

## Supporting Information

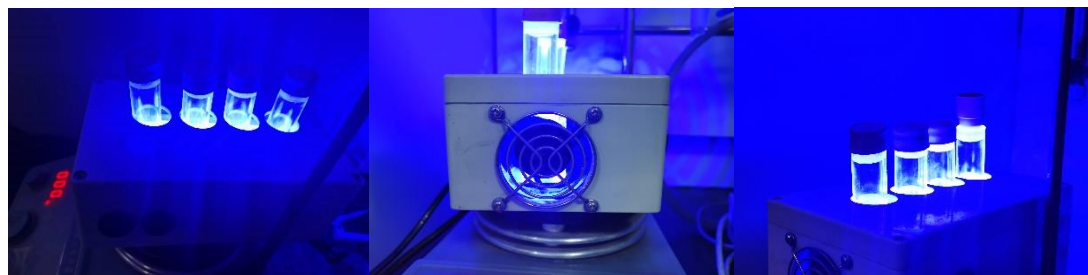
### **Photocatalyst-Free Visible-Light Induced Highly Selective Acylation of Purine Nucleosides at C6 Position**

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## 1. General Information

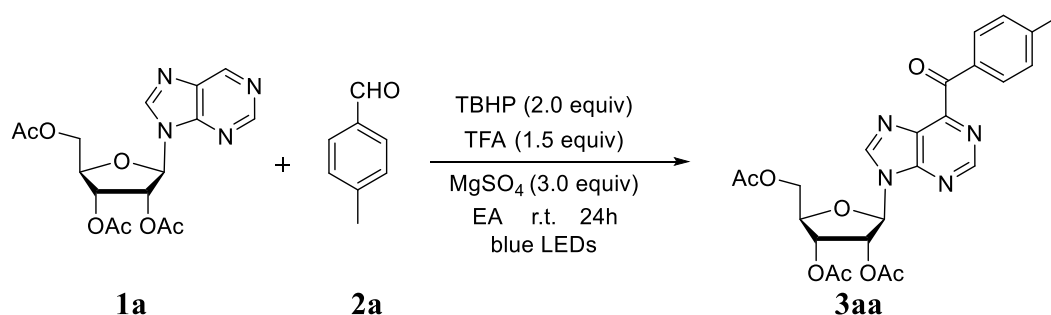
All commercial reagents were purchased from Sigma-Aldrich, Alfa-Aesar, Acros and were used without further purification unless specified. The progress of the reaction was monitored by TLC.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AV-400 spectrometers operating respectively at 400 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ . The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. Peak multiplicities are reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet, hept = heptet, dd = doublet of doublets. The high-resolution mass spectra (HRMS) of the new compounds were acquired on a Bruker microTOF-Q III spectrometer. Melting points were determined using X-4 apparatus and not corrected. The source of the blue LEDs is common LED lights. The power of each light is 24W. There is 3.0 cm distance between the reactor and the LEDs. This reaction could be well-performed using a quartz reaction tube (20 mL). Below we showed some photos of the setup for the photochemical reaction and at the beginning of the experiment, the WATTCAS parallel photoreactor (WP-TEC-1020HPL) was used to find a suitable light source.



## 2. General Procedures for Preparation 3 (3aa as an example)

A mixture of (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate **1a** (0.2 mmol), 4-methylbenzaldehyde **2a** (1.0 mmol), TBHP (0.4 mmol), TFA (0.3 mmol) and dry  $\text{MgSO}_4$  (0.6mmol) were stirred in ethyl acetate (2 mL) for 24 hours at room temperature irradiated by blue LEDs. After completion of the reaction, saturated aqueous  $\text{NaHCO}_3$  solution (10 mL) was added, then extracted with ethyl acetate 3 times (3×20 mL). The extract was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 1/2) to afford product **3aa**.

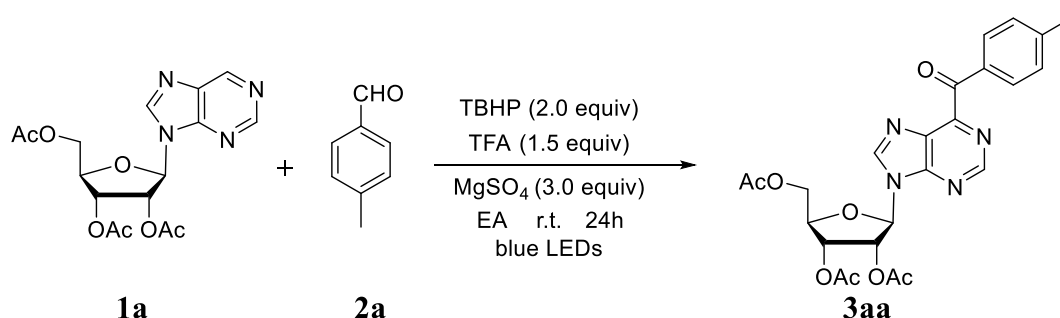
### 3. The Exploration of Reaction Conditions<sup>a</sup>



Entry	Variation from “standard conditions”	Yield <sup>b</sup> (%)
1	None	82
2	No light irradiation	n.r.
3	No light irradiation, 120°C	19
4	No TBHP	n.r.
5	No TFA	n.r.
6	No MgSO <sub>4</sub>	46
7	20 mol % of AgNO <sub>3</sub> instead of TFA	23
8	20 mol % of AgCO <sub>3</sub> instead of TFA	trace
9	20 mol % of Ag <sub>2</sub> O instead of TFA	trace
10	20 mol % of CF <sub>3</sub> COOAg instead of TFA	19
11	20 mol % of K <sub>2</sub> CO instead of TFA	trace
12	1.5 equiv of TFAA instead of TFA	17
13	1.5 equiv of TsOH instead of TFA	42
14	1.5 equiv of TsOH·H <sub>2</sub> O instead of TFA	35
15	1.5 equiv of Ts <sub>2</sub> O instead of TFA	n.r.
16	1.5 equiv of AcOH instead of TFA	trace
17	1.5 equiv of Ac <sub>2</sub> O instead of TFA	n.r.
18	1.5 equiv of TfOH instead of TFA	n.r.
19	2.0 equiv of TBHP (in water) instead of TBHP (in decane)	29
20	2.0 equiv of DTBP instead of TBHP (in decane)	56
21	2.0 equiv of K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> instead of TBHP (in decane)	trace
22	2.0 equiv of (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> instead of TBHP (in decane)	trace
23	2.0 equiv of BPO instead of TBHP (in decane)	37
24	2.0 equiv of PIFA instead of TBHP (in decane)	n.r.
25	DCM as the solvent	43
26	THF as the solvent	25
27	DCE as the solvent	39
28	CH <sub>3</sub> CN as the solvent	33

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), TBHP (0.4 mmol), TFA (0.3 mmol) and dry MgSO<sub>4</sub> (0.6 mmol) were stirred in ethyl acetate (2 mL) for 24 hours at room temperature irradiated by blue LEDs. <sup>b</sup> Isolated yield.

## 4. Scale-up Reaction

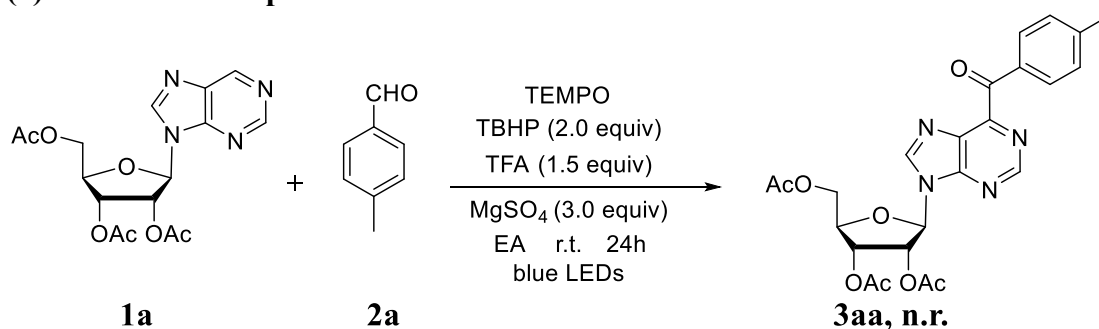


A mixture of (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate **1a** (1.0 mmol), 4-methylbenzaldehyde **2a** (5.0 mmol), TBHP (2.0 mmol), TFA (1.5 mmol) and dry MgSO<sub>4</sub> (3.0 mmol) were stirred in ethyl acetate (5 mL) for 24 hours at room temperature irradiated by blue LEDs. After completion of the reaction, saturated aqueous NaHCO<sub>3</sub> solution (10 mL) was added, then extracted with ethyl acetate 3 times (3×20 mL). The extract was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude mixture was purified by flash chromatography (petroleum ether/ethyl acetate = 1/2) as a yellow oil 307 mg, 0.618 mmol, 62% yield.

## 5. Radical Trapped Experiments

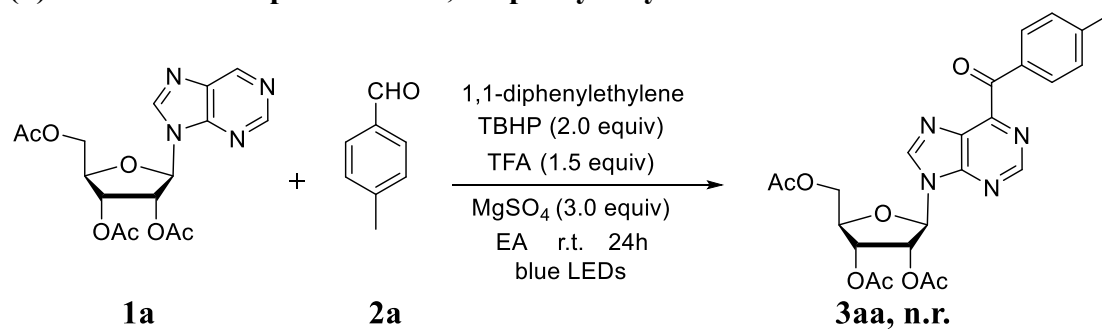
To further investigate the reaction mechanism for this acylation reaction, radical scavengers, including TEMPO and 1,1-diphenylethylene, were employed in the standard reaction, and the process was inhibited obviously. This result suggested that a free radical process might be involved in the present acylation reaction.

### (a) Reaction in the presence of TEMPO



A mixture of (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate **1a** (0.2 mmol), 4-methylbenzaldehyde **2a** (1.0 mmol), TBHP (0.4 mmol), TFA (0.3 mmol), 1,1-diphenylethylene and dry MgSO<sub>4</sub> (0.6 mmol) were stirred in ethyl acetate (2 mL) for 24 hours at room temperature irradiated by blue LEDs. The reaction was completely suppressed.

### (b) Reaction in the presence of 1,1-diphenylethylene



A mixture of (2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate **1a** (0.2 mmol), 4-methylbenzaldehyde **2a** (1.0 mmol), TBHP (0.4 mmol), TFA (0.3 mmol), 1,1-diphenylethylene and dry MgSO<sub>4</sub> (0.6 mmol) were stirred in ethyl acetate (2 mL) for 24 hours at room temperature irradiated by blue LEDs. The reaction was completely suppressed.

## 6. UV-visible Study

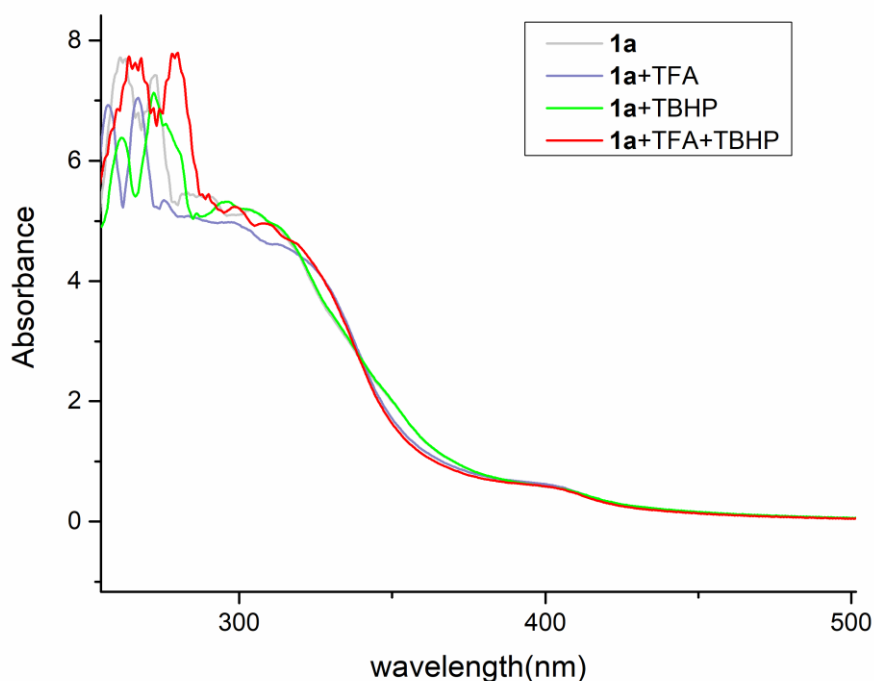
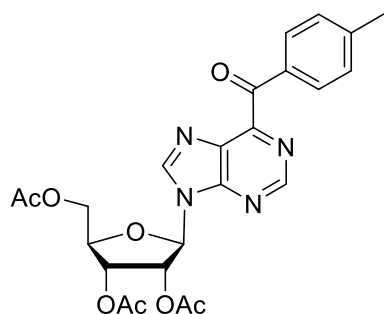


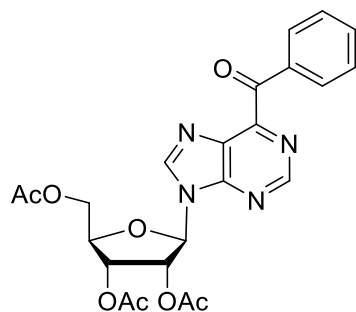
Figure S1. UV-vis absorption spectra.

## 7. Characterization of Compounds



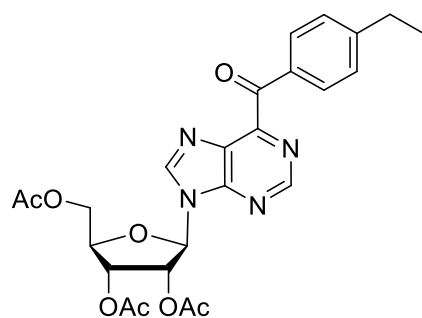
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3aa):**

Yield: 82%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.10 (s, 1H), 8.35 (s, 1H), 7.93 (d,  $J = 8.2$  Hz, 2H), 7.28 (d,  $J = 8.2$  Hz, 2H), 6.29 (d,  $J = 5.2$  Hz, 1H), 6.00 (t,  $J = 5.4$  Hz, 1H), 5.67 (t,  $J = 5.4$  Hz, 1H), 4.51 – 4.35 (m, 3H), 2.42 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.8, 170.3, 169.6, 169.3, 153.8, 152.7, 152.1, 145.3, 145.0, 132.7, 132.4, 130.9, 129.3, 86.6, 80.5, 73.0, 70.5, 62.9, 21.8, 20.7, 20.5, 20.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{24}\text{N}_4\text{NaO}_8^+$   $[\text{M}+\text{Na}]^+$ : 519.1487; found: 519.1477.



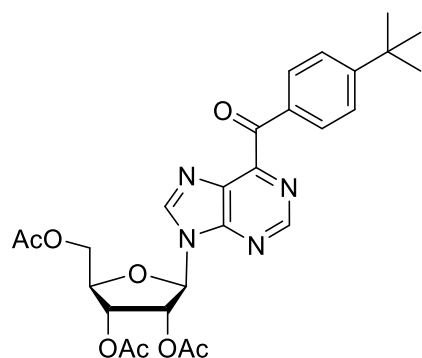
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-benzoyl-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ab):**

Yield: 83%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.12 (s, 1H), 8.37 (s, 1H), 8.04 (d,  $J = 8.2$  Hz, 2H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.49 ((t,  $J = 7.8$  Hz, 2H), 6.30 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.4$  Hz, 1H), 5.67 (t,  $J = 5.0$  Hz, 1H), 4.55 – 4.37 (m, 3H), 2.15 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  191.1, 170.2, 169.5, 169.3, 153.4, 152.7, 152.1, 145.1, 135.1, 134.1, 132.4, 130.7, 128.5, 86.6, 80.5, 73.0, 70.5, 62.9, 20.7, 20.5, 20.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{N}_4\text{NaO}_8^+$   $[\text{M}+\text{Na}]^+$ : 505.1330; found: 505.1323.



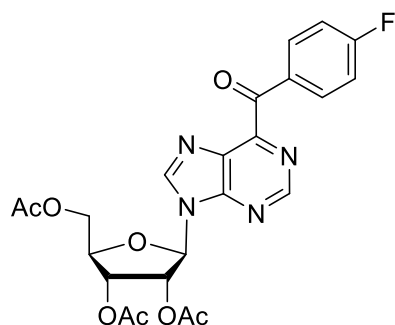
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-ethylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ac):**

Yield: 74%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.35 (s, 1H), 7.97 (d,  $J = 8.2$  Hz, 2H), 7.32 (d,  $J = 8.2$  Hz, 2H), 6.30 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.4$  Hz, 1H), 5.67 (t,  $J = 5.2$  Hz, 1H), 4.53 – 4.36 (m, 3H), 2.72 (q,  $J = 7.6$  Hz, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 1.26 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  190.8, 170.3, 169.6, 169.3, 153.8, 152.7, 152.1, 151.4, 144.9, 132.8, 132.4, 131.0, 128.1, 86.6, 80.5, 73.0, 70.5, 62.9, 29.1, 20.7, 20.5, 20.4, 15.0; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_4\text{NaO}_8^+$  [ $\text{M}+\text{Na}$ ] $^+$ : 533.1643; found: 533.1641.



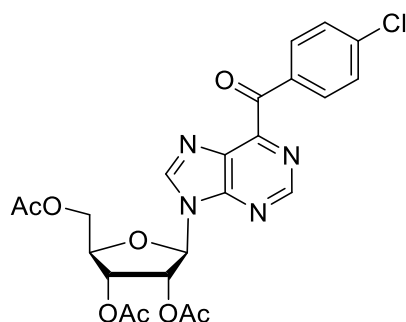
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-(tert-butyl)benzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ad):**

Yield: 69%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.37 (s, 1H), 7.98 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 8.4$  Hz, 2H), 6.30 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.4$  Hz, 1H), 5.68 (t,  $J = 5.0$  Hz, 1H), 4.52 – 4.37 (m, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.33 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.8, 170.3, 169.6, 169.3, 158.1, 153.7, 152.7, 152.1, 145.0, 132.5, 132.3, 130.7, 125.6, 86.6, 80.5, 73.0, 70.5, 62.9, 35.2, 31.0, 20.7, 20.5, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{31}\text{N}_4\text{O}_8^+$  [ $\text{M}+\text{H}$ ] $^+$ : 539.2137; found: 539.2127.



**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-fluorobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ae):**

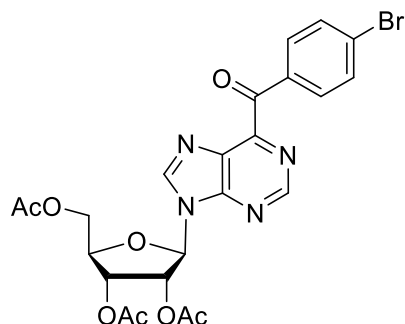
Yield: 47%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.37 (s, 1H), 8.15 – 8.10 (m, 2H), 7.21 – 7.12 (m, 2H), 6.29 (d, *J* = 5.2 Hz, 1H), 6.00 (t, *J* = 5.2 Hz, 1H), 5.67 (t, *J* = 5.4 Hz, 1H), 4.52 – 4.37 (m, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 189.4, 170.2, 169.6, 169.3, 166.4 (d, *J* = 257.0 Hz), 153.0, 152.8, 152.0, 145.2, 133.6 (d, *J* = 9.6 Hz), 132.5, 131.5 (d, *J* = 2.8 Hz), 115.8 (d, *J* = 22.0 Hz), 86.7, 80.5, 73.0, 70.4, 62.9, 20.7, 20.5, 20.4; HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>22</sub>FN<sub>4</sub>O<sub>8</sub><sup>+</sup> [M+H]<sup>+</sup>: 501.1417; found: 501.1391.



**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-chlorobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3af):**

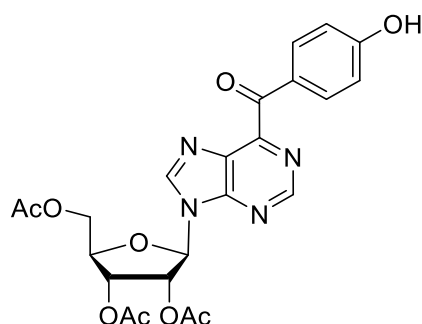
Yield: 51%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.44 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 6.31 (d, *J* = 5.0 Hz, 1H), 6.01 (t, *J* = 5.4 Hz, 1H), 5.67 (t, *J* = 5.2 Hz, 1H), 4.54 – 4.40 (m, 3H), 2.17 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 189.8, 170.2, 169.5, 169.3, 152.9, 152.6, 152.0, 145.3, 140.7, 133.5, 132.5, 132.1, 128.9, 86.7, 80.5, 73.0, 70.4, 62.9, 20.7, 20.5, 20.3; HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>21</sub>ClN<sub>4</sub>NaO<sub>8</sub><sup>+</sup> [M+Na]<sup>+</sup>: 539.0941; found: 539.0949.





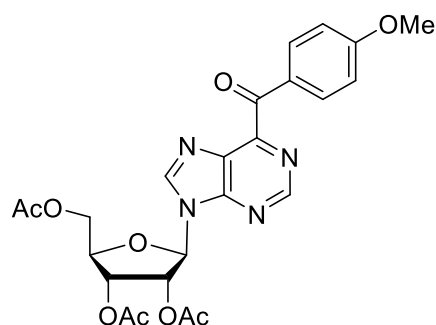
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-bromobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ag):**

Yield: 58%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.13 (s, 1H), 8.39 (s, 1H), 7.99 – 7.94 (m, 2H), 7.68 – 7.64 (m, 2H), 6.30 (d,  $J = 5.2$  Hz, 1H), 6.00 (t,  $J = 5.4$  Hz, 1H), 5.69 – 5.65 (m, 1H), 4.53 – 4.49 (m, 1H), 4.44 (dd,  $J = 15.4, 3.8$  Hz, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  190.1, 170.3, 169.6, 169.4, 152.9, 152.5, 152.1, 145.4, 133.9, 132.2, 131.9, 131.6, 129.7, 86.7, 80.5, 73.0, 70.5, 62.9, 20.8, 20.5, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{BrN}_4\text{NaO}_8^+$   $[\text{M}+\text{Na}]^+$ : 585.0415; found: 585.0424.



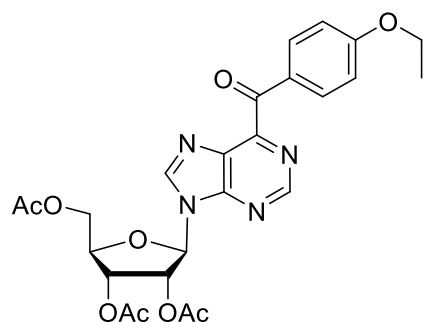
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-hydroxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ah):**

Yield: 43%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.43 (s, 1H), 7.74 (d,  $J = 8.4$  Hz, 2H), 6.71 (d,  $J = 8.8$  Hz, 2H), 6.31 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.4$  Hz, 1H), 5.67 (t,  $J = 5.2$  Hz, 1H), 4.54 – 4.39 (m, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  189.2, 170.4, 169.6, 169.4, 162.6, 154.8, 152.4, 152.2, 144.9, 133.3, 131.5, 127.2, 115.9, 86.8, 80.5, 73.0, 70.4, 62.9, 20.8, 20.5, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_4\text{O}_9^+$   $[\text{M}+\text{H}]^+$ : 499.1460; found: 499.1465.



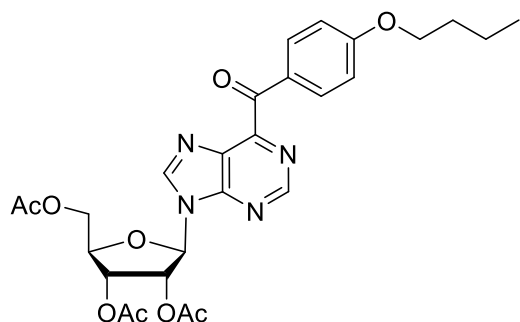
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-methoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ai):**

Yield: 64%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.12 (s, 1H), 8.34 (s, 1H), 8.13 – 8.02 (m, 2H), 7.07 – 6.92 (m, 2H), 6.30 (d,  $J = 5.4$  Hz, 1H), 6.02 (t,  $J = 5.4$  Hz, 1H), 5.68 (dd,  $J = 5.5, 4.4$  Hz, 1H), 4.52 – 4.39 (m, 3H), 3.89 (s, 3H), 2.17 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  189.5, 170.2, 169.5, 169.3, 164.4, 154.1, 152.5, 152.1, 144.8, 133.2, 132.3, 128.1, 113.9, 86.5, 80.4, 72.9, 70.4, 62.9, 55.5, 20.7, 20.5, 20.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{24}\text{N}_4\text{NaO}_9^+$   $[\text{M}+\text{Na}]^+$ : 535.1436; found: 535.1431.



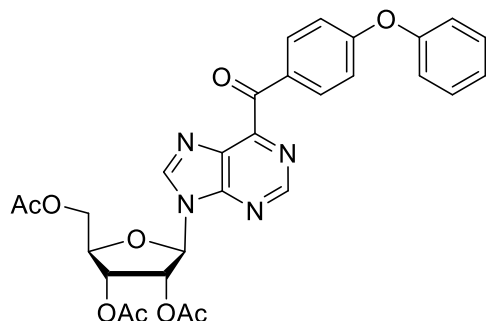
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-ethoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3aj):**

Yield: 52%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.10 (s, 1H), 8.34 (s, 1H), 8.03 (d,  $J = 8.8$  Hz, 2H), 6.94 (d,  $J = 8.8$  Hz, 2H), 6.29 (d,  $J = 5.2$  Hz, 1H), 6.00 (t,  $J = 5.4$  Hz, 1H), 5.71 – 5.62 (m, 1H), 4.51 – 4.36 (m, 3H), 4.11 (q,  $J = 7.0$  Hz, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.43 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  189.4, 170.3, 169.6, 169.3, 163.9, 154.2, 152.5, 152.1, 144.8, 133.3, 132.3, 127.9, 114.3, 86.5, 80.4, 72.9, 70.5, 63.8, 62.9, 20.7, 20.5, 20.4, 14.6; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_4\text{NaO}_9^+$   $[\text{M}+\text{Na}]^+$ : 549.1592; found: 549.1590.



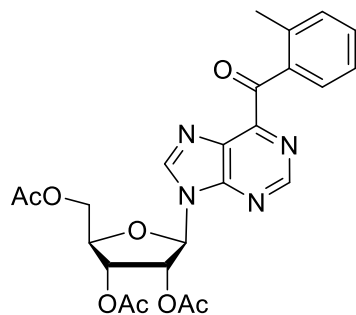
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-butoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ak):**

Yield: 63%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.09 (s, 1H), 8.33 (s, 1H), 8.04 – 7.96 (m, 2H), 6.97 – 6.89 (m, 2H), 6.28 (d,  $J = 5.2$  Hz, 1H), 6.00 (t,  $J = 5.4$  Hz, 1H), 5.66 (t,  $J = 5.0$  Hz, 1H), 4.49 – 4.35 (m, 3H), 4.02 (t,  $J = 6.4$  Hz, 2H), 2.14 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 1.76 (p,  $J = 6.6$  Hz, 2H), 1.54 – 1.40 (m, 2H), 0.95 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  189.4, 170.2, 169.5, 169.3, 164.1, 154.2, 152.5, 152.0, 144.8, 133.2, 132.2, 127.8, 114.3, 86.5, 80.4, 72.9, 70.4, 67.9, 62.8, 30.9, 20.7, 20.4, 20.3, 19.0, 13.7; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{27}\text{H}_{31}\text{N}_4\text{O}_9^+$   $[\text{M}+\text{H}]^+$ : 555.2086; found: 555.2077.



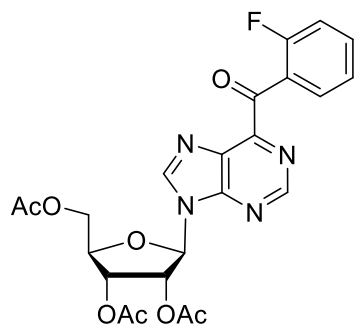
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(4-phenoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3al):**

Yield: 60%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.10 (s, 1H), 8.35 (s, 1H), 8.05 (d,  $J = 8.8$  Hz, 2H), 7.43 – 7.35 (m, 2H), 7.20 (t,  $J = 7.4$  Hz, 1H), 7.08 (d,  $J = 7.4$  Hz, 2H), 7.01 (d,  $J = 8.8$  Hz, 2H), 6.30 (d,  $J = 5.2$  Hz, 1H), 6.00 (t,  $J = 5.4$  Hz, 1H), 5.72 – 5.61 (m, 1H), 4.53 – 4.37 (m, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  189.5, 170.3, 169.6, 169.3, 163.1, 155.0, 153.7, 152.7, 152.1, 144.9, 133.2, 132.4, 130.1, 129.5, 124.9, 120.4, 117.1, 86.6, 80.5, 73.0, 70.5, 62.9, 20.8, 20.5, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{29}\text{H}_{26}\text{N}_4\text{NaO}_9^+$   $[\text{M}+\text{Na}]^+$ : 597.1592; found: 597.1595.



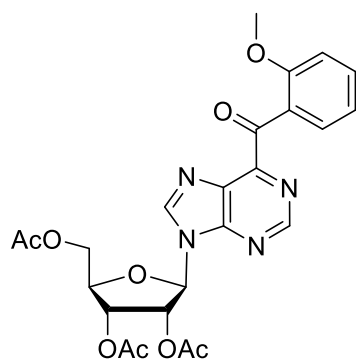
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(2-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3am):**

Yield: 32%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.10 (s, 1H), 8.37 (s, 1H), 7.55 – 7.32 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.30 (d, *J* = 5.2 Hz, 1H), 6.01 (t, *J* = 5.2 Hz, 1H), 5.68 (t, *J* = 5.0 Hz, 1H), 4.55 – 4.37 (m, 3H), 2.61 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 194.0, 170.3, 169.5, 169.3, 153.7, 152.9, 152.2, 145.2, 140.3, 135.0, 132.6, 132.3, 132.2, 131.9, 125.4, 86.6, 80.5, 73.0, 70.5, 62.9, 21.4, 20.7, 20.5, 20.3; HRMS (ESI): *m/z* calcd for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>NaO<sub>8</sub><sup>+</sup> [*M*+Na]<sup>+</sup>: 519.1487; found: 519.1489.



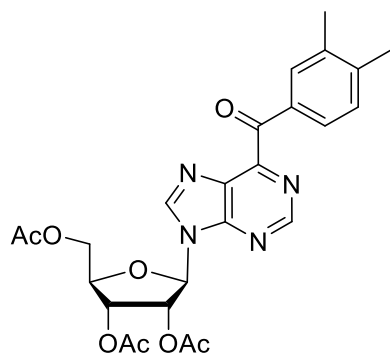
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(2-fluorobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3an):**

Yield: 43%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.39 (s, 1H), 7.91 (td, *J* = 7.4, 1.8 Hz, 1H), 7.66 – 7.56 (m, 1H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.11 (ddd, *J* = 10.2, 8.2, 1.0 Hz, 1H), 6.30 (d, *J* = 5.2 Hz, 1H), 5.99 (t, *J* = 5.4 Hz, 1H), 5.68 (t, *J* = 5.0 Hz, 1H), 4.51 – 4.36 (m, 3H), 2.15 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 190.0, 170.3, 169.6, 169.3, 161.7 (d, *J* = 256.2 Hz), 153.1, 152.4, 152.3, 145.5, 135.4 (d, *J* = 8.8 Hz), 131.5, 131.5 (d, *J* = 1.8 Hz), 125.2 (d, *J* = 12.0 Hz), 124.6 (d, *J* = 3.4 Hz), 116.4 (d, *J* = 21.8 Hz), 86.6, 80.5, 73.0, 70.5, 62.9, 20.7, 20.5, 20.4; HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>21</sub>FN<sub>4</sub>NaO<sub>8</sub><sup>+</sup> [*M*+Na]<sup>+</sup>: 523.1236; found: 523.1230.



