

# Supplementary material for First Total Synthesis of 5'-O- $\alpha$ -D-Glucopyranosyl Tubercidin

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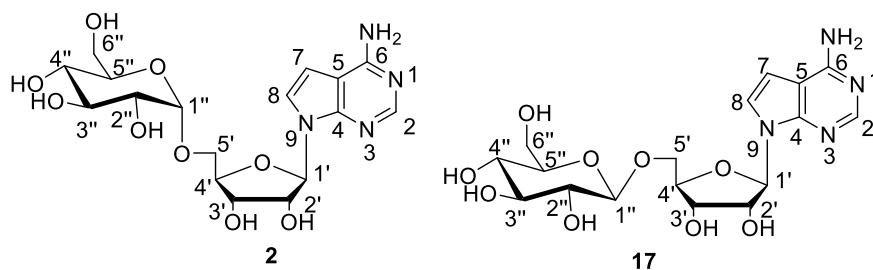
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1. Chemical shifts of naturally occurring nucleoside **2**, Synthetic nucleoside **2** and **17**



**Table S1.**  $^{13}\text{C}$  NMR chemical shifts of naturally occurring nucleoside **2**, synthetic nucleoside **2** and **17**

Chemical shifts ( $\delta$ ) Position of carbon	Naturally occurring nucleoside <b>2</b> / ppm	Synthetic nucleoside <b>2</b> / ppm	Synthetic nucleoside <b>17</b> / ppm
C-6	157.3	157.3	157.5
CH-2	151.5	151.5	151.7
C-4	150.6	150.6	150.7
CH-8	122.2	122.4	122.2
C-5	103.0	102.8	103.1
CH-7	99.8	100.0	100.5
CH-1''	98.7	98.5	103.5
CH-1'	85.8	85.9	87.1
CH-4'	83.0	83.2	83.1
CH-2'	74.0	74.2	77.2
CH-4''	73.4	73.3	74.2
CH-5''	72.9	72.7	74.1
CH-2''	71.8	71.5	77.4
CH-3'	71.1	70.9	71.1
CH-3''	70.2	70.0	70.5
CH <sub>2</sub> -5'	67.2	67.0	69.5
CH <sub>2</sub> -6''	60.9	60.9	61.5

**Table S2.** <sup>1</sup>H NMR chemical shifts and coupling constants of naturally occurring nucleoside 2, synthetic 2 and 17

Chemical shifts (δ) Hydrogen	Naturally occurring nucleoside 2 (coupling constants) / ppm	Synthetic nucleoside 2 (coupling constants) / ppm	Synthetic nucleoside 17 (coupling constants) / ppm
H-2	8.03 (s)	8.09 (s)	8.07 (s)
H-8	7.69(d, J = 3.7 Hz)	7.76 (d, J = 3.2 Hz)	7.38 (d, J = 3.7 Hz)
NH <sub>2</sub>	6.95 (s)	7.20 (s)	7.09 (s)
H-7	6.53 (d, J = 3.7 Hz)	6.61 (d, J = 3.4 Hz)	6.61 (d, J = 3.6 Hz)
H-1'	6.12(d, J = 7.0 Hz)	6.14 (d, J = 7.0 Hz)	6.08 (d, J = 5.6 Hz)
3'-OH	5.19 (d, J = 4.8 Hz)	5.21 (d, J = 4.6 Hz)	5.17 (d, J = 4.6 Hz)
2''-OH	5.19 (d, J = 4.8 Hz)	5.21 (d, J = 4.6 Hz)	5.03 (d, J = 3.7 Hz)
2'-OH	5.10 (d, J = 4.8 Hz)	5.10 (d, J = 4.3 Hz)	5.26 (d, J = 5.5 Hz)
3''-OH	4.93 (d, J = 3.8 Hz)	4.92 (d, J = 4.9 Hz)	4.95 (s)
4''-OH	4.85 (d, J = 4.6 Hz)	4.84 (d, J = 3.6 Hz)	4.91 (s)
H-1''	4.70 (d, J = 3.5 Hz)	4.72 (d, J = 3.1 Hz)	4.21 (d, J = 7.8 Hz)
6''-OH	4.50 (d, J = 4.7 Hz)	4.49 (m)	4.51 (s)
H-2'	4.41 (td, J = 6.3 Hz, 4.8, 4.8 Hz)	4.43 (m)	4.36 (d, J = 5.0 Hz)
H-4'	4.09 (td, J = 4.9 Hz, 4.9, 2.1 Hz)	4.11 (m)	4.02–3.95 (m)
H-3'	4.05 (m)	4.08 (d, J = 1.7 Hz)	4.14 (d, J = 4.4 Hz)
H-5'	3.76 (dd, J = 11.1, 3.1 Hz)	3.78 (dd, J = 10.9, 2.8 Hz)	4.02–3.95 (m)
H-6''	3.64 (ddd, J = 10.9, 4.8, 1.2 Hz)	3.66–3.63 (m)	3.68 (d, J = 9.2 Hz)
H-4''	3.45 (m)	3.47–3.42 (m)	3.12–3.04 (m)
H-6' ''	3.44 (m)	3.47–3.42 (m)	3.44 (d, J = 6.7 Hz)
H-5'	3.41 (dd, J = 11.1, 4.9 Hz)	3.47–3.42 (m)	3.59 (dd, J = 11.9, 5.7 Hz)
H-5''	3.34 (m)	3.40–3.34 (m)	3.12–3.04 (m)
H-2''	3.26 (m)	3.40–3.34 (m)	3.00 (d, J = 7.8 Hz)
H-3''	3.10 (td, J = 9.3, 3.8 Hz)	3.13–3.07 (m)	3.15 (d, J = 9.9 Hz)

2. Optimization of glycosylation of **11** and **6**

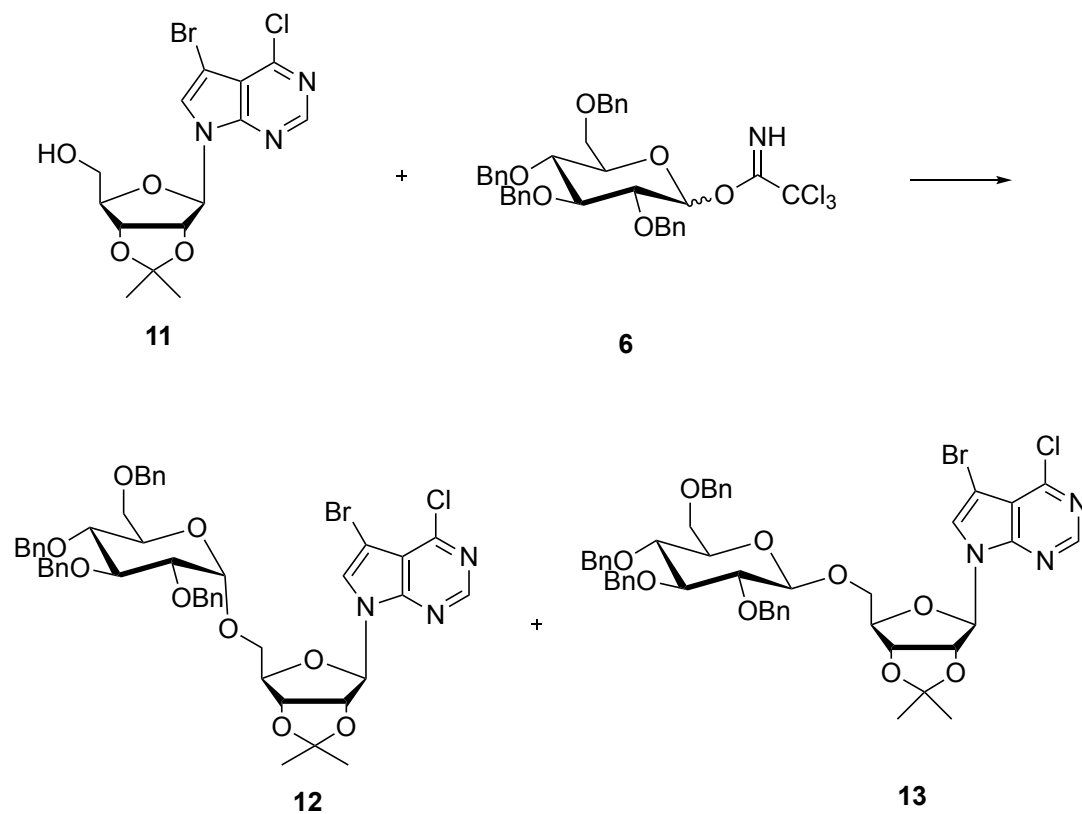
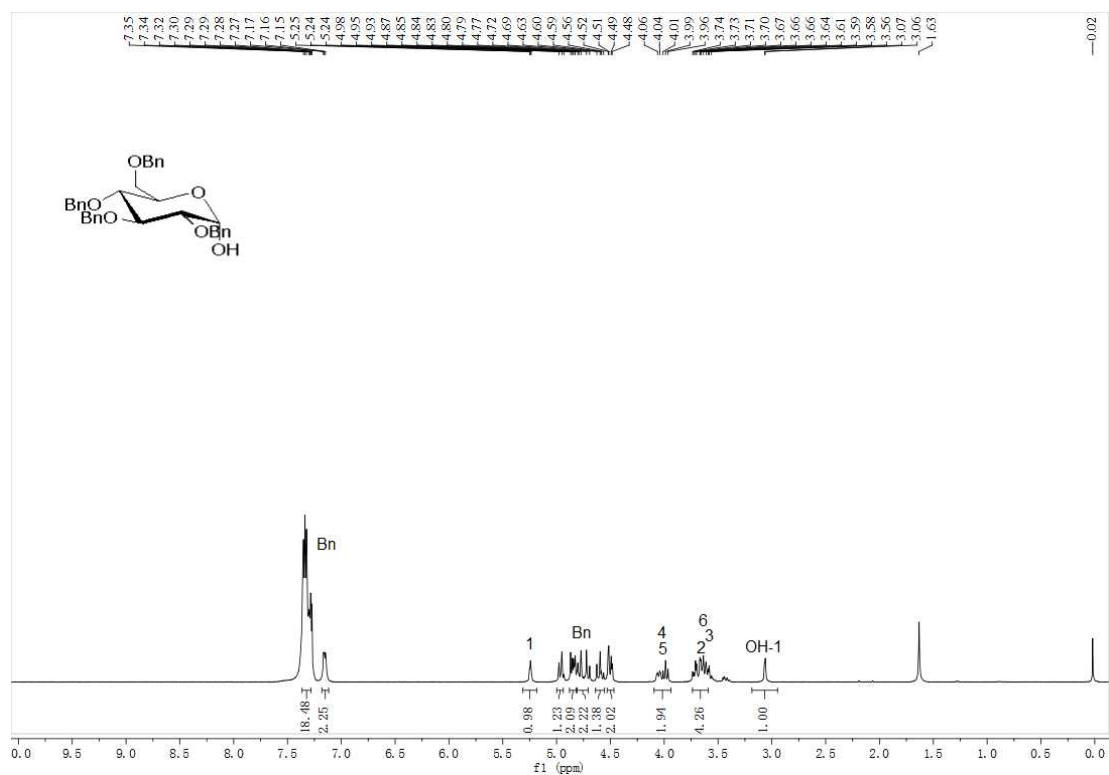


