Supporting information for

Sulfurization of H-phosphonate diesters by elemental sulfur under aqueous conditions

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Contents

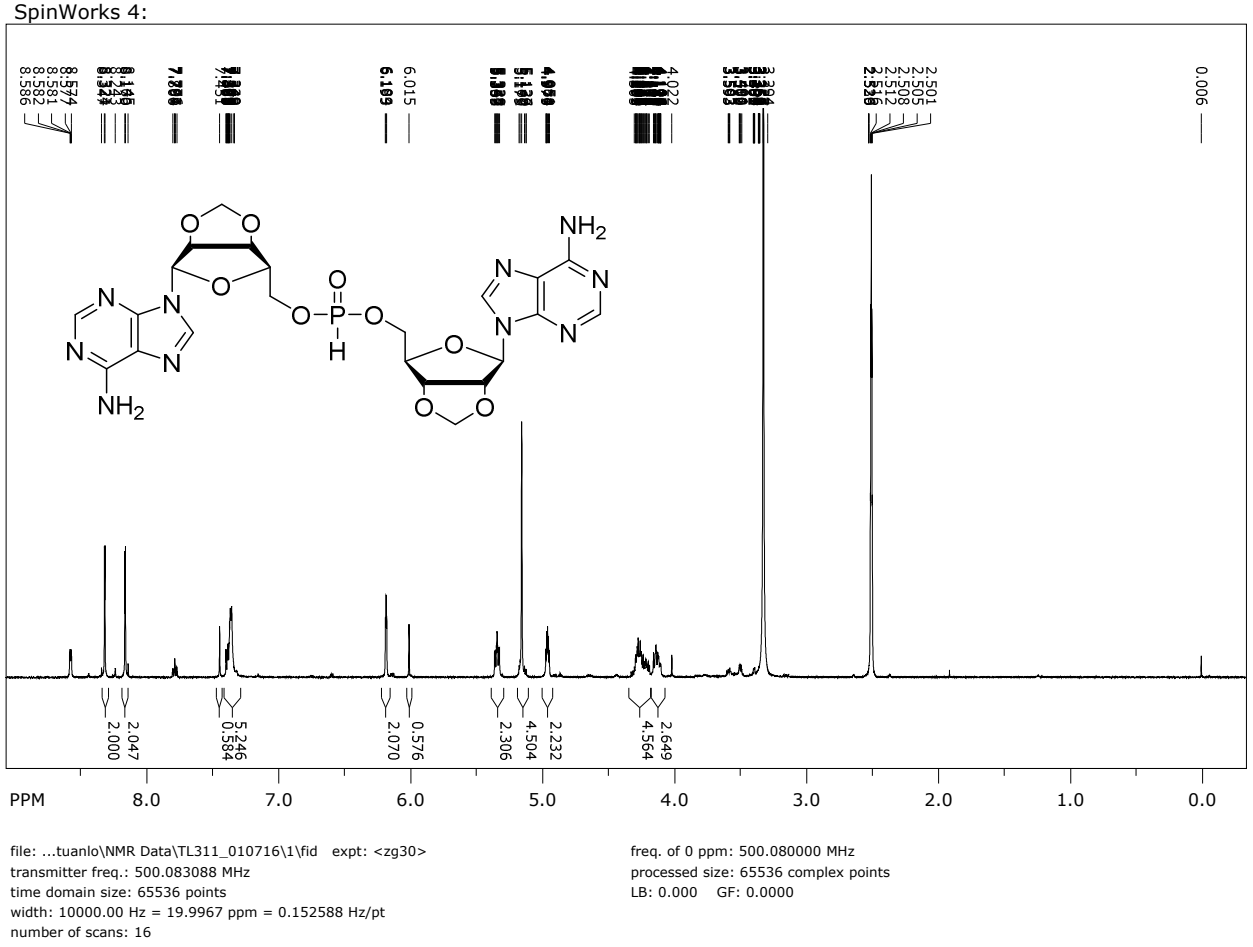

Figure S1 ^{1}H NMR spectrum of bis(2´,3´-*O*-methyleneadenosin-5´-yl)-H-phosphonate (**1h**)

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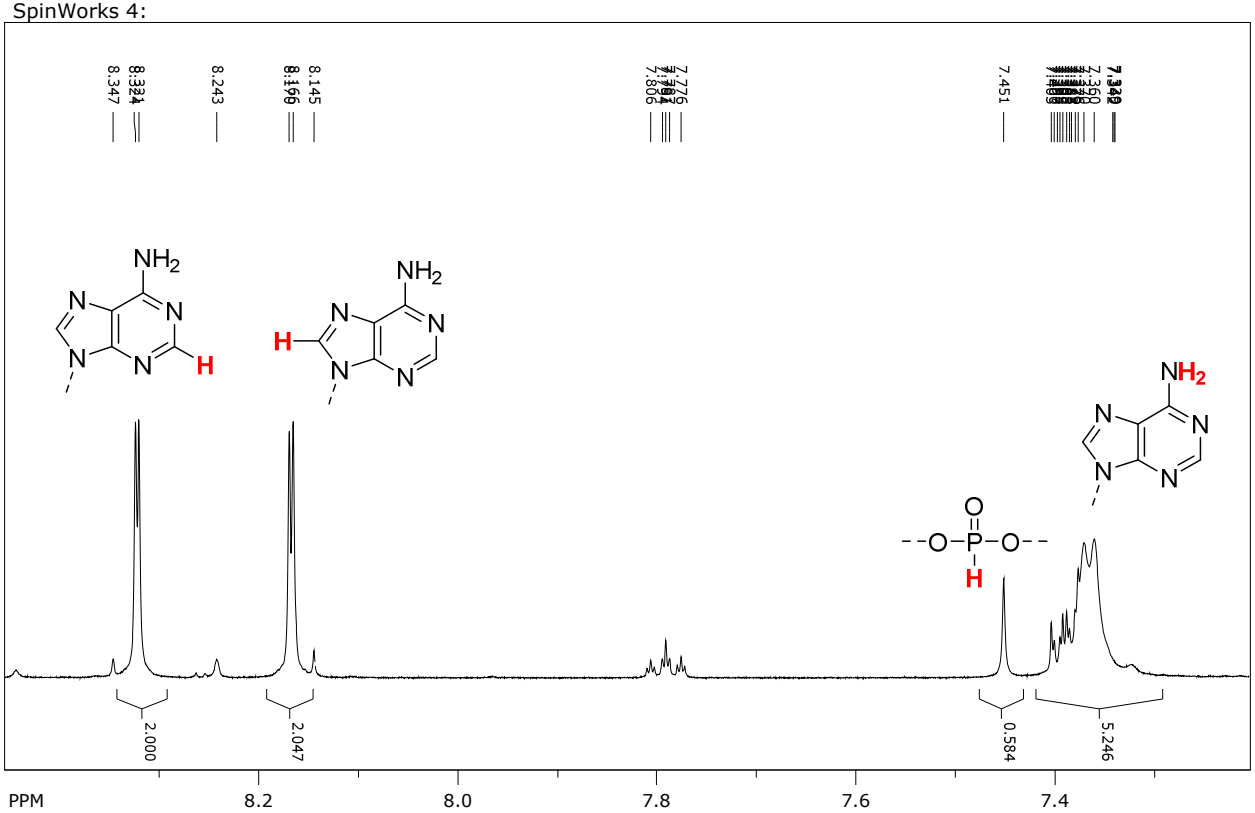

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Figure S1 ^{1}H NMR spectrum of bis(2´,3´-*O*-methyleneadenosin-5´-yl)-H-phosphonate (**1h**) (continued)

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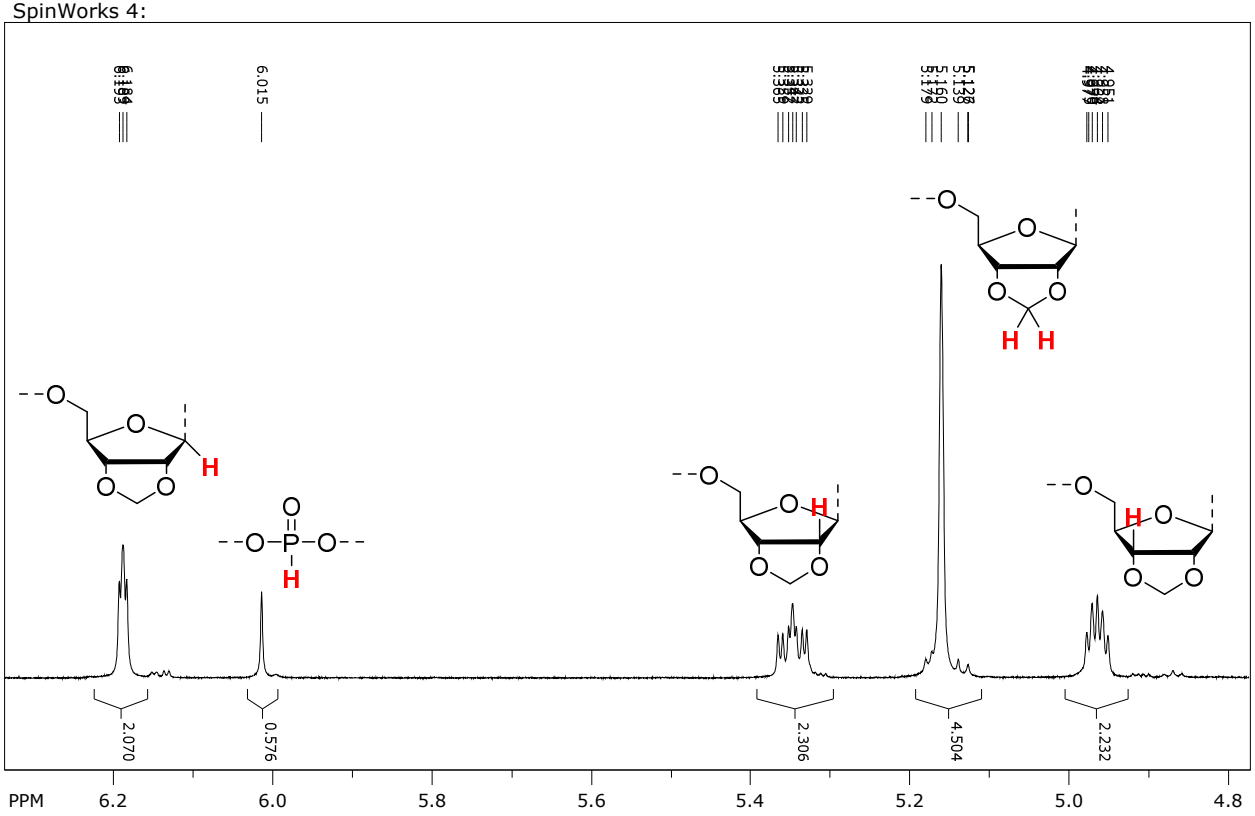

