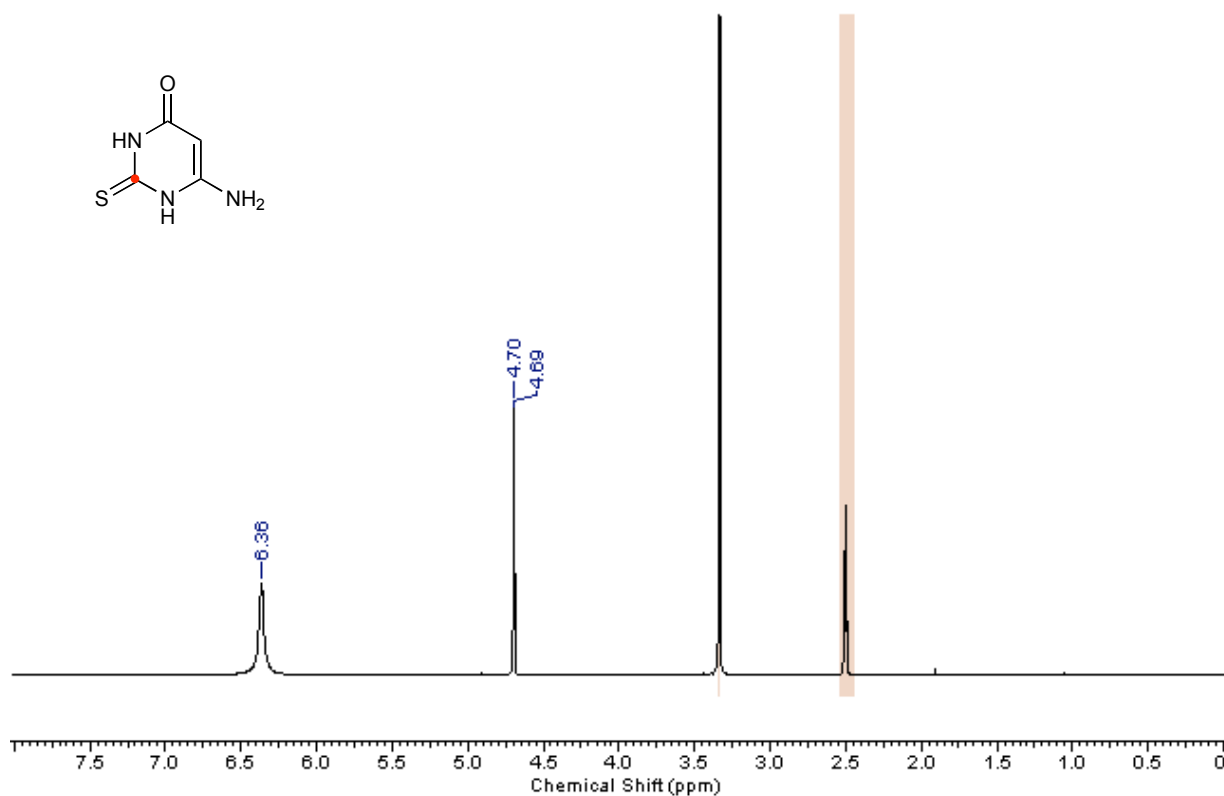


**7-Deazapurine biosynthesis: NMR study of toyocamycin biosynthesis in *Streptomyces rimosus*
using 2-¹³C-7-¹⁵N-adenine**

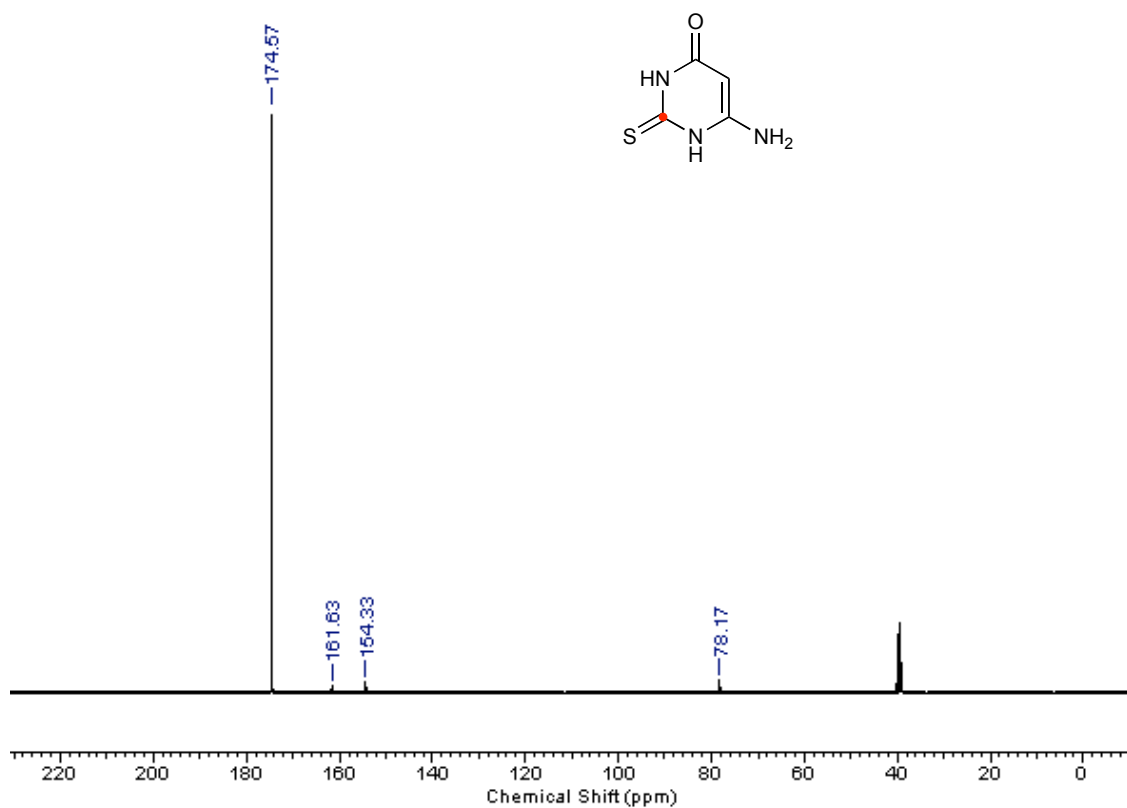
Ugo Battaglia, Jed E. Long, Mark S. Searle and Christopher J. Moody

ELECTRONIC SUPPLEMENTARY INFORMATION

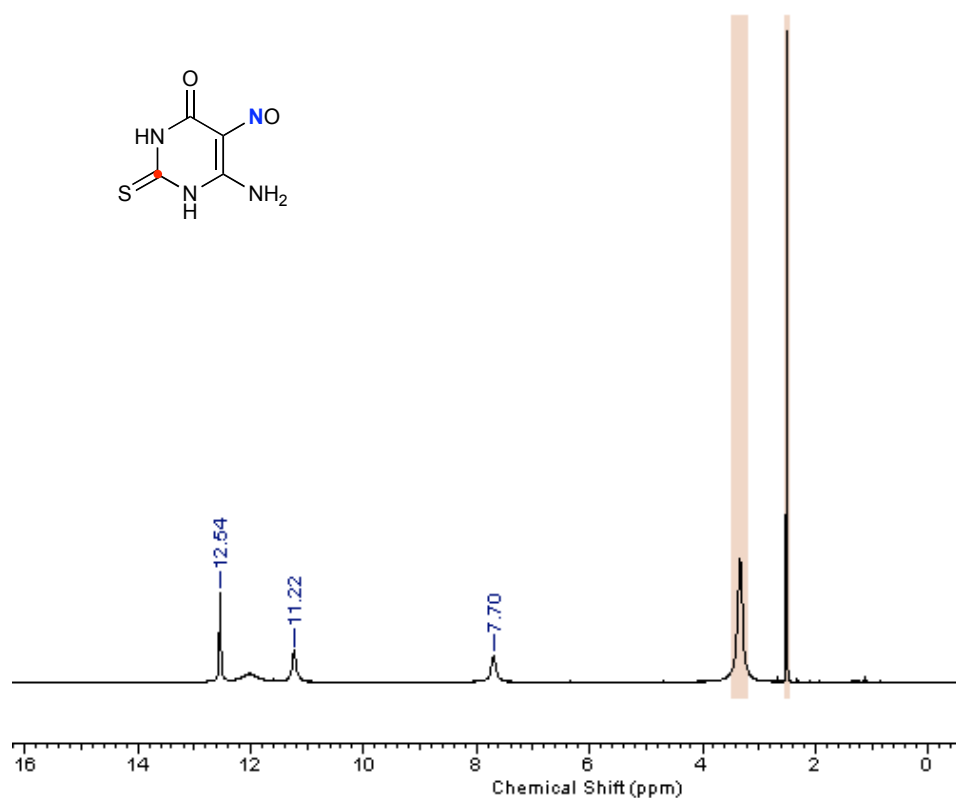
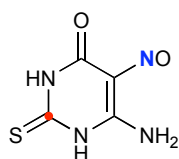
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C]-6-Amino-2-thioxo-1,2-dihydro-4(3H)-pyrimidone 4