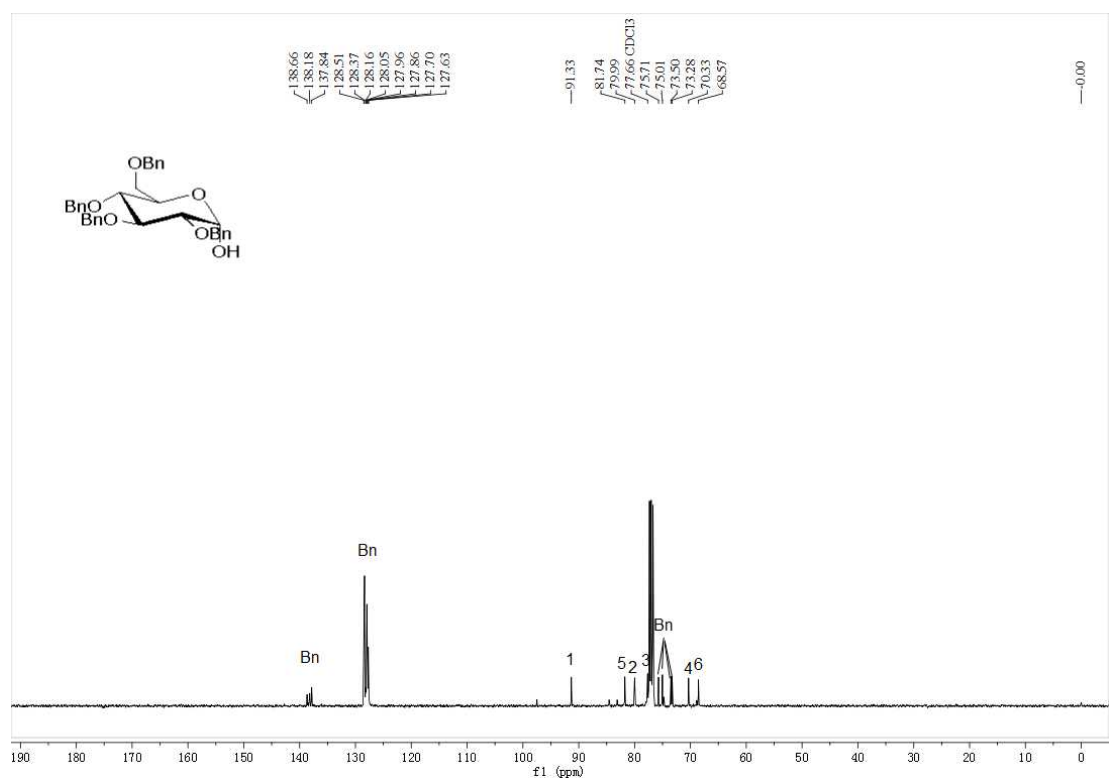
Table S3 Optimization of glycosylation of **11** and **6**

Entry	Solvent	Lewis Acid	Temperature	Ratio of		Yield
				<b>12:13</b>		
1	DCM	TMSOTf	-78 °C	2.6:1		71%
2	DCM	TMSOTf	-30 °C	4:1		79%
3	DCM	TMSOTf	0 °C	1.6:1		67%
4	DCM	BF <sub>3</sub> .Et <sub>2</sub> O	0 °C	1.2:1		43%
5	DCM	BF <sub>3</sub> .Et <sub>2</sub> O	-30 °C	3:1		59%
6	DCM	BF <sub>3</sub> .Et <sub>2</sub> O	-78 °C	1.5:1		57%

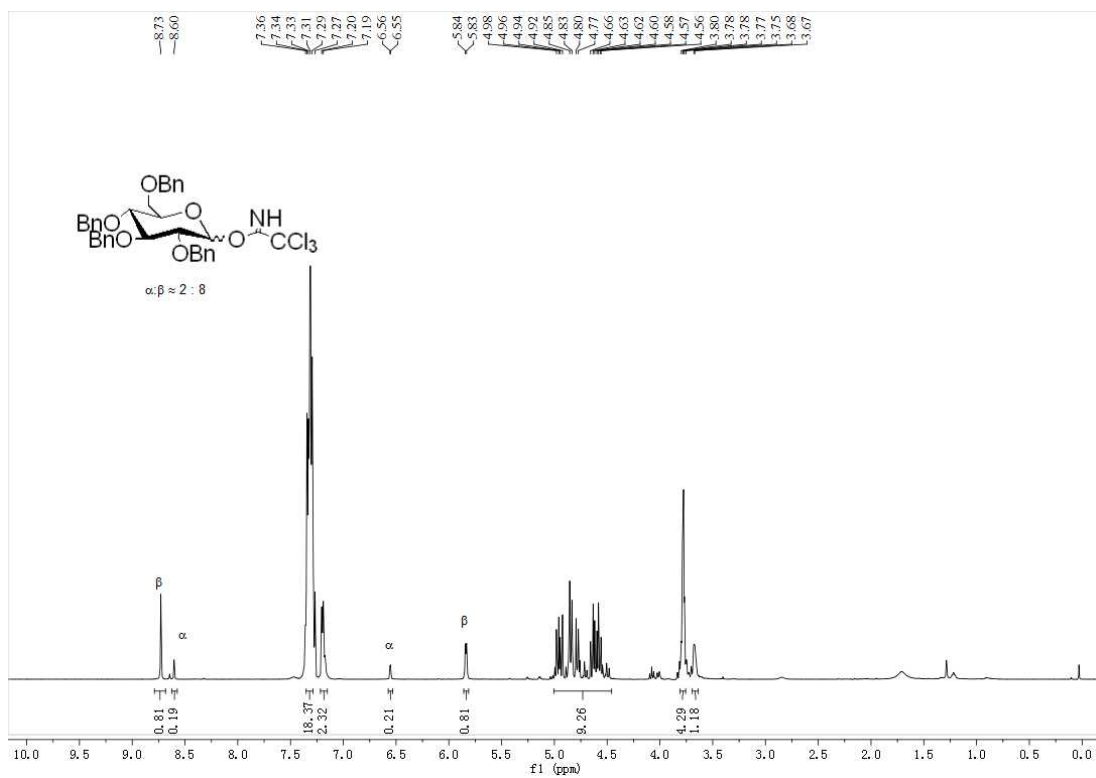
3.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds 2 – 17.



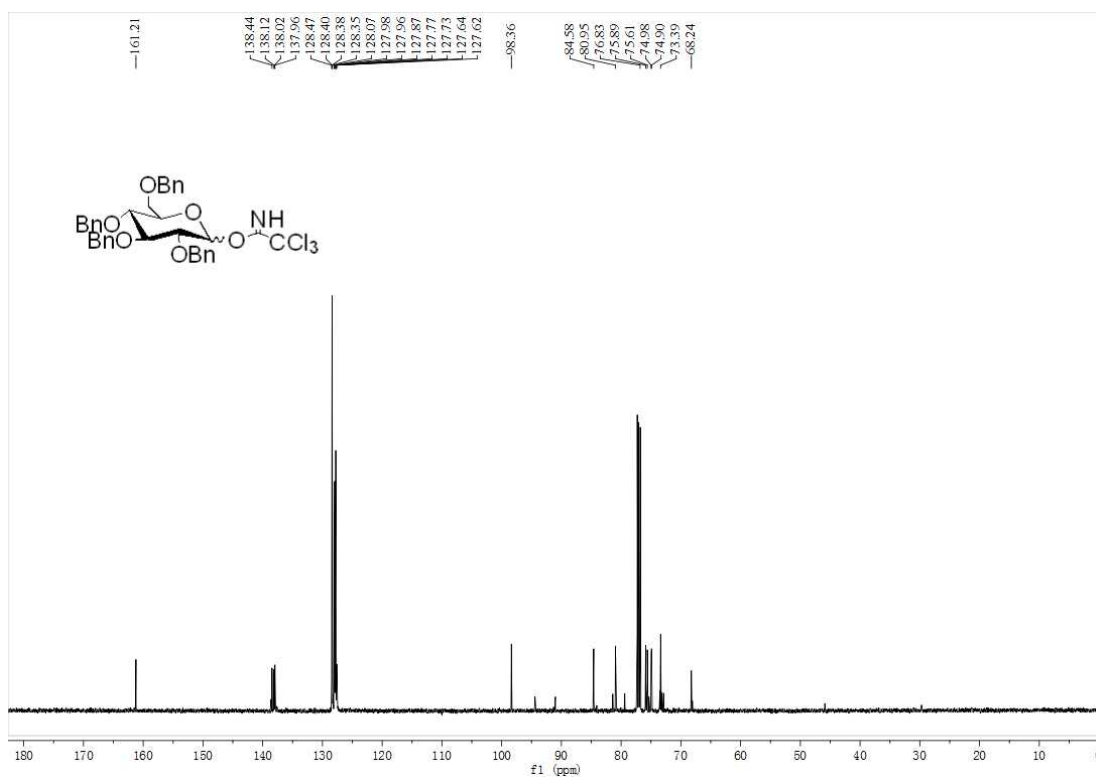
$^1\text{H}$  NMR (CDCl<sub>3</sub>) of 2,3,4,6-*O*-tetrabenzyl- $\text{D}$ -glucopyranose.



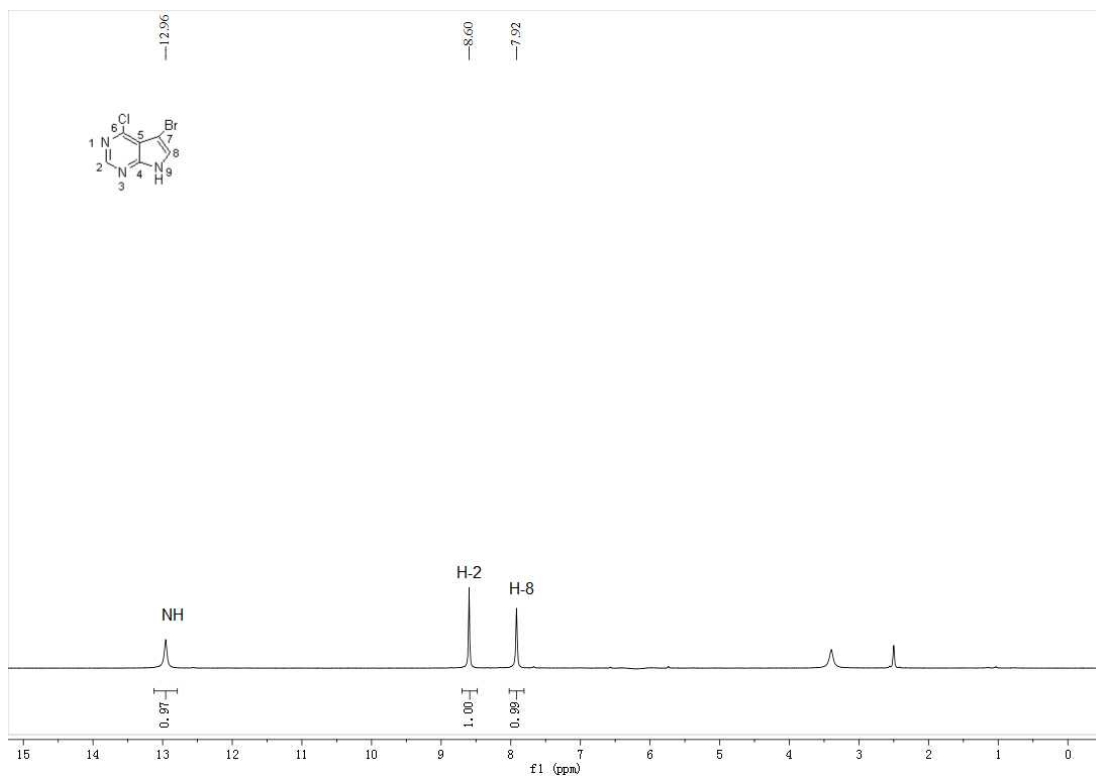
$^{13}\text{C}$  NMR (CDCl<sub>3</sub>) of 2,3,4,6-*O*-tetrabenzyl- $\text{D}$ -glucopyranose.



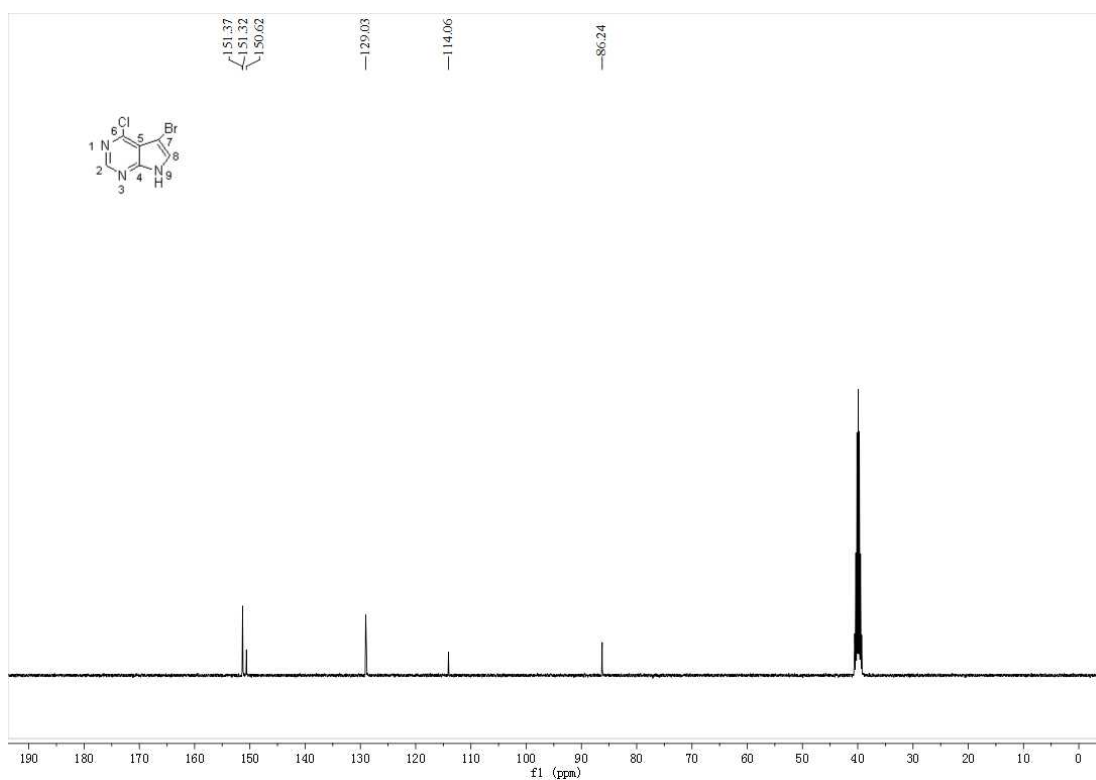
<sup>1</sup>H NMR (CDCl<sub>3</sub>) of 6.