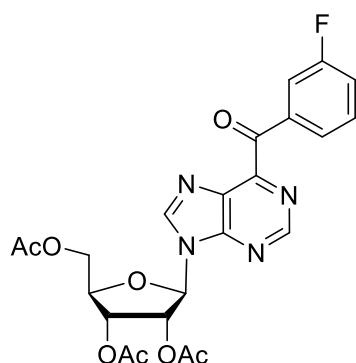
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(2-methoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ao):**

Yield: 56%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.01 (s, 1H), 7.85 – 7.76 (m, 1H), 7.54 (ddd,  $J = 8.6, 7.4, 1.8$  Hz, 1H), 7.09 (td,  $J = 7.4, 0.8$  Hz, 1H), 6.92 (d,  $J = 8.2$  Hz, 1H), 6.27 (d,  $J = 5.2$  Hz, 1H), 5.96 (t,  $J = 5.4$  Hz, 1H), 5.66 (t,  $J = 5.0$  Hz, 1H), 4.49 – 4.34 (m, 3H), 3.46 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  192.5, 170.2, 169.5, 169.3, 159.4, 154.4, 152.6, 152.1, 144.7, 134.8, 131.1, 131.0, 126.5, 120.9, 111.8, 86.5, 80.3, 72.9, 70.4, 62.8, 55.5, 20.7, 20.4, 20.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{24}\text{H}_{24}\text{N}_4\text{NaO}_9^+$   $[\text{M}+\text{Na}]^+$ : 535.1436; found: 535.1444.



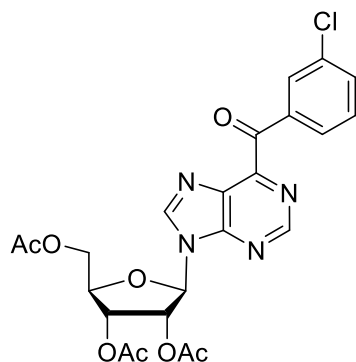
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(3,4-dimethylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ap):**

Yield: 48%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.34 (s, 1H), 7.81 (d,  $J = 1.8$  Hz, 1H), 7.72 (dd,  $J = 7.8, 1.8$  Hz, 1H), 7.23 (d,  $J = 7.8$  Hz, 1H), 6.29 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.4$  Hz, 1H), 5.68 (t,  $J = 5.0$  Hz, 1H), 4.53 – 4.36 (m, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  191.1, 170.3, 169.6, 169.3, 154.0, 152.6, 152.2, 144.9, 144.2, 137.1, 133.0, 132.3, 131.5, 129.8, 128.7, 86.6, 80.4, 72.9, 70.5, 62.9, 20.7, 20.5, 20.4, 20.2, 19.7; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_4\text{NaO}_8^+$   $[\text{M}+\text{Na}]^+$ : 533.1643; found: 533.1644.



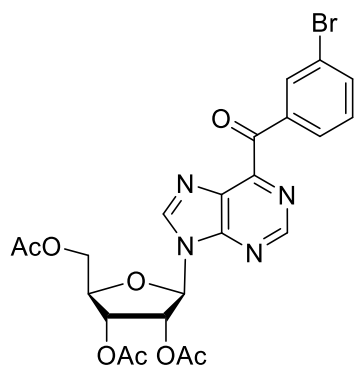
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(3-fluorobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3aq):**

Yield: 35%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.14 (s, 1H), 8.40 (s, 1H), 7.88 – 7.79 (m, 2H), 7.49 (td, *J* = 8.0, 5.4 Hz, 1H), 7.38 – 7.32 (m, 1H), 6.31 (d, *J* = 5.2 Hz, 1H), 6.01 (t, *J* = 5.4 Hz, 1H), 5.67 (dd, *J* = 5.4, 4.6 Hz, 1H), 4.53 – 4.48 (m, 1H), 4.47 – 4.39 (m, 2H), 2.17 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 189.8 (d, *J* = 2.2 Hz), 170.3, 169.6, 169.3, 162.6 (d, *J* = 248.0 Hz), 152.9, 152.4, 152.0, 145.4, 137.1 (d, *J* = 6.8 Hz), 132.4, 130.2 (d, *J* = 7.8 Hz), 126.8 (d, *J* = 3.2 Hz), 121.2 (d, *J* = 21.6 Hz), 117.3 (d, *J* = 22.8 Hz), 86.7, 80.5, 73.0, 70.5, 62.9, 20.8, 20.5, 20.4; HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>22</sub>FN<sub>4</sub>O<sub>8</sub><sup>+</sup> [M+H]<sup>+</sup>: 501.1417; found: 501.1379.



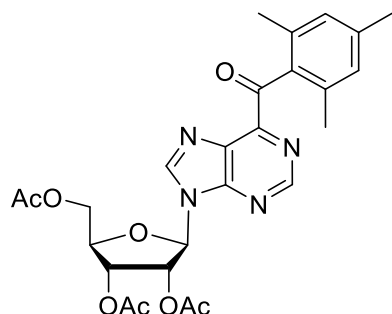
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(3-chlorobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ar):**

Yield: 39%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.39 (s, 1H), 8.06 (t, *J* = 1.9 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 6.30 (d, *J* = 5.2 Hz, 1H), 6.00 (t, *J* = 5.4 Hz, 1H), 5.72 – 5.62 (m, 1H), 4.52 – 4.38 (m, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 189.8, 170.3, 169.6, 169.3, 152.9, 152.2, 152.0, 145.4, 136.7, 134.8, 134.0, 132.5, 130.6, 129.8, 128.9, 86.7, 80.5, 73.0, 70.4, 62.9, 20.7, 20.5, 20.4; HRMS (ESI): *m/z* calcd for C<sub>23</sub>H<sub>22</sub>ClN<sub>4</sub>O<sub>8</sub><sup>+</sup> [M+H]<sup>+</sup>: 517.1121; found: 517.1117.



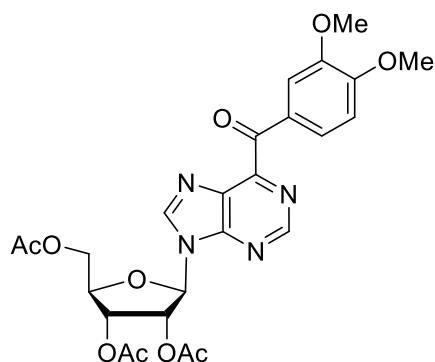
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(3-bromobenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3as):**

Yield: 46%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.14 (s, 1H), 8.40 (s, 1H), 8.23 (t,  $J = 1.8$  Hz, 1H), 8.01 (dt,  $J = 7.8, 1.4$  Hz, 1H), 7.77 (ddd,  $J = 8.0, 2.0, 1.0$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz, 1H), 6.31 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.2$  Hz, 1H), 5.67 (t,  $J = 5.0$  Hz, 1H), 4.52 – 4.39 (m, 3H), 2.17 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  189.8, 170.4, 169.6, 169.4, 153.0, 152.2, 152.1, 145.5, 136.9, 133.6, 132.5, 130.1, 129.5, 128.6, 122.8, 86.7, 80.6, 73.1, 70.5, 63.0, 20.8, 20.6, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{BrN}_4\text{O}_8^+$   $[\text{M}+\text{H}]^+$ : 563.0596; found: 563.0597.



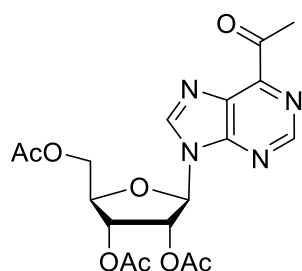
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(2,4,6-trimethylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3at):**

Yield: 34%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.07 (s, 1H), 8.46 (s, 1H), 6.91 (s, 2H), 6.29 (d,  $J = 5.0$  Hz, 1H), 5.98 (t,  $J = 5.4$  Hz, 1H), 5.66 (t,  $J = 5.2$  Hz, 1H), 4.52 – 4.35 (m, 3H), 2.32 (s, 3H), 2.15 (s, 3H), 2.13 (s, 6H), 2.12 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (10 MHz, Chloroform-*d*)  $\delta$  199.7, 170.2, 169.5, 169.3, 153.7, 152.6, 150.4, 146.2, 139.6, 136.1, 135.0, 131.7, 128.5, 86.7, 80.3, 73.0, 70.3, 62.8, 21.3, 20.7, 20.5, 20.3, 19.7; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{26}\text{H}_{29}\text{N}_4\text{O}_8^+$   $[\text{M}+\text{H}]^+$ : 525.1980; found: 525.1981.



**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-(3,4-dimethoxybenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3au):**

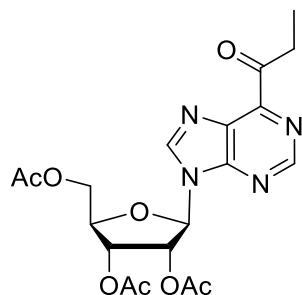
Yield: 32%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.34 (s, 1H), 7.75 (d,  $J = 2.0$  Hz, 1H), 7.54 (dd,  $J = 8.4, 2.0$  Hz, 1H), 6.88 (d,  $J = 8.4$  Hz, 1H), 6.29 (d,  $J = 5.2$  Hz, 1H), 6.01 (t,  $J = 5.2$  Hz, 1H), 5.67 (t,  $J = 5.0$  Hz, 1H), 4.53 – 4.36 (m, 3H), 3.95 (d,  $J = 1.6$  Hz, 6H), 2.16 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  189.5, 170.2, 169.5, 169.3, 154.4, 154.3, 152.5, 152.1, 149.3, 144.8, 132.4, 128.3, 127.2, 111.5, 109.9, 86.6, 80.5, 73.0, 70.5, 62.9, 56.1, 56.1, 20.7, 20.5, 20.4; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_4\text{NaO}_{10}^+$   $[\text{M}+\text{Na}]^+$ : 565.1542; found: 565.1538.



**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-acetyl-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3av):**

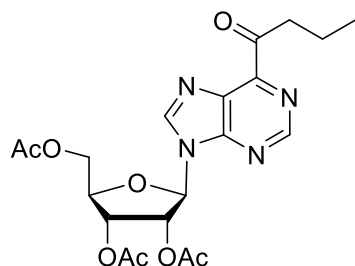
Yield: 65%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.11 (s, 1H), 8.42 (s, 1H), 6.28 (d,  $J = 5.2$  Hz, 1H), 5.96 (t,  $J = 5.4$  Hz, 1H), 5.64 (t,  $J = 5.2$  Hz, 1H), 4.50 – 4.34 (m, 3H), 2.88 (s, 3H), 2.15 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  198.7, 170.2, 169.5, 169.3, 153.7, 152.2, 149.2, 145.9, 131.5, 86.6, 80.4, 73.0, 70.4, 62.9, 27.9, 20.7, 20.5, 20.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_4\text{NaO}_8^+$   $[\text{M}+\text{Na}]^+$ : 433.1174; found: 433.1167.





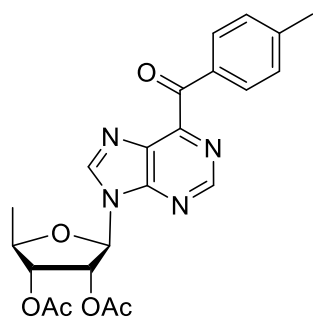
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-propionyl-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3aw):**

Yield: 70%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.10 (s, 1H), 8.43 (s, 1H), 6.28 (d,  $J = 5.2$  Hz, 1H), 5.96 (t,  $J = 5.2$  Hz, 1H), 5.65 (t,  $J = 5.2$  Hz, 1H), 4.50 – 4.36 (m, 3H), 3.35 (q,  $J = 7.2$  Hz, 2H), 2.15 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.27 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  201.3, 170.3, 169.5, 169.3, 153.6, 152.3, 149.7, 145.7, 131.4, 86.6, 80.5, 73.0, 70.5, 62.9, 33.7, 20.7, 20.5, 20.3, 7.6; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{22}\text{N}_4\text{NaO}_8^+ [\text{M}+\text{Na}]^+$ : 457.1330; found: 457.1336.



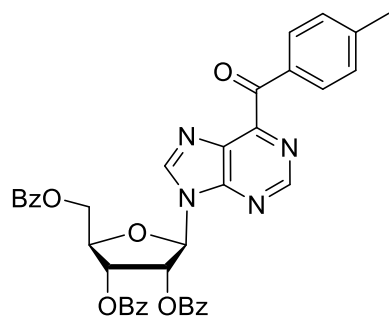
**(2*R*,3*R*,4*R*,5*R*)-2-(acetoxymethyl)-5-(6-butyryl-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ax):**

Yield: 79%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.09 (s, 1H), 8.41 (s, 1H), 6.27 (d,  $J = 5.2$  Hz, 1H), 5.96 (t,  $J = 5.4$  Hz, 1H), 5.68 – 5.61 (m, 1H), 4.53 – 4.36 (m, 3H), 3.30 (t,  $J = 7.4$  Hz, 2H), 2.23 – 2.03 (m, 10H), 1.82 (q,  $J = 7.4$  Hz, 2H), 1.03 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  200.8, 170.3, 169.6, 169.3, 153.6, 152.3, 149.7, 145.7, 131.5, 86.6, 80.4, 73.0, 70.5, 62.9, 42.0, 20.7, 20.5, 20.3, 17.2, 13.8; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{25}\text{N}_4\text{O}_8^+ [\text{M}+\text{H}]^+$ : 449.1667; found: 449.1678.



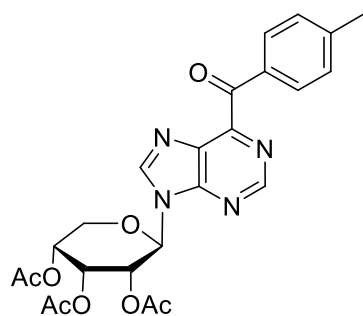
**(2*R*,3*R*,4*R*,5*R*)-2-methyl-5-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3ba):**

Yield: 80%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.27 (s, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.19 (d, *J* = 5.0 Hz, 1H), 6.06 (t, *J* = 5.2 Hz, 1H), 5.44 (t, *J* = 5.2 Hz, 1H), 4.38 (dt, *J* = 11.6, 6.2 Hz, 1H), 2.43 (s, 3H), 2.16 (s, 3H), 2.10 (s, 3H), 1.55 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 190.8, 169.7, 169.4, 153.7, 152.6, 152.1, 145.3, 145.2, 132.7, 132.5, 130.9, 129.3, 87.0, 79.0, 74.4, 73.0, 21.8, 20.5, 20.4, 18.7; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>NaO<sub>6</sub><sup>+</sup> [M+Na]<sup>+</sup>: 461.1432; found: 461.1423.



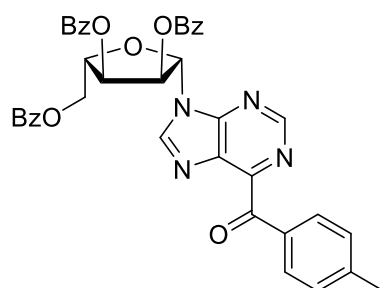
**(2*R*,3*R*,4*R*,5*R*)-2-((benzyloxy)methyl)-5-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl dibenzoate (3ca):**

Yield: 57%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 8.36 (s, 1H), 8.15 – 8.08 (m, 2H), 8.06 – 7.99 (m, 2H), 7.97 – 7.89 (m, 4H), 7.64 – 7.51 (m, 3H), 7.50 – 7.33 (m, 6H), 7.31 – 7.24 (m, 2H), 6.56 – 6.47 (m, 2H), 6.30 (t, *J* = 5.2 Hz, 1H), 4.96 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.91 – 4.84 (m, 1H), 4.73 (dd, *J* = 12.2, 4.2 Hz, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 190.7, 166.1, 165.3, 165.1, 153.7, 152.7, 152.1, 145.4, 145.2, 133.9, 133.8, 133.5, 132.7, 132.4, 130.8, 129.8, 129.8, 129.7, 129.2, 129.2, 128.6, 128.6, 128.6, 128.5, 128.2, 87.2, 80.9, 73.6, 71.4, 63.34, 21.8; HRMS (ESI): *m/z* calcd for C<sub>39</sub>H<sub>31</sub>N<sub>4</sub>O<sub>8</sub><sup>+</sup> [M+H]<sup>+</sup>: 683.2137; found: 683.2135.



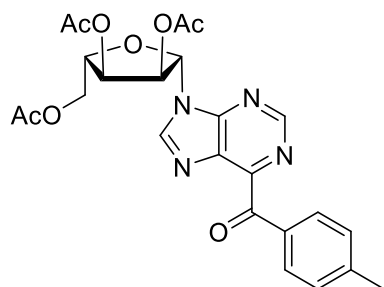
**(2*R*,3*R*,4*R*,5*R*)-2-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3da):**

Yield: 82%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.12 (s, 1H), 8.31 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.13 (d, *J* = 9.6 Hz, 1H), 5.88 (t, *J* = 2.8 Hz, 1H), 5.75 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.27 (ddd, *J* = 10.4, 6.0, 2.8 Hz, 1H), 4.14 – 4.00 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H), 1.81 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 190.8, 169.8, 169.3, 168.8, 153.6, 153.2, 152.3, 145.3, 144.6, 132.6, 131.8, 130.9, 129.3, 78.7, 68.0, 67.7, 65.7, 63.8, 21.8, 20.8, 20.6, 20.3; HRMS (ESI): *m/z* calcd for C<sub>24</sub>H<sub>25</sub>N<sub>4</sub>O<sub>8</sub><sup>+</sup> [M+H]<sup>+</sup>: 497.1667; found: 497.1658.



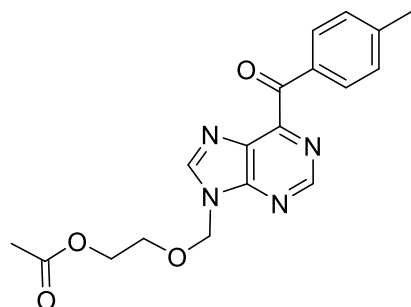
**(2*R*,3*S*,4*S*,5*R*)-2-((benzoyloxy)methyl)-5-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl dibenzoate (3ea):**

Yield: 68%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.94 (s, 1H), 8.36 (s, 1H), 8.14 – 8.09 (m, 2H), 8.05 – 8.01 (m, 2H), 7.95 – 7.90 (m, 4H), 7.63 – 7.53 (m, 3H), 7.48 – 7.35 (m, 6H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.55 – 6.49 (m, 2H), 6.30 (t, *J* = 5.2 Hz, 1H), 4.96 (dd, *J* = 12.2, 3.2 Hz, 1H), 4.90 – 4.85 (m, 1H), 4.73 (dd, *J* = 12.2, 4.2 Hz, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 166.1, 165.3, 165.1, 153.7, 152.7, 152.1, 145.4, 145.2, 133.9, 133.8, 133.5, 132.7, 132.4, 130.8, 129.8, 129.8, 129.7, 129.2, 129.2, 128.6, 128.6, 128.5, 128.5, 128.2, 87.2, 80.9, 73.6, 71.3, 63.4, 21.8; HRMS (ESI): *m/z* calcd for C<sub>39</sub>H<sub>30</sub>N<sub>4</sub>NaO<sub>8</sub><sup>+</sup> [M+Na]<sup>+</sup>: 705.1956; found: 705.1949.



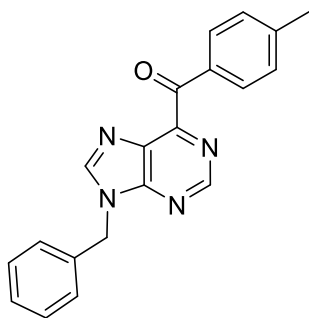
**(2*R*,3*S*,4*S*,5*R*)-2-(acetoxymethyl)-5-(6-(4-methylbenzoyl)-9*H*-purin-9-yl) tetrahydrofuran-3,4-diyl diacetate (3fa):**

Yield: 80%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 8.33 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 9.6 Hz, 1H), 5.89 (d, *J* = 2.8 Hz, 1H), 5.75 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.28 (ddd, *J* = 10.4, 6.0, 2.8 Hz, 1H), 4.17 – 4.00 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H), 1.82 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 169.8, 169.4, 168.8, 153.6, 153.2, 152.3, 145.4, 144.7, 132.7, 130.9, 129.3, 129.1, 78.8, 68.1, 67.8, 65.8, 63.8, 21.9, 20.9, 20.6, 20.4; HRMS (ESI): *m/z* calcd for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>NaO<sub>8</sub><sup>+</sup> [M+Na]<sup>+</sup>: 519.1487; found: 519.1479.



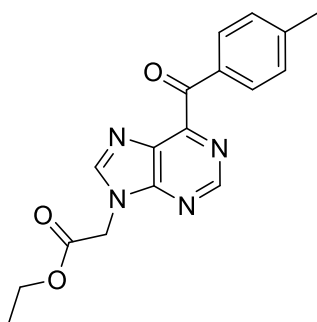
**2-((6-(4-methylbenzoyl)-9*H*-purin-9-yl) methoxy) ethyl acetate (3ga):**

Yield: 81%, Yellow oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 8.34 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.77 (s, 2H), 4.19 (t, *J* = 4.6 Hz, 2H), 3.80 (t, *J* = 4.6 Hz, 2H), 2.41 (s, 3H), 2.01 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 170.7, 153.4, 152.3, 146.5, 145.3, 132.7, 131.4, 130.8, 129.2, 72.8, 68.0, 62.7, 21.8, 20.7. HRMS (ESI): *m/z* calcd for C<sub>18</sub>H<sub>19</sub>N<sub>4</sub>O<sub>4</sub>[M+H]<sup>+</sup>: 355.1401; found: 355.1408.



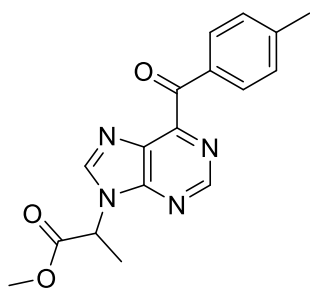
**(9-benzyl-9H-purin-6-yl) (p-tolyl) methanone (3ha):**

Yield: 56%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.05 (s, 1H), 7.87 (d,  $J$  = 8.2 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.20 (d,  $J$  = 7.8 Hz, 2H), 5.42 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.2, 153.2, 153.1, 151.9, 146.5, 145.1, 134.6, 132.8, 131.5, 130.8, 129.2, 129.1, 128.7, 127.9, 47.4, 21.8; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{NaO}^+$  [ $\text{M}+\text{Na}$ ] $^+$ : 351.1217; found: 351.1215.



**ethyl 2-(6-(4-methylbenzoyl)-9H-purin-9-yl) acetate (3ia):**

Yield: 78%, Yellow solid; mp 129–133 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.09 (s, 1H), 8.28 (s, 1H), 7.94 (d,  $J$  = 8.2 Hz, 2H), 7.28 (d,  $J$  = 7.8 Hz, 2H), 5.11 (s, 2H), 4.28 (q,  $J$  = 7.2 Hz, 2H), 2.42 (s, 3H), 1.31 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.1, 166.7, 153.3, 153.2, 152.2, 147.0, 145.3, 132.9, 131.3, 131.0, 129.3, 62.7, 44.3, 21.9, 14.1. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_4\text{O}_3^+$  [ $\text{M}+\text{H}$ ] $^+$ : 325.1296; found: 325.1297.

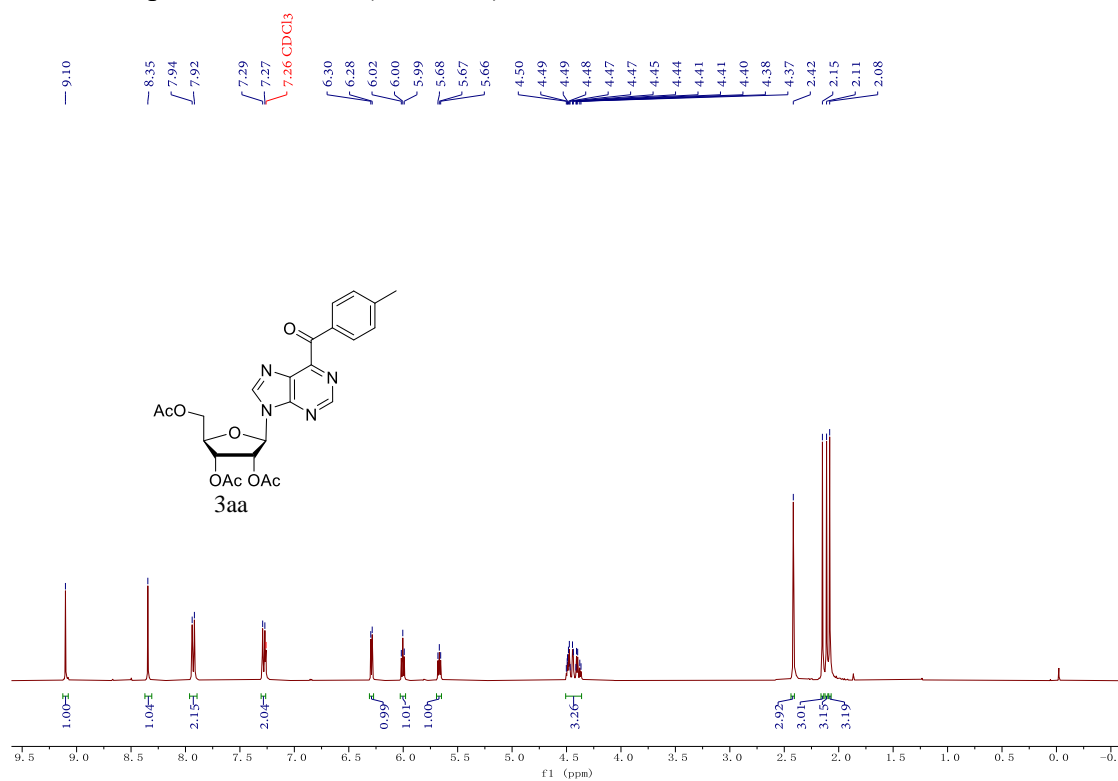


**methyl 2-(6-(4-methylbenzoyl)-9H-purin-9-yl) propanoate (3ja):**

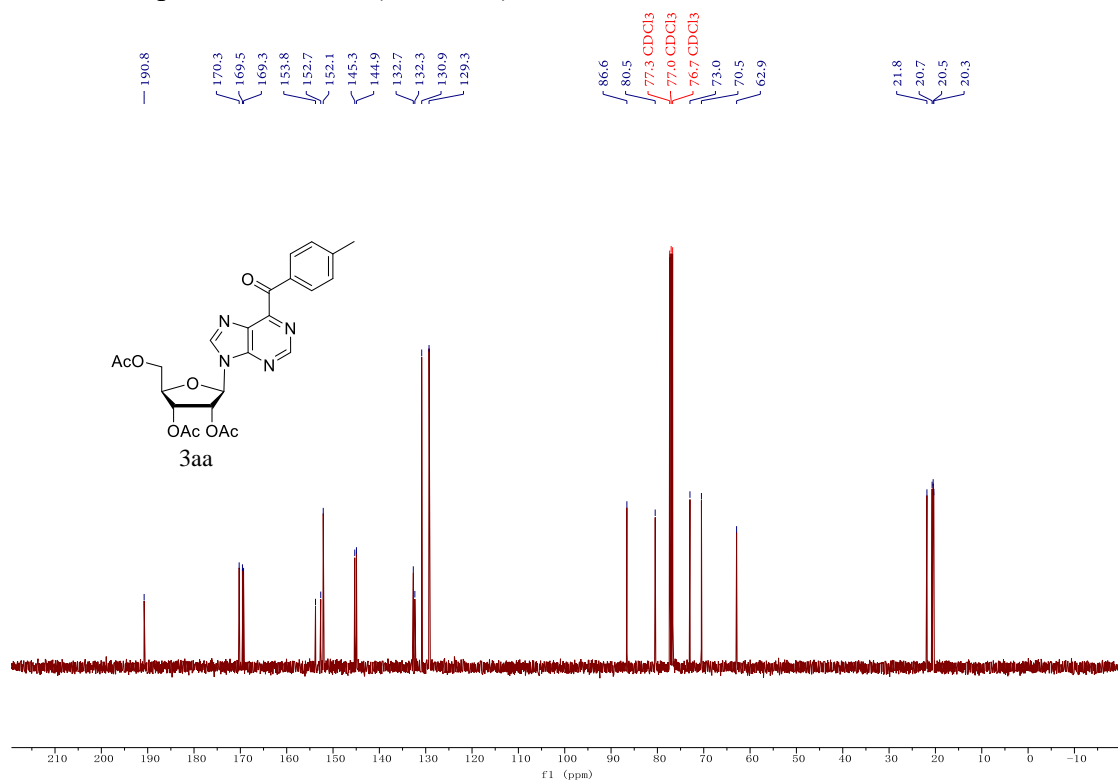
Yield: 76%, Yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.08 (s, 1H), 8.38 (s, 1H), 7.95 (d,  $J = 8.2$  Hz, 2H), 7.29 (d,  $J = 7.6$  Hz, 2H), 5.59 (q,  $J = 7.6$  Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H), 1.94 (d,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  191.1, 170.1, 153.2, 153.0, 151.9, 145.2, 132.8, 131.4, 130.9, 129.3, 53.3, 52.0, 21.9, 18.0. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_4\text{O}_3^+$   $[\text{M}+\text{H}]^+$ : 325.1296; found: 325.1285.