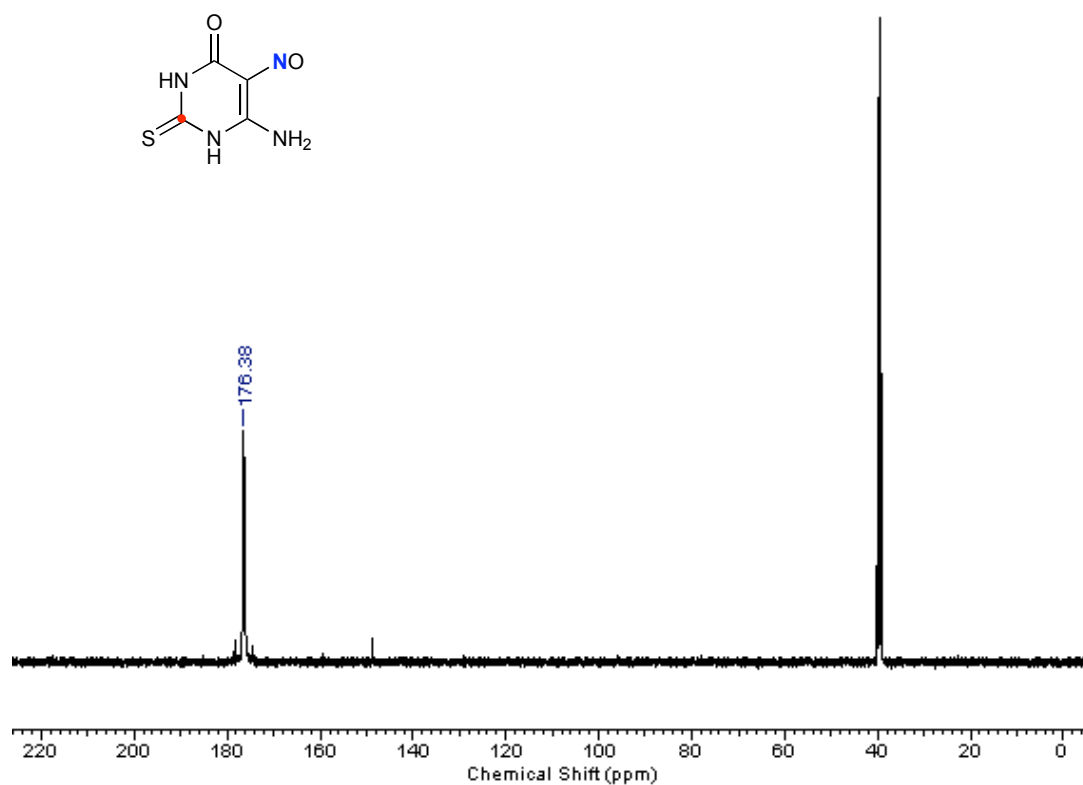
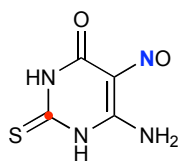
^{13}C NMR (100MHz; DMSO- d_6)



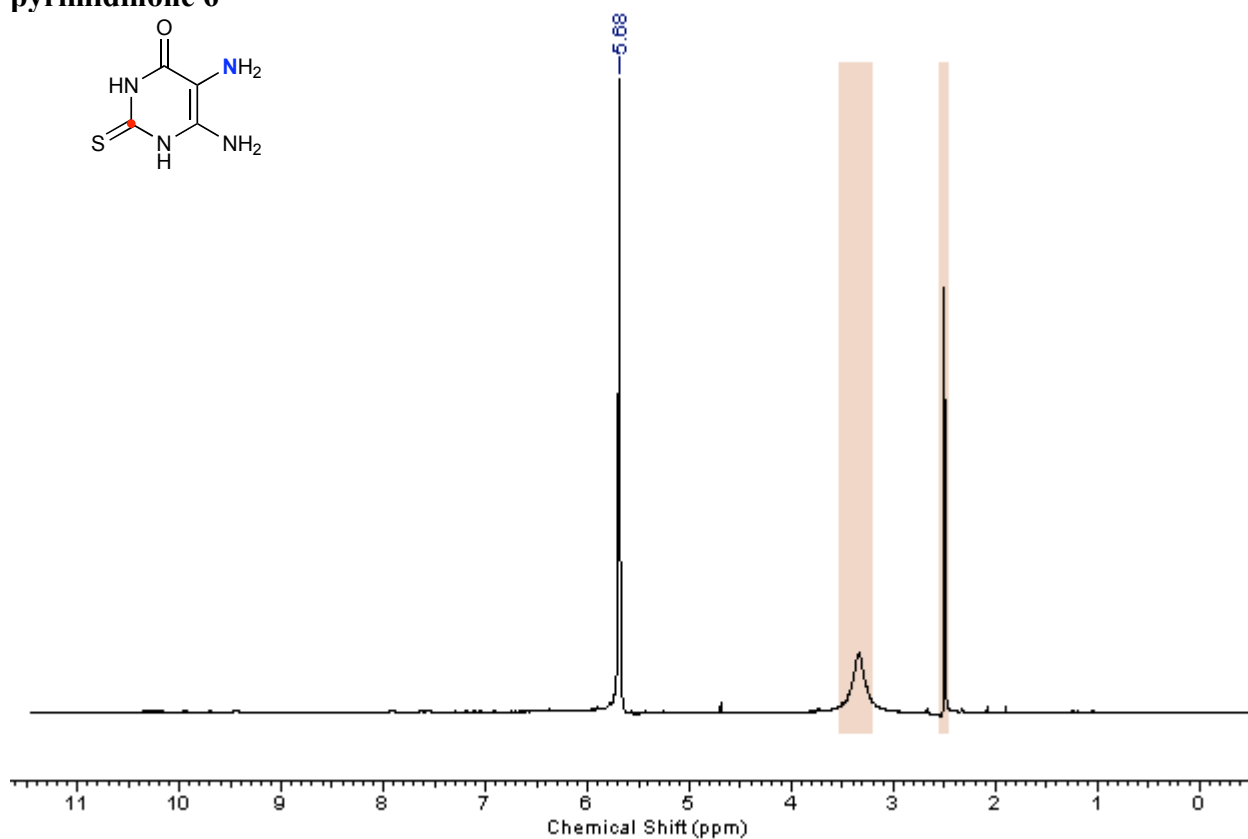
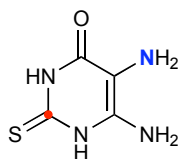
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 5- ^{15}N]-6-Amino-5-nitroso-2-thioxo-1,2-dihydro-4(3*H*)-pyrimidinone 5



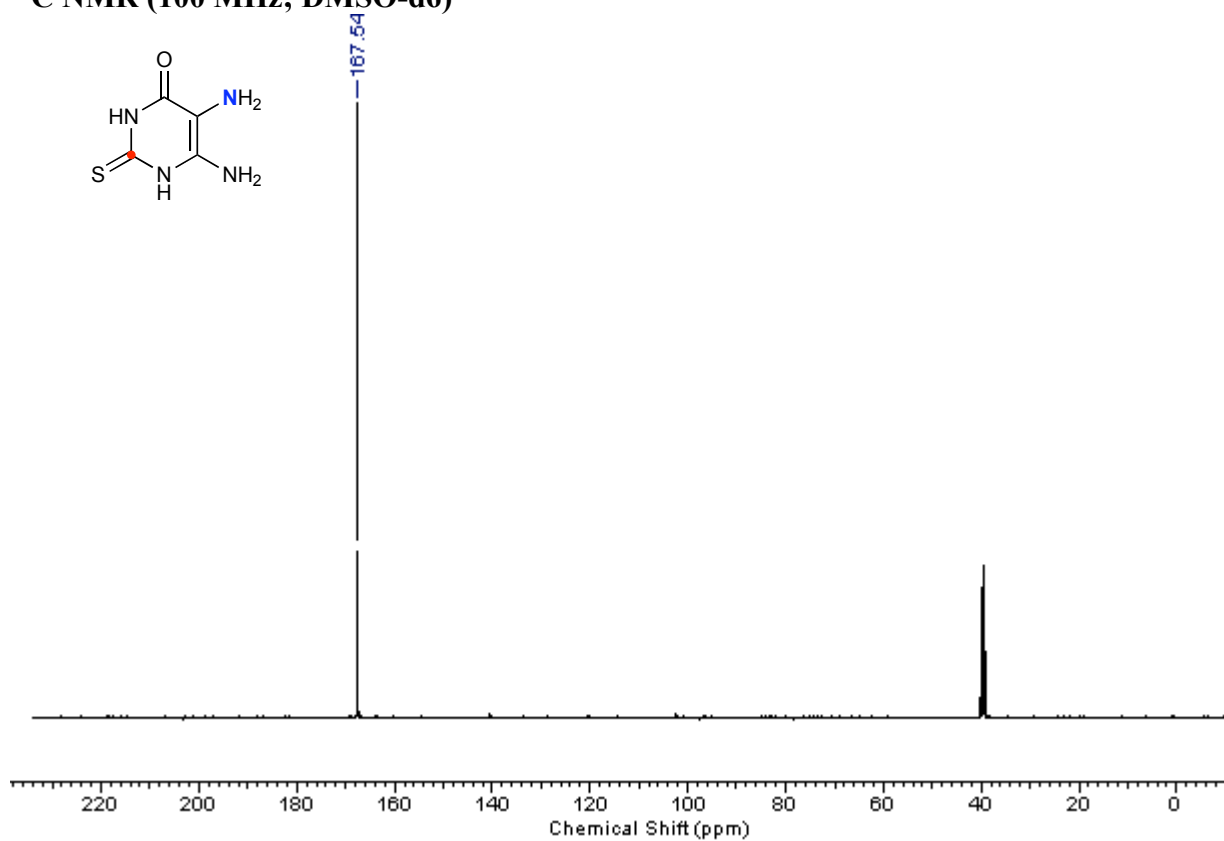
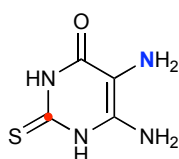
^{13}C NMR (100 MHz; DMSO- d_6)



