

## Supporting Information for

# Electrochemical Enantioselective Dihydroxylation Reaction of *N*-Alkenyl nucleobases for the Construction of Chiral Acyclic Nucleosides

Qi-Ying Zhang<sup>\*a</sup>, Pei-Xian Lu<sup>a</sup>, Song-Lin Wang<sup>b</sup> Lu-Xin Li<sup>a</sup>, Gui-Rong Qu<sup>a</sup>, and Hai-Ming Guo<sup>\*a</sup>

<sup>a</sup>NMPA Key Laboratory for Research and Evaluation of Innovative Drug, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.

<sup>b</sup>School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China.

E-mail: zhangqiyi@htu.edu.cn; ghm@htu.edu.cn

## Table of Contents

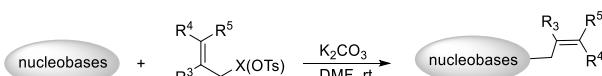
1. General information.....	2
2. Experimental Section .....	2
2.1 Synthesis methods for starting materials <sup>[1-4]</sup> .....	2
2.2 Graphical guide for the electrochemical set-up.....	3
2.3 Optimization of reaction conditions.....	3
2.4 General procedure for electrochemical enantioselective dihydroxylation reaction of N-alkenyl nucleobases .....	4
2.5 Scale-up synthesis of model product 2a.....	5
3. The X-ray data of 2a .....	5
4. The analytical and spectral characterization data.....	7
5. Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra.....	26
6. Copies of HPLC spectra for racemic and chiral products .....	77
7. References.....	105

## 1. General information

All the electrochemical oxidations were performed in an undivided cell equipped with carbon felt anode (1.5 cm × 1.5 cm × 0.3 cm) and platinum cathode (1.5 cm × 1.5 cm × 0.2 mm) unless otherwise noted. Source (HSPY-600) was purchased from Beijing Hansheng Puyuan Technology Co., LTD. All commercial reagents were purchased from TCI, Sigma-Aldrich, laajoo and Adamas-beta of the highest purity grade and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane with the solvent resonance as the internal standard. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants ( $J$ ) are in Hertz (Hz), and integration. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/ ID/OD-H/IC in comparison with the authentic racemates. Chiral HPLC analysis was recorded on Thermo Scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were recorded on Autopol Automatic Polarimeter, and were reported as follows:  $[\alpha]_D^T$  (c: g/100 mL, in  $\text{CH}_3\text{OH}$ ). High resolution mass spectra (HRMS) were recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. Melting point (m.p.) data were obtained on X-5 micro melting point apparatus. For column chromatography, silica gel (200-300 mesh) was used as the stationary phase.

## 2. Experimental Section

### 2.1 Synthesis methods for starting materials<sup>[1-4]</sup>



To a mixture of nucleobases (10.0 mmol) and  $\text{K}_2\text{CO}_3$  (2.07 g, 15.0 mmol) in DMF (20.0 mL), the solution of alkenes compounds (12.0 mmol) was added. Then, the resulting mixture was stirred at rt until the starting materials were consumed as indicated by TLC analysis. Afterwards, the resulting mixture was filtered through a Celite pad, and the brine (40 mL) was added into the filtrate. Subsequently, the mixture was extracted with ethyl acetate (30.0 mL×3). The combined

organic layers were washed with brine ( $100.0\text{ mL} \times 2$ ), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography with petroleum ether: ethyl acetate (2:1) as the eluant to afford the N-alkenyl nucleobases.

## 2.2 Graphical guide for the electrochemical set-up



**Figure S1.** Reaction set-up for milligram-scale electrolysis. The anode is carbon felt electrode ( $1.5\text{ cm} \times 1.5\text{ cm} \times 0.3\text{ cm}$ ) while the cathode is platinum electrode ( $1.5\text{ cm} \times 1.5\text{ cm} \times 0.2\text{ mm}$ ).



**Figure S2.** Reaction set-up for gram-scale electrolysis. The anode is carbon felt electrode ( $4.0\text{ cm} \times 4.0\text{ cm} \times 0.6\text{ cm}$ ) while the cathode is platinum electrode ( $4.0\text{ cm} \times 4.0\text{ cm} \times 0.2\text{ mm}$ ).

## 2.3 Optimization of reaction conditions

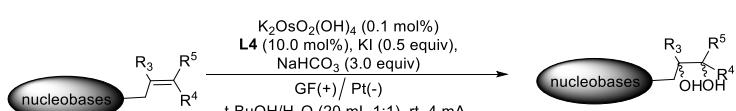
Table S1. Screening of Reaction Conditions<sup>a</sup>

entry	anode	cathode	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	Pt (1.0*1.0 cm <sup>2</sup> )	Pt (1.0*1.0 cm <sup>2</sup> )	33	89
2	Pt (1.5*1.0 cm <sup>2</sup> )	Pt (1.0*1.0 cm <sup>2</sup> )	49	90
3	Pt (1.5*1.5 cm <sup>2</sup> )	Pt (1.0*1.0 cm <sup>2</sup> )	56	91
4	Pt (1.5*1.5 cm <sup>2</sup> )	Pt (1.5*1.5 cm <sup>2</sup> )	66	91
5	Graphite Felt (1.5*1.5 cm <sup>2</sup> )	Pt (1.5*1.5 cm <sup>2</sup> )	94	96
6	RVC <sup>d</sup> (1.5*1.5 cm <sup>2</sup> )	Pt (1.5*1.5 cm <sup>2</sup> )	56	92
7	Carbon Rod	Pt (1.5*1.5 cm <sup>2</sup> )	35	92
8	Ni foam (1.5*1.5 cm <sup>2</sup> )	Pt (1.5*1.5 cm <sup>2</sup> )	n.r.	n.r.
9	Carbon Rod	Carbon Rod	n.r.	n.r.

<sup>a</sup>Unless otherwise noted, the reaction conditions were: **1a** (1.0 mmol), K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.1 mol%), **L4** (DHQD)<sub>2</sub>PHAL (10.0 mol%), KI (0.5 equiv), NaHCO<sub>3</sub> (3.0 equiv), t-BuOH/H<sub>2</sub>O (20 mL, 1:1), constant current of 4 mA, rt, the reaction time of 40 h, in an undivided cell. <sup>b</sup>Isolated yields.

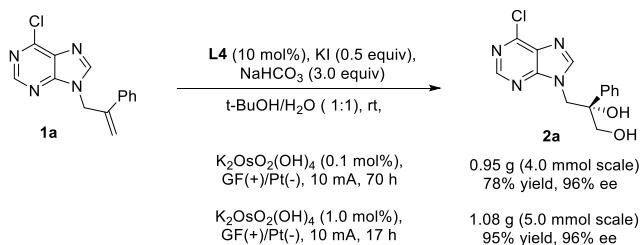
<sup>c</sup>Determined by chiral HPLC analysis. <sup>d</sup>RVC: Reticulated Vitreous Carbon

## 2.4 General procedure for electrochemical enantioselective dihydroxylation reaction of N-alkenyl nucleobases



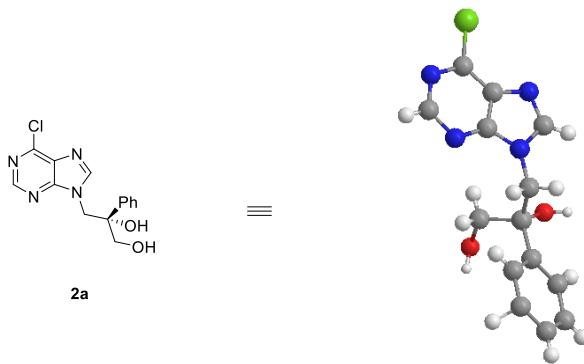
The electrocatalysis was carried out in an undivided cell under air with carbon felt anode (1.5 cm × 1.5 cm × 0.3 cm) and platinum cathode (1.5 cm × 1.5 cm × 0.2 mm). The N-alkenyl nucleobases (1.0 mmol), K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.001 mmol), **L4** (0.1 mmol), KI (0.5 mmol), NaHCO<sub>3</sub> (3.0 mmol) were dissolved in t-BuOH/H<sub>2</sub>O (20 mL, 1:1). Electrocatalysis was performed at rt with a constant current of 4.0 mA maintained for 40 h. After the reaction, the electrodes were washed with ethyl acetate (3×10.0 mL). The mixture was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (40/1) to afford the corresponding products.

## 2.5 Scale-up synthesis of model product **2a**



The electrocatalysis was carried out in an undivided cell under air with carbon felt anode (4.0 cm × 4.0 cm × 0.6 cm) and platinum cathode (4.0 cm × 4.0 cm × 0.2 mm). To one vial, **1a** (4.0 mmol), K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.004 mmol), **L4** (0.4 mmol), KI (2.0 mmol), NaHCO<sub>3</sub> (12.0 mmol) and t-BuOH/H<sub>2</sub>O (80.0 mL, 1:1) were added. To another vial, **1a** (5.0 mmol), K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.05 mmol), **L4** (0.5 mmol), KI (2.5 mmol), NaHCO<sub>3</sub> (15.0 mmol) and t-BuOH/H<sub>2</sub>O (100.0 mL, 1:1) were added. Electrocatalysis was performed at rt with a constant current of 10.0 mA until the starting materials were consumed as indicated by TLC analysis. After these reactions, the electrodes were washed with ethyl acetate (3×30.0 mL). The mixture was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The resulting residue was purified by flash column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (40/1) afforded the product **2a**.

## 3. The X-ray data of **2a**



The chiral product of **2a** was recrystallized by ethyl acetate/ petroleum ether/methanol (30/10/1). CCDC 2150120 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1** Crystal data and structure refinement for **2a**.

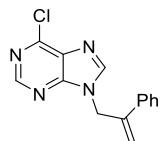
Identification code	LPX-20211213
Empirical formula	C <sub>14</sub> H <sub>16</sub> ClN <sub>4</sub> O <sub>4</sub>

Formula weight	339.76
Temperature/K	293 (2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	10.76520(10)
b/Å	6.84890(10)
c/Å	11.20770(10)
$\alpha/^\circ$	90
$\beta/^\circ$	110.1070(10)
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	775.977(16)
Z	2
$\rho_{\text{calc}} \text{g/cm}^3$	1.454
$\mu/\text{mm}^{-1}$	2.427
F(000)	354.0
Crystal size/mm <sup>3</sup>	0.01 × 0.01 × 0.01
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/°	8.402 to 142.808
Index ranges	-13 ≤ h ≤ 13, -8 ≤ k ≤ 7, -13 ≤ l ≤ 13
Reflections collected	18673
Independent reflections	2824 [ $R_{\text{int}} = 0.0417$ , $R_{\text{sigma}} = 0.0195$ ]
Data/restraints/parameters	2824/1/216
Goodness-of-fit on F <sup>2</sup>	1.149
Final R indexes [I>=2σ (I)]	$R_1 = 0.0435$ , $wR_2 = 0.1066$
Final R indexes [all data]	$R_1 = 0.0436$ , $wR_2 = 0.1067$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.31/-0.62
Flack parameter	0.023(11)

#### 4. The analytical and spectral characterization data

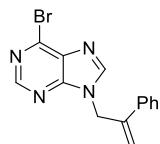
##### (1) The analytical and spectral characterization data of starting materials

###### **6-chloro-9-(2-phenylallyl)-9H-purine (1a)**



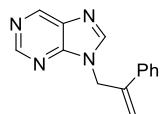
White solid, m.p. 87.0-88.5 °C, 1.48 g, 55% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.77 (s, 1H), 8.08 (s, 1H), 7.43-7.40 (m, 2H), 7.30-7.28 (m, 3H), 5.63 (s, 1H), 5.33 (s, 2H), 5.21 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.1, 151.8, 151.0, 145.1, 141.9, 136.9, 131.3, 128.81, 128.75, 126.0, 116.9, 47.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 271.0745, found m/z 271.0741.

###### **6-bromo-9-(2-phenylallyl)-9H-purine (1b)**



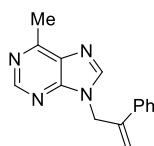
White solid, m.p. 106.7-108.6 °C, 2.01 g, 64% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 8.09 (s, 1H), 7.42-7.41 (m, 2H), 7.32-7.26 (m, 3H), 5.63 (s, 1H), 5.32 (s, 2H), 5.21 (s, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 152.0, 150.6, 145.0, 143.1, 141.9, 136.9, 133.9, 128.84, 128.79, 126.0, 116.9, 47.6; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 315.0240, found m/z 315.0245.

###### **9-(2-phenylallyl)-9H-purine (1c)**



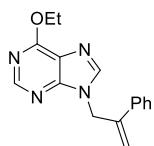
White solid, m.p. 61.9-64.0 °C, 1.26 g, 53% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.12 (s, 1H), 9.03 (s, 1H), 8.06 (s, 1H), 7.45-7.42 (m, 2H), 7.32-7.27 (m, 3H), 5.63 (s, 1H), 5.32 (s, 2H), 5.18 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.8, 151.4, 148.6, 145.1, 142.2, 137.1, 133.8, 128.8, 128.7, 126.0, 116.5, 46.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>12</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 237.1135, found m/z 237.1137.

###### **6-methyl-9-(2-phenylallyl)-9H-purine (1d)**



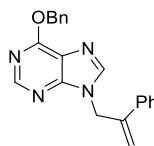
White solid, m.p. 66.5-67.2 °C, 0.78 g, 31% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.87 (s, 1H), 7.96 (s, 1H), 7.44-7.41 (m, 2H), 7.32-7.28 (m, 3H), 5.61 (s, 1H), 5.29 (s, 2H), 5.16 (s, 1H), 2.83 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.4, 152.6, 150.7, 143.7, 142.5, 137.3, 132.9, 128.9, 128.8, 126.1, 116.5, 47.1, 19.6; **HRMS** (ESI-TOF): exact mass calcd for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 251.1291, found m/z 251.1298.

#### 6-ethoxy-9-(2-phenylallyl)-9H-purine (1f)



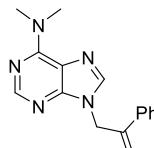
White solid, m.p. 29.2-32.1 °C, 1.54 g, 55% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.56 (s, 1H), 7.87 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.30-7.26 (m, 3H), 5.59 (s, 1H), 5.27 (s, 2H), 5.12 (s, 1H), 4.67-4.63 (m, 2H), 1.50 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 160.9, 152.3, 152.1, 142.5, 142.0, 137.3, 128.7, 128.6, 126.0, 121.2, 116.0, 63.2, 47.1, 14.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O (M+Na)<sup>+</sup> requires m/z 303.1216, found m/z 303.1209.

#### 6-(benzyloxy)-9-(2-phenylallyl)-9H-purine (1g)



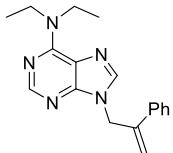
White solid, m.p. 102.9-104.3 °C, 2.01 g, 59% yield, **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.58 (s, 1H), 7.86 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.43-7.41 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.27 (m, 4H), 5.66 (s, 2H), 5.59 (s, 1H), 5.26 (s, 2H), 5.12 (s, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 160.7, 152.4, 152.2, 142.5, 142.2, 137.3, 136.2, 128.8, 128.7, 128.53, 128.45, 128.2, 126.1, 121.3, 116.2, 68.5, 47.2; **HRMS** (ESI-TOF): exact mass calcd for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O (M+H)<sup>+</sup> requires m/z 343.1553, found m/z 343.1559.

#### N,N-dimethyl-9-(2-phenylallyl)-9H-purin-6-amine (1h)



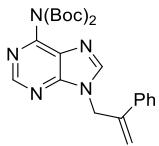
White solid, m.p. 126.5-127.5 °C, 1.45 g, 52% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.67 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.31-7.27 (m, 3H), 5.58 (s, 1H), 5.20 (s, 2H), 5.08 (s, 1H), 3.51 (s, 6H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 155.0, 152.7, 150.7, 142.8, 138.2, 137.6, 128.7, 128.5, 126.1, 119.9, 115.7, 46.7, 38.6; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>17</sub>N<sub>5</sub> (M+H)<sup>+</sup> requires m/z 280.1557, found m/z 280.1556.

**N,N-diethyl-9-(2-phenylallyl)-9H-purin-6-amine (1i)**



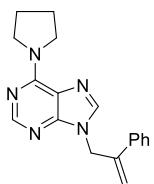
White solid, m.p. 85.7-87.6 °C, 1.84 g, 60% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.68 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 5.58 (s, 1H), 5.19 (s, 2H), 5.07 (s, 1H), 3.97 (s, 4H), 1.28 (t, *J* = 7.2 Hz, 6H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 153.9, 152.8, 150.7, 142.8, 138.2, 137.6, 128.7, 128.4, 126.1, 119.4, 115.6, 46.6, 43.0, 13.6; **HRMS** (ESI-TOF): exact mass calcd for C<sub>18</sub>H<sub>21</sub>N<sub>5</sub> (M+H)<sup>+</sup> requires m/z 308.1870, found m/z 308.1864.

**tert-butyl (tert-butoxycarbonyl)(9-(2-phenylallyl)-9H-purin-6-yl)carbamate (1j)**



White solid, m.p. 86.4-89.0 °C, 1.80 g, 40% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.89 (s, 1H), 8.01 (s, 1H), 7.42-7.40 (m, 2H), 7.31-7.25 (m, 3H), 5.61 (s, 1H), 5.32 (s, 2H), 5.19 (s, 1H), 1.39 (s, 18H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.4, 152.2, 150.4, 150.3, 144.6, 142.4, 137.1, 128.8, 128.7, 128.6, 126.1, 116.6, 83.7, 47.3, 27.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>24</sub>H<sub>29</sub>N<sub>5</sub>O<sub>4</sub> (M+H)<sup>+</sup> requires m/z 452.2292, found m/z 452.2282.

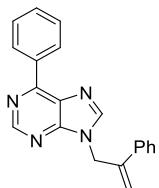
**9-(2-phenylallyl)-6-(pyrrolidin-1-yl)-9H-purine (1k)**



White solid, m.p. 177.7-181.6 °C, 2.01 g, 53% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.40 (s, 1H), 7.67 (s, 1H), 7.46-7.44 (m, 2H), 7.33-7.25 (m, 3H), 5.58 (s, 1H), 5.21 (s, 2H), 5.08 (s, 1H), 4.14 (s, 2H), 3.76 (s, 2H), 2.02 (s, 4H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.2, 153.1, 150.3, 142.9, 138.7,

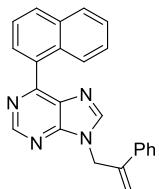
137.6, 128.8, 128.5, 126.1, 120.1, 115.7, 46.7, 26.3, 24.4; **HRMS** (ESI-TOF): exact mass calcd for C<sub>18</sub>H<sub>19</sub>N<sub>5</sub> (M+H)<sup>+</sup> requires m/z 306.1713, found m/z 306.1714.

**6-phenyl-9-(2-phenylallyl)-9H-purine (1l)**



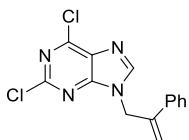
White solid, m.p. 123.8-125.4 °C, 1.03 g, 33% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.06 (s, 1H), 8.78-8.77 (m, 2H), 8.06 (s, 1H), 7.56-7.50 (m, 3H), 7.46-7.45 (m, 2H), 7.33-7.28 (m, 3H), 5.63 (s, 1H), 5.34 (s, 2H), 5.19 (s, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 155.0, 152.7, 152.6, 144.3, 142.5, 137.4, 135.7, 131.1, 130.9, 129.9, 128.9, 128.8, 126.1, 116.5, 47.1; **HRMS** (ESI-TOF): exact mass calcd for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 313.1448, found m/z 313.1493.

**6-(naphthalen-1-yl)-9-(2-phenylallyl)-9H-purine (1m)**



White solid, m.p. 108.8-109.9 °C, 1.41 g, 39% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 9.19 (s, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.05-8.03 (m, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.92-7.91 (m, 1H), 7.62 (t, *J* = 6.6, 1H), 7.52-7.47 (m, 4H), 7.35-7.29 (m, 3H), 5.63 (s, 1H), 5.33 (s, 2H), 5.19 (s, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 158.0, 152.4, 144.7, 142.3, 137.3, 134.1, 132.5, 132.4, 131.1, 130.7, 130.0, 128.8, 128.7, 128.5, 126.8, 126.10, 126.08, 125.8, 125.1, 116.4, 47.0; **HRMS** (ESI-TOF): exact mass calcd for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 363.1604, found m/z 363.1603.

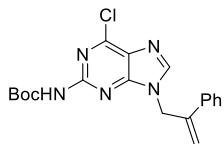
**2,6-dichloro-9-(2-phenylallyl)-9H-purine (1n)**



White solid, m.p. 114.8-115.6 °C, 1.31 g, 43% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.06 (s, 1H), 7.41-7.39 (m, 2H), 7.32-7.28 (m, 3H), 5.65 (s, 1H), 5.29 (s, 2H), 5.24, (s, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 153.1, 153.0, 151.6, 145.7, 141.5, 136.6, 130.4, 128.84, 128.82, 125.9, 117.3, 47.7; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 305.0355, found m/z

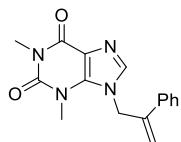
305.0346.

**tert-butyl (6-chloro-9-(2-phenylallyl)-9H-purin-2-yl)carbamate (1o)**



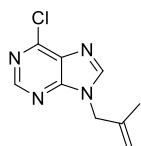
White solid, 149.5-151.9 °C, 2.50 g, 65% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 1H), 7.62 (s, 1H), 7.46-7.44 (m, 2H), 7.33-7.27 (m, 3H), 5.65 (s, 1H), 5.26-5.25 (m, 3H), 1.56 (s, 9H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.0, 152.6, 151.3, 150.3, 144.1, 142.1, 137.0, 128.9, 128.8, 127.6, 126.2, 117.2, 81.8, 47.5, 28.3; **HRMS** (ESI-TOF): exact mass calcd for C<sub>19</sub>H<sub>20</sub>ClN<sub>5</sub>O<sub>2</sub> (M+Na)<sup>+</sup> requires m/z 408.1198, found m/z 408.1208.

**1,3-dimethyl-9-(2-phenylallyl)-3,9-dihydro-1H-purine-2,6-dione (1p)**



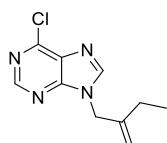
White solid, m.p. 112.3-114.3 °C, 1.94 g, 49% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.49 (s, 1H), 7.44-7.42 (m, 2H), 7.35-7.29 (m, 3H), 5.55 (s, 1H), 5.38 (s, 2H), 5.12 (s, 1H), 3.55 (d, J = 1.2 Hz, 3H), 3.41 (d, J = 1.2 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 155.4, 151.8, 148.7, 143.1, 141.3, 137.5, 128.9, 128.7, 126.3, 116.3, 107.0, 50.2, 29.9, 28.1; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> (M+Na)<sup>+</sup> requires m/z 319.1165, found m/z 319.1162.

**6-chloro-9-(2-methylallyl)-9H-purine (1q)**



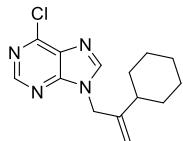
Yellow oil, 1.00 g, 48% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.64-8.62 (m, 1H), 8.07 (s, 1H), 4.91 (s, 1H), 4.75 (s, 2H), 4.68 (s, 1H), 1.64 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.0, 151.8, 150.8, 145.4, 139.0, 131.2, 114.6, 49.5, 19.9; **HRMS** (ESI-TOF): exact mass calcd for C<sub>9</sub>H<sub>9</sub>ClN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 209.0589, found m/z 209.0598.

**6-chloro-9-(2-methylenebutyl)-9H-purine (1r)**



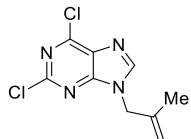
Colorless oil; 0.89 g, 40% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 8.09 (s, 1H), 5.01 (s, 1H), 4.84 (s, 2H), 4.79 (s, 1H), 2.00 (q, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.2, 152.0, 151.2, 145.4, 144.8, 131.5, 112.8, 48.7, 26.4, 11.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>10</sub>H<sub>11</sub>ClN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 223.0745, found m/z 223.0750.

#### **6-chloro-9-(2-cyclohexylallyl)-9H-purine (1s)**



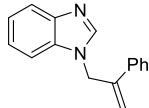
White solid, m.p. 61.4-62.7 °C, 0.74 g, 42% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.74 (s, 1H), 8.09 (s, 1H), 5.02 (s, 1H), 4.86 (s, 2H), 4.70 (s, 1H), 1.81-1.75 (m, 5H), 1.67-1.64 (m, 1H), 1.22-1.17 (m, 5H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.2, 152.1, 151.2, 148.7, 145.5, 131.5, 112.2, 47.7, 41.9, 32.2, 26.5, 26.1; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>17</sub>ClN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 277.1215, found m/z 277.1215.

#### **2,6-dichloro-9-(2-methylallyl)-9H-purine (1t)**



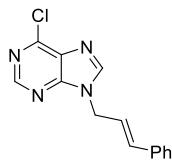
White solid, 66.6-67.1 °C, 1.52 g, 63% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.09 (s, 1H), 5.05 (s, 1H), 4.80 (s, 1H), 4.78 (s, 2H), 1.75 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.4, 153.3, 152.0, 146.0, 138.7, 130.7, 115.3, 49.8, 20.1; **HRMS** (ESI-TOF): exact mass calcd for C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 243.0199, found m/z 243.0205.

#### **1-(2-phenylallyl)-1H-benzo[d]imidazole (1x)**



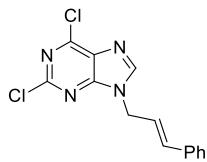
White solid, m.p. 106.4-108.4 °C, 1.24 g, 53% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 1H), 7.81-7.79 (m, 1H), 7.40-7.36 (m, 3H), 7.35-7.20 (m, 6H), 5.51 (s, 1H), 5.12 (s, 2H), 4.94 (s, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 143.9, 143.4, 142.3, 138.0, 128.8, 128.6, 126.7, 126.0, 123.1, 122.3, 120.5, 115.3, 110.1, 48.7; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub> (M+H)<sup>+</sup> requires m/z 235.1230, found m/z 235.1237.

#### **6-chloro-9-cinnamyl-9H-purine (3a)**



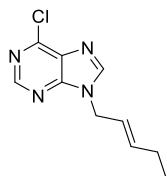
White solid, m.p. 80.1-83.6 °C, 1.70 g, 63% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.77 (s, 1H), 8.21 (s, 1H), 7.38-7.26 (m, 5H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.40-6.33 (m, 1H), 5.07 (d, *J* = 6.4 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.1, 151.8, 151.1, 145.0, 135.5, 135.3, 131.7, 128.8, 128.7, 126.7, 121.5, 46.1; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>4</sub> (M+Na)<sup>+</sup> requires m/z 293.0564, found m/z 293.0556.

### **(2,6-dichloro-9-cinnamyl-9H-purine (3b))**



White solid, m.p. 136.8-138.0 °C, 1.52 g, 50% yield; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.39-7.28 (m, 5H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.37-6.30 (m, 1H), 5.03 (d, *J* = 6.4 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.3, 153.1, 152.0, 145.6, 136.1, 135.2, 130.9, 128.9, 126.9, 121.0, 46.4; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>4</sub> (M+H)<sup>+</sup> requires m/z 305.0355, found m/z 305.0352.

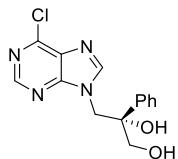
### **(E)-6-chloro-9-(pent-2-en-1-yl)-9H-purine (3c))**



White solid, m.p. 26.6-29.7 °C, 0.98 g, 44% yield; **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.69 (s, 1H), 8.08 (s, 1H), 5.80-5.76 (m, 1H), 5.58-5.54 (m, 1H), 4.88 (d, *J* = 7.2 Hz, 2H), 2.25-2.20 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 2H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ 151.9, 151.7, 150.9, 144.7, 138.8, 131.6, 120.9, 40.8, 20.9, 13.9; **HRMS** (ESI-TOF): exact mass calcd for C<sub>10</sub>H<sub>11</sub>ClN<sub>4</sub> (M+H)<sup>+</sup> requires m/z 223.0745, found m/z 223.0741.

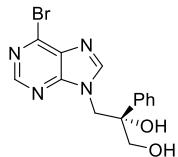
## **(2) The analytical and spectral characterization data of the products**

### **(S)-3-(6-chloro-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2a))**



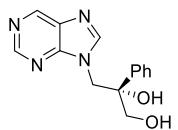
White solid, m.p. 66.2-69.2 °C, 288.8 mg, 95% yield, 96% ee;  $[\alpha]_D^{20} = 21.79$  ( $c = 0.257$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 11.053 min, 17.538 min; **TLC**:  $R_f = 0.25$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.57 (s, 1H), 8.30 (s, 1H), 7.43 (d,  $J = 7.2$  Hz, 2H), 7.18 (dt,  $J = 36.6, 7.8$  Hz, 3H), 4.76 (s, 2H), 3.90 (d,  $J = 11.4$  Hz, 1H), 3.75 (d,  $J = 11.4$  Hz, 1H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  153.8, 152.6, 150.8, 149.1, 142.4, 131.3, 129.1, 128.6, 126.8, 77.5, 68.6, 52.0; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 305.0800, found m/z 305.0801.

**(S)-3-(6-bromo-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2b)**



Brown oil, 327.1 mg, 94% yield, 95% ee;  $[\alpha]_D^{22} = 22.73$  ( $c = 0.274$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 12.903 min, 17.563 min; **TLC**:  $R_f = 0.27$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.52 (s, 1H), 8.30 (s, 1H), 7.44-7.42 (m, 2H), 7.18 (dt,  $J = 25.2, 7.2$  Hz, 3H), 4.75 (s, 2H), 3.90 (d,  $J = 11.6$  Hz, 1H), 3.75 (d,  $J = 11.6$  Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  152.5, 148.9, 142.7, 142.4, 134.0, 129.1, 128.6, 126.8, 77.5, 68.6, 52.0; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>13</sub>BrN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 349.0295, found m/z 349.0292.

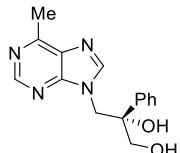
**(S)-2-phenyl-3-(9H-purin-9-yl)propane-1,2-diol (2c)**



White solid, m.p. 107.6-108.9 °C, 72.9 mg, 27% yield, 84% ee;  $[\alpha]_D^{21} = 56.73$  ( $c = 0.241$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 10.295 min, 17.490 min; **TLC**:  $R_f = 0.32$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.94 (s, 1H), 8.79 (s, 1H), 8.29 (s, 1H), 7.45-7.44 (m,

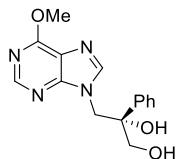
2H), 7.16 (dt,  $J$  = 37.8, 7.2 Hz, 3H), 4.76 (dd,  $J$  = 16.8, 14.4 Hz, 2H), 3.89 (d,  $J$  = 11.4 Hz, 1H), 3.76 (d,  $J$  = 11.4 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz, CD<sub>3</sub>OD)  $\delta$  153.3, 152.9, 149.2, 148.1, 142.6, 134.0, 129.1, 128.5, 126.8, 77.6, 68.6, 51.4; HRMS (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 271.1190, found m/z 271.1193.

**(S)-3-(6-methyl-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2d)**



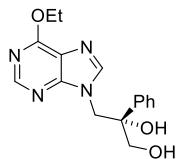
White solid, m.p. 161.9-162.9 °C, 264.2 mg, 93% yield, 94% ee;  $[\alpha]_D^{20} = 9.49$  ( $c = 0.260$ , CH<sub>3</sub>OH); HPLC CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda$  = 250 nm, retention time: 9.499 min, 13.586 min; TLC: R<sub>f</sub> = 0.29 (dichloromethane: methanol = 20:1) [UV];  $^1\text{H}$  NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.65 (s, 1H), 8.21 (s, 1H), 7.46-7.44 (m, 2H), 7.19 (dt,  $J$  = 37.2, 7.2 Hz, 3H), 4.74 (s, 2H), 3.86 (d,  $J$  = 11.4 Hz, 1H), 3.73 (d,  $J$  = 11.4 Hz, 1H), 2.74 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz, CD<sub>3</sub>OD)  $\delta$  159.4, 152.51, 152.47, 147.9, 142.7, 132.8, 129.1, 128.5, 126.9, 77.6, 68.7, 51.6, 18.9; HRMS (ESI-TOF): exact mass calcd for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 285.1346, found m/z 285.1343.

**(S)-3-(6-methoxy-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2e)**



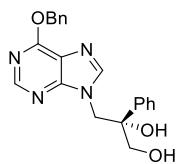
White solid, m.p. 140.9-142.6 °C, 285.1 mg, 95% yield, 96% ee;  $[\alpha]_D^{22} = 11.27$  ( $c = 0.284$ , CH<sub>3</sub>OH); HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 75/25, flow rate = 0.8 mL/min,  $\lambda$  = 254 nm, retention time: 18.705 min, 19.487 min; TLC: R<sub>f</sub> = 0.28 (dichloromethane: methanol = 20:1) [UV];  $^1\text{H}$  NMR (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.37 (s, 1H), 8.01 (s, 1H), 7.46-7.44 (m, 2H), 7.23-7.14 (m, 3H), 4.68 (dd,  $J$  = 30.0, 21.0 Hz, 2H), 4.10 (s, 3H), 3.77 (dd,  $J$  = 64.2, 16.8 Hz, 2H), 3.35 (s, 2H);  $^{13}\text{C}$  NMR (150 MHz, CD<sub>3</sub>OD)  $\delta$  162.0, 153.6, 152.8, 145.6, 142.7, 129.1, 128.4, 126.8, 121.0, 77.6, 68.5, 54.8, 51.8; HRMS (ESI-TOF): exact mass calcd for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub> (M+H)<sup>+</sup> requires m/z 301.1295, found m/z 301.1292.

**(S)-3-(6-ethoxy-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2f)**



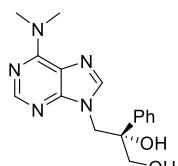
White solid, m.p. 142.9-143.8 °C, 279.6 mg, 89% yield, 93% ee;  $[\alpha]_D^{21} = 16.48$  ( $c = 0.267$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 11.142 min, 23.589 min; **TLC**:  $R_f = 0.31$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.38 (s, 1H), 8.02 (s, 1H), 7.46 (d,  $J = 7.2$  Hz, 2H), 7.20 (dt,  $J = 38.4, 7.8$  Hz, 3H), 4.69 (dd,  $J = 21.6, 14.4$  Hz, 2H), 4.60 (dd,  $J = 13.8, 7.2$  Hz, 2H), 3.82 (d,  $J = 12.0$  Hz, 2H), 3.71 (d,  $J = 12.0$  Hz, 2H), 1.45 (t,  $J = 7.2$  Hz, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  161.7, 153.7, 152.8, 145.5, 142.8, 129.1, 128.5, 126.9, 121.0, 77.6, 68.6, 64.3, 51.7, 14.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub> (M+H)<sup>+</sup> requires m/z 315.1452, found m/z 315.1447.