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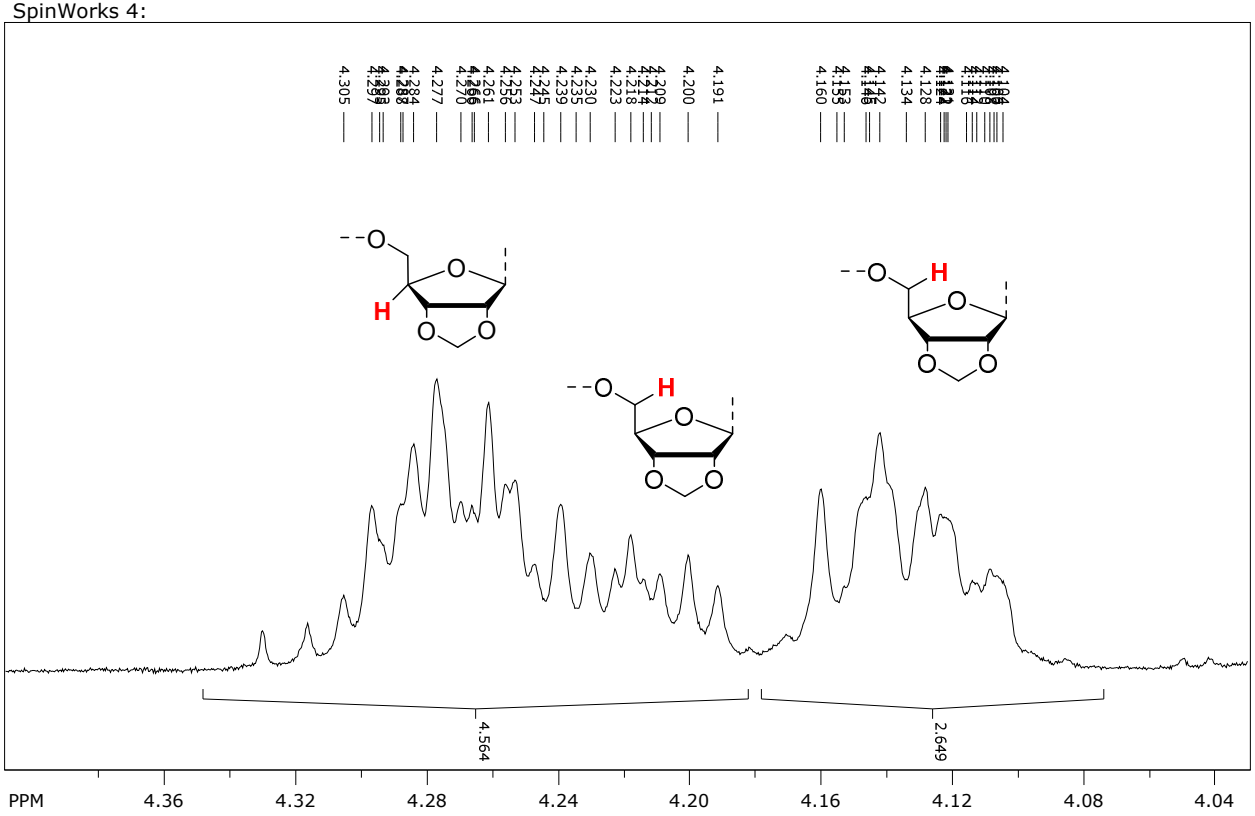

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Figure S1 ^{1}H NMR spectrum of bis(2´,3´-*O*-methyleneadenosin-5´-yl)-H-phosphonate (**1h**) (continued)

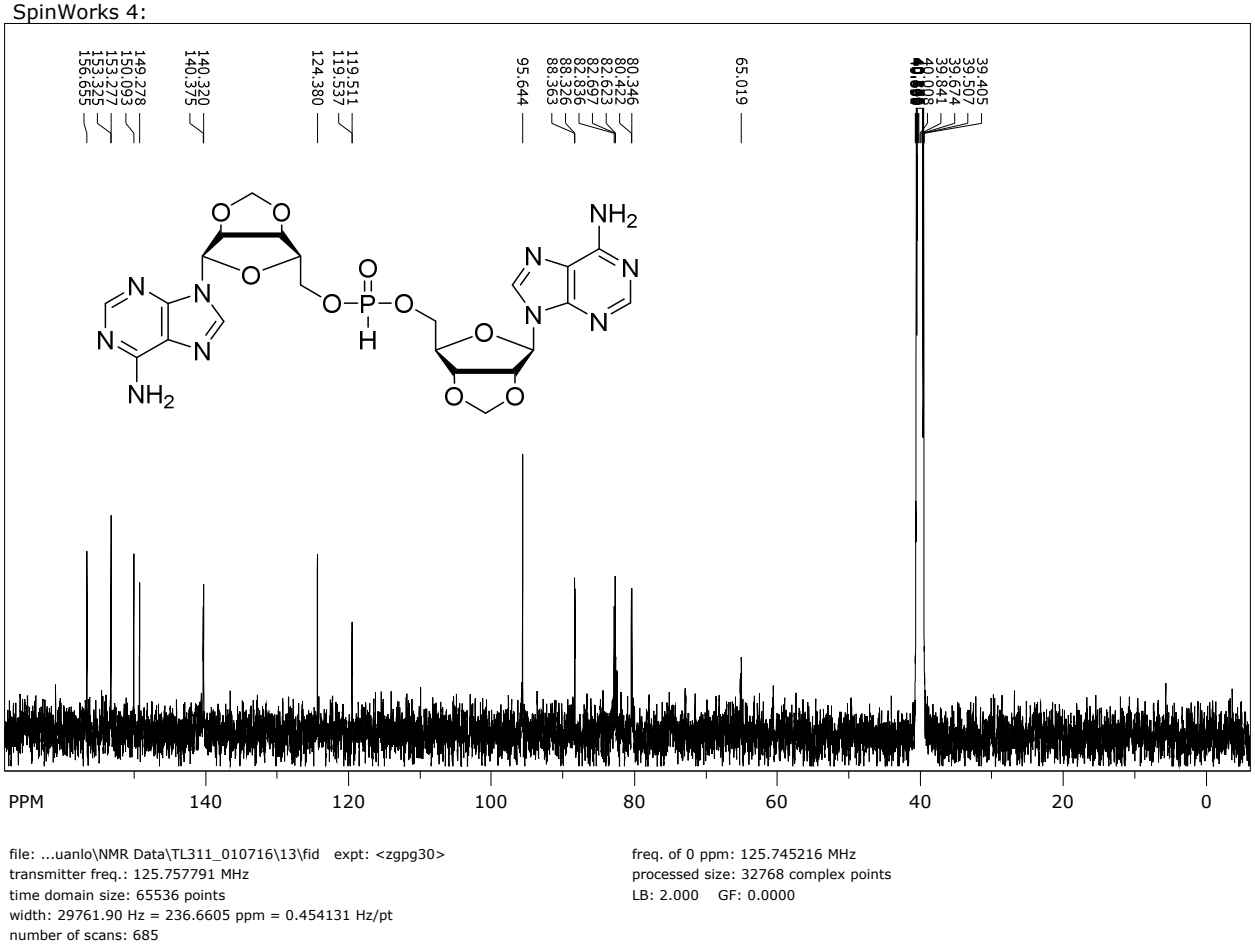

Figure S2 ^{13}C NMR spectrum of bis(2´,3´-*O*-methyleneadenosin-5´-yl)-H-phosphonate (**1h**)