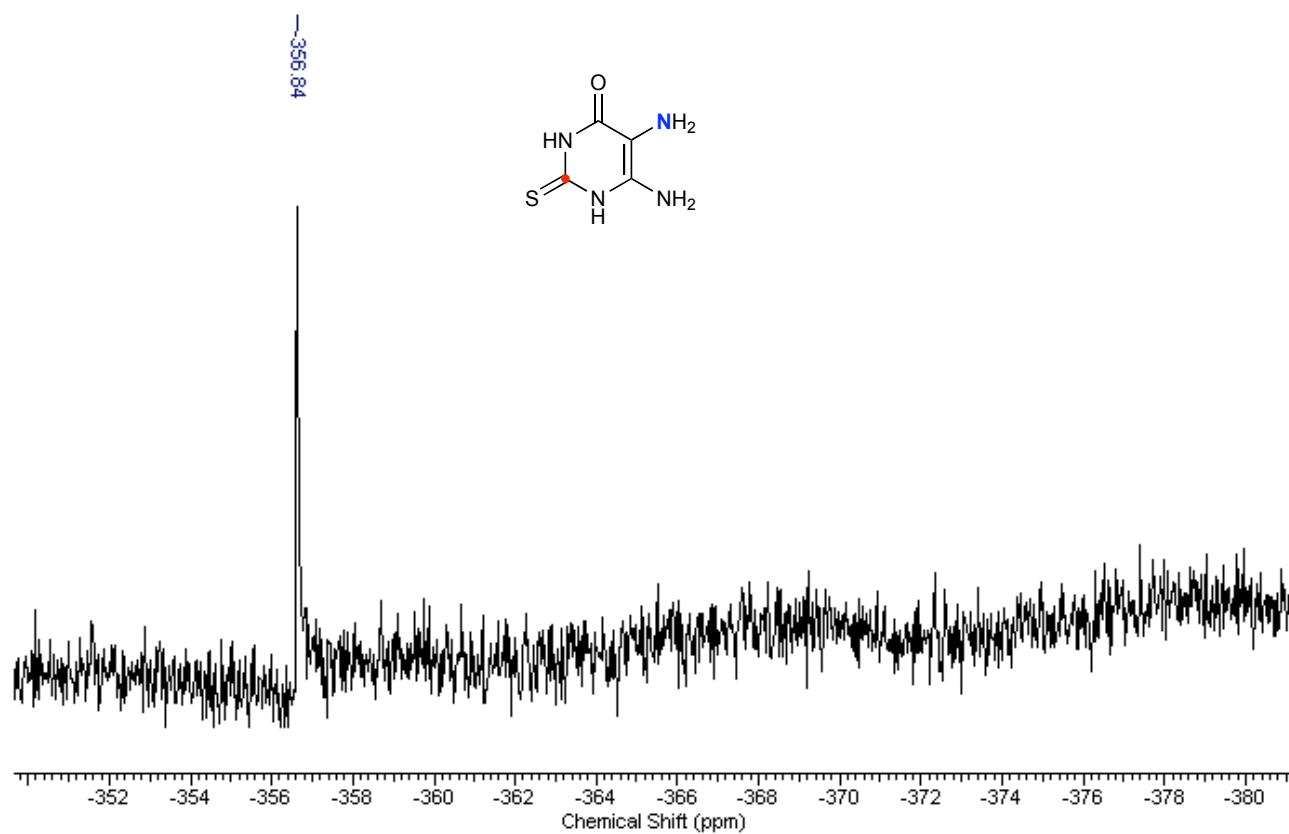
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 5- ^{15}N]-5,6-Diamino-2-thioxo-1,2-dihydro-4-pyrimidinone 6



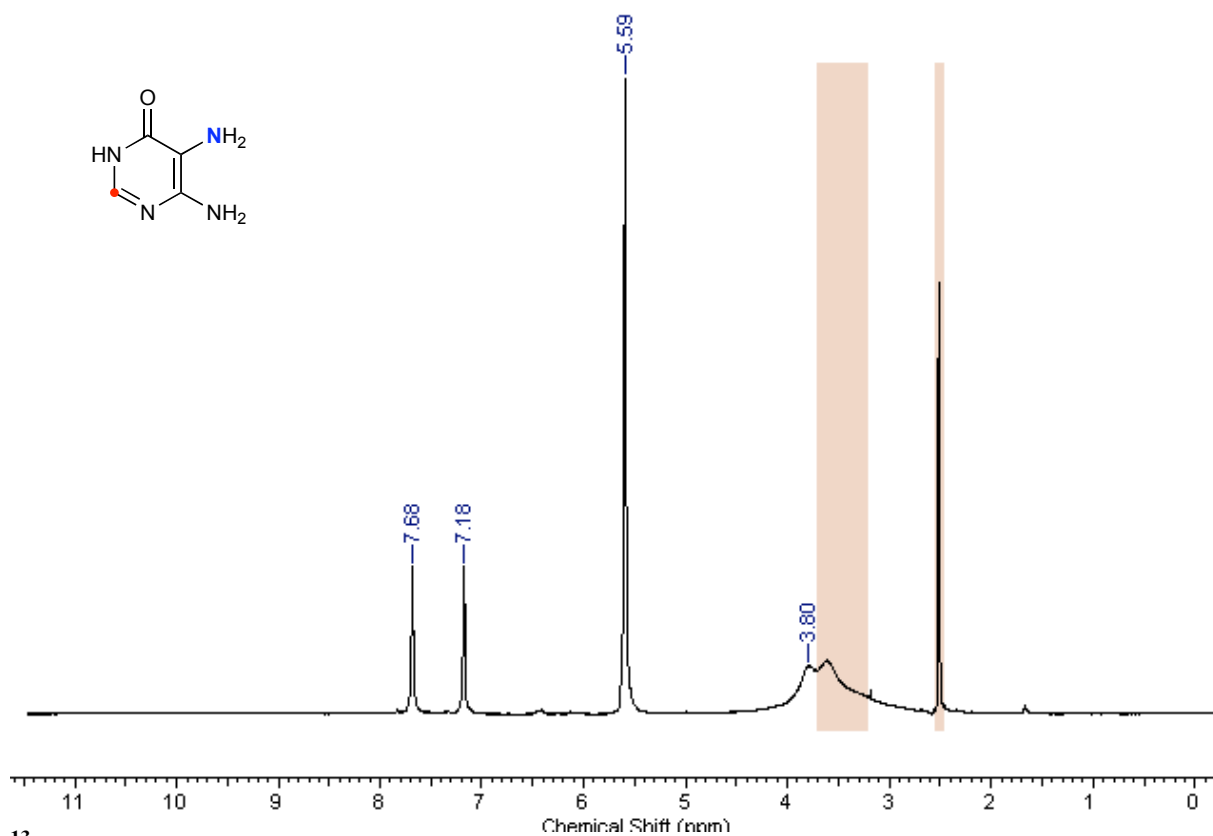
^{13}C NMR (100 MHz; DMSO- d_6)



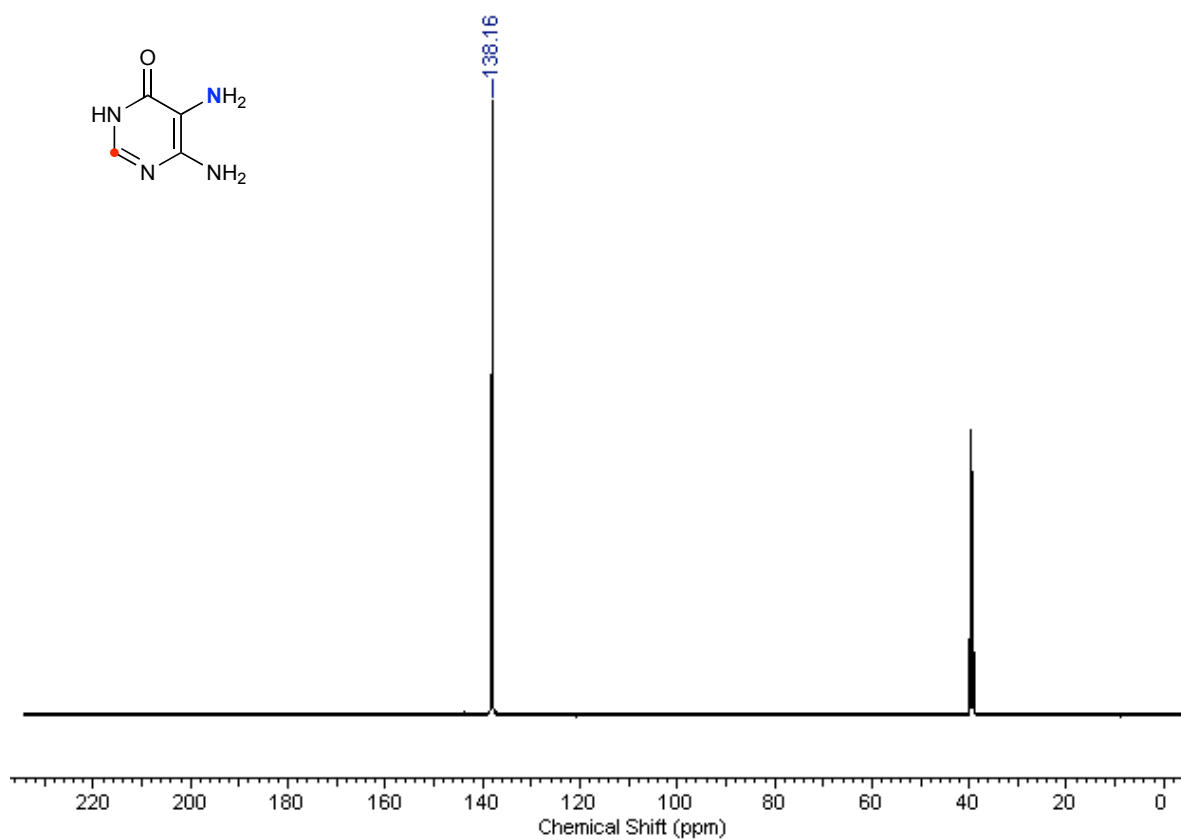
^{15}N NMR (40.5 MHz; DMSO- d_6): [2- ^{13}C , 5- ^{15}N]-5,6-Diamino-2-thioxo-1,2-dihydro-4-pyrimidinone 6