**(S)-3-(6-(benzyloxy)-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2g)**



White solid, m.p. 135.3-138.1 °C, 331.0 mg, 88% yield, 93% ee;  $[\alpha]_D^{20} = 17.16$  ( $c = 0.268$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 10.383 min, 18.422 min; **TLC**:  $R_f = 0.25$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.40 (s, 1H), 8.01 (s, 1H), 7.49-7.44 (m, 4H), 7.35-7.28 (m, 3H), 7.23-7.13 (m, 3H), 5.58 (s, 2H), 4.68 (dd,  $J = 21.6, 14.4$  Hz, 2H), 3.76 (dd,  $J = 45.2, 11.6$  Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  161.4, 153.8, 152.7, 145.7, 142.7, 137.5, 129.5, 129.4, 129.2, 129.1, 128.5, 126.8, 121.0, 77.5, 69.7, 68.5, 51.7; **HRMS** (ESI-TOF): exact mass calcd for C<sub>21</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub> (M+H)<sup>+</sup> requires m/z 377.1608, found m/z 377.1610.

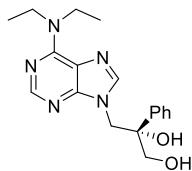
**(S)-3-(6-(dimethylamino)-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2h)**



White solid, m.p. 112.1-113.3 °C, 291.2 mg, 93% yield, 95% ee;  $[\alpha]_D^{22} = 21.62$  ( $c = 0.260$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda =$

256 nm, retention time: 9.975 min, 13.920 min; **TLC**:  $R_f = 0.32$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.13 (s, 1H), 7.74 (s, 1H), 7.50-7.48 (m, 2H), 7.22 (dt,  $J = 28.8, 7.2$  Hz, 3H), 4.57 (dd,  $J = 36.4, 14.4$  Hz, 2H), 3.69 (dd,  $J = 37.2, 11.2$  Hz, 2H), 3.42 (s, 6H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  156.0, 152.6, 151.8, 143.2, 142.0, 129.1, 128.4, 126.9, 120.1, 77.6, 68.4, 51.5, 39.0; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>19</sub>N<sub>5</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 314.1612, found m/z 314.1609.

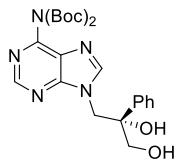
**(S)-3-(6-(diethylamino)-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2i)**



White solid, m.p. 78.3-82.0 °C, 276.4 mg, 81% yield, 92% ee;  $[\alpha]_D^{22} = -32.68$  ( $c = 0.284$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 7.002 min, 10.013 min; **TLC**:  $R_f = 0.32$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.15 (s, 1H), 7.75 (s, 1H), 7.52-7.49 (m, 2H), 7.30-7.19 (m, 3H), 4.59 (dd,  $J = 44.0, 14.4$  Hz, 2H), 3.94 (s, 4H), 3.69 (dd,  $J = 35.6, 11.2$  Hz, 2H), 1.24 (t,  $J = 6.8$  Hz, 6H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  154.9, 152.8, 151.9, 143.3, 142.1, 129.1, 128.4, 126.9, 119.6, 77.6, 68.4, 51.4, 44.3, 13.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>18</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 342.1925, found m/z 342.1926.

**tert-butyl**

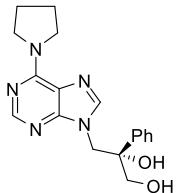
**(S)-(tert-butoxycarbonyl)(9-(2,3-dihydroxy-2-phenylpropyl)-9H-purin-6-yl)carbamate (2j)**



White solid, m.p. 145.9-149.6 °C, 470.6 mg, 97% yield, 95% ee;  $[\alpha]_D^{22} = 29.64$  ( $c = 0.227$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 75/25, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 9.779 min, 11.579 min; **TLC**:  $R_f = 0.29$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.73 (s, 1H), 8.34 (s, 1H), 7.47 (d,  $J = 7.8$  Hz, 2H), 7.17 (dt,  $J = 40.2, 7.2$  Hz, 3H), 4.89 (d,  $J = 14.4$  Hz, 1H), 4.77 (d,  $J = 14.4$  Hz, 1H), 3.93 (d,  $J = 11.4$  Hz, 1H), 3.77 (d,  $J = 11.4$  Hz, 1H), 1.33 (s, 18H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  155.4, 152.4, 151.2, 150.4, 149.0, 142.4, 129.2, 129.1, 128.5, 126.9, 85.08, 85.06, 77.6, 68.9, 51.8, 28.0;

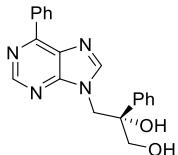
**HRMS** (ESI-TOF): exact mass calcd for C<sub>24</sub>H<sub>31</sub>N<sub>5</sub>O<sub>6</sub> (M+H)<sup>+</sup> requires m/z 486.2347, found m/z 486.2340.

**(S)-2-phenyl-3-(6-(pyrrolidin-1-yl)-9H-purin-9-yl)propane-1,2-diol (2k)**



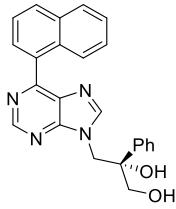
White solid, m.p. 136.7-139.4 °C, 287.4 mg, 85% yield, 97% ee; [α]<sub>D</sub><sup>22</sup> = 24.69 (c = 0.243, CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, λ = 250 nm, retention time: 11.884 min, 16.558 min; **TLC**: R<sub>f</sub> = 0.29 (dichloromethane: methanol = 30:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, DMSO-*d*<sup>6</sup>) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.21 (dt, *J* = 45.6, 7.8 Hz, 3H), 5.76 (s, 1H), 5.32 (t, *J* = 6.0 Hz, 1H), 4.55 (dd, *J* = 39.6, 14.4 Hz, 2H), 3.99 (s, 2H), 3.86-3.46 (m, 4H), 1.90 (d, *J* = 33.0 Hz, 4H); **<sup>13</sup>C NMR** (150 MHz, DMSO-*d*<sup>6</sup>) δ 152.4, 151.8, 150.3, 142.9, 141.0, 127.6, 126.8, 126.0, 118.6, 76.0, 67.4, 49.6, 48.4, 47.0, 43.2, 25.7, 23.7; **HRMS** (ESI-TOF): exact mass calcd for C<sub>18</sub>H<sub>21</sub>N<sub>5</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 340.1768, found m/z 340.1763.

**(S)-2-phenyl-3-(6-phenyl-9H-purin-9-yl)propane-1,2-diol (2l)**



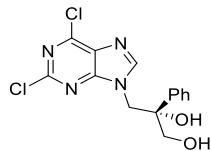
White solid, m.p. 117.0-119.9 °C, 308.0 mg, 89% yield, 98% ee; [α]<sub>D</sub><sup>22</sup> = 39.78 (c = 0.238, CH<sub>3</sub>OH); **HPLC** CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL/min, λ = 256 nm, retention time: 20.137 min, 21.135 min; **TLC**: R<sub>f</sub> = 0.35 (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD) δ 8.78 (s, 1H), 8.54-8.52 (m, 2H), 8.20 (s, 1H), 7.51-7.46 (m, 5H), 7.24-7.13 (m, 3H), 4.72 (dd, *J* = 22.0, 14.4 Hz, 2H), 3.80 (dd, *J* = 44.0, 11.2 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD) δ 155.6, 154.2, 152.7, 148.3, 142.7, 136.5, 132.0, 131.1, 130.8, 129.6, 129.1, 128.5, 126.9, 77.6, 68.5, 51.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 347.1503, found m/z 347.1504.

**(S)-3-(6-(naphthalen-1-yl)-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2m)**



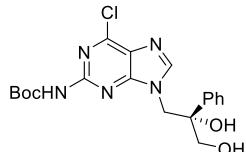
White solid, m.p. 83.3-86.0 °C, 273.3 mg, 69% yield, 99% ee;  $[\alpha]_D^{22} = 13.22$  ( $c = 0.227$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL ID, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 24.455 min, 27.318 min; **TLC**:  $R_f = 0.27$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.92 (s, 1H), 8.25 (s, 1H), 8.05 (d,  $J = 8.4$  Hz, 1H), 7.96 (d,  $J = 7.8$  Hz, 1H), 7.81-7.77 (m, 2H), 7.62 (t,  $J = 7.2$  Hz, 1H), 7.53-7.48 (m, 3H), 7.45-7.42 (m, 1H), 7.24 (t,  $J = 7.8$  Hz, 2H), 7.17 (t,  $J = 7.8$  Hz, 1H), 4.79 (s, 2H), 3.91 (d,  $J = 11.4$  Hz, 1H), 3.78 (d,  $J = 11.4$  Hz, 1H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  158.3, 154.0, 152.7, 148.9, 142.7, 135.3, 133.6, 132.7, 132.3, 131.5, 130.1, 129.5, 129.1, 128.5, 127.7, 127.3, 126.9, 126.5, 126.2, 77.7, 68.6, 51.7; **HRMS** (ESI-TOF): exact mass calcd for C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 397.1659, found m/z 397.1660.

#### (S)-3-(2,6-dichloro-9H-purin-9-yl)-2-phenylpropane-1,2-diol (2n)



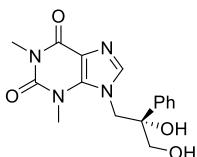
White solid, m.p. 167.8-169.3 °C, 189.3 mg, 56% yield, 94% ee;  $[\alpha]_D^{22} = -29.69$  ( $c = 0.274$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 10.197 min, 14.640 min; **TLC**:  $R_f = 0.32$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.28 (s, 1H), 7.41-7.39 (m, 2H), 7.18 (dt,  $J = 34.2$ , 7.2 Hz, 3H), 4.69 (dd,  $J = 18.6$ , 14.4 Hz, 2H), 3.95 (d,  $J = 11.4$  Hz, 1H), 3.77 (d,  $J = 11.4$  Hz, 1H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  155.2, 153.4, 151.3, 149.7, 142.2, 130.6, 129.1, 128.6, 126.9, 77.4, 68.5, 52.4; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 339.0410, found m/z 339.0401.

#### tert-butyl-(S)-(6-chloro-9-(2,3-dihydroxy-2-phenylpropyl)-9H-purin-2-yl)carbamate (2o)



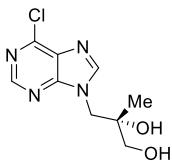
White solid, m.p. 161.7-164.3 °C, 373.0 mg, 89% yield, 98% ee;  $[\alpha]_D^{22} = -29.76$  ( $c = 0.336$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL IA, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 11.552 min, 13.834 min; **TLC**:  $R_f = 0.34$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  7.99 (s, 1H), 7.51 (d,  $J = 7.2$  Hz, 2H), 7.24 (dt,  $J = 39.6, 7.2$  Hz, 3H), 4.77 (d,  $J = 15.0$  Hz, 1H), 4.67 (d,  $J = 15.0$  Hz, 1H), 3.76 (d,  $J = 12.0$  Hz, 1H), 3.62 (d,  $J = 11.4$  Hz, 1H), 1.57 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  154.6, 154.2, 153.3, 151.4, 148.0, 143.1, 129.1, 128.5, 127.5, 127.0, 82.3, 77.2, 68.0, 51.5, 28.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>19</sub>H<sub>22</sub>ClN<sub>5</sub>O<sub>4</sub> (M+H)<sup>+</sup> requires m/z 420.1433, found m/z 420.1430.

**(S)-9-(2,3-dihydroxy-2-phenylpropyl)-1,3-dimethyl-3,9-dihydro-1H-purine-2,6-dione (2p)**



White solid, m.p. 138.0-140.3 °C, 280.6 mg, 85% yield, 88% ee;  $[\alpha]_D^{22} = 22.81$  ( $c = 0.300$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 12.671 min, 14.628 min; **TLC**:  $R_f = 0.30$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  7.60 (s, 1H), 7.43 (d,  $J = 7.2$  Hz, 2H), 7.26 (t,  $J = 7.2$  Hz, 2H), 7.20 (t,  $J = 7.2$  Hz, 2H), 4.85 (d,  $J = 13.2$  Hz, 1H), 4.72 (d,  $J = 14.4$  Hz, 1H), 3.82 (d,  $J = 11.4$  Hz, 1H), 3.71 (d,  $J = 11.4$  Hz, 1H), 3.44 (s, 3H), 3.29 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  157.1, 152.9, 149.2, 144.6, 142.5, 129.1, 128.5, 126.8, 108.7, 77.6, 68.5, 53.9, 30.1, 28.3; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> (M+H)<sup>+</sup> requires m/z 331.1401, found m/z 331.1392.

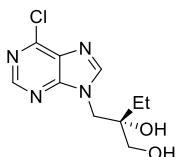
**(S)-3-(6-chloro-9H-purin-9-yl)-2-methylpropane-1,2-diol (2q)**



White solid, m.p. 128.0-130.2 °C, 222.7 mg, 92% yield, 57% ee;  $[\alpha]_D^{22} = -10.67$  ( $c = 0.300$  CH<sub>3</sub>OH); **HPLC** CHIRALCEL IC, *n*-hexane/2-propanol = 75/25, flow rate = 0.8 mL/min,  $\lambda = 254$  nm, retention time: 13.296 min, 14.619 min; **TLC**:  $R_f = 0.22$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.72 (s, 1H), 8.53 (s, 1H), 4.41 (dd,  $J = 25.2, 10.8$  Hz, 2H), 3.43-3.39 (m, 2H), 1.11 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  154.0, 152.9, 151.1, 149.5,

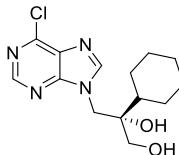
131.7, 73.3, 68.4, 51.5, 22.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>9</sub>H<sub>11</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 243.0643, found m/z 243.0644.

**(S)-2-((6-chloro-9H-purin-9-yl)methyl)butane-1,2-diol (2r)**



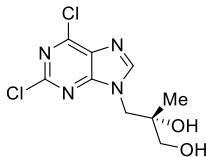
White solid, m.p. 98.7-100.7 °C, 225.3 mg, 88% yield, 84% ee;  $[\alpha]_D^{21} = -18.59$  ( $c = 0.283$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL IC, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 11.190 min, 12.856 min; **TLC**:  $R_f = 0.32$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.71 (s, 1H), 8.52 (s, 1H), 4.42 (dd,  $J = 21.6, 14.4$  Hz, 2H), 3.43 (d,  $J = 11.4$  Hz, 1H), 3.31 (d,  $J = 11.4$  Hz, 1H), 1.61-1.54 (sext,  $J = 7.2$  Hz, 1H), 1.48-1.42 (sext,  $J = 7.2$  Hz, 1H), 0.96 (t,  $J = 7.2$  Hz, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  154.0, 152.8, 151.1, 149.6, 131.7, 75.1, 64.9, 50.3, 28.5, 7.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>10</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 257.0800, found m/z 257.0791.

**(S)-3-(6-chloro-9H-purin-9-yl)-2-cyclohexylpropane-1,2-diol (2s)**



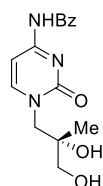
White solid, m.p. 158.8-159.3 °C, 272.9 mg, 88% yield, 75% ee;  $[\alpha]_D^{22} = 18.45$  ( $c = 0.300$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL ID, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 14.102 min, 15.310 min; **TLC**:  $R_f = 0.36$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.73 (s, 1H), 8.53 (s, 1H), 4.49 (dd,  $J = 30.0, 14.4$  Hz, 2H), 3.42 (d,  $J = 11.6$  Hz, 1H), 3.34 (d,  $J = 11.2$  Hz, 1H), 2.03-1.91 (m, 2H), 1.79 (s, 2H), 1.67 (s, 1H), 1.49-1.43 (m, 1H), 1.28-1.12 (m, 6H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  154.2, 152.8, 151.1, 149.9, 131.7, 76.3, 64.0, 44.2, 28.0, 28.0, 27.93, 27.86, 27.8, 27.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>19</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 311.1269, found m/z 311.1266.

**(S)-3-(2,6-dichloro-9H-purin-9-yl)-2-methylpropane-1,2-diol (2t)**



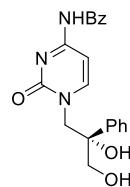
White solid, m.p. 149.1-149.9 °C, 237.4 mg, 86% yield, 68% ee;  $[\alpha]_D^{20} = -22.31$  ( $c = 0.260$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 7.564 min, 8.475 min; **TLC**:  $R_f = 0.35$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.51 (s, 1H), 4.36 (dd,  $J = 22.2, 7.8$  Hz, 2H), 3.43 (dd,  $J = 14.4, 11.4$  Hz, 2H), 1.11 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  155.4, 153.7, 151.7, 150.2, 131.0, 73.3, 68.4, 51.7, 22.4; **HRMS** (ESI-TOF): exact mass calcd for C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 277.0254, found m/z 277.0251.

**(S)-N-(1-(2,3-dihydroxy-2-methylpropyl)-2-oxo-1,2-dihydropyrimidin-4-yl)benzamide (2u)**



White solid, m.p. 177.2-178.3 °C, 245.5 mg, 81% yield, 80% ee;  $[\alpha]_D^{25} = -31.6$  ( $c = 0.336$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 27.841 min, 31.883 min; **TLC**:  $R_f = 0.26$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.04 (d,  $J = 10.8$  Hz, 1H), 7.98-7.96 (m, 2H), 7.65-7.51 (m, 4H), 4.05 (dd,  $J = 20.4, 14.0$  Hz, 2H), 3.35 (dd,  $J = 14.4, 11.6$  Hz, 2H), 1.20 (s, 3H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  169.1, 164.8, 159.8, 152.9, 134.7, 134.1, 129.8, 129.1, 98.2, 74.0, 68.2, 56.6, 22.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub> (M+H)<sup>+</sup> requires m/z 304.1292, found m/z 304.1290.

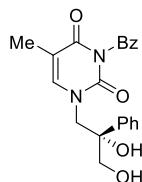
**(S)-N-(1-(2,3-dihydroxy-2-phenylpropyl)-2-oxo-1,2-dihydropyrimidin-4-yl)benzamide (2v)**



White solid, m.p. 147.5-148.2 °C, 204.4 mg, 56% yield, 95% ee;  $[\alpha]_D^{25} = -38.3$  ( $c = 0.283$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 18.002 min, 26.105 min; **TLC**:  $R_f = 0.29$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  7.96-7.94 (m, 2H), 7.87 (d,  $J = 7.6$  Hz, 1H), 7.65-7.61 (m, 1H), 7.57-7.51 (m, 4H), 7.44 (d,  $J = 7.2$  Hz, 1H), 7.36-7.33 (m, 2H), 7.28-7.25 (m, 1H), 4.61 (d,  $J = 14.0$  Hz, 1H), 4.17 (d,  $J = 14.0$  Hz, 1H), 3.78 (d,  $J = 11.6$  Hz, 1H), 3.69 (d,  $J =$

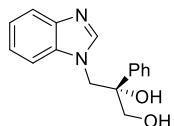
11.6 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD) δ 164.7, 152.7, 143.3, 134.7, 134.1, 129.8, 129.3, 129.1, 128.6, 127.0, 98.0, 78.0, 68.4, 57.3; **HRMS** (ESI-TOF): exact mass calcd for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub> (M+H)<sup>+</sup> requires m/z 366.1448, found m/z 366.1446.

**(S)-3-benzoyl-1-(2,3-dihydroxy-2-phenylpropyl)-5-methylpyrimidine-2,4(1H,3H)-dione (2w)**



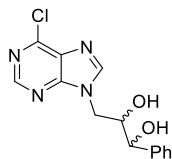
White solid, m.p. 138.4-139.2 °C, 315.5 mg, 83% yield, 98% ee; [α]<sub>D</sub><sup>25</sup> = 59.5 (c = 0.600, CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, λ = 250 nm, retention time: 17.108 min, 23.746 min; **TLC**: R<sub>f</sub> = 0.31 (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD) δ 7.67 (t, *J* = 7.8 Hz, 2H), 7.53-7.48 (m, 6H), 7.35-7.48 (m, 3H), 4.19 (s, 2H), 3.86 (d, *J* = 11.4 Hz, 1H), 3.71 (d, *J* = 11.4 Hz, 1H), 1.82 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD) δ 170.2, 164.9, 151.9, 144.6, 142.7, 136.2, 132.7, 131.3, 130.3, 129.7, 129.5, 129.21, 129.16, 128.9, 128.6, 127.0, 109.8, 78.0, 68.6, 54.83, 54.79, 12.2; **HRMS** (ESI-TOF): exact mass calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub> (M+Na)<sup>+</sup> requires m/z 403.1264, found m/z 403.1261.

**(S)-3-(1H-benzo[d]imidazol-1-yl)-2-phenylpropane-1,2-diol (2x)**



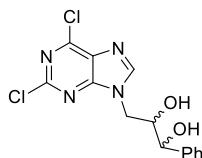
White solid, m.p. 137.7-140.2 °C, 185.0 mg, 69% yield, 85% ee; [α]<sub>D</sub><sup>22</sup> = 17.20 (c = 0.283, CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, λ = 250 nm, retention time: 9.235 min, 13.211 min; **TLC**: R<sub>f</sub> = 0.34 (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD) δ 7.82 (s, 1H), 7.56-7.54 (m, 1H), 7.41-7.37 (m, 3H), 7.25-7.13 (m, 5H), 4.58 (dd, *J* = 59.4, 14.4 Hz, 2H), 3.81 (dd, *J* = 71.4, 11.4 Hz, 2H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD) δ 145.7, 143.4, 143.0, 129.2, 128.5, 126.9, 123.8, 123.0, 119.5, 112.1, 77.6, 67.9, 52.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 269.1285, found m/z 269.1285.

**3-(6-chloro-9H-purin-9-yl)-1-phenylpropane-1,2-diol (4a)**



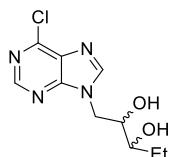
White solid, m.p. 140.0-141.7 °C, 273.6 mg, 90% yield, >20/1 dr, 97% ee;  $[\alpha]_D^{21} = 9.61$  ( $c = 0.222$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 256$  nm, retention time: 9.170 min, 10.773 min; **TLC**:  $R_f = 0.31$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.66 (s, 1H), 8.46 (s, 1H), 7.44 (d,  $J = 7.8$  Hz, 2H), 7.34-7.24 (m, 3H), 4.70 (d,  $J = 4.8$  Hz, 1H), 4.42 (dd,  $J = 14.4, 3.0$  Hz, 1H), 4.29-4.25 (m, 1H), 4.19-4.16 (m, 1H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  153.34, 153.31, 152.7, 150.9, 149.2, 142.6, 132.1, 129.3, 128.8, 128.0, 76.2, 74.1, 48.5; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 305.0800, found m/z 305.0791.

### 3-(2,6-dichloro-9H-purin-9-yl)-1-phenylpropane-1,2-diol (4b)



White solid, m.p. 63.1-65.9 °C, 202.8 mg, 60% yield, >20/1 dr, 93% ee;  $[\alpha]_D^{21} = 20.58$  ( $c = 0.243$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 8.786 min, 10.319 min; **TLC**:  $R_f = 0.30$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (600 MHz, CD<sub>3</sub>OD)  $\delta$  8.45 (s, 1H), 7.43 (d,  $J = 7.2$  Hz, 2H), 7.29 (dt,  $J = 45.0, 7.2$  Hz, 3H), 4.69 (d,  $J = 4.8$  Hz, 1H), 4.37 (dd,  $J = 13.8, 3.0$  Hz, 1H), 4.26-4.22 (m, 1H), 4.17-4.14 (m, 1H); **<sup>13</sup>C NMR** (150 MHz, CD<sub>3</sub>OD)  $\delta$  154.7, 153.5, 151.5, 149.8, 142.4, 131.3, 129.2, 128.7, 128.0, 76.0, 74.0; **HRMS** (ESI-TOF): exact mass calcd for C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 339.0410, found m/z 339.0403.

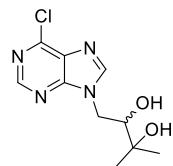
### 1-(6-chloro-9H-purin-9-yl)pentane-2,3-diol (4c)



White solid, m.p. 72.4-75.1 °C, 227.9 mg, 89% yield, >20/1 dr, 53% ee;  $[\alpha]_D^{22} = -23.35$  ( $c = 0.260$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 250$  nm, retention time: 6.624 min, 7.814 min; **TLC**:  $R_f = 0.38$  (dichloromethane: methanol = 20:1) [UV]; **<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.73 (s, 1H), 8.53 (s, 1H), 4.71 (dd,  $J = 14.4, 3.2$  Hz, 1H),

4.34-4.28 (m, 1H), 3.80-3.76 (m, 1H), 3.41-3.37 (m, 1H), 1.83-1.76 (m, 1H), 1.51-1.43 (s, 1H), 1.02 (t,  $J = 7.2$  Hz, 3H);  **$^{13}\text{C}$  NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  153.6, 152.8, 151.0, 149.4, 132.2, 75.6, 73.5, 27.3, 10.3; **HRMS** (ESI-TOF): exact mass calcd for C<sub>10</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 257.0800, found m/z 257.0806.

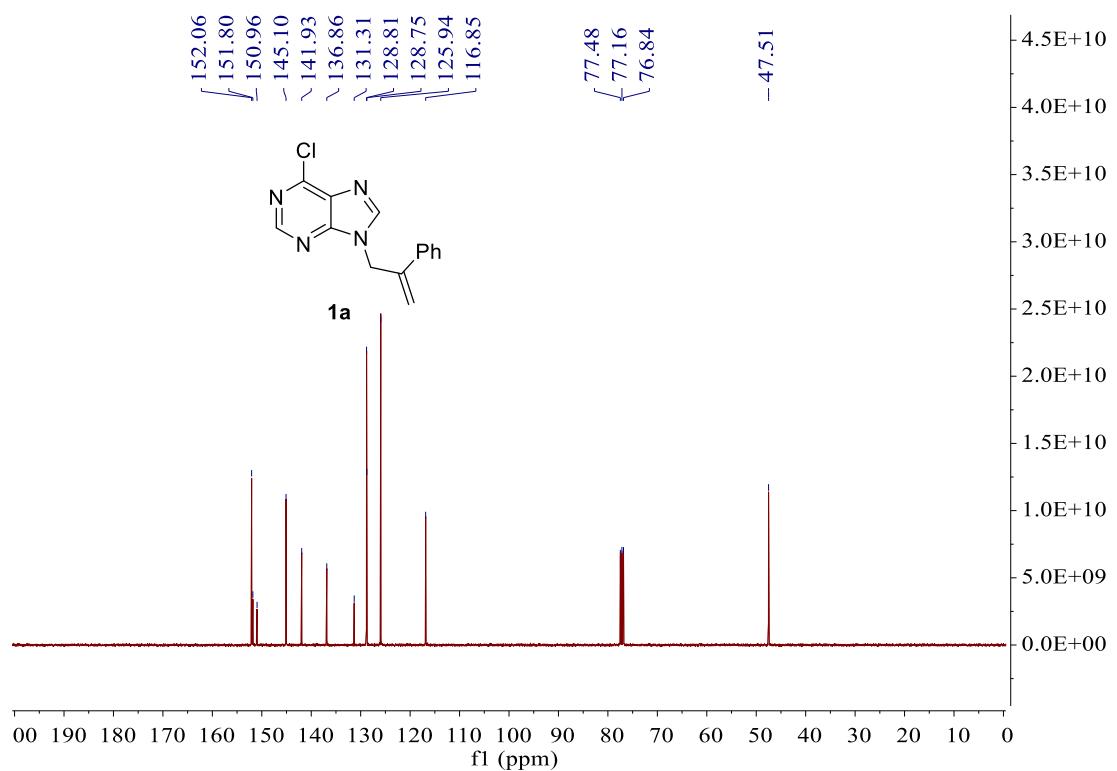
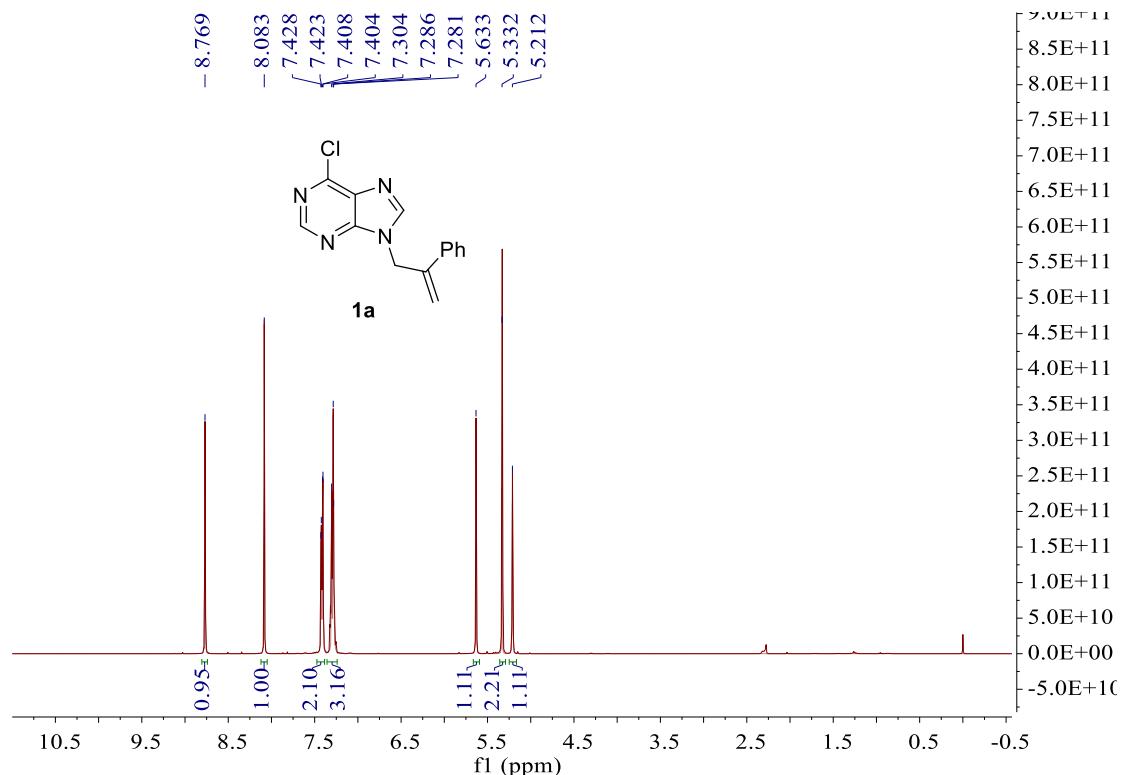
**1-(6-chloro-9H-purin-9-yl)-3-methylbutane-2,3-diol (4d)**

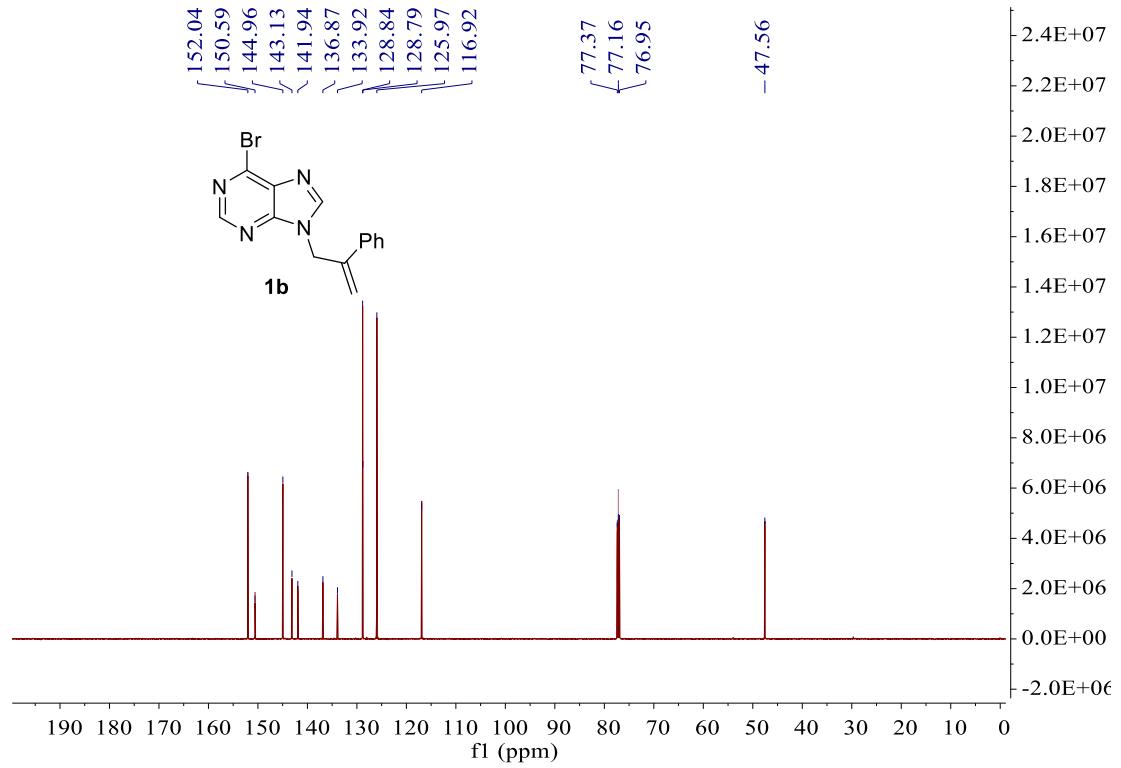
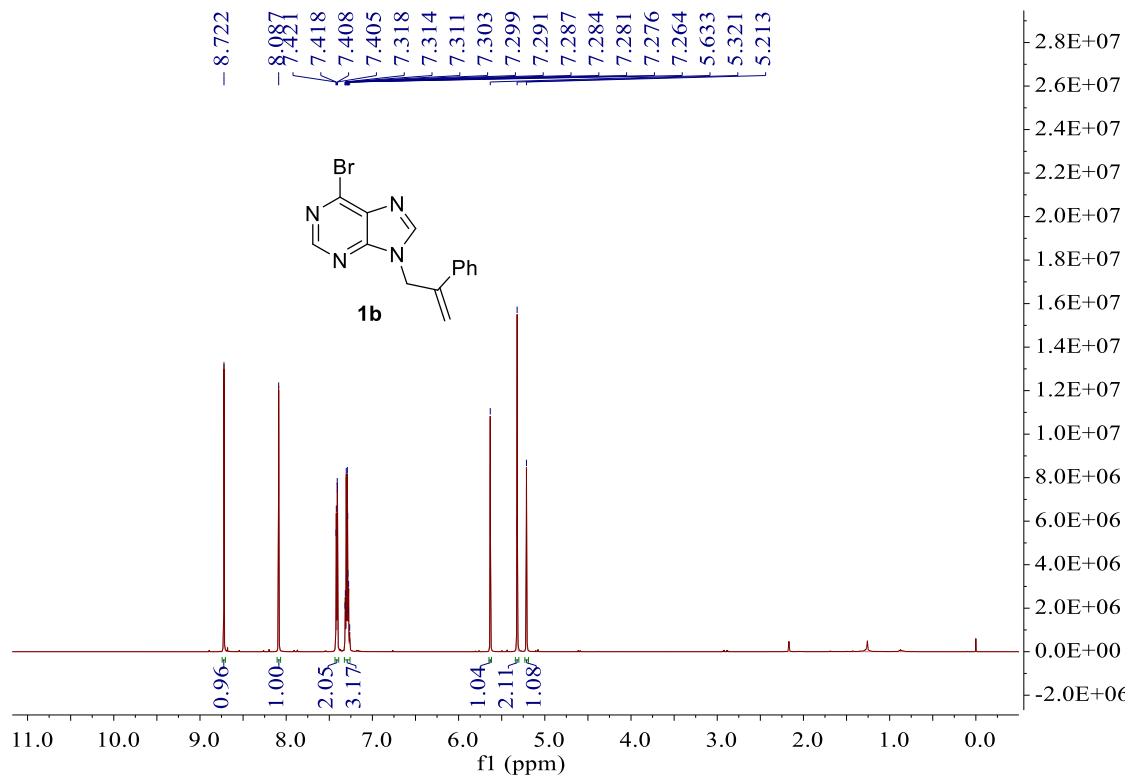