## 8. NMR Spectra of Products

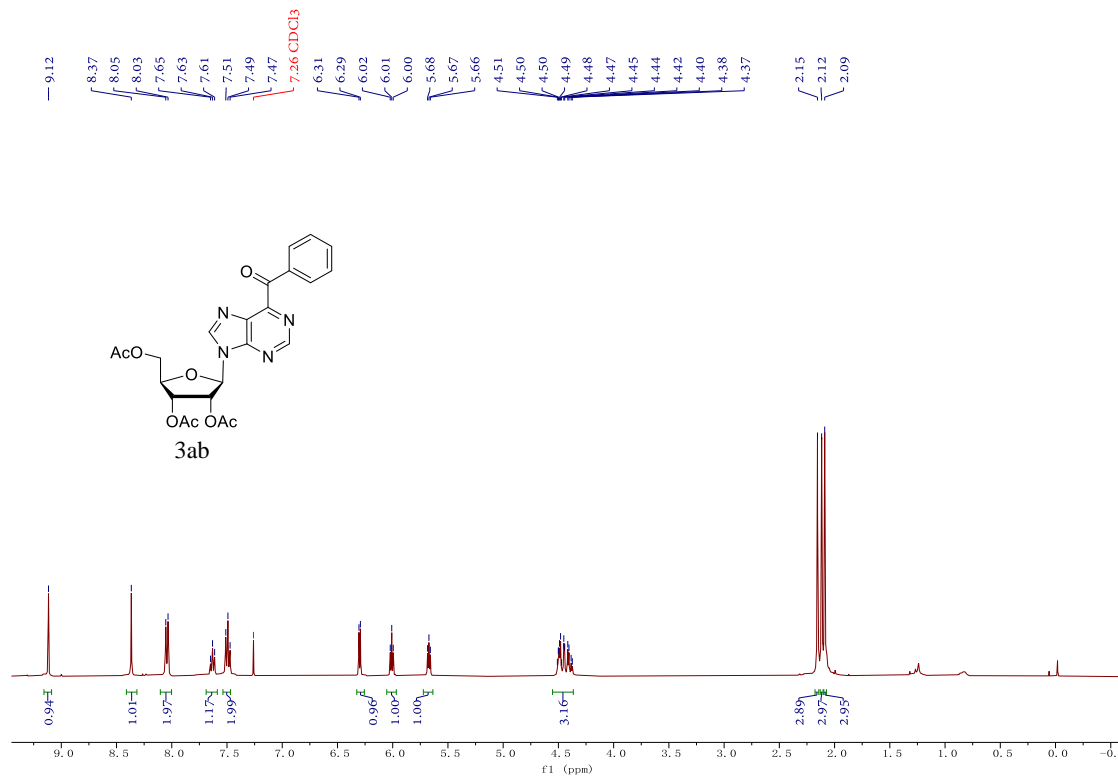
$^1\text{H-NMR}$  spectrum for **3aa** (in  $\text{CDCl}_3$ )



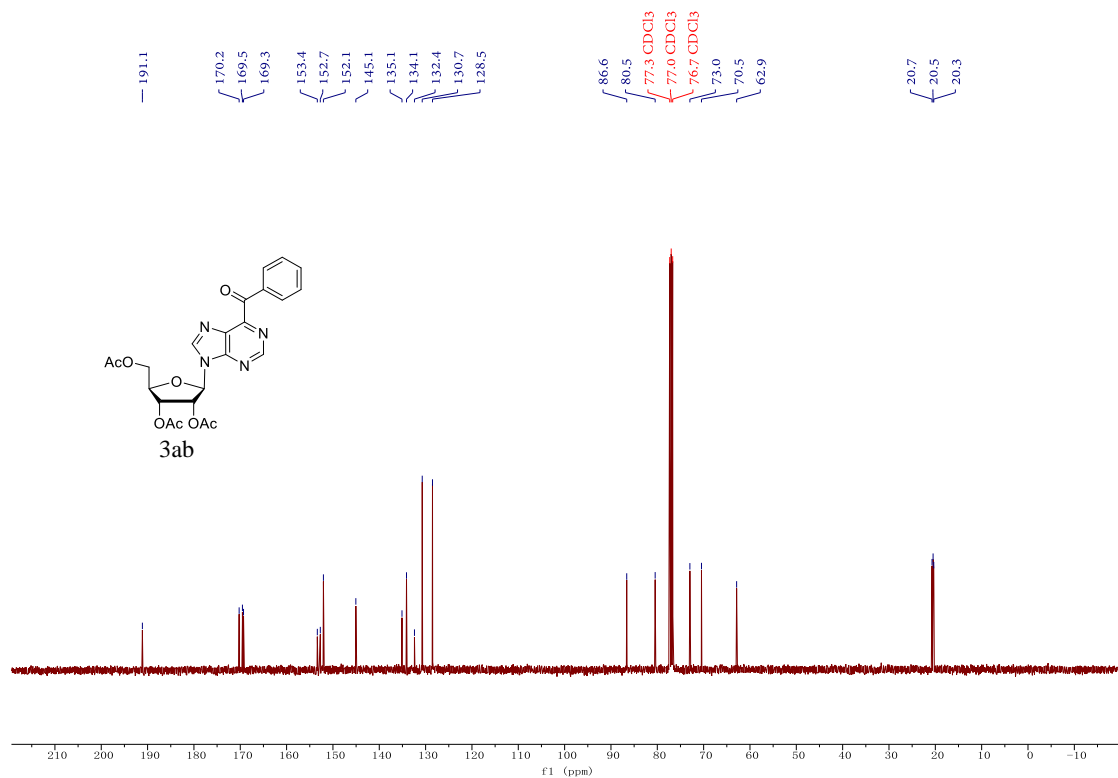
$^{13}\text{C-NMR}$  spectrum for **3aa** (in  $\text{CDCl}_3$ )



<sup>1</sup>H-NMR spectrum for **3ab** (in CDCl<sub>3</sub>)

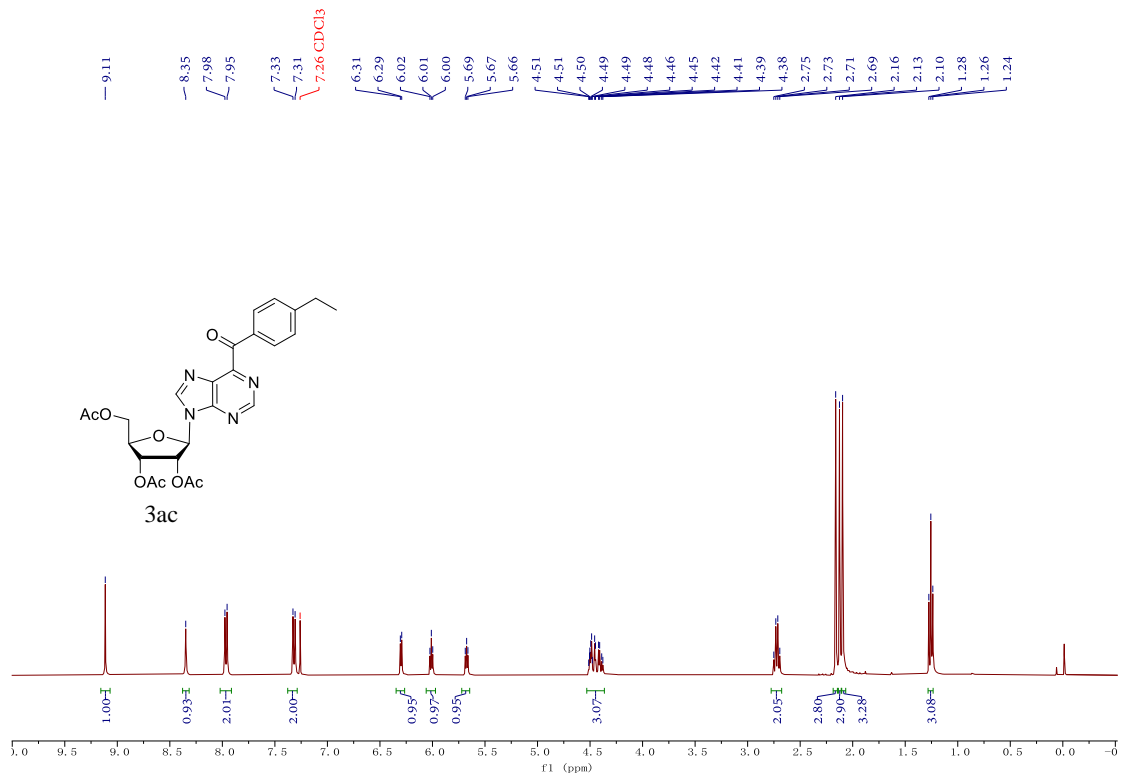


<sup>13</sup>C-NMR spectrum for **3ab** (in CDCl<sub>3</sub>)

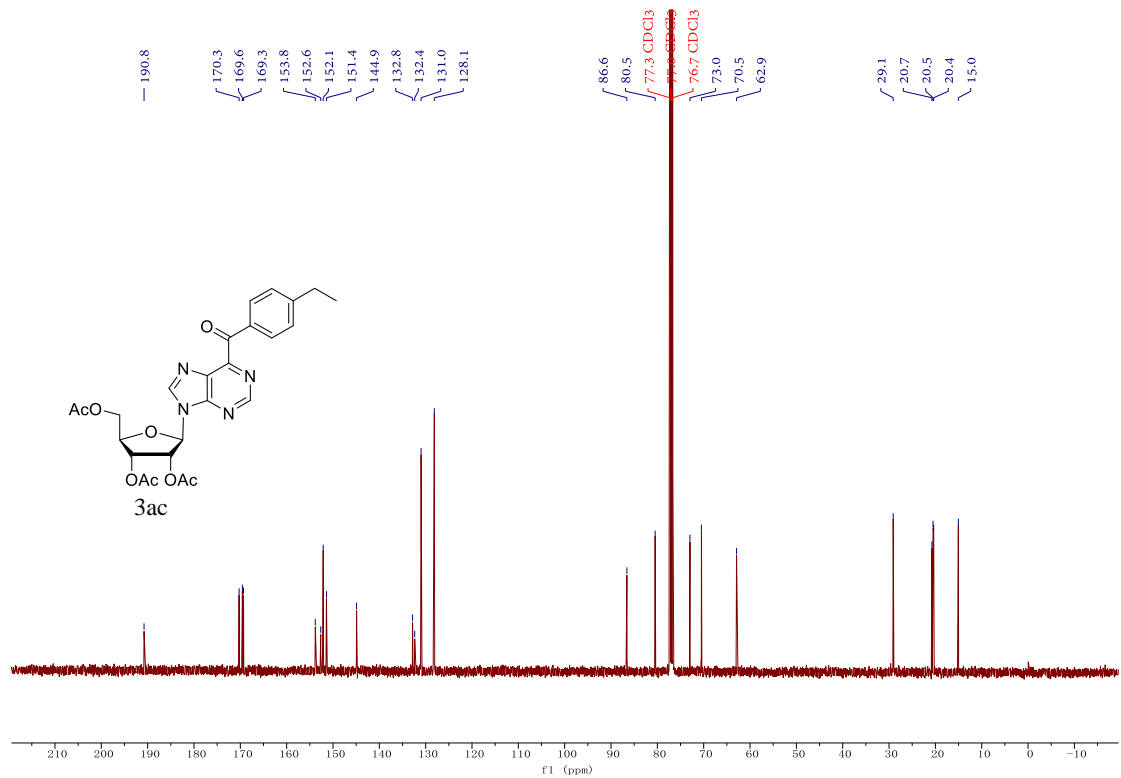




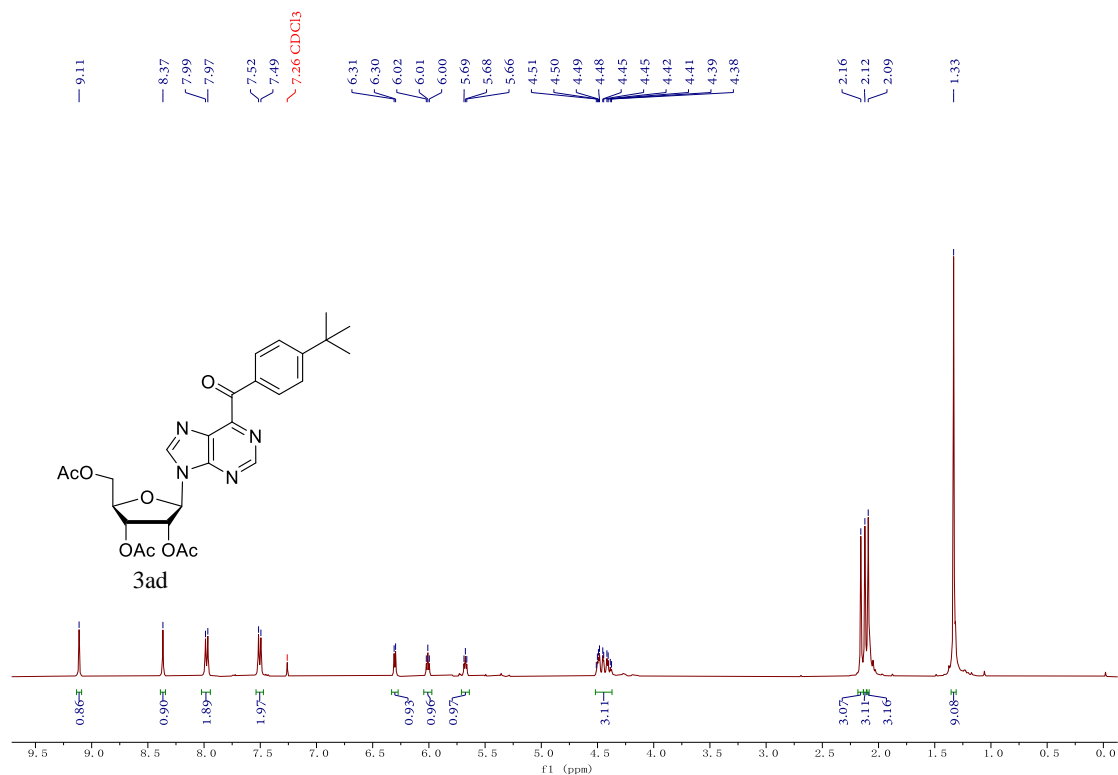
$^1\text{H-NMR}$  spectrum for **3ac** (in  $\text{CDCl}_3$ )



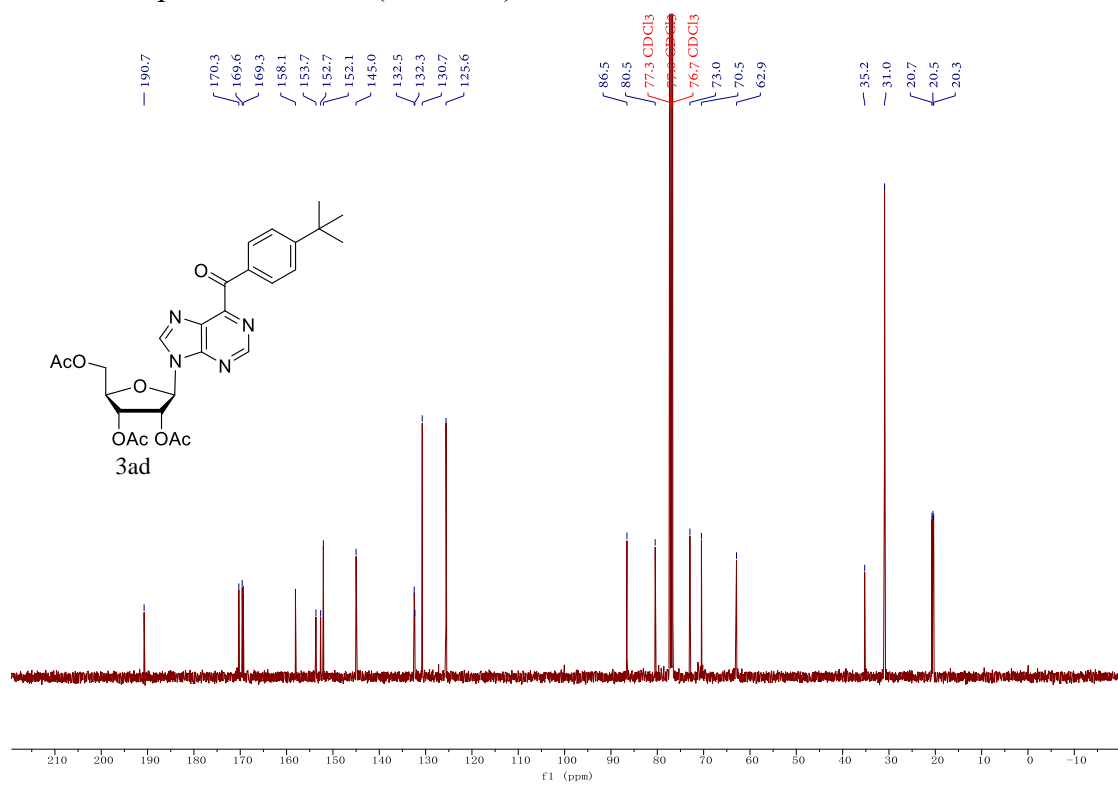
$^{13}\text{C-NMR}$  spectrum for **3ac** (in  $\text{CDCl}_3$ )



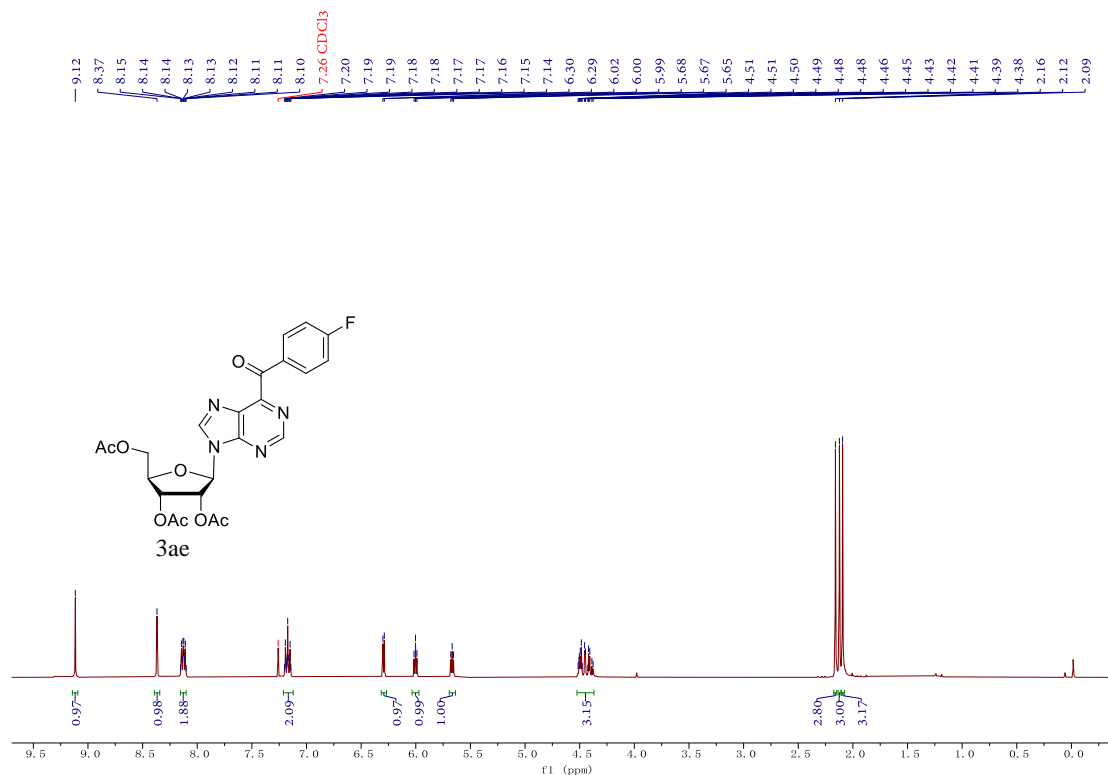
<sup>1</sup>H-NMR spectrum for **3ad** (in CDCl<sub>3</sub>)



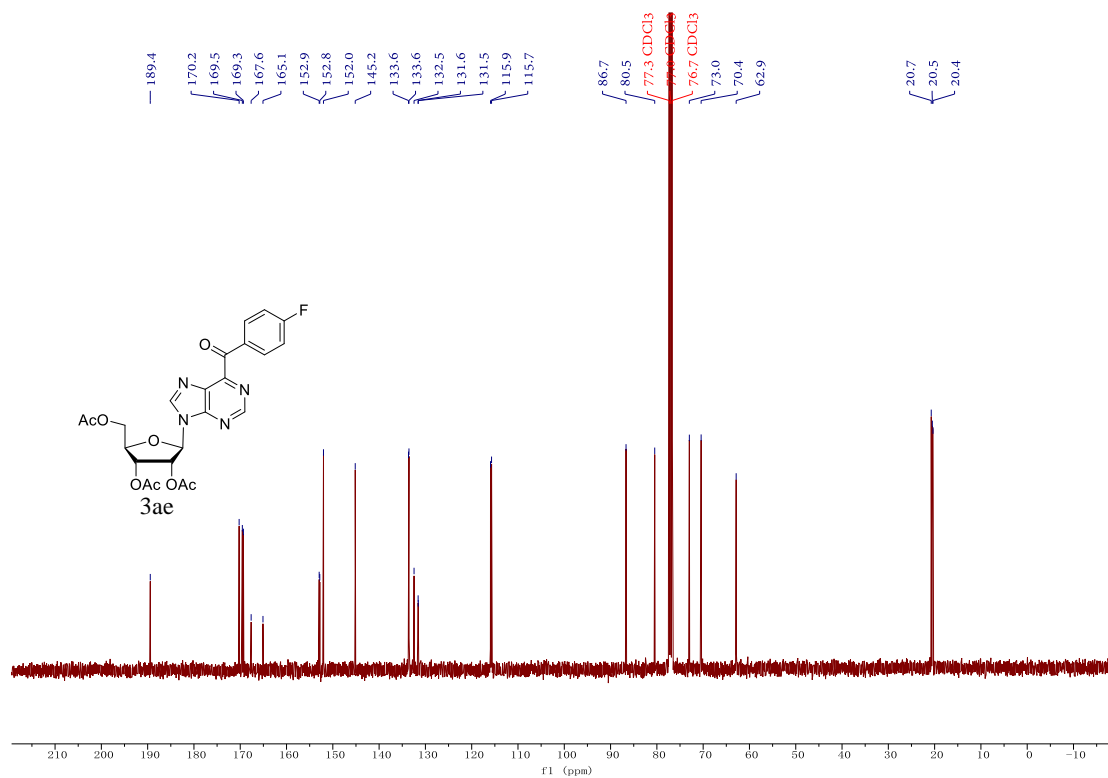
<sup>13</sup>C-NMR spectrum for **3ad** (in CDCl<sub>3</sub>)



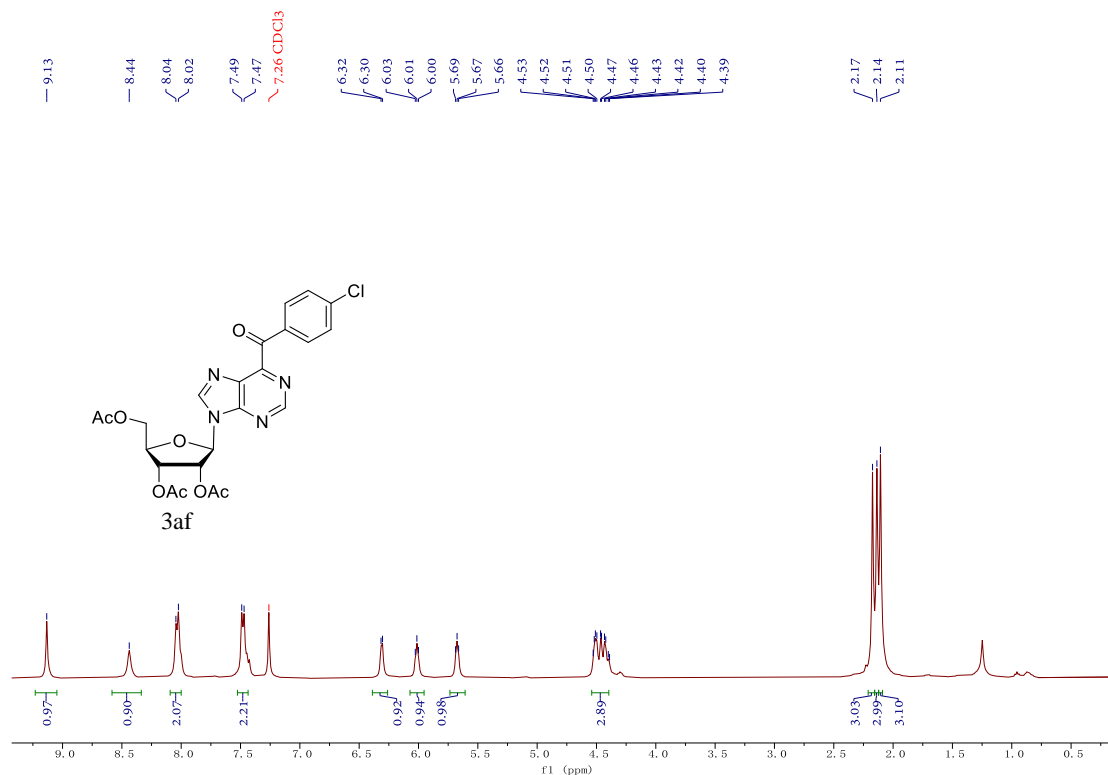
<sup>1</sup>H-NMR spectrum for **3ae** (in CDCl<sub>3</sub>)



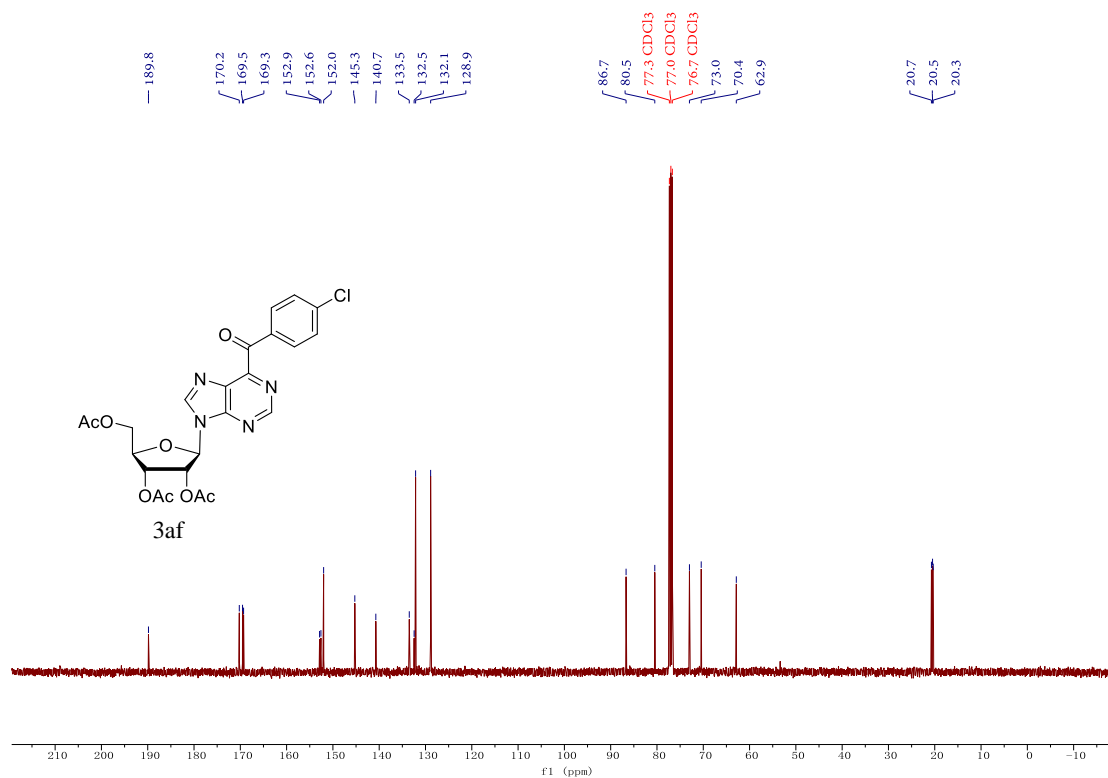
<sup>13</sup>C-NMR spectrum for **3ae** (in CDCl<sub>3</sub>)



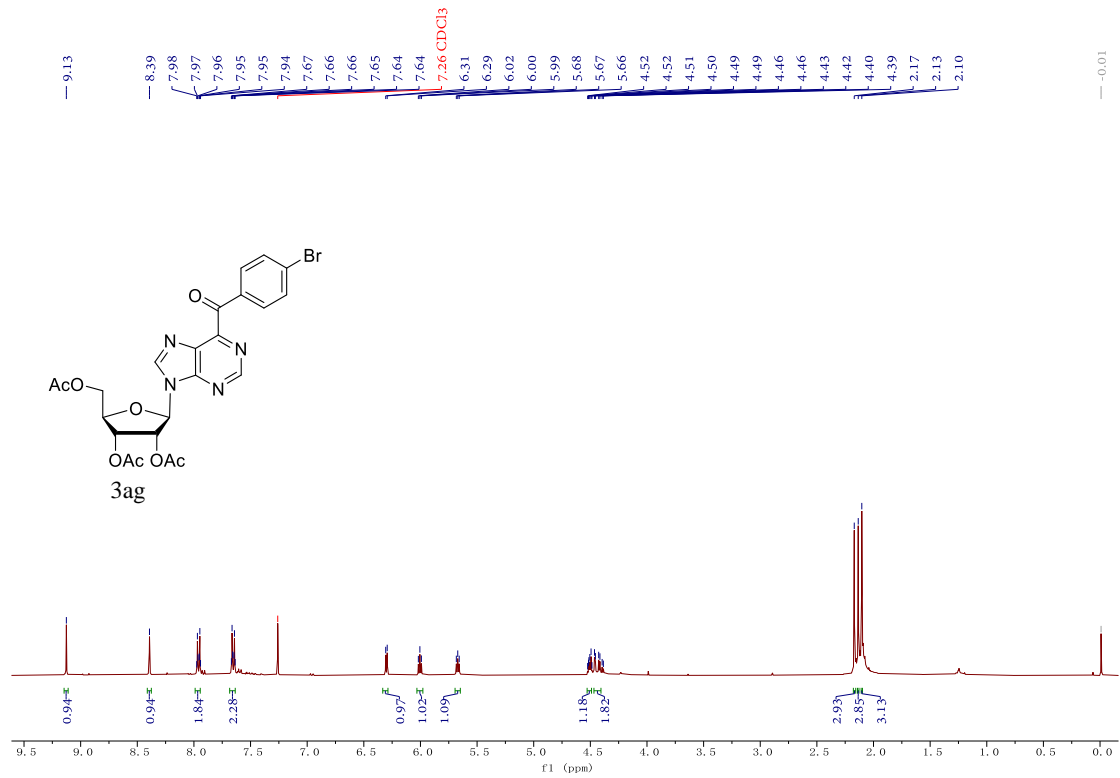
$^1\text{H-NMR}$  spectrum for **3af** (in  $\text{CDCl}_3$ )



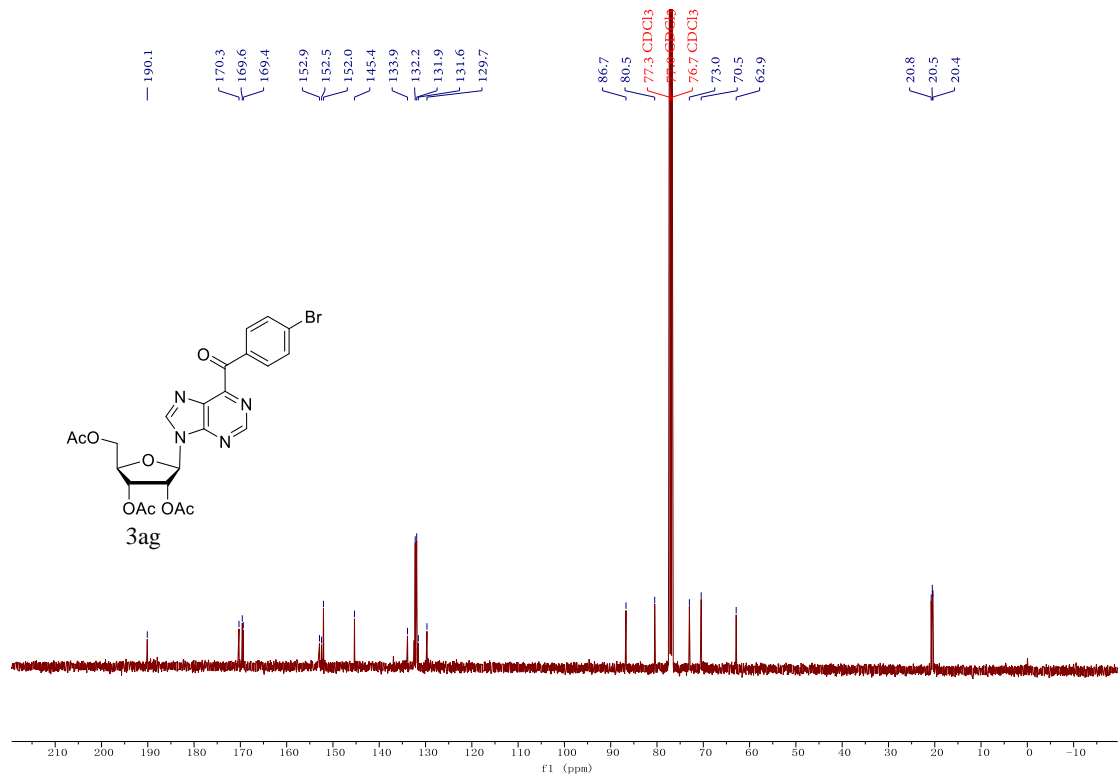
$^{13}\text{C-NMR}$  spectrum for **3af** (in  $\text{CDCl}_3$ )