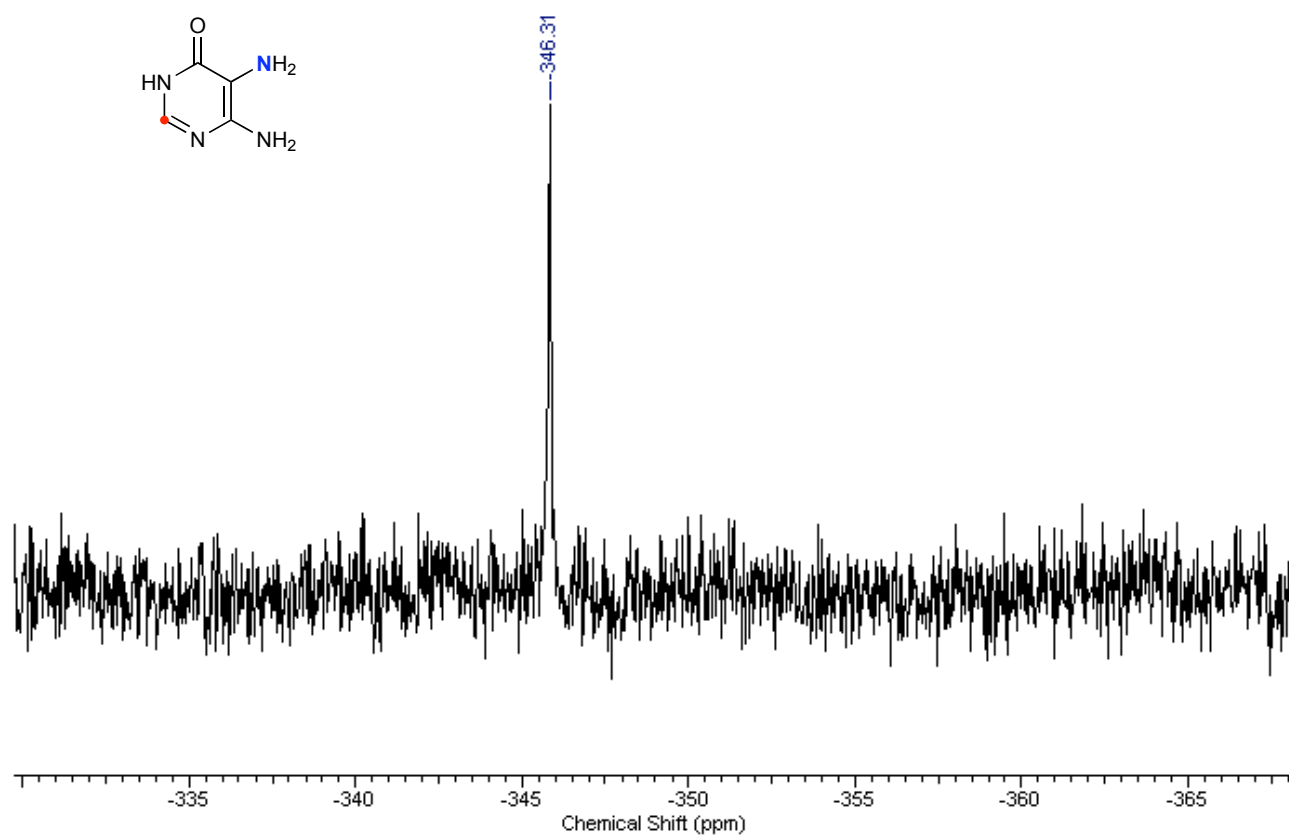
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 5- ^{15}N]-5,6-Diamino-4-pyrimidinone 7



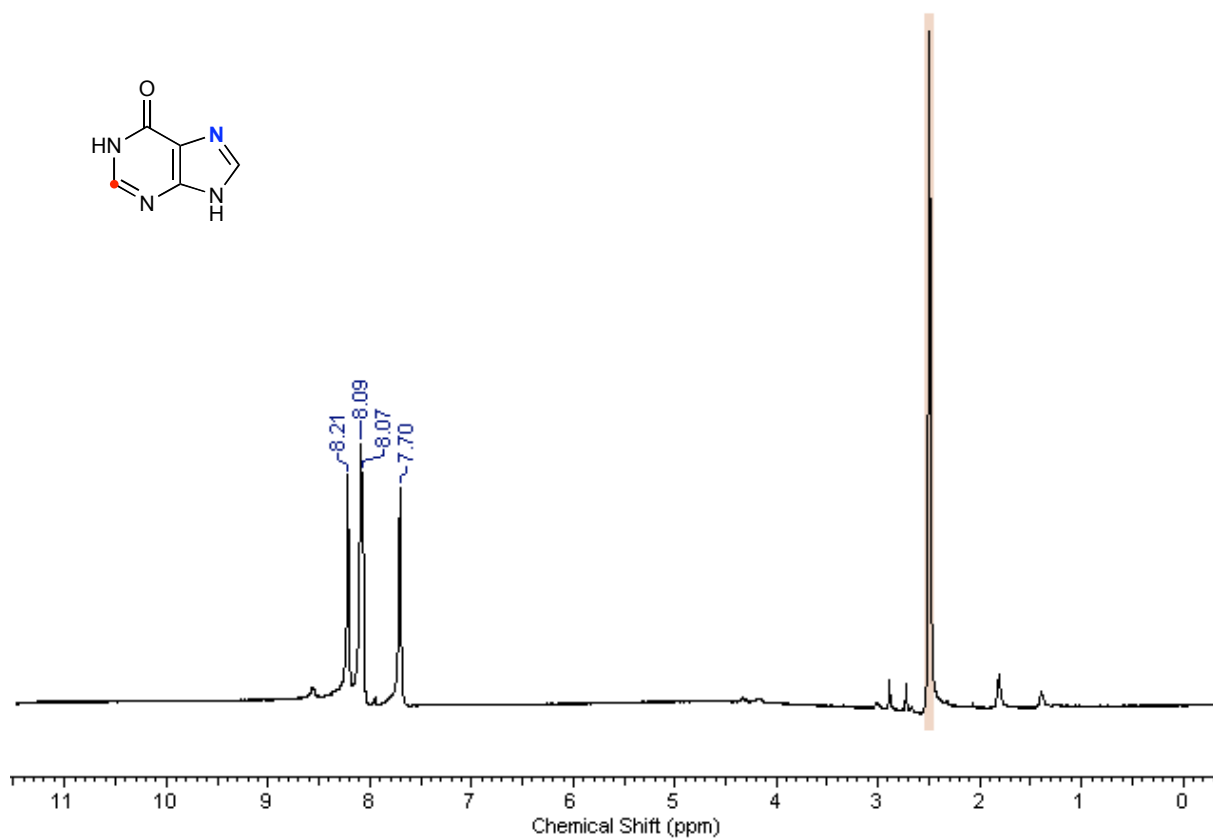
^{13}C NMR (100 MHz; DMSO- d_6)



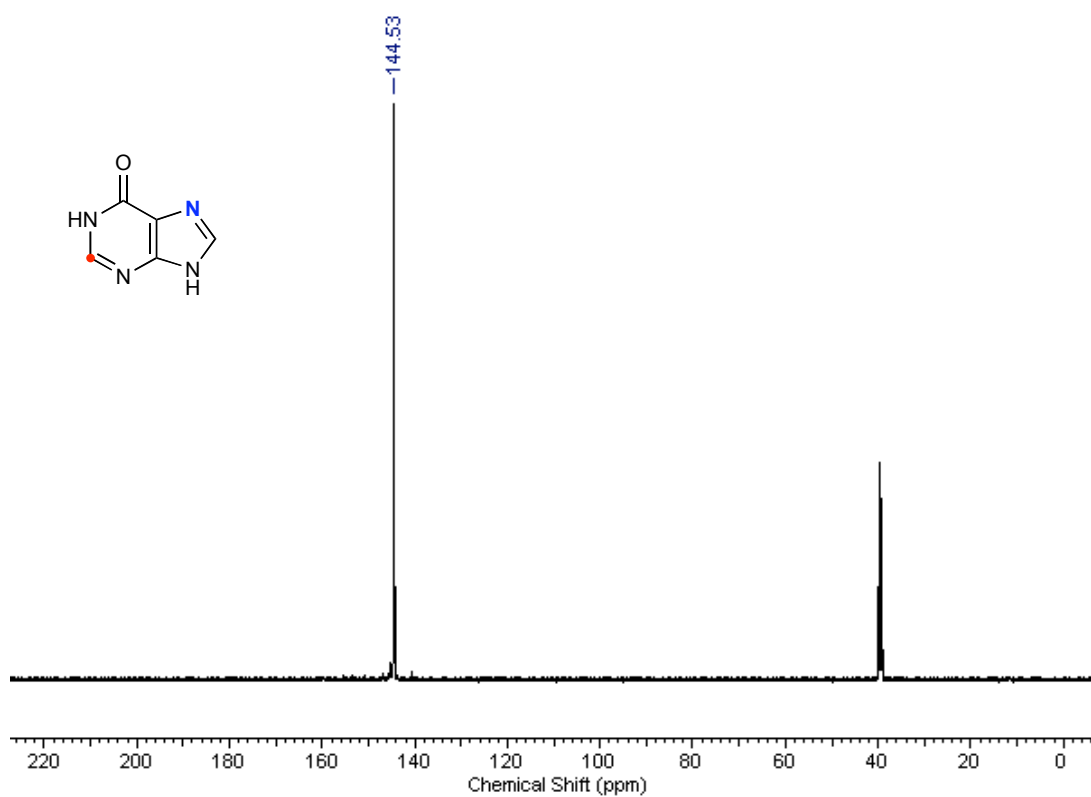
^{15}N NMR (40.5 MHz; DMSO- d_6): [2- ^{13}C , 5- ^{15}N]-5,6-Diamino-4-pyrimidinone 7