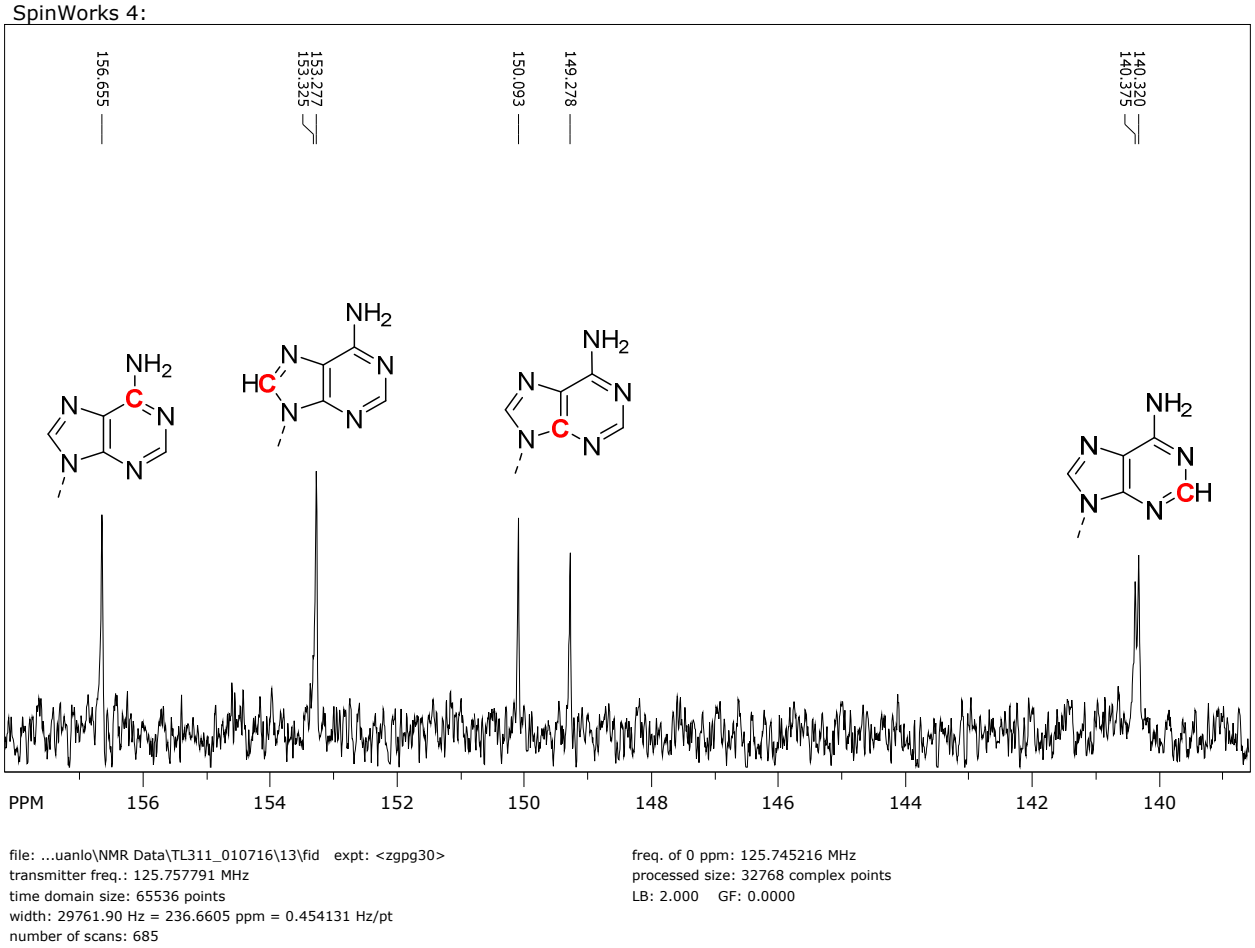

Figure S2 ^{13}C NMR spectrum of bis(2′,3′-*O*-methyleneadenosin-5′-yl)-H-phosphonate (**1h**) (continued)

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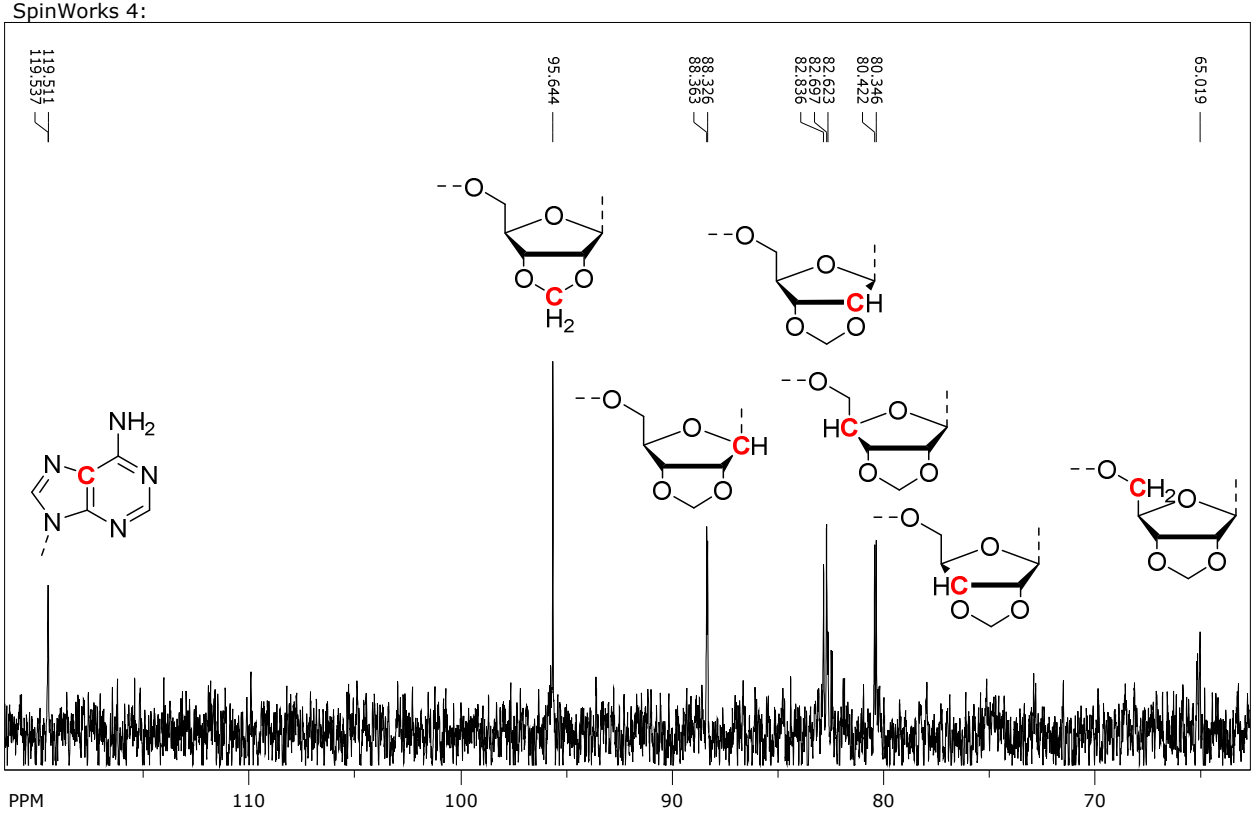

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Figure S2 ^{13}C NMR spectrum of bis(2′,3′-*O*-methyleneadenosin-5′-yl)-H-phosphonate (**1h**) (continued)

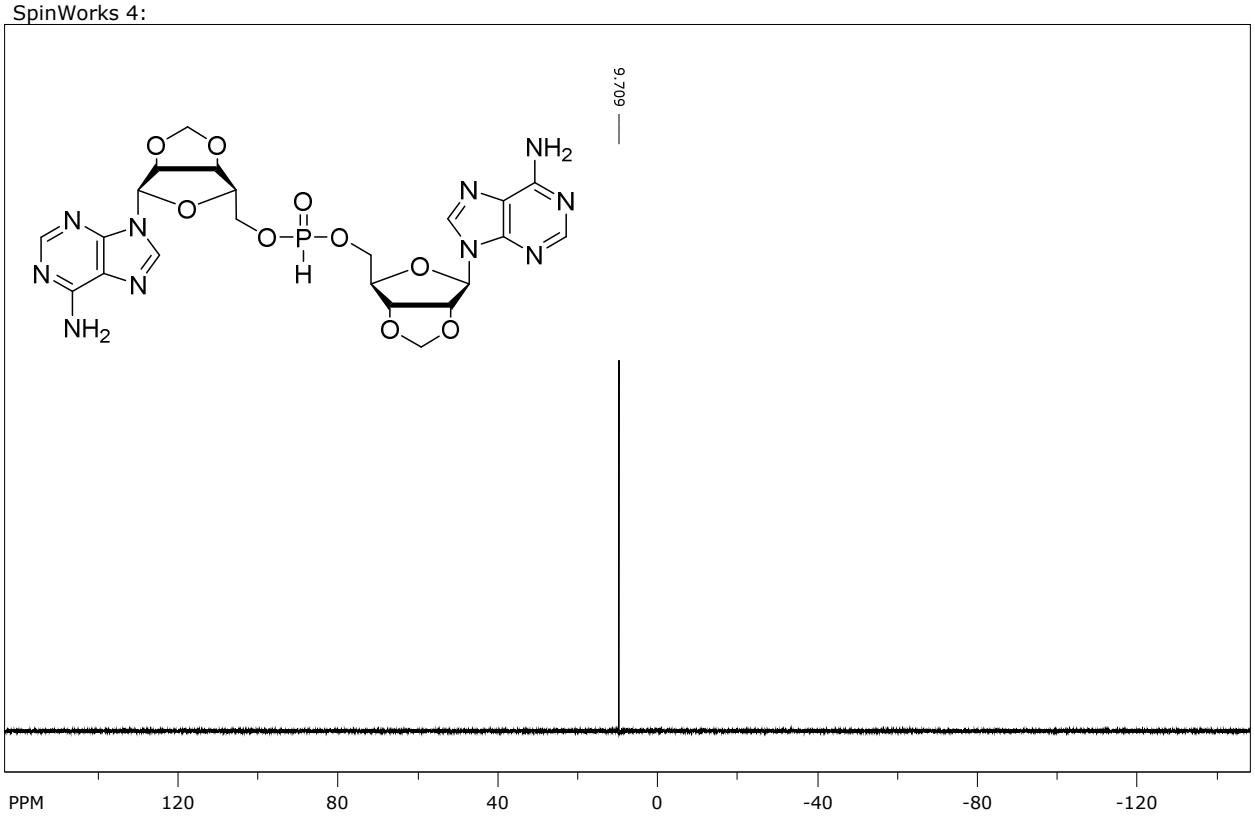

Figure S3 ^{31}P NMR spectrum of bis(2´,3´-*O*-methyleneadenosin-5´-yl)-H-phosphonate (**1h**)