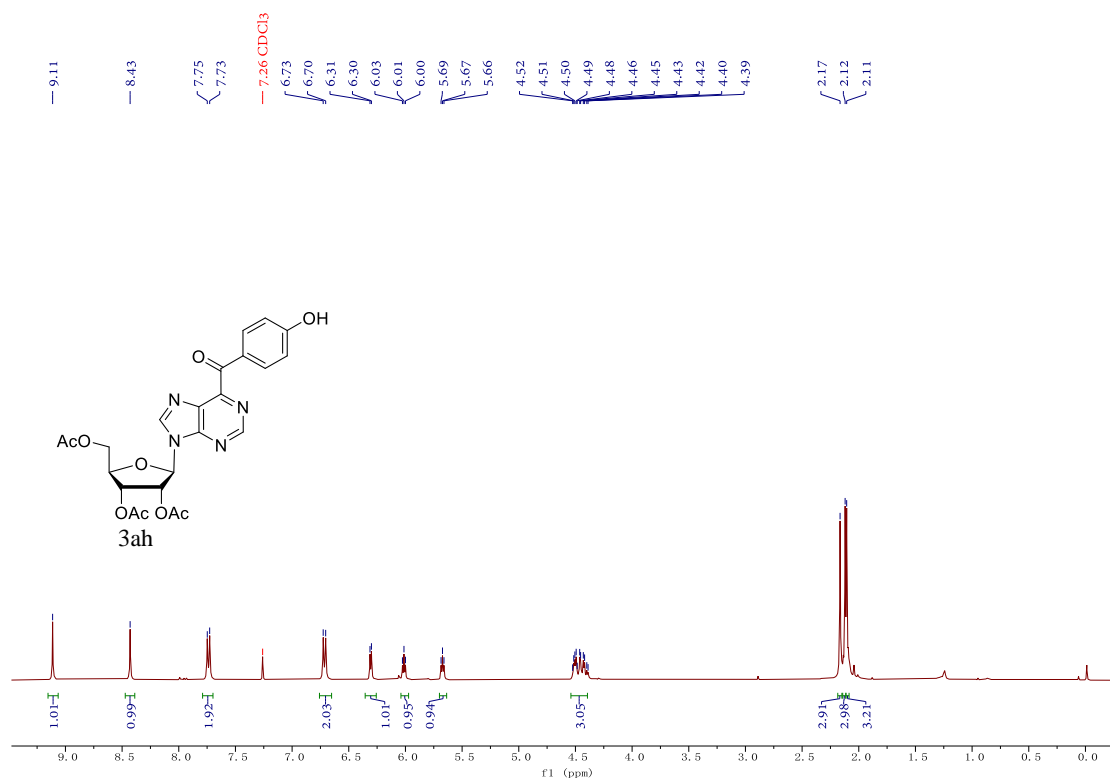
$^1\text{H-NMR}$  spectrum for **3ag** (in  $\text{CDCl}_3$ )



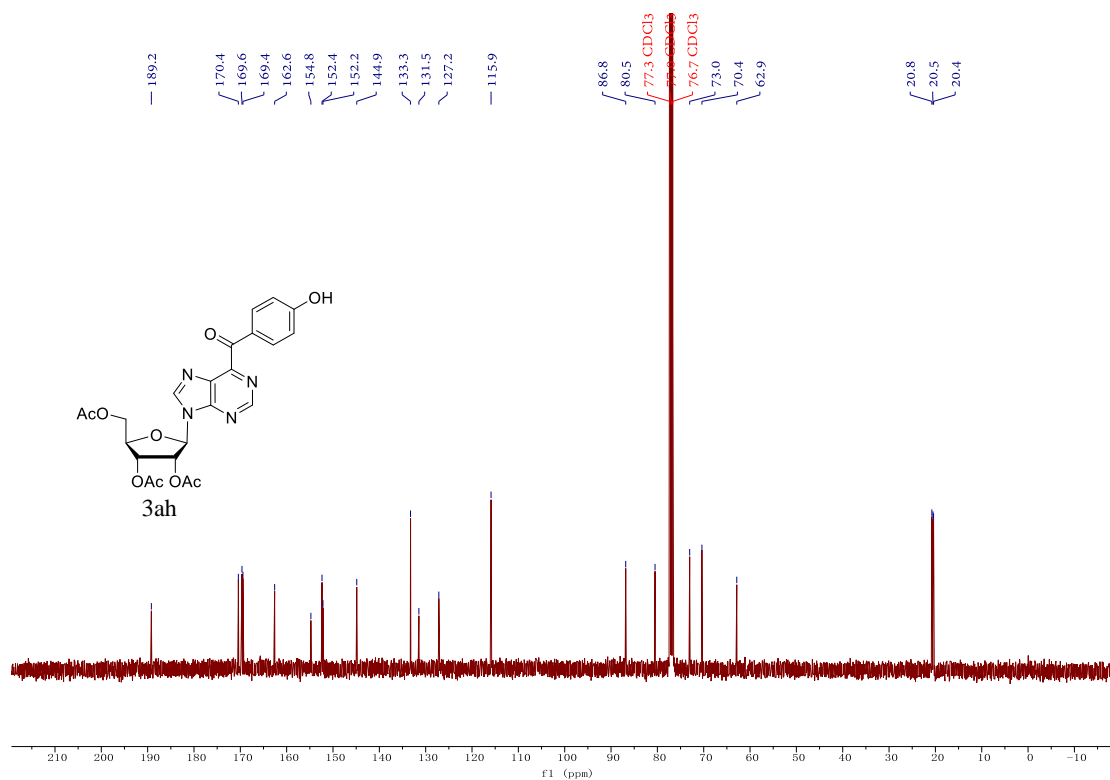
$^{13}\text{C-NMR}$  spectrum for **3ag** (in  $\text{CDCl}_3$ )



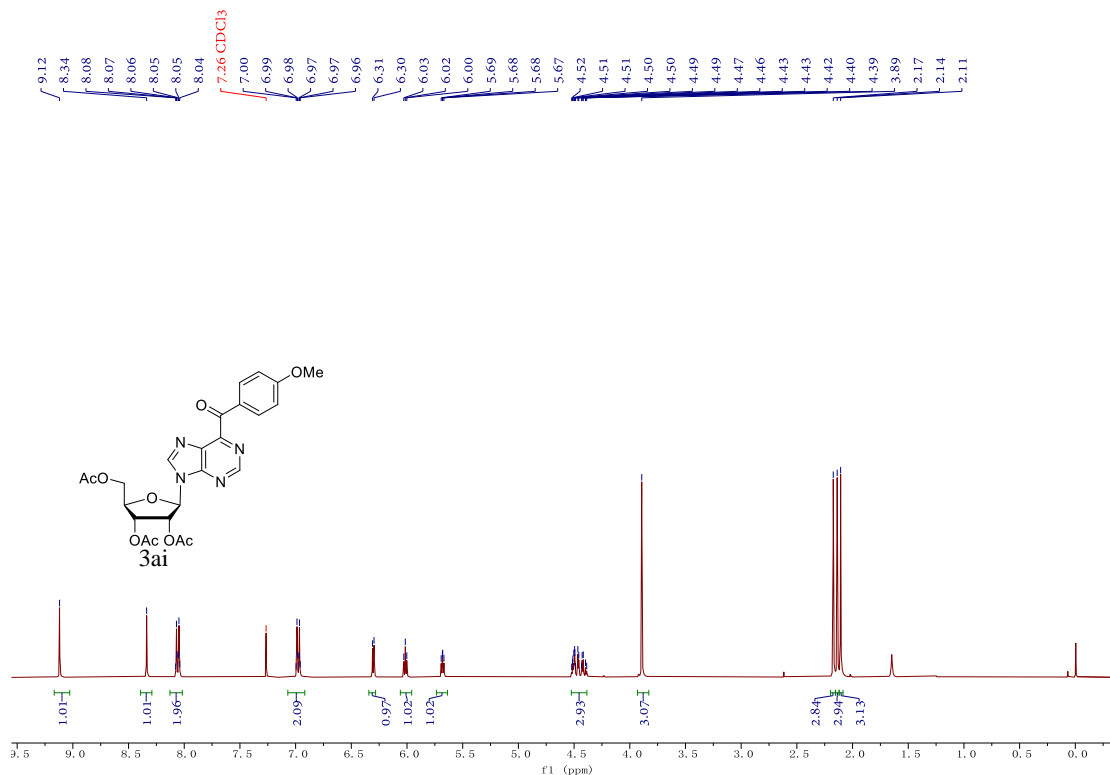
$^1\text{H-NMR}$  spectrum for **3ah** (in  $\text{CDCl}_3$ )



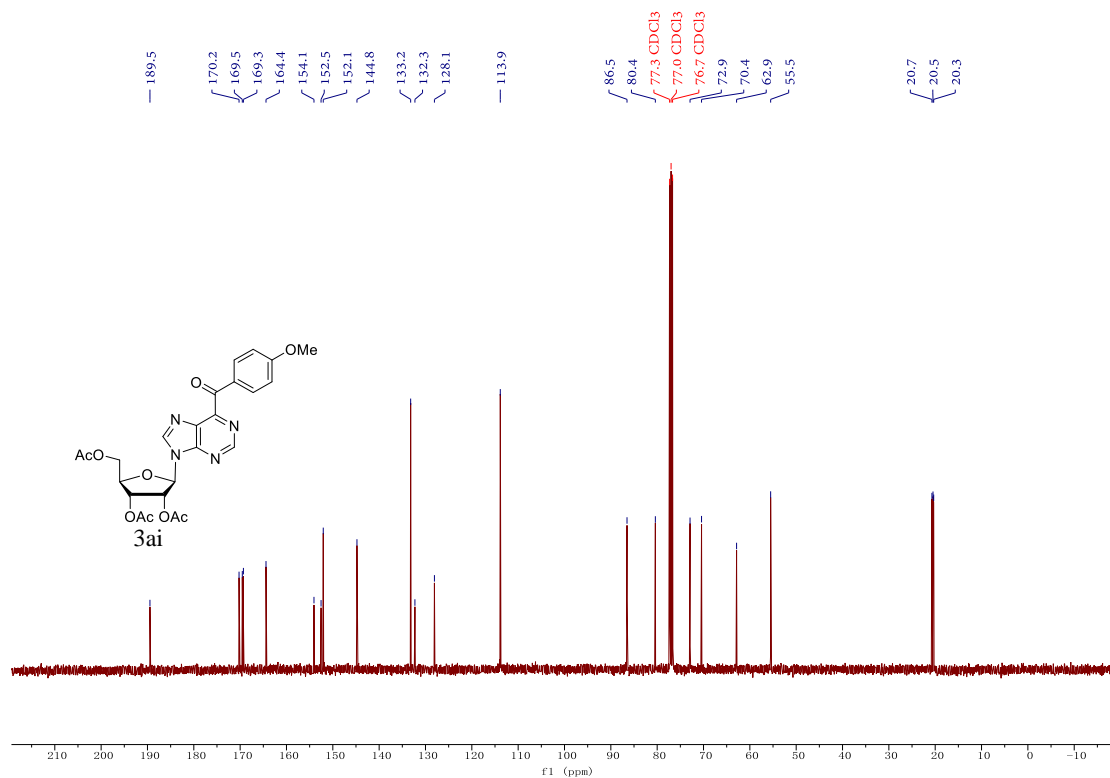
$^{13}\text{C-NMR}$  spectrum for **3ah** (in  $\text{CDCl}_3$ )



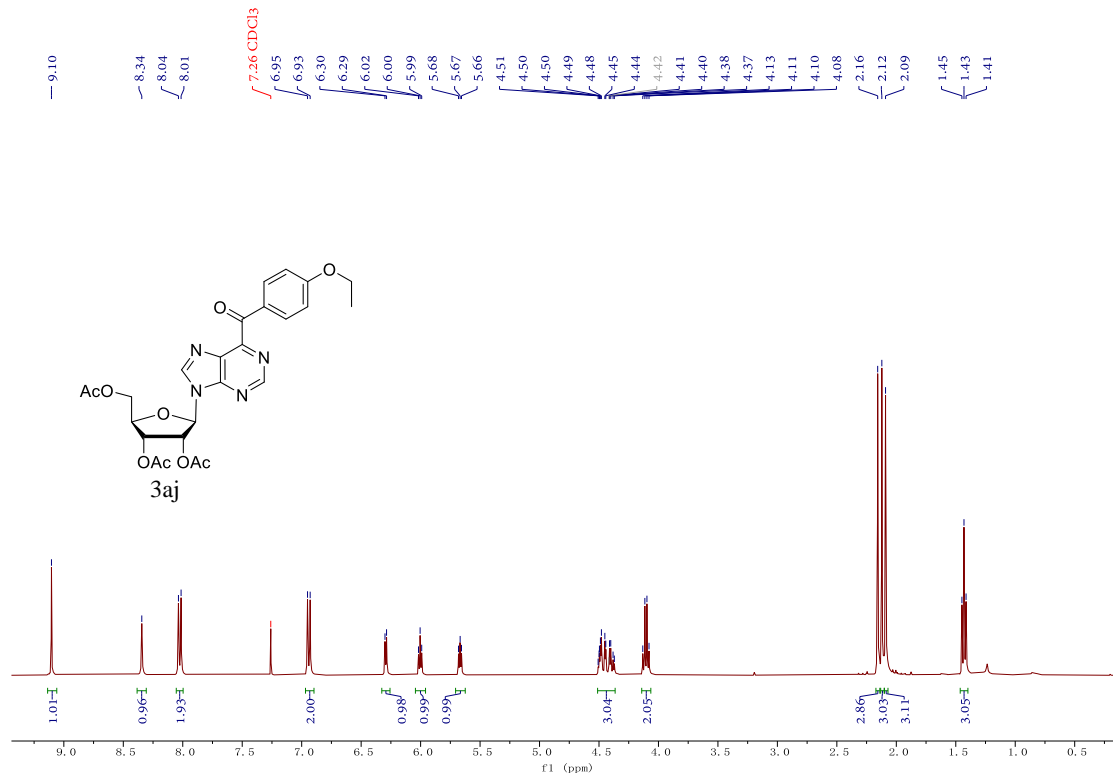
<sup>1</sup>H-NMR spectrum for **3ai** (in CDCl<sub>3</sub>)



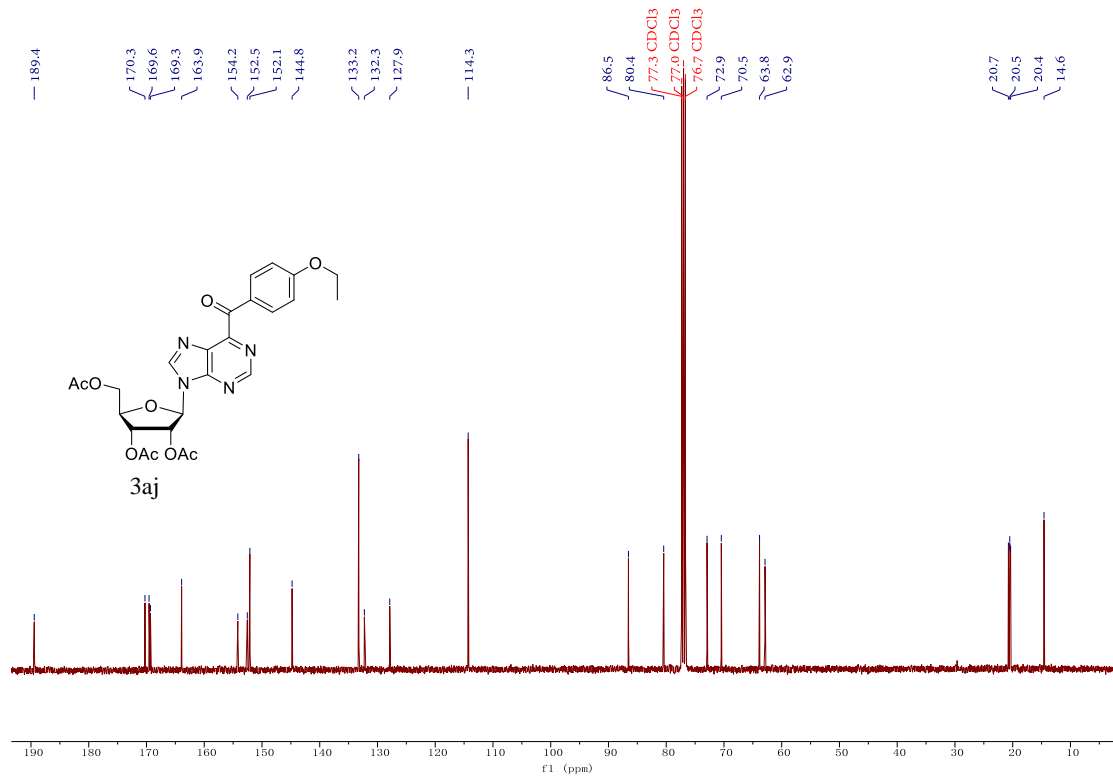
<sup>13</sup>C-NMR spectrum for **3ai** (in CDCl<sub>3</sub>)



<sup>1</sup>H-NMR spectrum for **3aj** (in CDCl<sub>3</sub>)

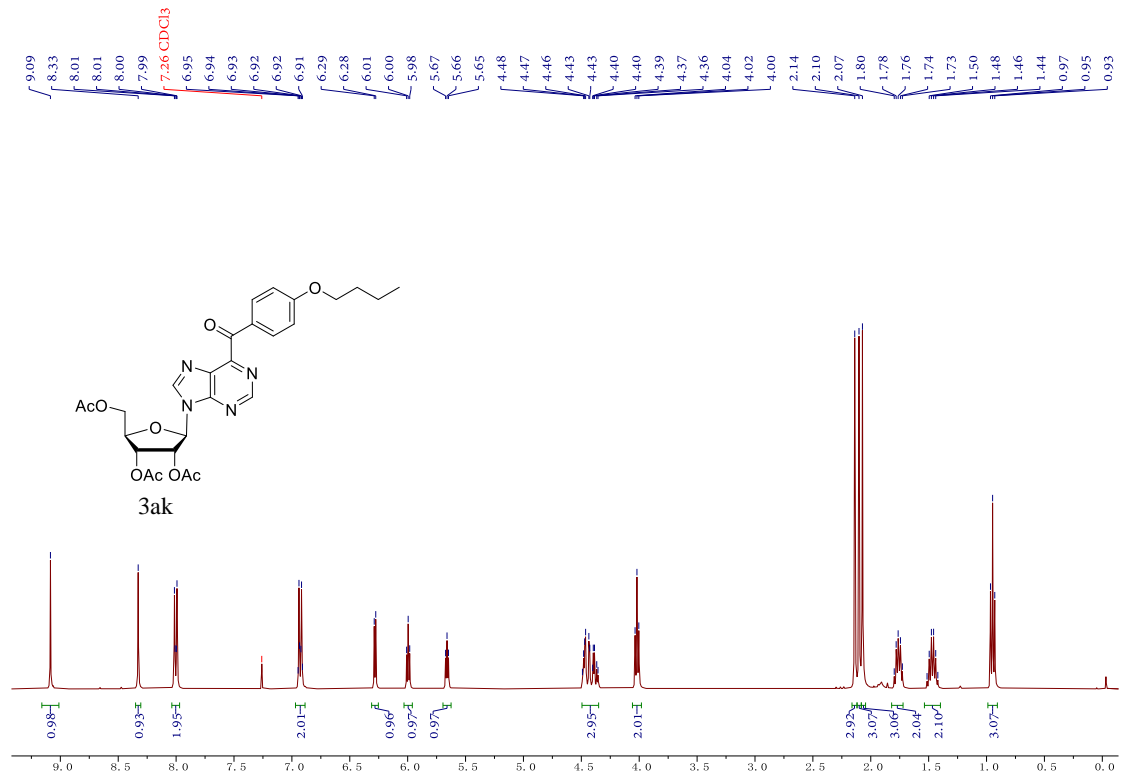


<sup>13</sup>C-NMR spectrum for **3aj** (in CDCl<sub>3</sub>)

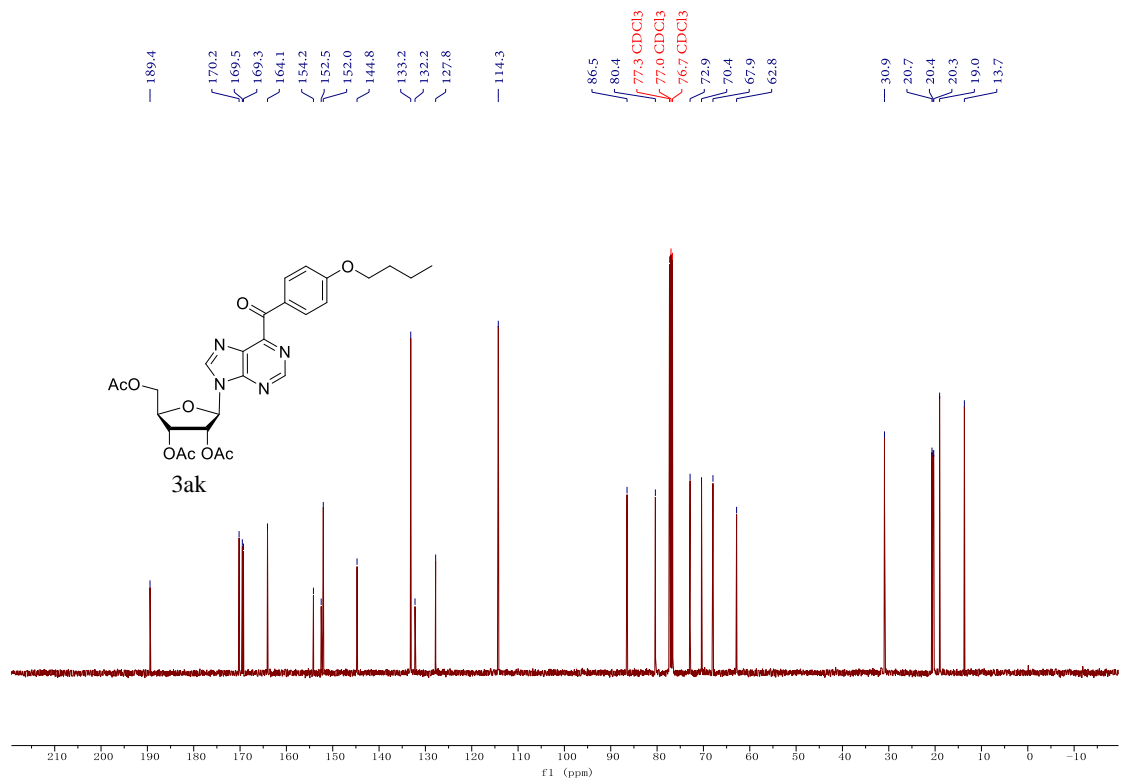




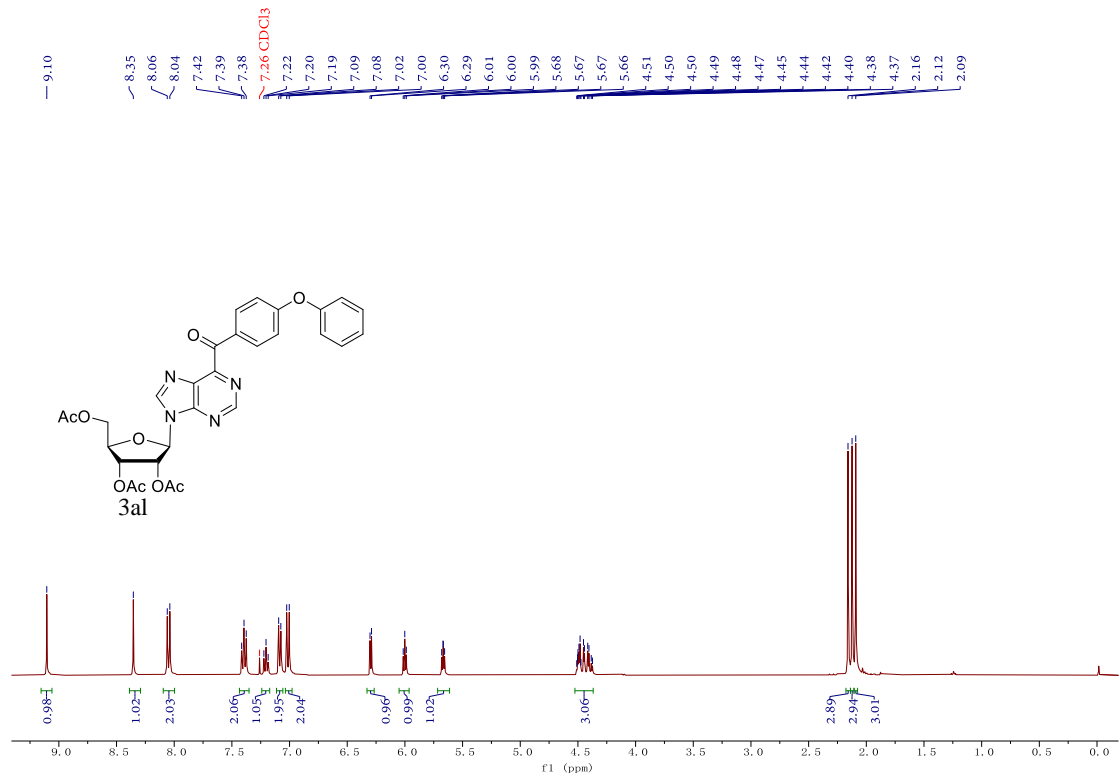
$^1\text{H-NMR}$  spectrum for **3ak** (in  $\text{CDCl}_3$ )



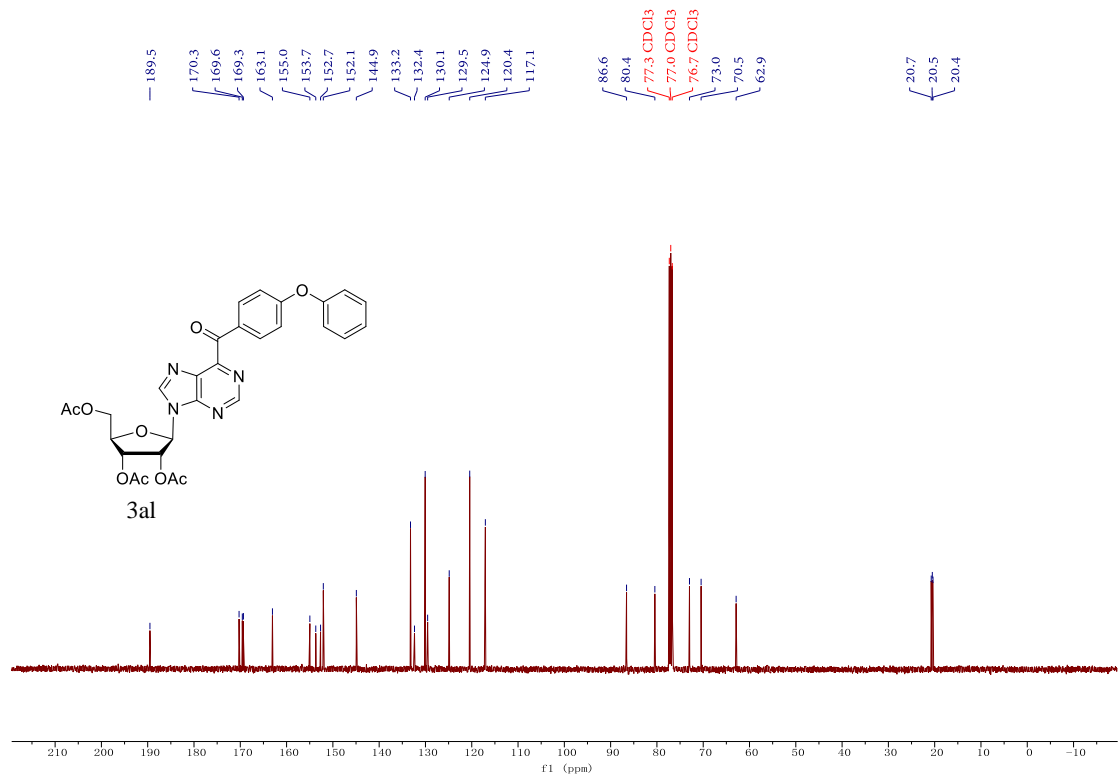
$^{13}\text{C-NMR}$  spectrum for **3ak** (in  $\text{CDCl}_3$ )



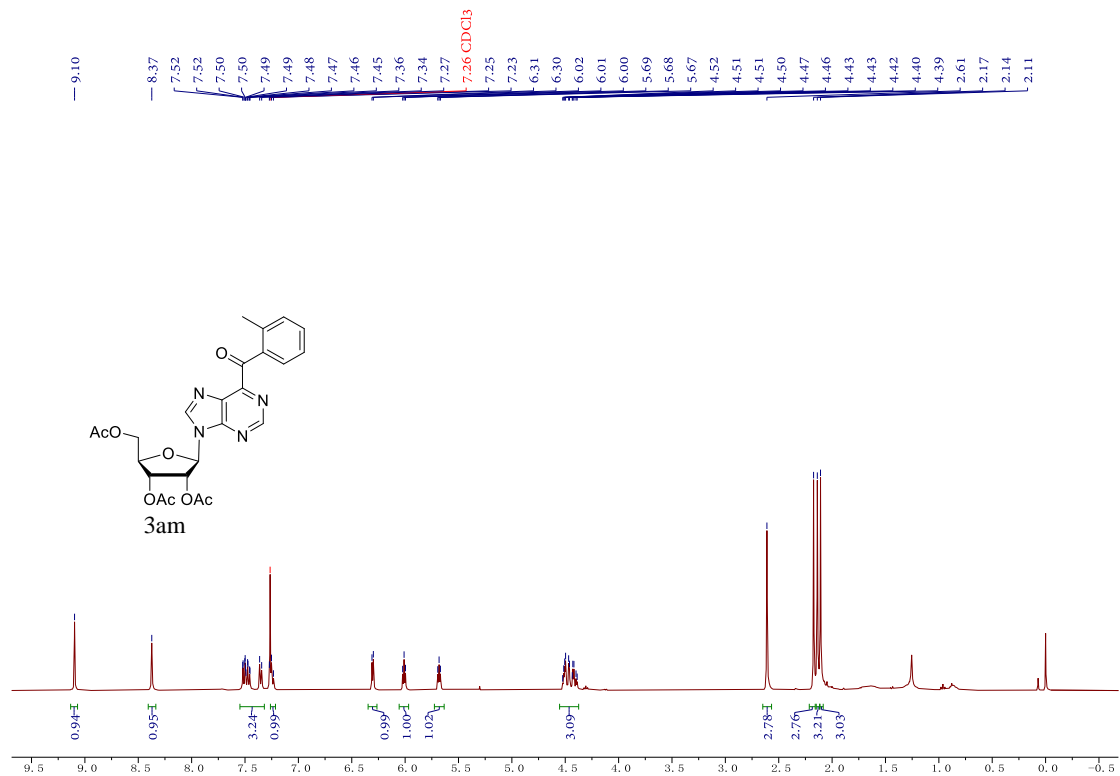
### <sup>1</sup>H-NMR spectrum for **3al** (in CDCl<sub>3</sub>)