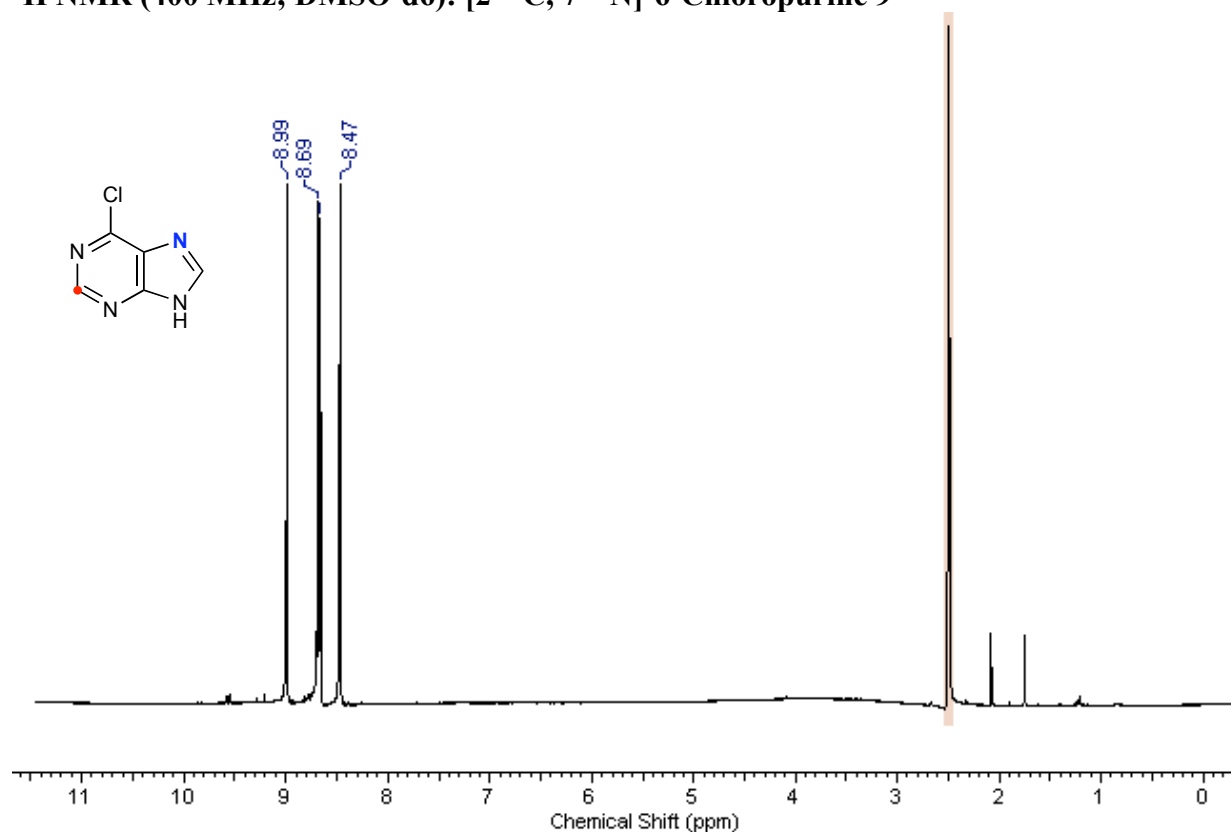
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 7- ^{15}N]-Hypoxanthine 8



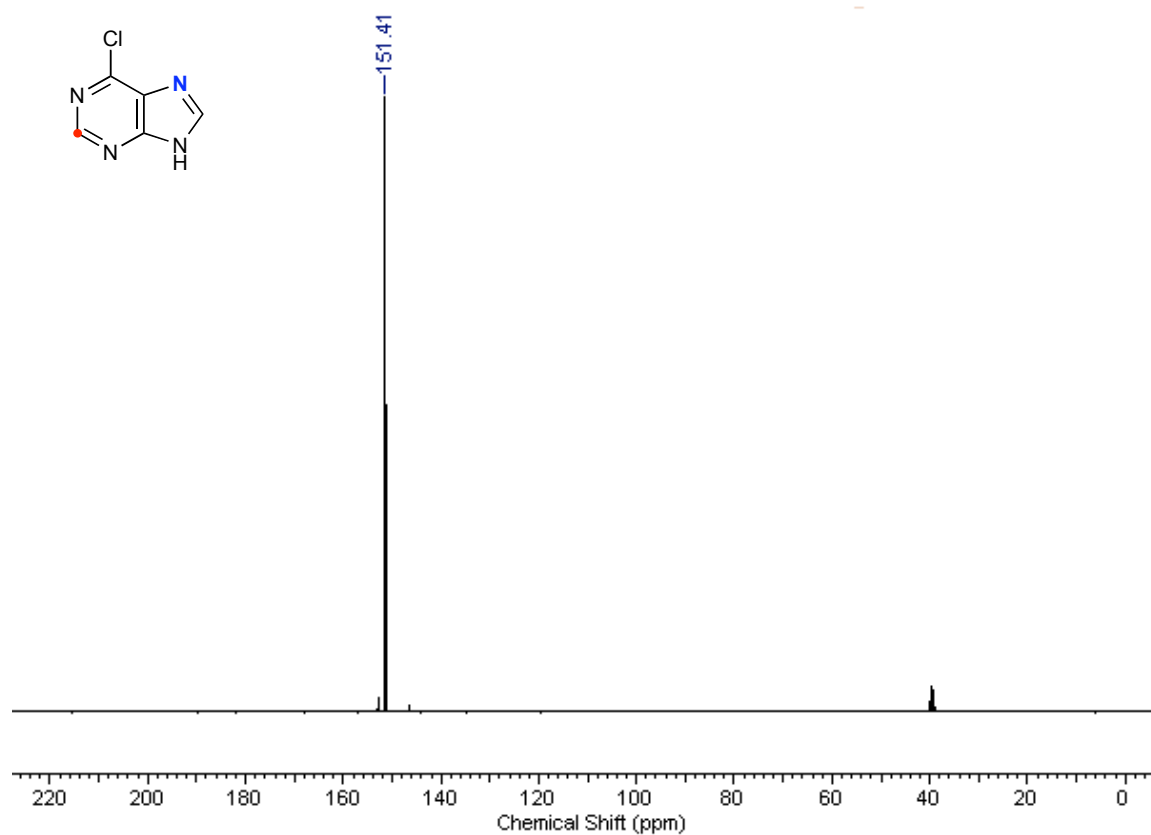
^{13}C NMR (100 MHz; DMSO- d_6)



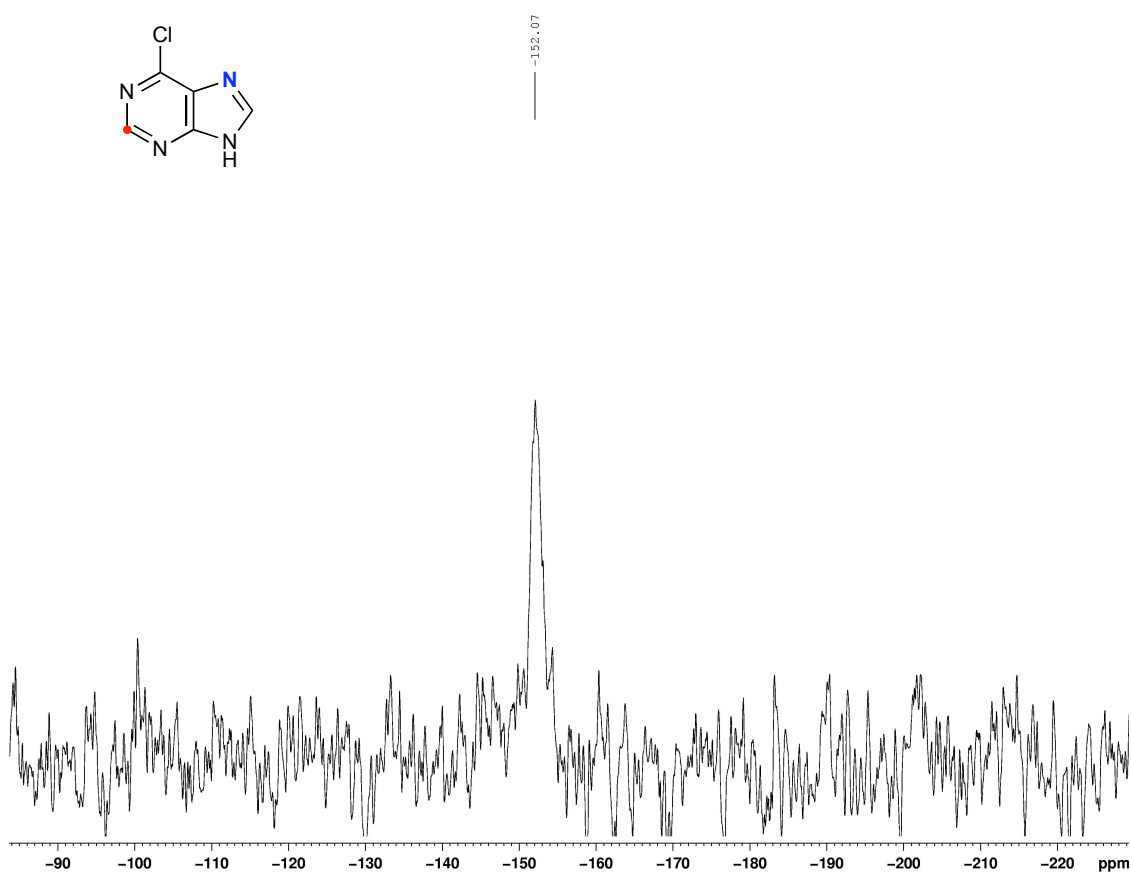
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 7- ^{15}N]-6-Chloropurine 9