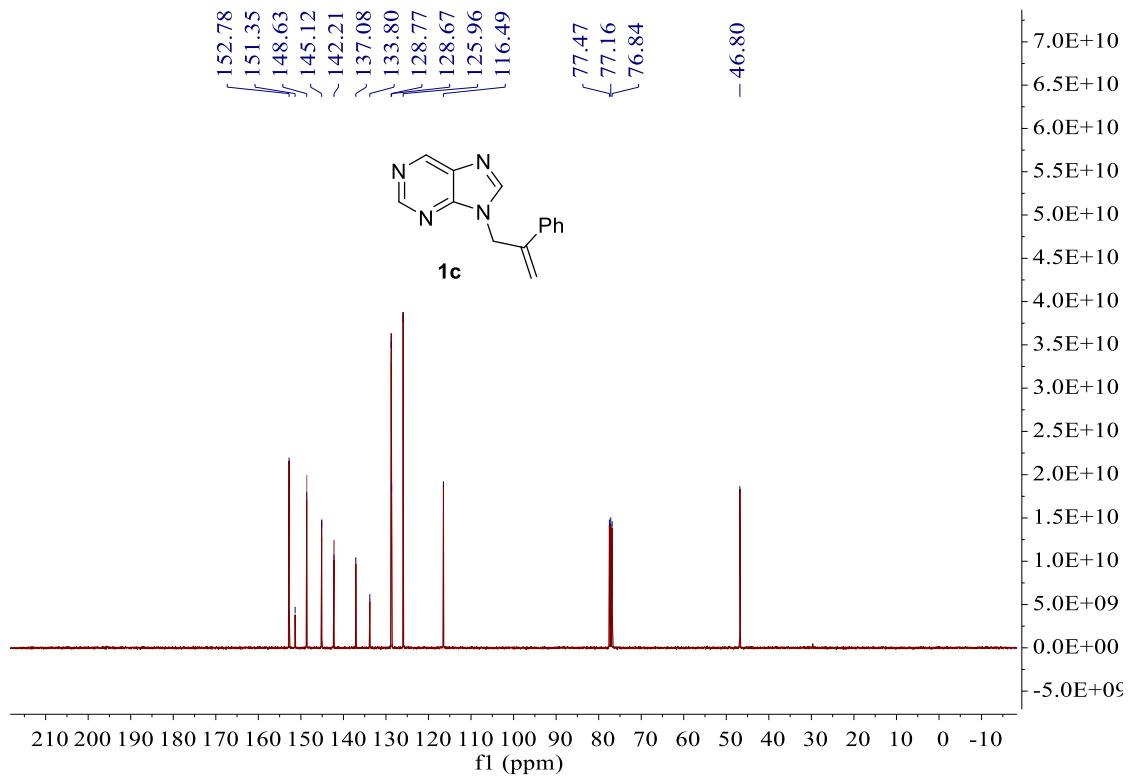
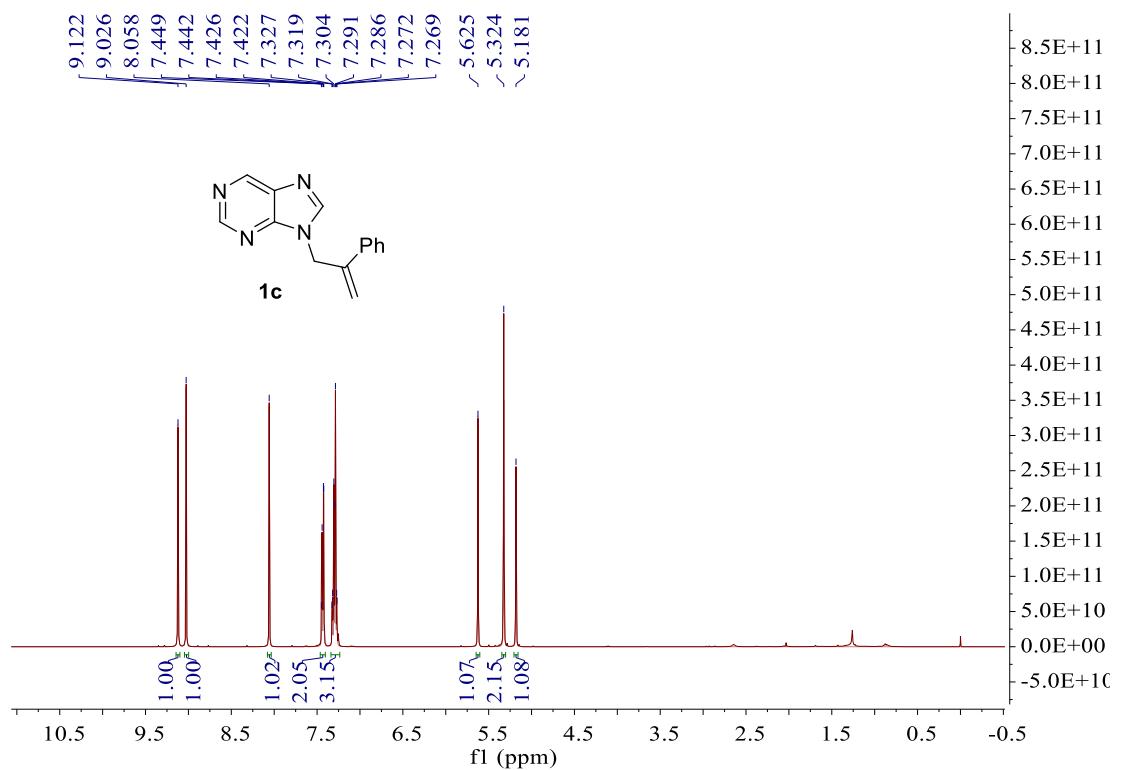
White solid, m.p. 98.1-100.2 °C, 197.2 mg, 77% yield, 92% ee;  $[\alpha]_D^{22} = 37.77$  ( $c = 0.274$ , CH<sub>3</sub>OH); **HPLC** CHIRALCEL OD-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min,  $\lambda = 254$  nm, retention time: 7.685 min, 8.924 min; **TLC**: R<sub>f</sub> = 0.23 (dichloromethane: methanol = 20:1) [UV];  **$^1\text{H}$  NMR** (400 MHz, CD<sub>3</sub>OD)  $\delta$  8.73 (s, 1H), 8.54 (s, 1H), 4.74 (dd,  $J = 14.0, 2.4$  Hz, 1H), 4.26-4.20 (m, 1H), 3.72 (dd,  $J = 10.4, 2.4$  Hz, 1H), 1.30 (d,  $J = 6.8$  Hz, 6H);  **$^{13}\text{C}$  NMR** (100 MHz, CD<sub>3</sub>OD)  $\delta$  153.5, 152.8, 150.9, 149.4, 132.2, 76.8, 72.8, 47.5, 26.7, 24.8; **HRMS** (ESI-TOF): exact mass calcd for C<sub>10</sub>H<sub>13</sub>ClN<sub>4</sub>O<sub>2</sub> (M+H)<sup>+</sup> requires m/z 257.0800, found m/z 257.0807.

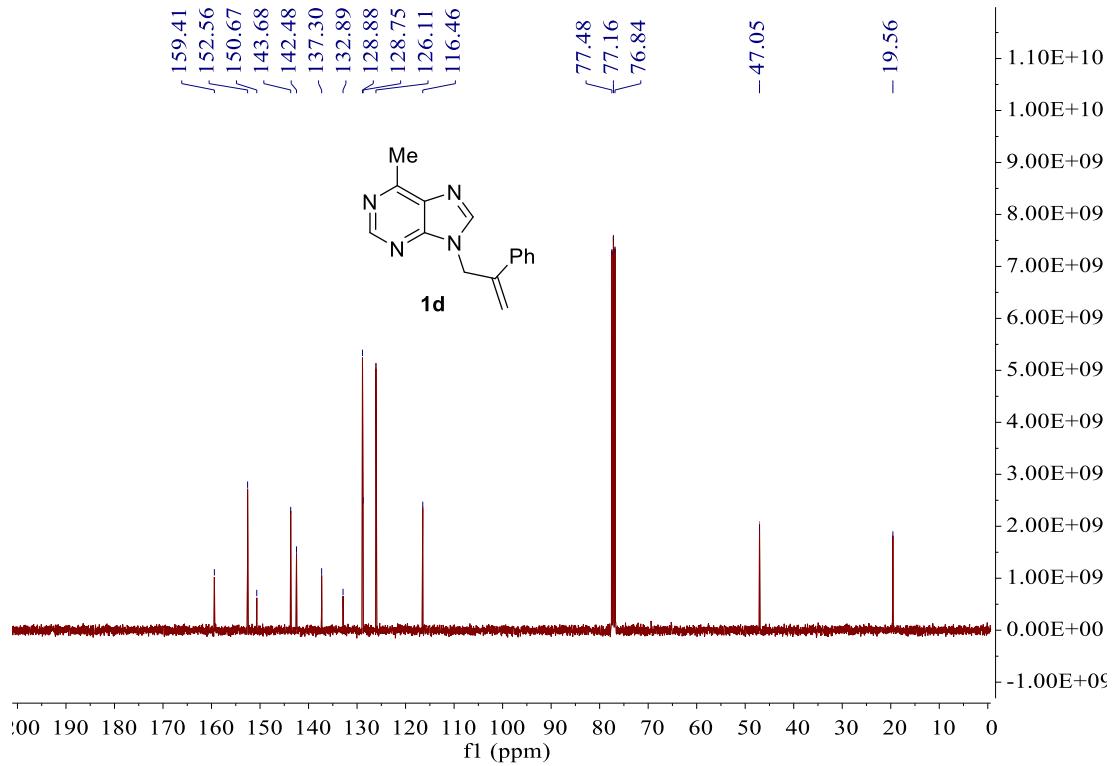
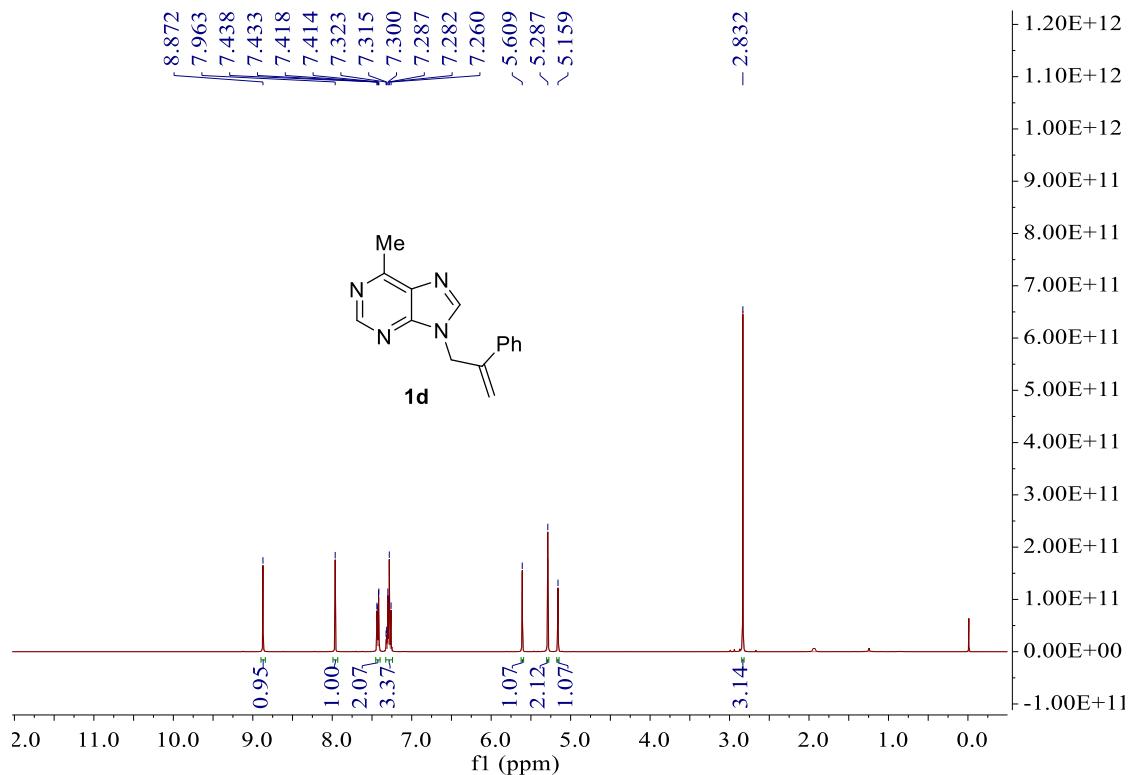
## 5. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

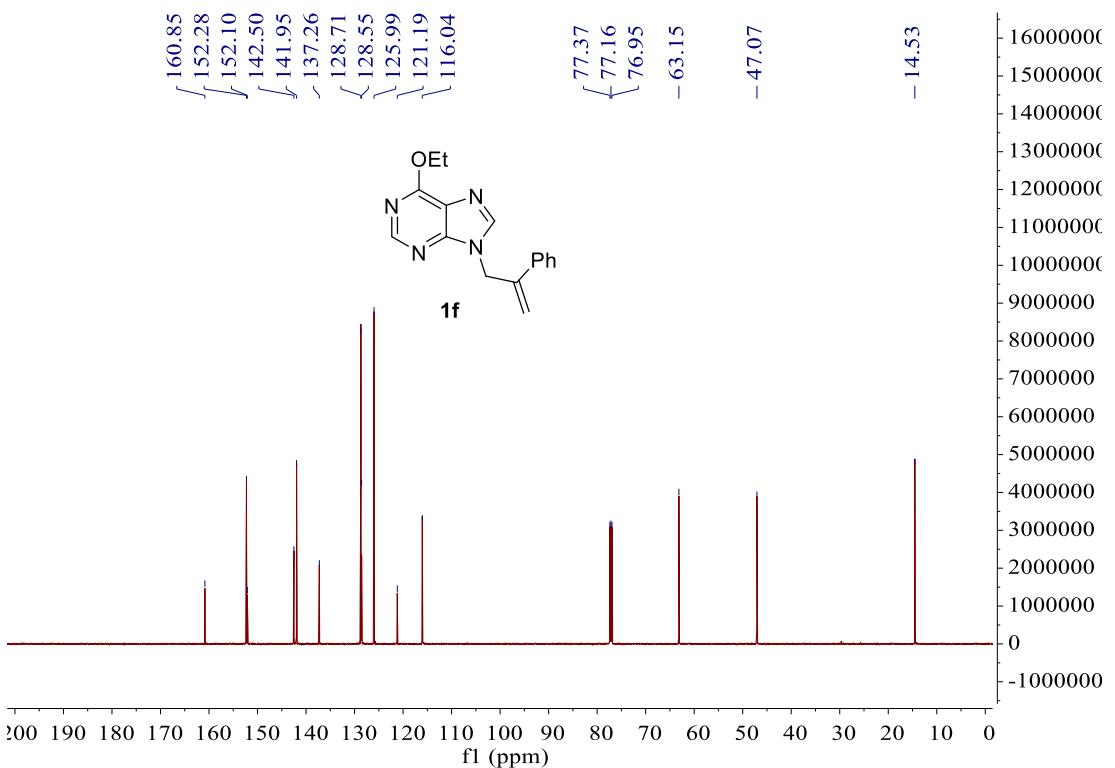
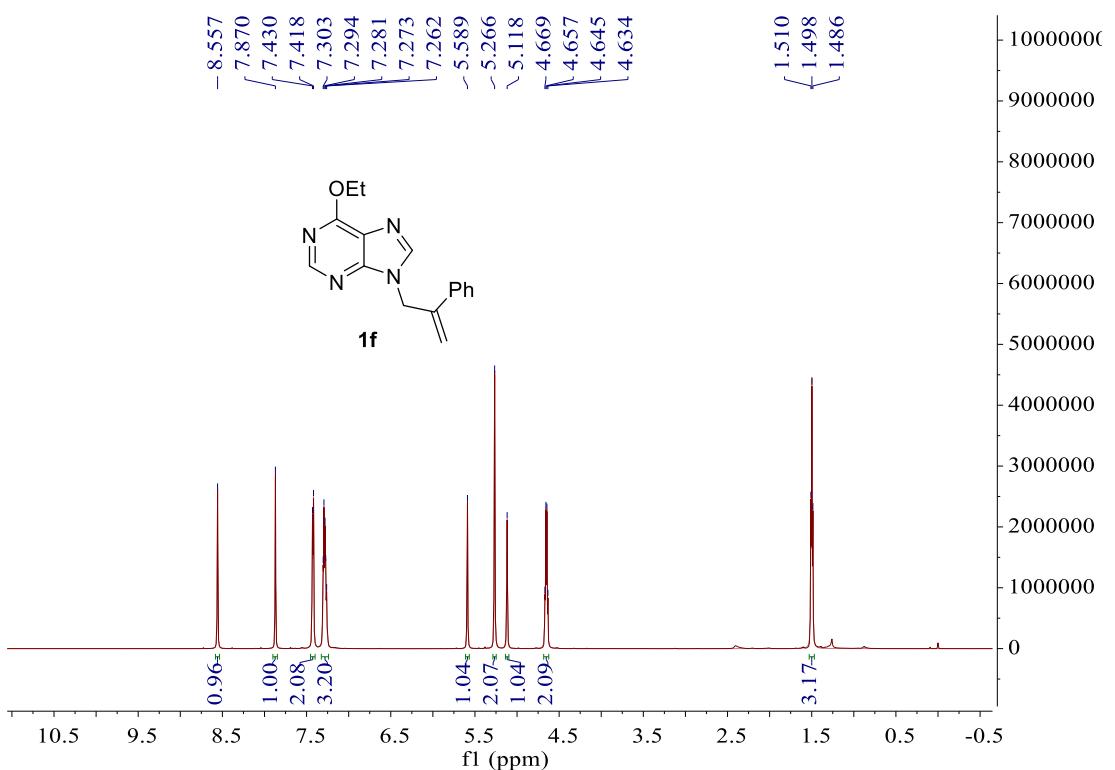
### (1) Copies of NMR spectra of starting materials

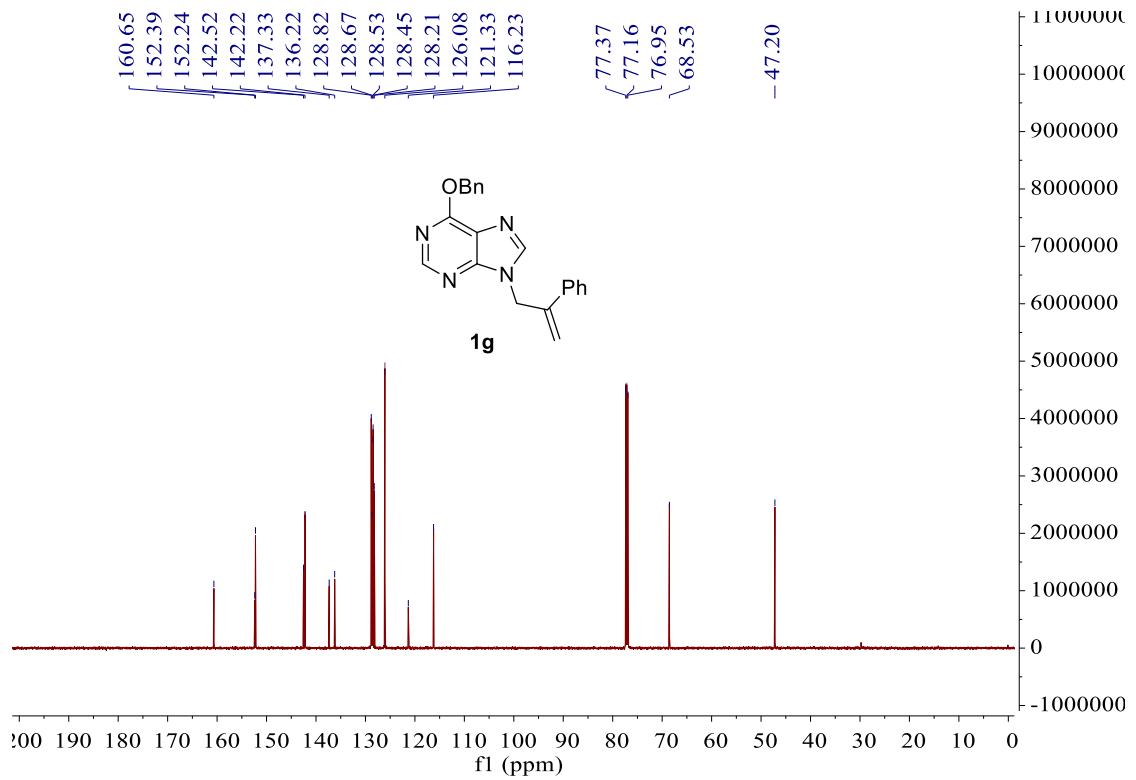
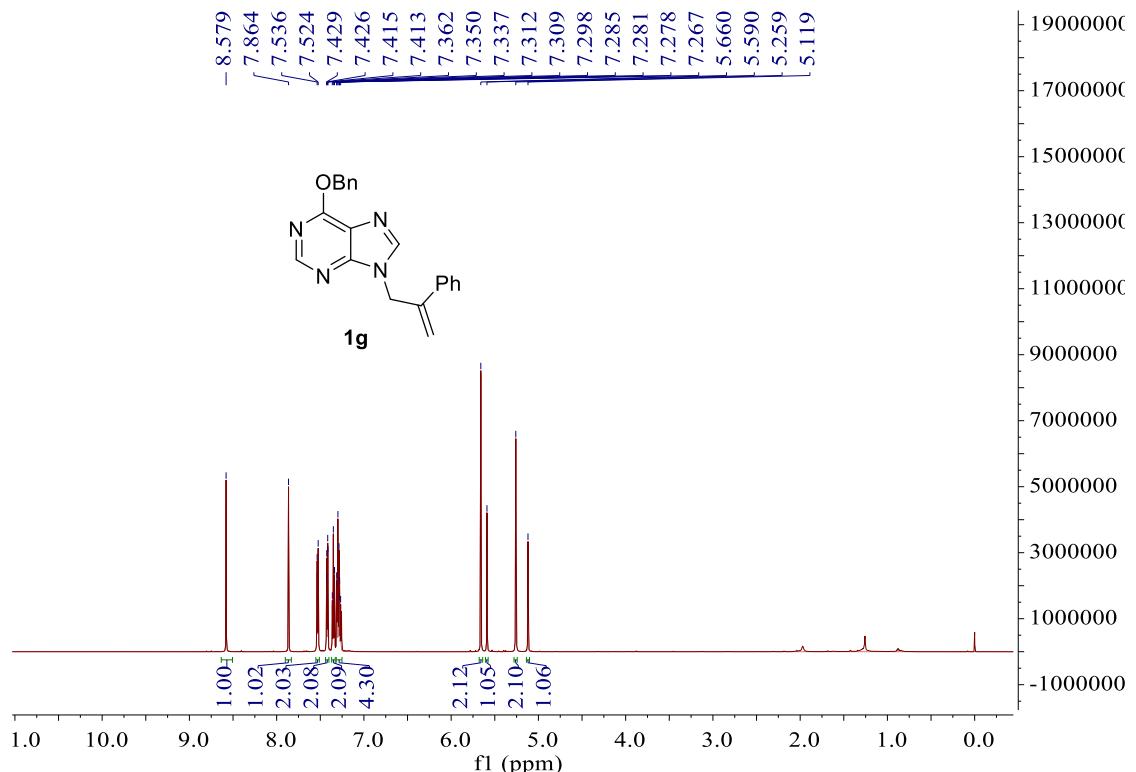


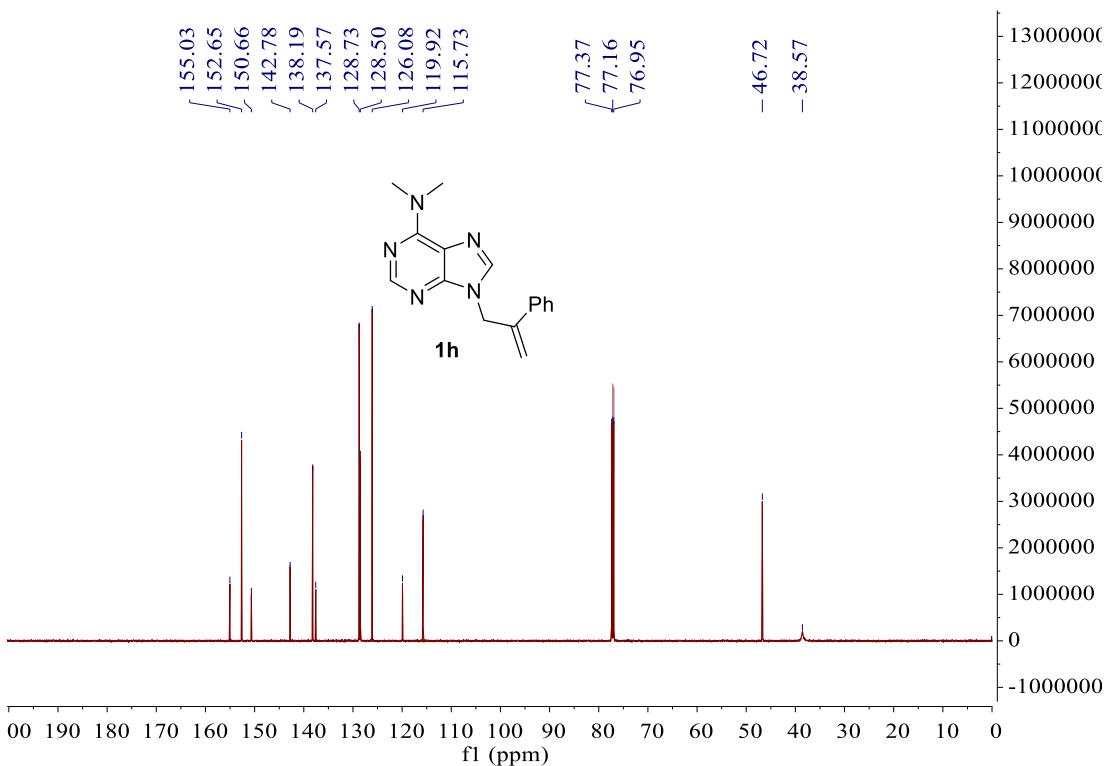
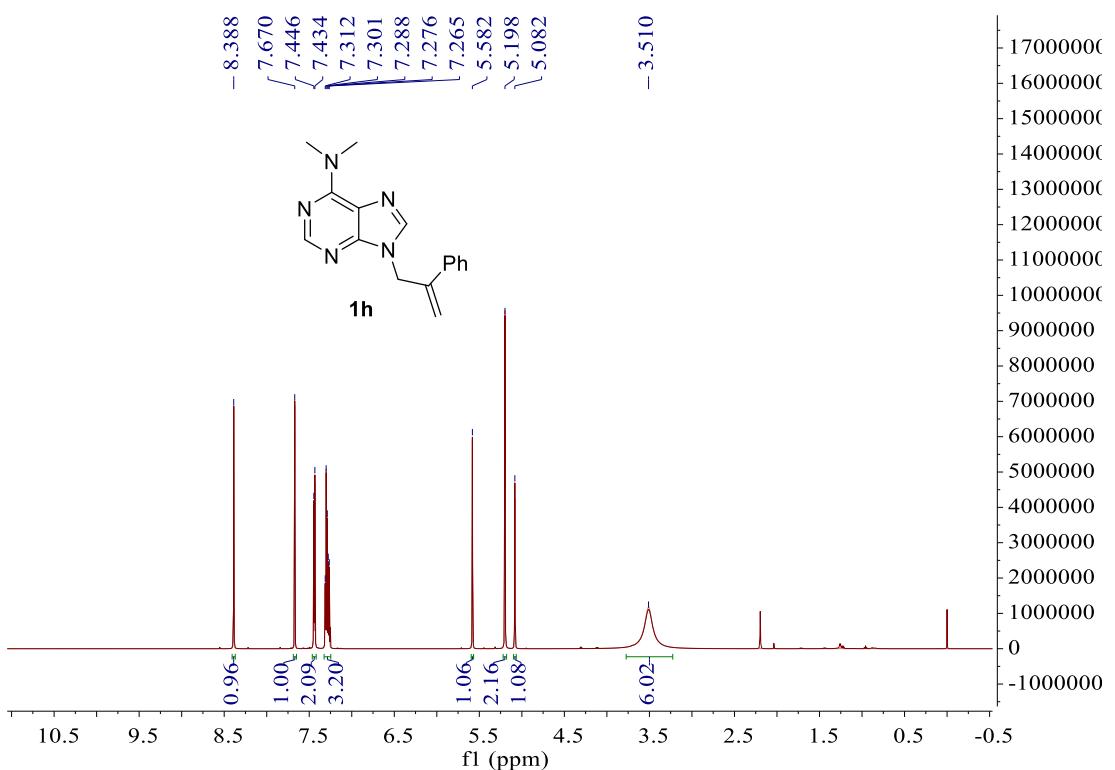


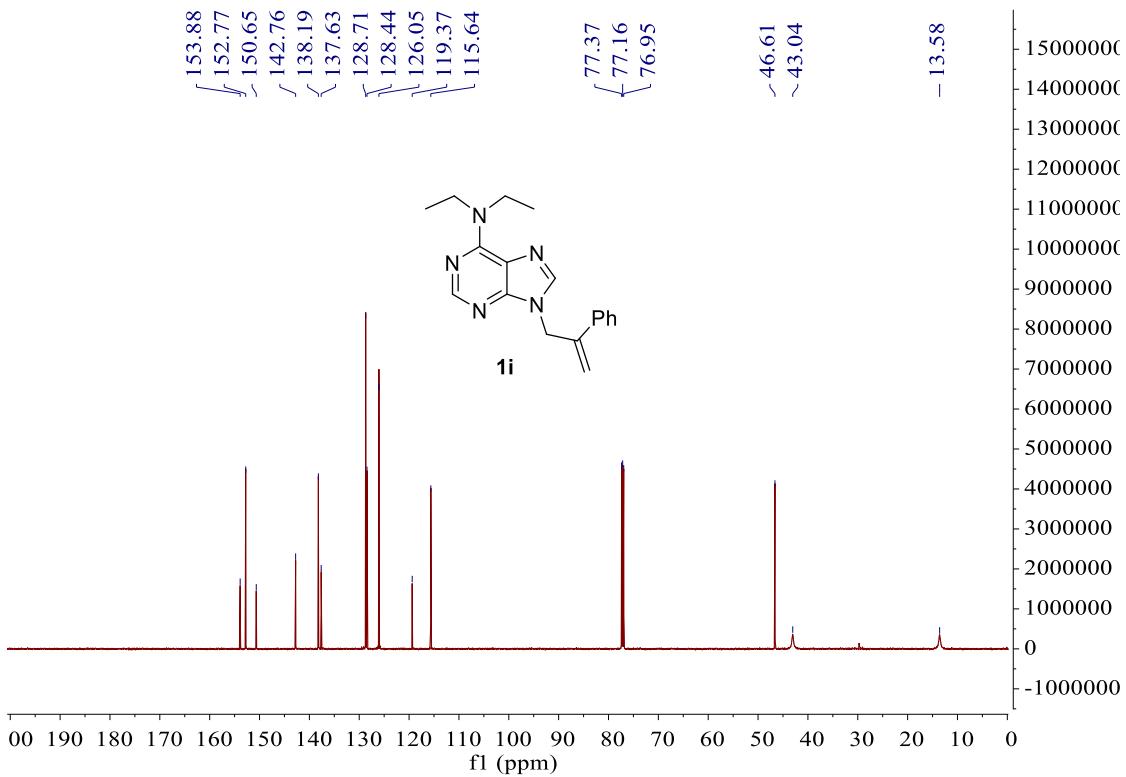
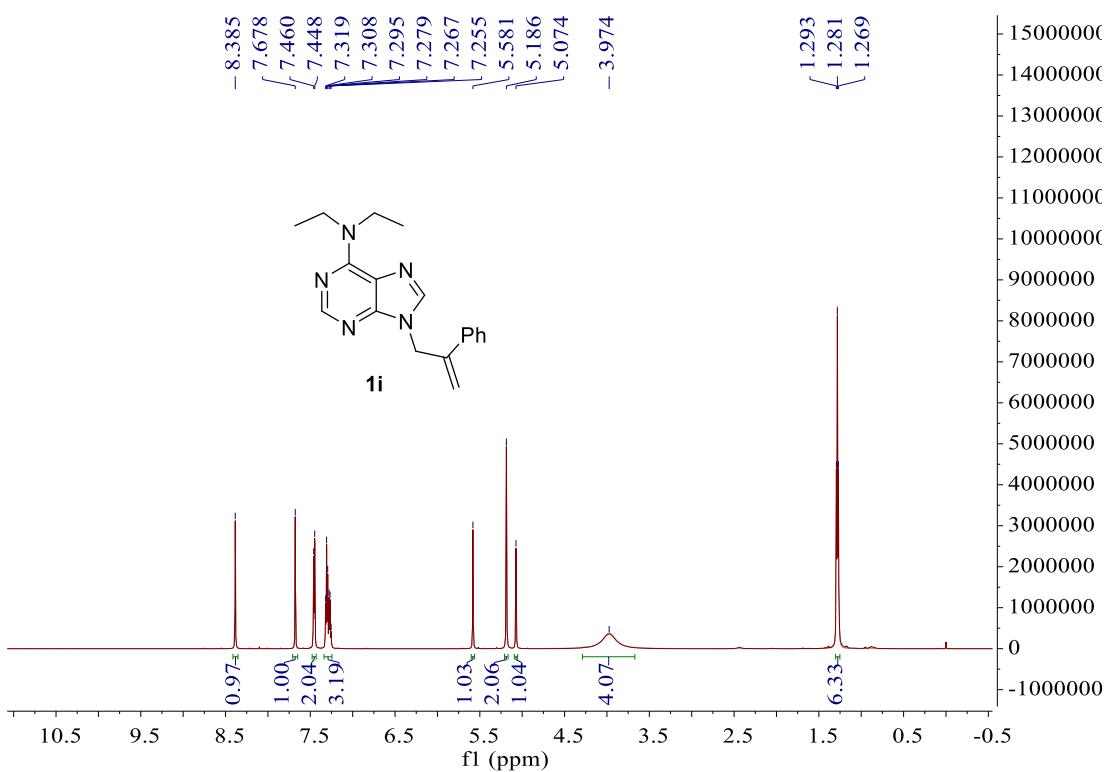