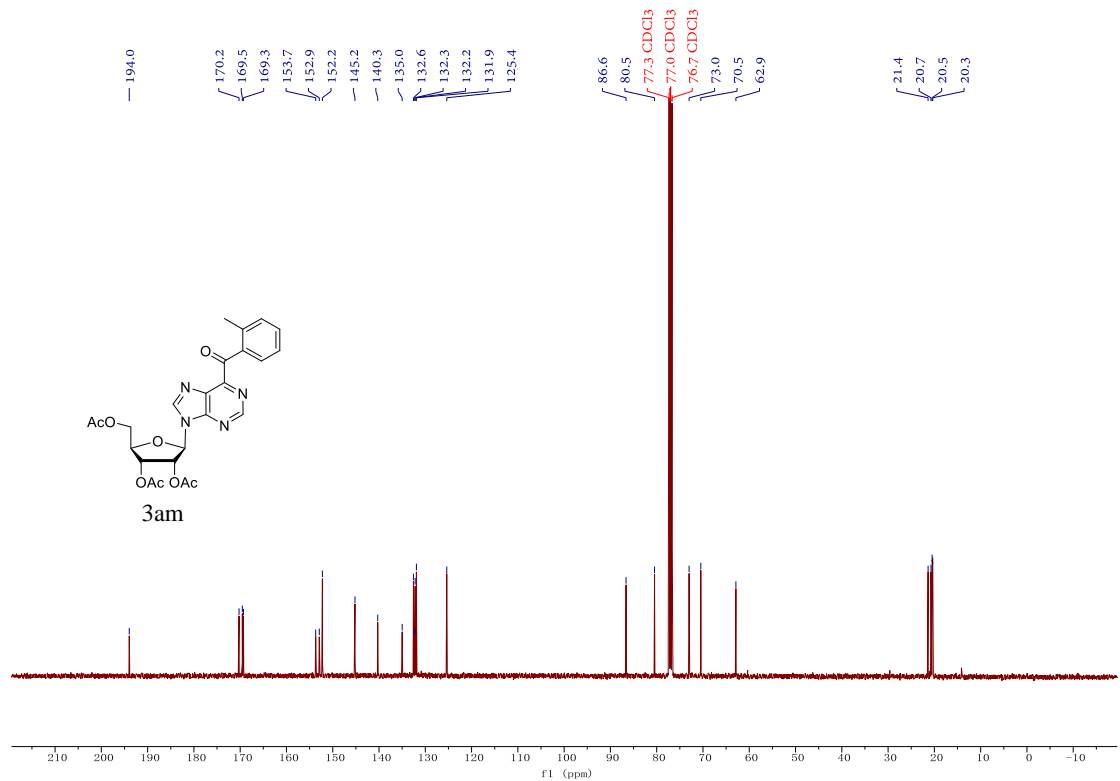
### <sup>13</sup>C-NMR spectrum for **3al** (in CDCl<sub>3</sub>)



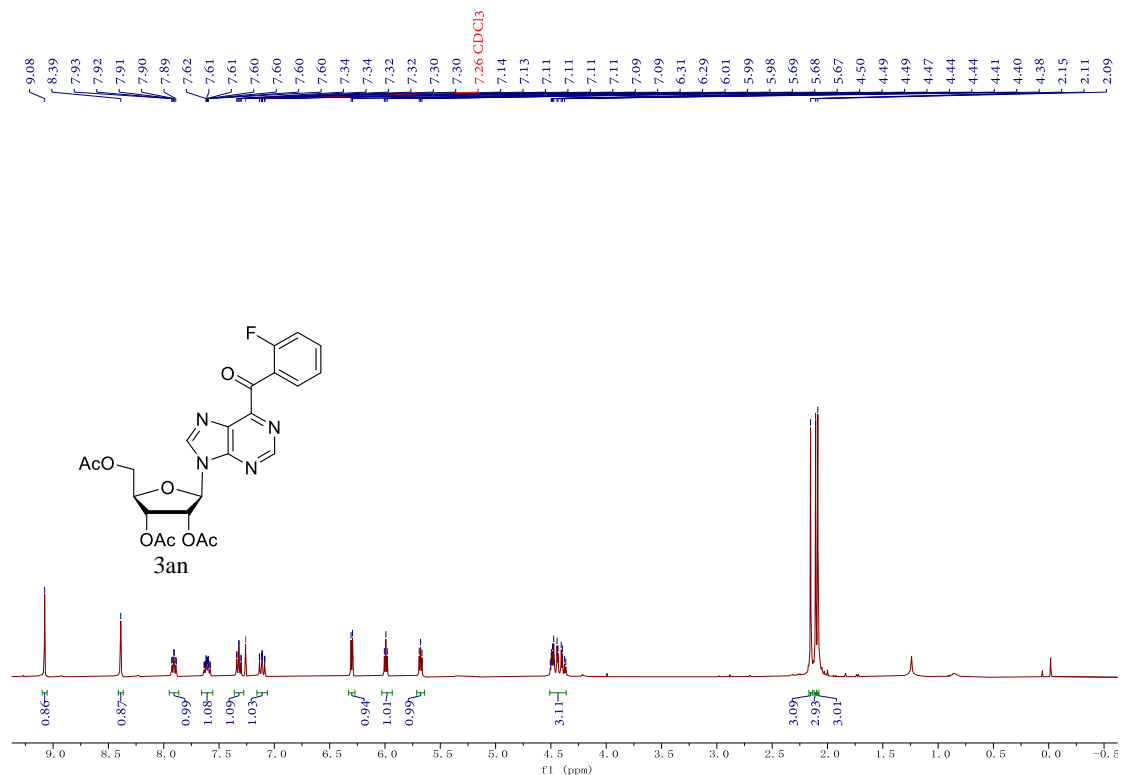
<sup>1</sup>H-NMR spectrum for **3am** (in CDCl<sub>3</sub>)



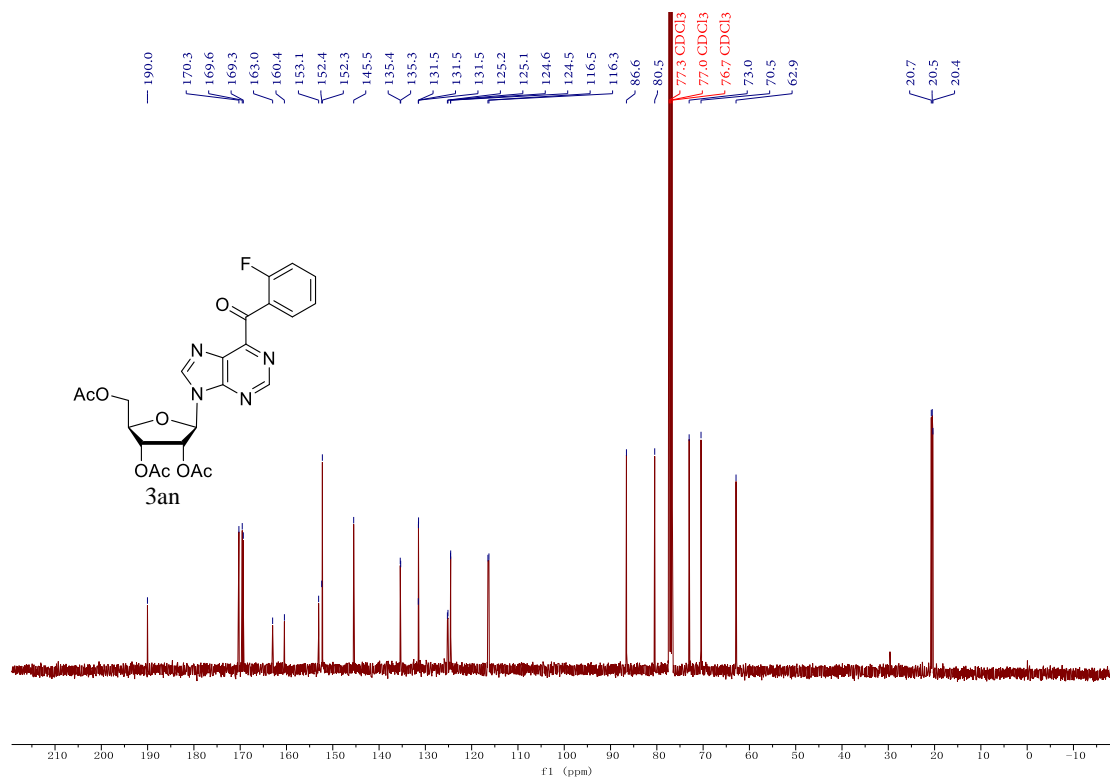
<sup>13</sup>C-NMR spectrum for **3am** (in CDCl<sub>3</sub>)



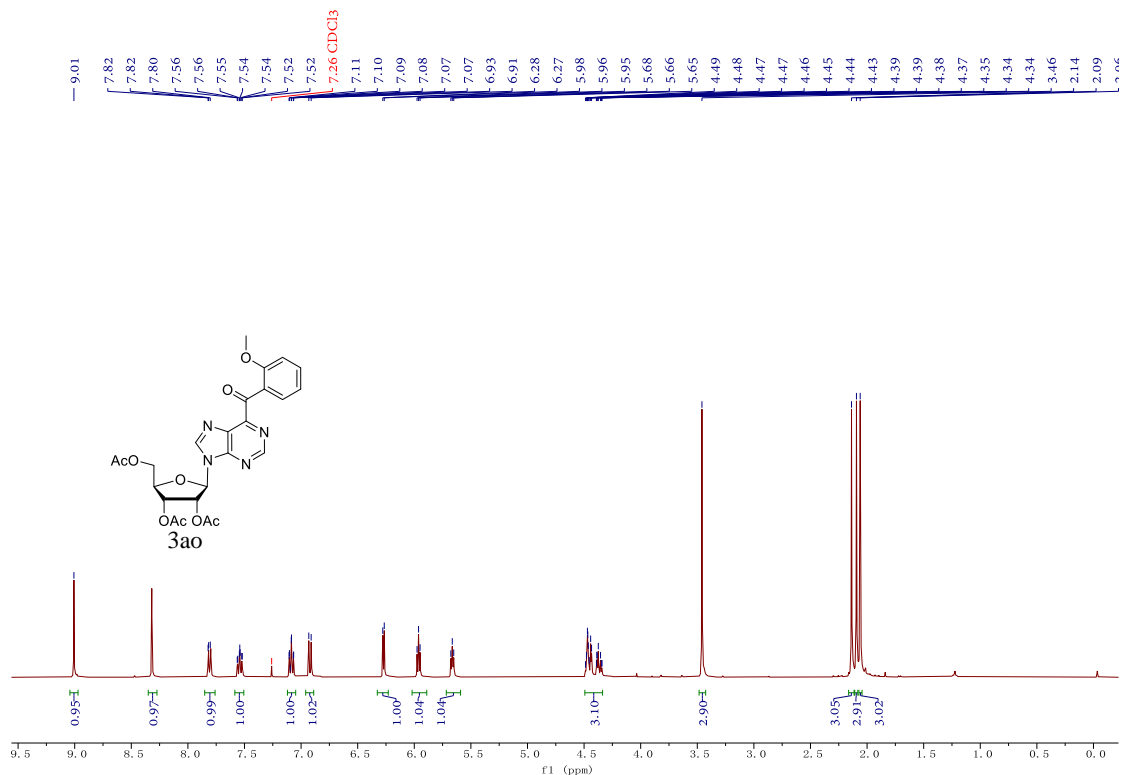
$^1\text{H-NMR}$  spectrum for **3an** (in  $\text{CDCl}_3$ )



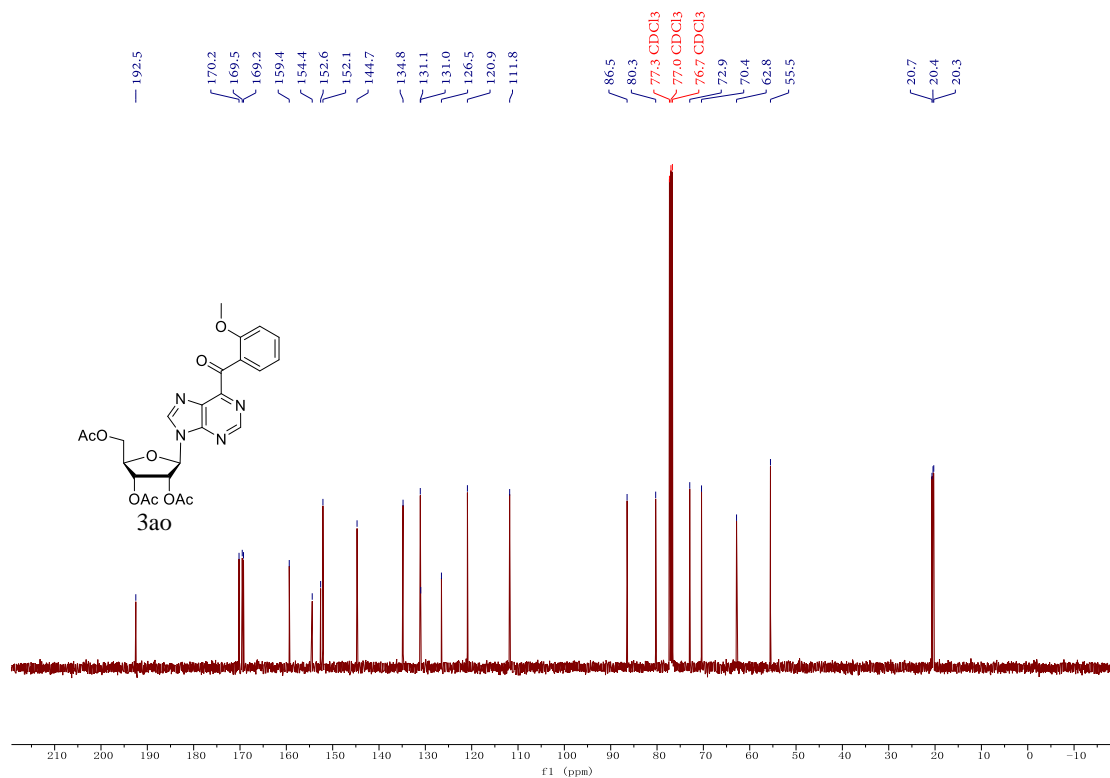
$^{13}\text{C-NMR}$  spectrum for **3an** (in  $\text{CDCl}_3$ )



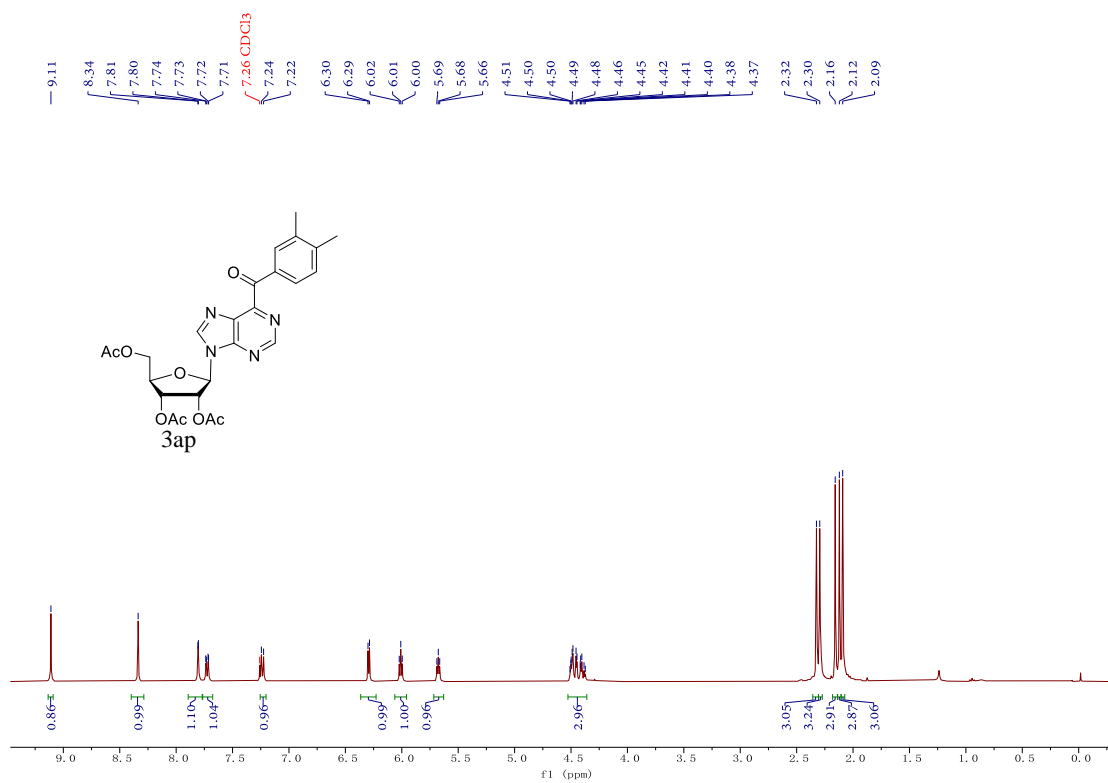
### $^1\text{H-NMR}$ spectrum for **3ao** (in $\text{CDCl}_3$ )



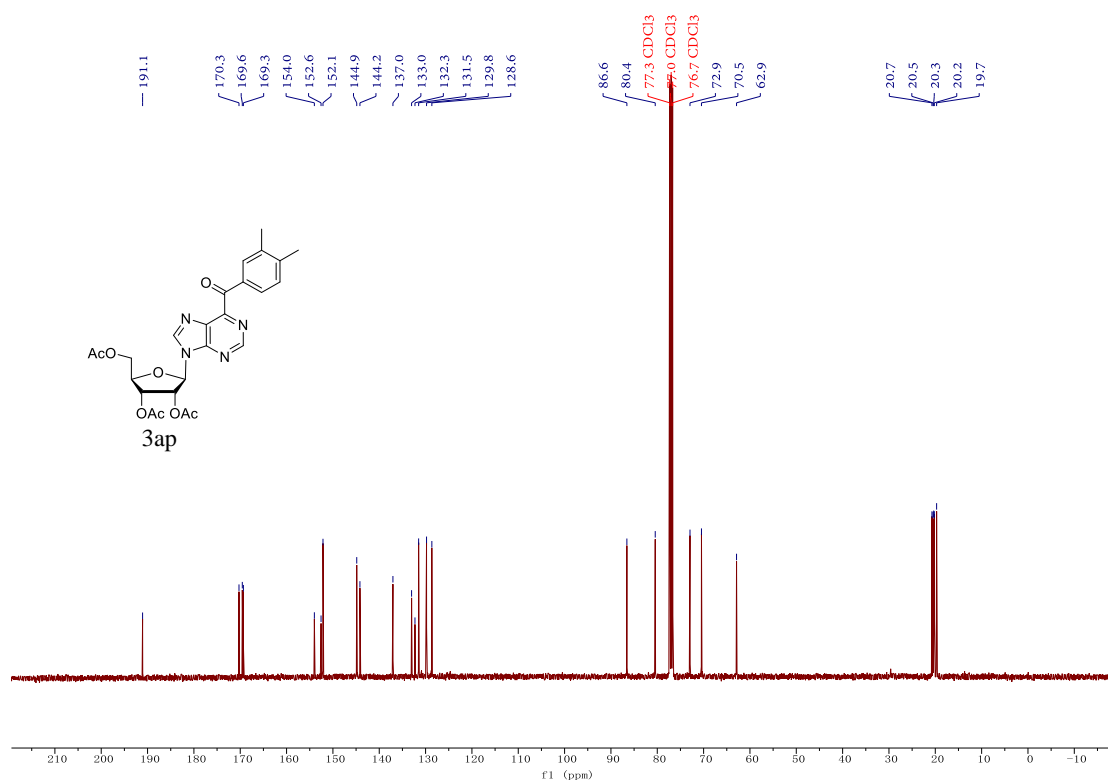
### $^{13}\text{C-NMR}$ spectrum for **3ao** (in $\text{CDCl}_3$ )



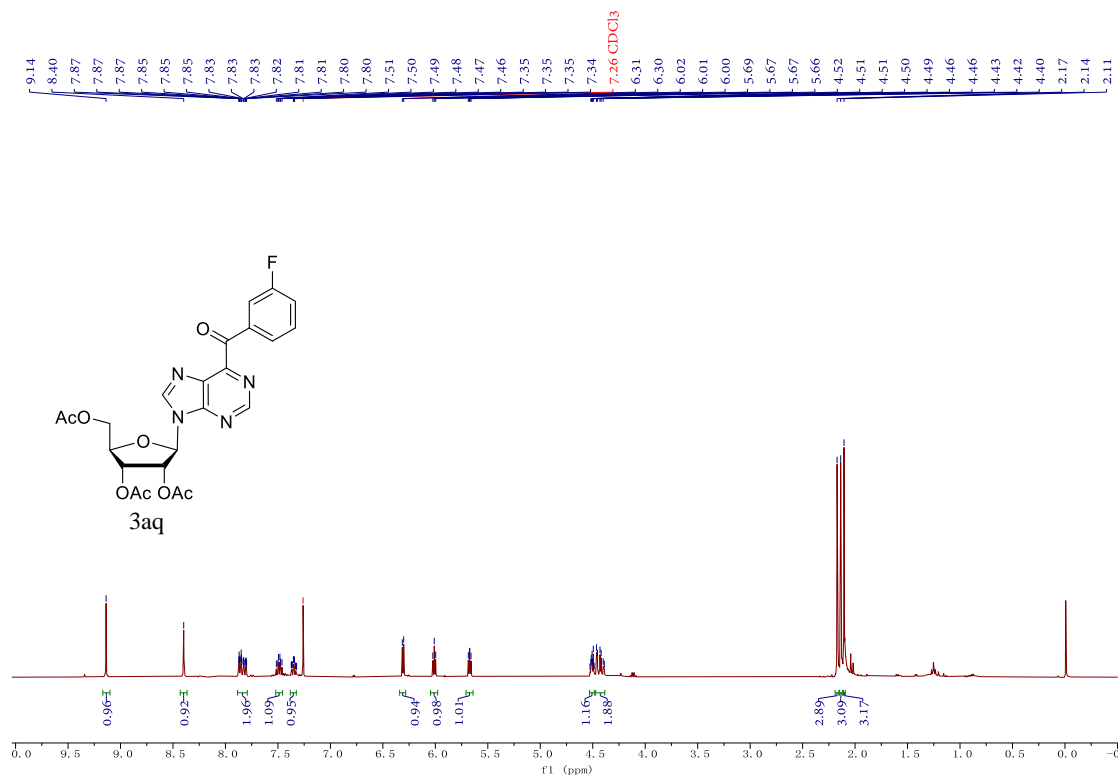
$^1\text{H-NMR}$  spectrum for **3ap** (in  $\text{CDCl}_3$ )



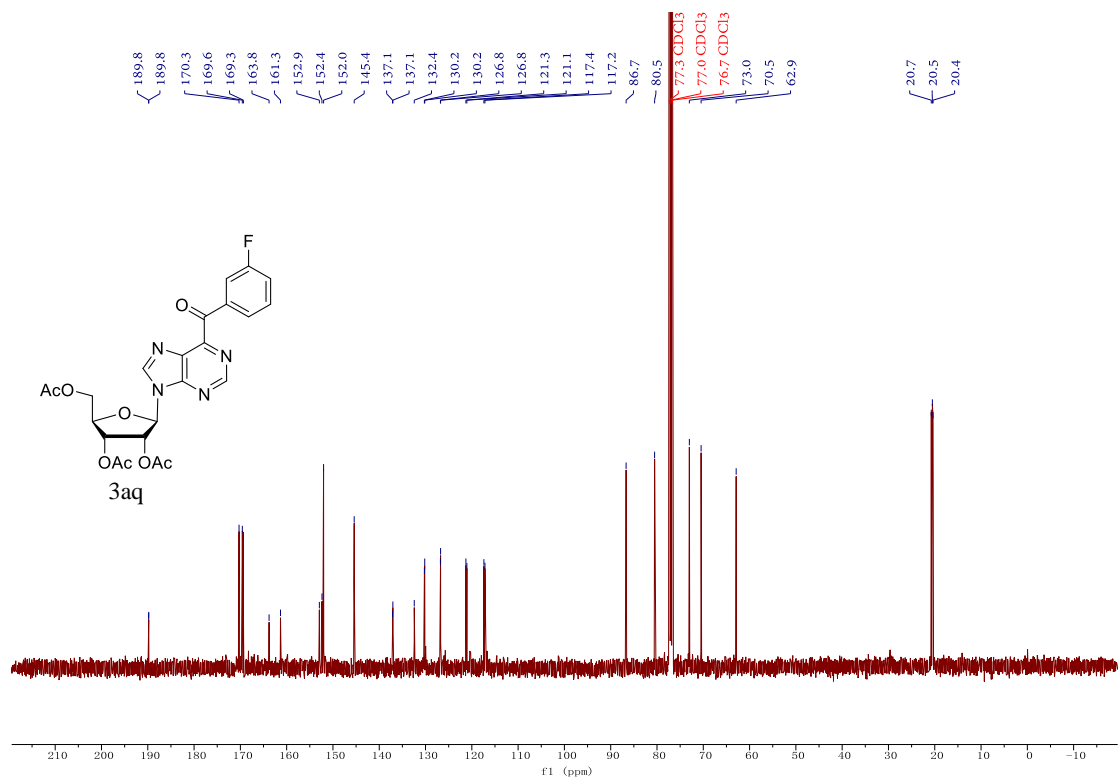
$^{13}\text{C-NMR}$  spectrum for **3ap** (in  $\text{CDCl}_3$ )



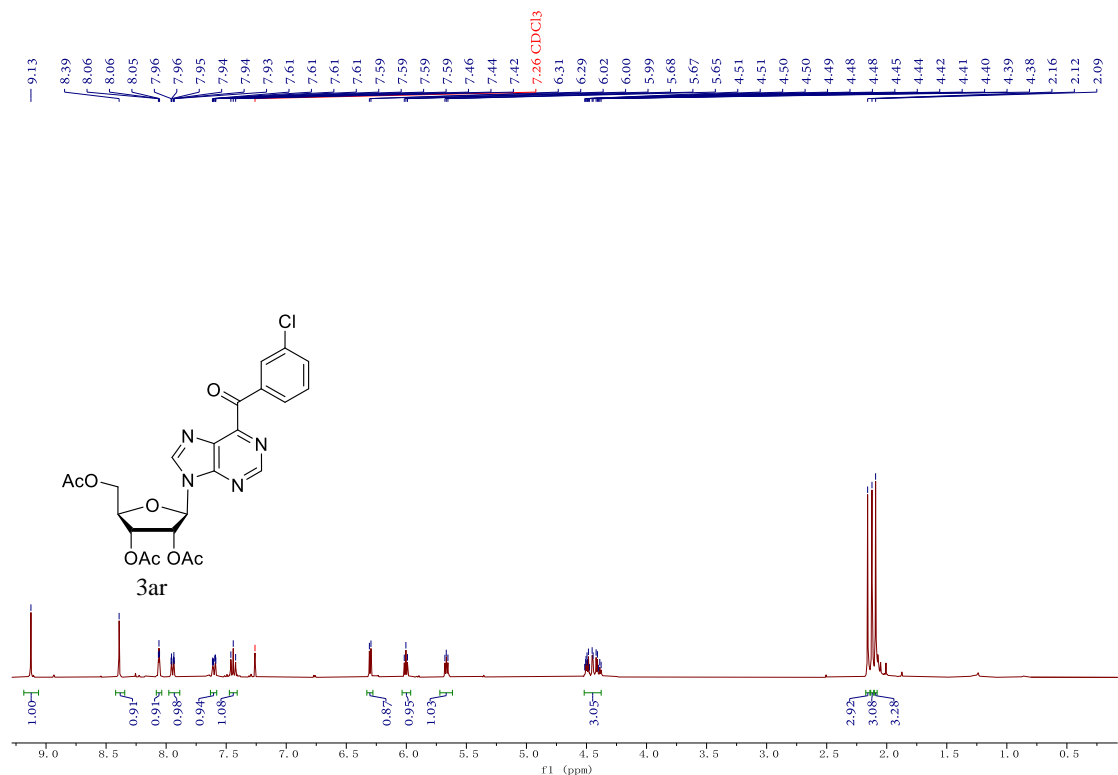
$^1\text{H-NMR}$  spectrum for **3aq** (in  $\text{CDCl}_3$ )



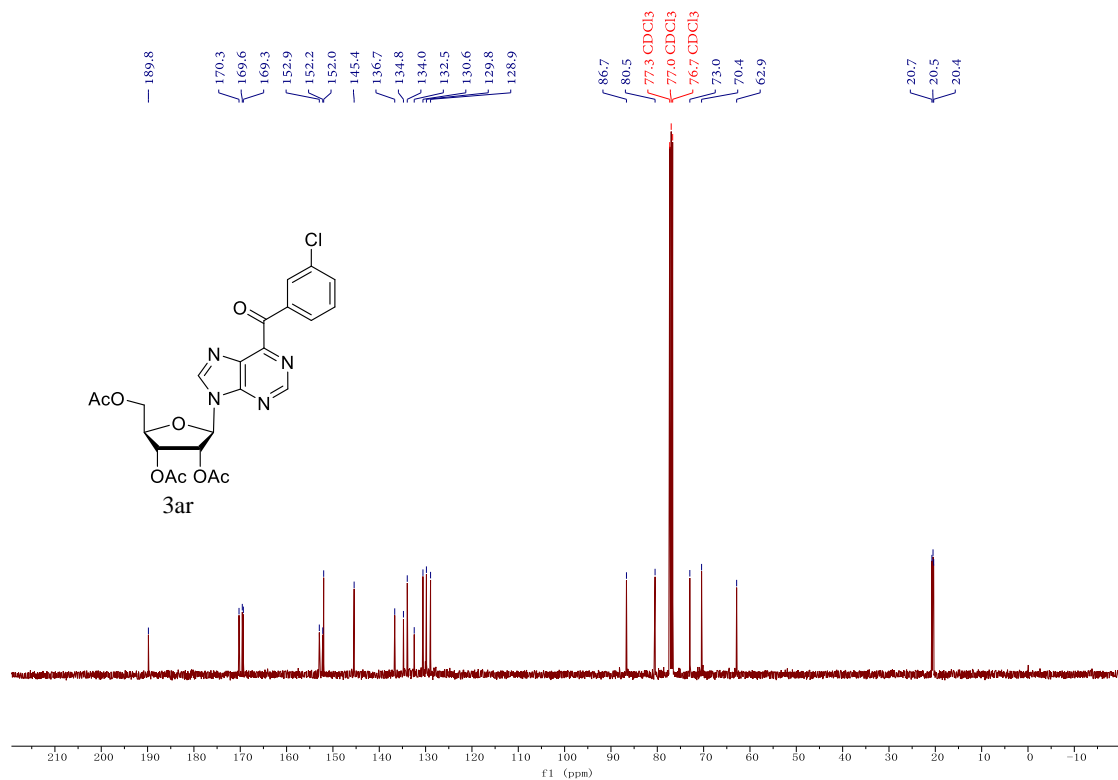
$^{13}\text{C-NMR}$  spectrum for **3aq** (in  $\text{CDCl}_3$ )



