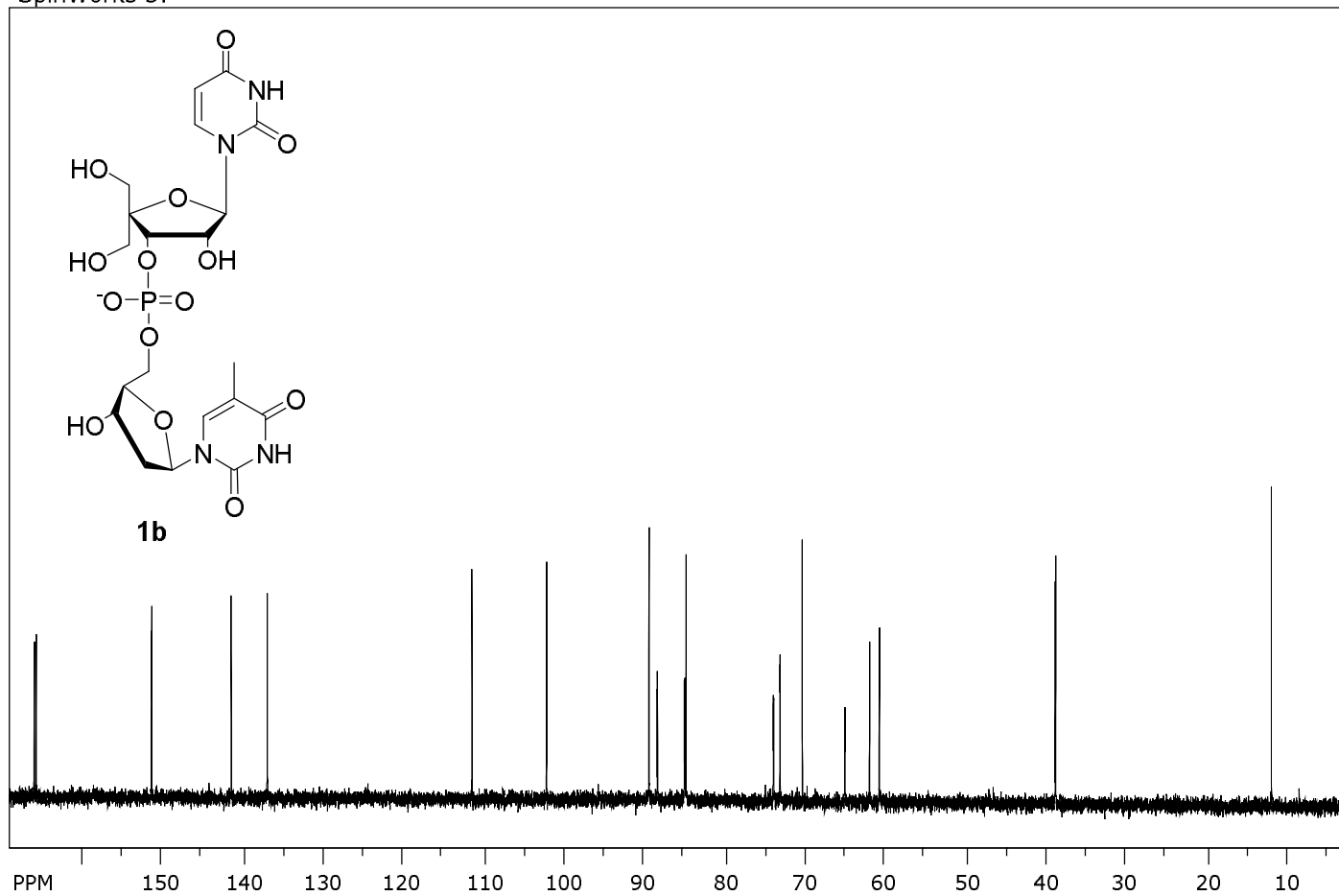
SpinWorks 3:



file: ...399-300614 (proton, cosy, P)\1\fid exp: <zgpr>
transmitter freq.: 600.132821 MHz
time domain size: 32768 points
width: 7309.94 Hz = 12.1805 ppm = 0.223082 Hz/pt
number of scans: 64

freq. of 0 ppm: 600.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 26.684 ppm/cm: 0.04446