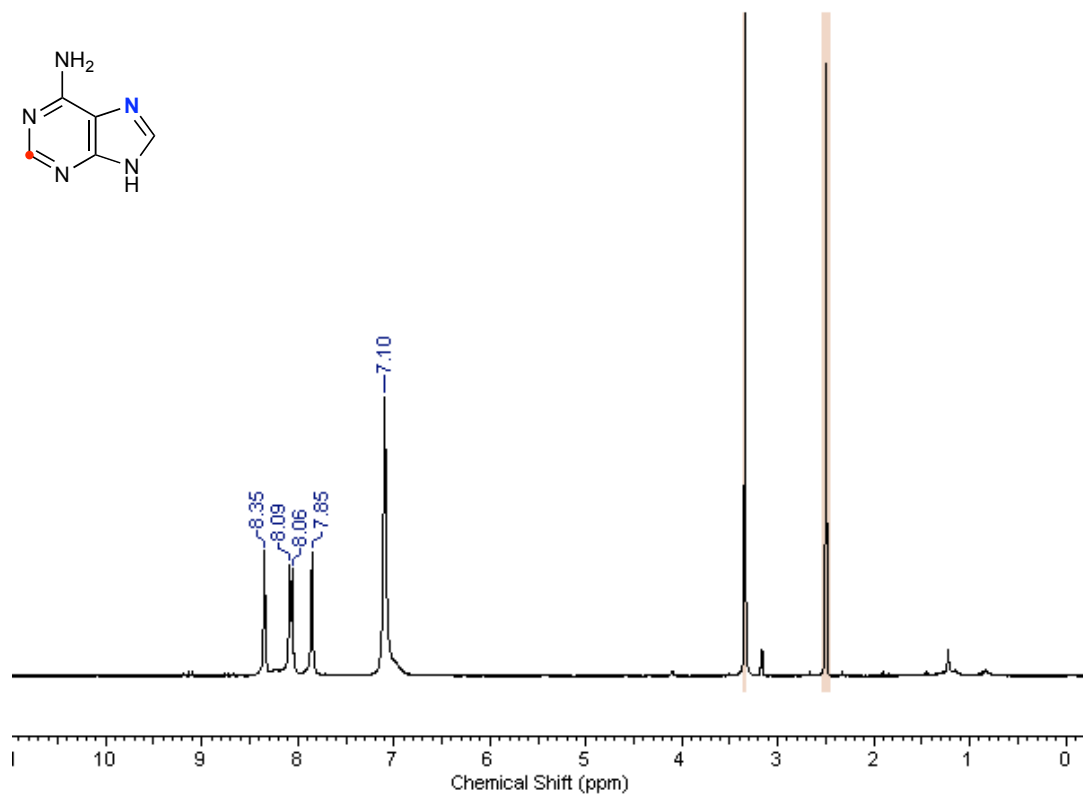
^{13}C NMR (100 MHz; DMSO- d_6)



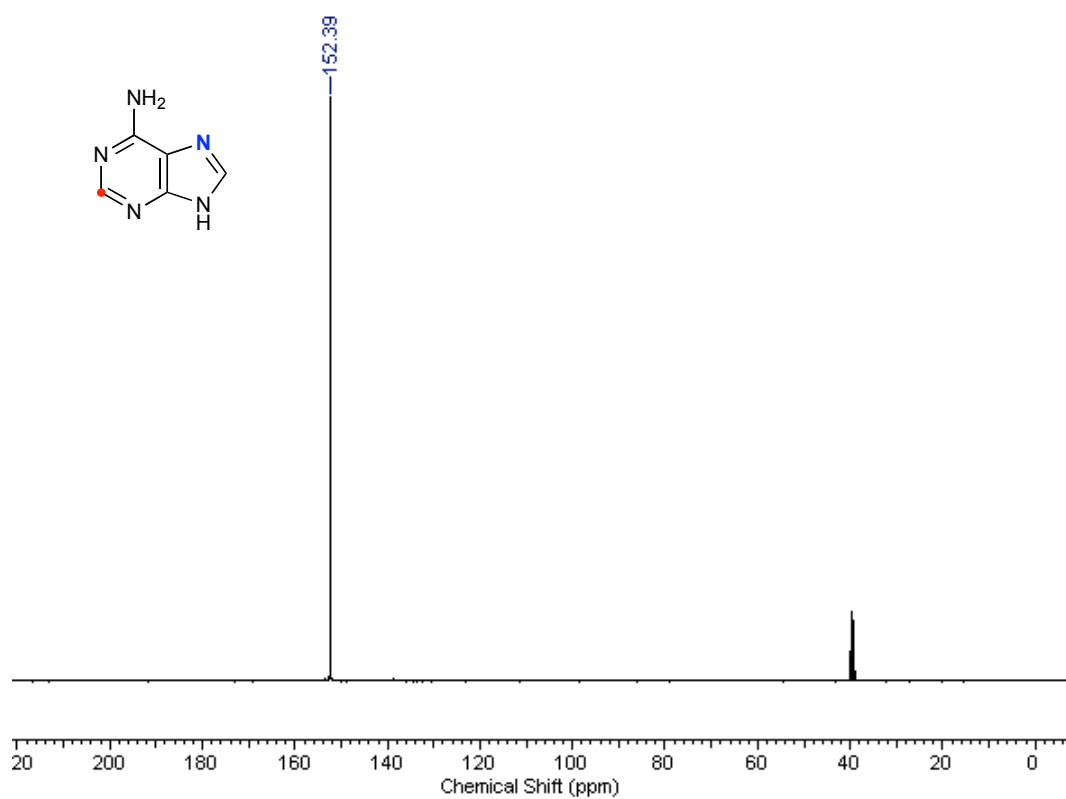
^{15}N NMR (40.5 MHz; DMSO- d_6): [2- ^{13}C , 7- ^{15}N]-6-Chloropurine 9



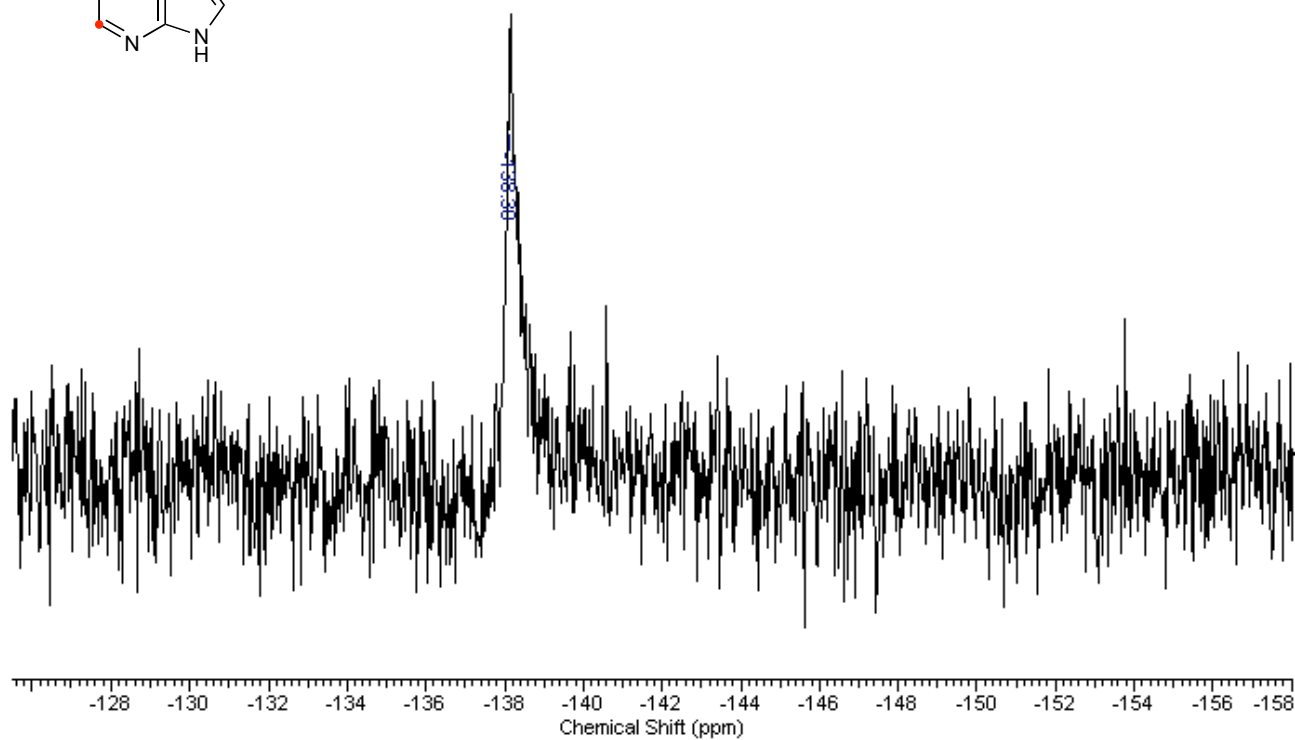
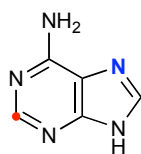
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C , 7- ^{15}N]-Adenine 10



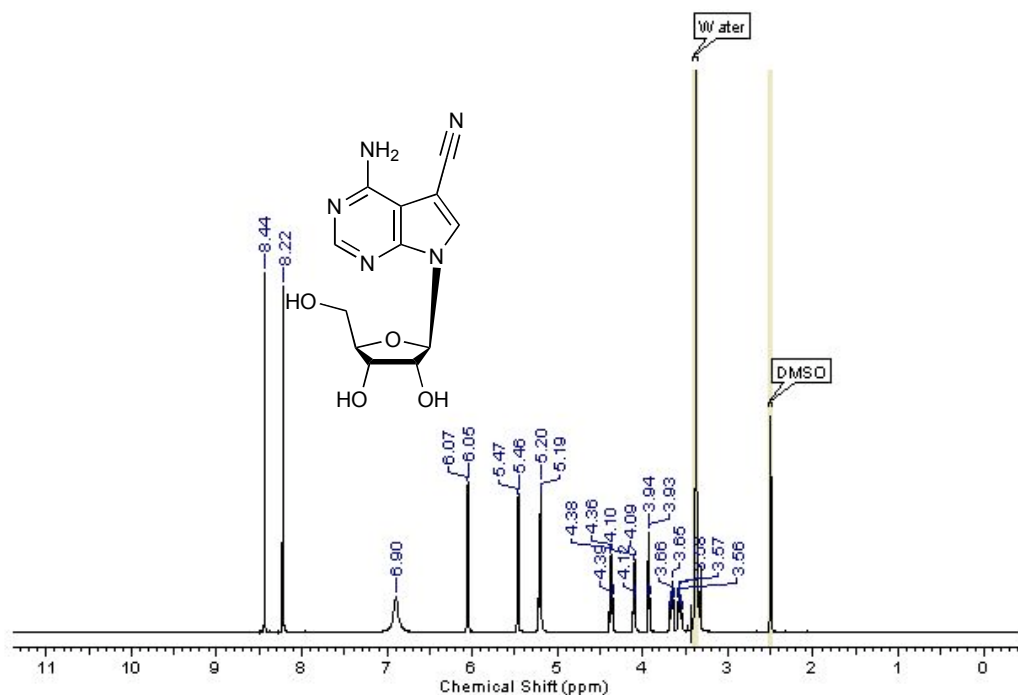
^{13}C NMR (100 MHz; DMSO- d_6)