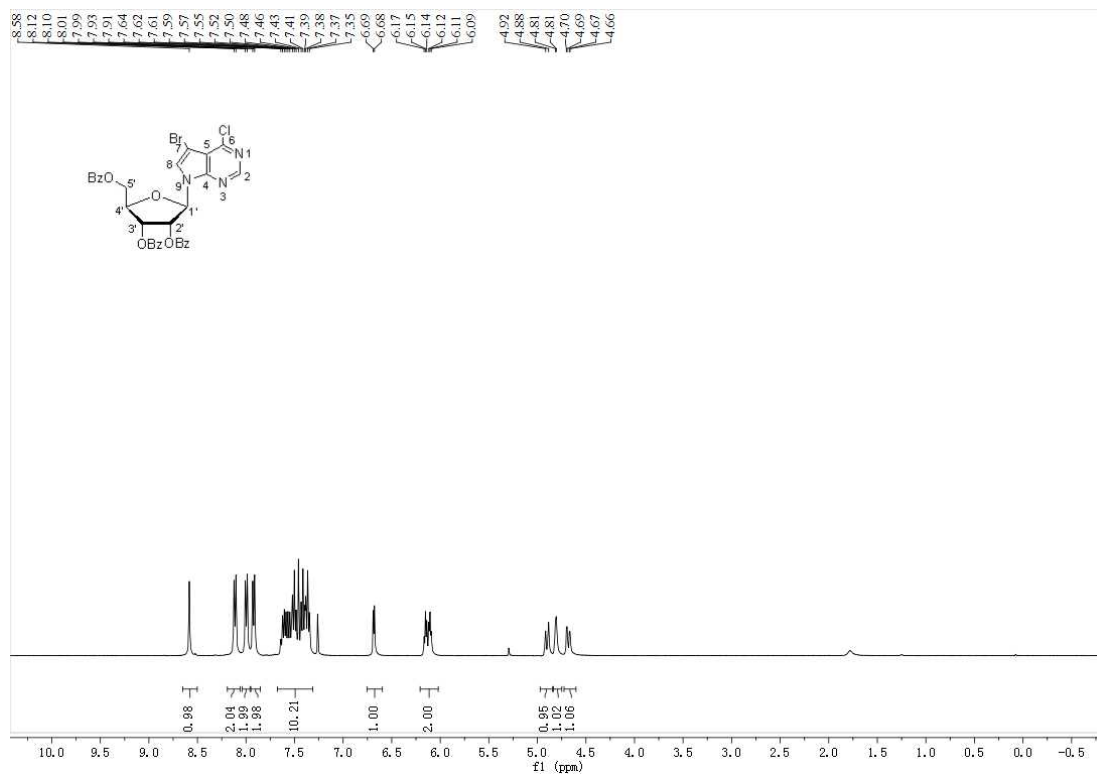
<sup>13</sup>C NMR (CDCl<sub>3</sub>) of 6.



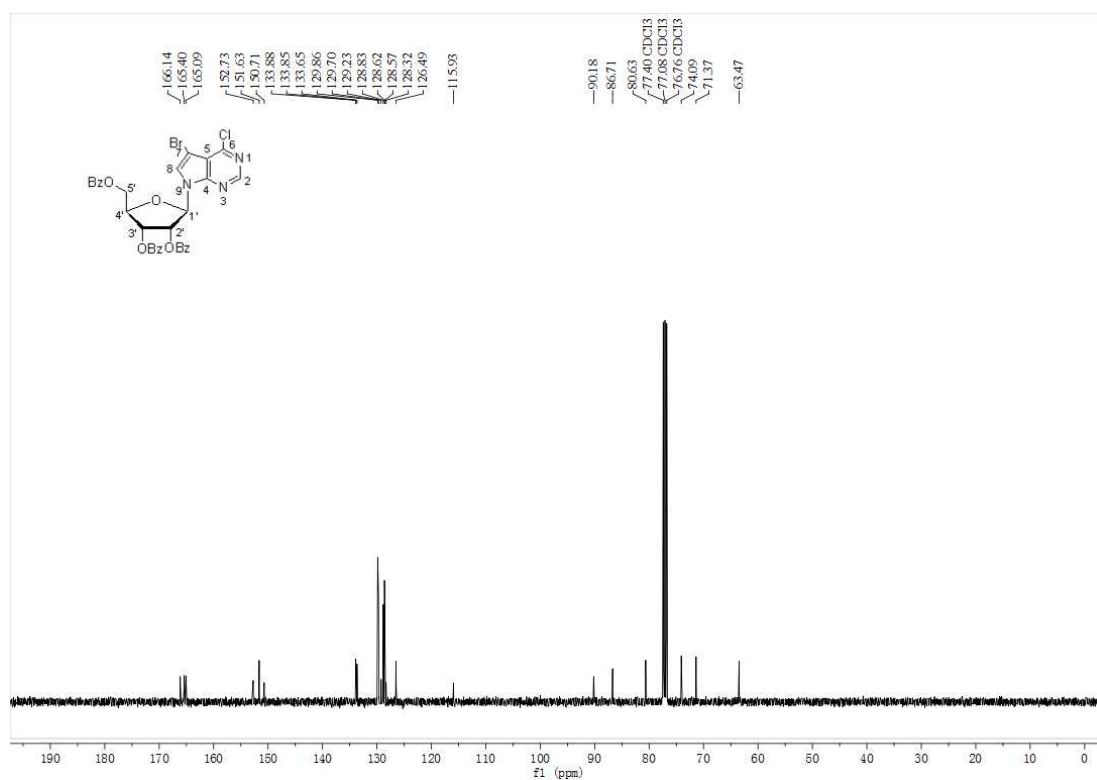
$^1\text{H NMR (DMSO)}$  of 8.



$^{13}\text{C NMR (DMSO)}$  of 8.

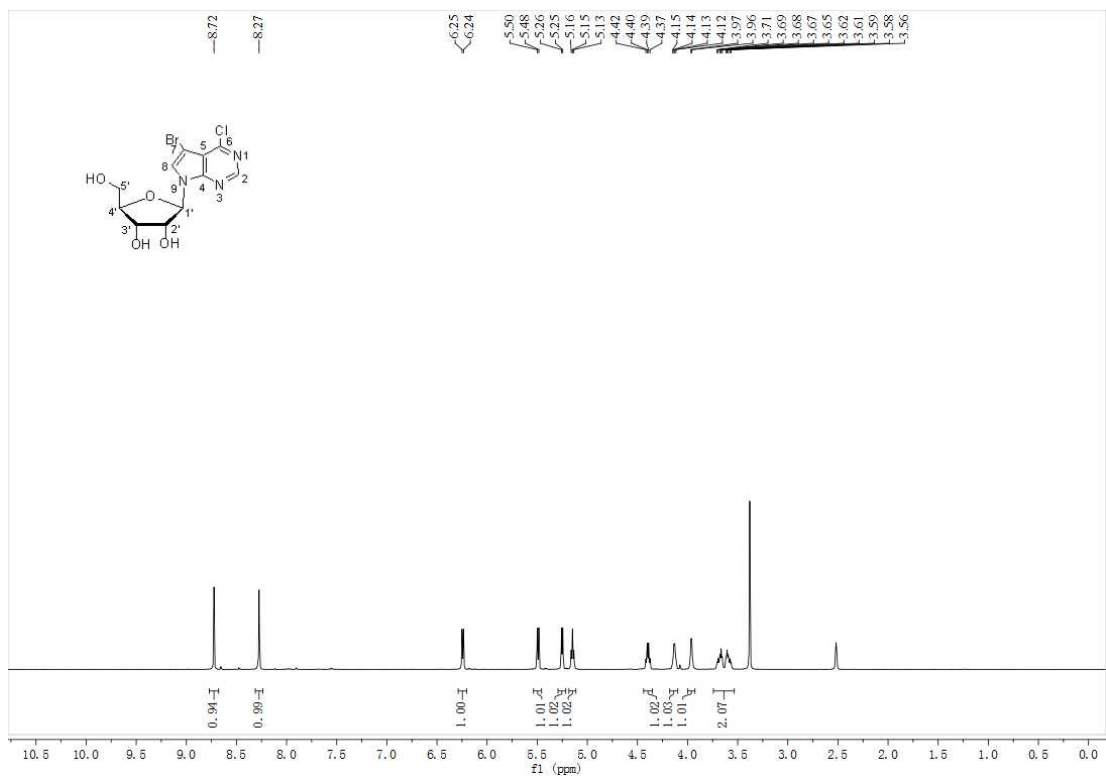


$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of **9**.