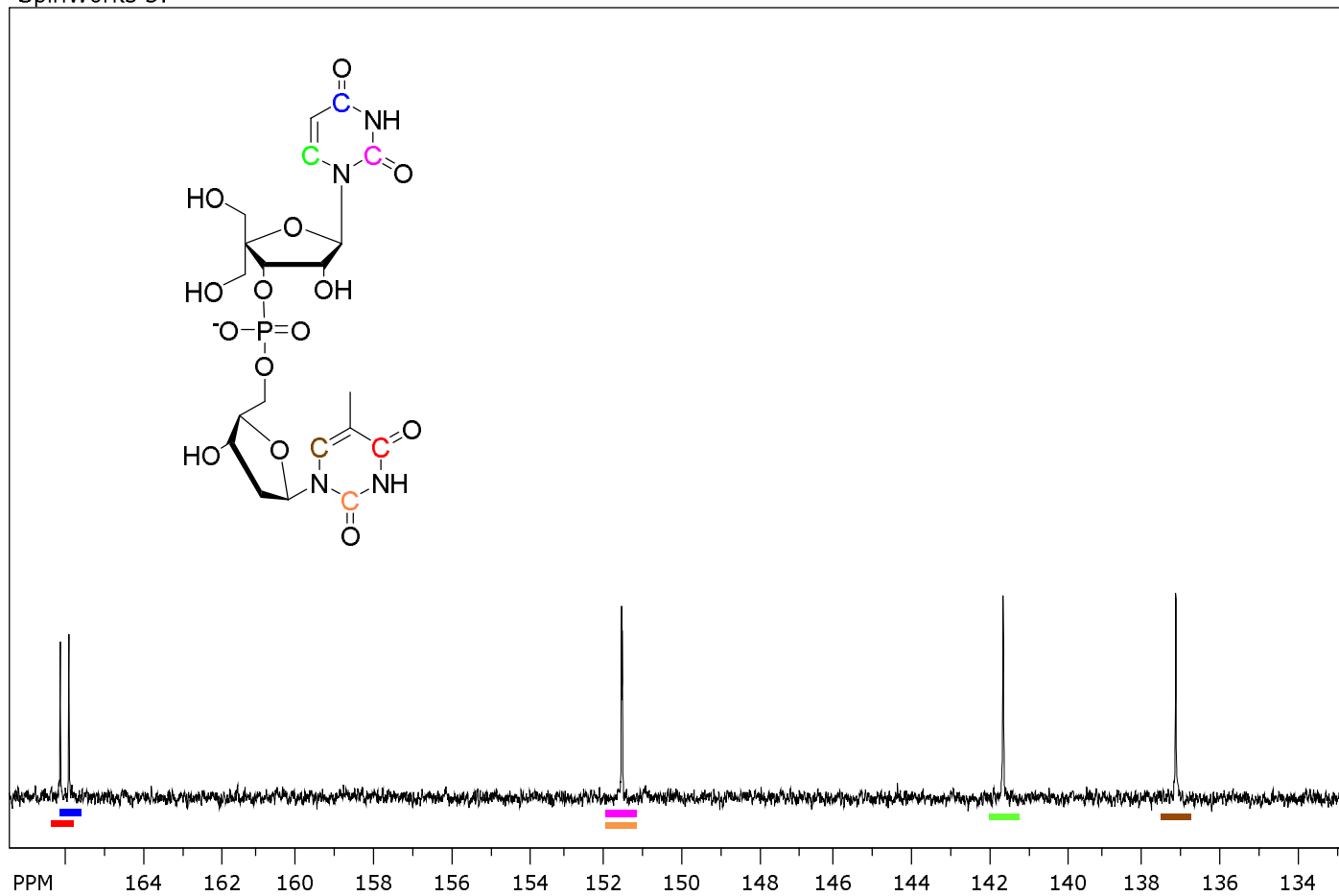
SpinWorks 3:



file: ...\\LL401-030714 (carbon, HSQC)\1\fid exp: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 877.068 ppm/cm: 6.97356