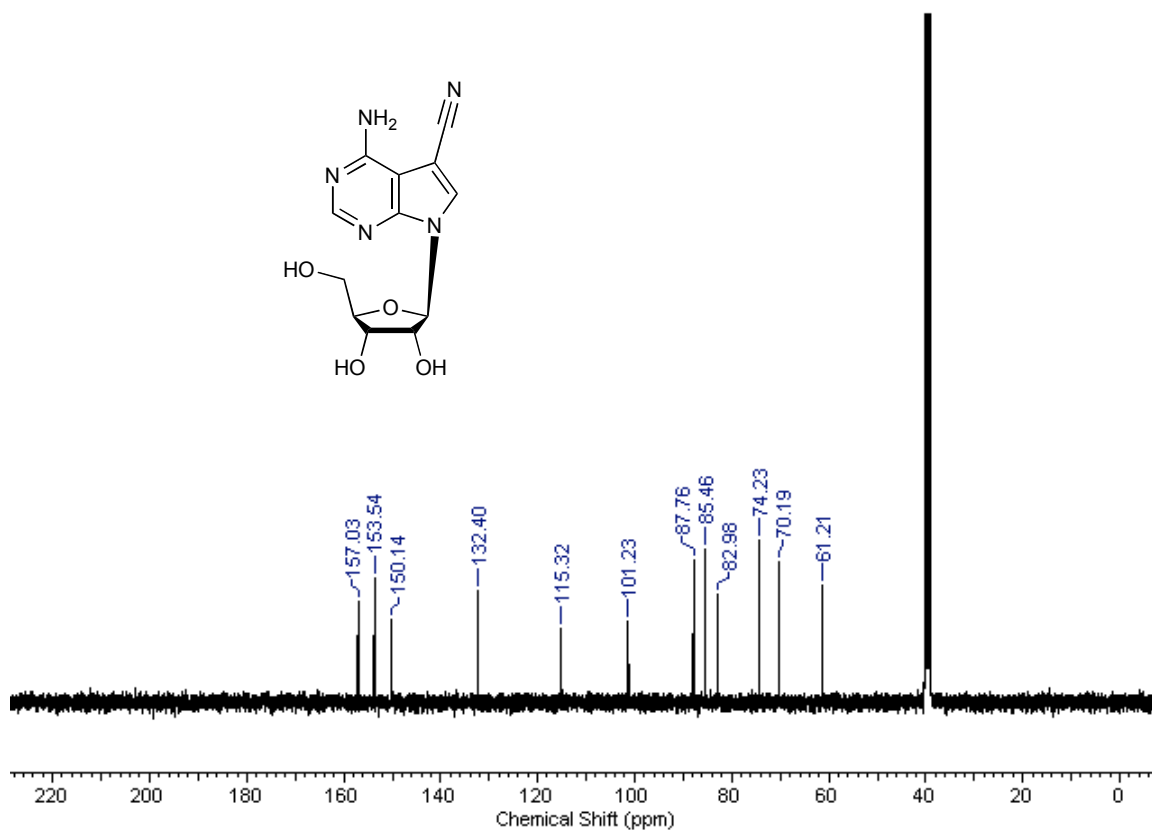
^{15}N NMR (40.5 MHz; DMSO- d_6): [2- ^{13}C , 7- ^{15}N]-Adenine 10



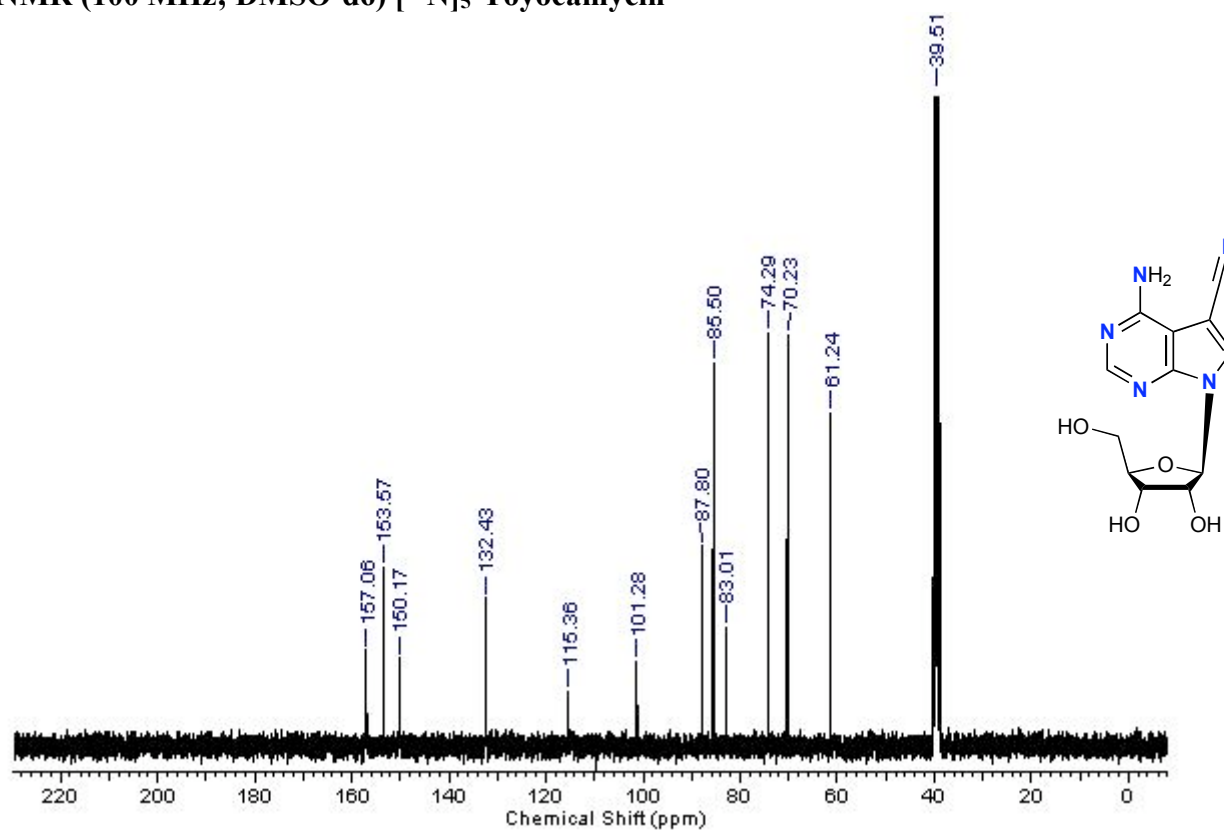
¹H NMR (400 MHz; DMSO-d₆): Toyocamycin



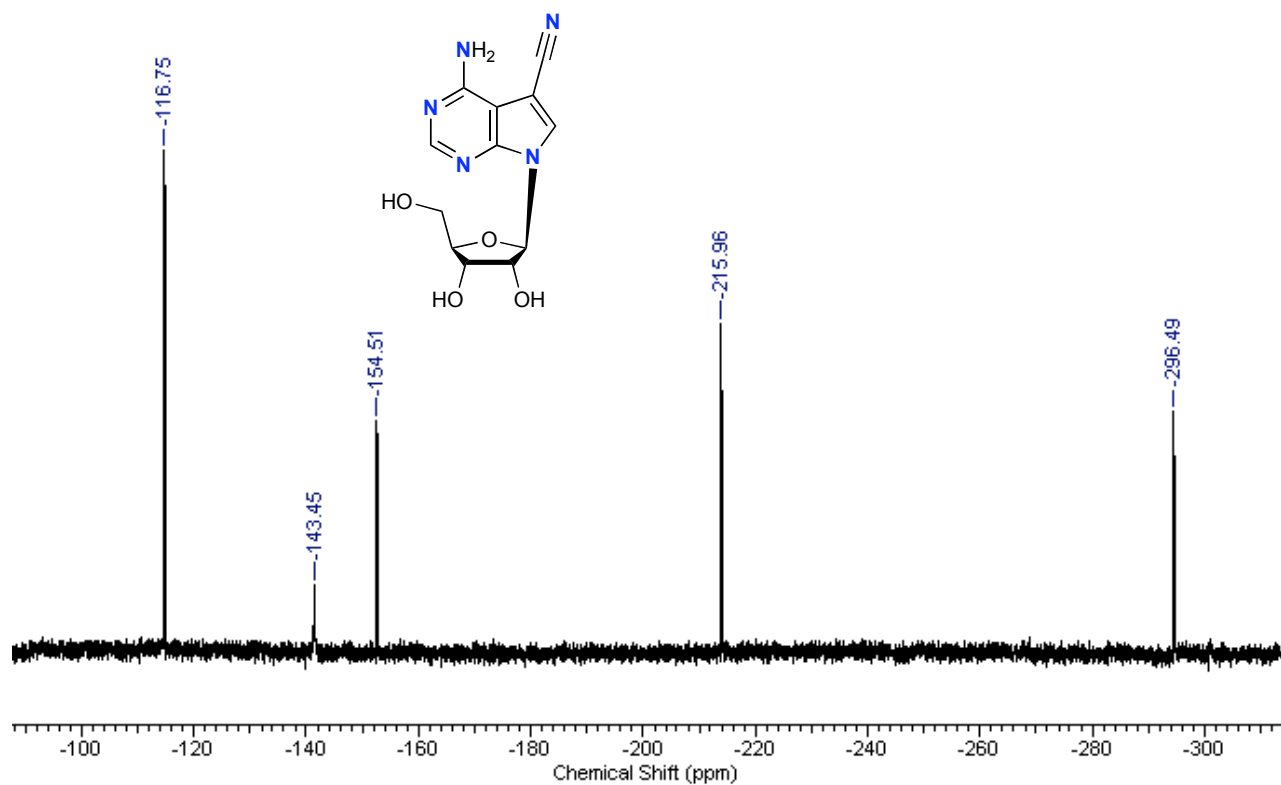
¹³C NMR (100 MHz; DMSO-d₆)