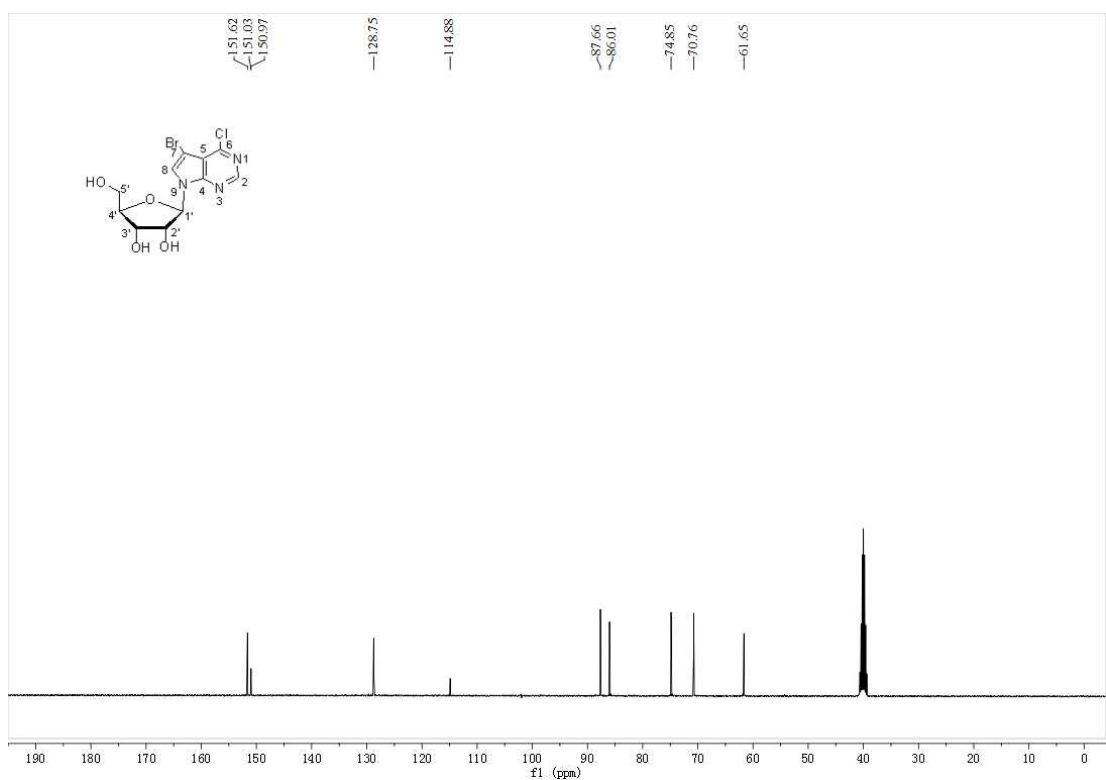


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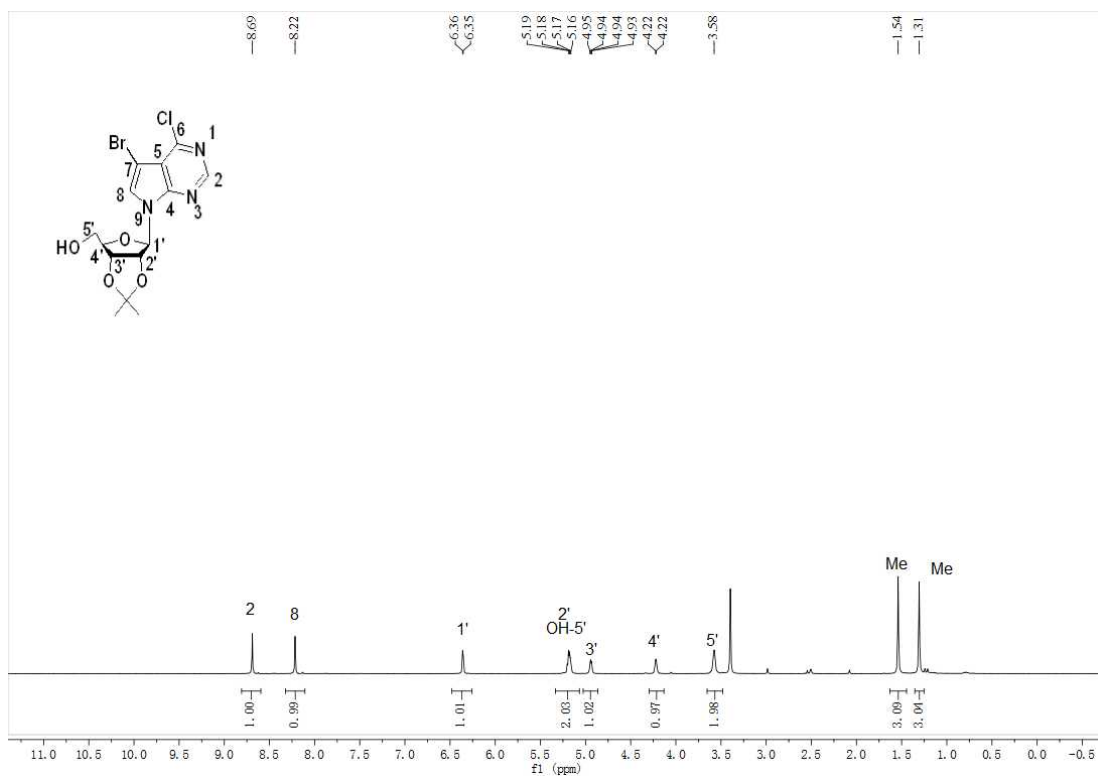




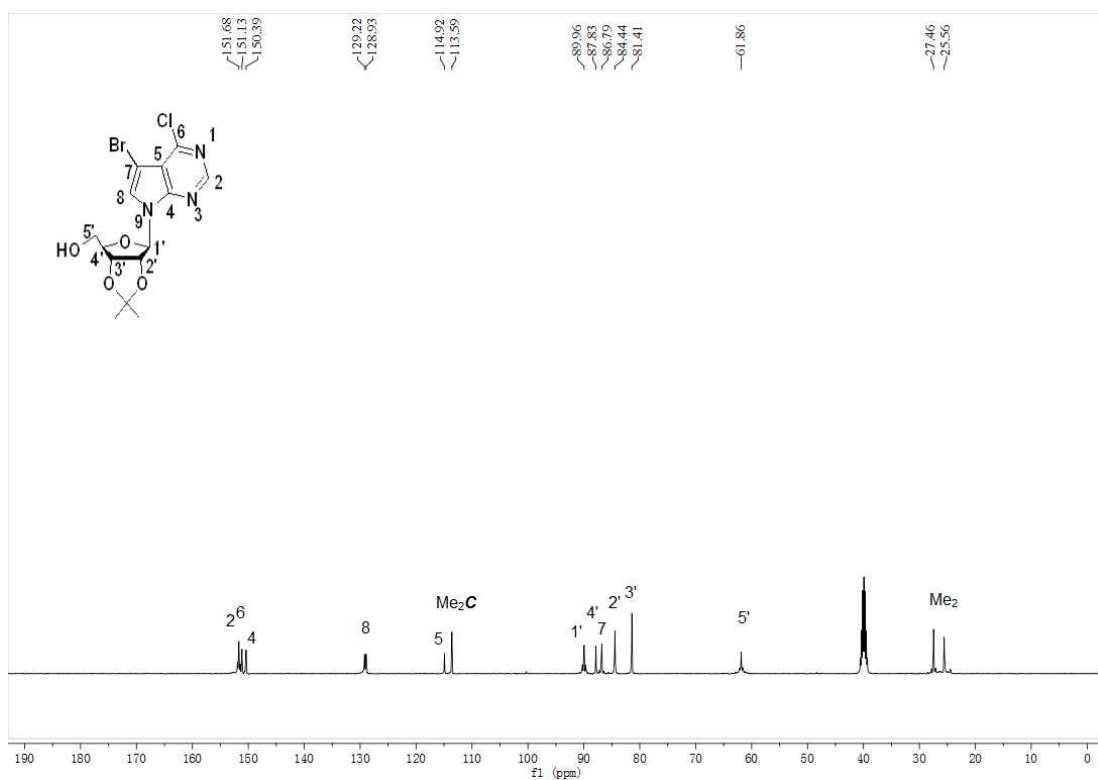
<sup>1</sup>H NMR (DMSO) of 10.



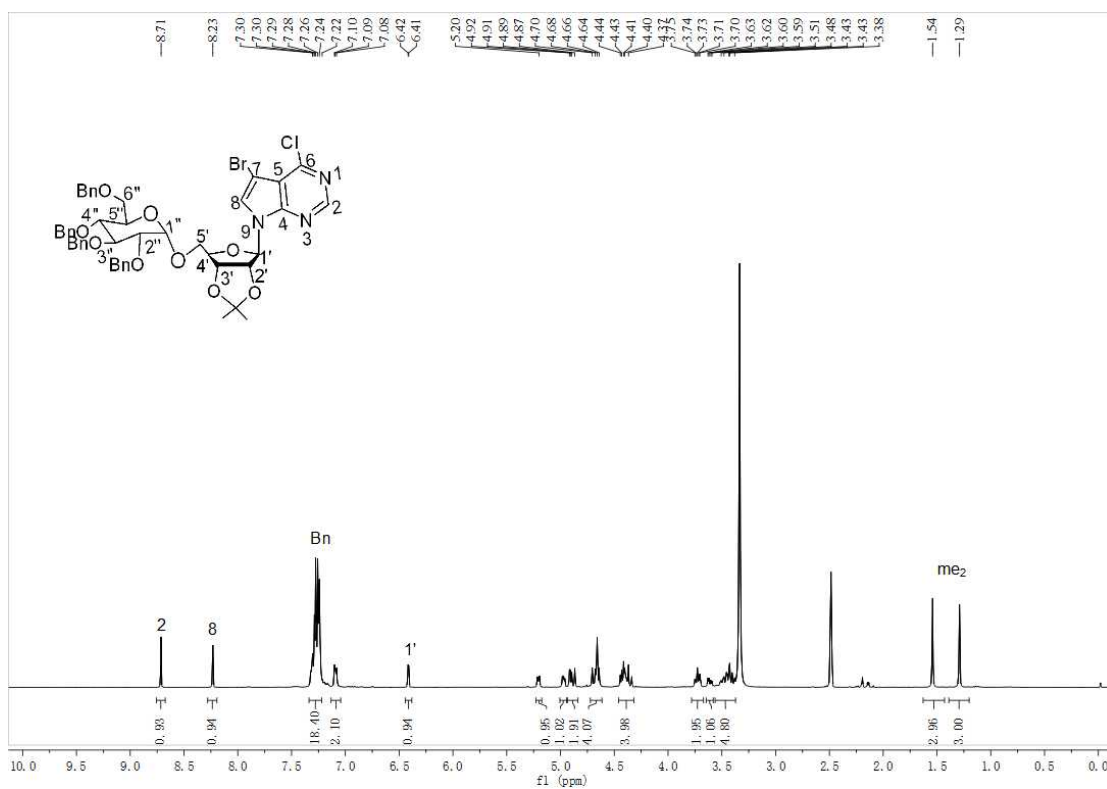
<sup>13</sup>C NMR (DMSO) of 10.