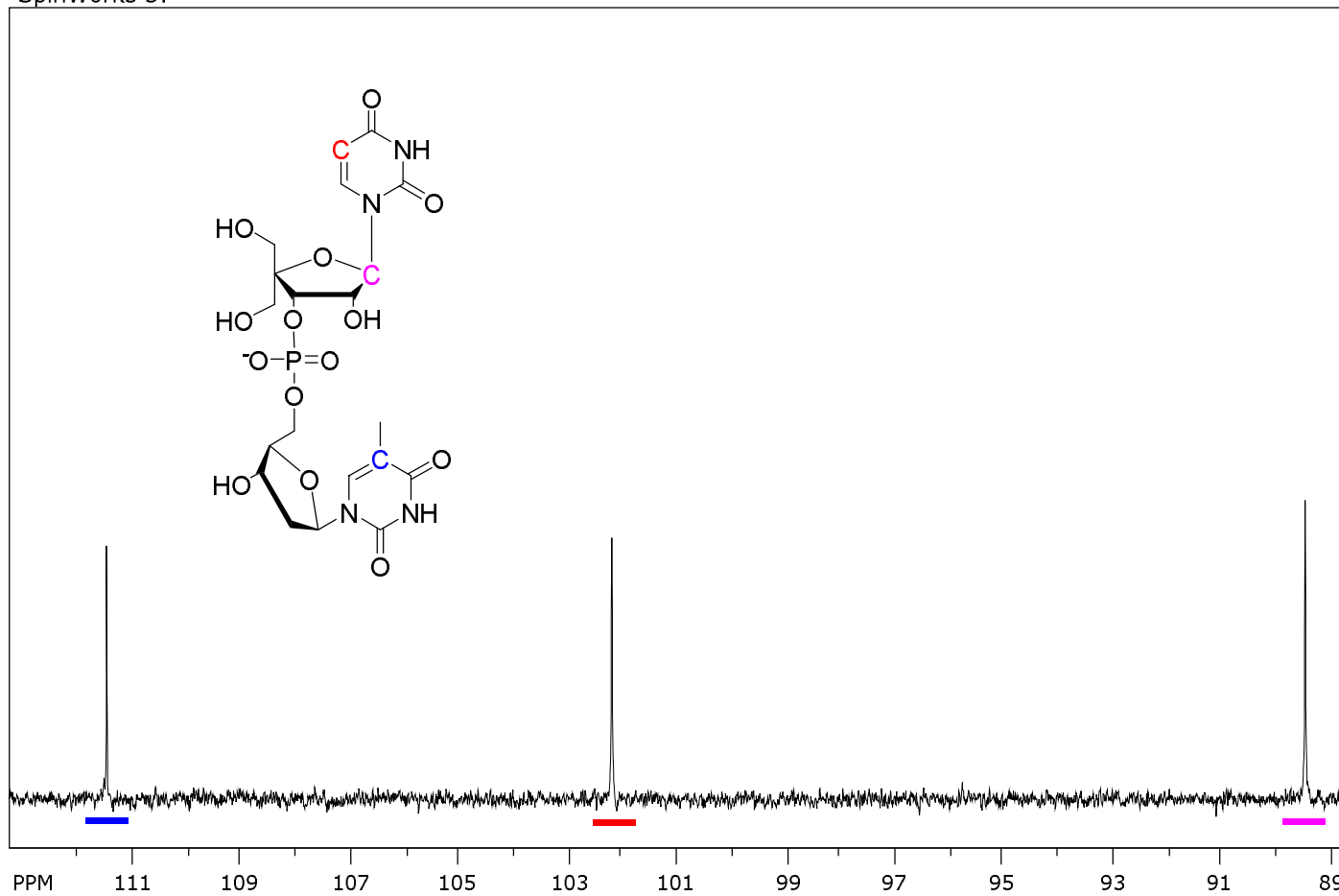
SpinWorks 3:



file: ...\\L401-030714 (carbon, HSQC)\1\fid exp: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 183.210 ppm/cm: 1.45670