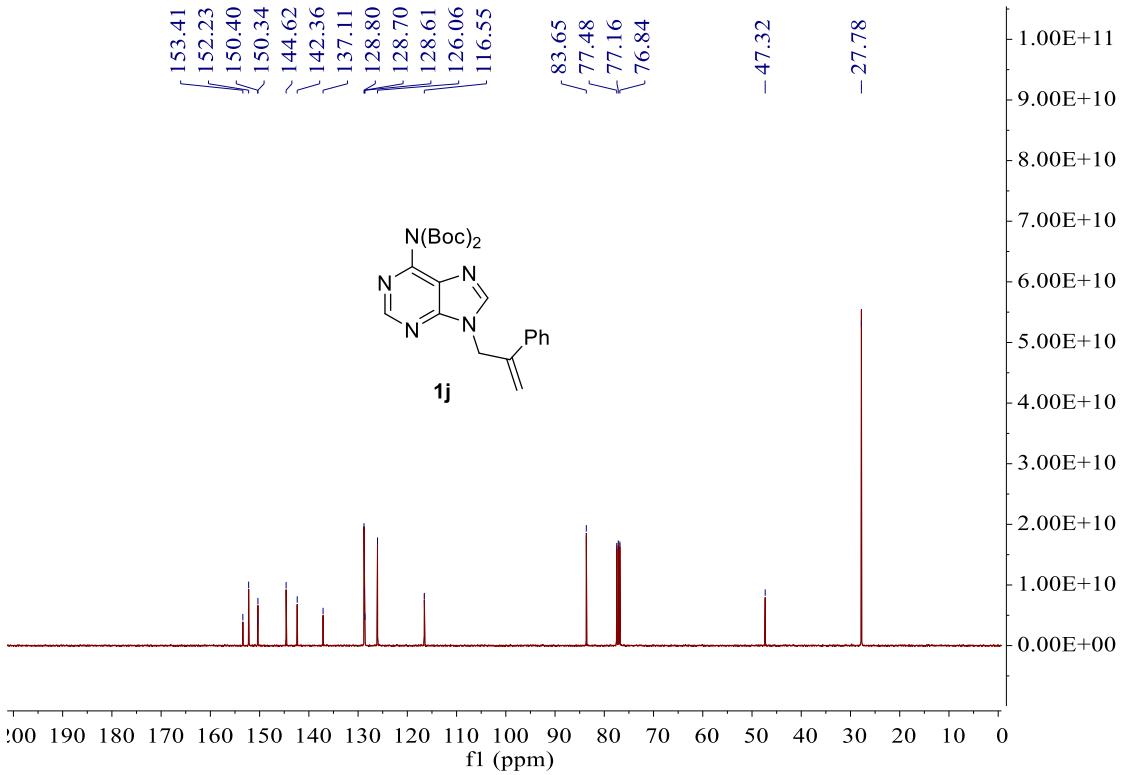
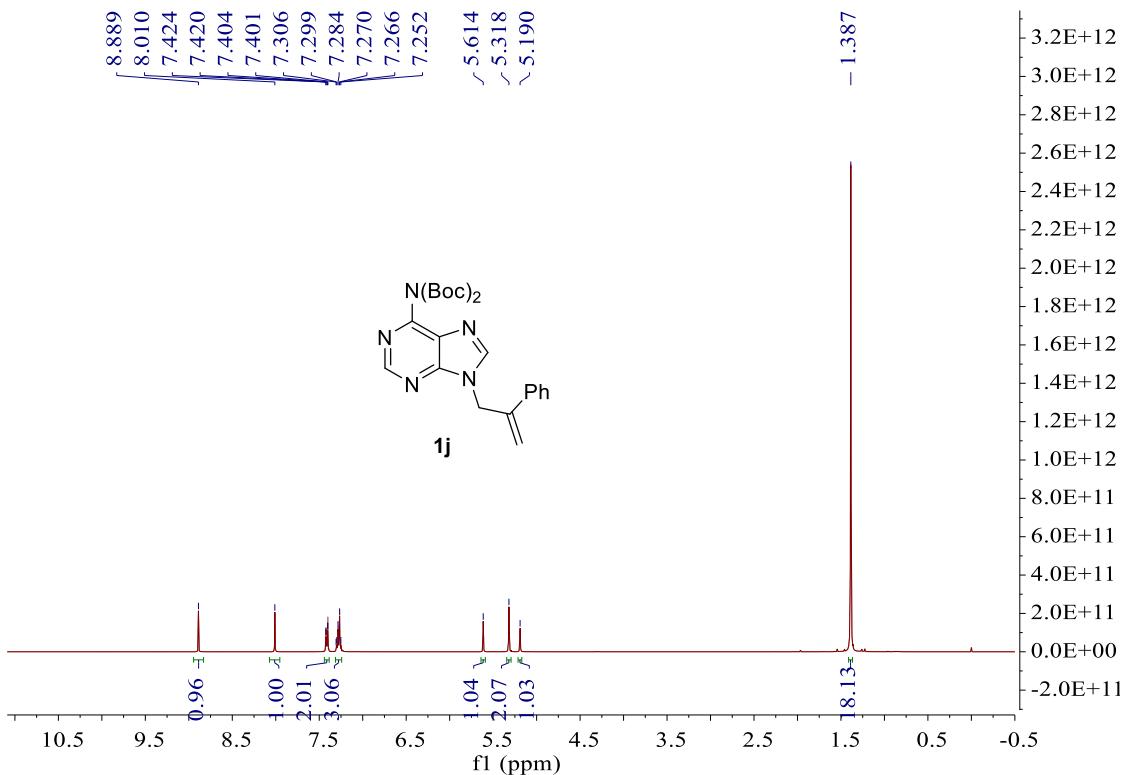


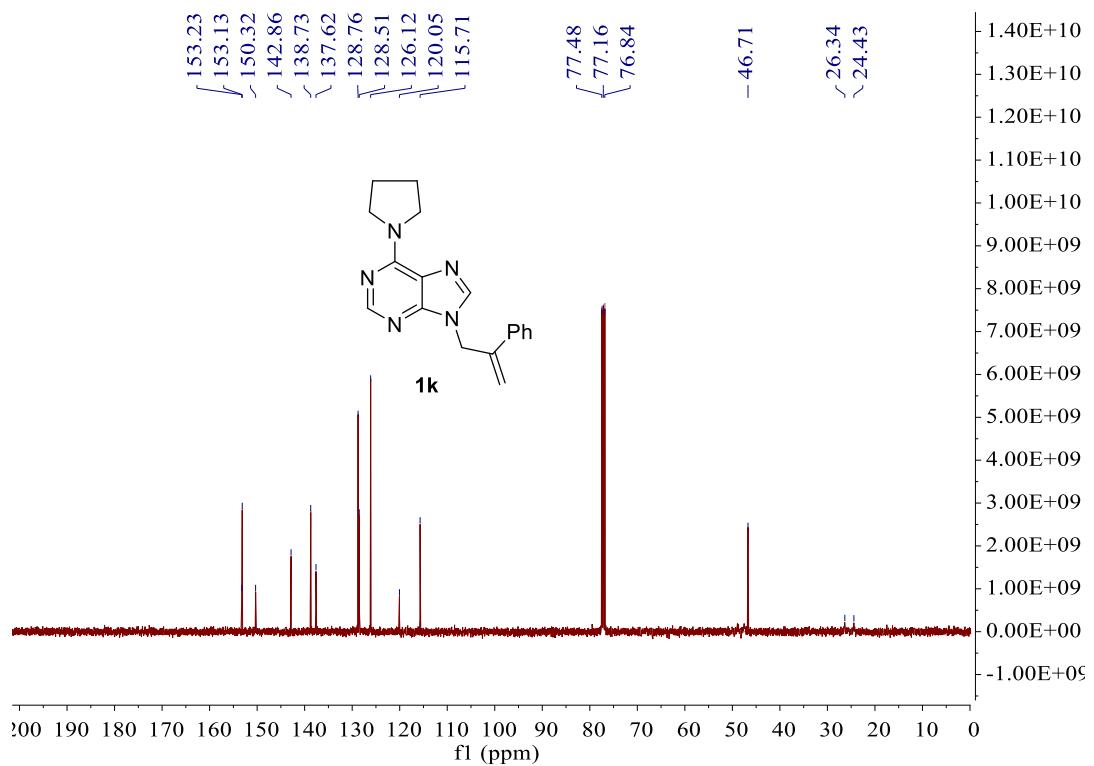
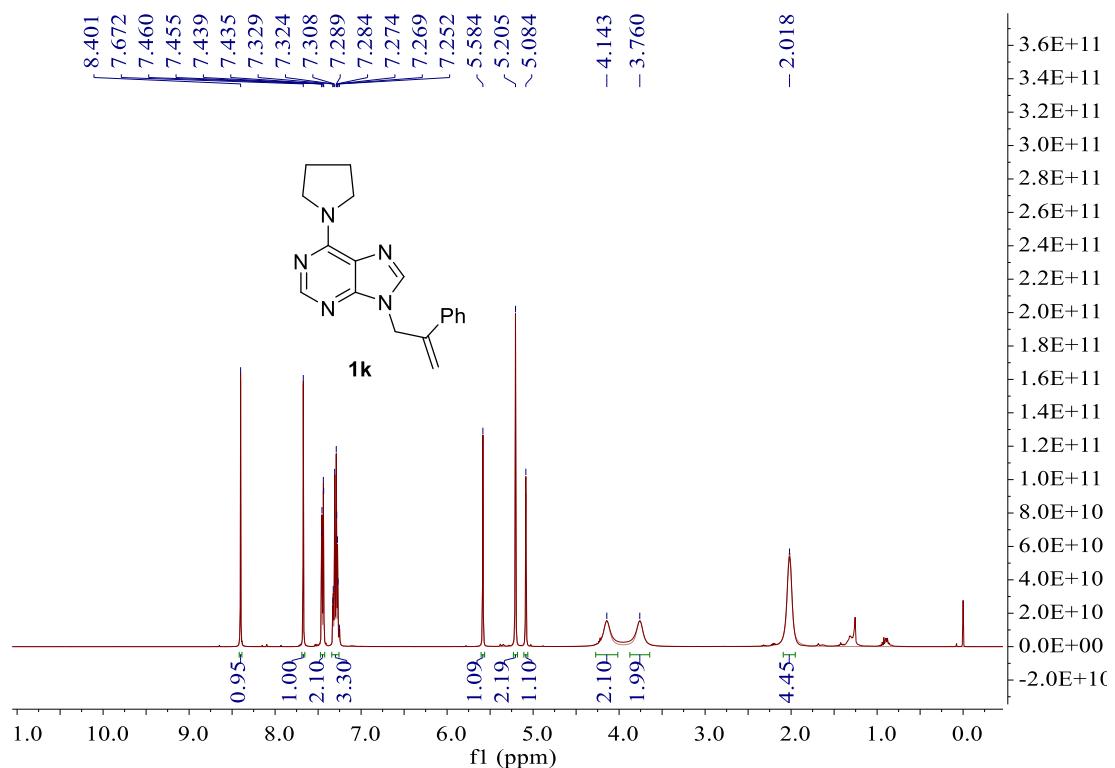


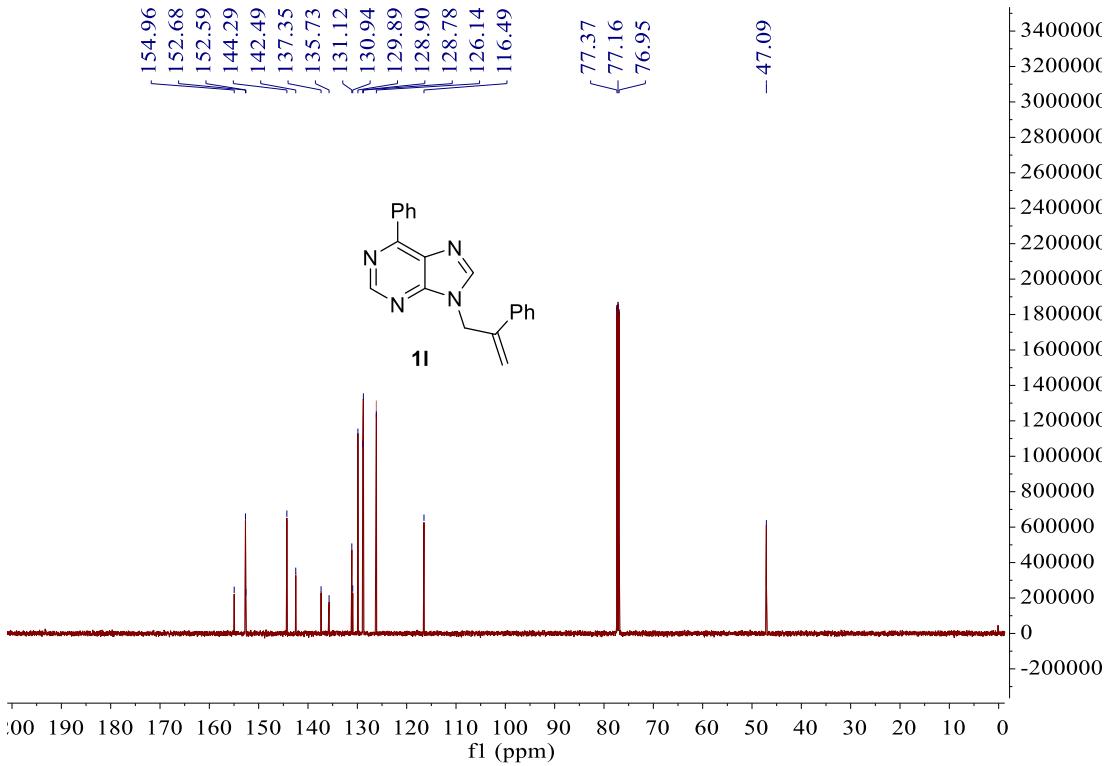
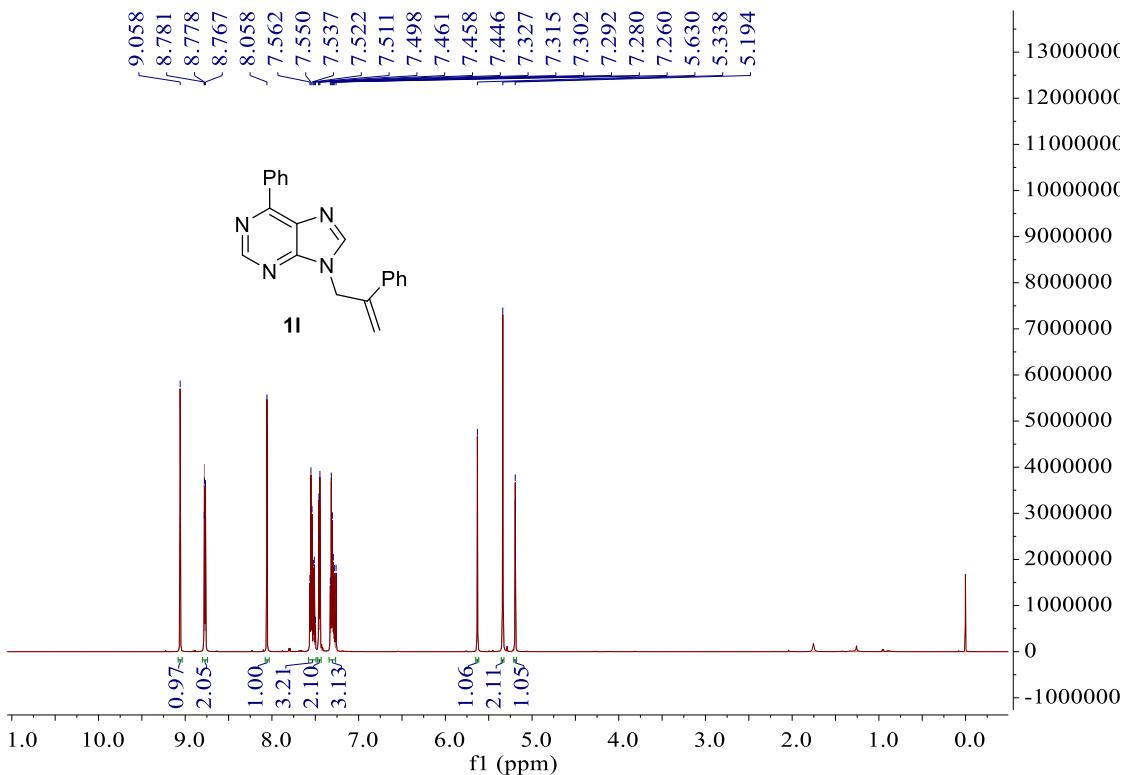


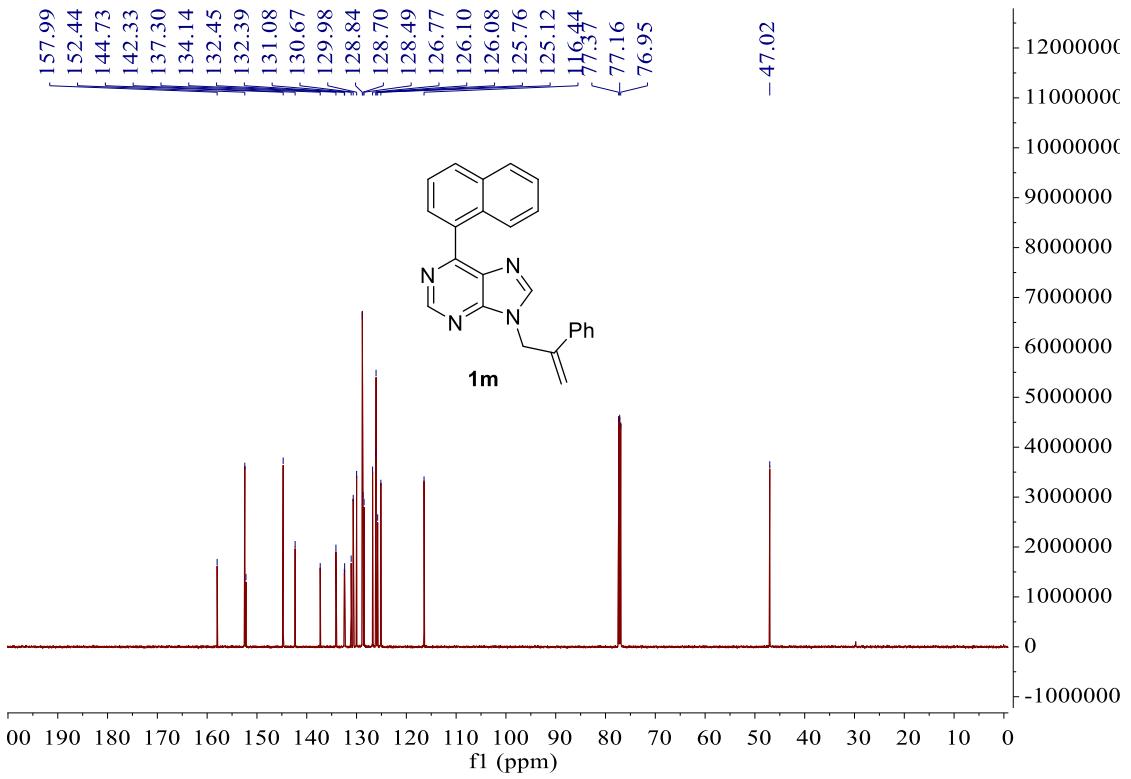
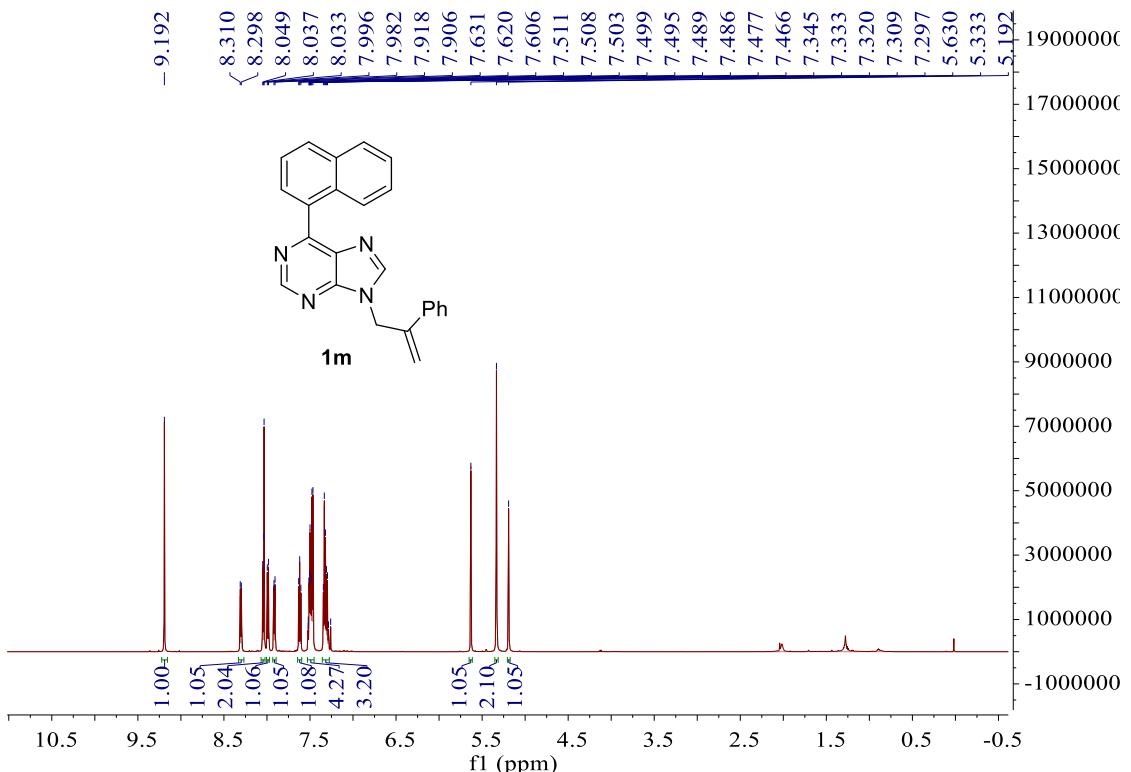


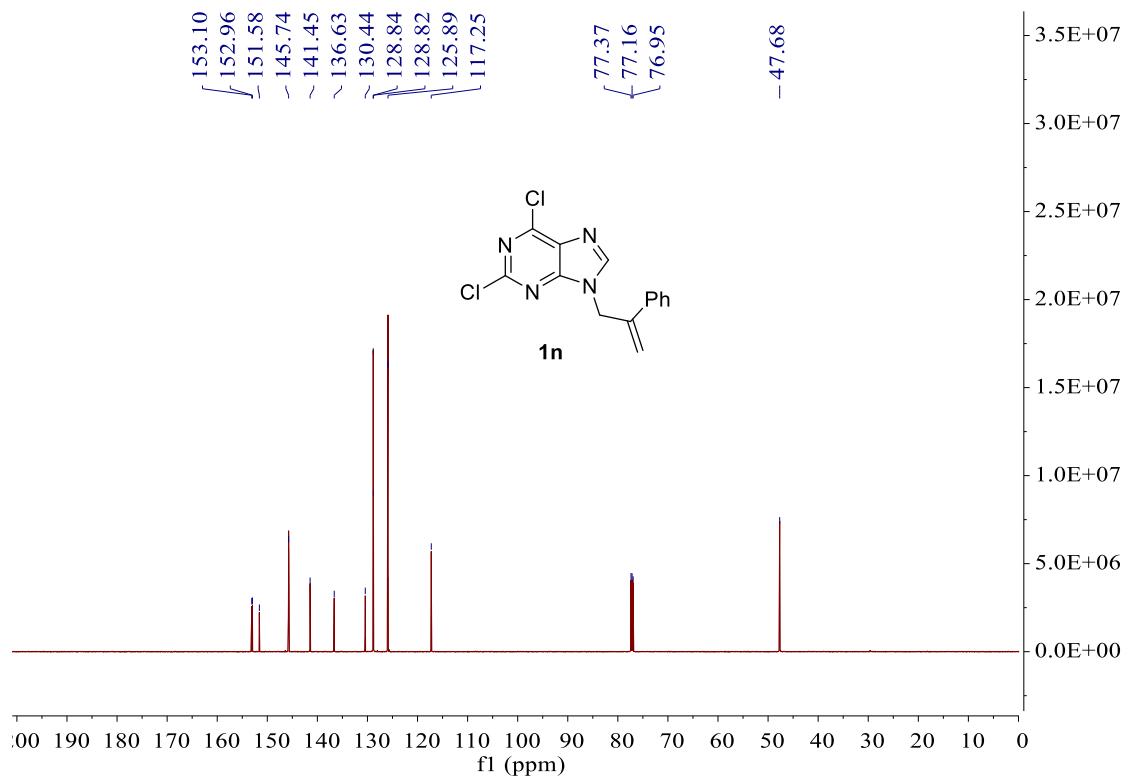
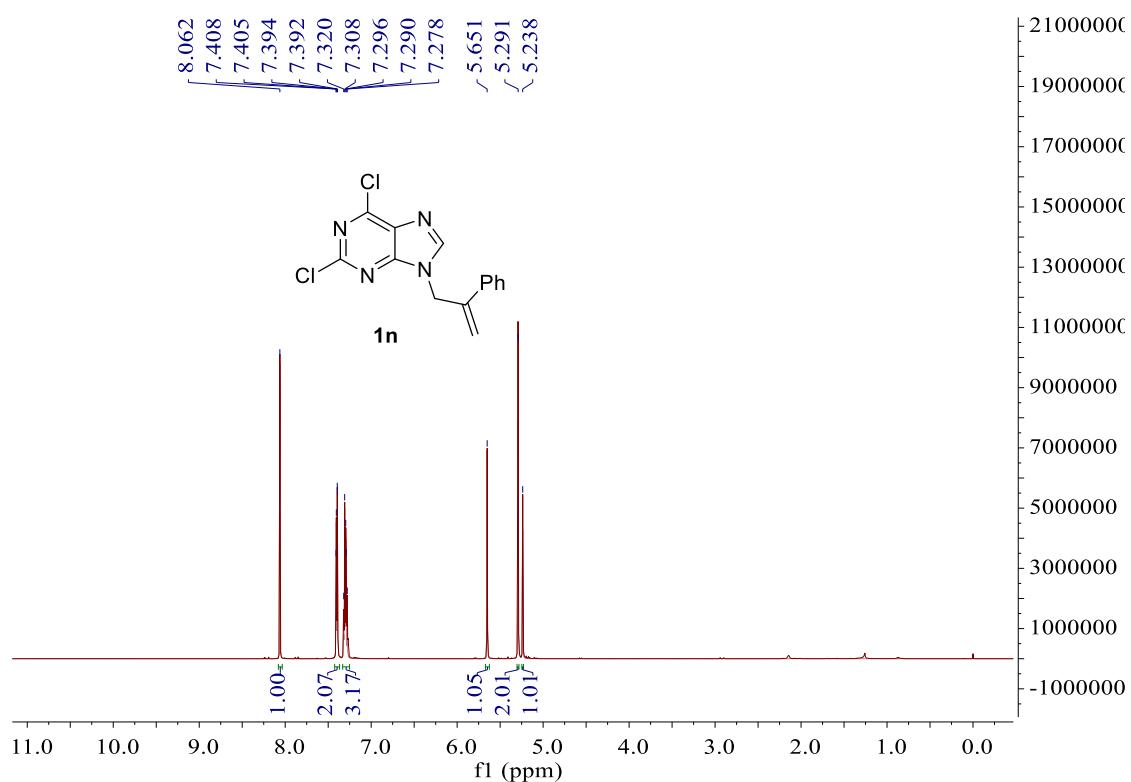


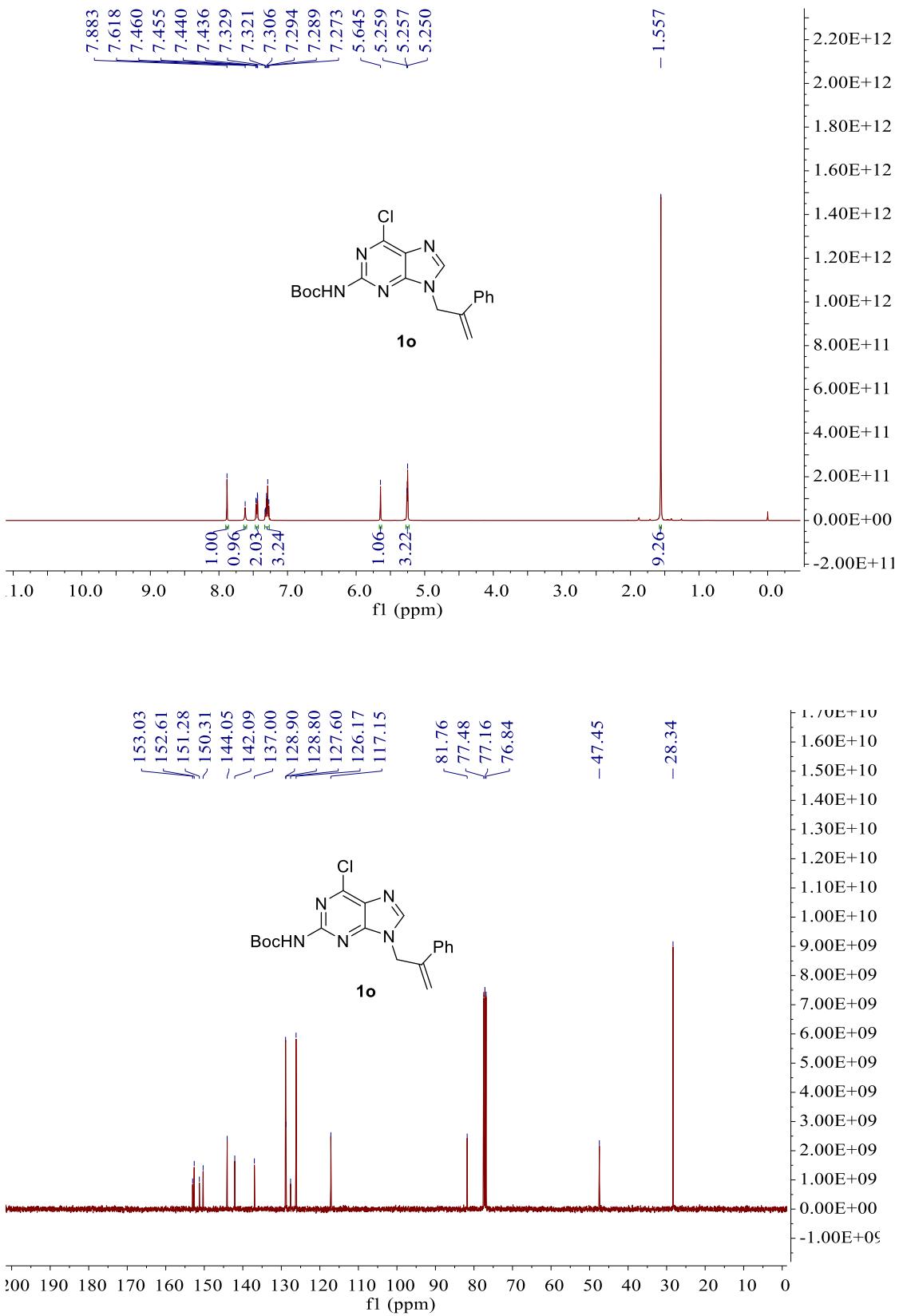


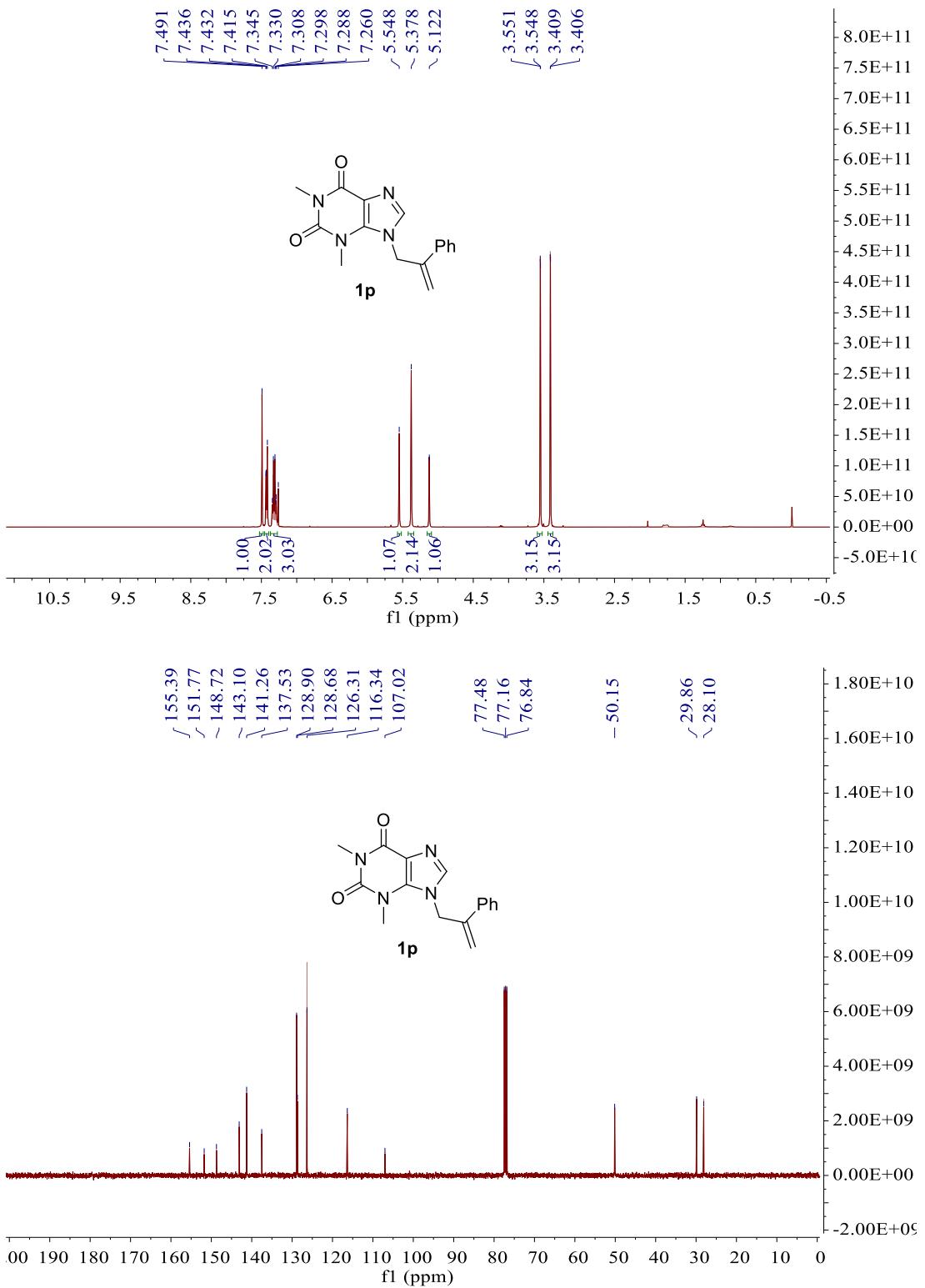


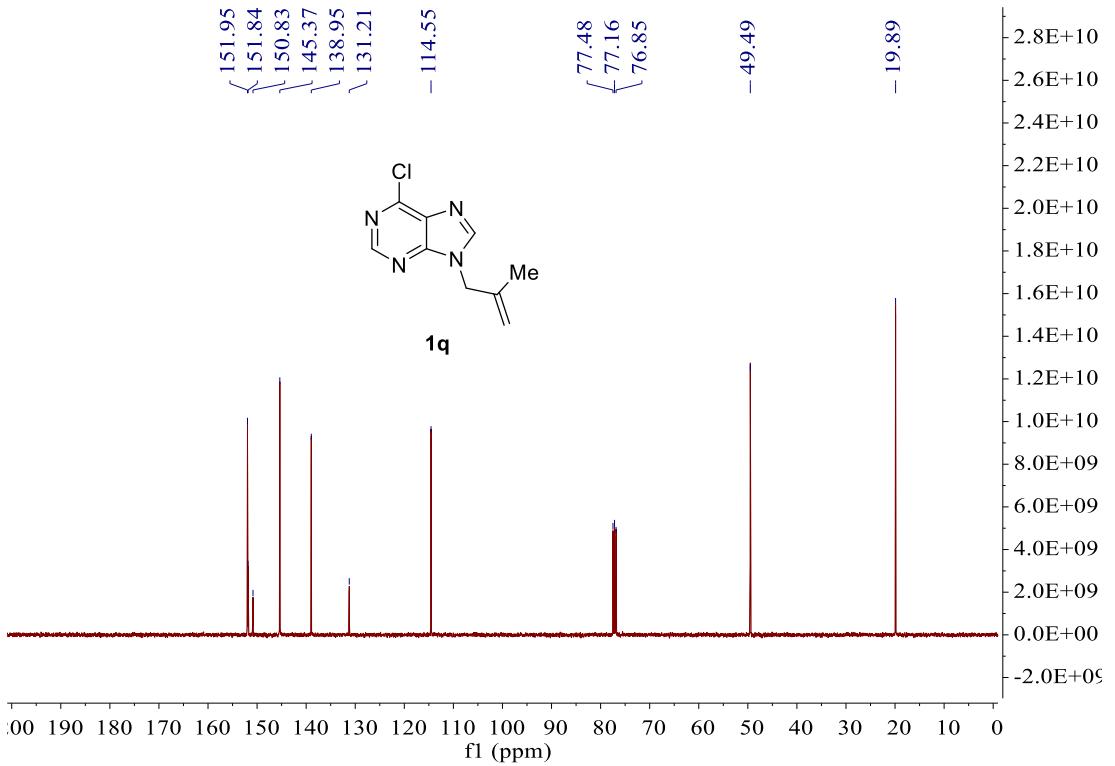
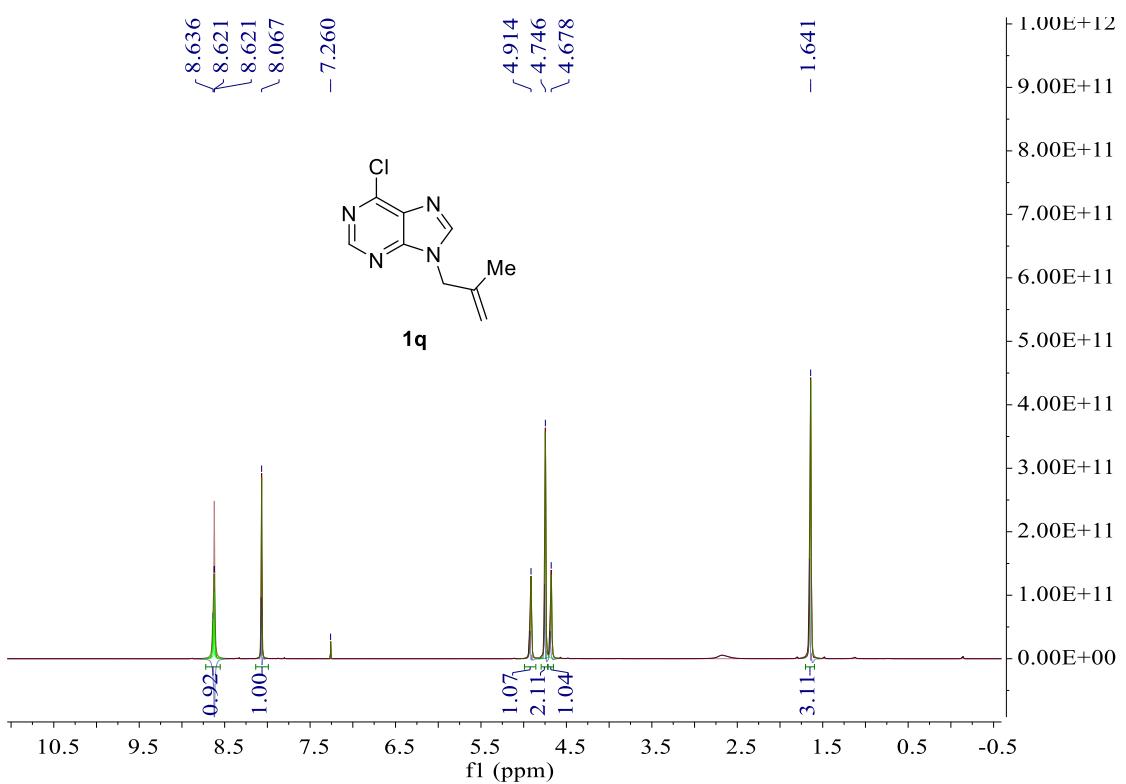