### $^1\text{H-NMR}$ spectrum for **3ar** (in $\text{CDCl}_3$ )

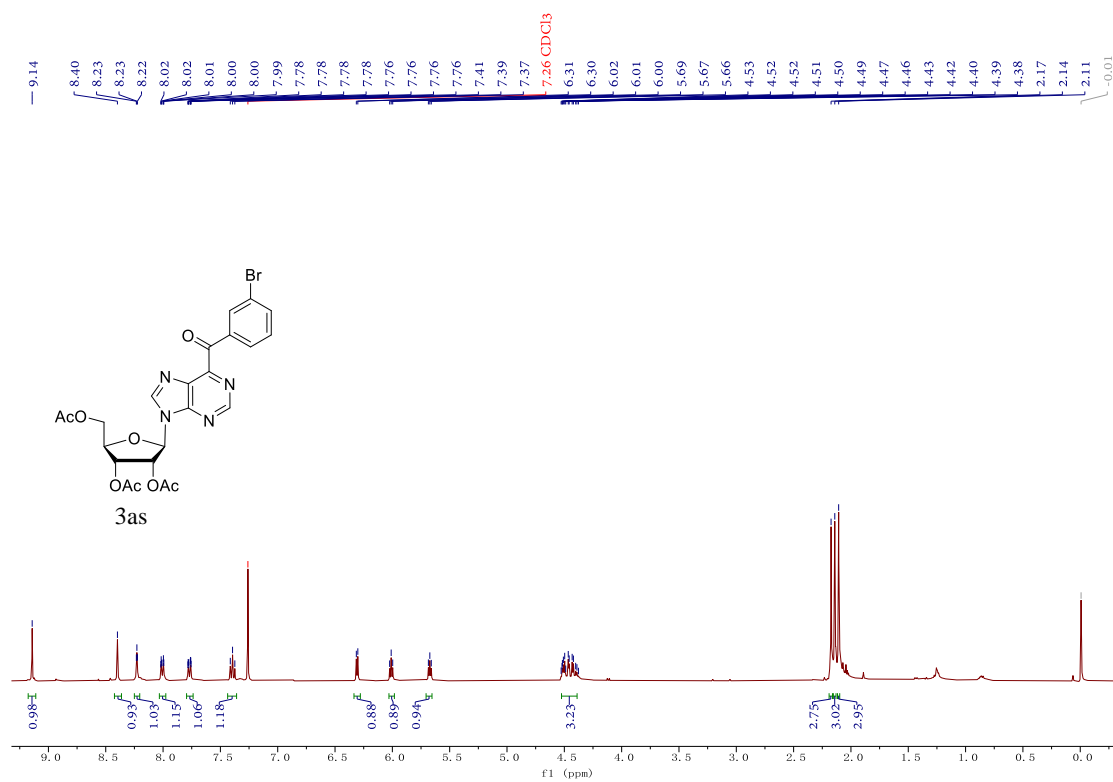


### $^{13}\text{C-NMR}$ spectrum for **3ar** (in $\text{CDCl}_3$ )

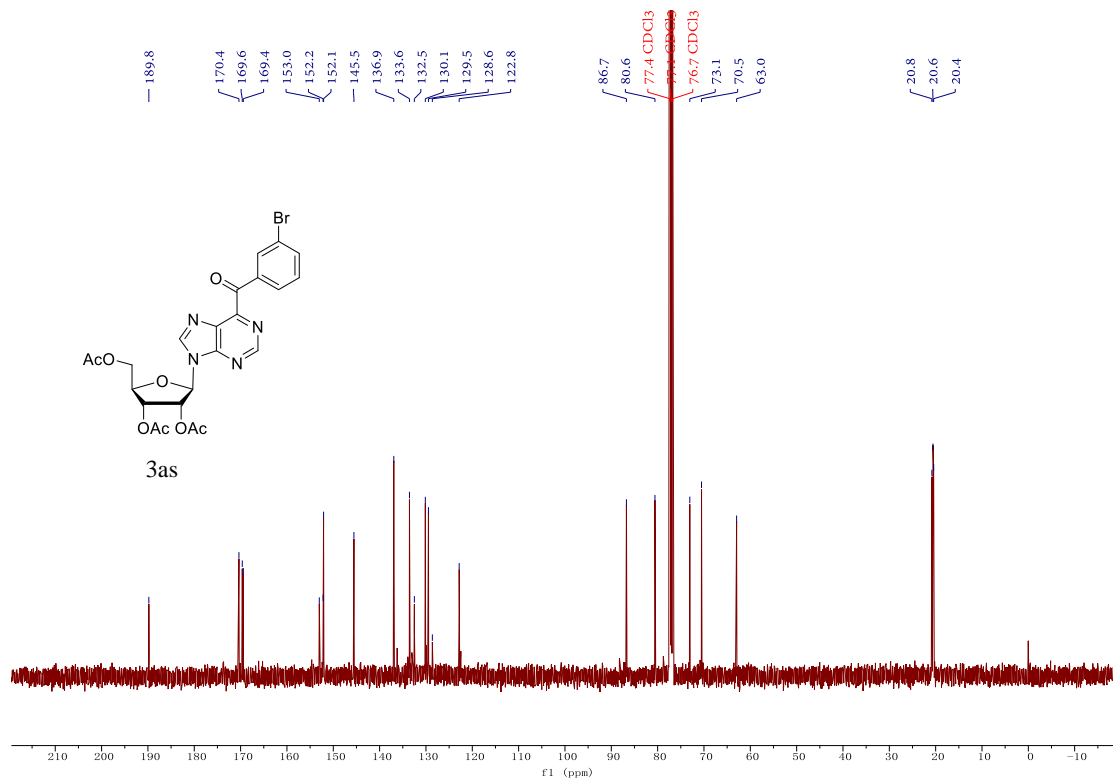




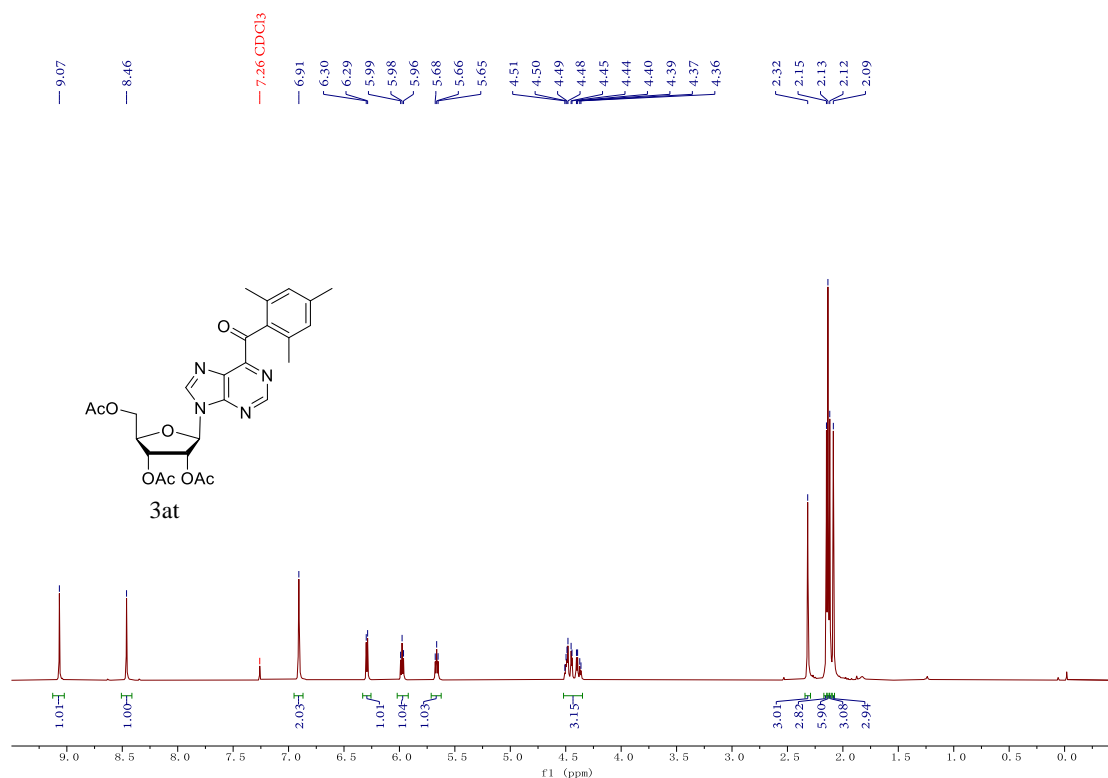
### <sup>1</sup>H-NMR spectrum for **3as** (in CDCl<sub>3</sub>)



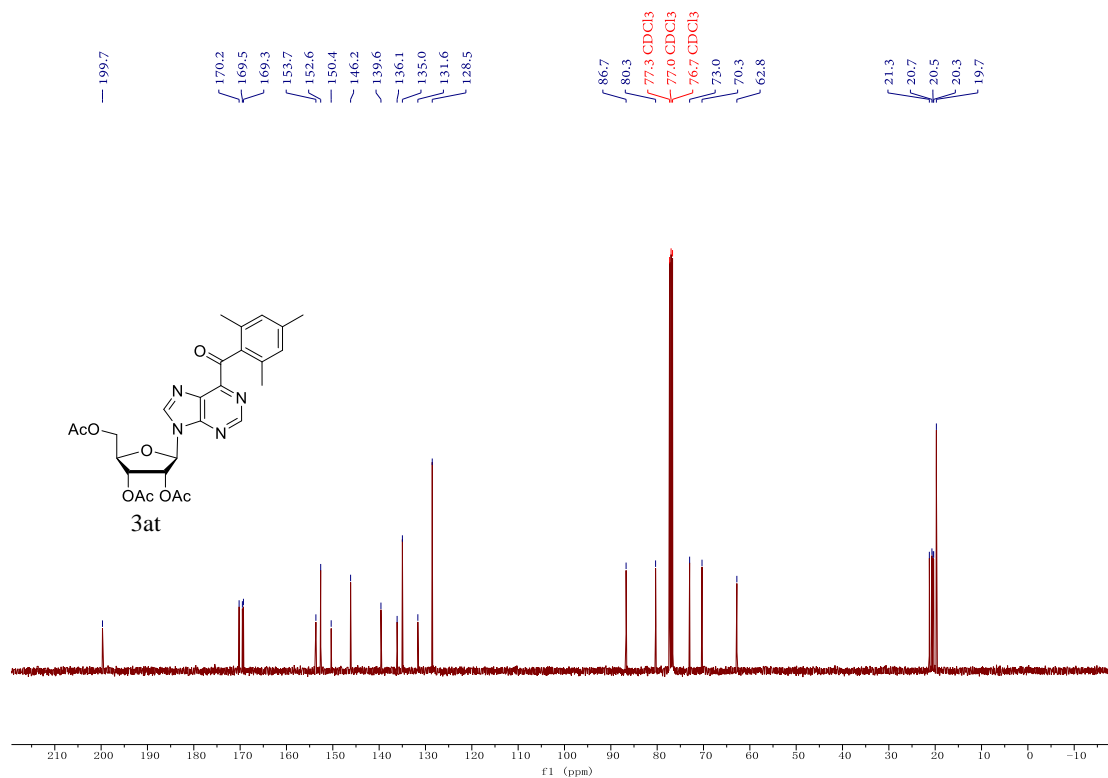
### <sup>13</sup>C-NMR spectrum for **3as** (in CDCl<sub>3</sub>)



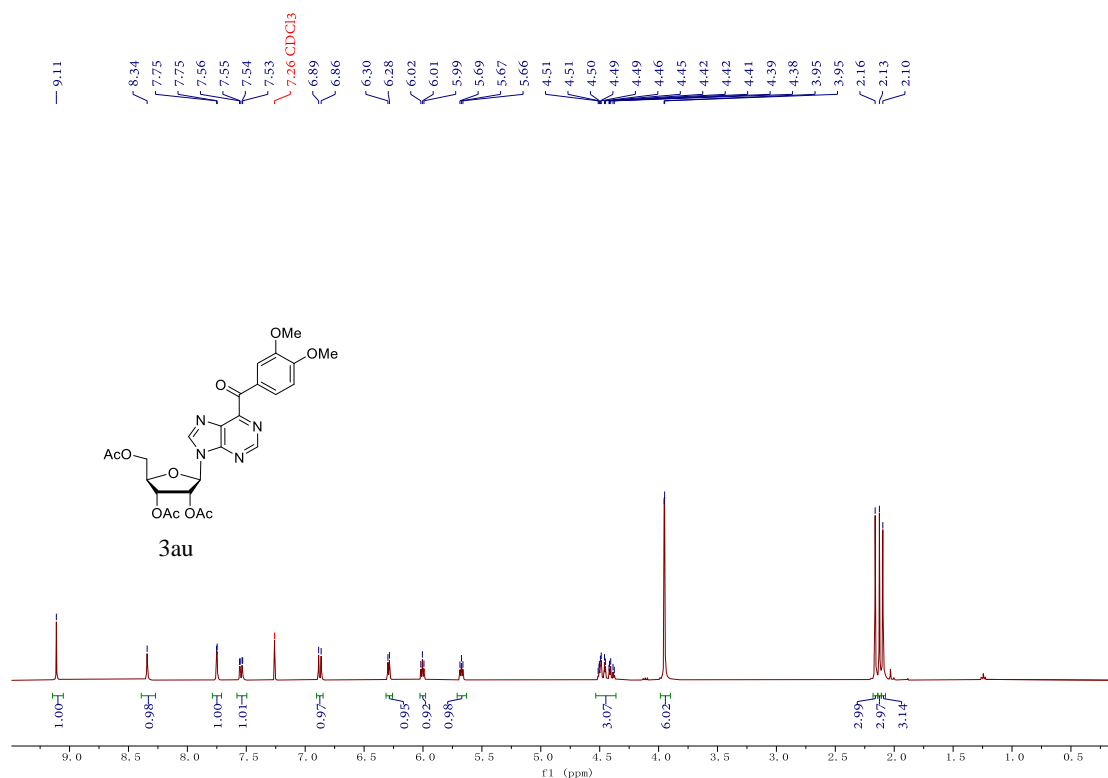
<sup>1</sup>H-NMR spectrum for **3at** (in CDCl<sub>3</sub>)



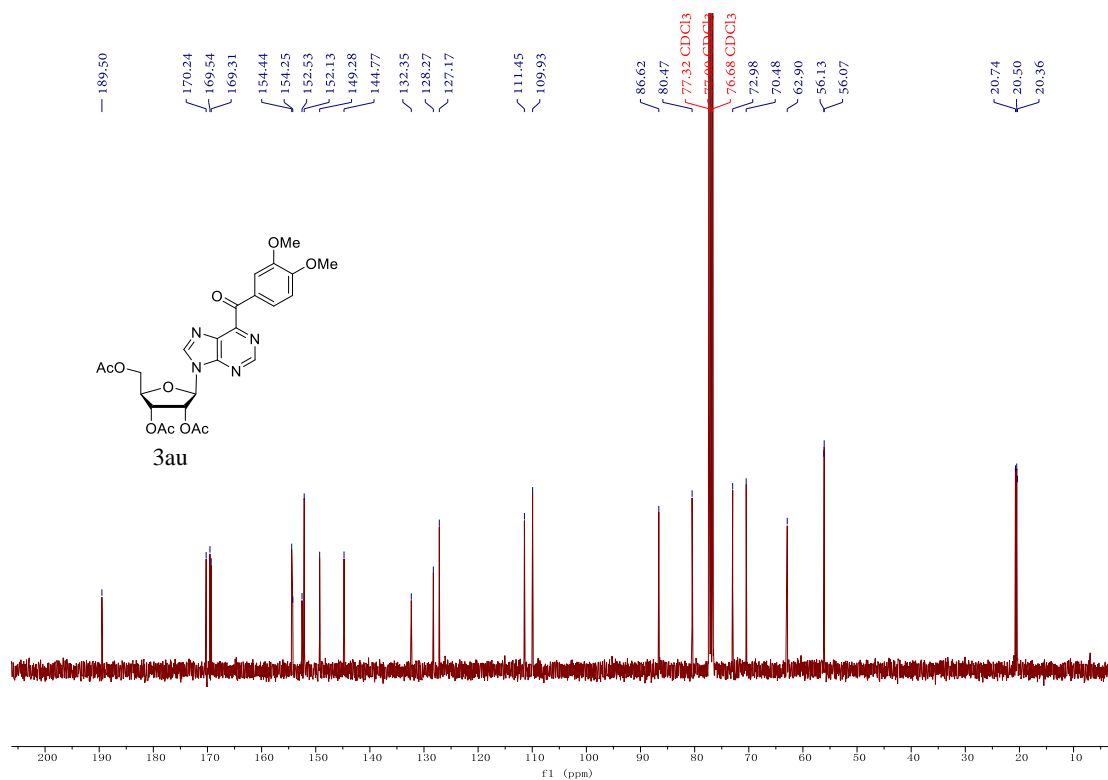
<sup>13</sup>C-NMR spectrum for **3at** (in CDCl<sub>3</sub>)



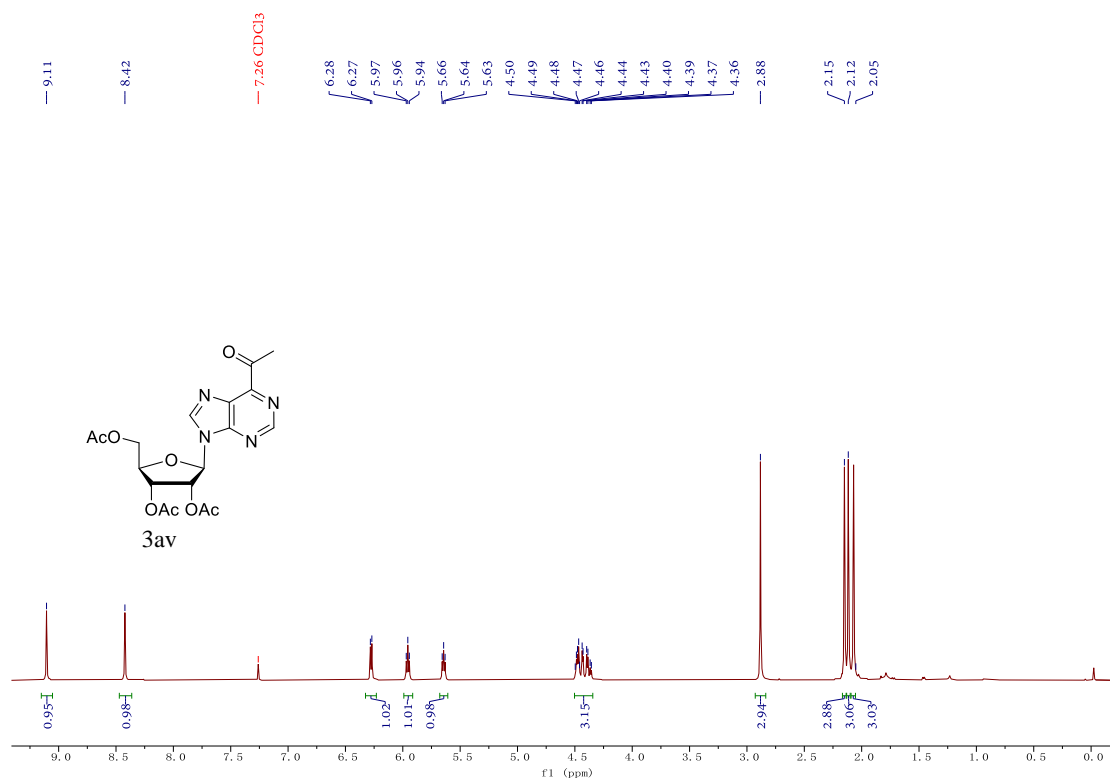
### $^1\text{H-NMR}$ spectrum for **3au** (in $\text{CDCl}_3$ )



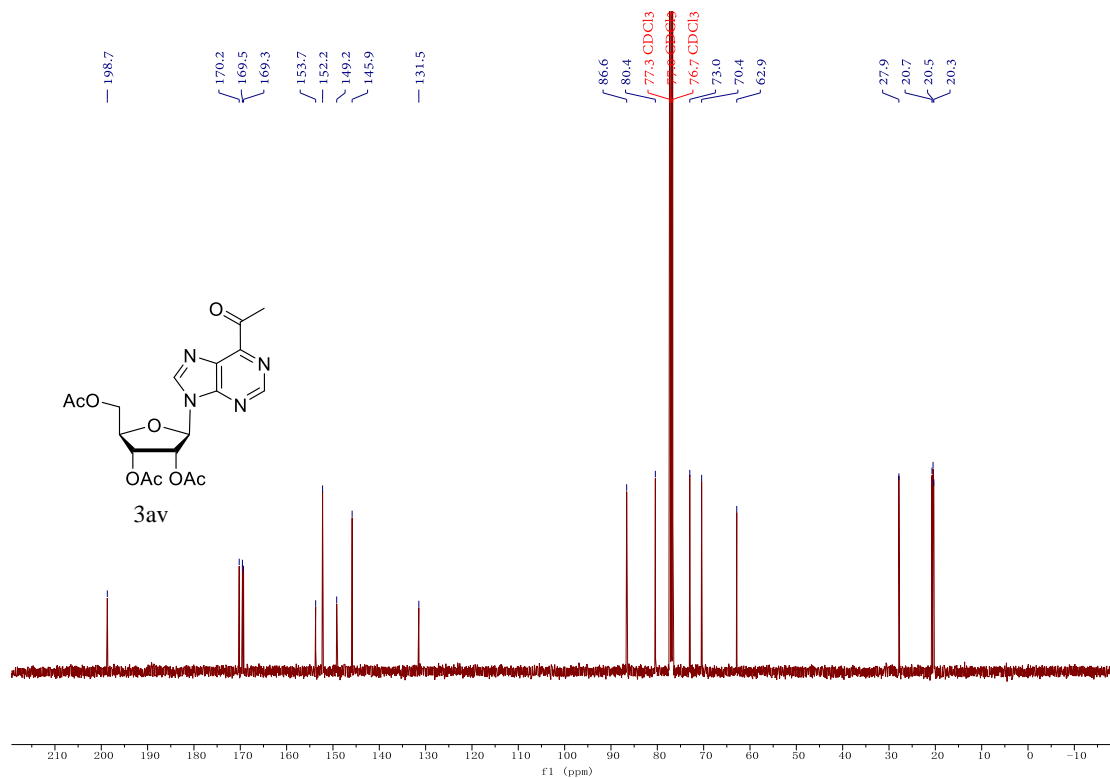
### $^{13}\text{C-NMR}$ spectrum for **3au** (in $\text{CDCl}_3$ )



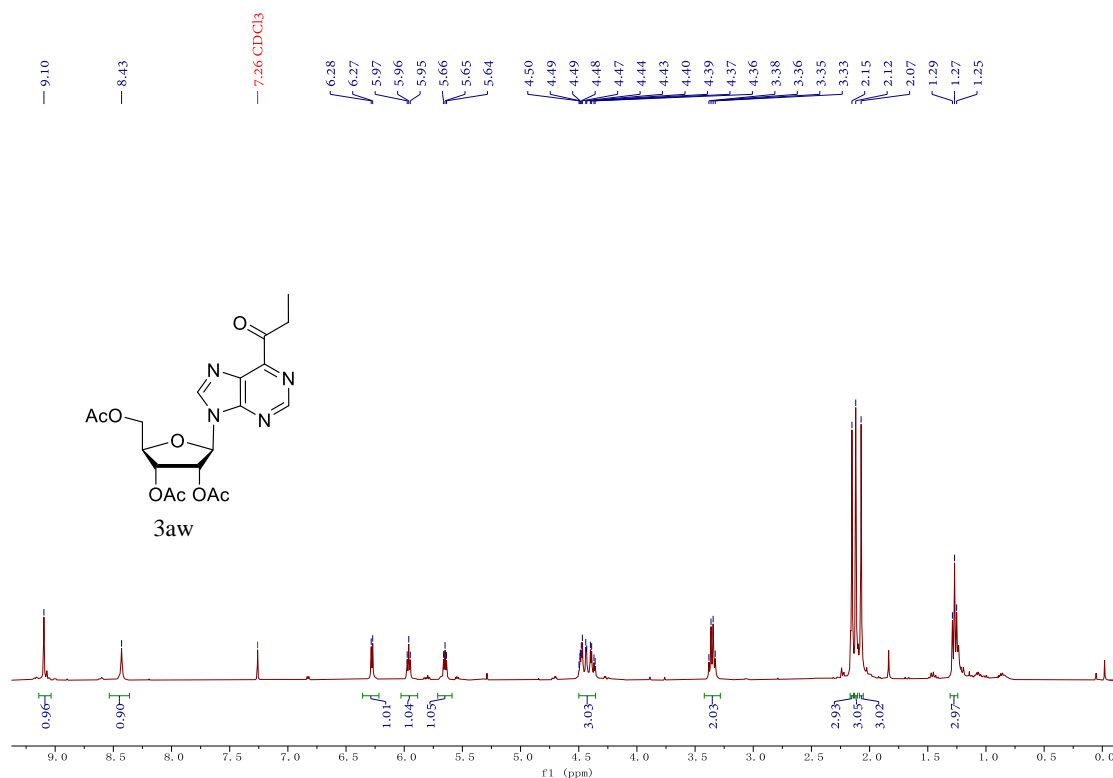
<sup>1</sup>H-NMR spectrum for **3av** (in CDCl<sub>3</sub>)



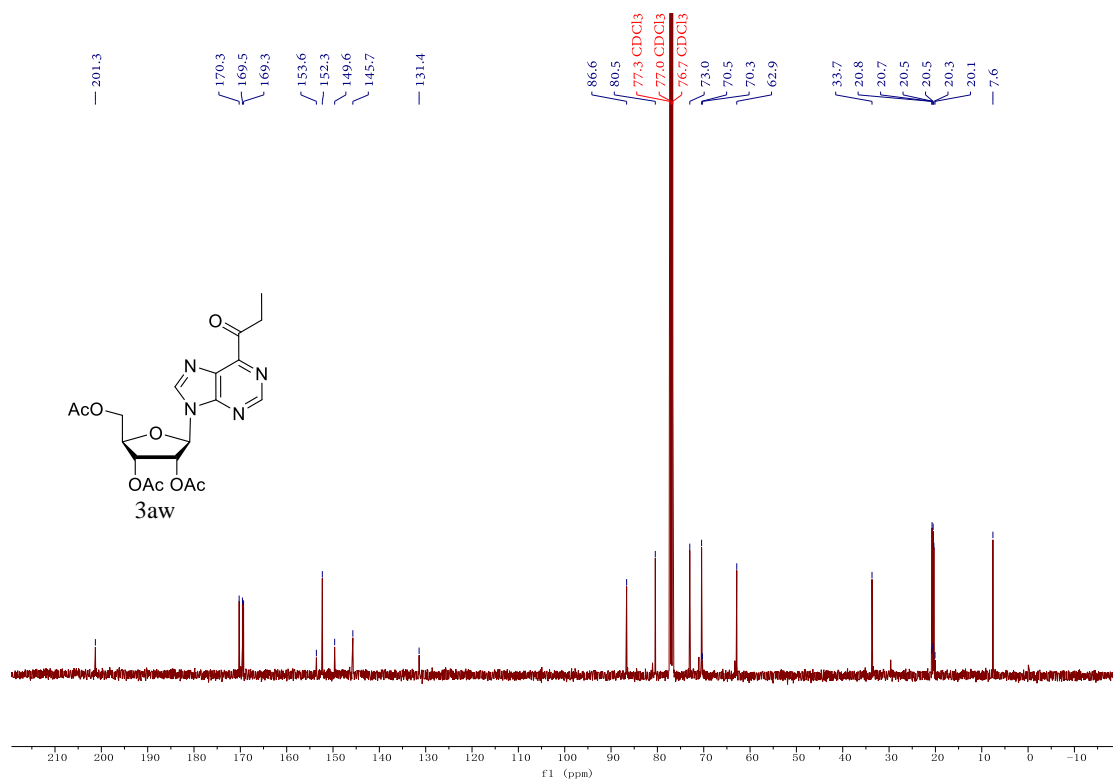
<sup>13</sup>C-NMR spectrum for **3av** (in CDCl<sub>3</sub>)



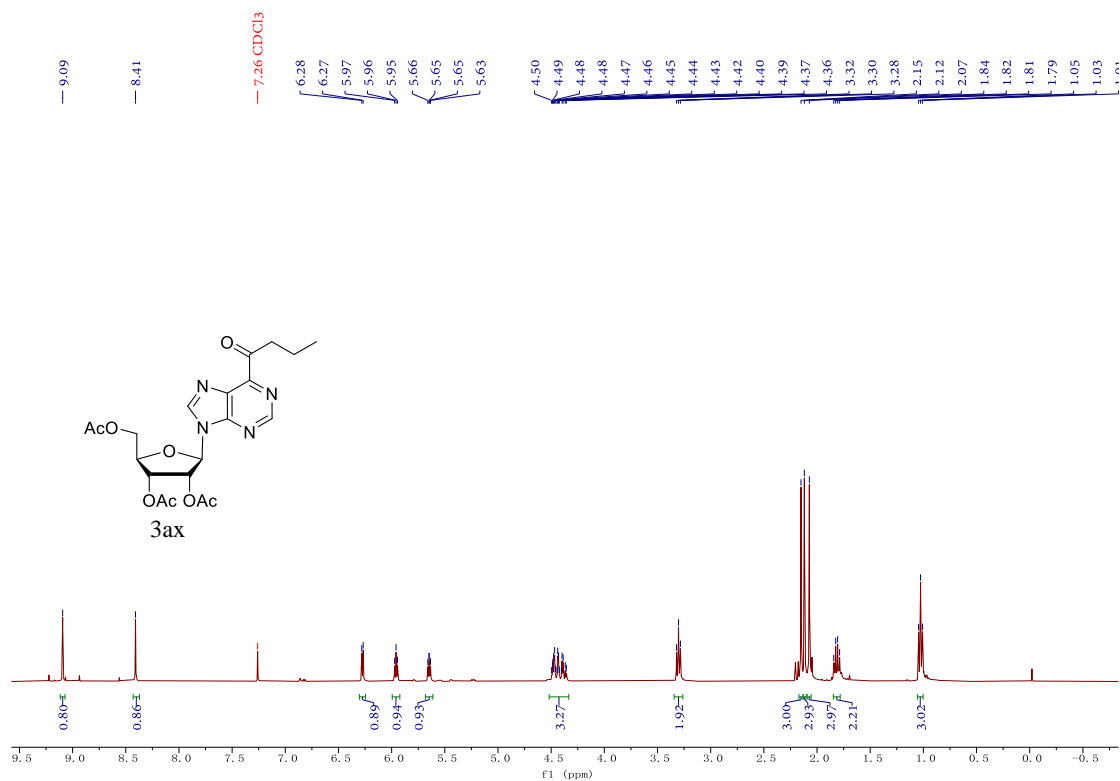
### <sup>1</sup>H-NMR spectrum for **3aw** (in CDCl<sub>3</sub>)



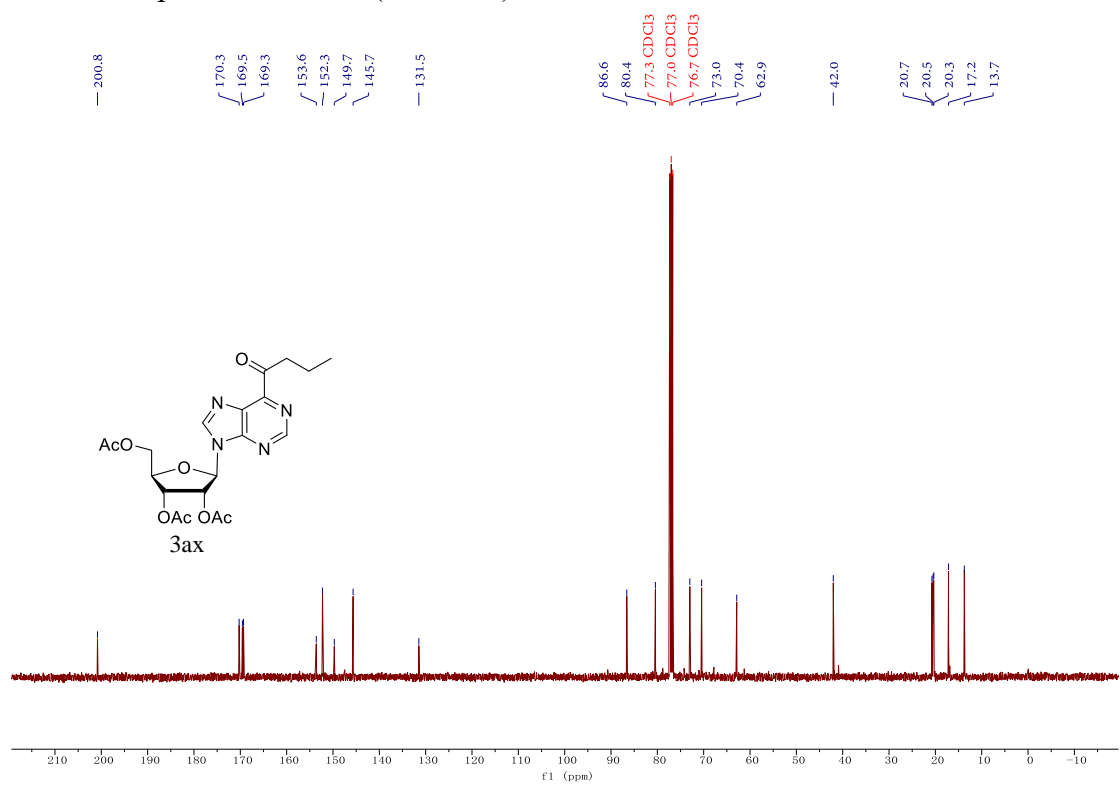
### <sup>13</sup>C-NMR spectrum for **3aw** (in CDCl<sub>3</sub>)