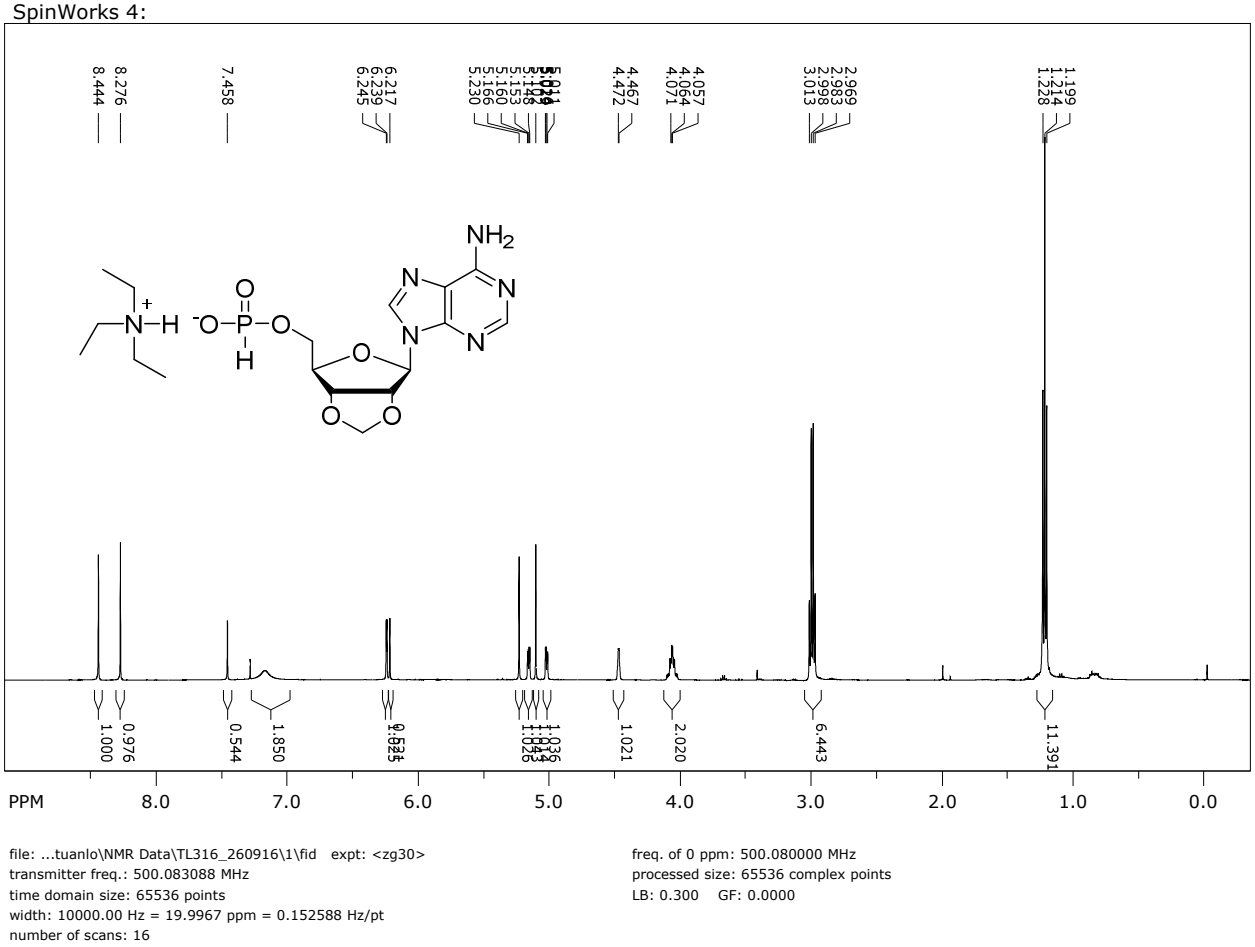

Figure S4 ^{1}H NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**)