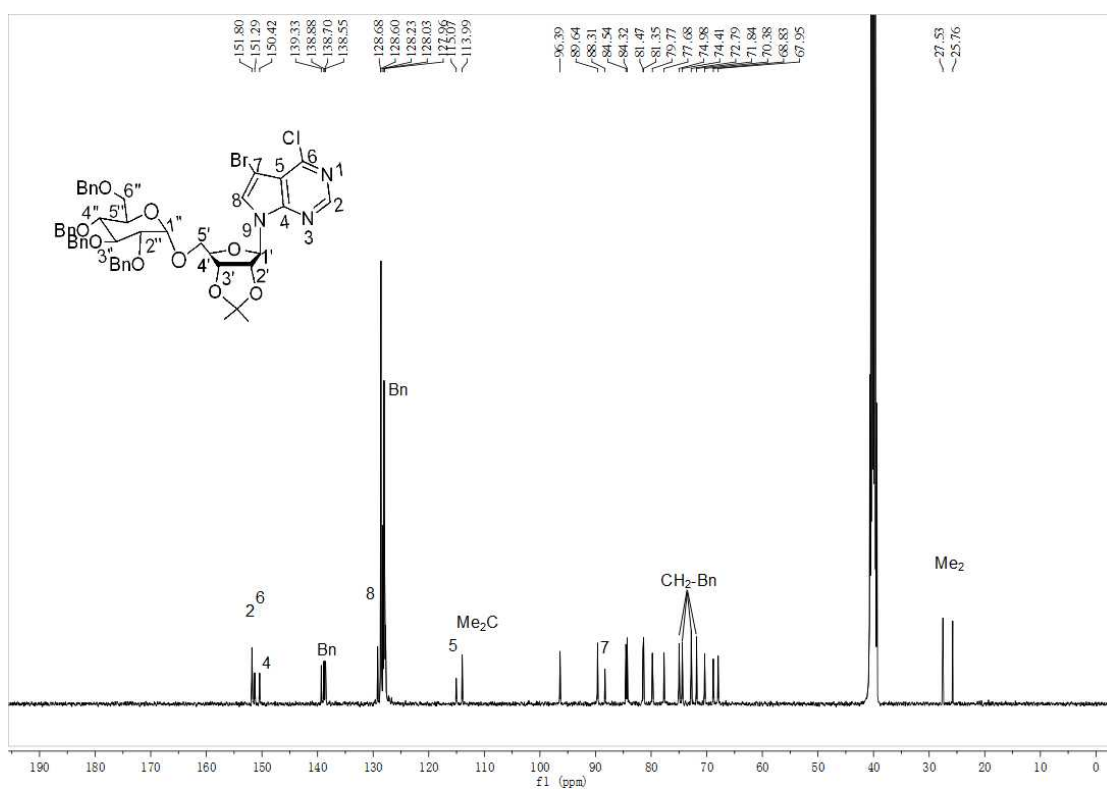
**<sup>1</sup>H NMR (DMSO) of 11.**



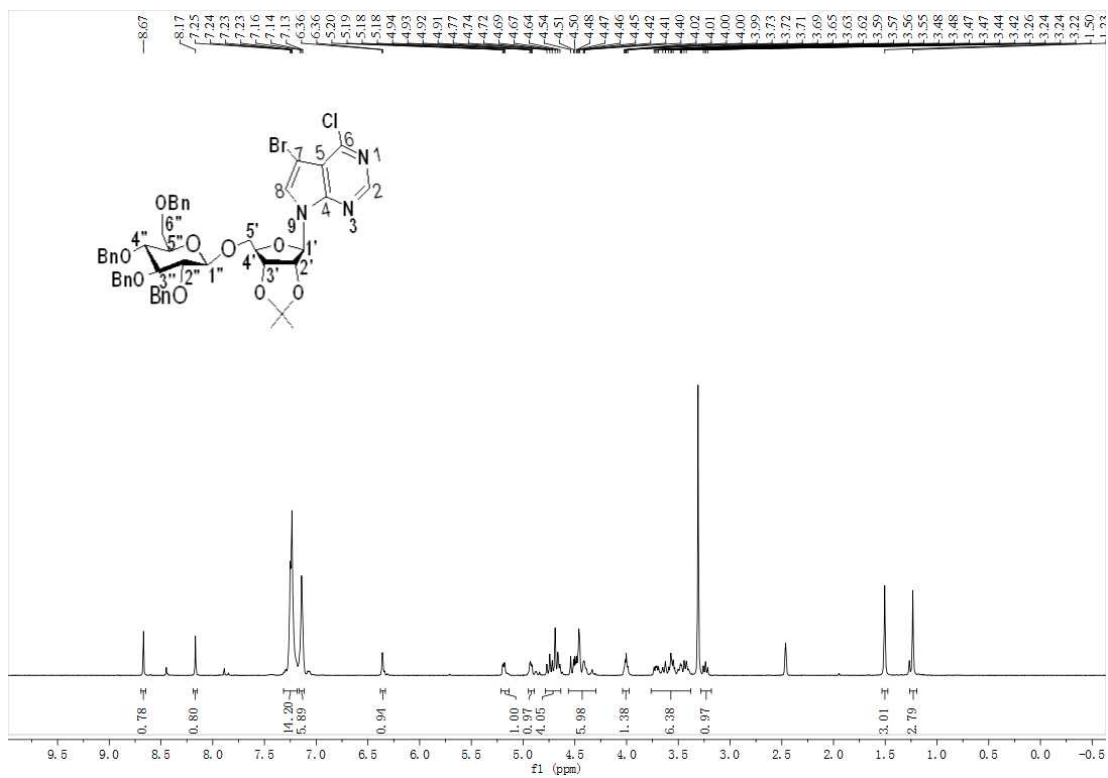
**<sup>13</sup>C NMR (DMSO) of 11.**



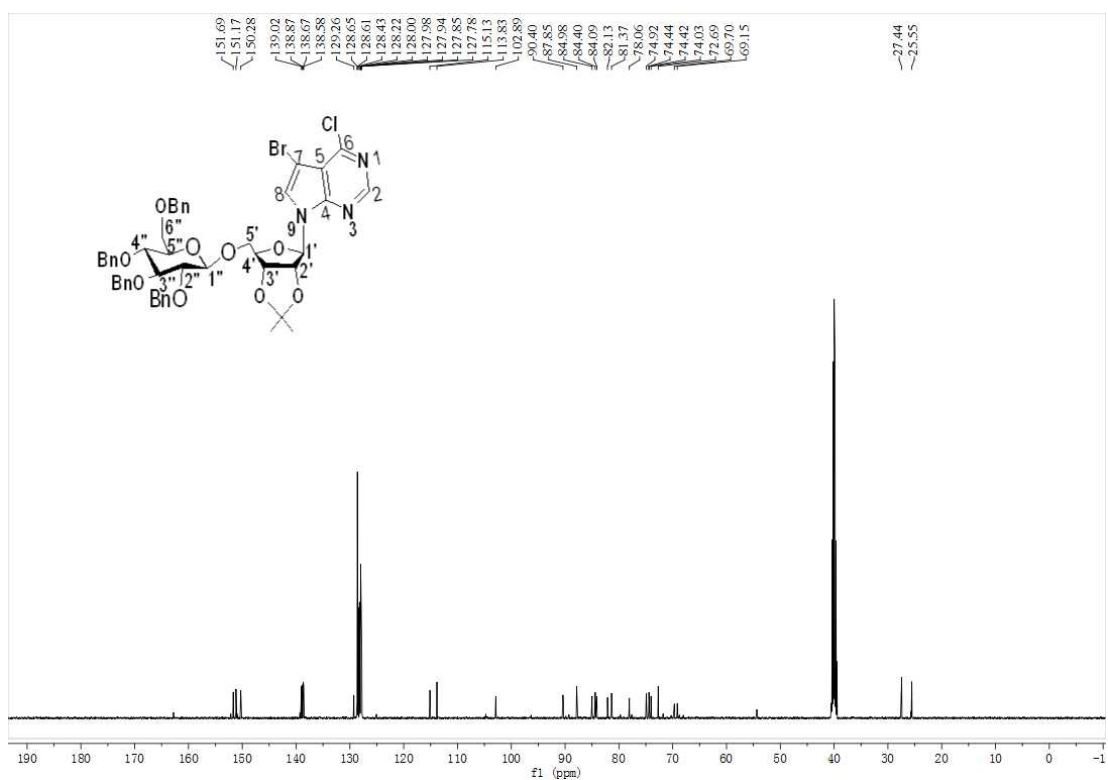
**<sup>1</sup>H NMR (DMSO) of 12.**



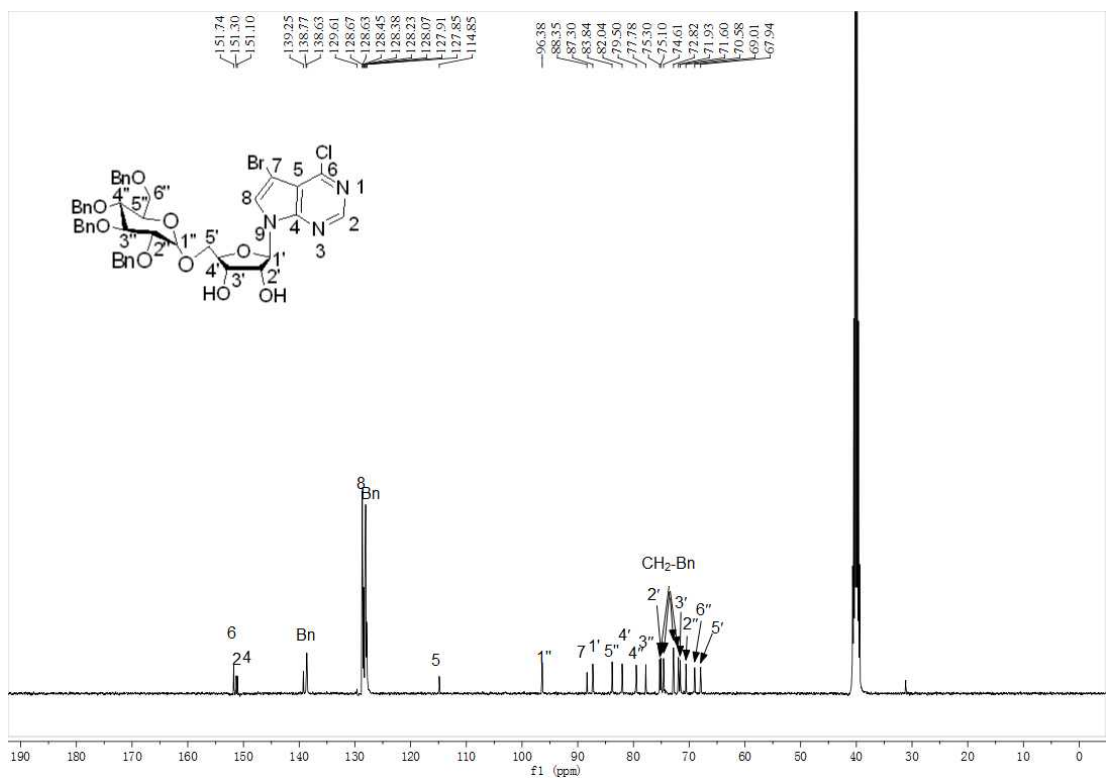
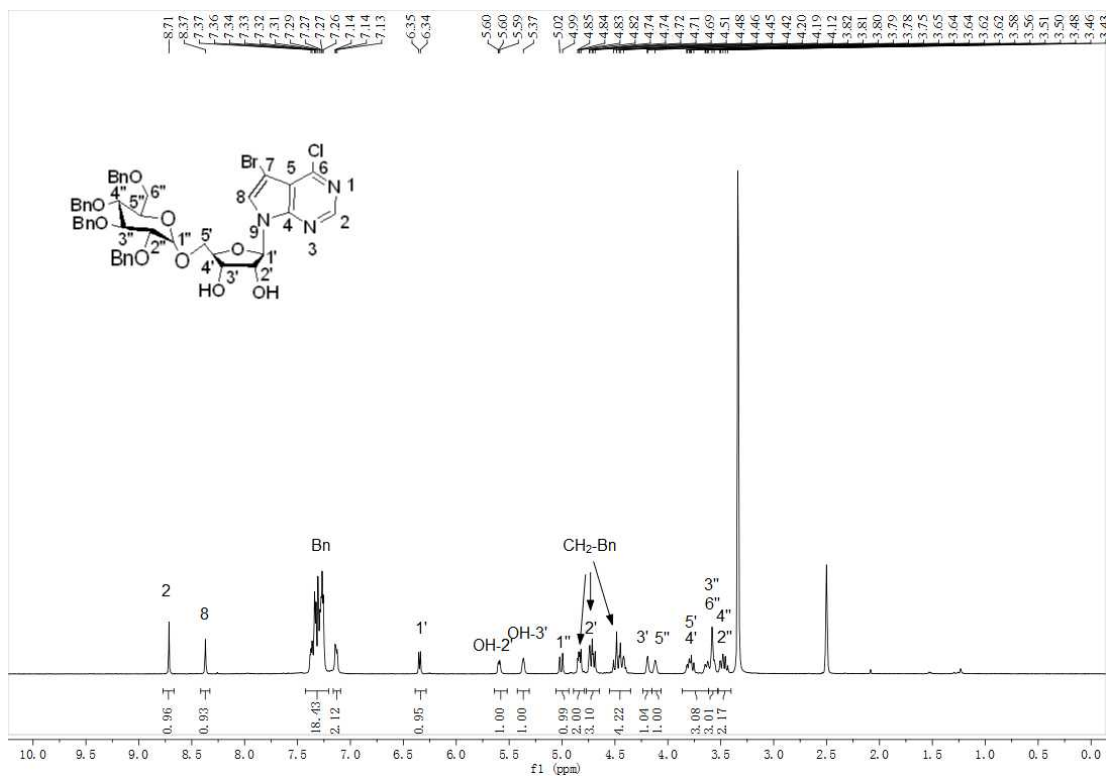
**<sup>13</sup>C NMR (DMSO) of 12.**

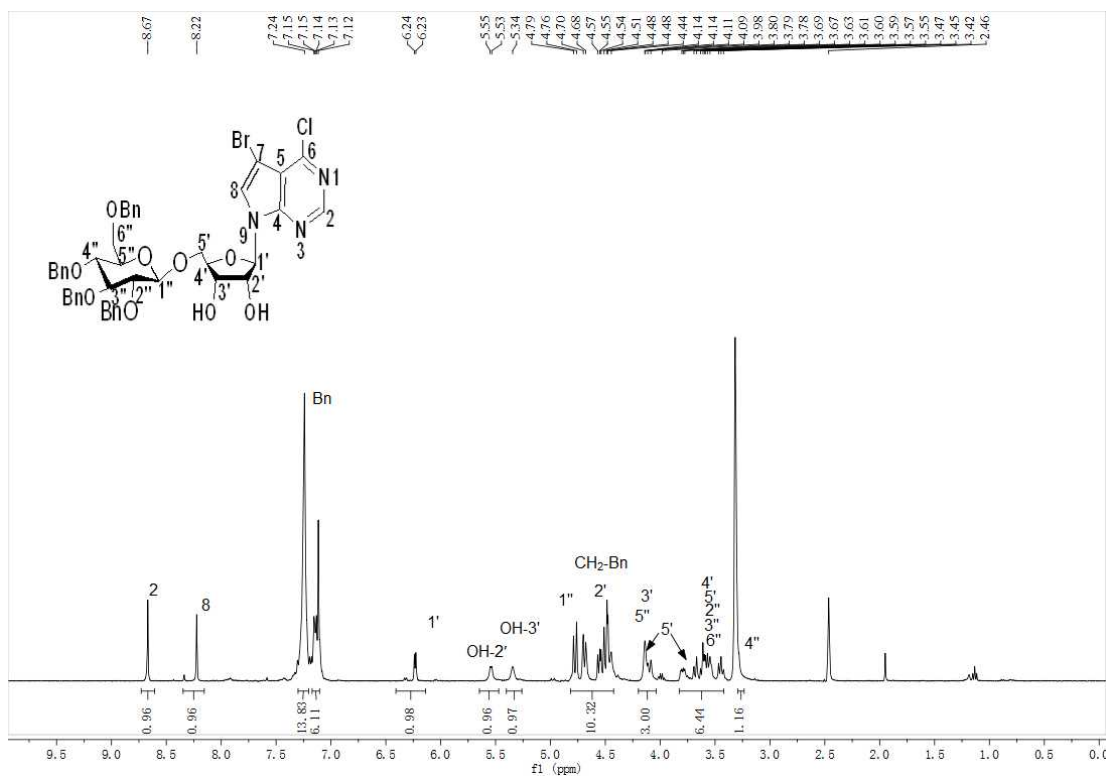


<sup>1</sup>H NMR (DMSO) of 13.