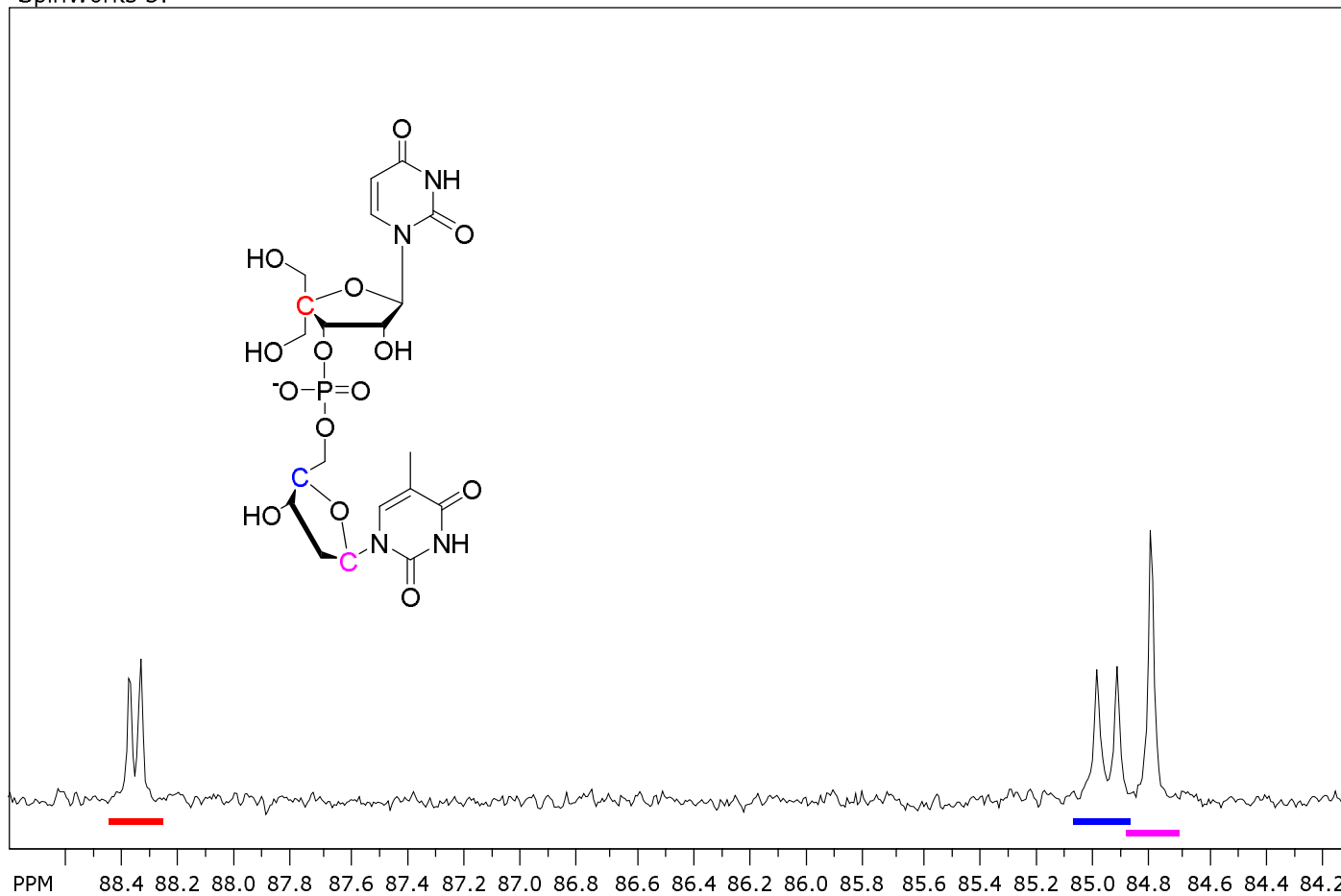
SpinWorks 3:



file: ...\\LL401-030714 (carbon, HSQC)\1\fid expt: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 129.470 ppm/cm: 1.02941