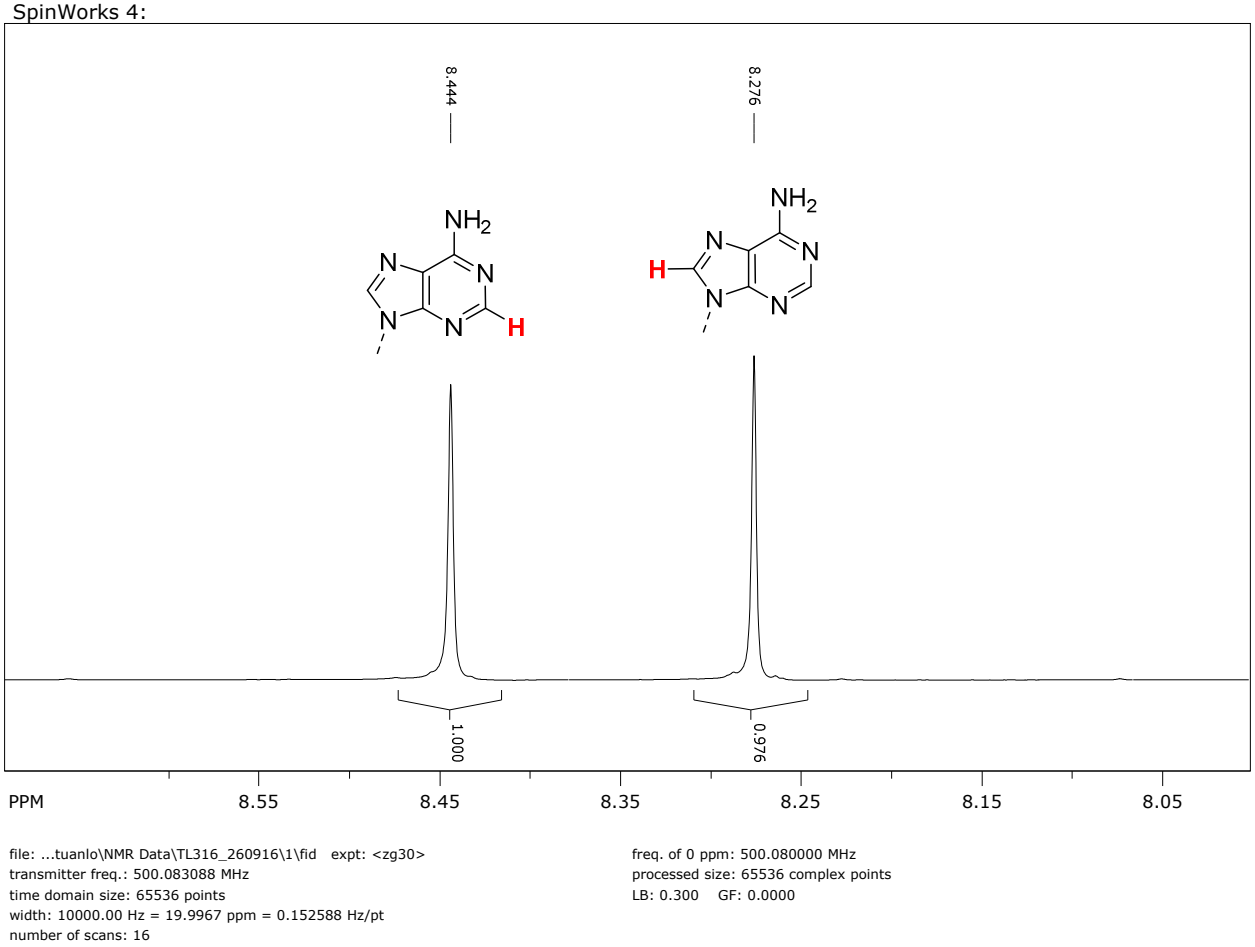

Figure S4 ^{1}H NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

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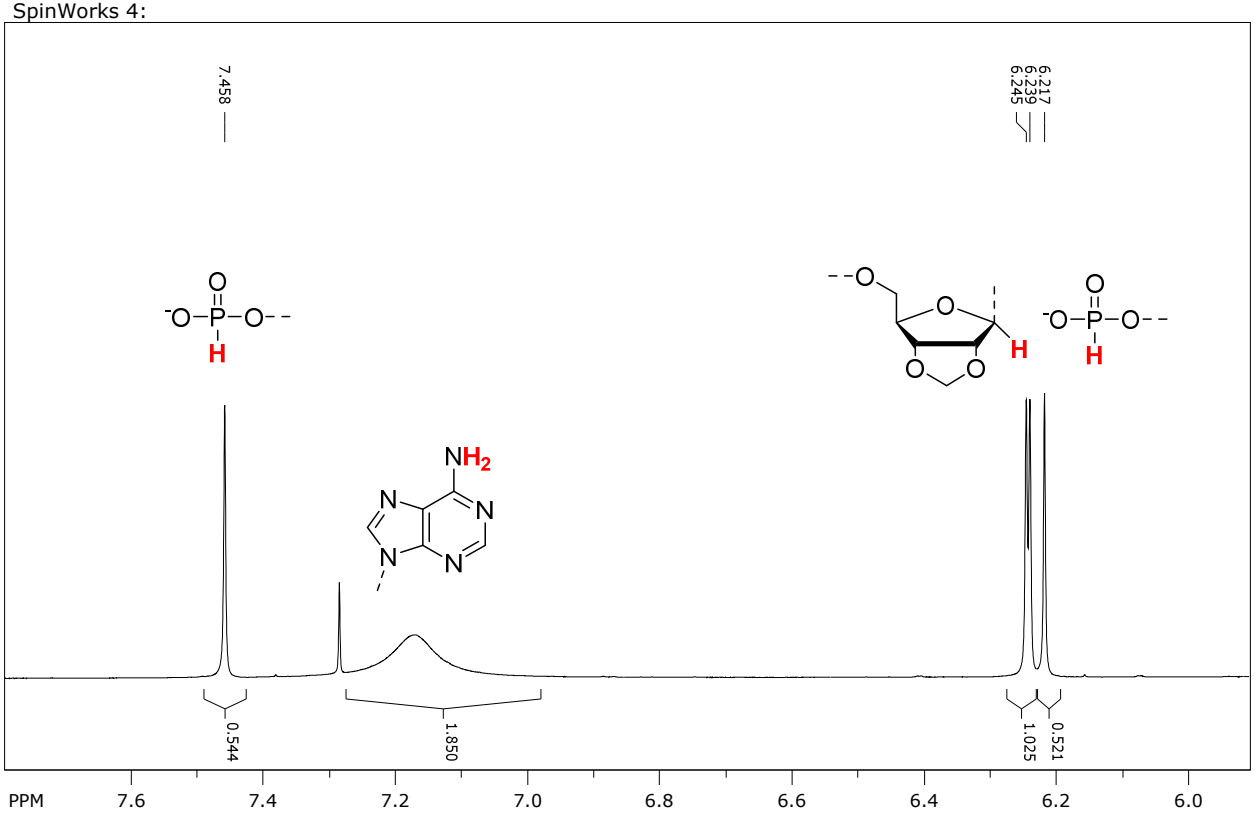

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Figure S4 ^{1}H NMR spectrum of 2´,3´-*O*-methyleneadenosine-5´-H-phosphonate (**3h**) (continued)

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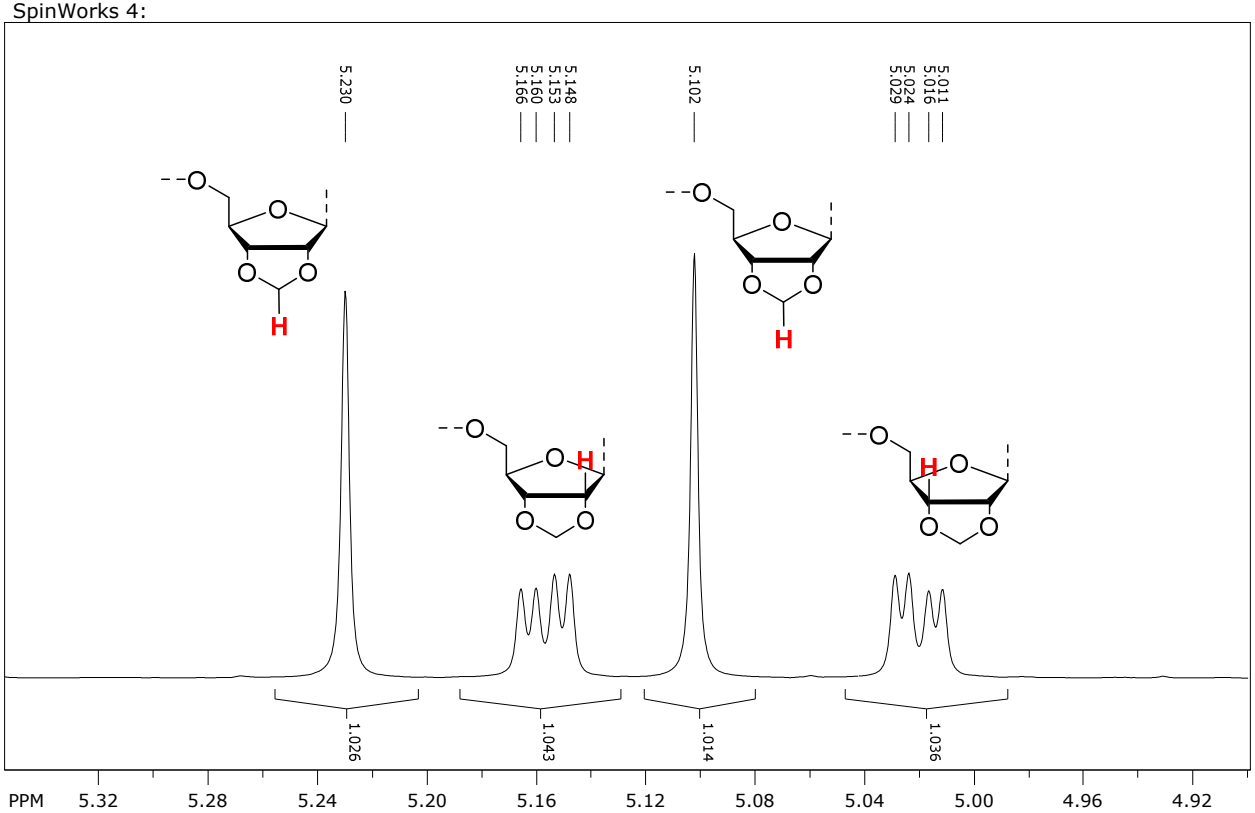

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Figure S4 ^{1}H NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

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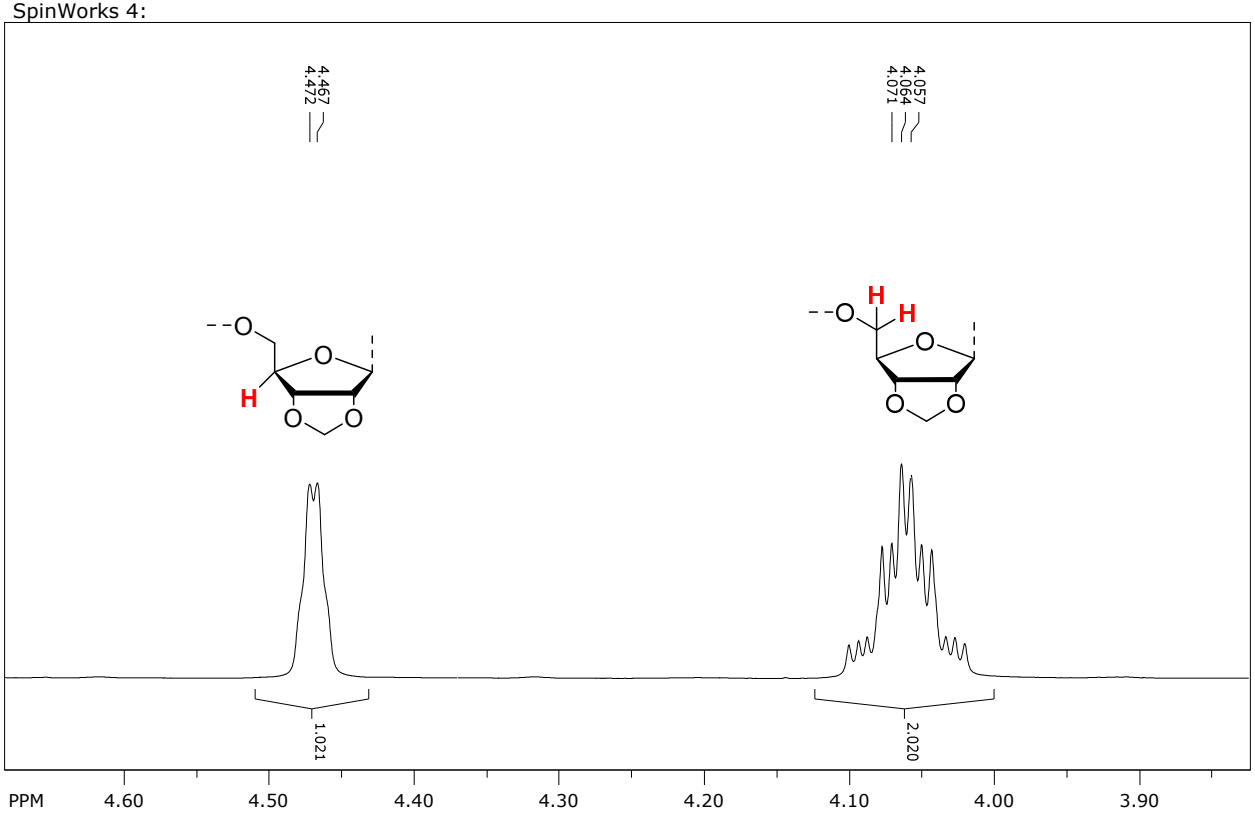