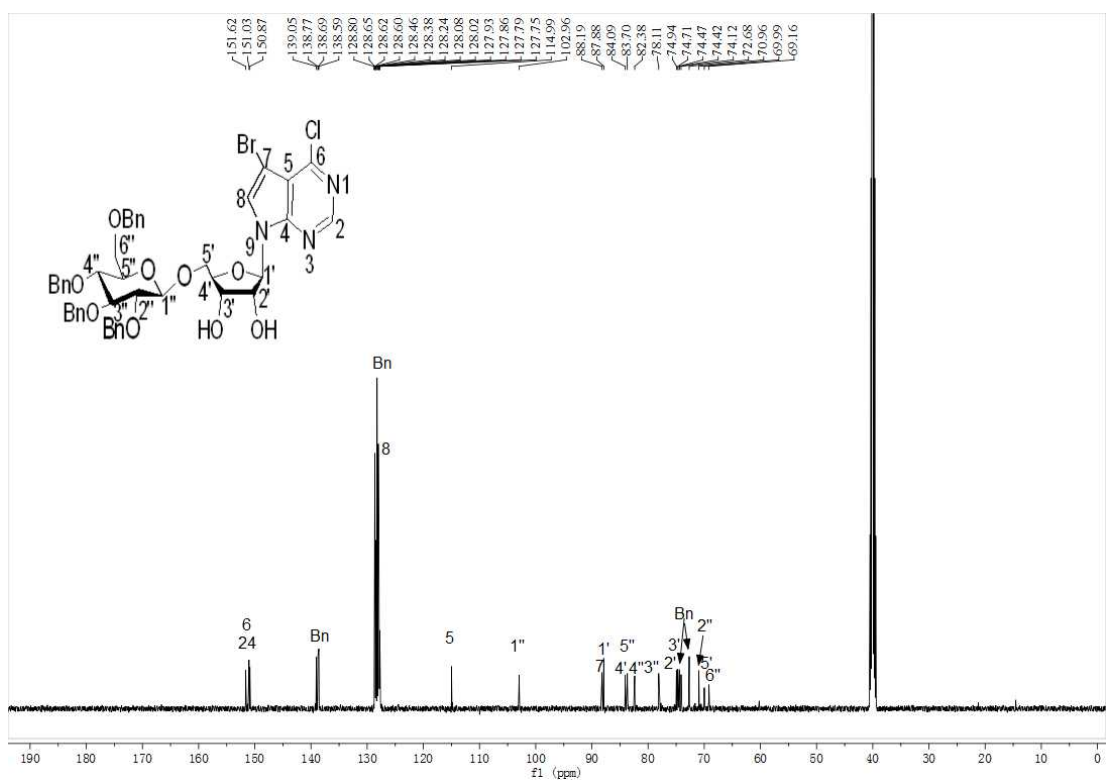


<sup>13</sup>C NMR (DMSO) of 13.

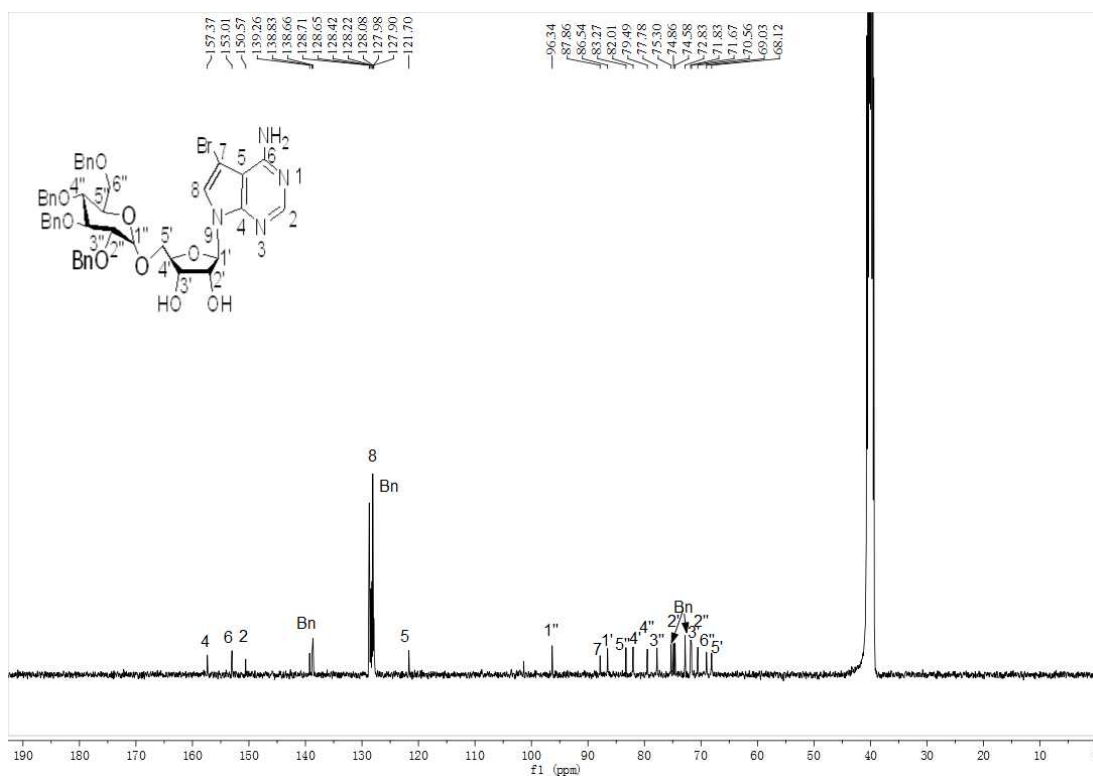
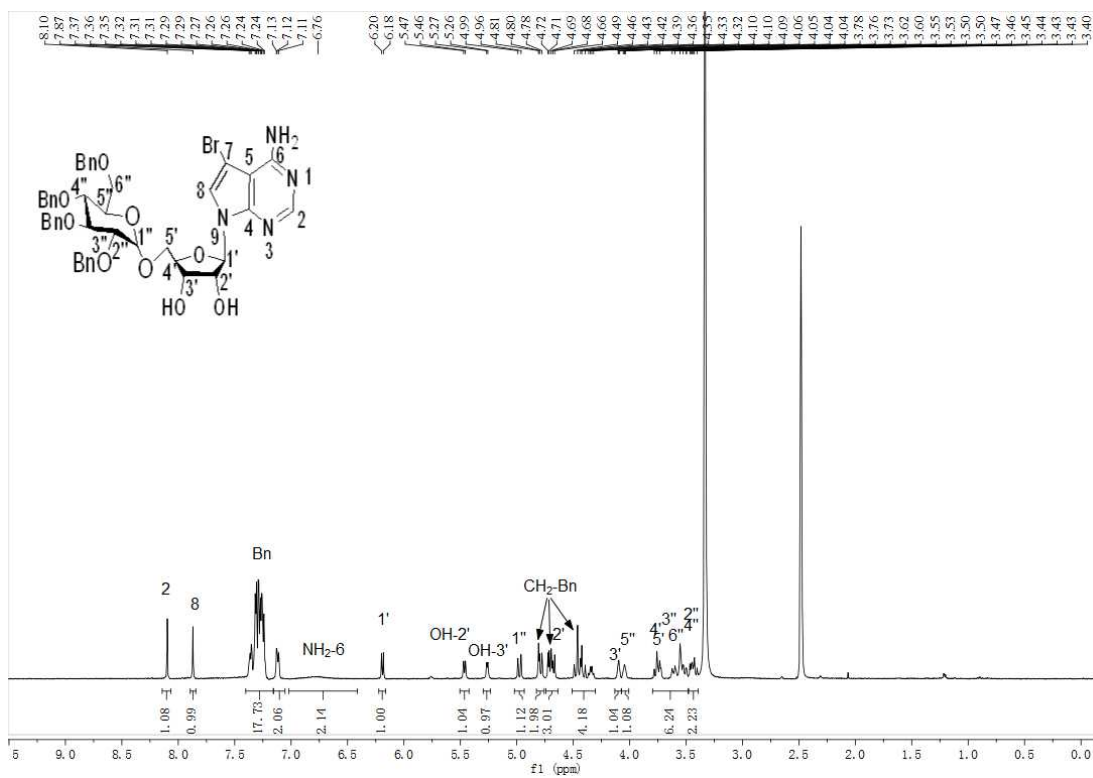


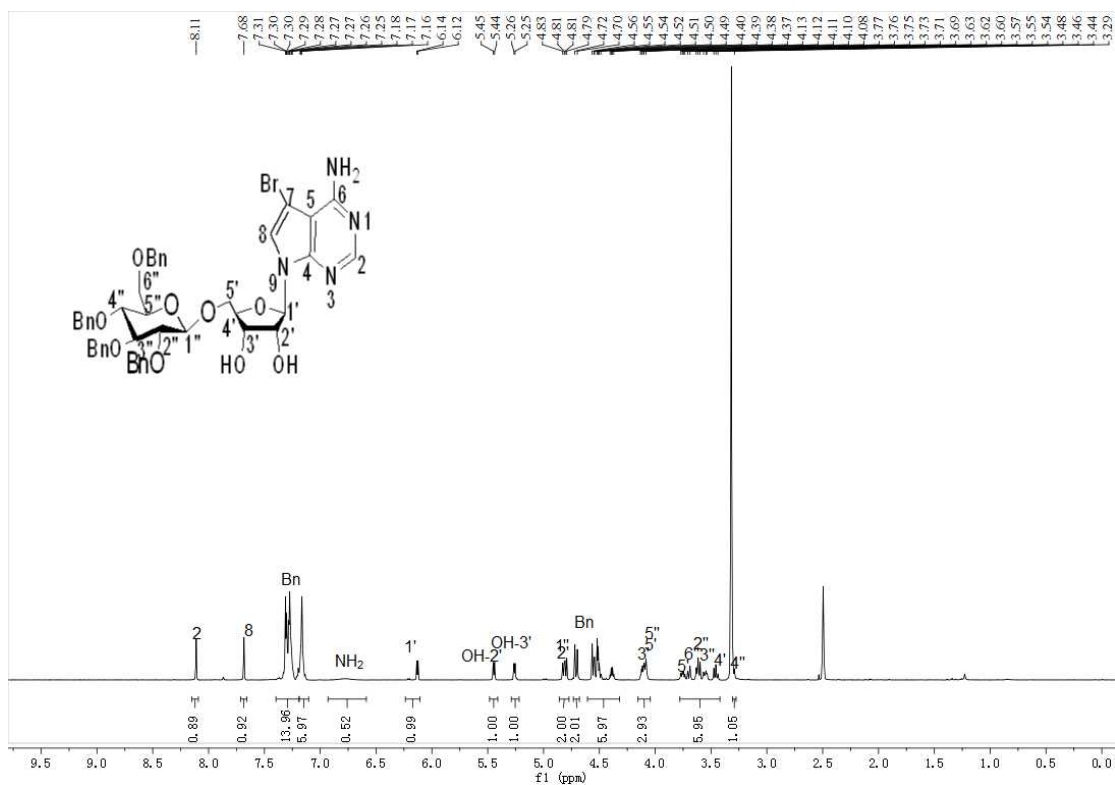


<sup>1</sup>H NMR (DMSO) of 14'.