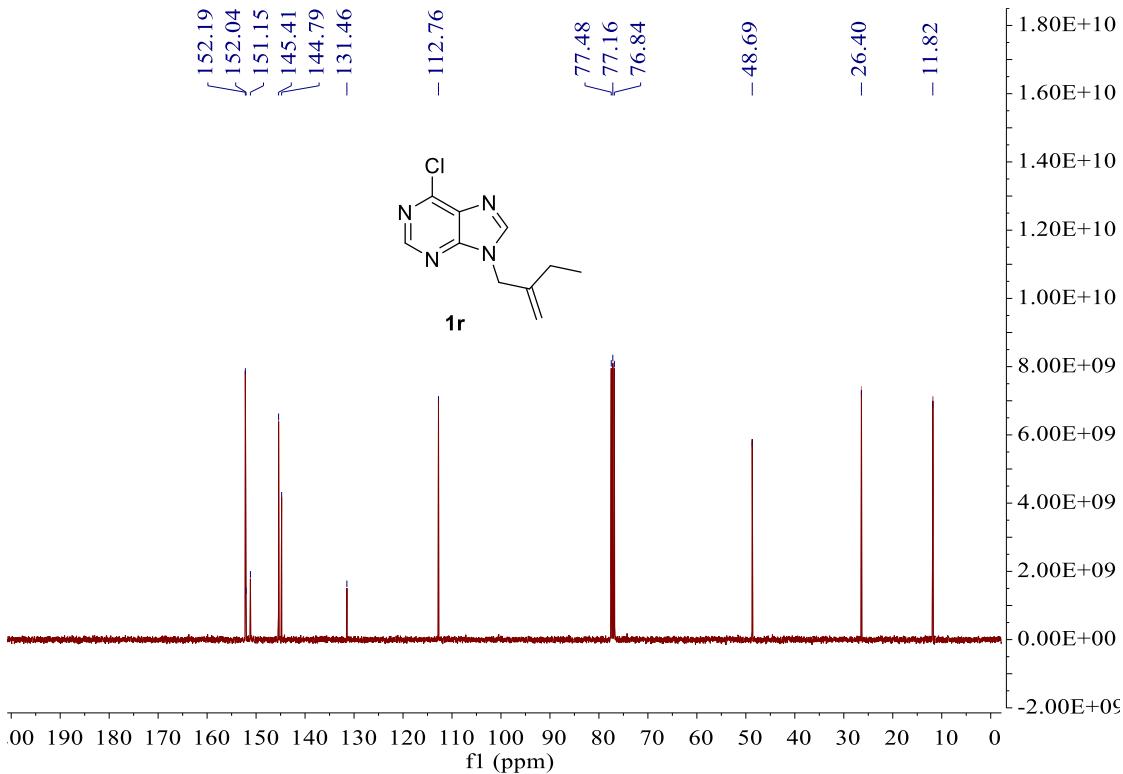
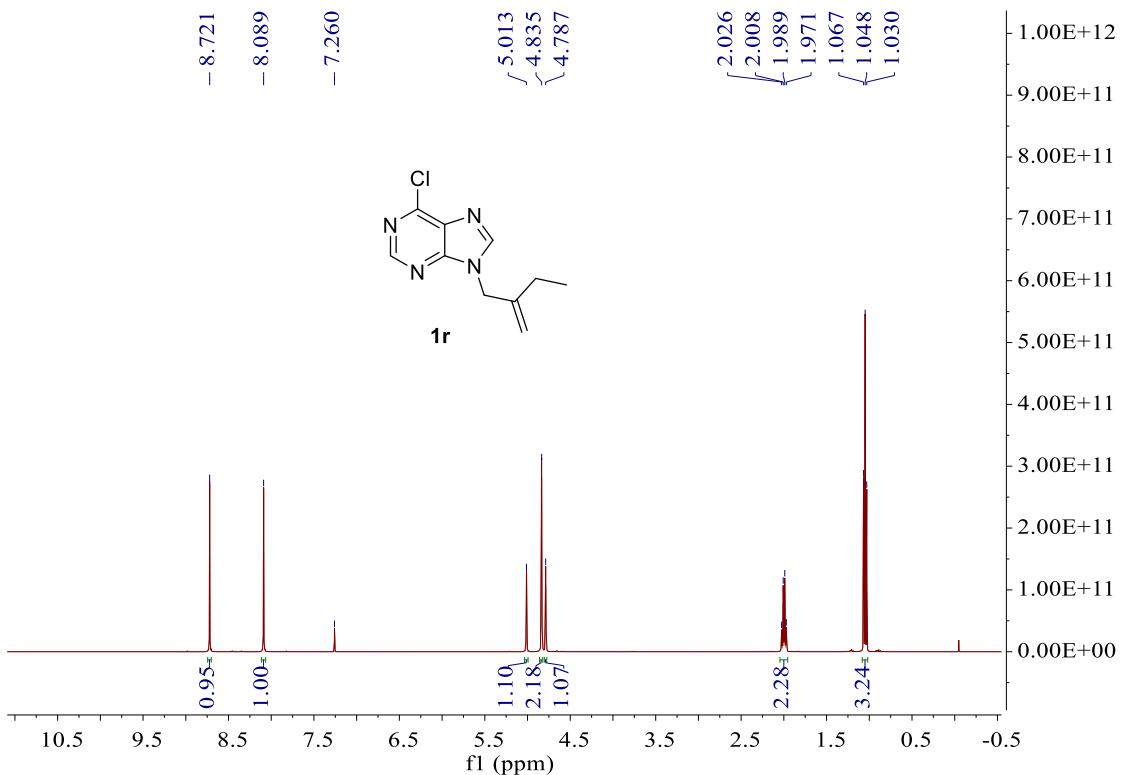


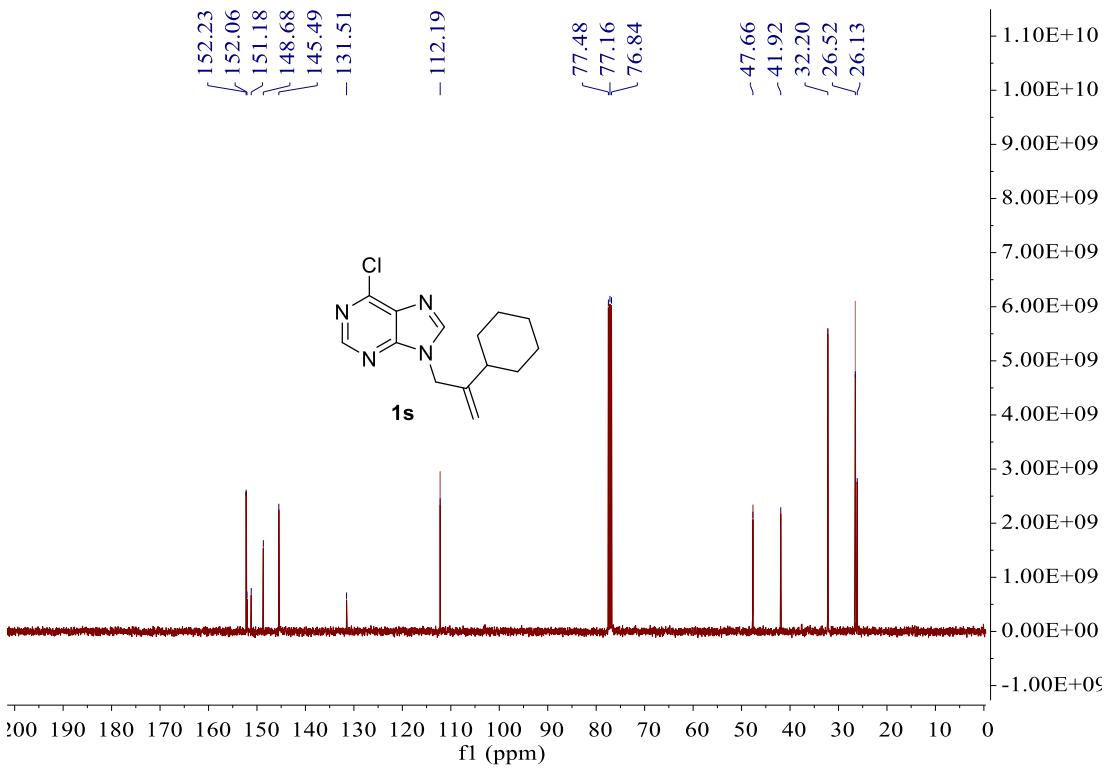
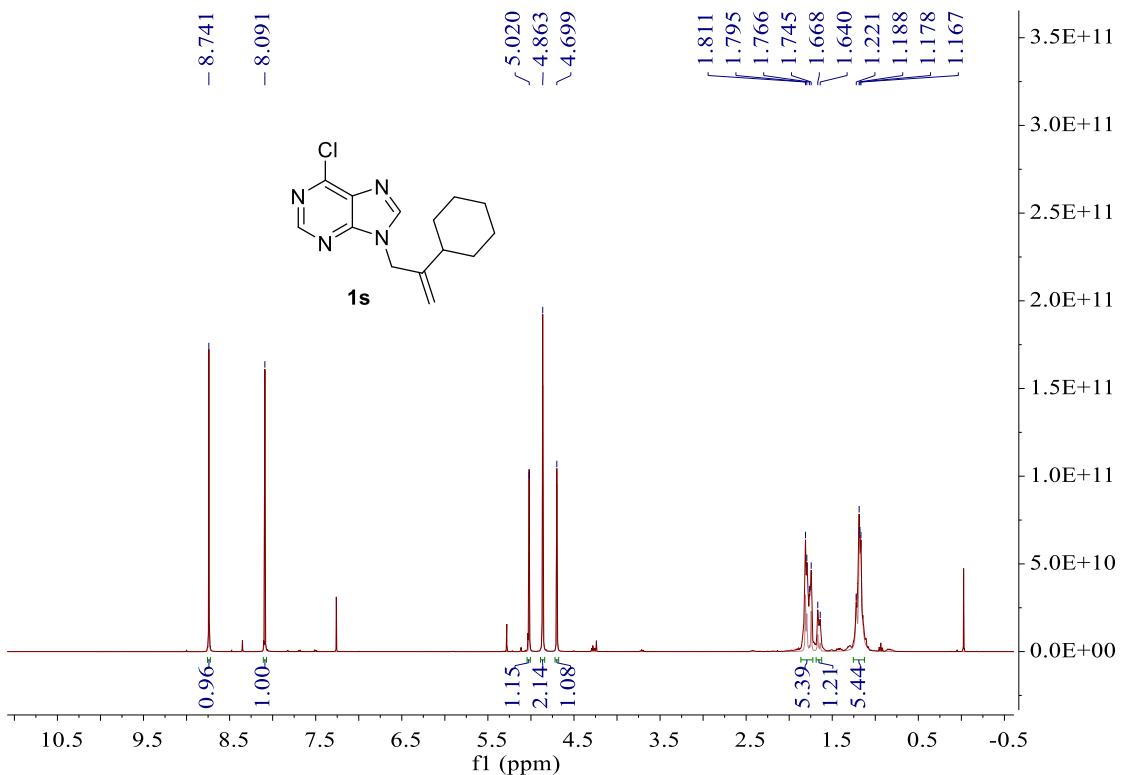


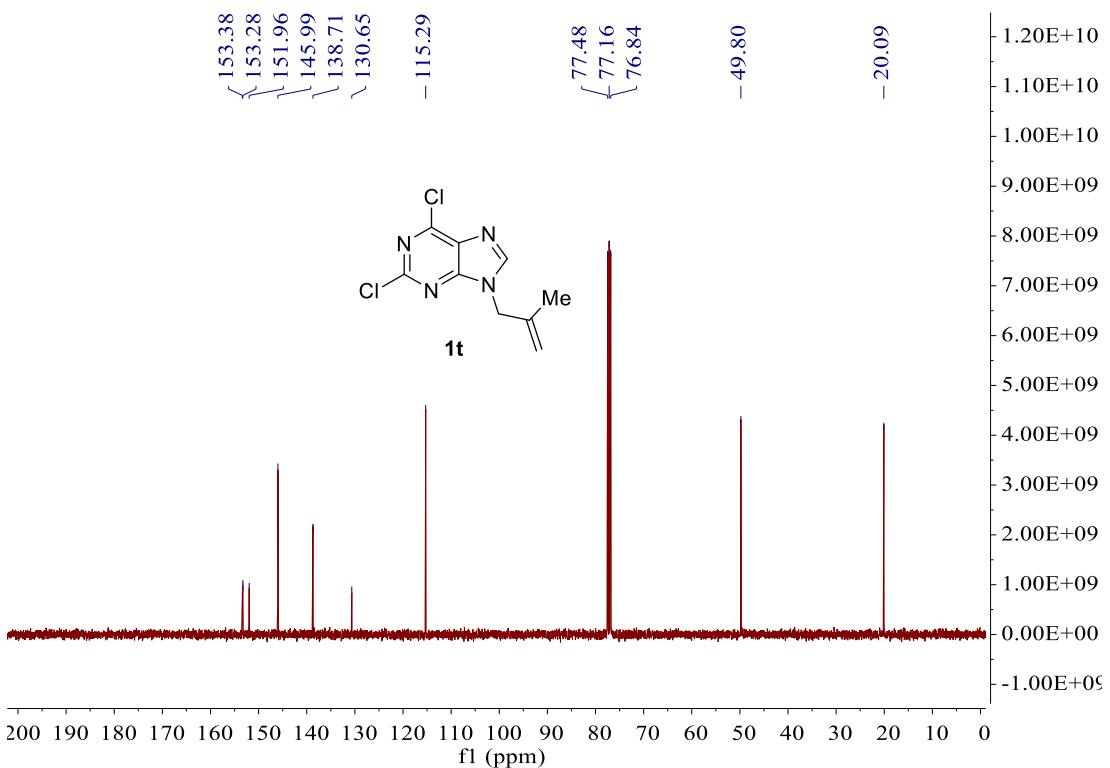
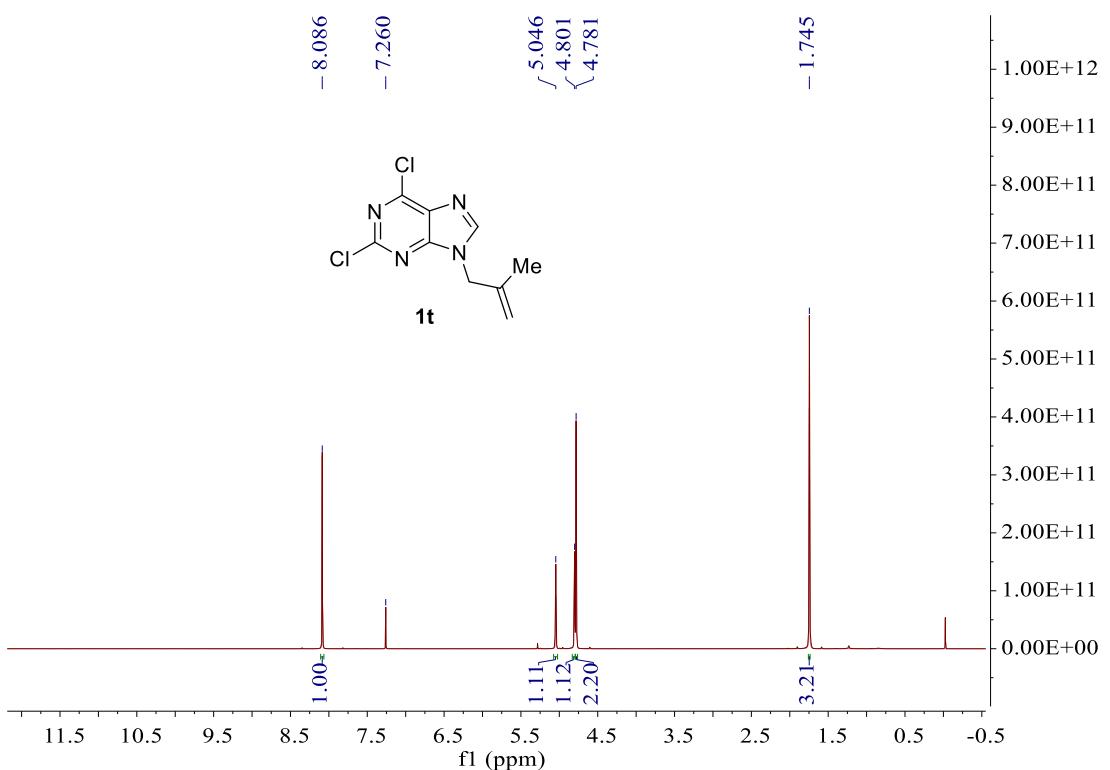


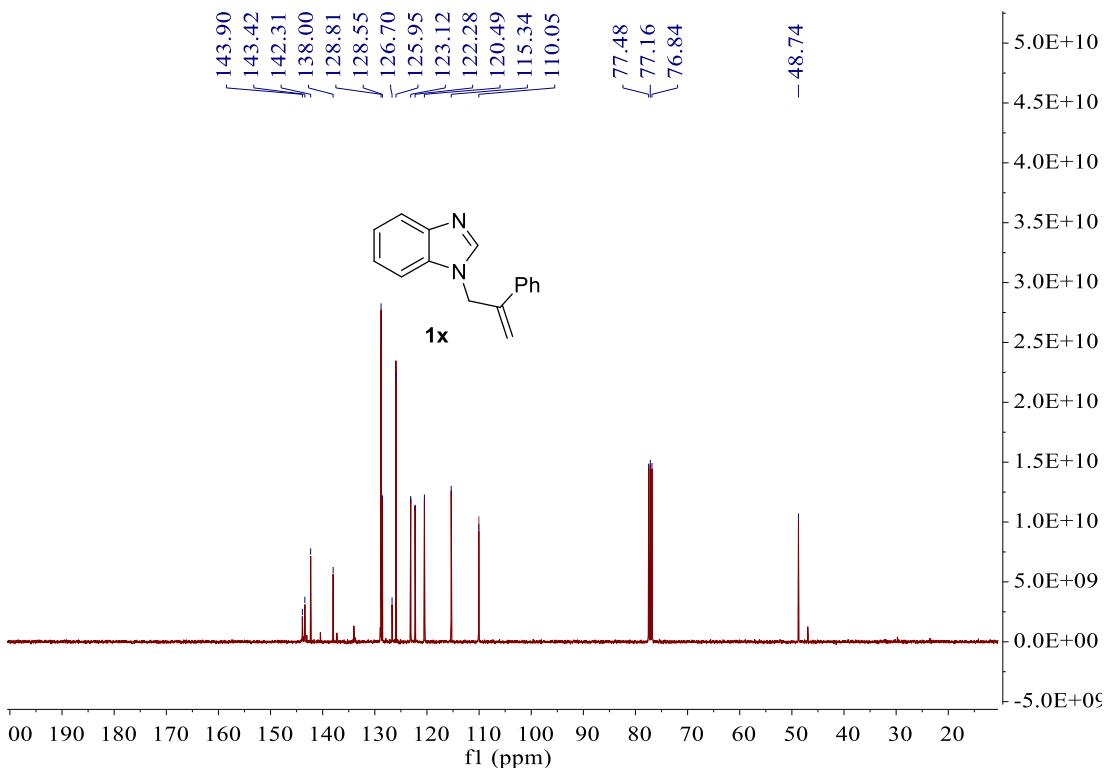
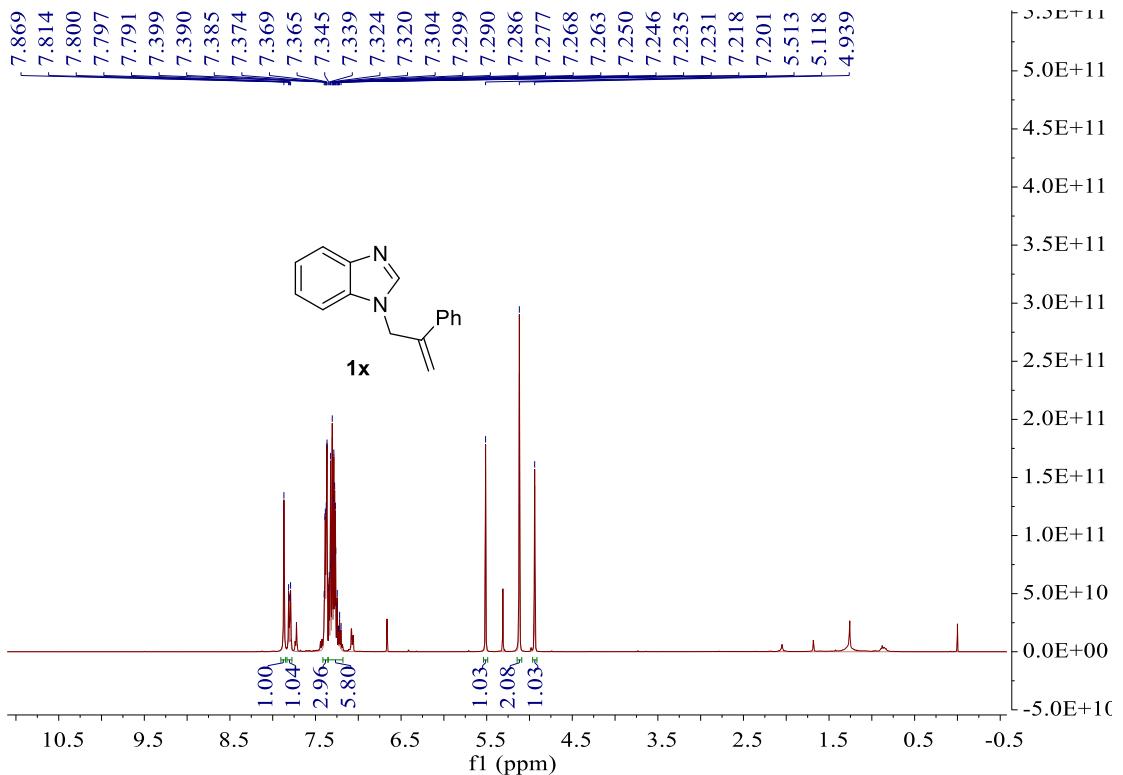


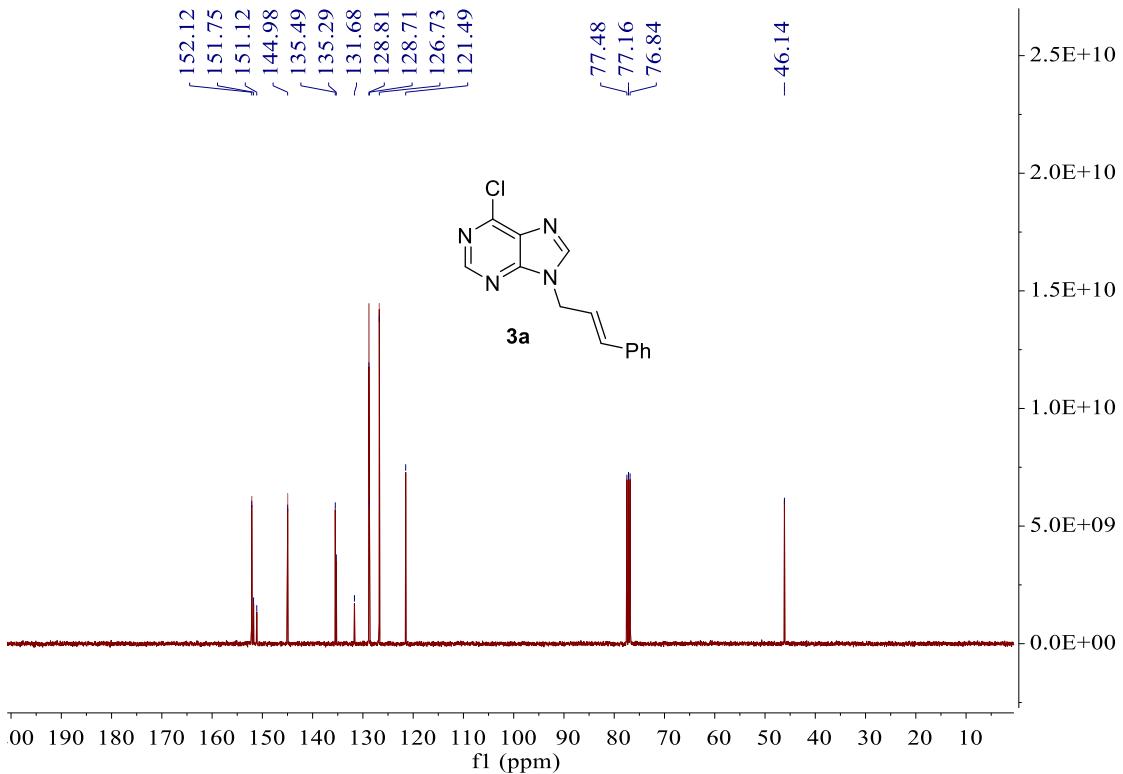
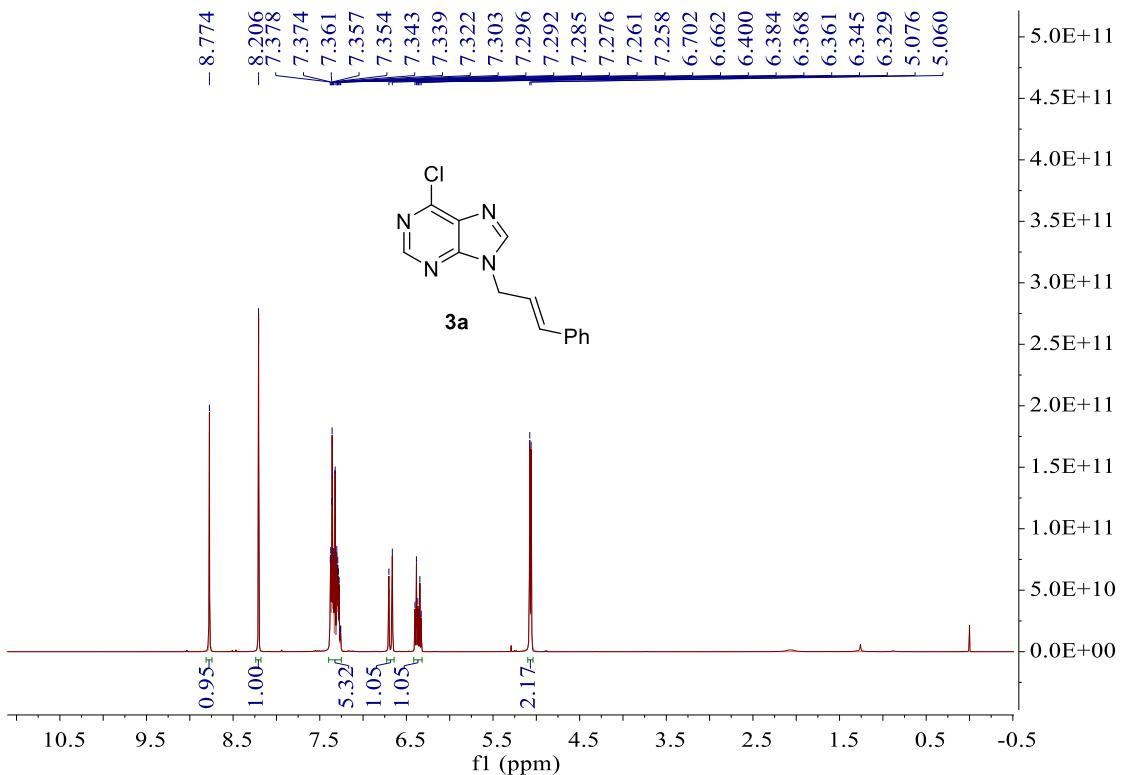