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Figure S4 ^{1}H NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

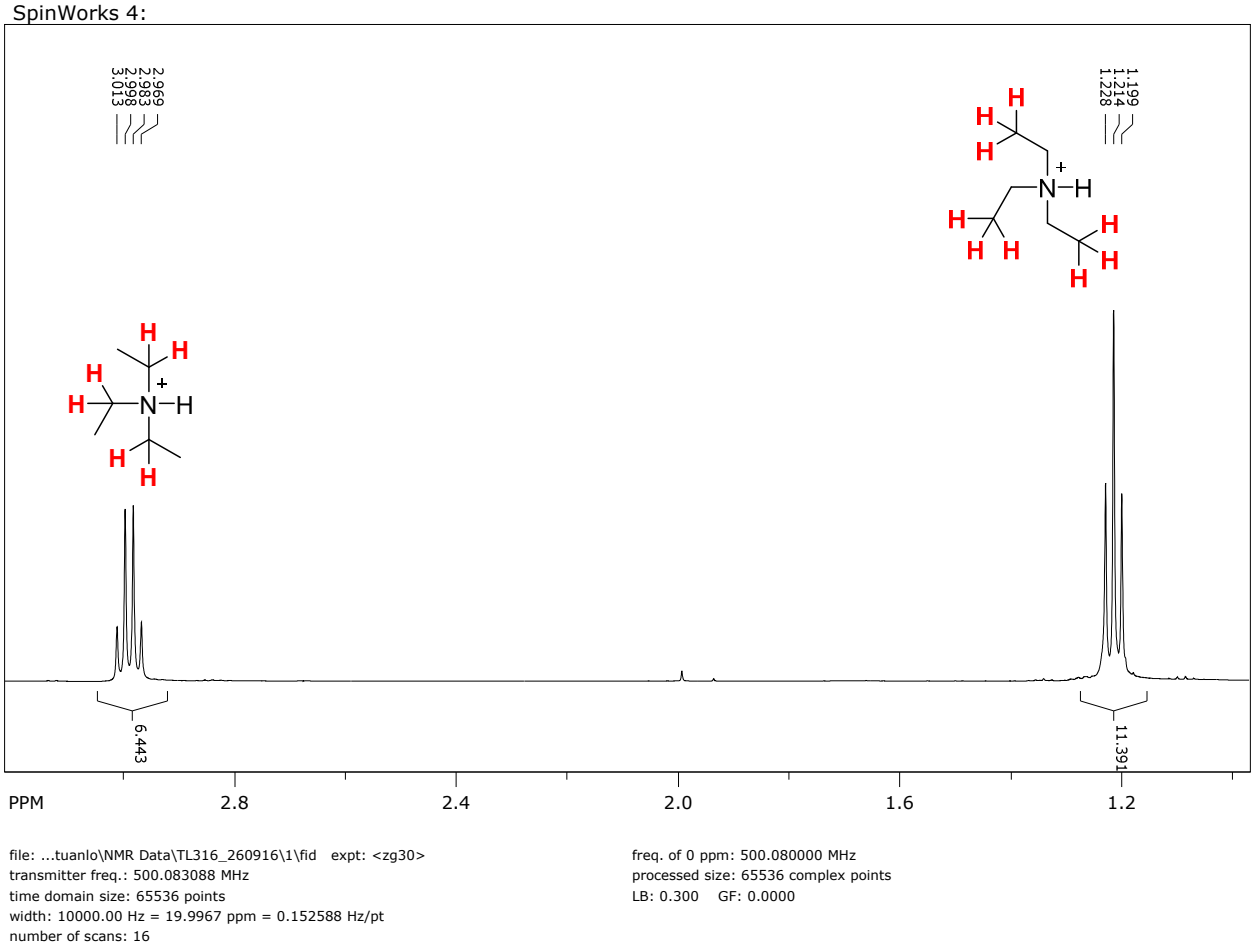

Figure S4 ^{1}H NMR spectrum of 2´,3´-*O*-methyleneadenosine-5´-H-phosphonate (**3h**) (continued)

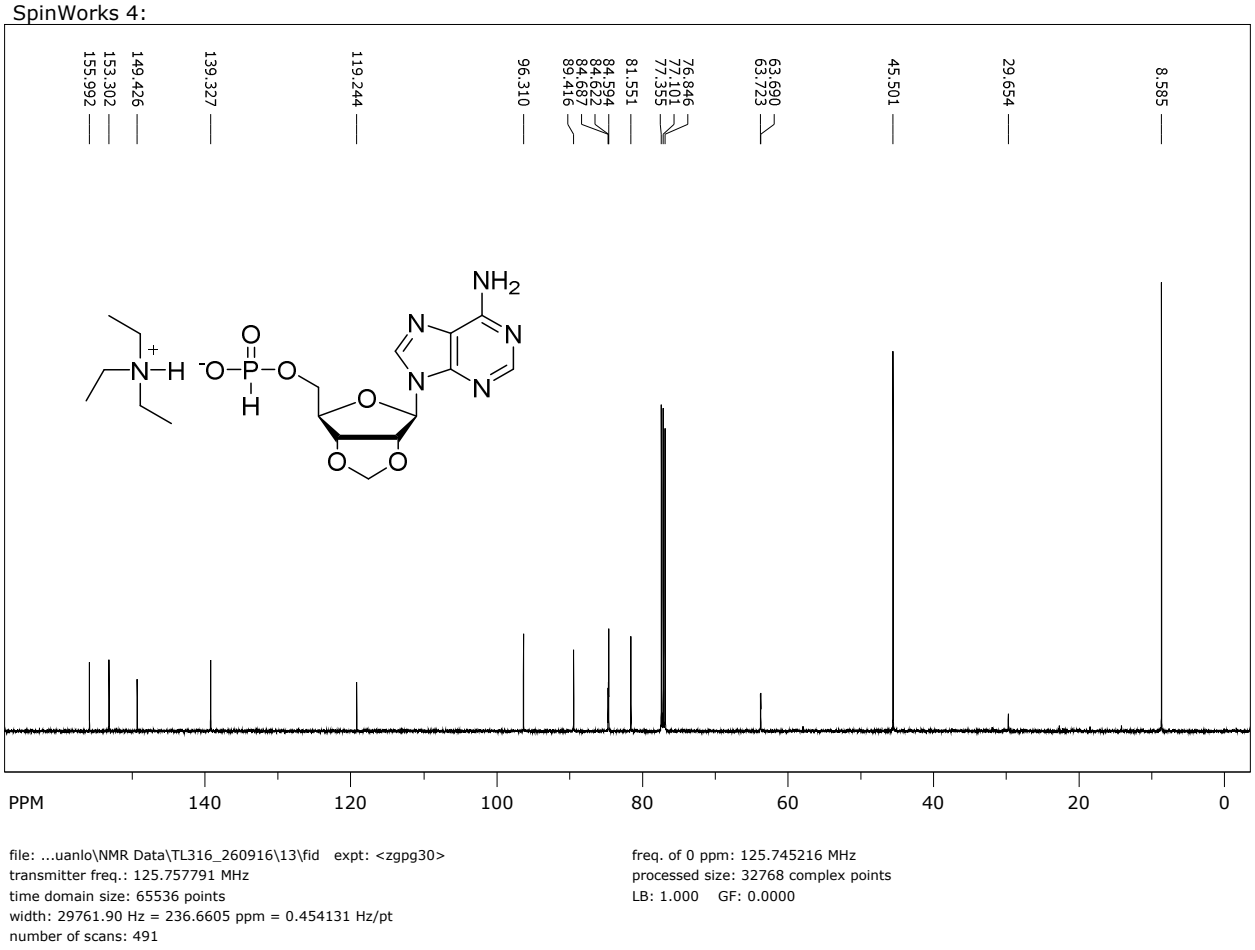

Figure S5 ^{13}C NMR spectrum of 2´,3´-*O*-methyleneadenosine-5´-H-phosphonate (**3h**)