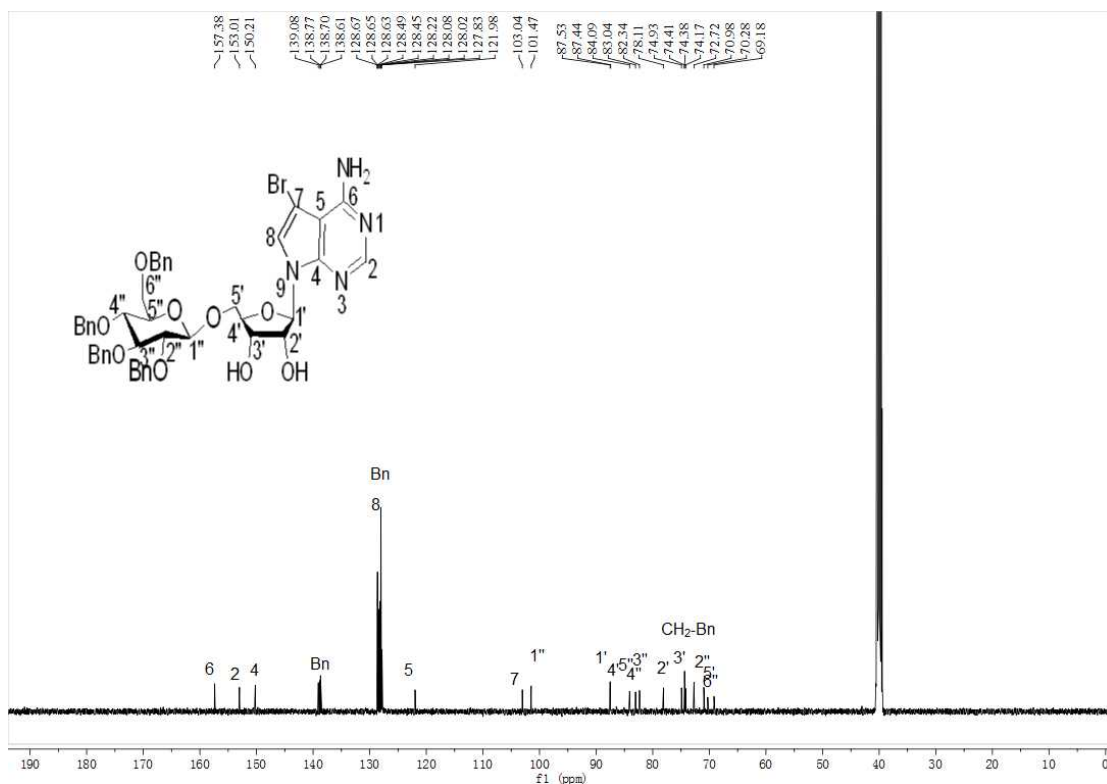


<sup>13</sup>C NMR (DMSO) of 14'.