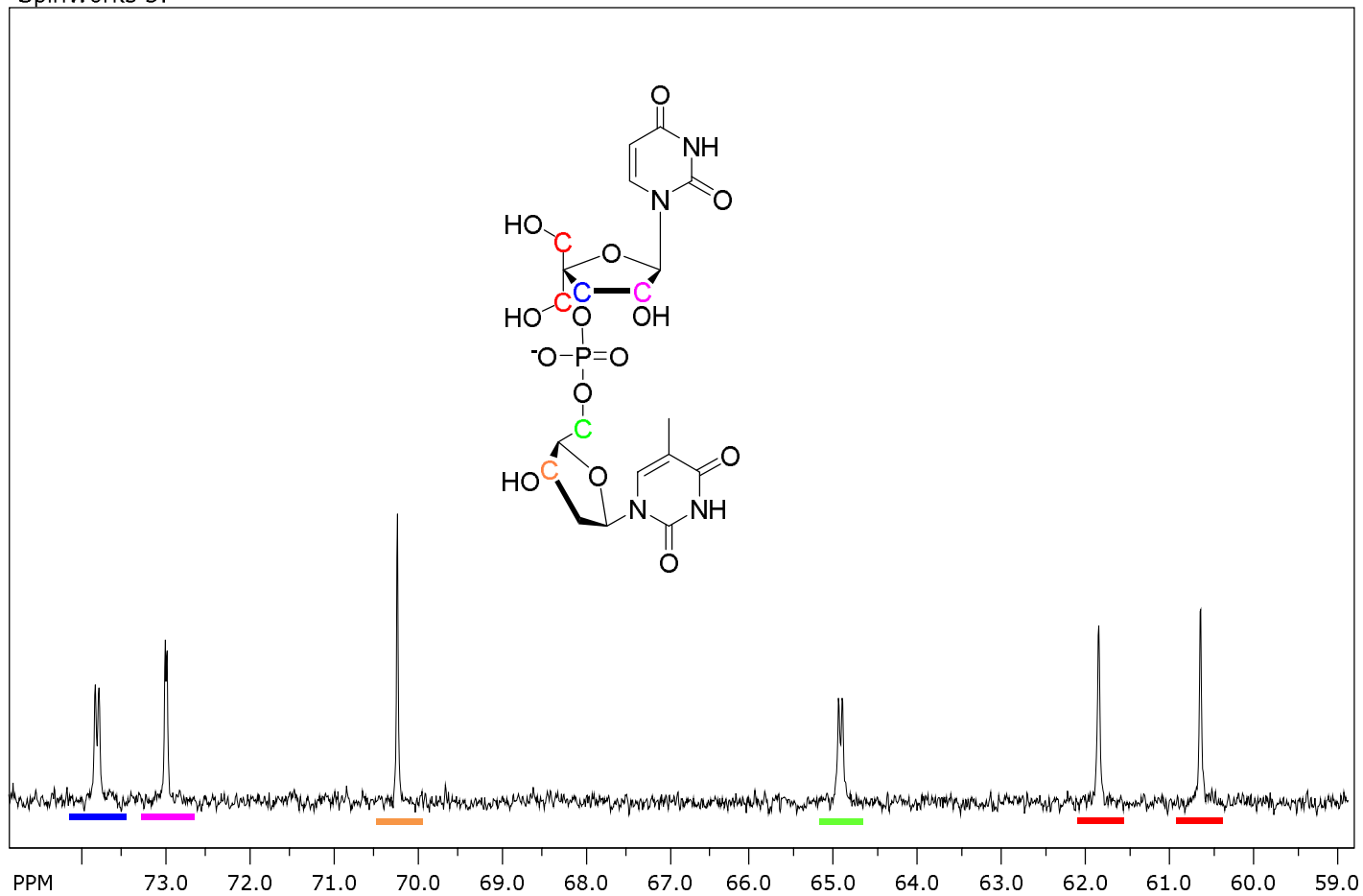
SpinWorks 3:



file: ...\\LL401-030714 (carbon, HSQC)\1\fid expt: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 24.661 ppm/cm: 0.19608