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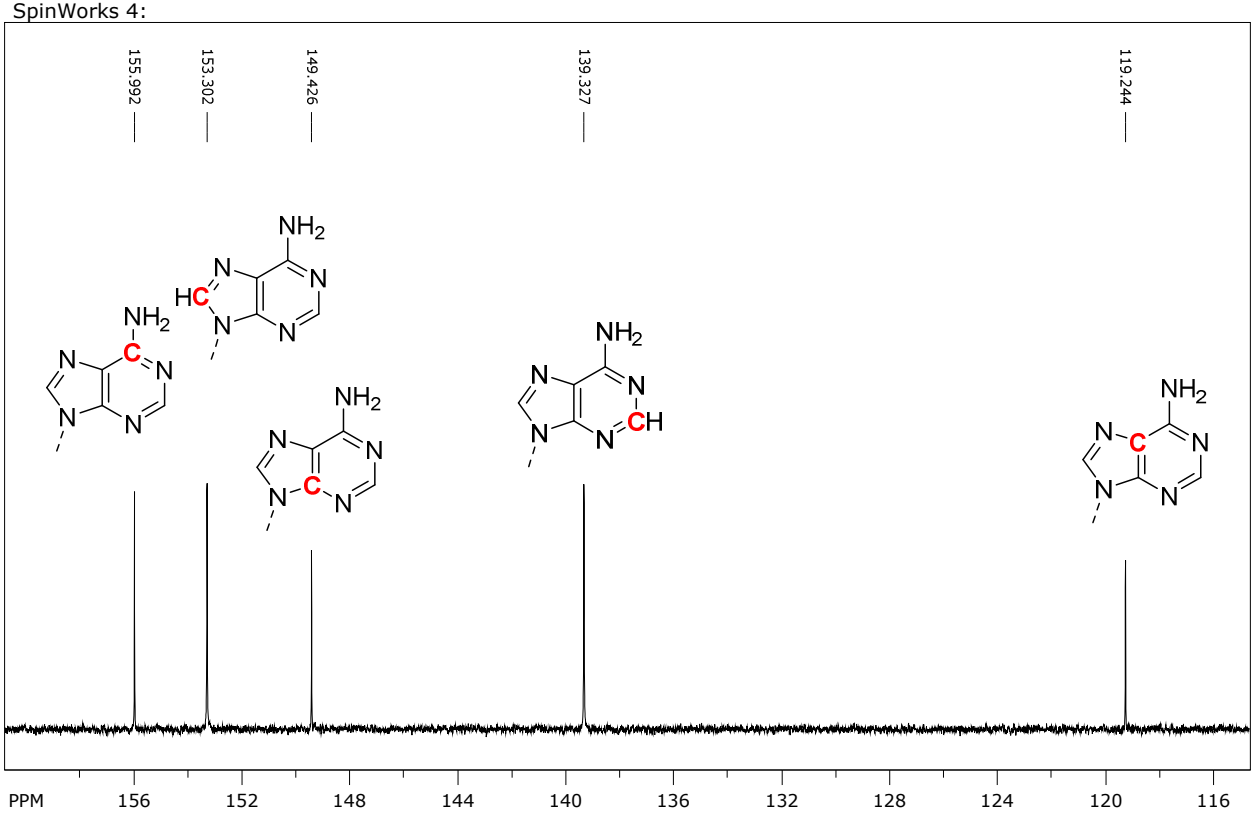

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Figure S5 ^{13}C NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

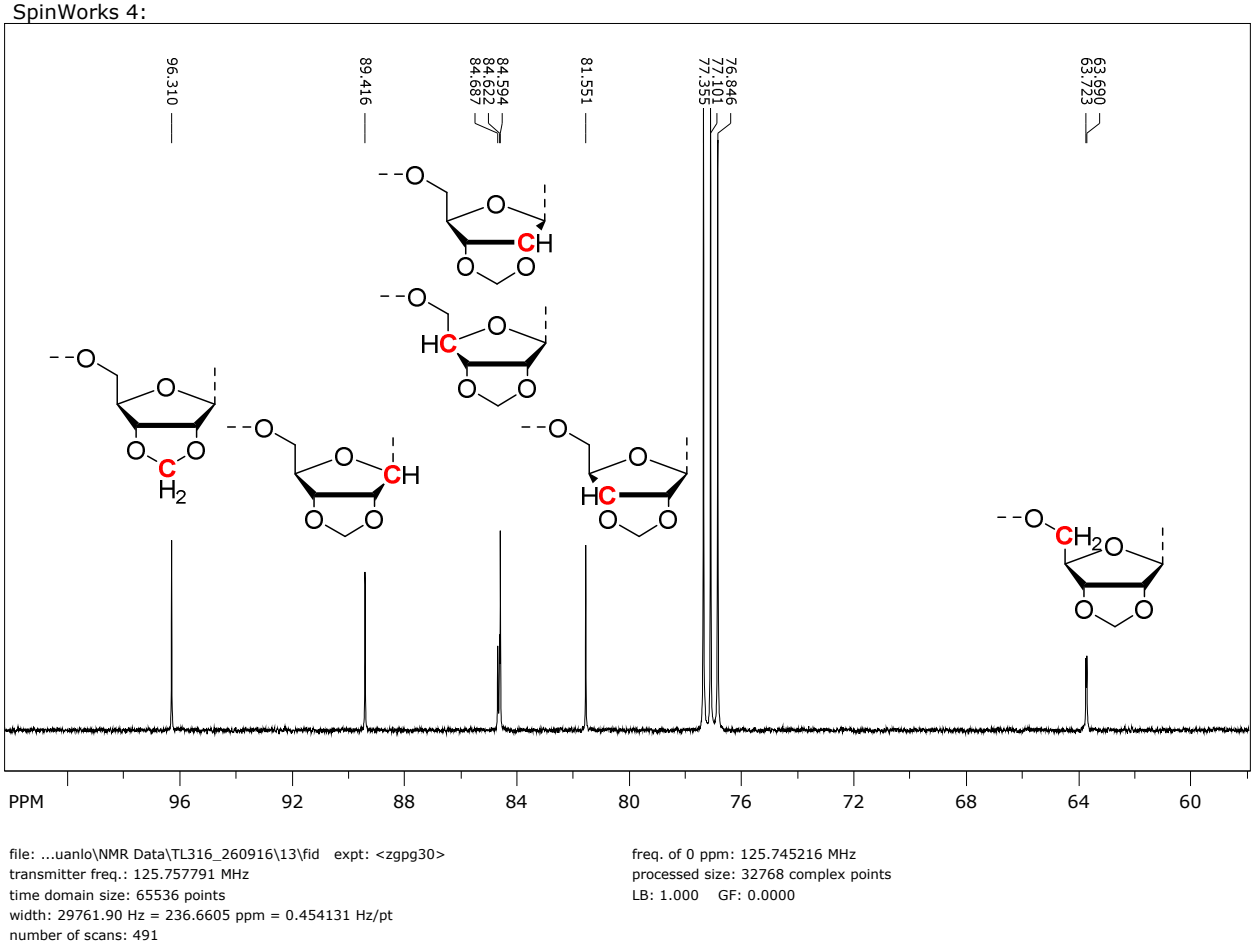

Figure S5 ^{13}C NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

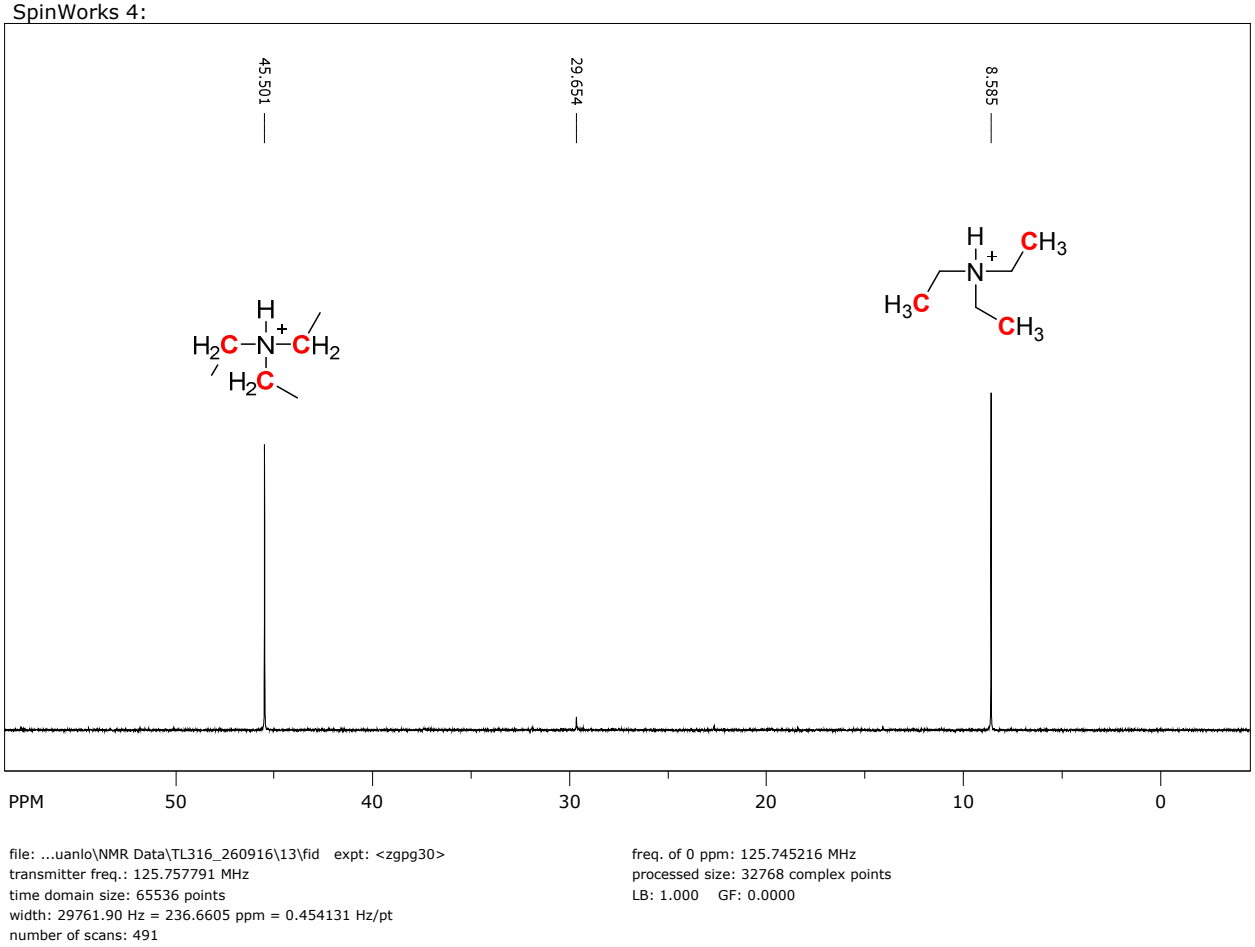

Figure S5 ^{13}C NMR spectrum of 2′,3′-*O*-methyleneadenosine-5′-H-phosphonate (**3h**) (continued)