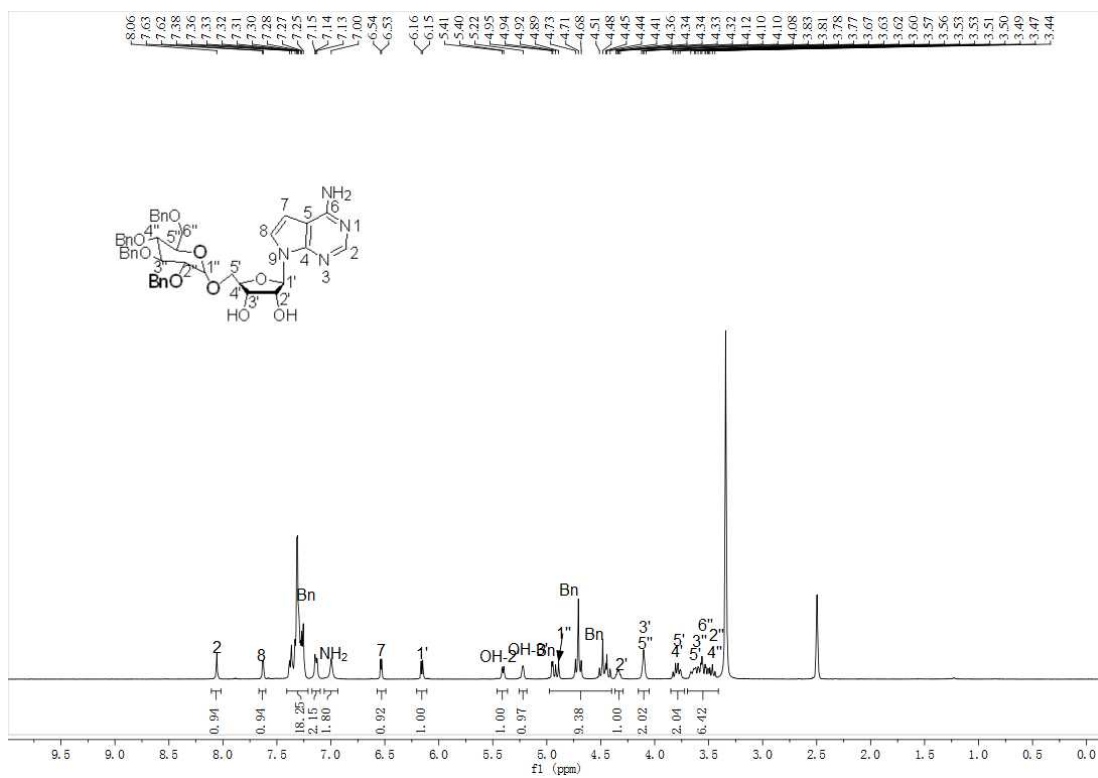


**<sup>1</sup>H NMR (DMSO) of 15'.**

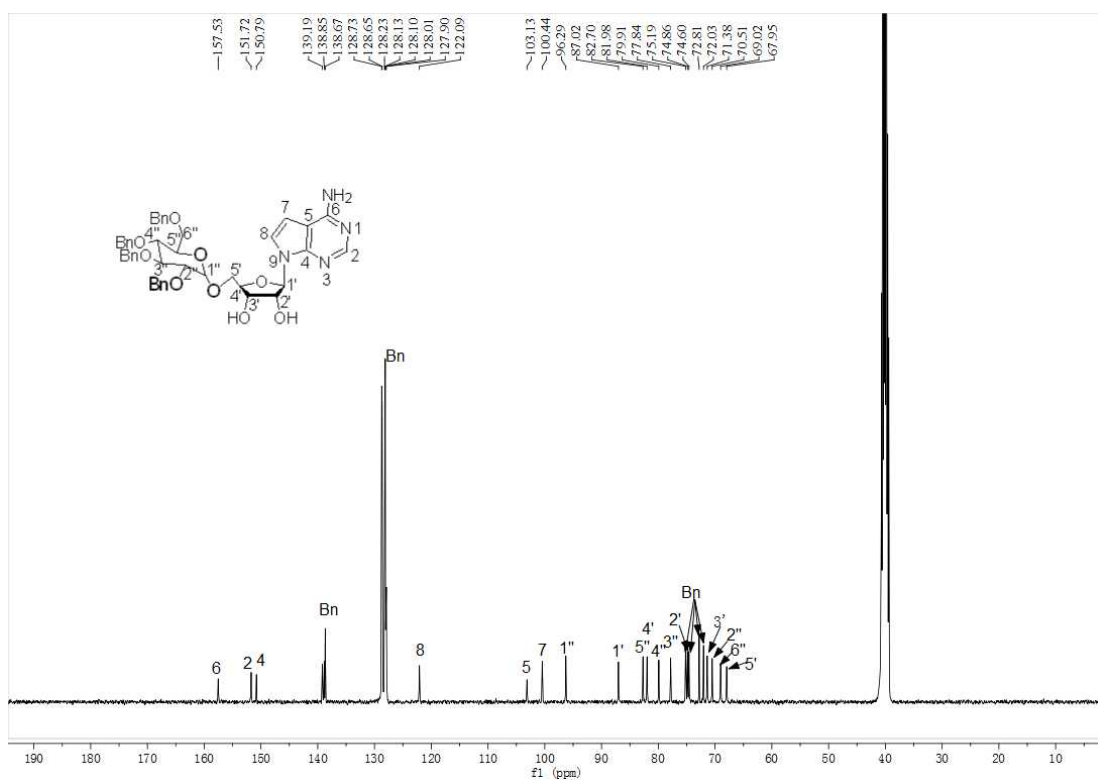


**<sup>13</sup>C NMR (DMSO) of 15'.**

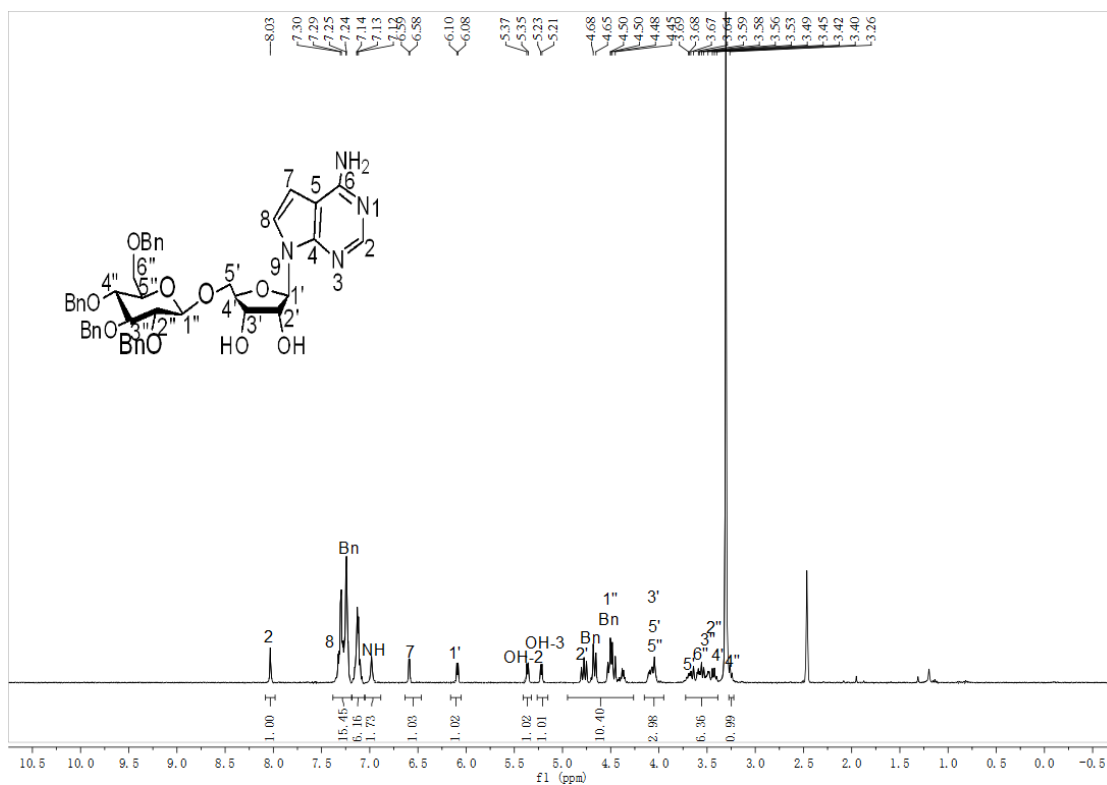




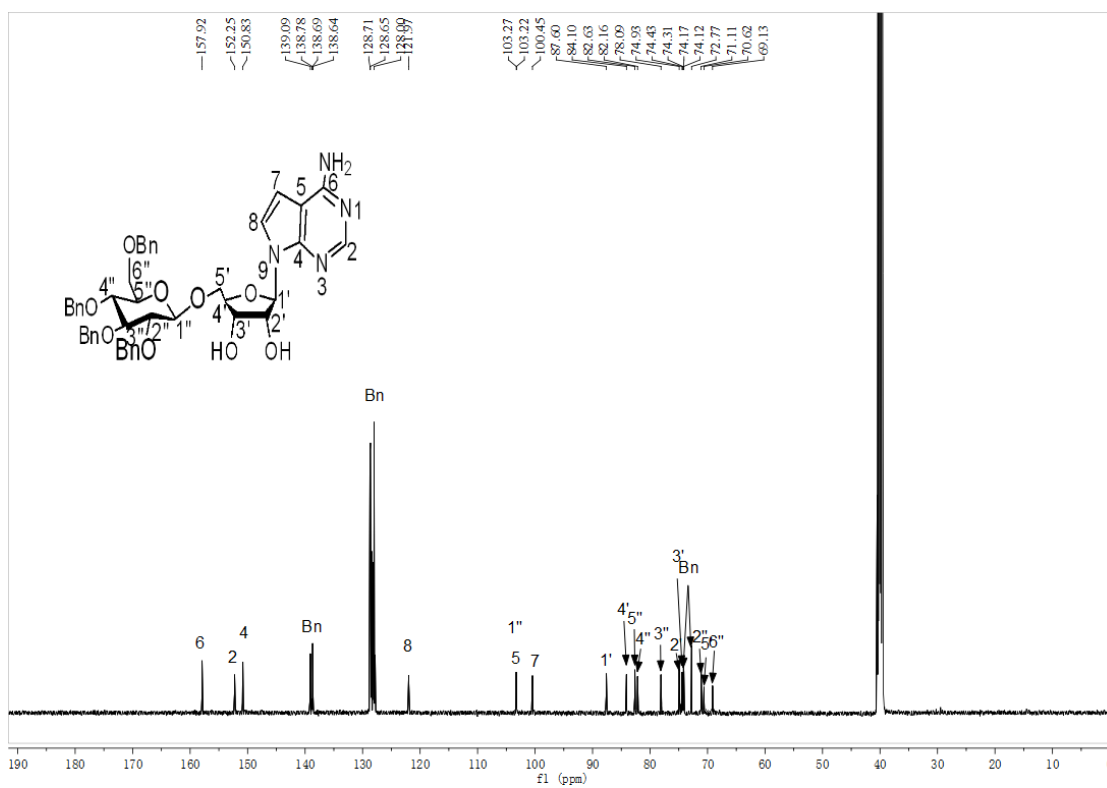
**<sup>1</sup>H NMR (DMSO) of 16.**



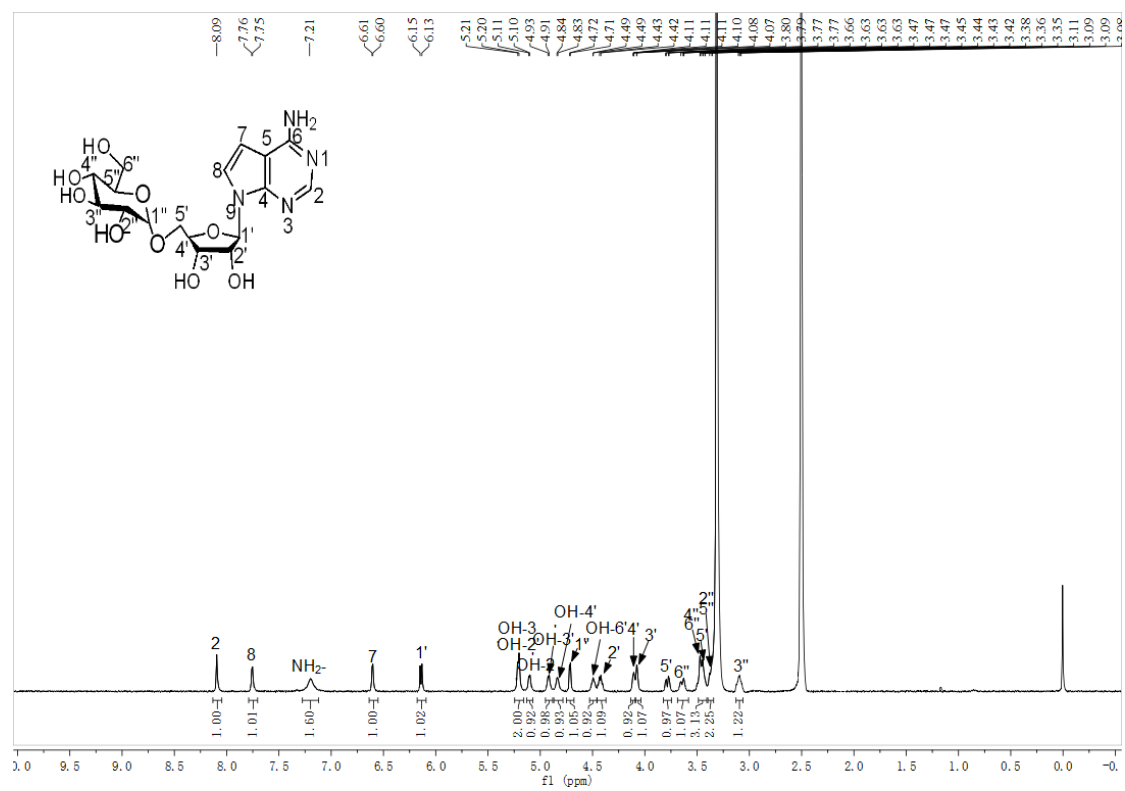
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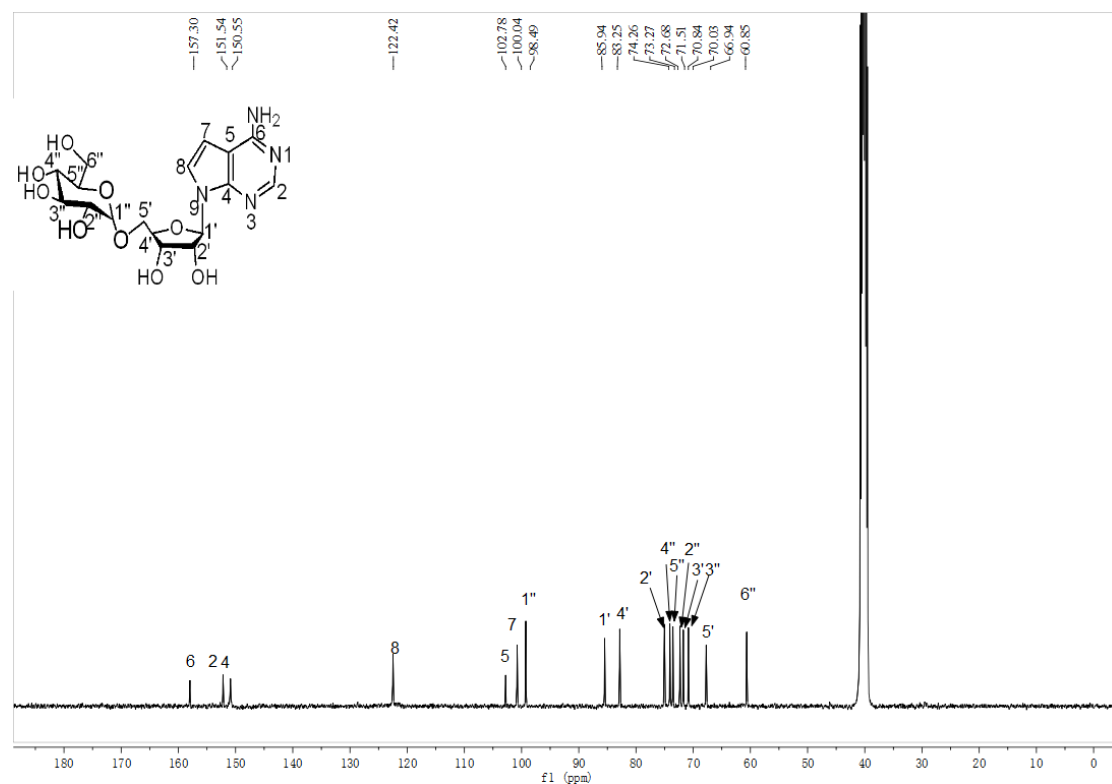
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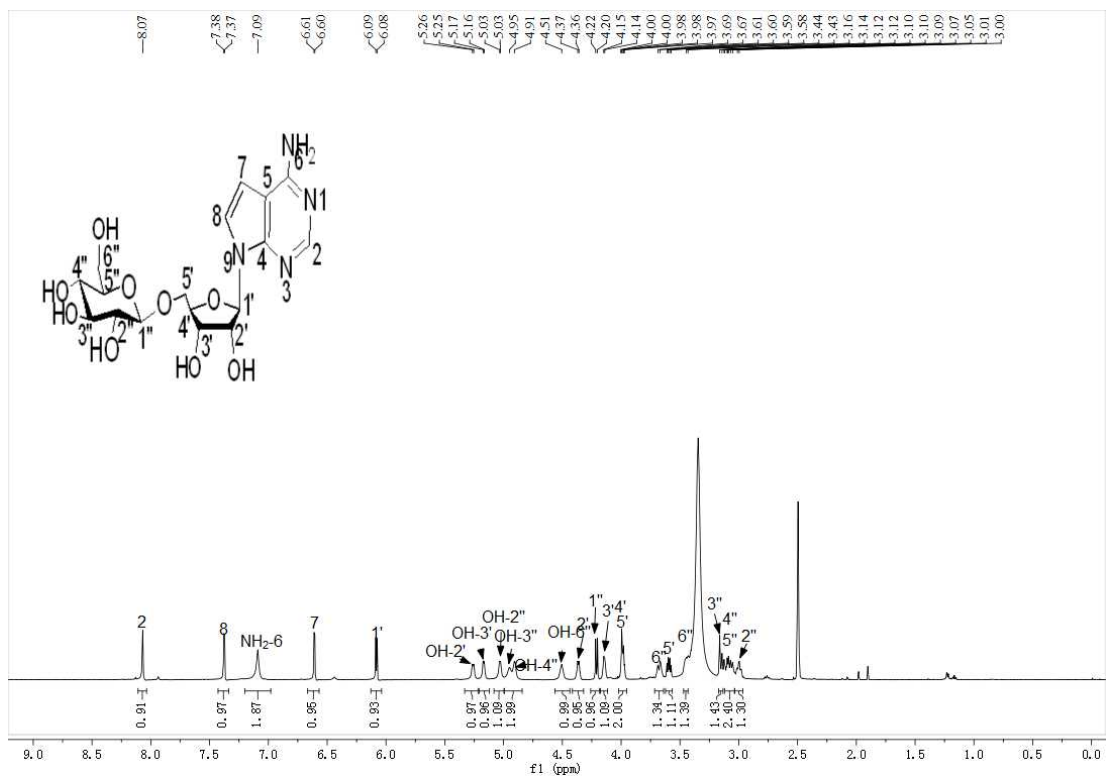
**<sup>13</sup>C NMR (DMSO) of 16'.**



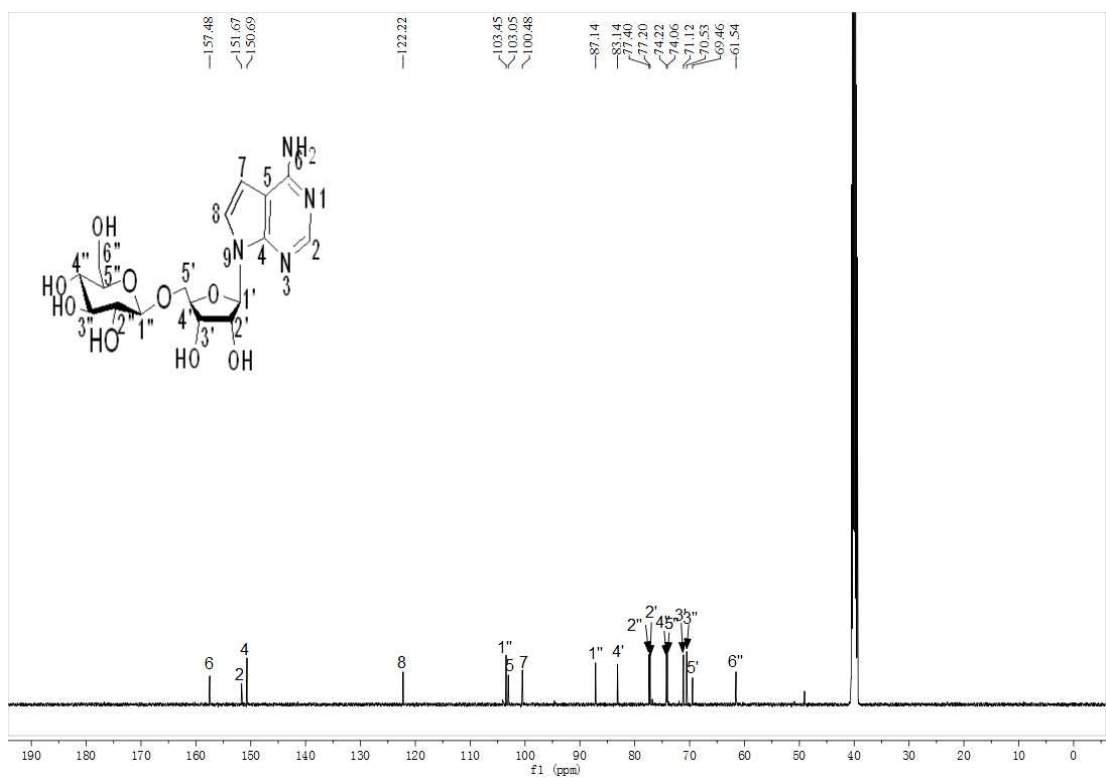
<sup>1</sup>H NMR (DMSO-*d*) of 2.



<sup>13</sup>C NMR (DMSO) of 2.



<sup>1</sup>H NMR (DMSO) of 17.



<sup>13</sup>C NMR (DMSO) of 17.