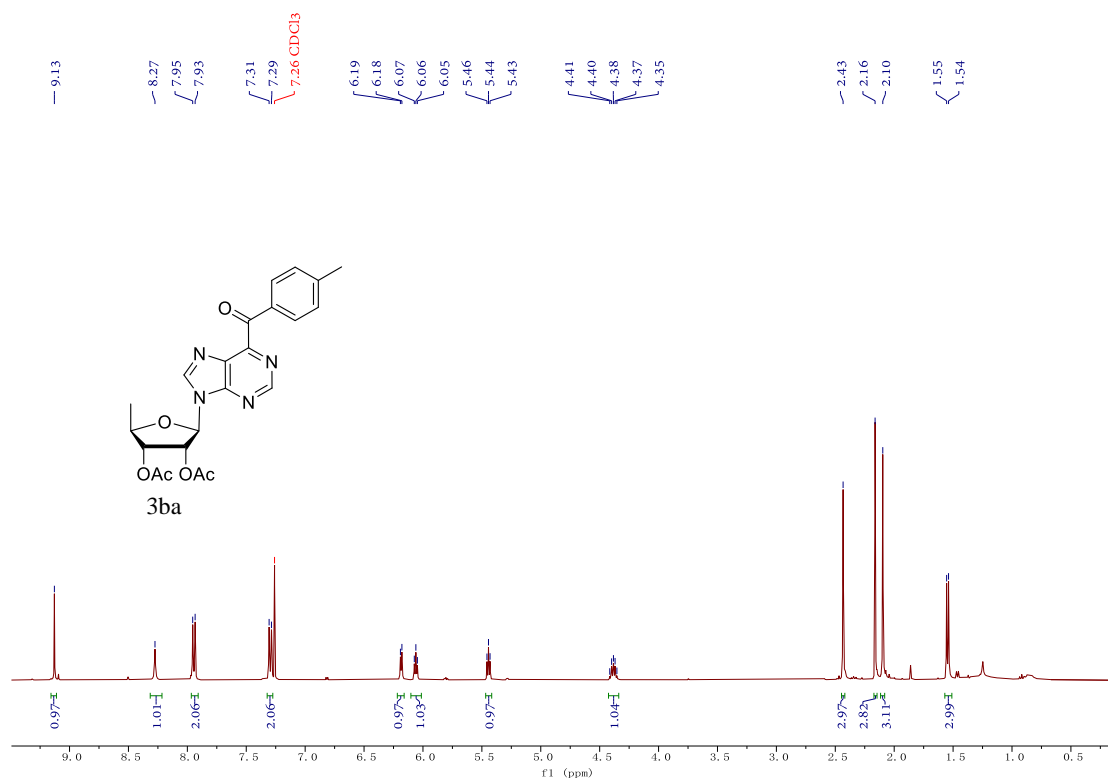
### $^1\text{H-NMR}$ spectrum for **3ax** (in $\text{CDCl}_3$ )



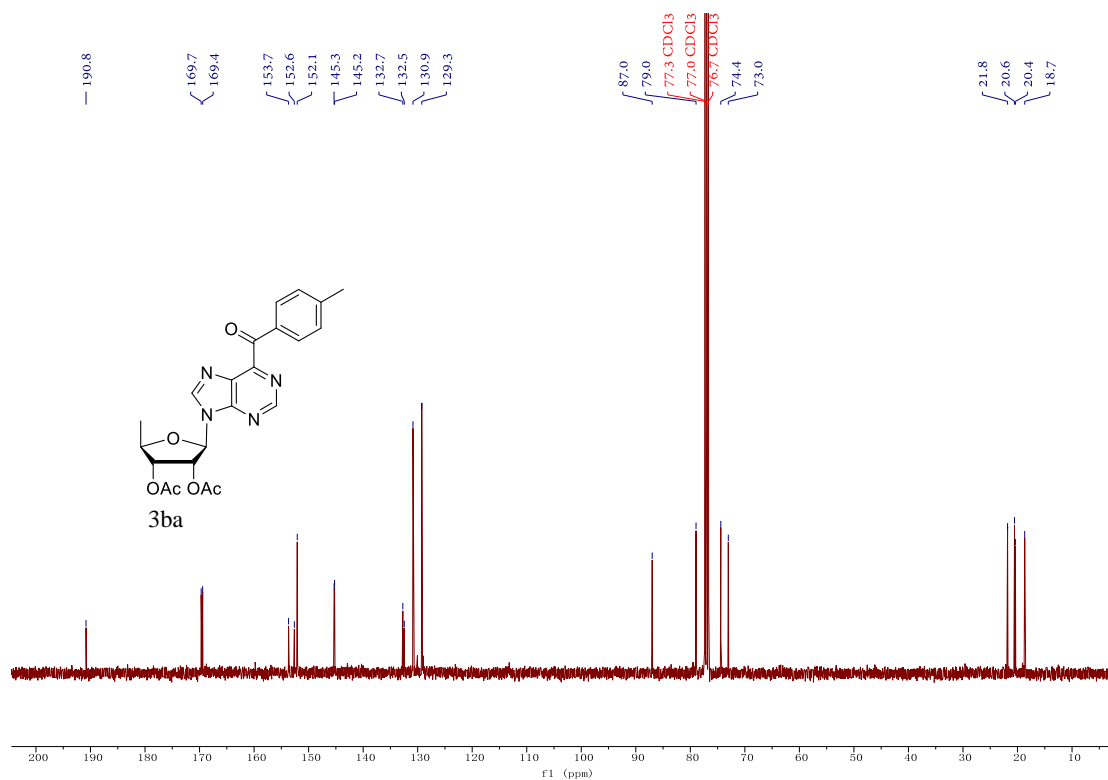
### $^{13}\text{C-NMR}$ spectrum for **3ax** (in $\text{CDCl}_3$ )



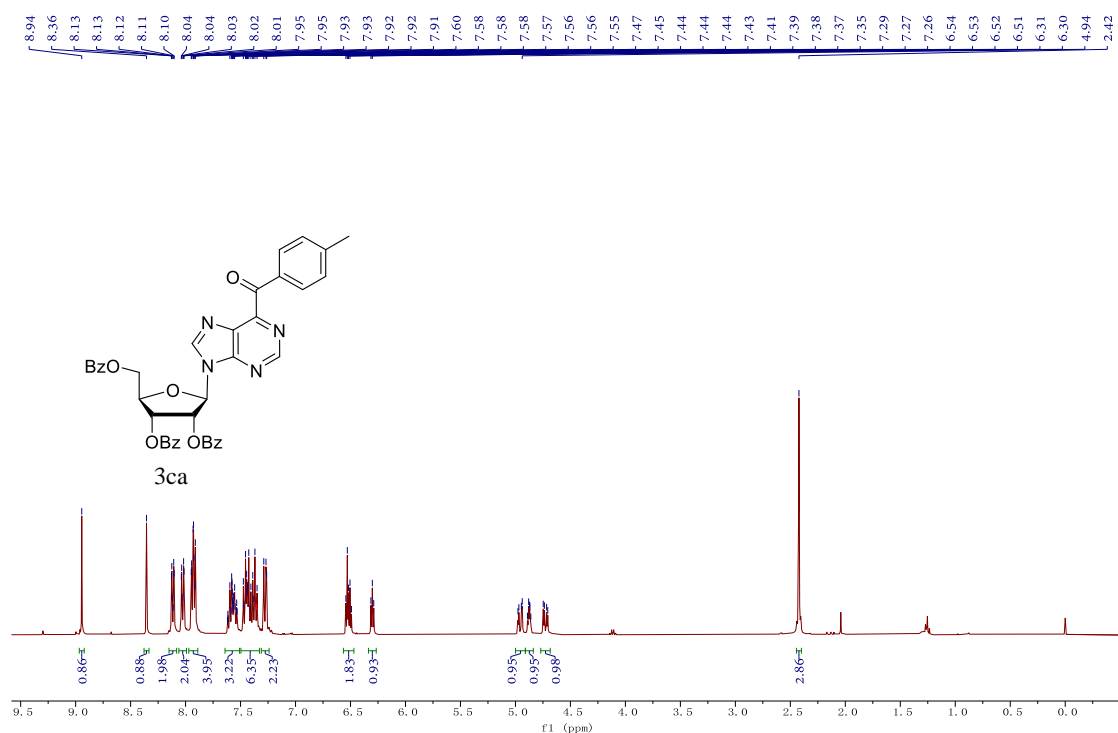
<sup>1</sup>H-NMR spectrum for **3ba** (in CDCl<sub>3</sub>)



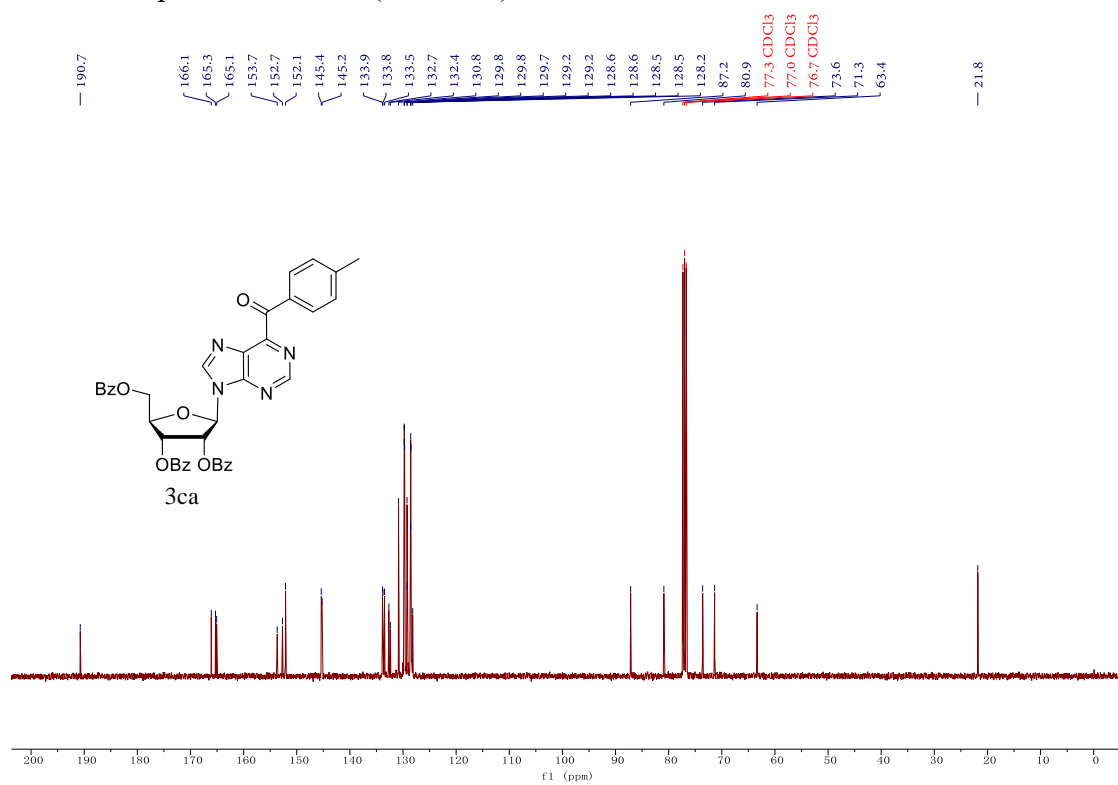
<sup>13</sup>C-NMR spectrum for **3ba** (in CDCl<sub>3</sub>)



$^1\text{H-NMR}$  spectrum for **3ca** (in  $\text{CDCl}_3$ )

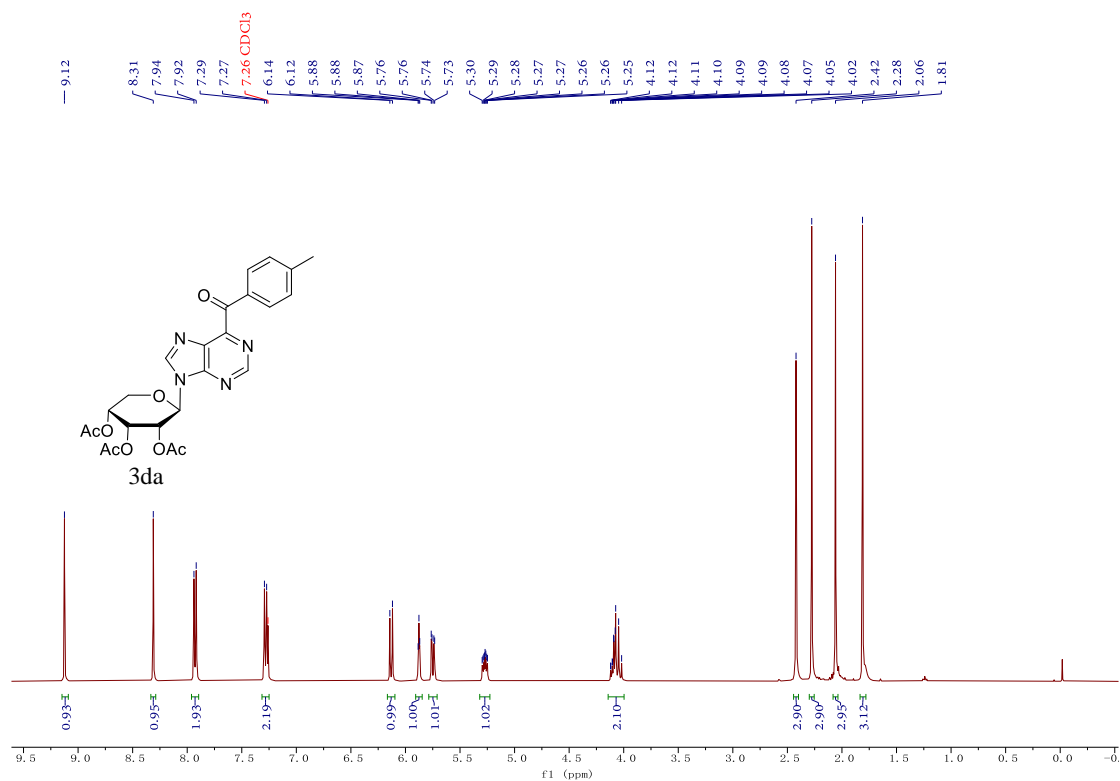


$^{13}\text{C-NMR}$  spectrum for **3ca** (in  $\text{CDCl}_3$ )

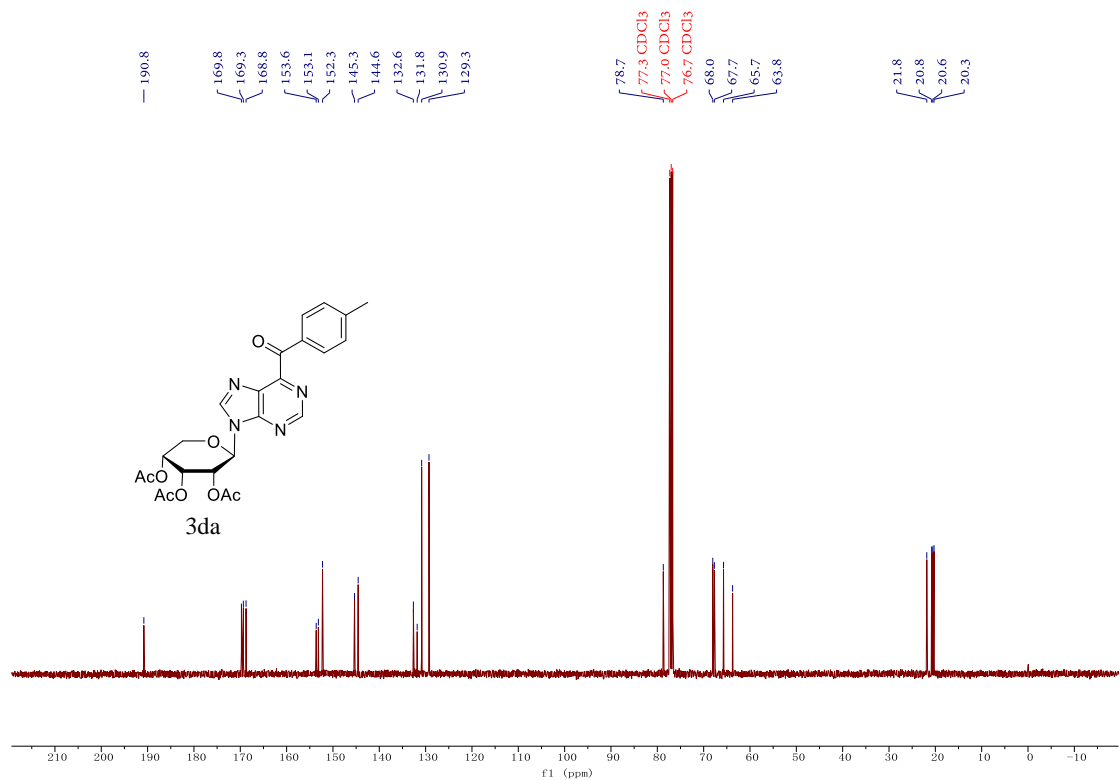




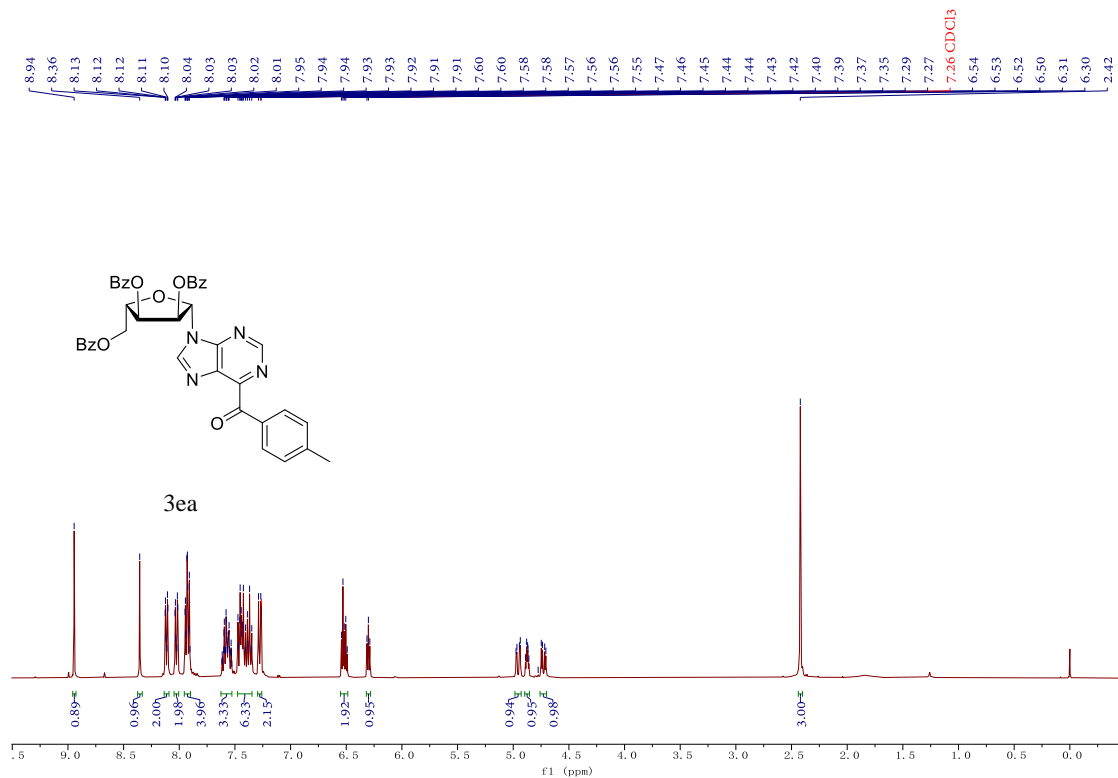
### $^1\text{H-NMR}$ spectrum for **3da** (in $\text{CDCl}_3$ )



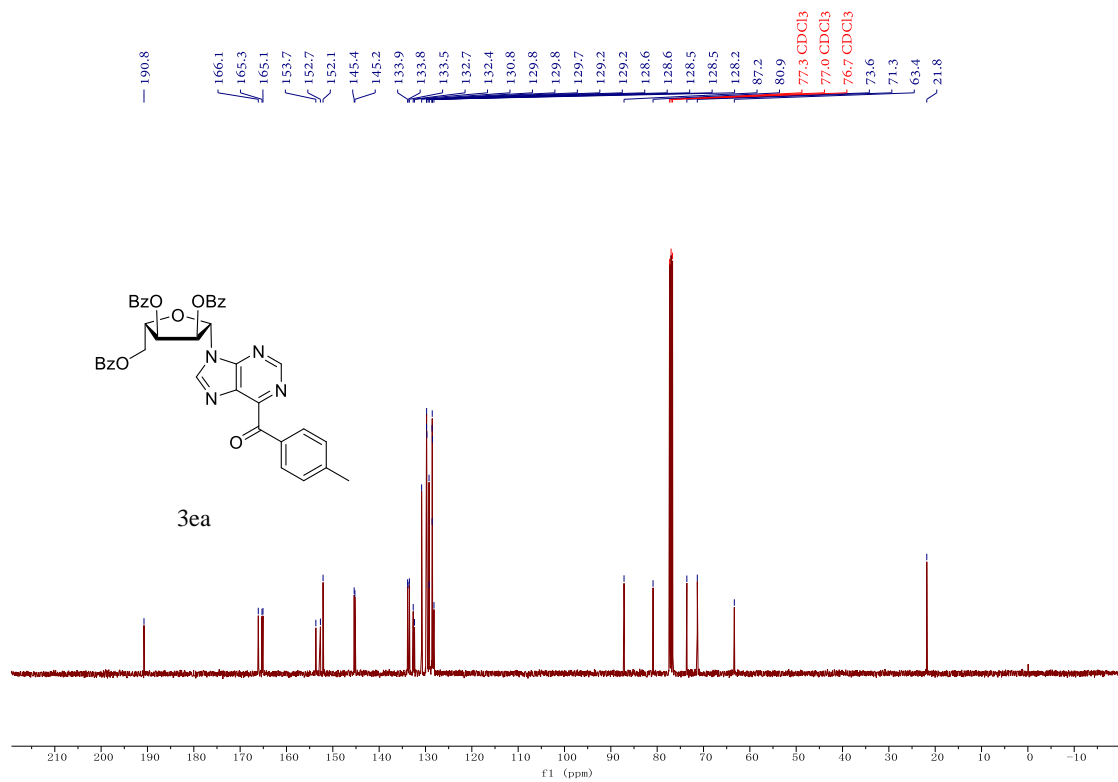
### $^{13}\text{C-NMR}$ spectrum for **3da** (in $\text{CDCl}_3$ )



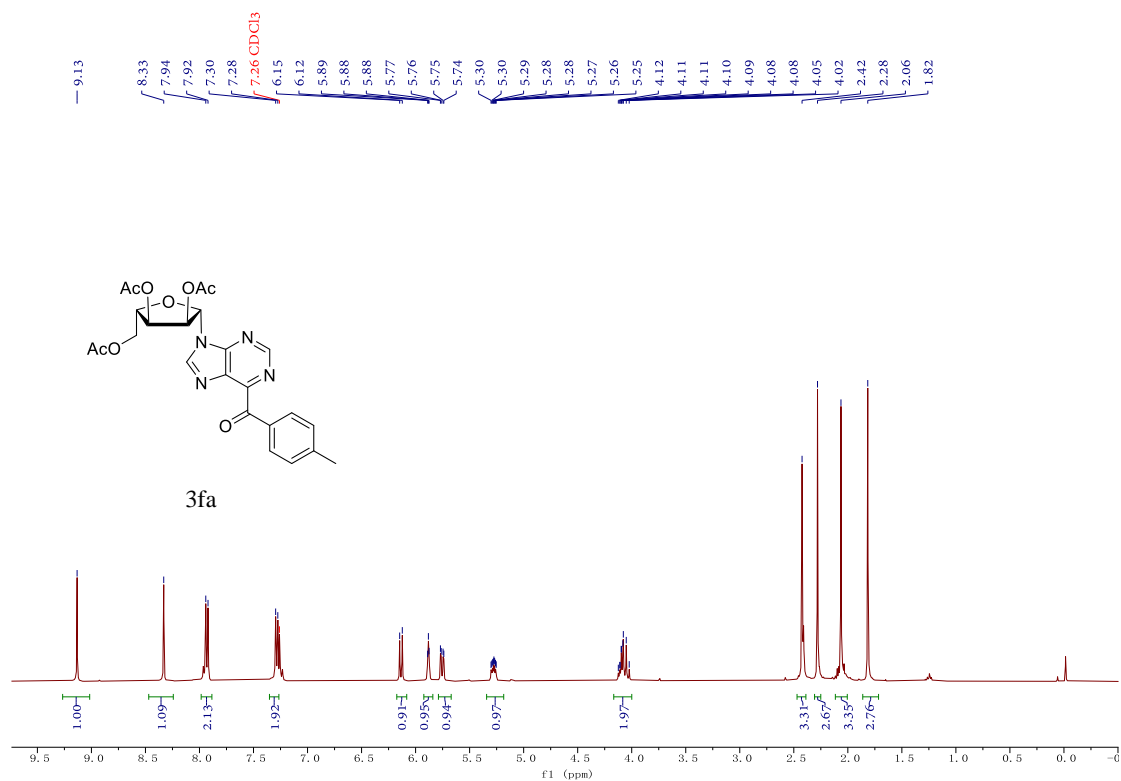
### <sup>1</sup>H-NMR spectrum for **3ea** (in CDCl<sub>3</sub>)



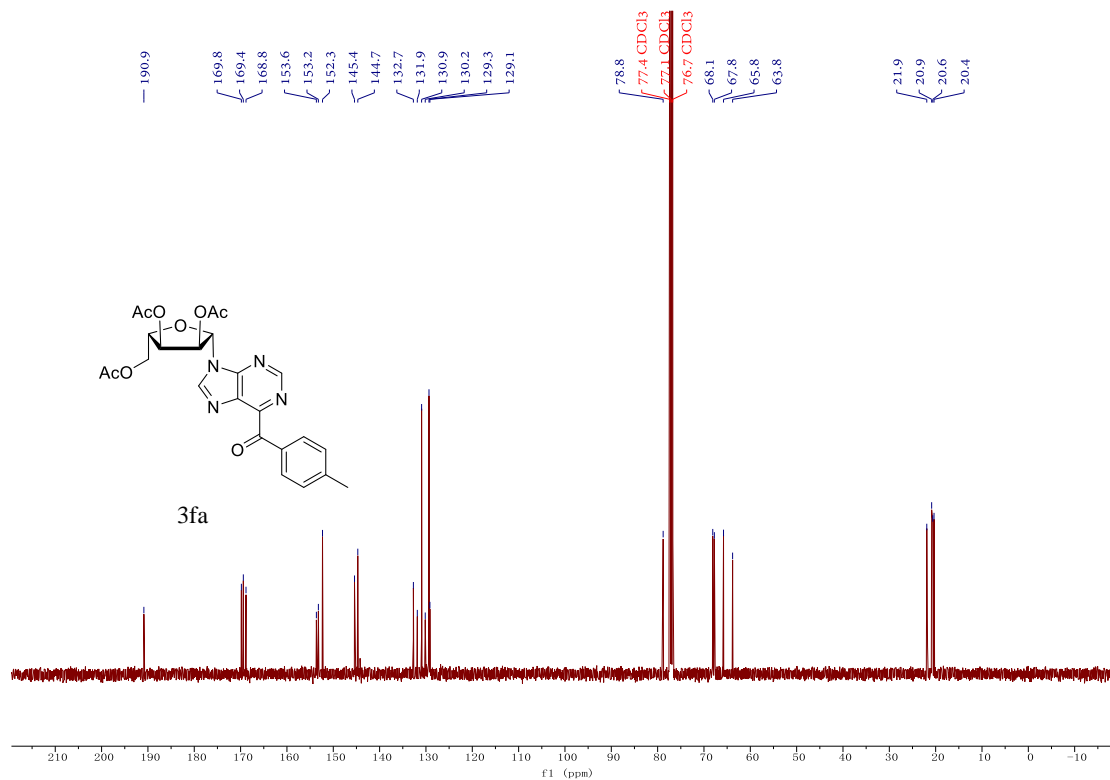
### <sup>13</sup>C-NMR spectrum for **3ea** (in CDCl<sub>3</sub>)



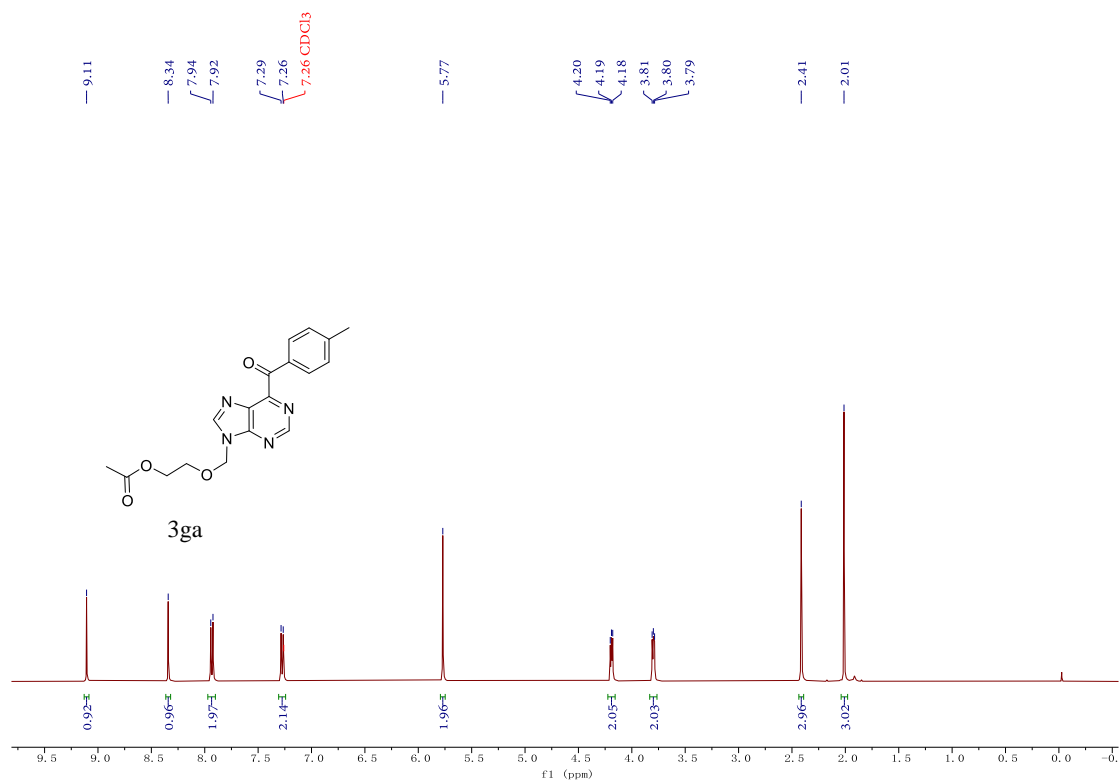
$^1\text{H-NMR}$  spectrum for **3fa** (in  $\text{CDCl}_3$ )