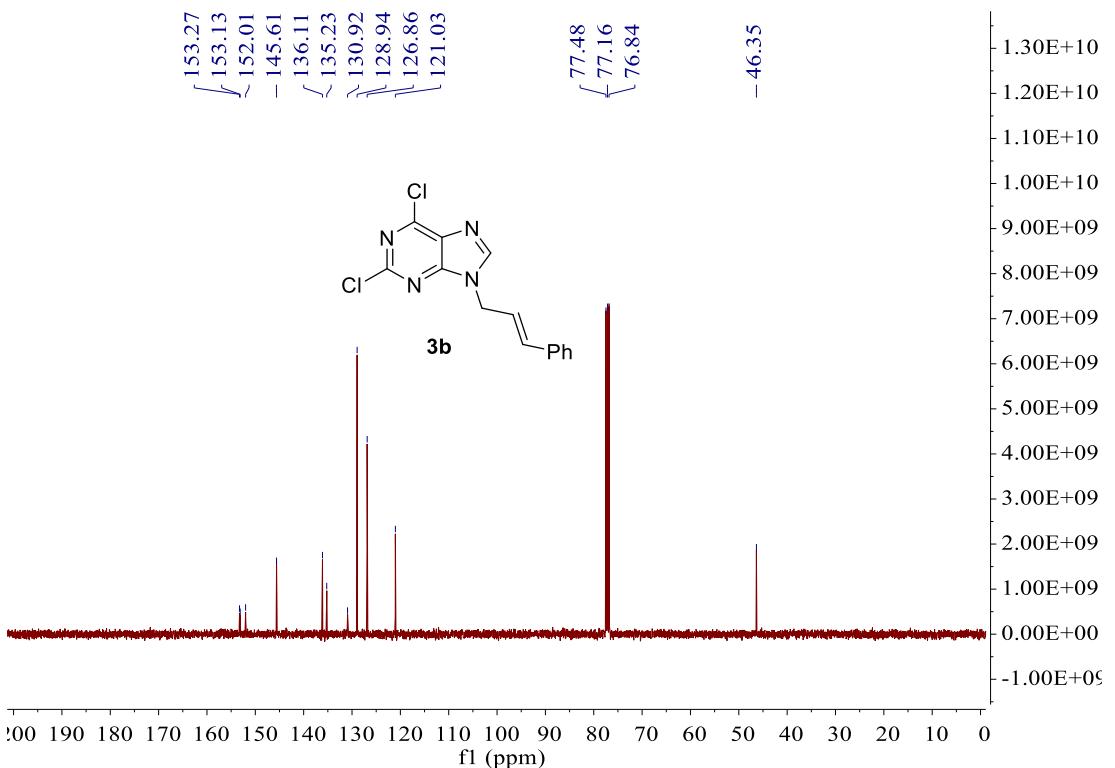
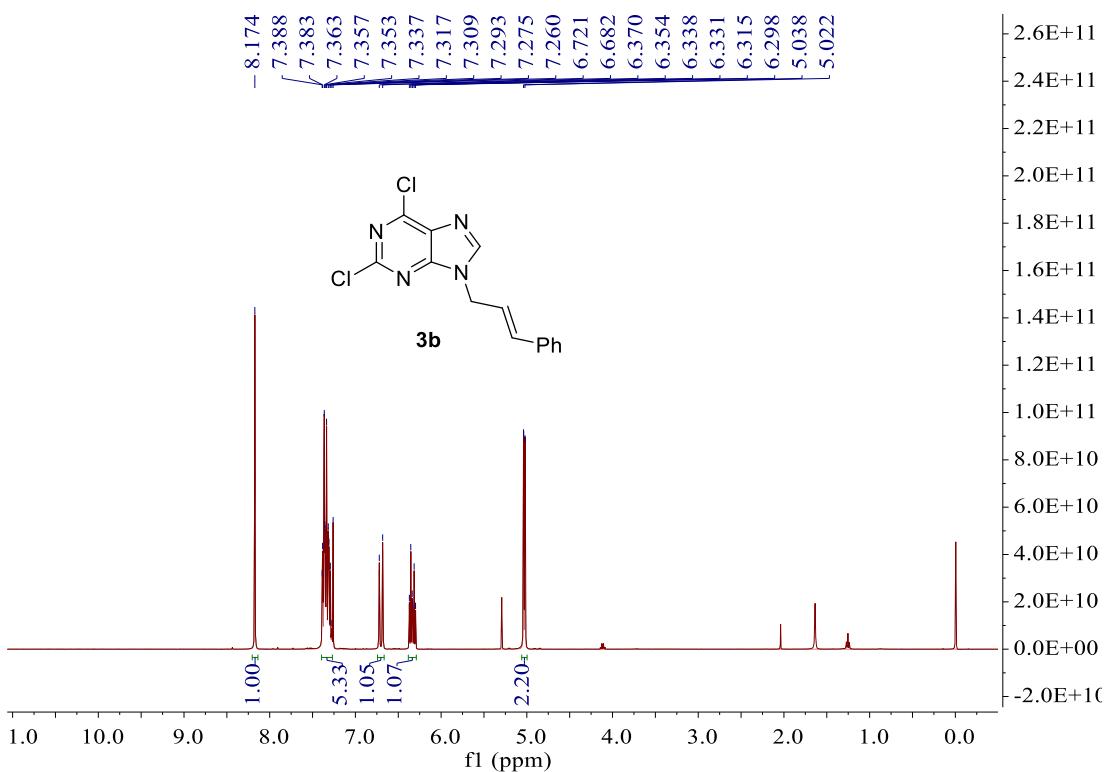


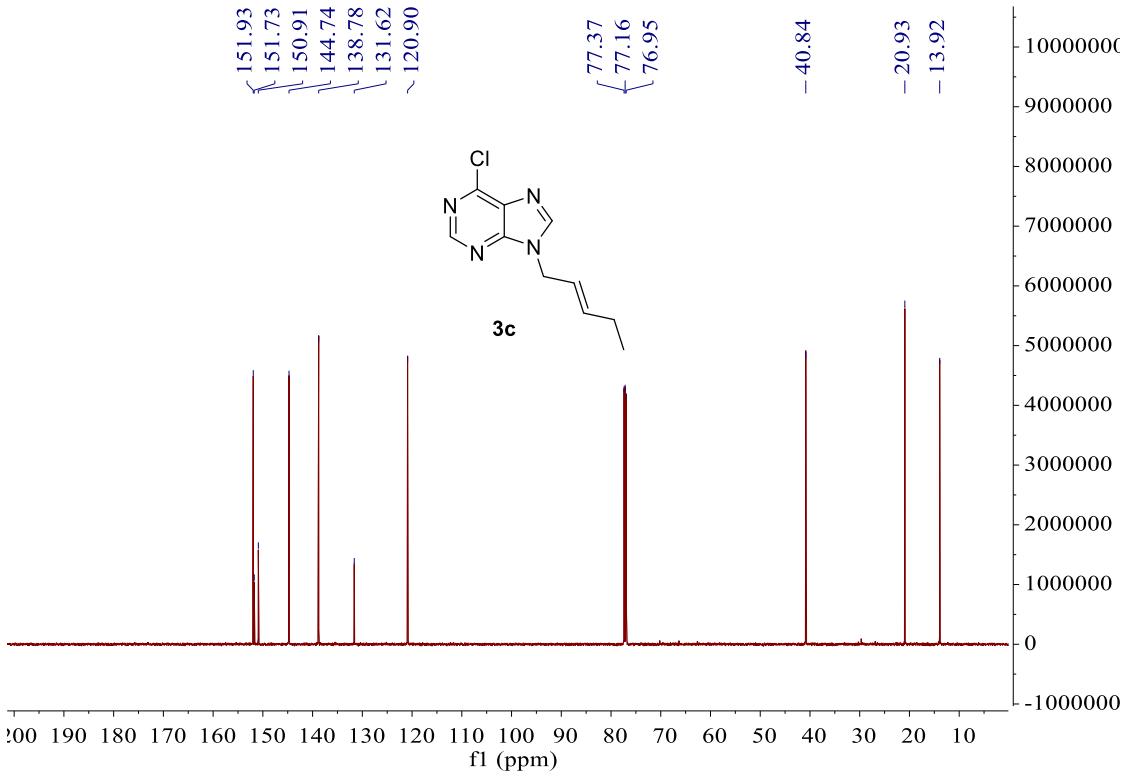
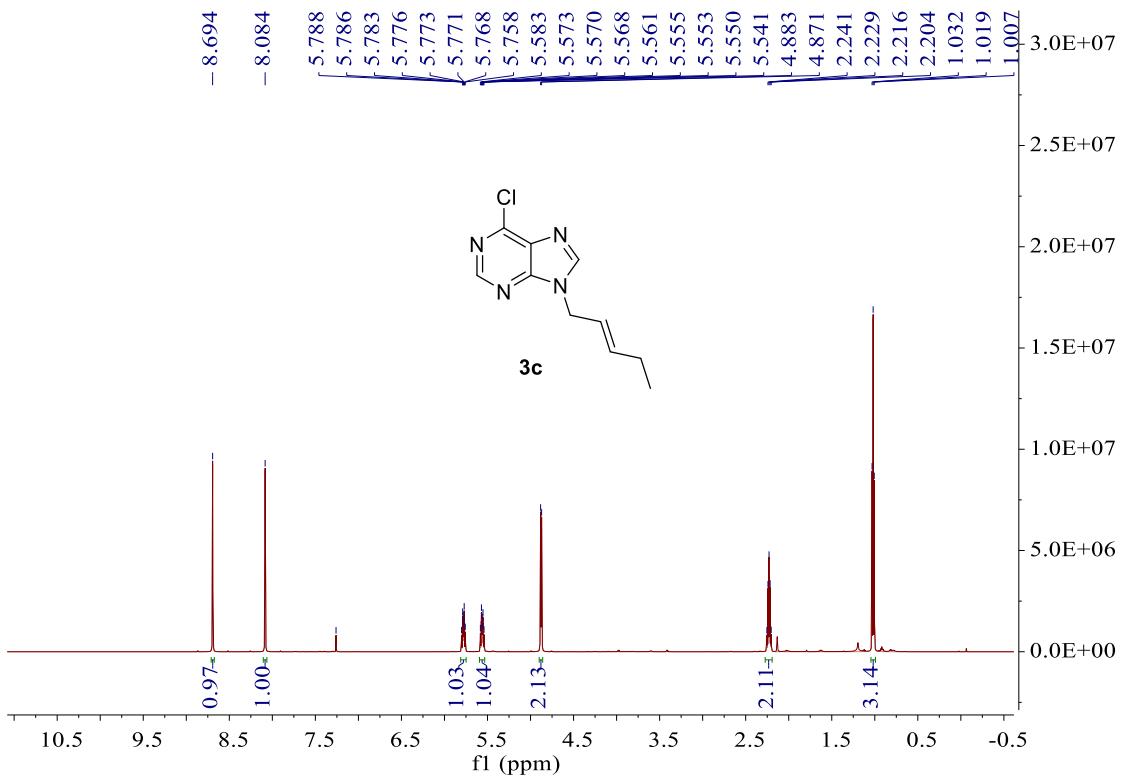




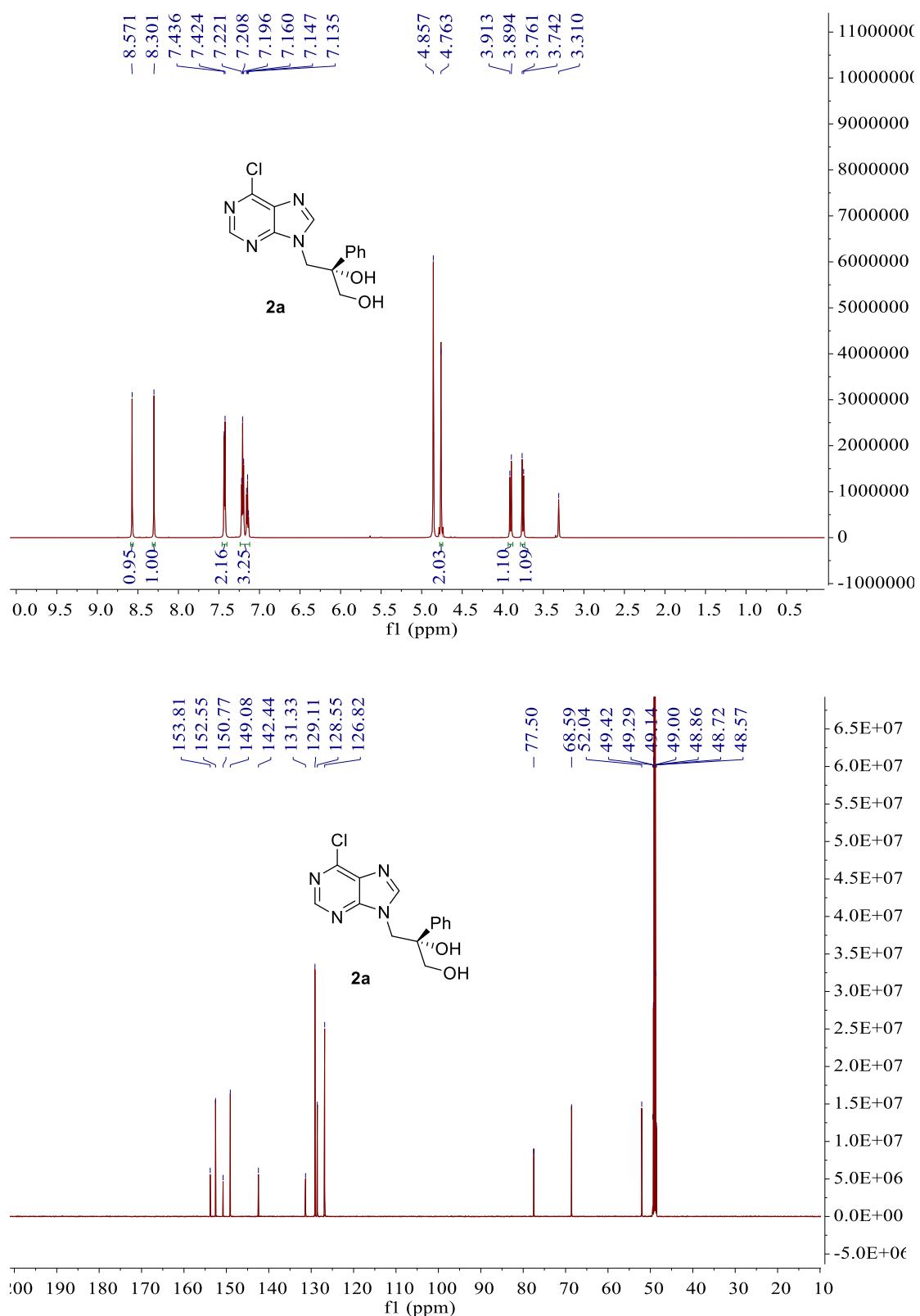


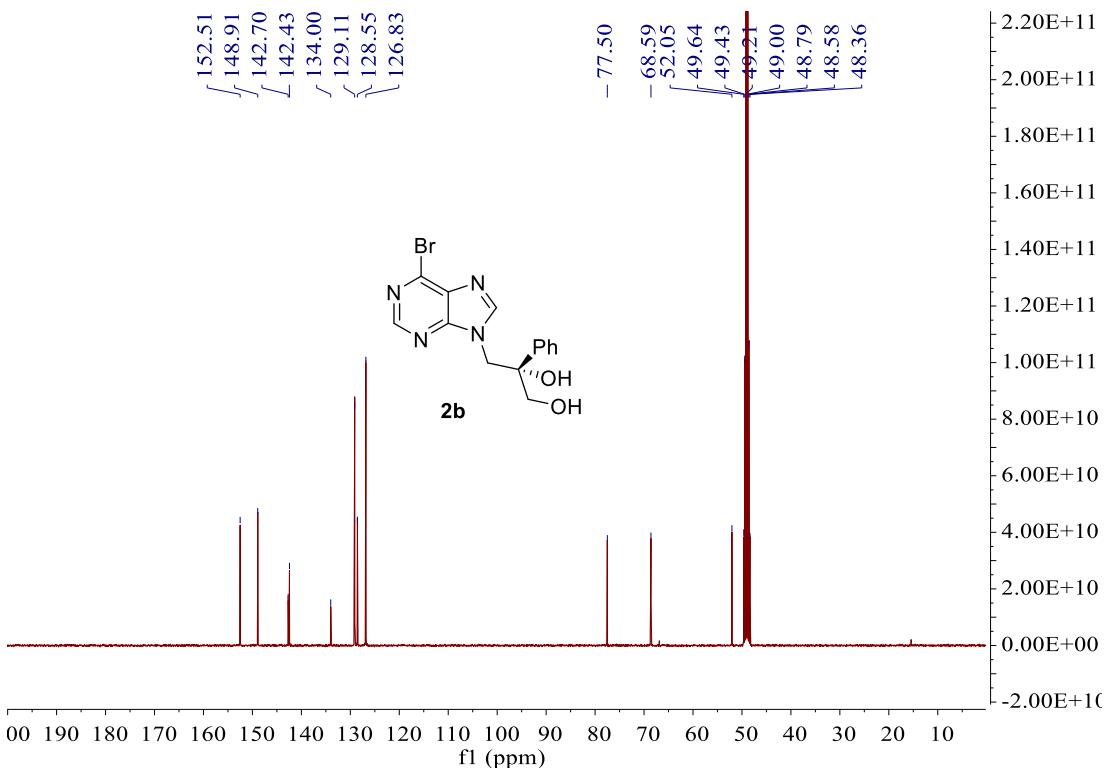
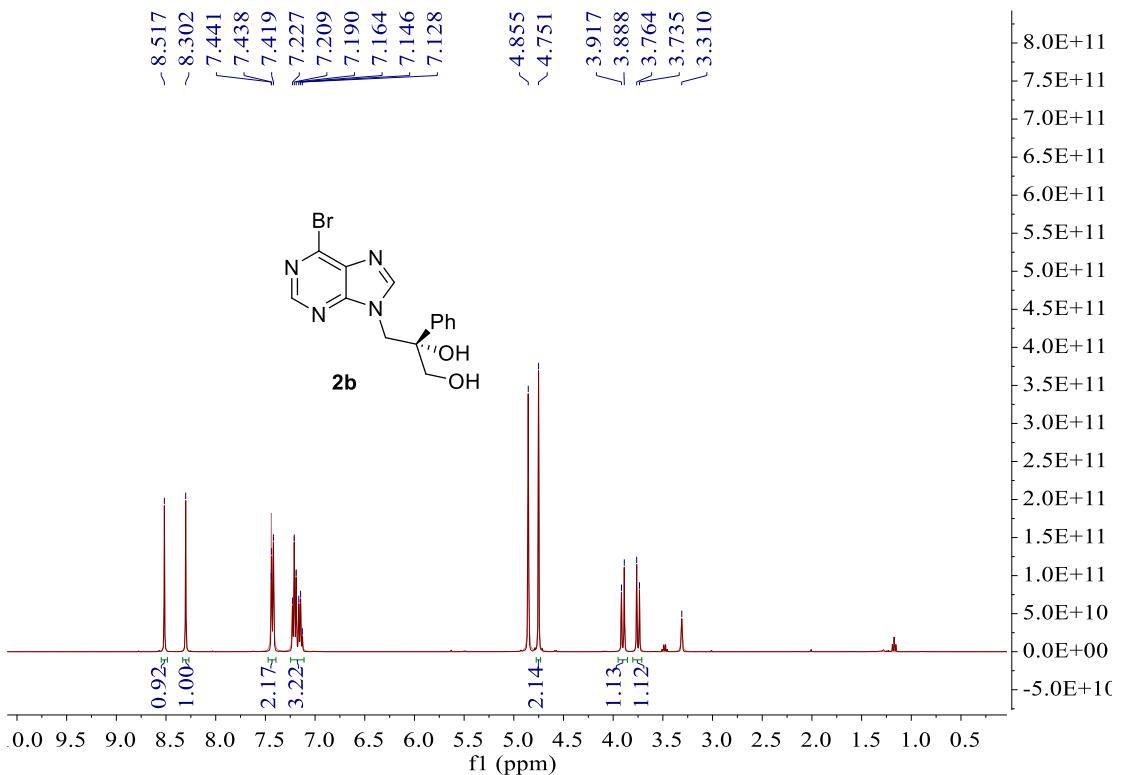


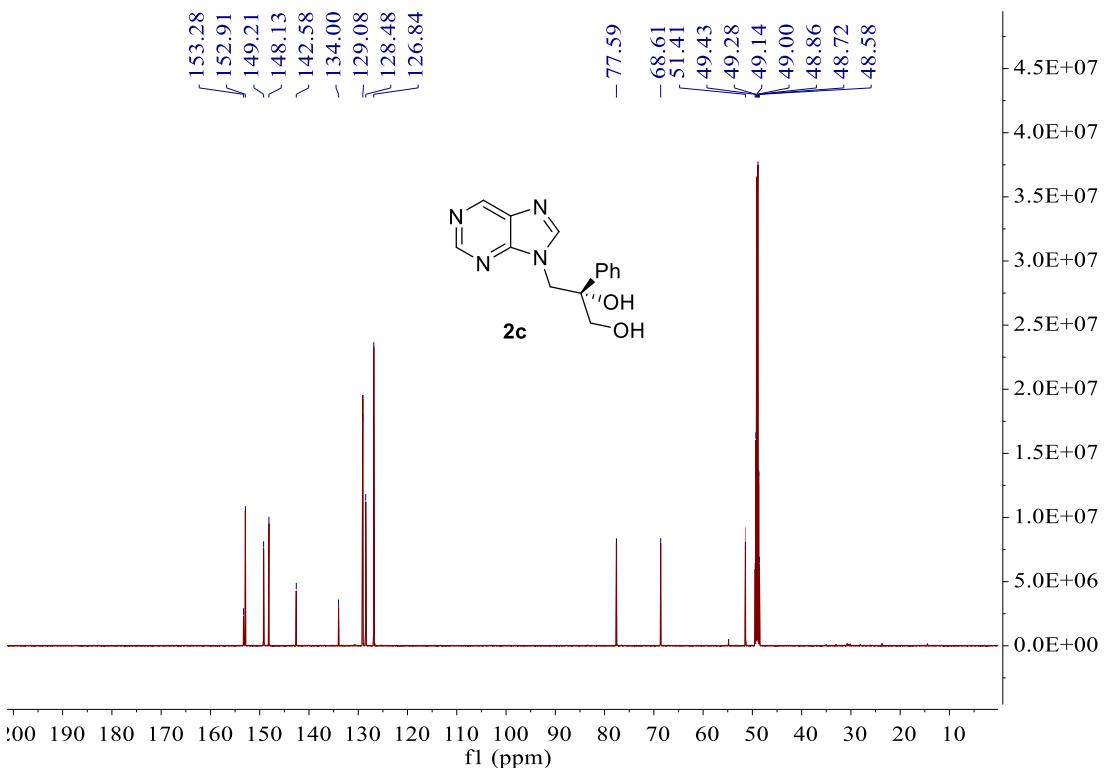
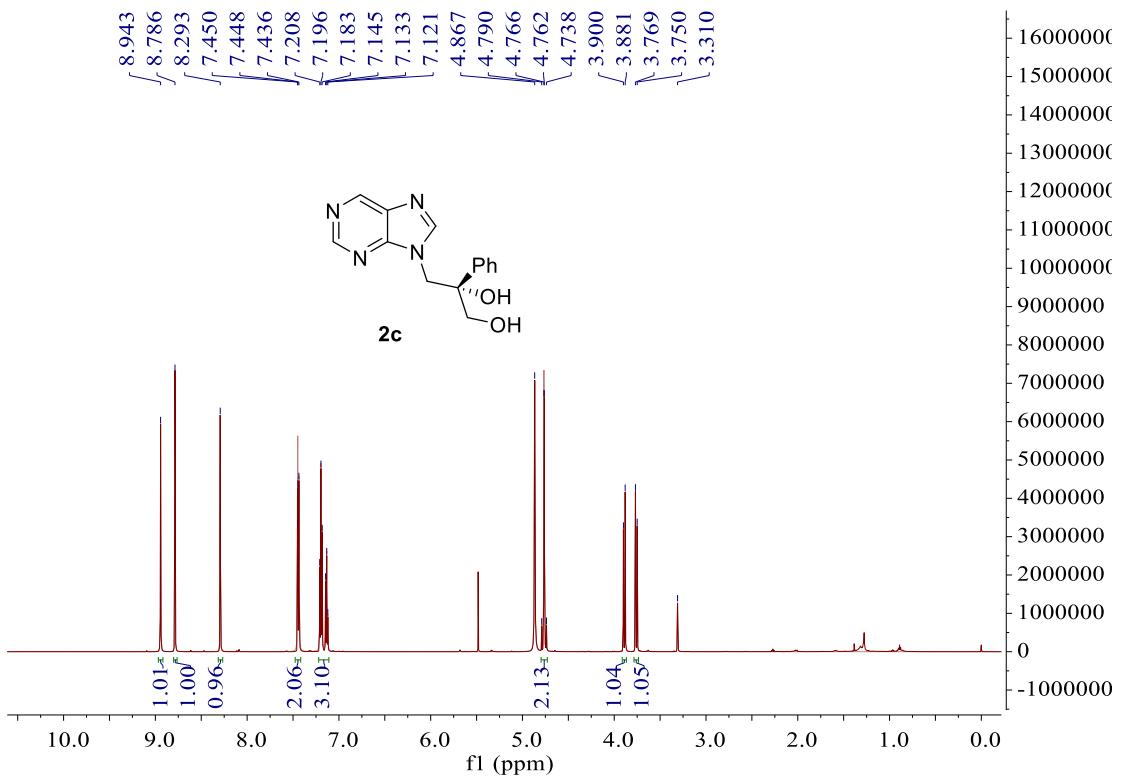


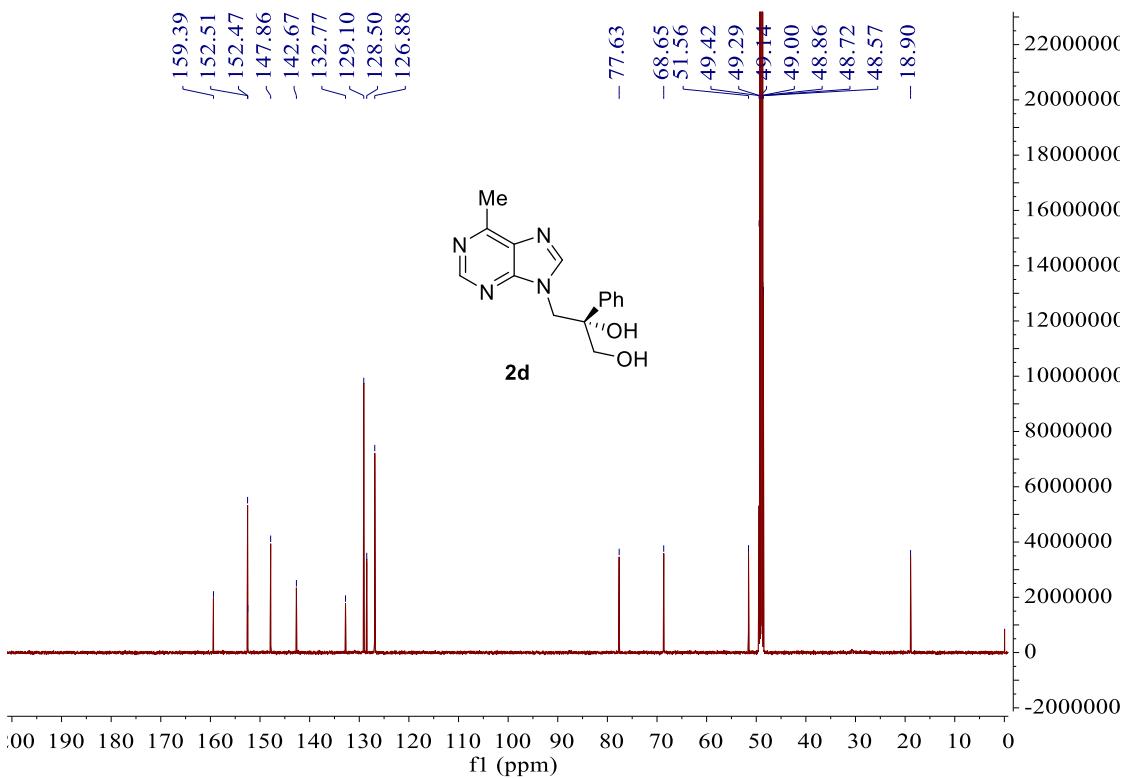
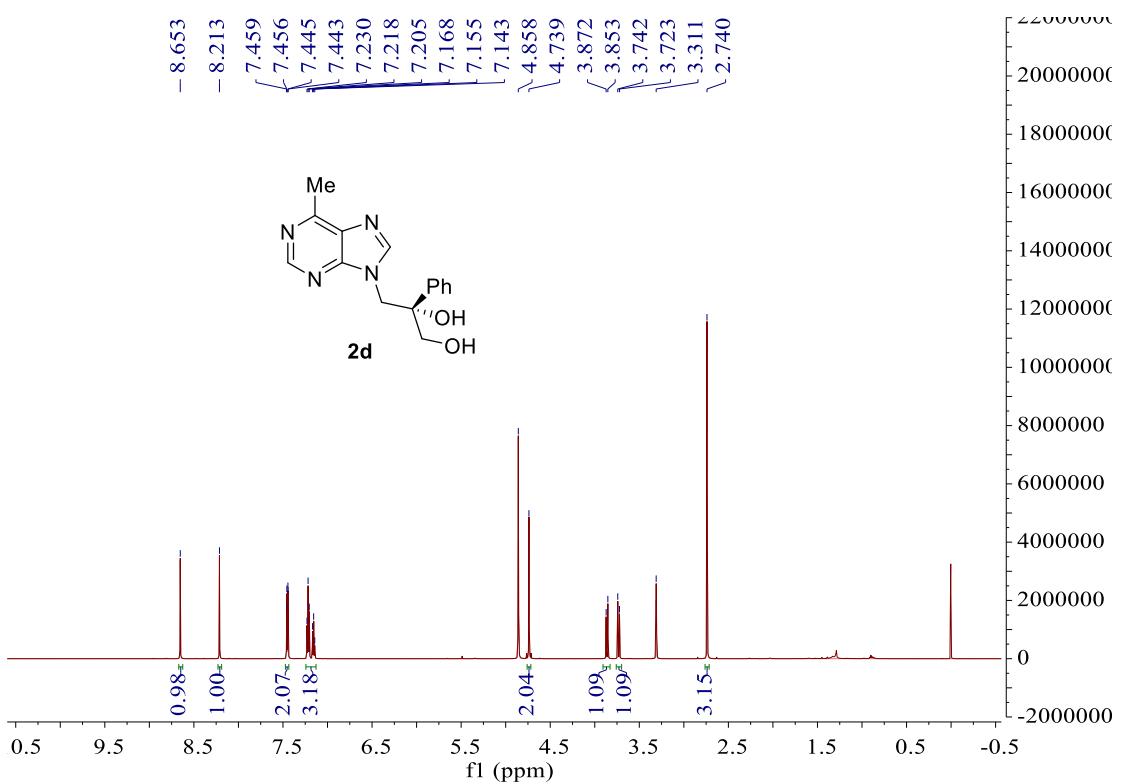


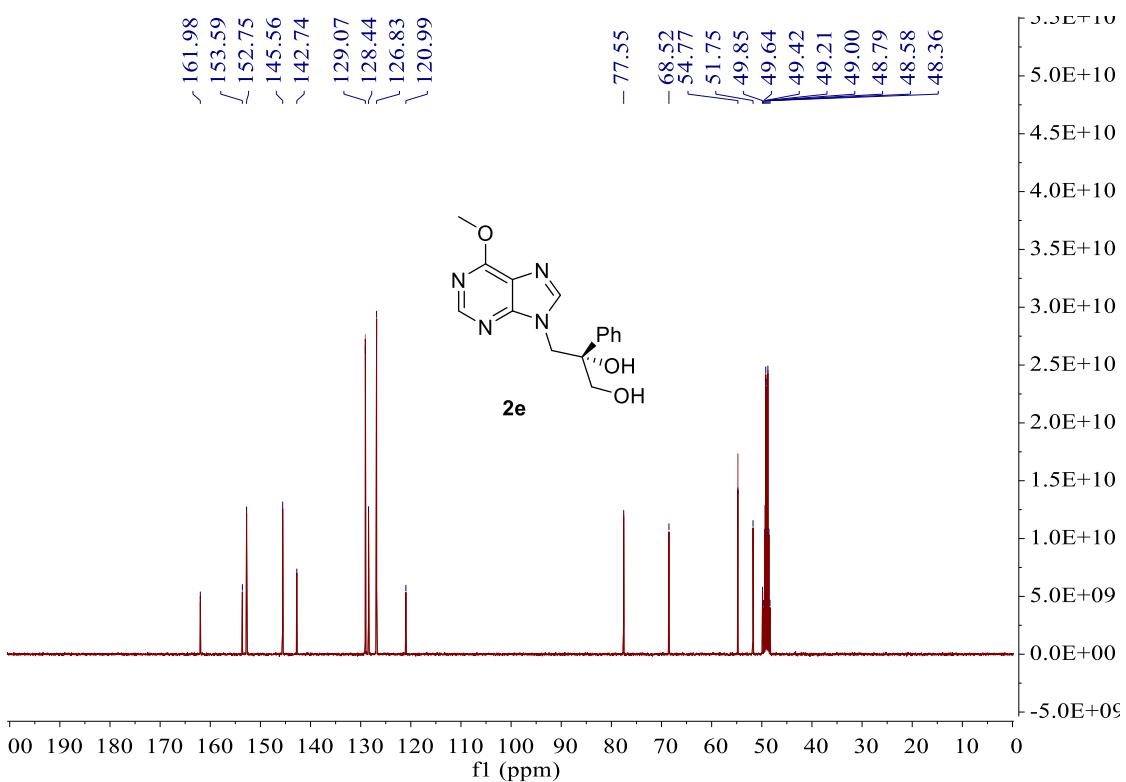
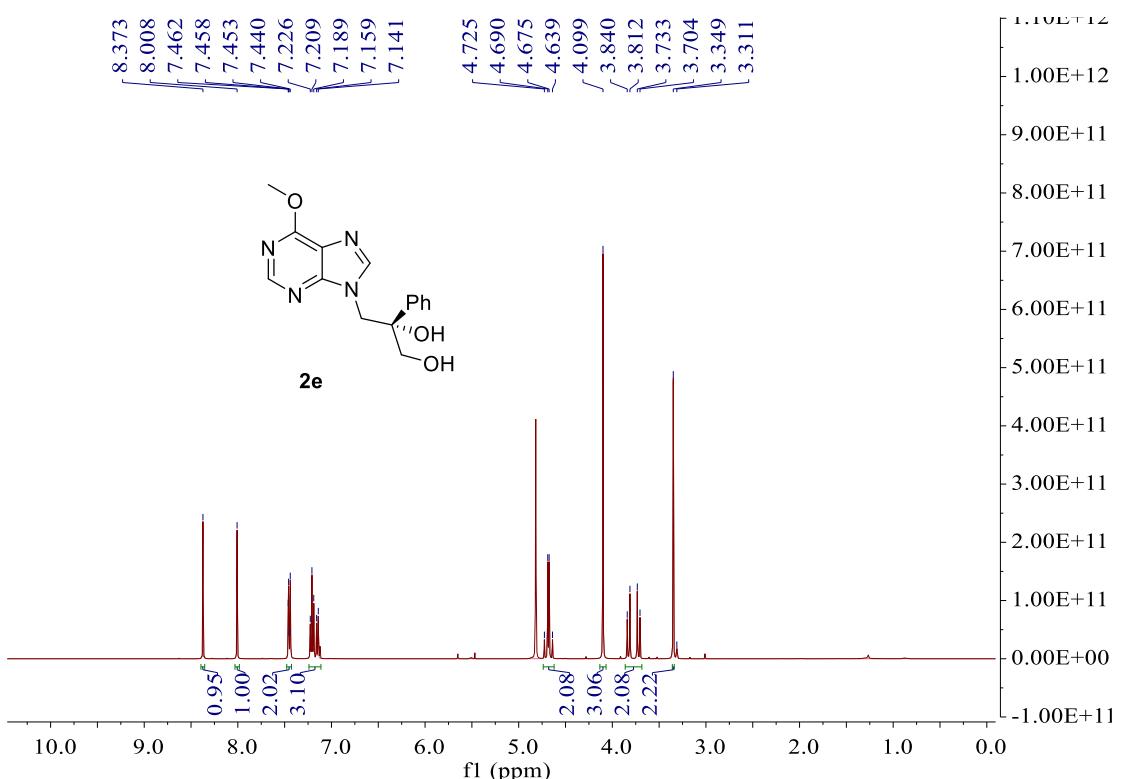
**(2) Copies of NMR spectra of products**