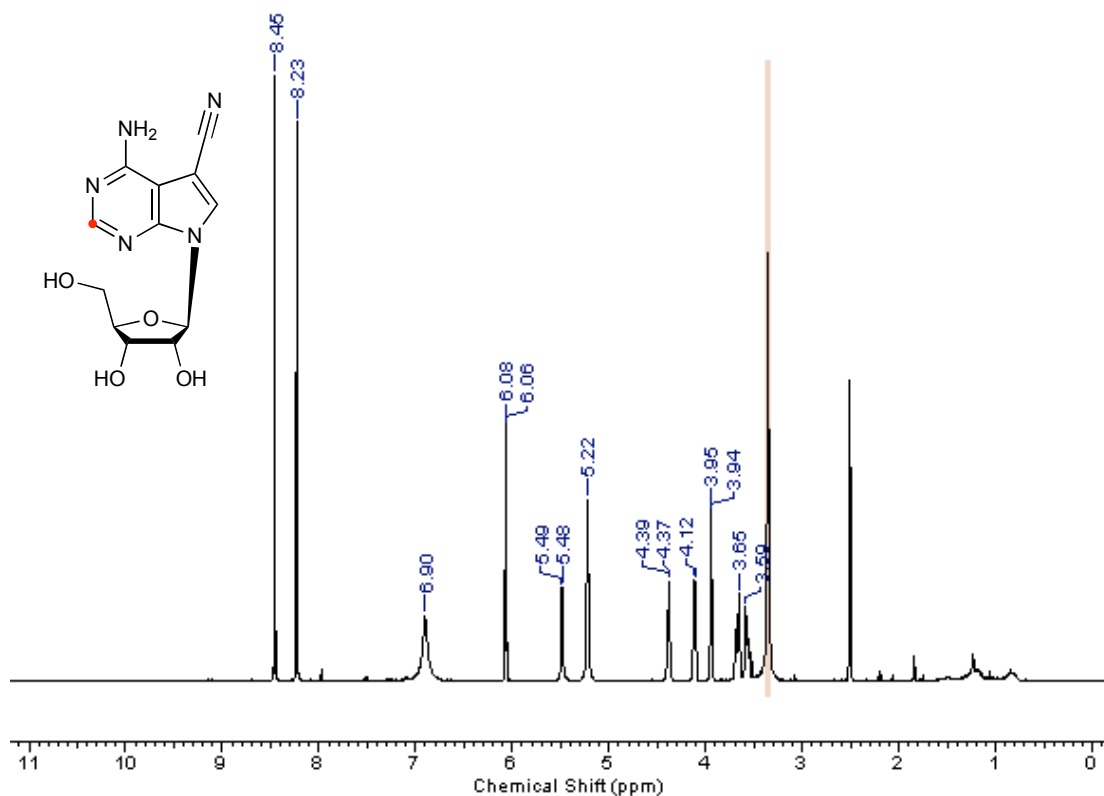
^{13}C NMR (100 MHz; DMSO- d_6) [^{15}N] $_5$ -Toyocamycin



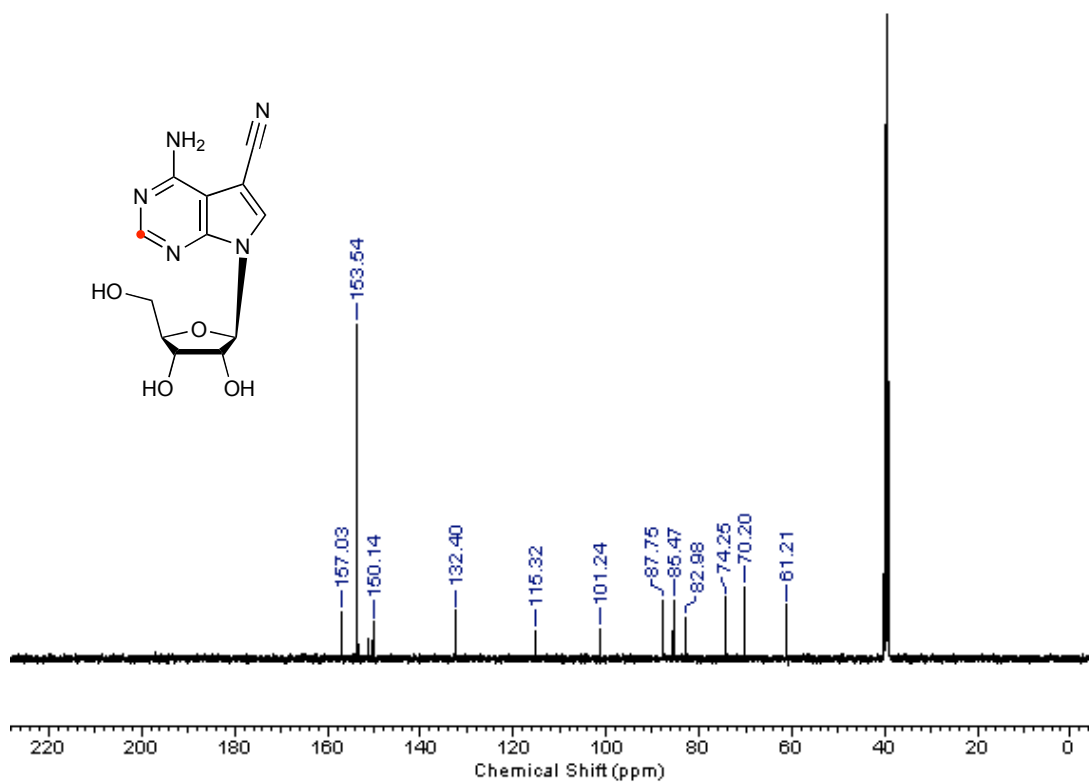
^{15}N NMR (40.5 MHz; DMSO- d_6)



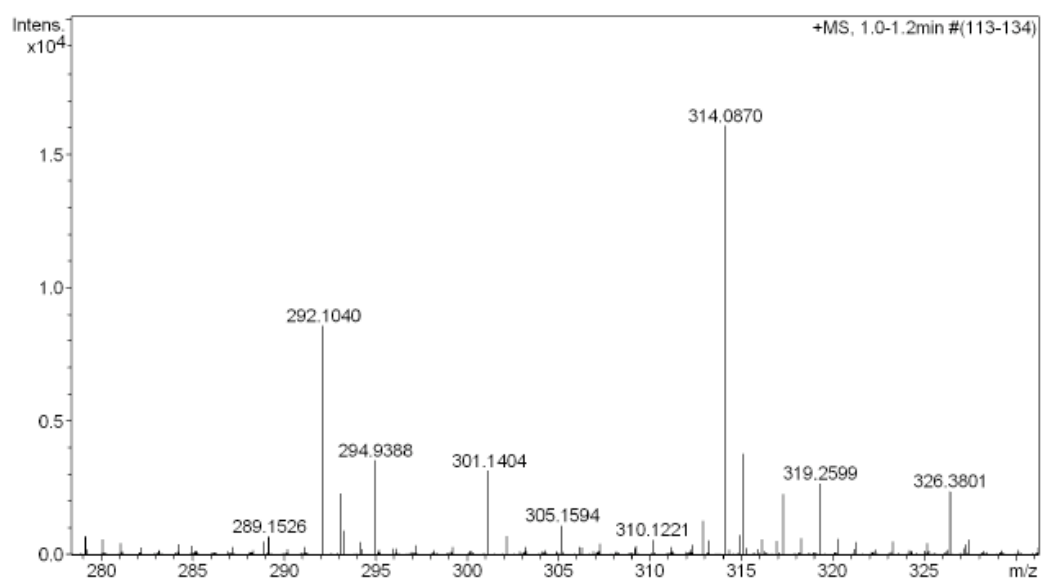
^1H NMR (400 MHz; DMSO- d_6): [2- ^{13}C]-Toyocamycin



^{13}C NMR (100 MHz; DMSO- d_6)



Mass spectrum



#	m/z	I %	#	m/z	I %
1	158.9642	16.1	16	314.0870	100.0
2	173.0767	11.0	17	315.0899	23.4
3	179.0772	15.3	18	317.2441	14.0
4	185.1132	34.9	19	319.2599	16.4
5	186.0944	11.5	20	326.3801	14.6
6	217.1031	11.7	21	362.9276	24.8
7	226.9508	69.4	22	382.0741	13.8
8	239.1056	7.3	23	399.1269	24.3
9	259.1152	7.1	24	400.1281	7.1
10	261.1291	7.5	25	413.2640	13.9
11	292.1040	53.3	26	430.9143	23.2
12	293.1110	14.1	27	498.8998	16.7
13	294.9388	21.8	28	566.8890	12.5
14	301.1404	19.4	29	605.1831	13.3
15	312.8899	7.7	30	634.8778	8.5