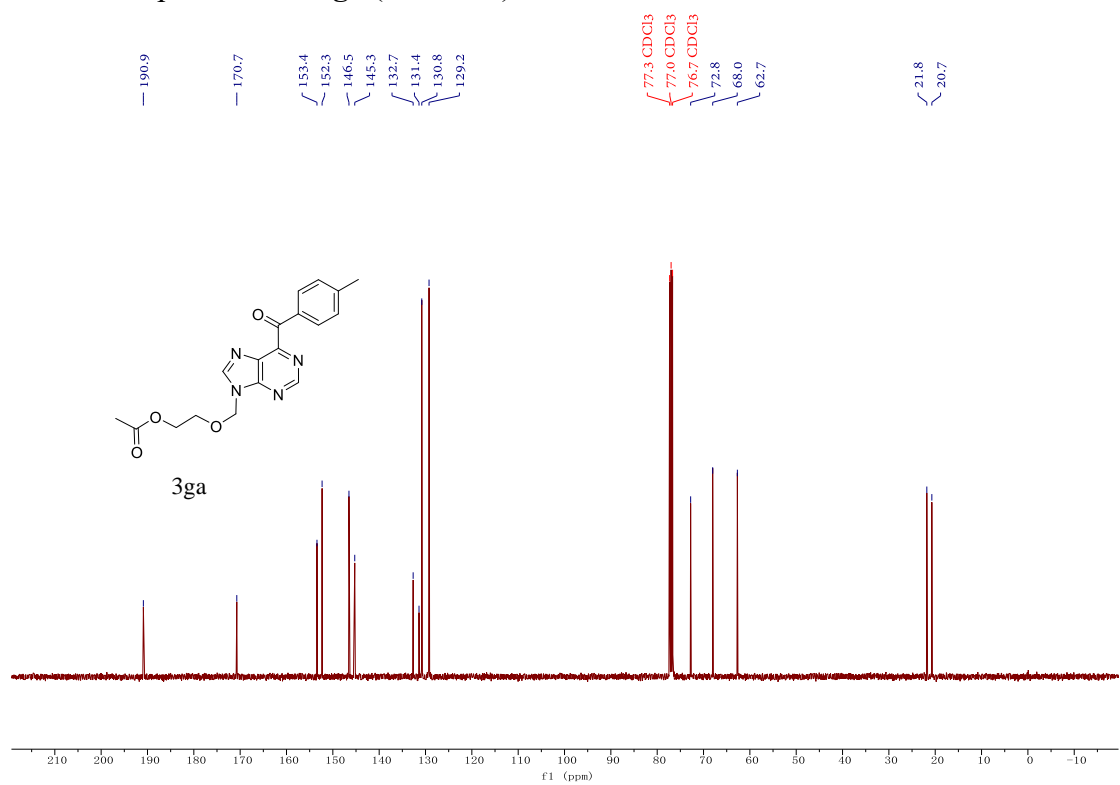
$^{13}\text{C-NMR}$  spectrum for **3fa** (in  $\text{CDCl}_3$ )



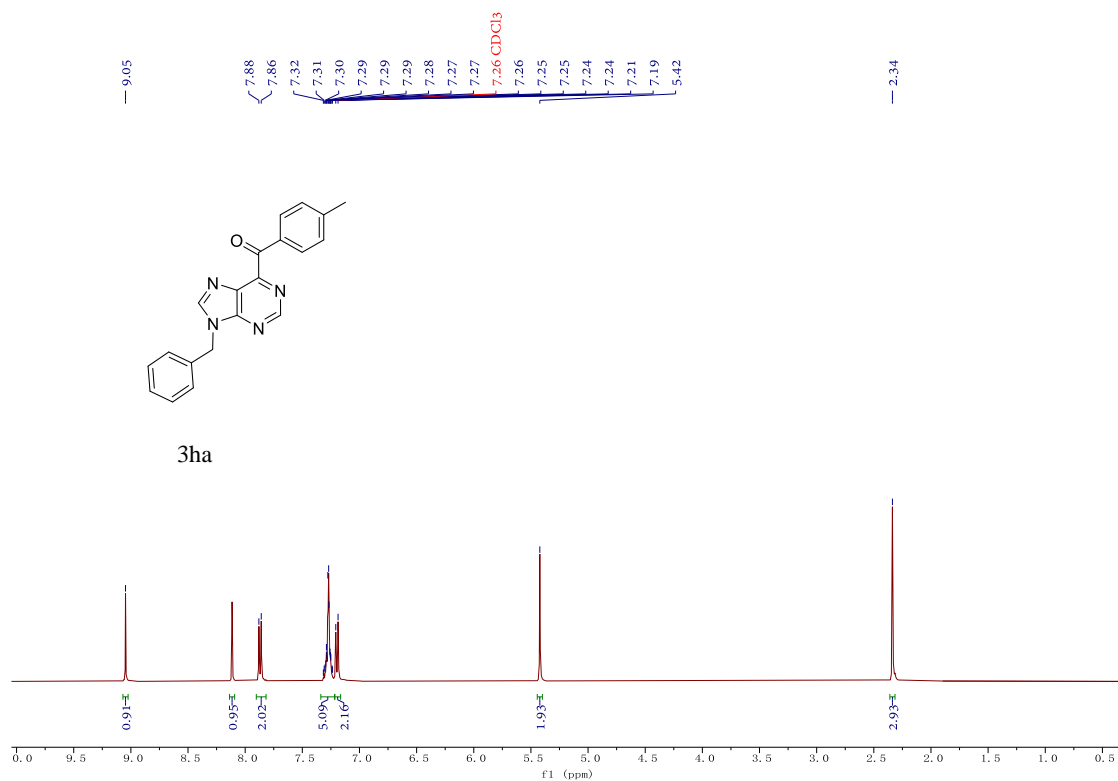
<sup>1</sup>H-NMR spectrum for **3ga** (in CDCl<sub>3</sub>)



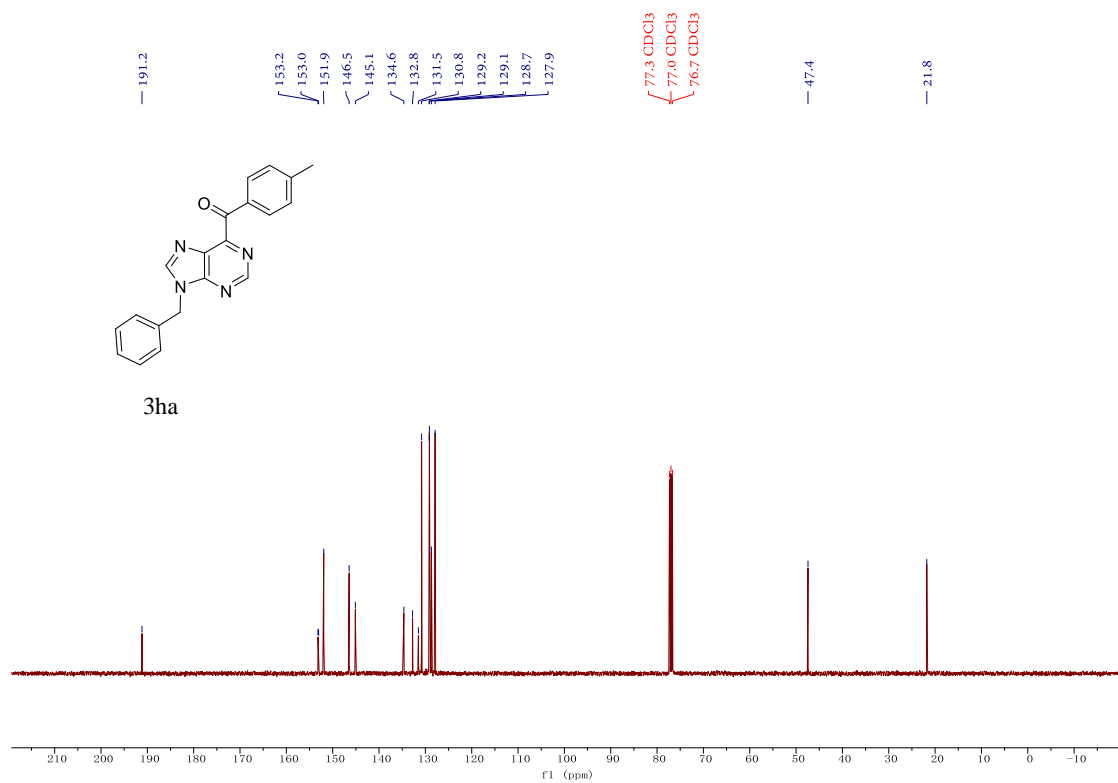
<sup>13</sup>C-NMR spectrum for **3ga** (in CDCl<sub>3</sub>)



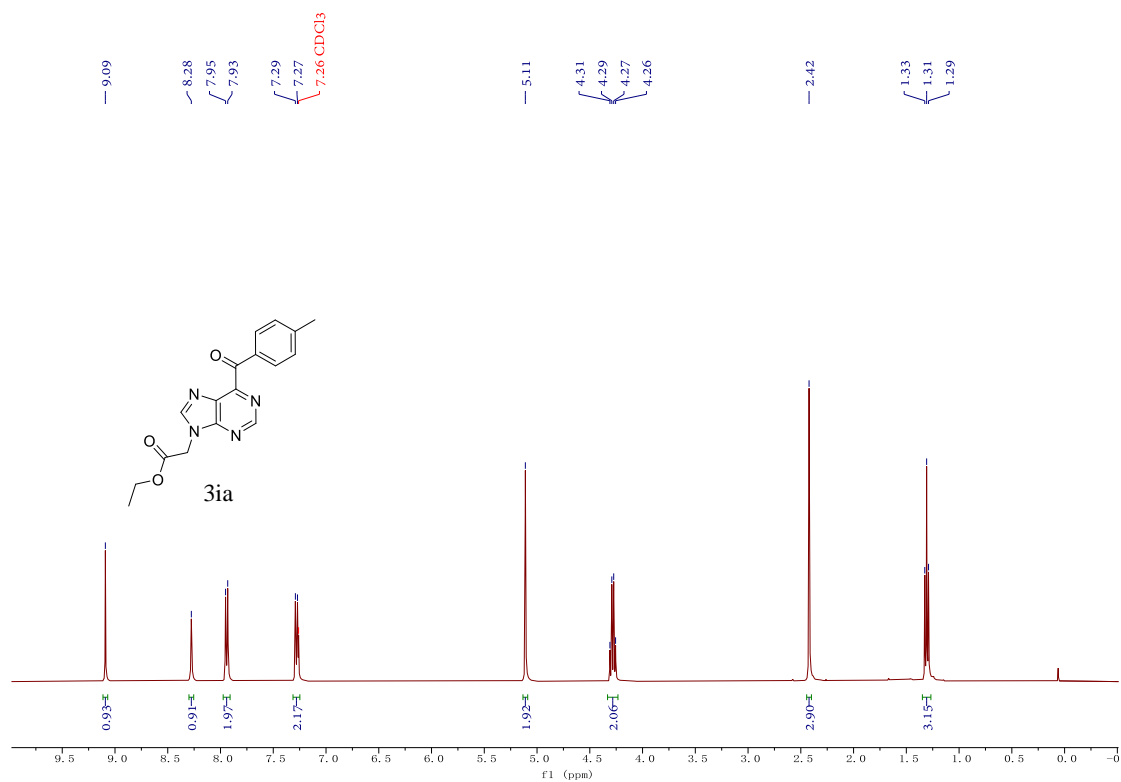
<sup>1</sup>H-NMR spectrum for **3ha** (in CDCl<sub>3</sub>)



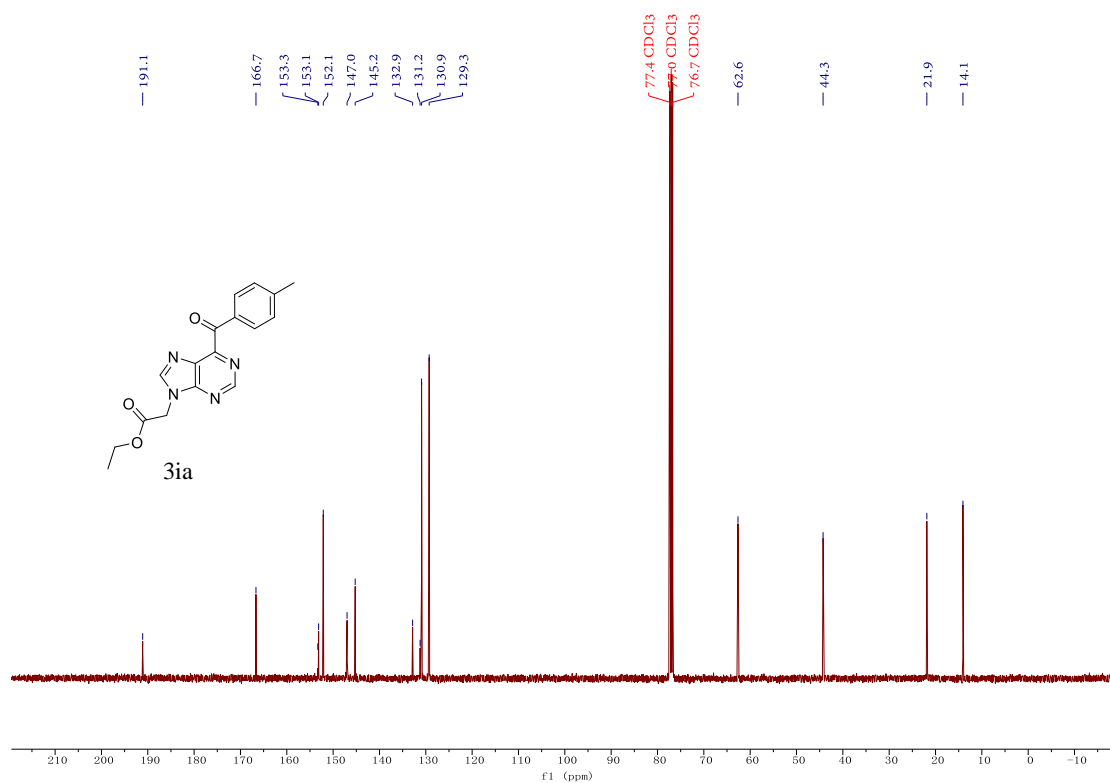
<sup>13</sup>C-NMR spectrum for **3ha** (in CDCl<sub>3</sub>)



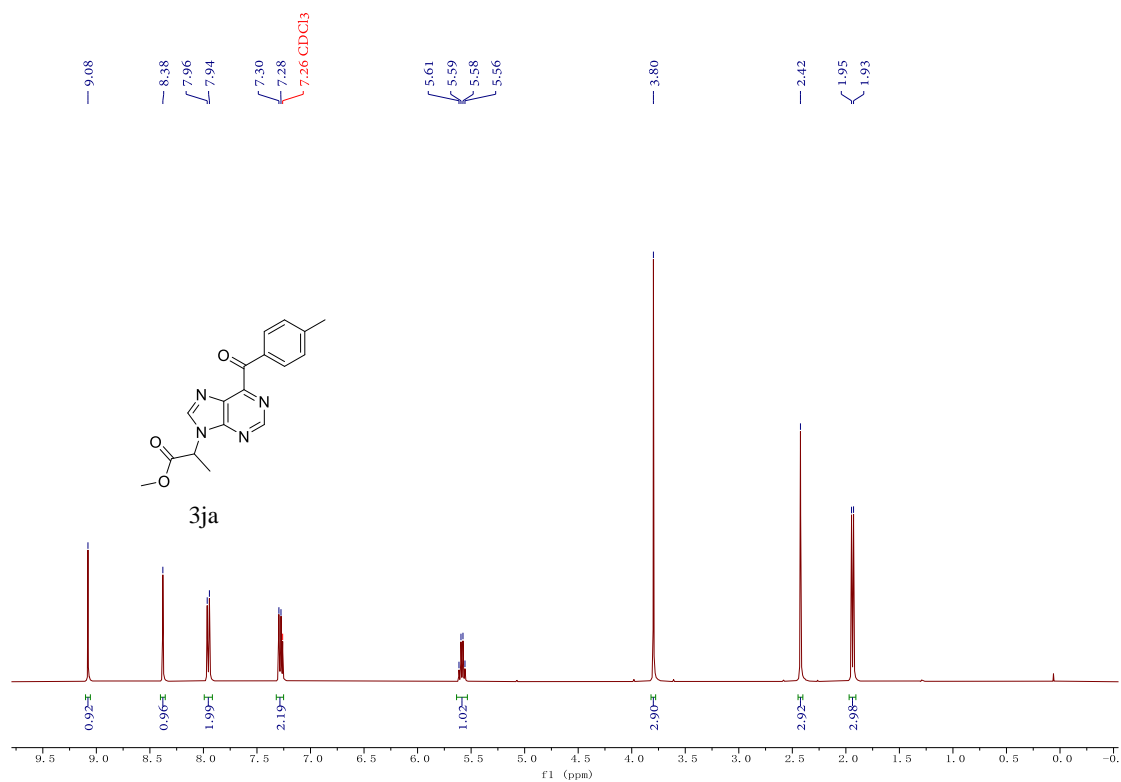
$^1\text{H-NMR}$  spectrum for **3ia** (in  $\text{CDCl}_3$ )



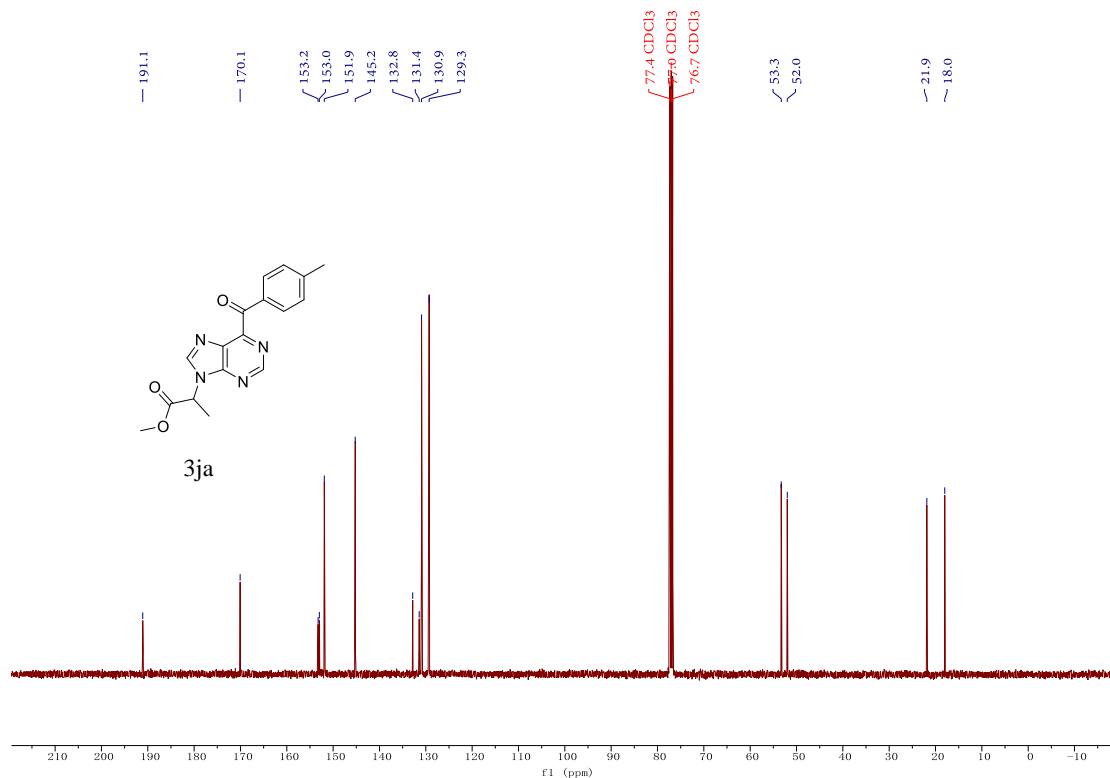
$^{13}\text{C-NMR}$  spectrum for **3ia** (in  $\text{CDCl}_3$ )



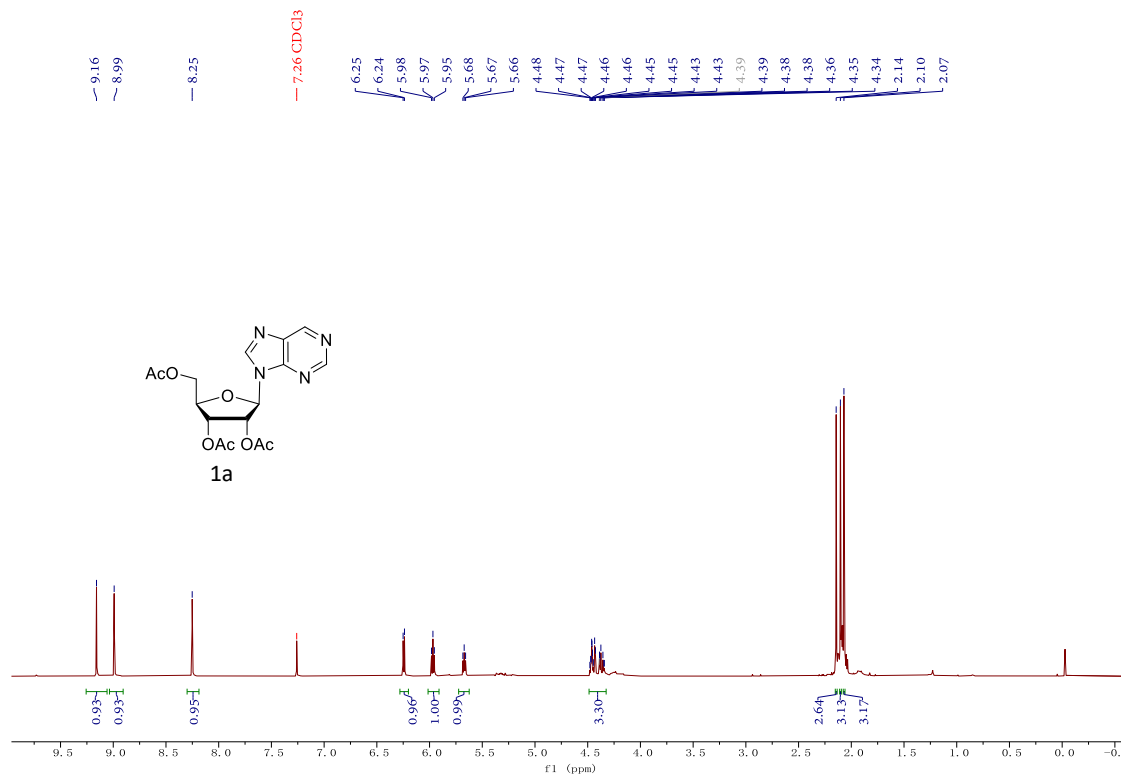
<sup>1</sup>H-NMR spectrum for **3ja** (in CDCl<sub>3</sub>)



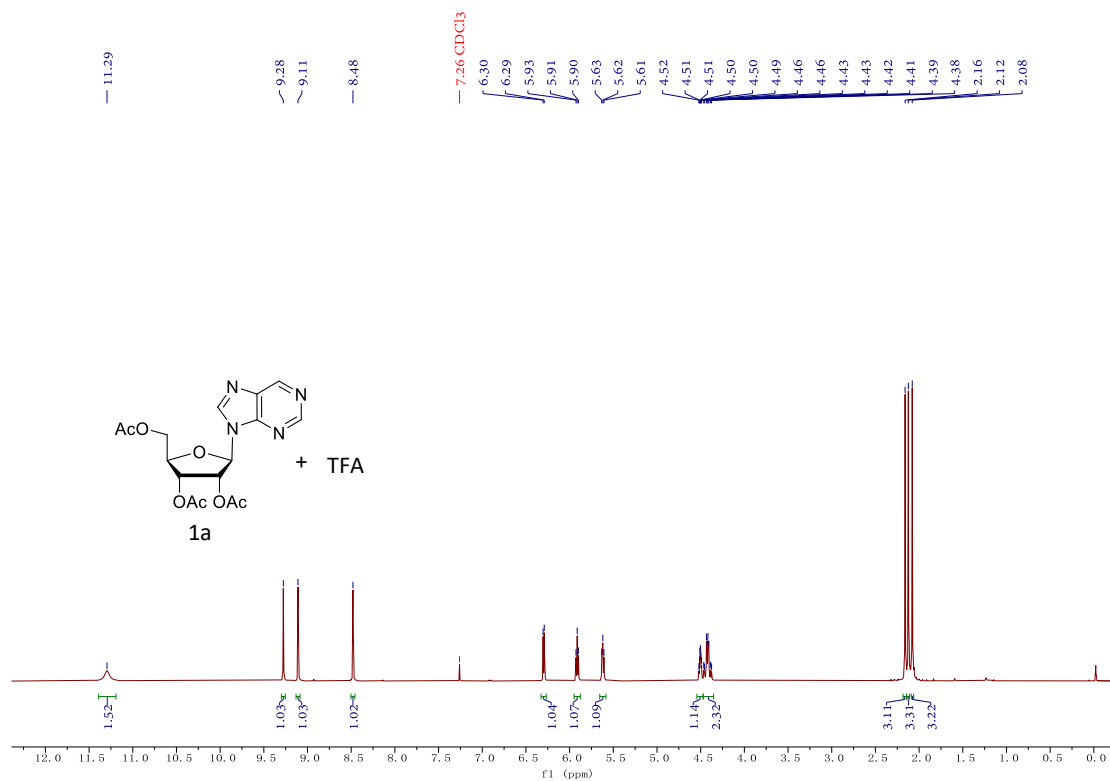
<sup>13</sup>C-NMR spectrum for **3ja** (in CDCl<sub>3</sub>)



<sup>1</sup>H-NMR spectrum for **1a** (in CDCl<sub>3</sub>)

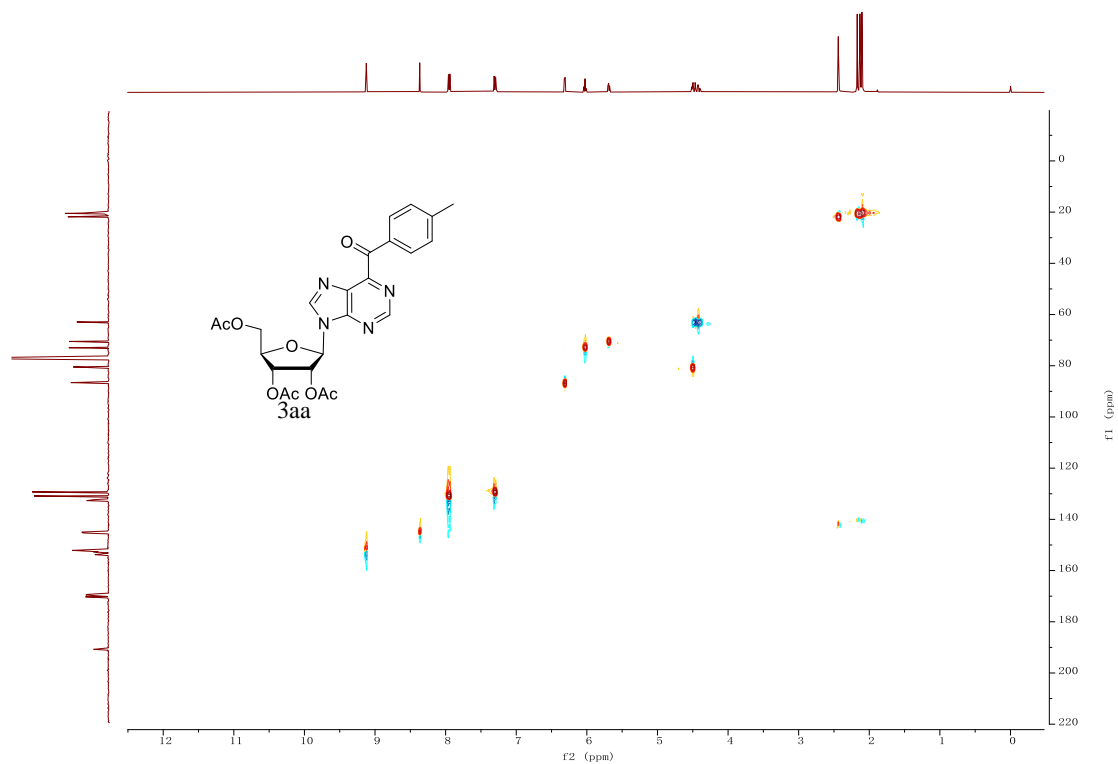


<sup>1</sup>H-NMR spectrum for **1a**+(1.5eq) TFA (in CDCl<sub>3</sub>)

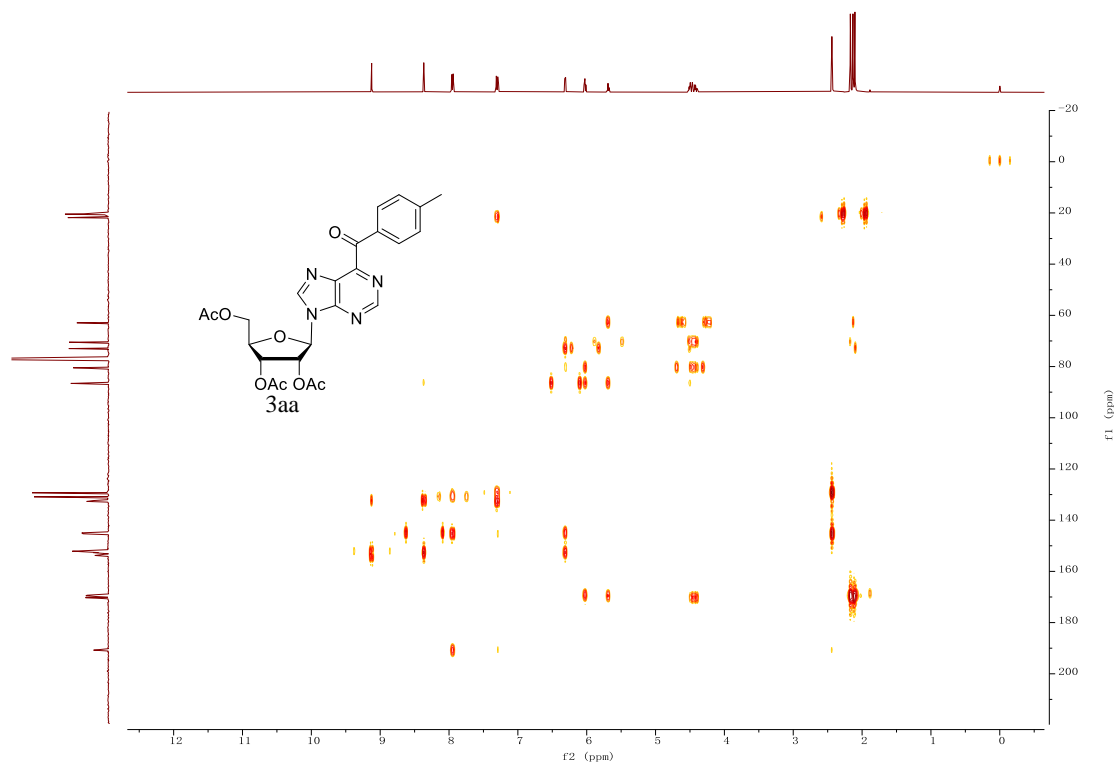




HSQC NMR Spectrum for **3aa** (in CDCl<sub>3</sub>)



HMBC NMR Spectrum for **3aa** (in CDCl<sub>3</sub>)



COSY NMR Spectrum for **3aa** (in CDCl<sub>3</sub>)