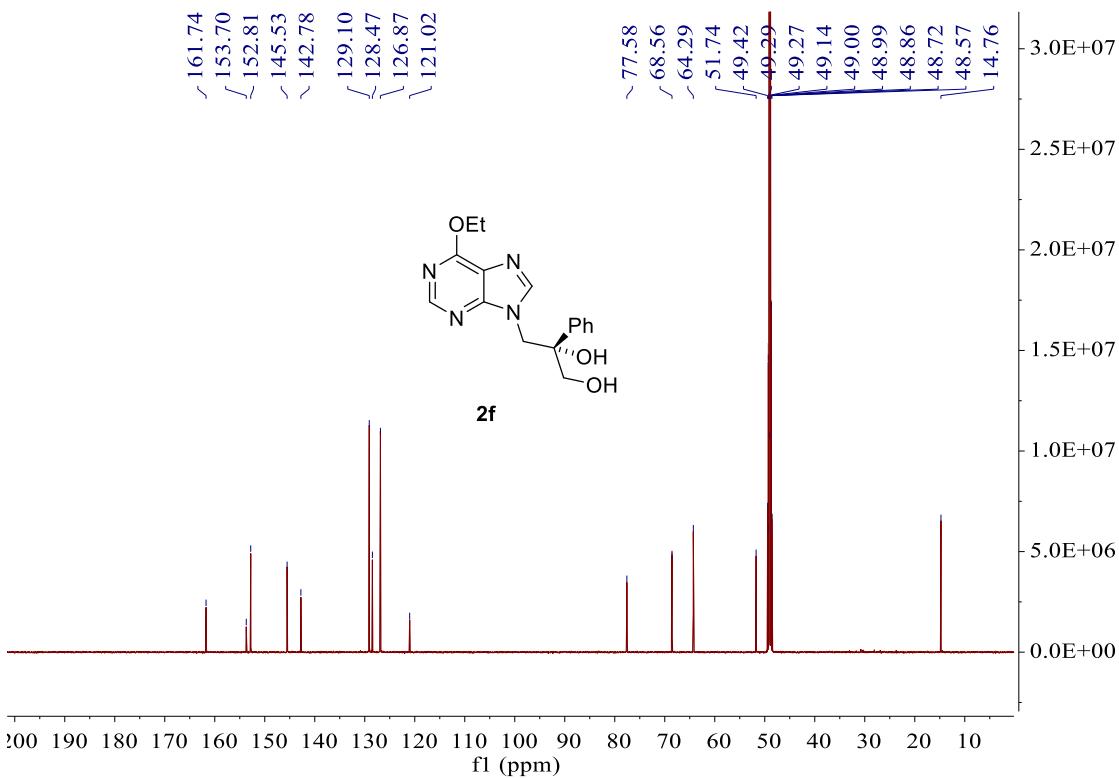
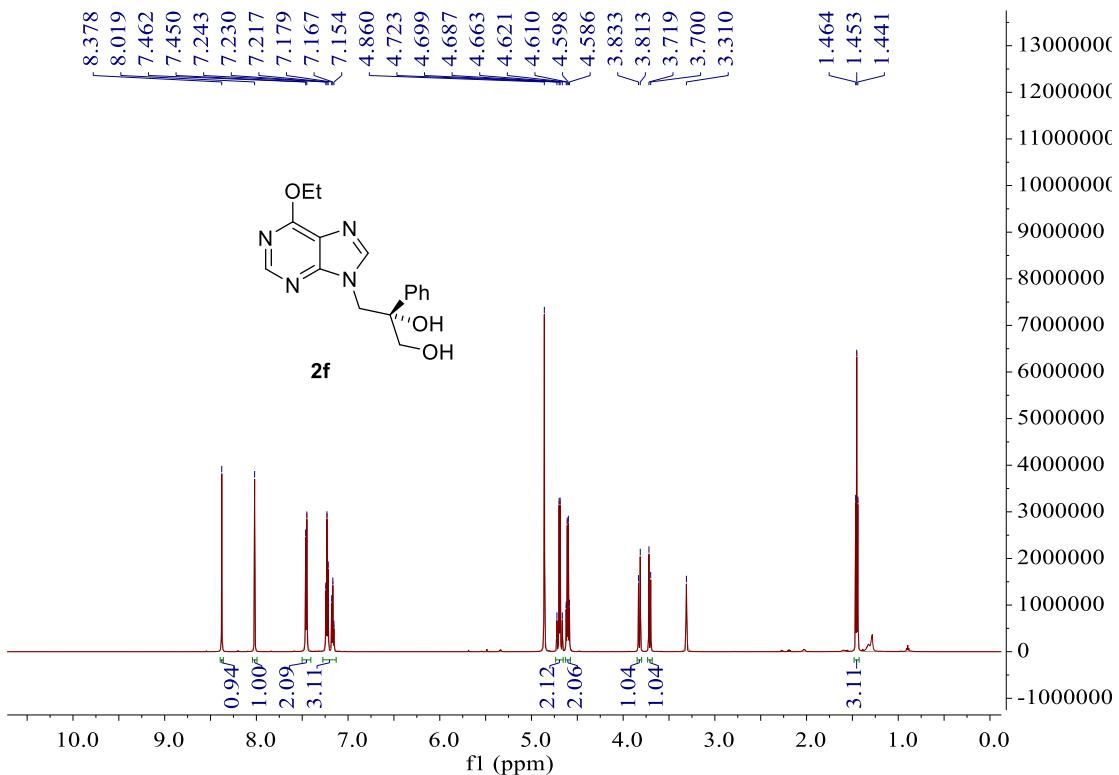


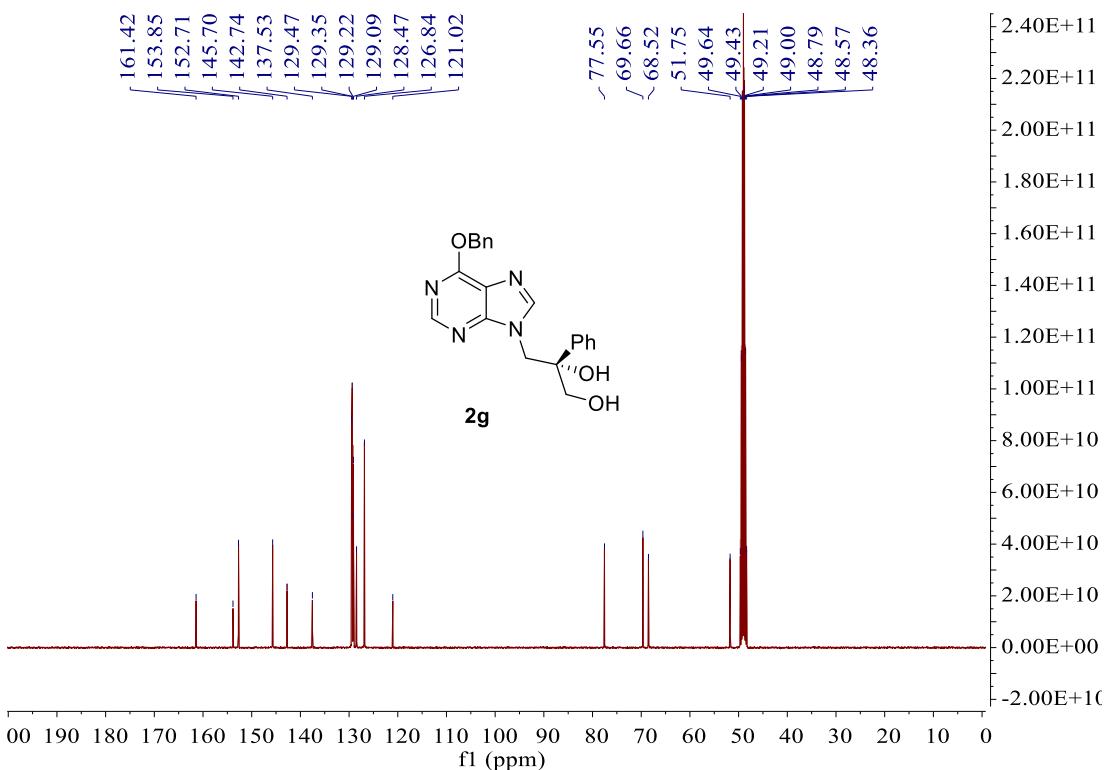
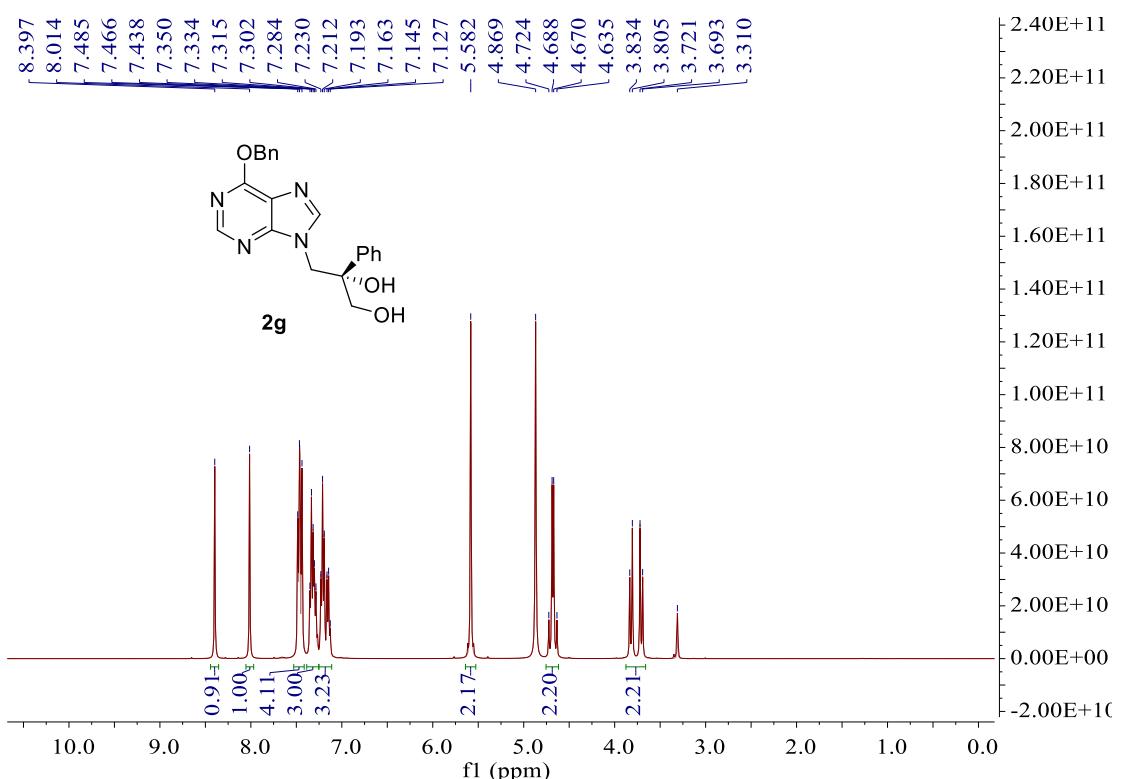


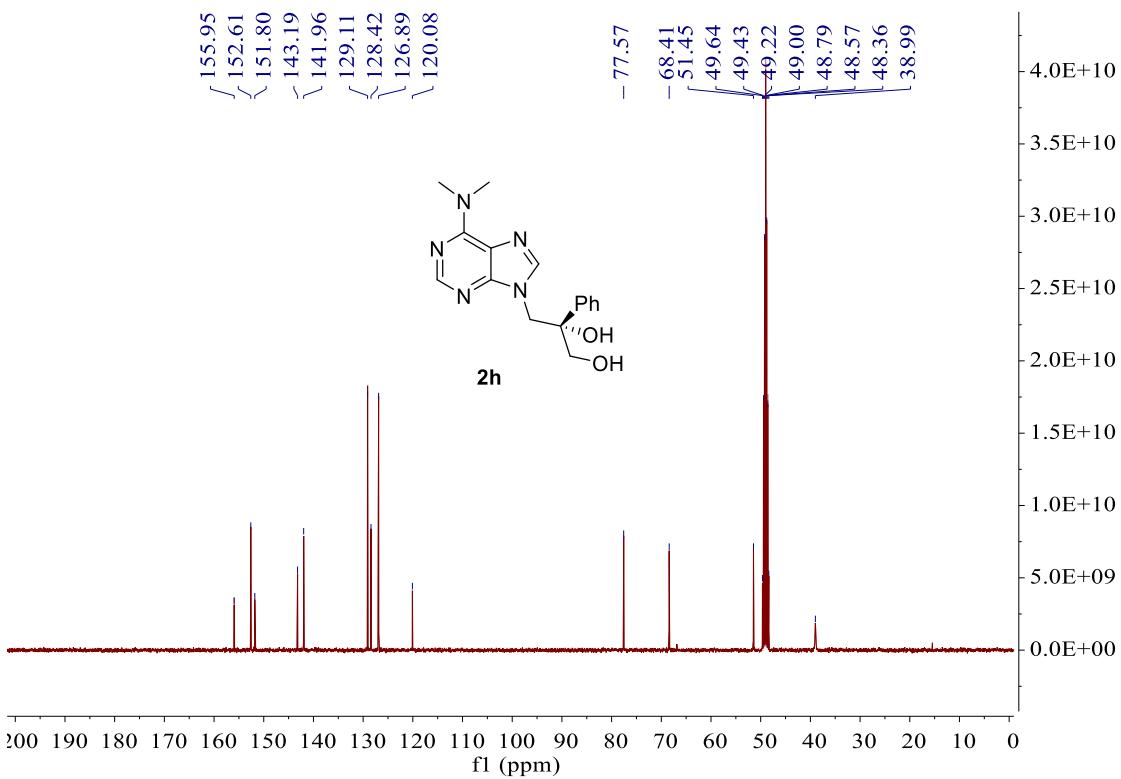
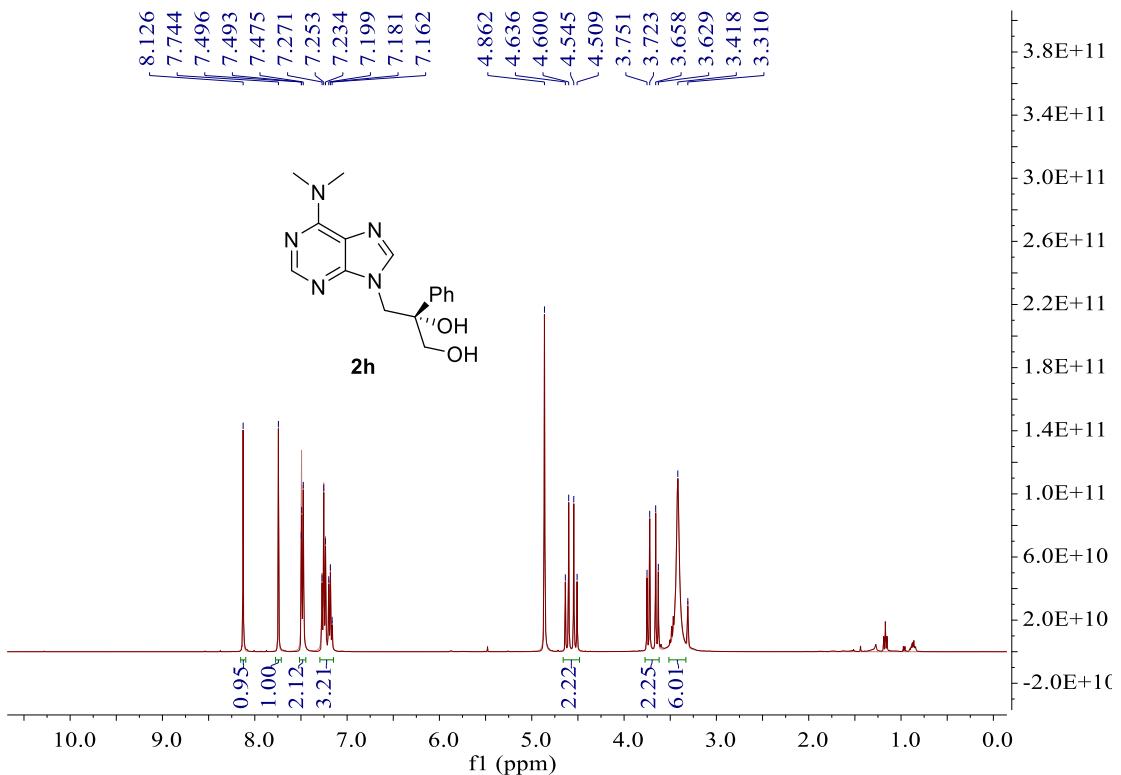


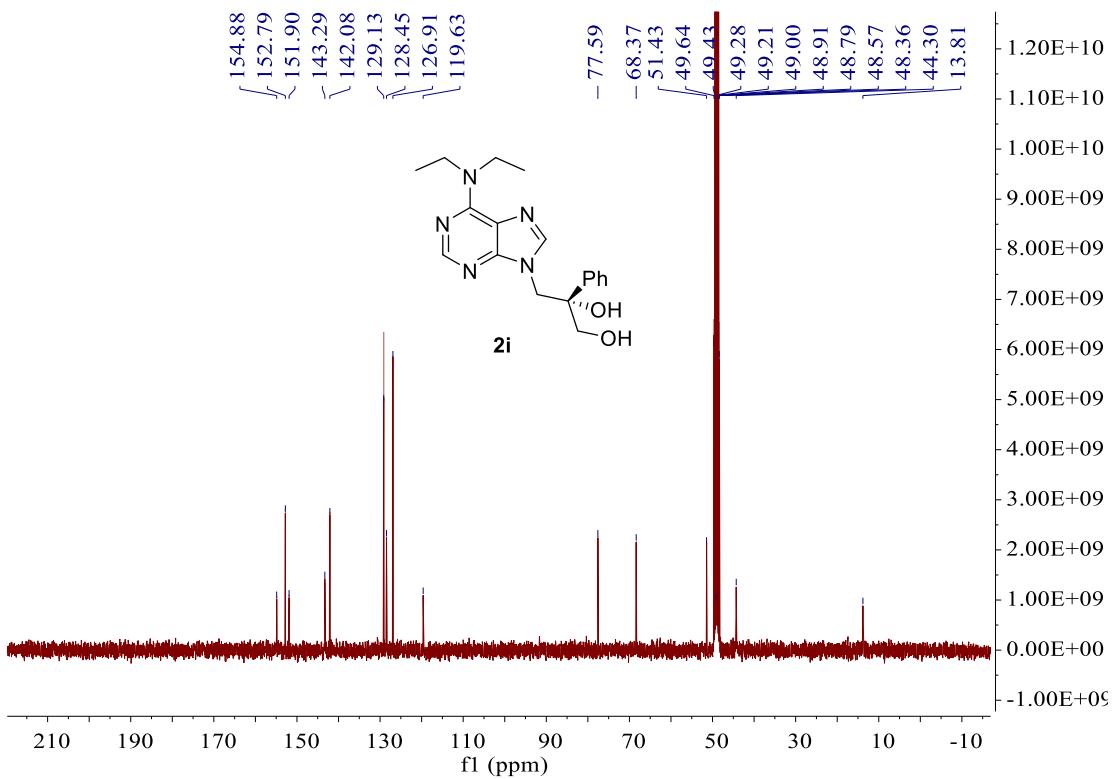
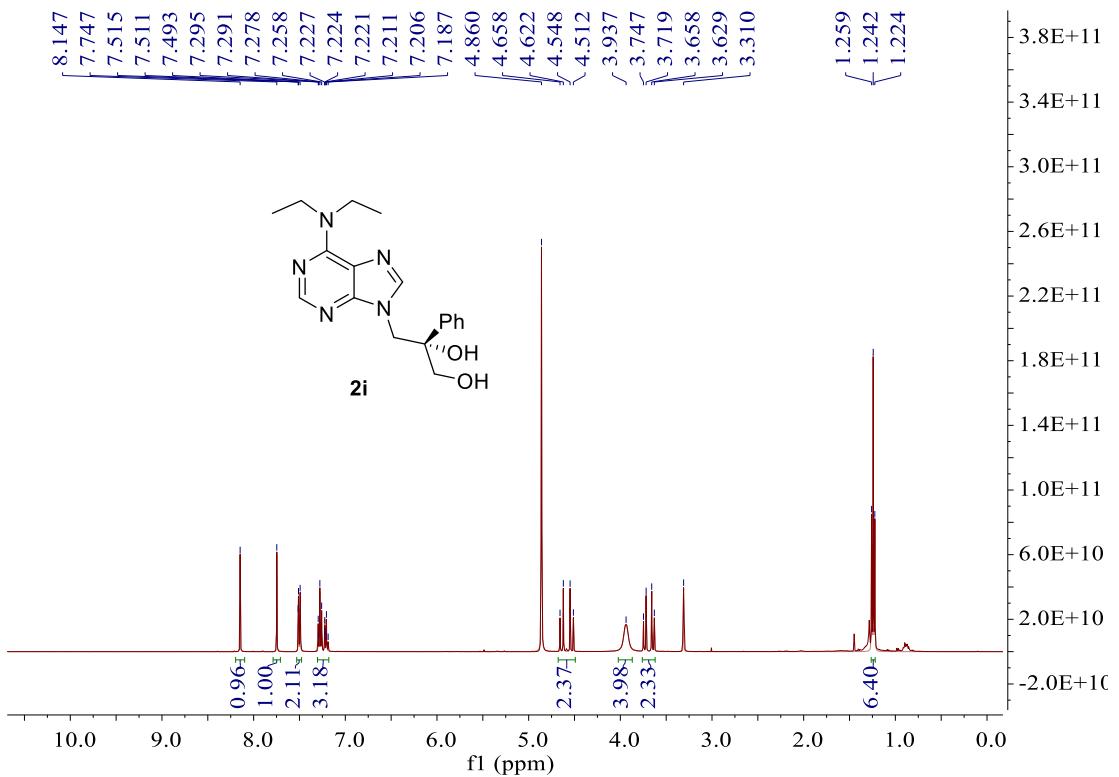


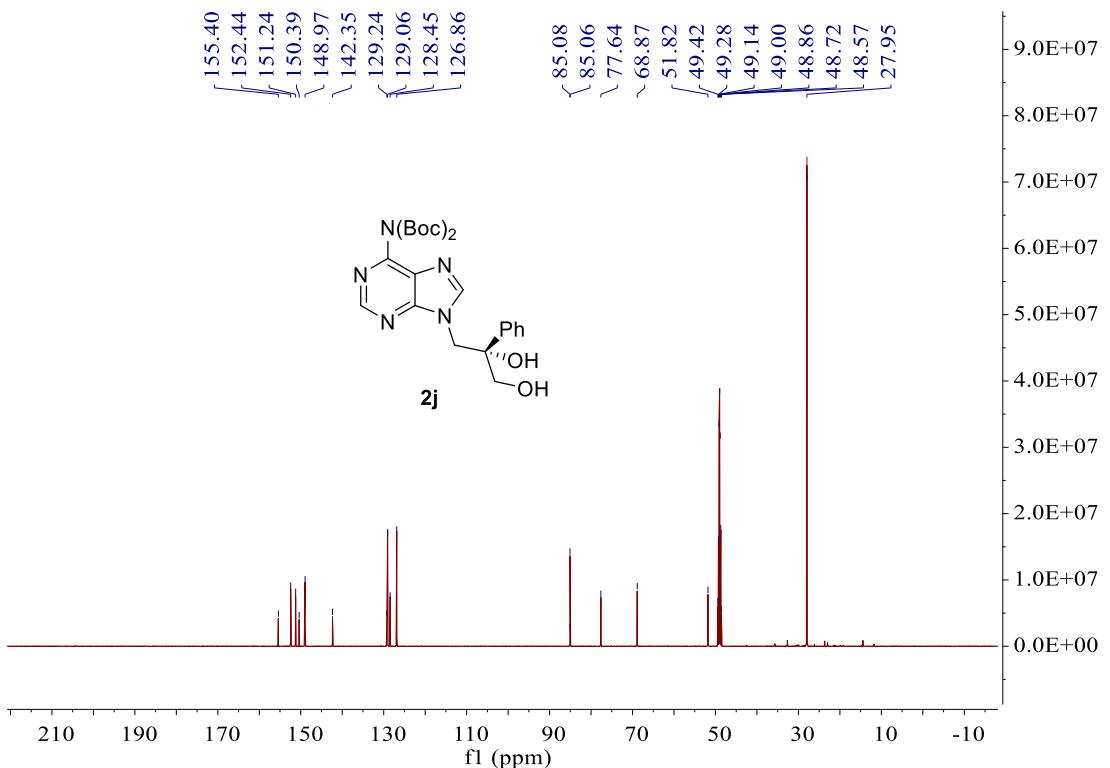
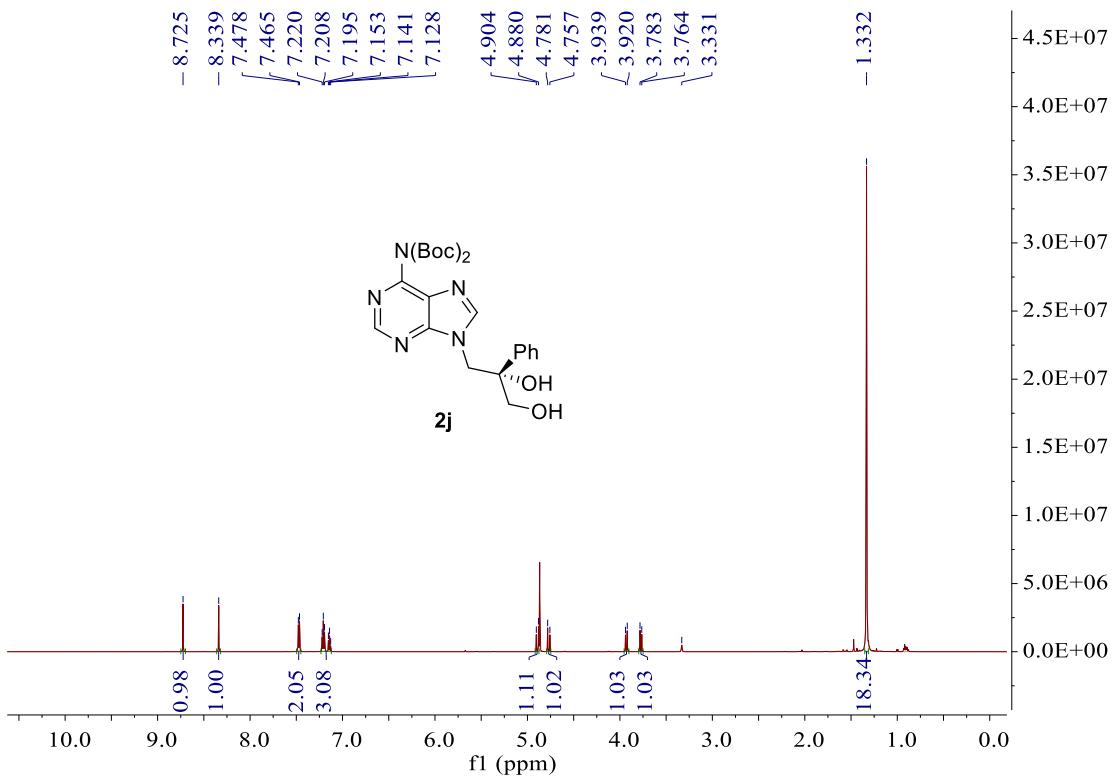


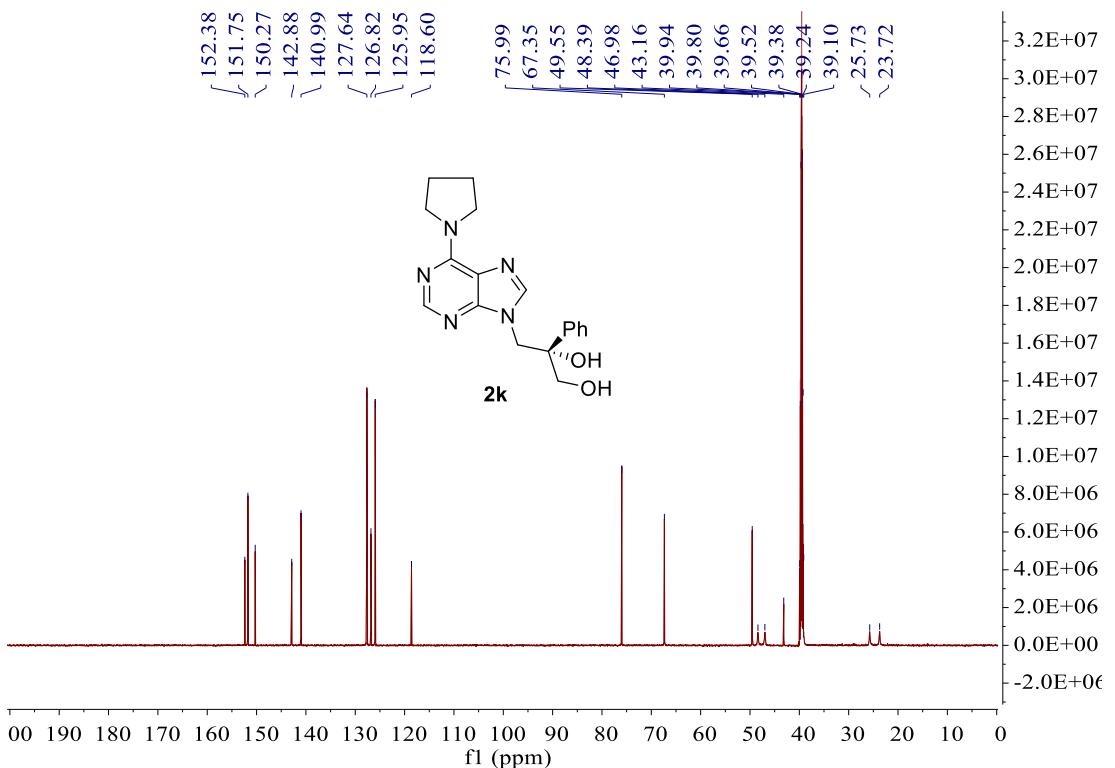
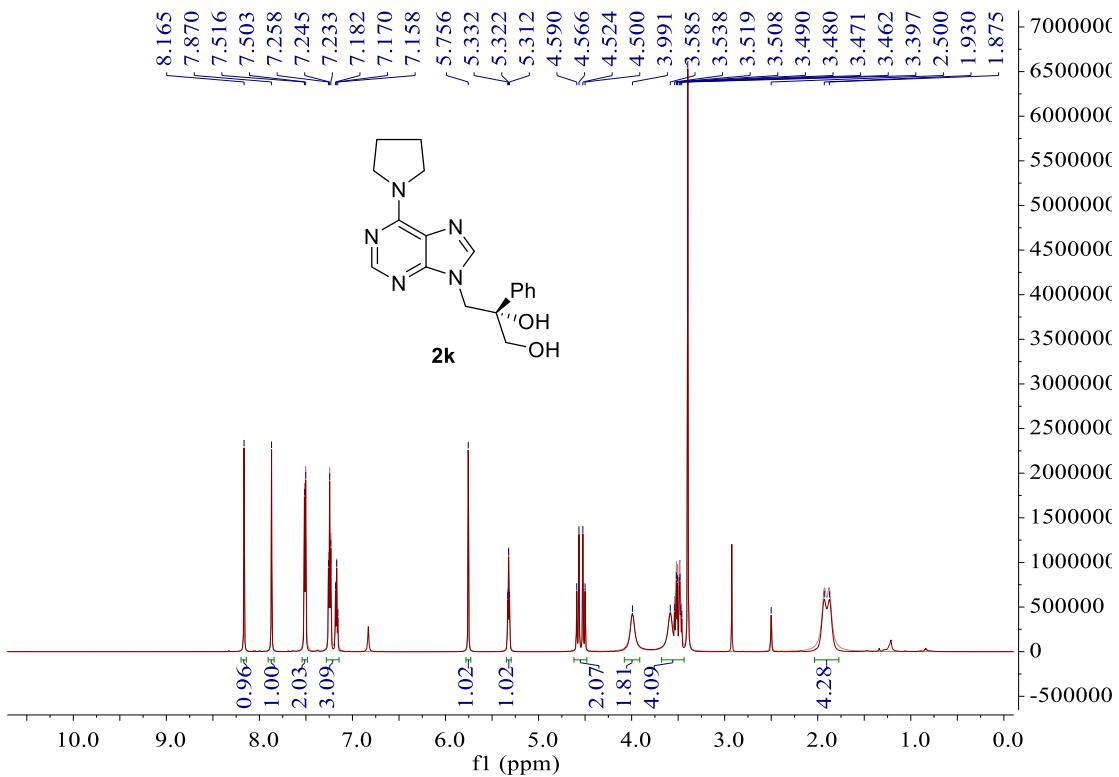


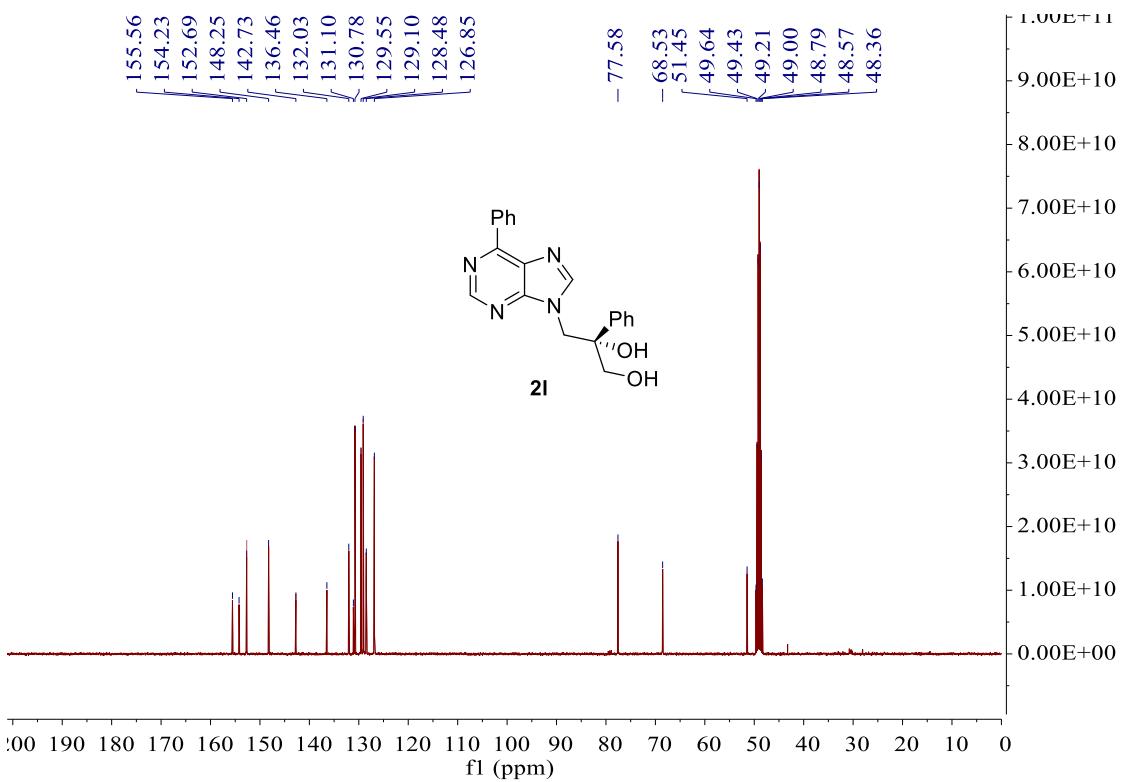
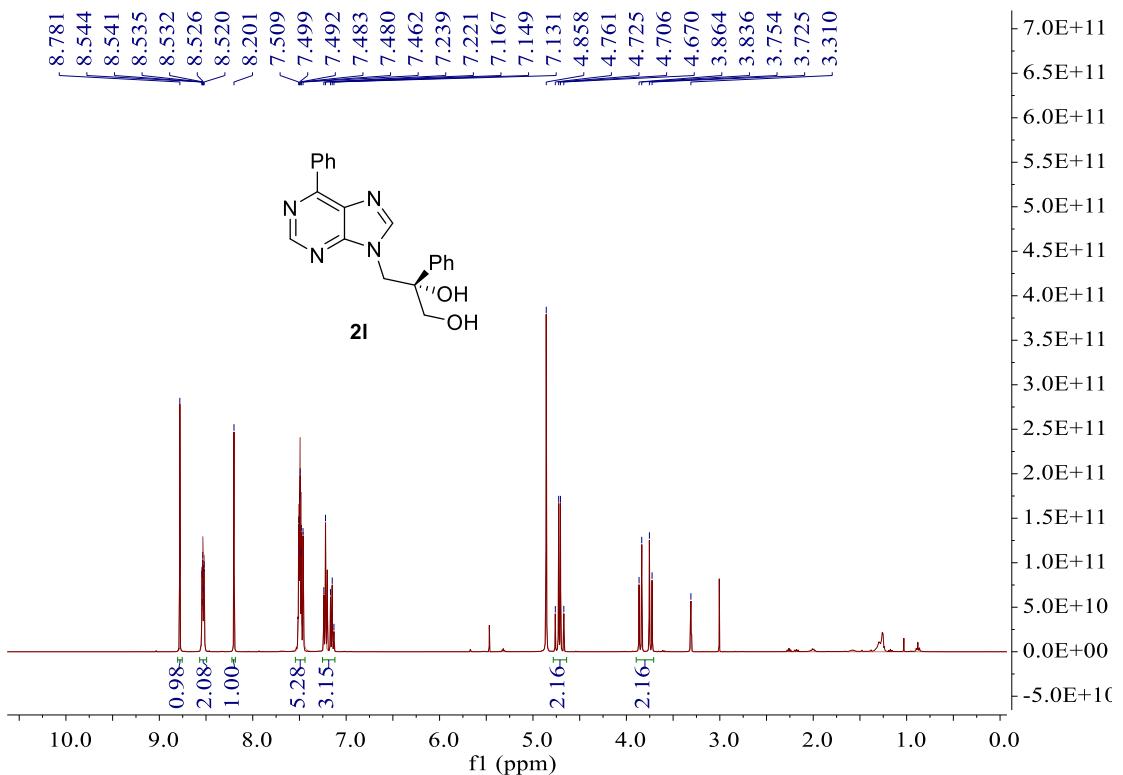