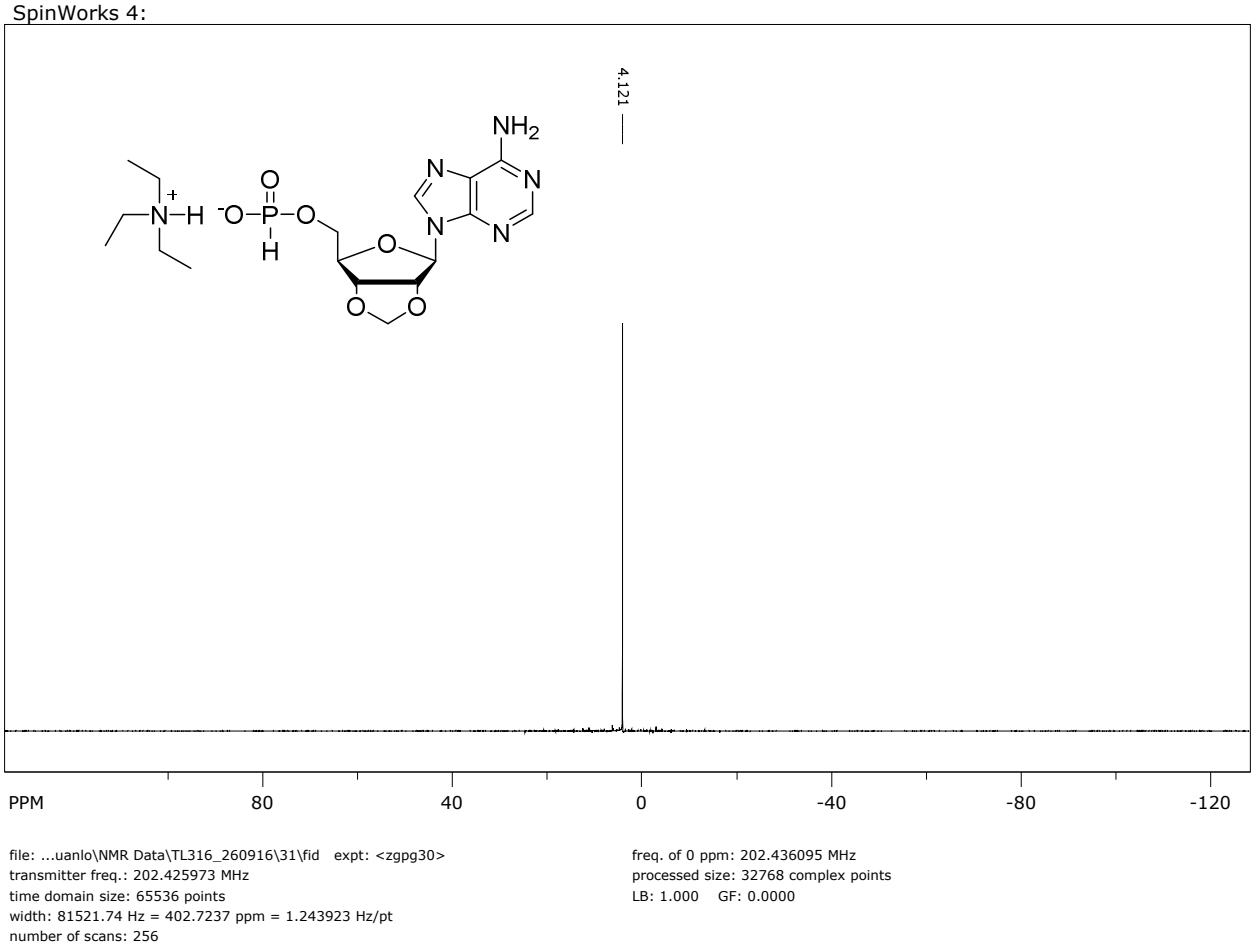

Figure S6 ^{31}P NMR spectrum of 2´,3´-*O*-methyleneadenosine-5´-H-phosphonate (**3h**)

Table S1 Observed rate constants for the hydrolysis of **1h** in the presence of 3.0 mg of sublimed elemental sulfur; *T* = 60 °C, *I*(NaCl) = 1.0 M.

			k_{obs} / 10^{-4} s^{-1}			log (k_{obs} / s^{-1})
pH	**[buffer] = 200 mM**	**[buffer] = 100 mM**	**[buffer] = 50 mM**	**[buffer] = 20 mM**	**[buffer] = 0 mM**	
0.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	44 ± 2	-2.35
1.00	n/a[a]	n/a[a]	n/a[a]	n/a[a]	14.5 ± 0.5	-2.84
1.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	5.4 ± 0.1	-3.27
2.00	n/a[a]	n/a[a]	n/a[a]	n/a[a]	2.79 ± 0.03	-3.55
2.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	1.39 ± 0.03	-3.86
3.07	1.46 ± 0.03	1.35 ± 0.03	1.22 ± 0.03	1.24 ± 0.04	1.19 ± 0.03[b]	-3.92
3.55	1.32 ± 0.02	1.36 ± 0.05	1.22 ± 0.05	1.17 ± 0.05	1.2 ± 0.1[b]	-3.92
4.08	1.81 ± 0.05	1.76 ± 0.04	1.68 ± 0.04	1.35 ± 0.05	1.5 ± 0.1[b]	-3.82
4.56	2.39 ± 0.04	2.1 ± 0.2	2.14 ± 0.03	1.86 ± 0.02	1.9 ± 0.1[b]	-3.72
5.03	3.5 ± 0.2	3.84 ± 0.08	3.8 ± 0.2	(1.59 ± 0.08)[c]	3.7 ± 0.2[b]	-3.43
5.82	10.2 ± 0.1	9.0 ± 0.5	8.2 ± 0.3	11 ± 1	10 ± 1[d]	-3.02
6.30	24.7 ± 0.9	22 ± 1	25 ± 2	22 ± 3	23 ± 3[d]	-2.64
6.78	53 ± 8	53 ± 3	60 ± 1	60 ± 1	56 ± 4[d]	-2.25
7.25	170 ± 30	170 ± 10	170 ± 10	220 ± 20	170 ± 20[d]	-1.77

[a] Kinetic runs at pH < 3 were carried out in aq. HCl, rather than buffer. [b] Linear extrapolation of values obtained at 20, 50, 100 and 200 mM buffer. [c] Excluded as an outlier. [d] Average of values obtained at 20, 50, 100 and 200 mM buffer.

Table S2 Observed rate constants for the sulfurization of **1h** in the presence of 3.0 mg of sublimed elemental sulfur; *T* = 60 °C, *I*(NaCl) = 1.0 M.

			k_{obs} / 10^{-4} s^{-1}			log (k_{obs} / s^{-1})
pH	**[buffer] = 200 mM**	**[buffer] = 100 mM**	**[buffer] = 50 mM**	**[buffer] = 20 mM**	**[buffer] = 0 mM**	
0.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	n/a[b]	n/a[b]
1.00	n/a[a]	n/a[a]	n/a[a]	n/a[a]	n/a[b]	n/a[b]
1.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	0.0140 ± 0.0002	-5.85
2.00	n/a[a]	n/a[a]	n/a[a]	n/a[a]	0.0337 ± 0.0003	-5.47
2.52	n/a[a]	n/a[a]	n/a[a]	n/a[a]	0.110 ± 0.002	-4.96
3.07	0.140 ± 0.003	0.161 ± 0.003	(0.068 ± 0.002)[c]	0.189 ± 0.006	0.16 ± 0.02[d]	-4.80
3.55	0.337 ± 0.004	0.218 ± 0.008	0.184 ± 0.007	(0.94 ± 0.04)[c]	0.25 ± 0.07[d]	-4.60
4.08	(0.090 ± 0.003)[c]	0.42 ± 0.01	0.43 ± 0.01	0.60 ± 0.02	0.49 ± 0.08[d]	-4.31
4.56	0.86 ± 0.01	1.02 ± 0.08	(0.38 ± 0.06)[c]	1.31 ± 0.07	1.1 ± 0.2[d]	-3.96
5.03	1.63 ± 0.07	(0.70 ± 0.01)[c]	2.1 ± 0.1	1.53 ± 0.08	1.7 ± 0.2[d]	-3.77
5.82	2.27 ± 0.03	3.4 ± 0.2	3.6 ± 0.1	5.4 ± 0.5	4 ± 1[d]	-3.40
6.30	2.59 ± 0.04	(1.6 ± 0.2)[c]	7.3 ± 0.3	5.9 ± 0.2	5 ± 2[d]	-3.30
6.78	7 ± 1	9.3 ± 0.8	(4.2 ± 0.1)[c]	9.8 ± 0.2	9 ± 1[d]	-3.05
7.25	19 ± 4	17 ± 1	53 ± 5	60 ± 6	40 ± 20[d]	-2.40

[a] Kinetic runs at pH < 3 were carried out in aq. HCl, rather than buffer. [b] Not detected owing to overwhelmingly faster hydrolysis. [c] Excluded as an outlier. [d] Average of values obtained at 20, 50, 100 and 200 mM buffer.