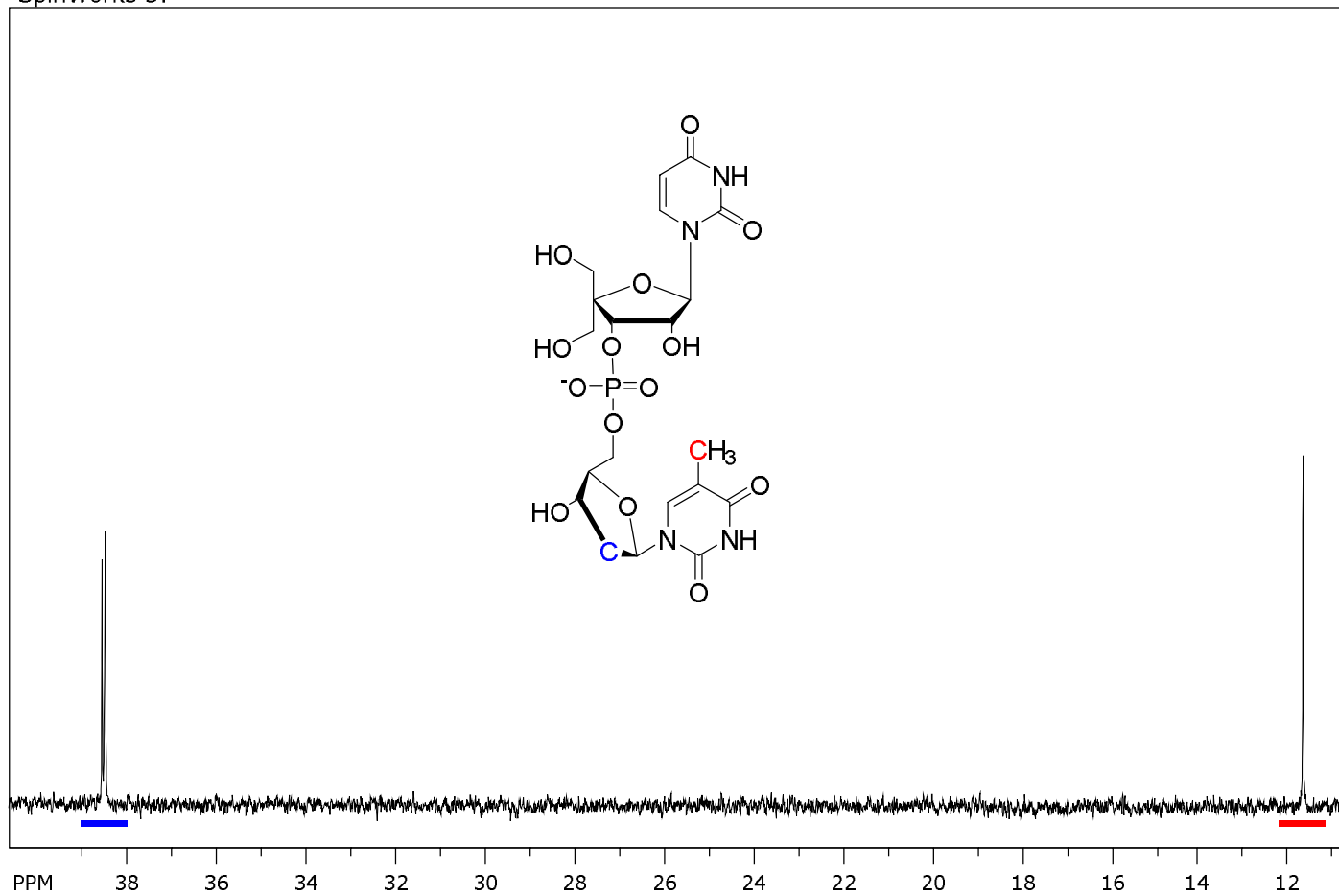
SpinWorks 3:



file: ...\\LL401-030714 (carbon, HSQC)\1\fid expt: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 84.211 ppm/cm: 0.66956

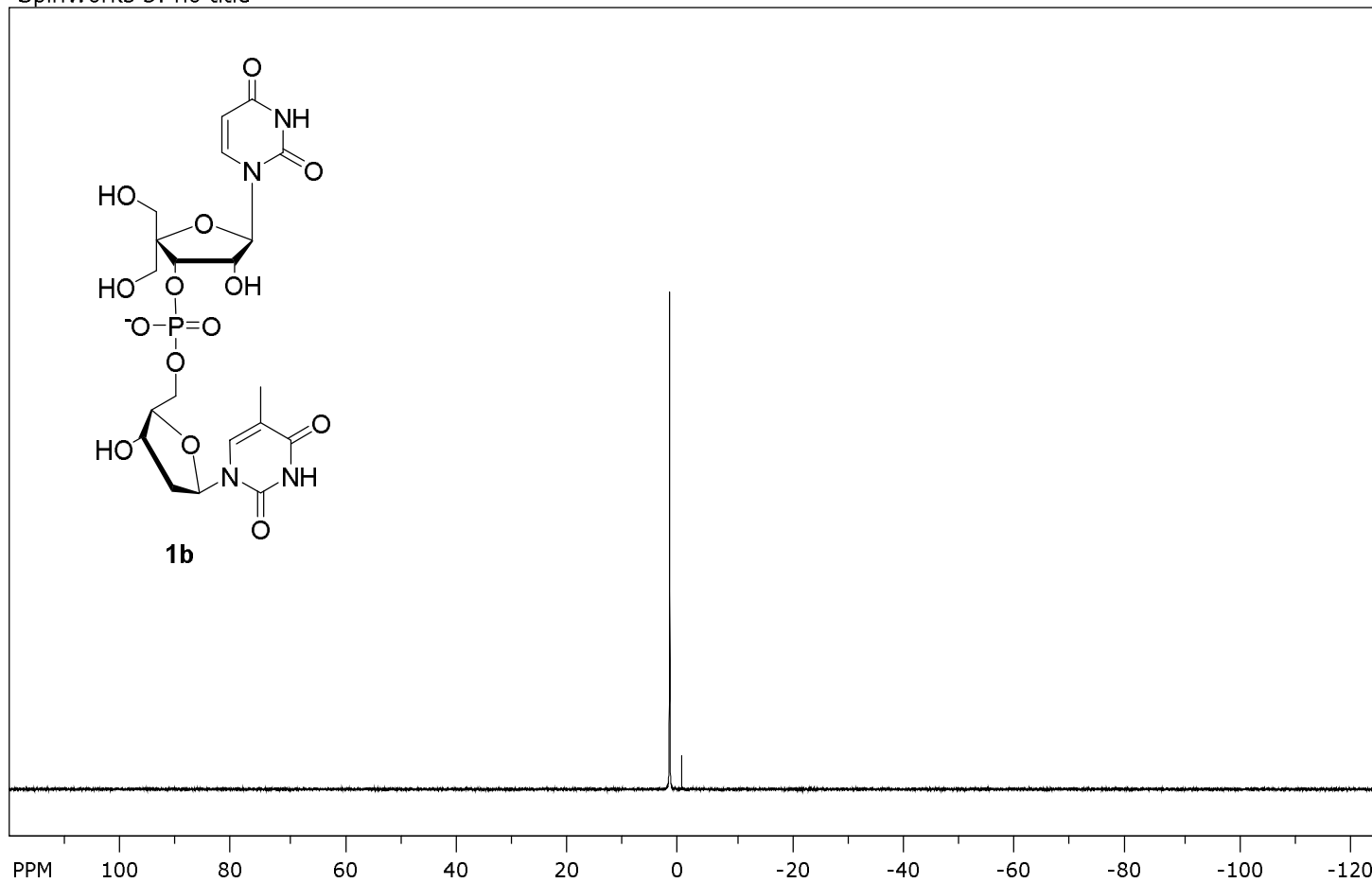
SpinWorks 3:



file: ...\\LL401-030714 (carbon, HSQC)\1\fid expt: <ph_zgpg45>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 20000

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 157.927 ppm/cm: 1.25567

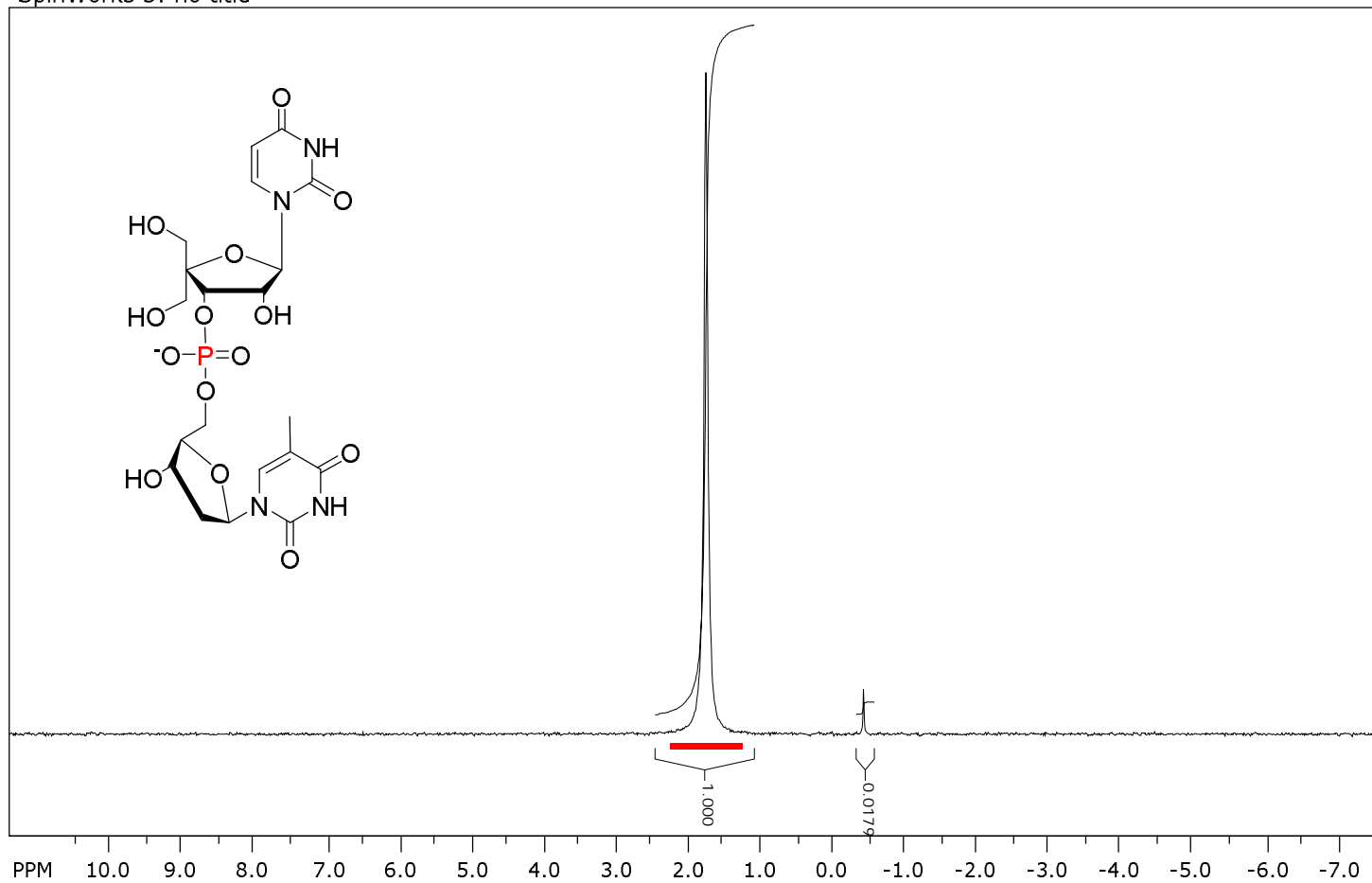
SpinWorks 3: no title



file: ...399-300614 (proton, cosy, P)\2\fid exp: <zgpg30>
transmitter freq.: 242.924900 MHz
time domain size: 65536 points
width: 97087.38 Hz = 399.6601 ppm = 1.481436 Hz/pt
number of scans: 32

freq. of 0 ppm: 242.937047 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 2399.137 ppm/cm: 9.87604

SpinWorks 3: no title



file: ...399-300614 (proton, cosy, P)\2\fid exp: <zgpg30>
transmitter freq.: 242.924900 MHz
time domain size: 65536 points
width: 97087.38 Hz = 399.6601 ppm = 1.481436 Hz/pt
number of scans: 32

freq. of 0 ppm: 242.937047 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 185.838 ppm/cm: 0.76500

Table S1 Observed rate constants for the cleavage and isomerization of 1b; $T = 90\text{ }^{\circ}\text{C}$; $I(\text{NaClO}_4) = 0.1\text{ mol L}^{-1}$.

Buffer	[HA] : [A]	[Buffer] / mol L ⁻¹	pH	$k_{\text{obs}}^{\text{civ}} / 10^{-7} \text{ s}^{-1}$	$\log(k^{\text{civ}} / \text{s}^{-1})$	$k_{\text{obs}}^{\text{iso}} / 10^{-5} \text{ s}^{-1}$	$\log(k^{\text{iso}} / \text{s}^{-1})$	
HClO ₄	N/A	0.98	0.02	345000 ^a	-1.46	604 ^a	-1.92	
		0.30	0.53	73100 ^a	-2.14	366 ^a	-2.21	
		0.10	1	18000 ^a	-2.74	99.6 ^a	-3.02	
		0.10	1	9690	-3.04	76.3	-3.12	
		0.03	1.52	1450	-3.89	13.6	-3.75	
		0.01	2	178	-4.75	1.77	-4.65	
		0.003	2.52	25.0	-5.65	0.426	-5.12	
Formic acid	4 : 1	0.10		16.0		0.536		
		0.03		6.85		0.277		
		0.01		3.79		0.209		
			3.10		-6.63 ^b		-5.48 ^b	
Acetic acid	1 : 1	0.10		1.86		0.193		
		0.03		0.901		0.160		
		0.01		0.932		0.145		
				4.81		-7.15 ^b		-5.55 ^b
	2 : 3	0.10		1.58		0.181		
		0.03		0.823		0.152		
0.01			0.759		0.144			
			4.98		-7.22 ^b		-5.55 ^b	
Cacodylic acid	1 : 3	0.10		654		14.1		
		0.03		644		14.0		
			6.99		-6.19 ^b		-5.55 ^b	
Glycine	1 : 4	0.10		490				
		0.03		400				
		0.0125		297				
			9.05		-4.48 ^b			
NaOH	N/A	0.01	10.21	8930	-3.04			
		0.10	11.21	88200	-2.04			
		0.10	11.21	201000 ^a	-1.70			
		0.30	11.70	246000 ^a	-1.61			

^a $I = 1.0\text{ mol L}^{-1}$

^b Extrapolated to buffer concentration zero.