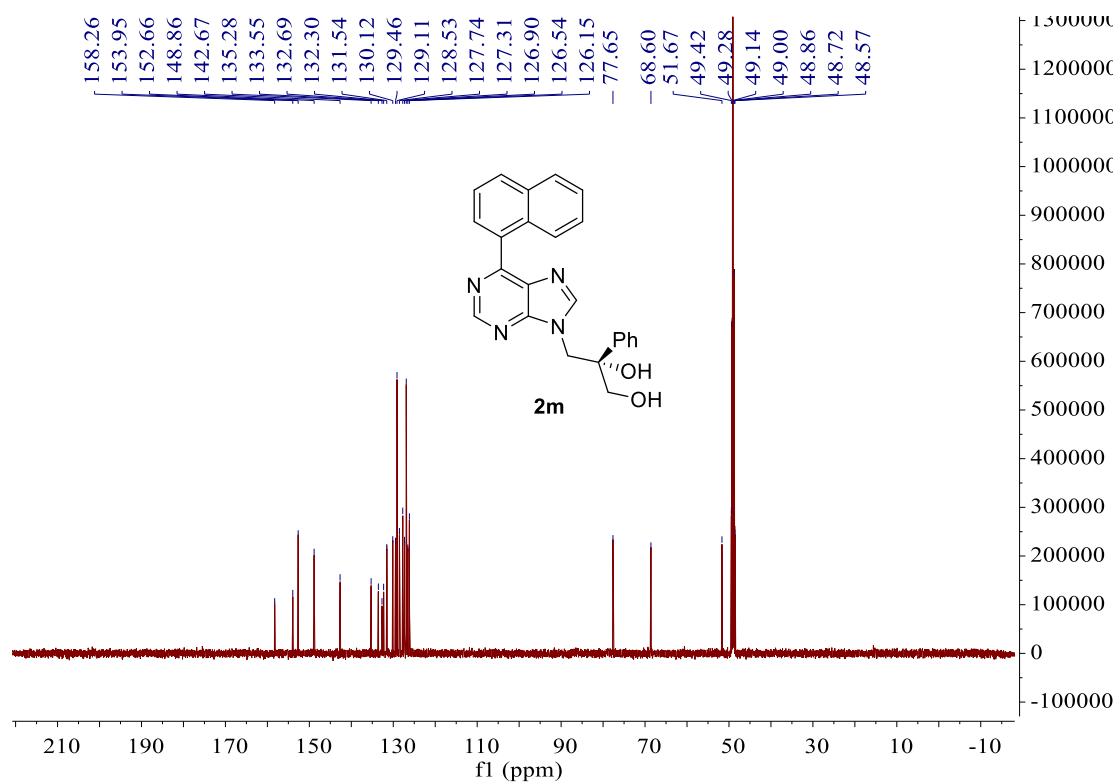
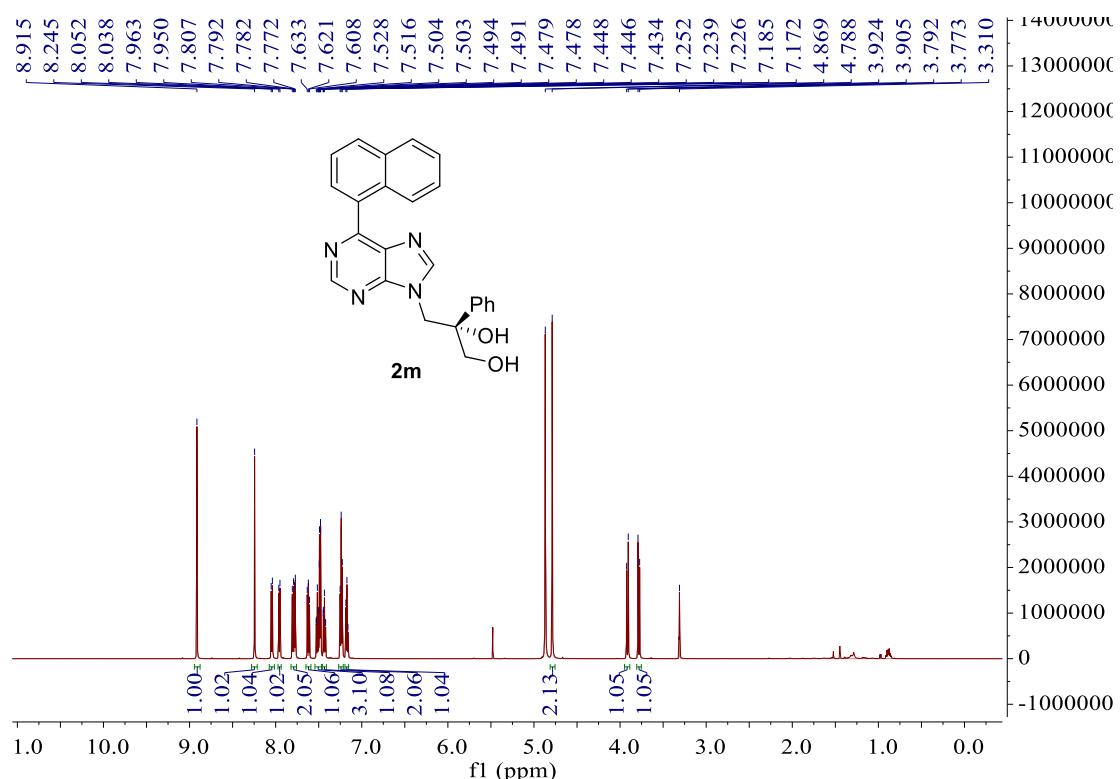


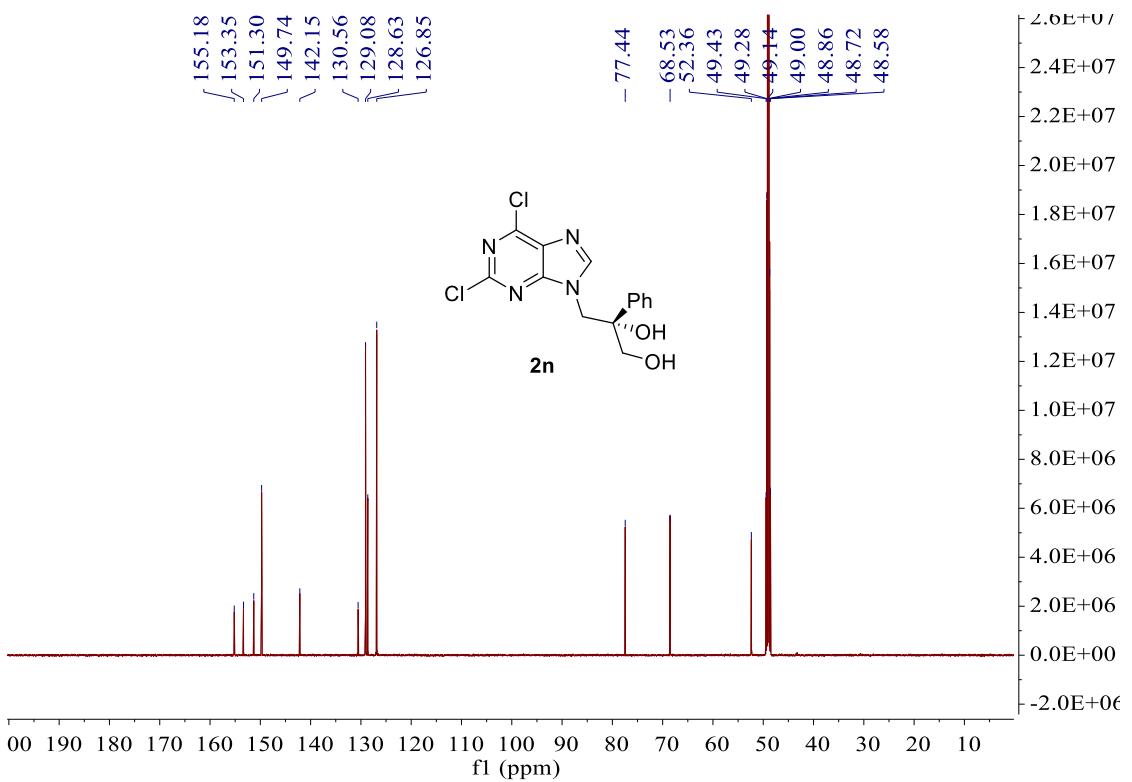
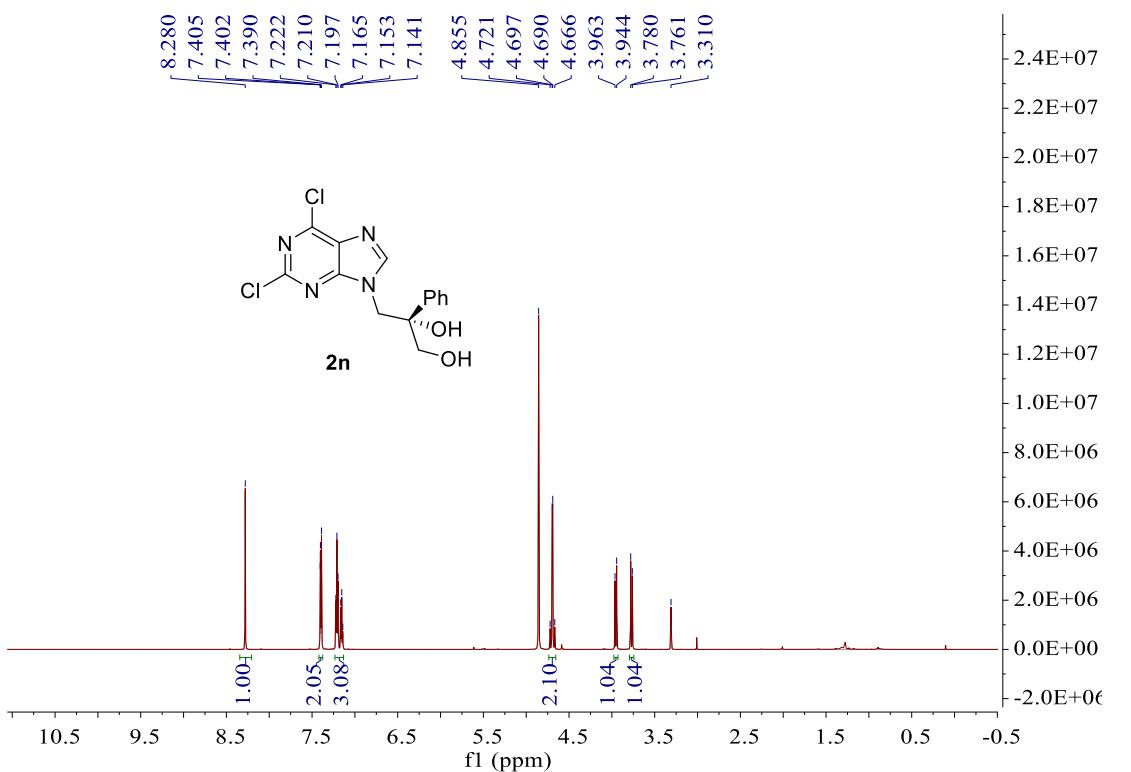


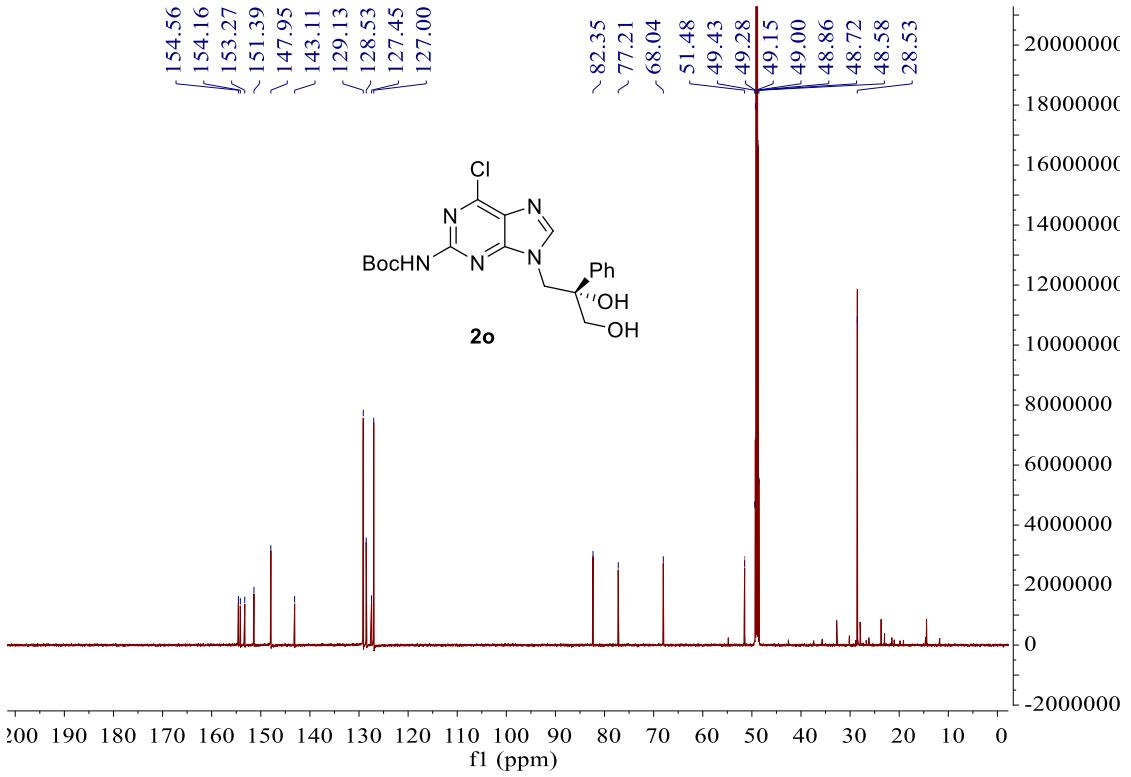
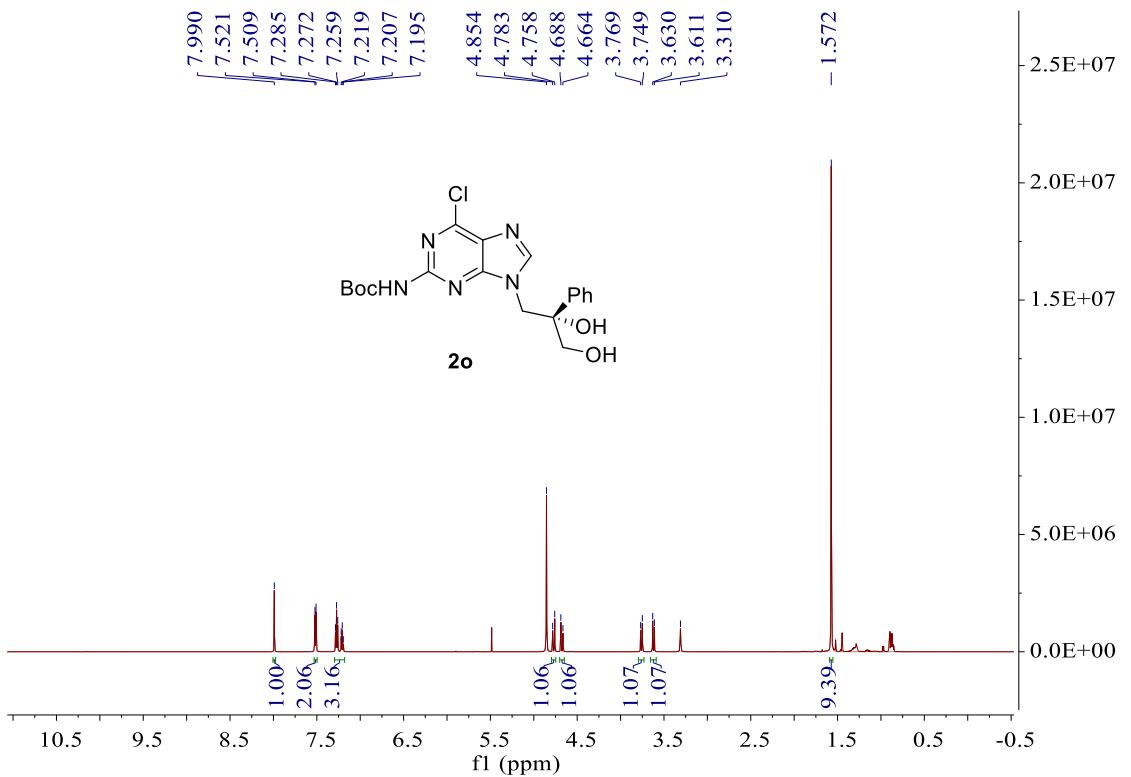


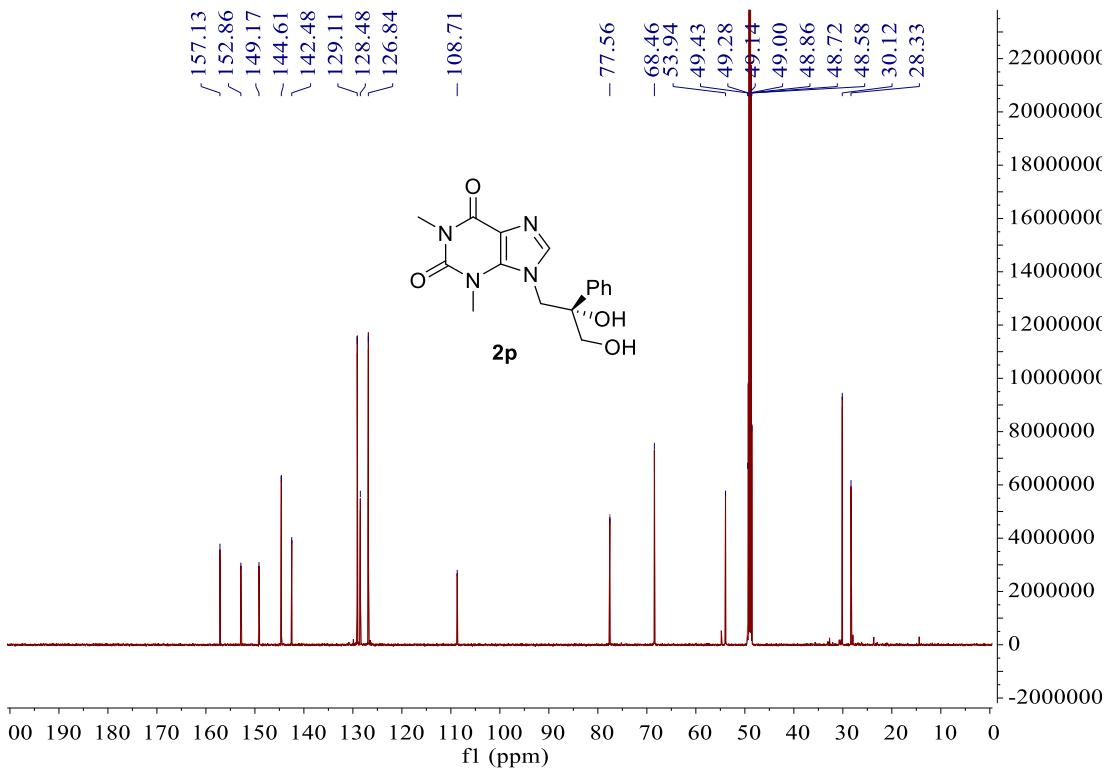
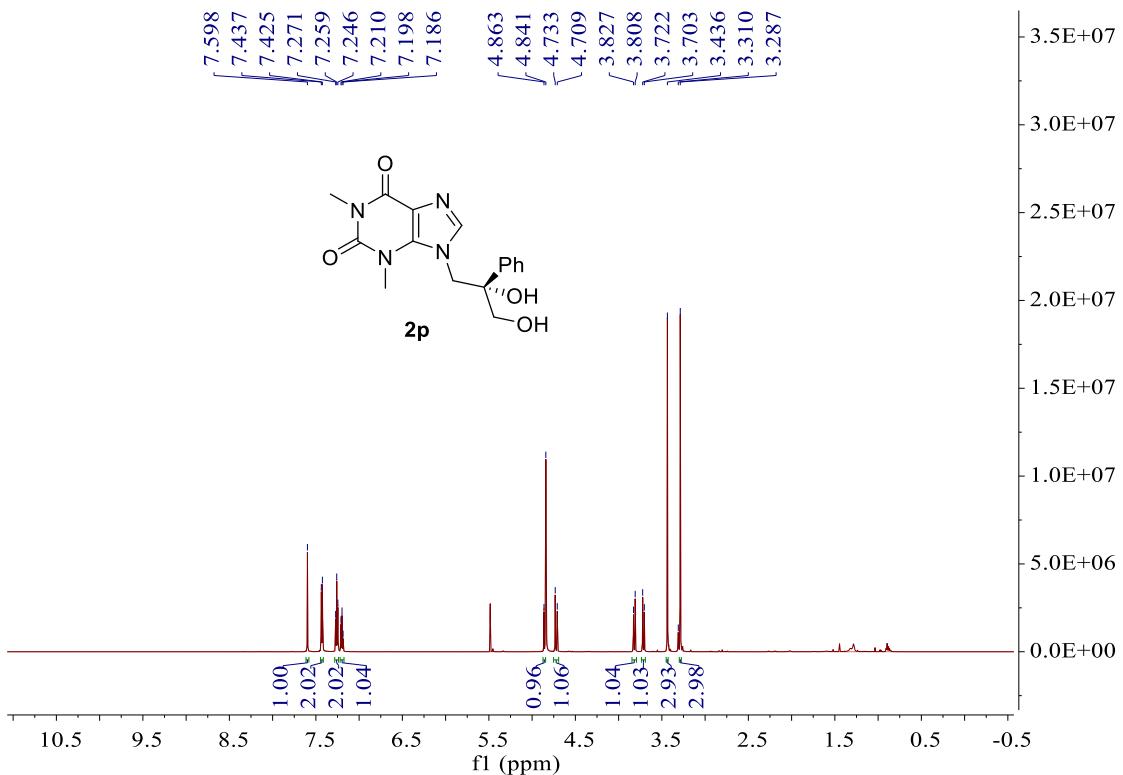


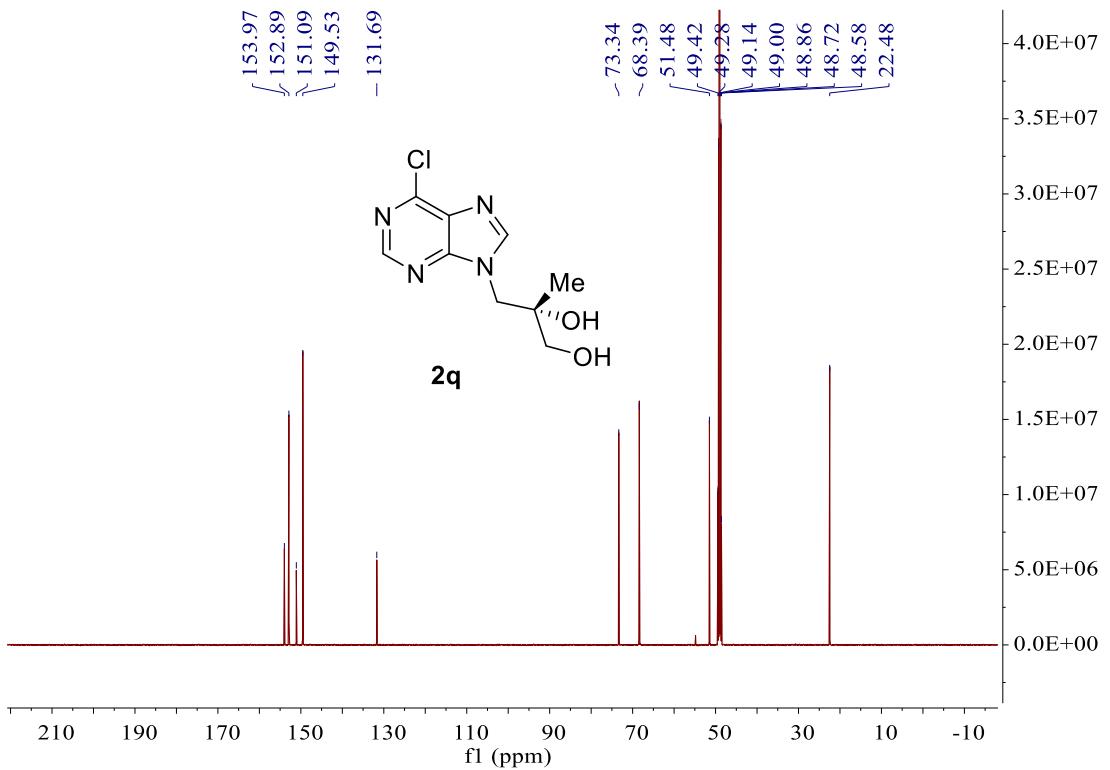
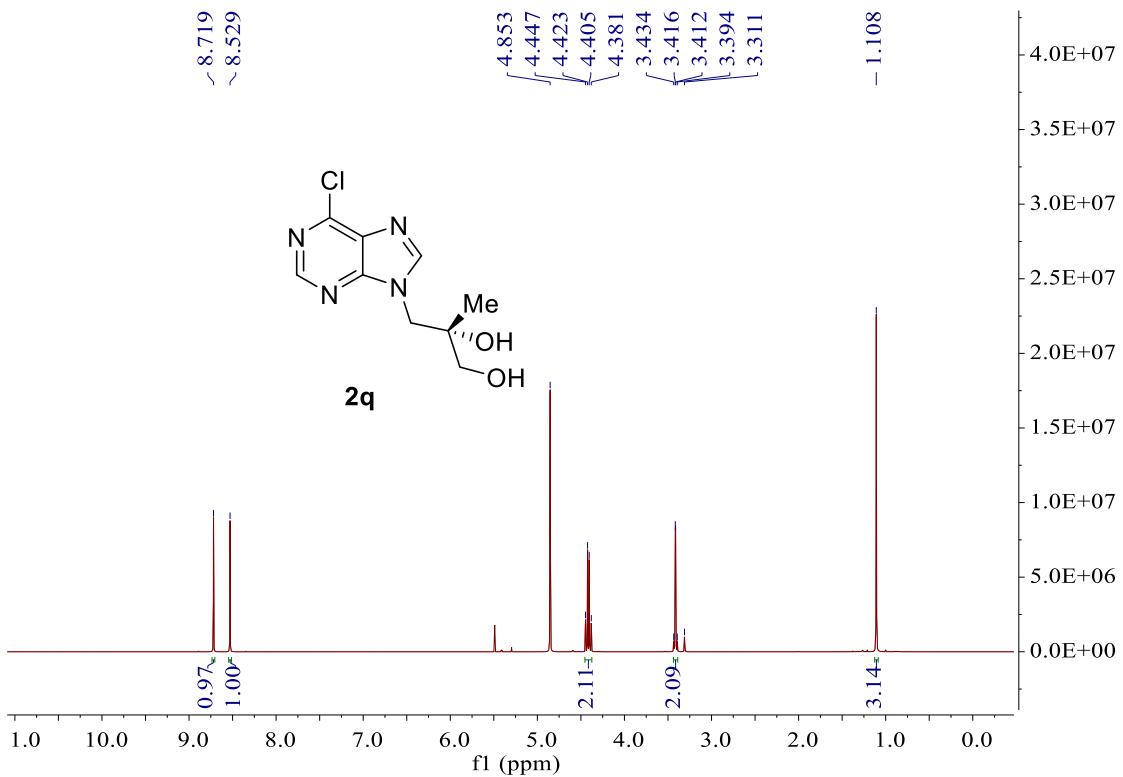


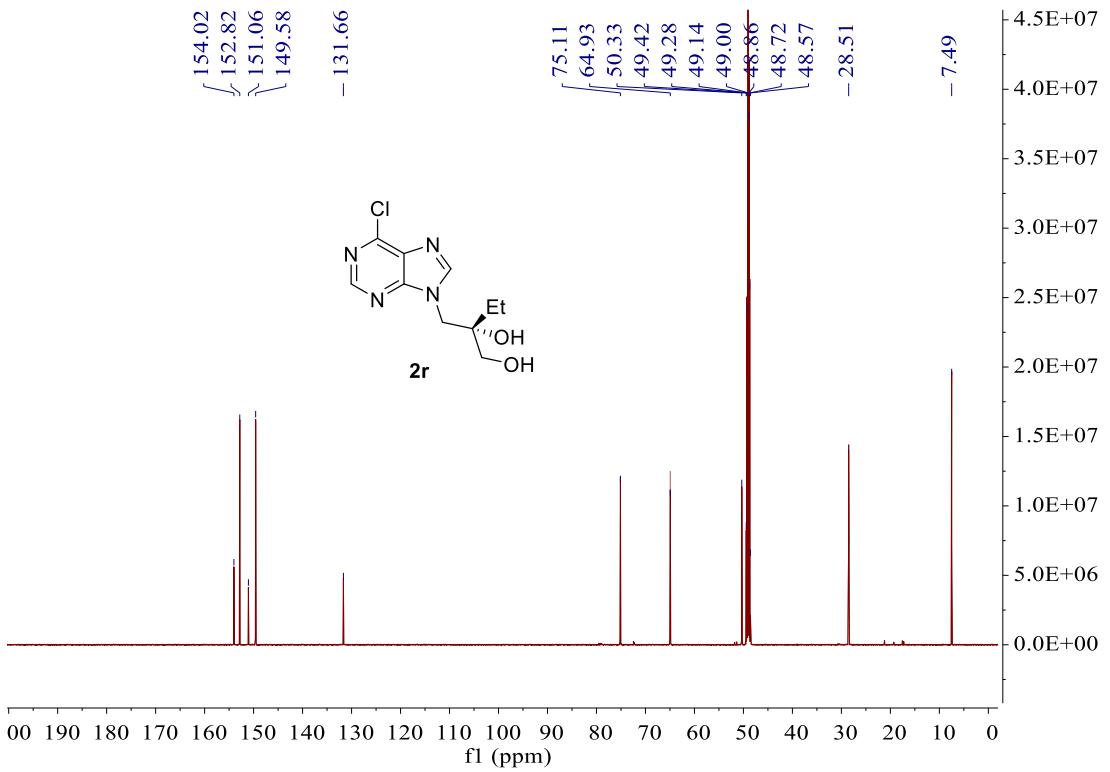
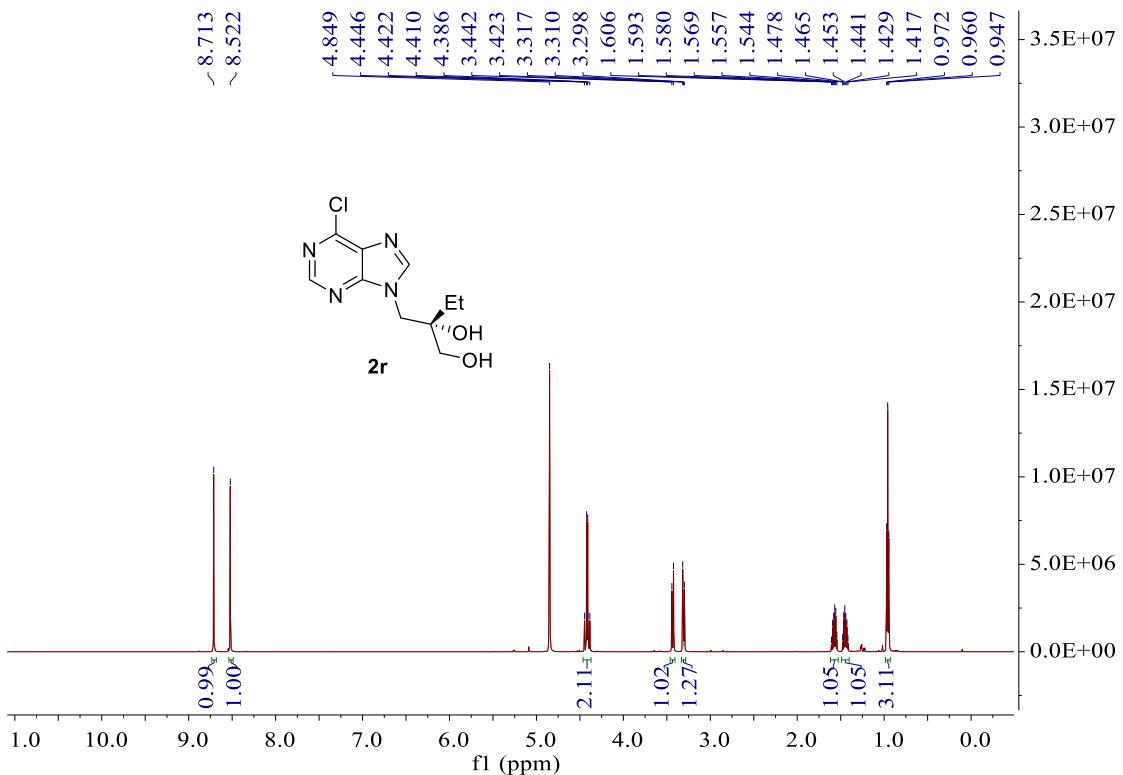


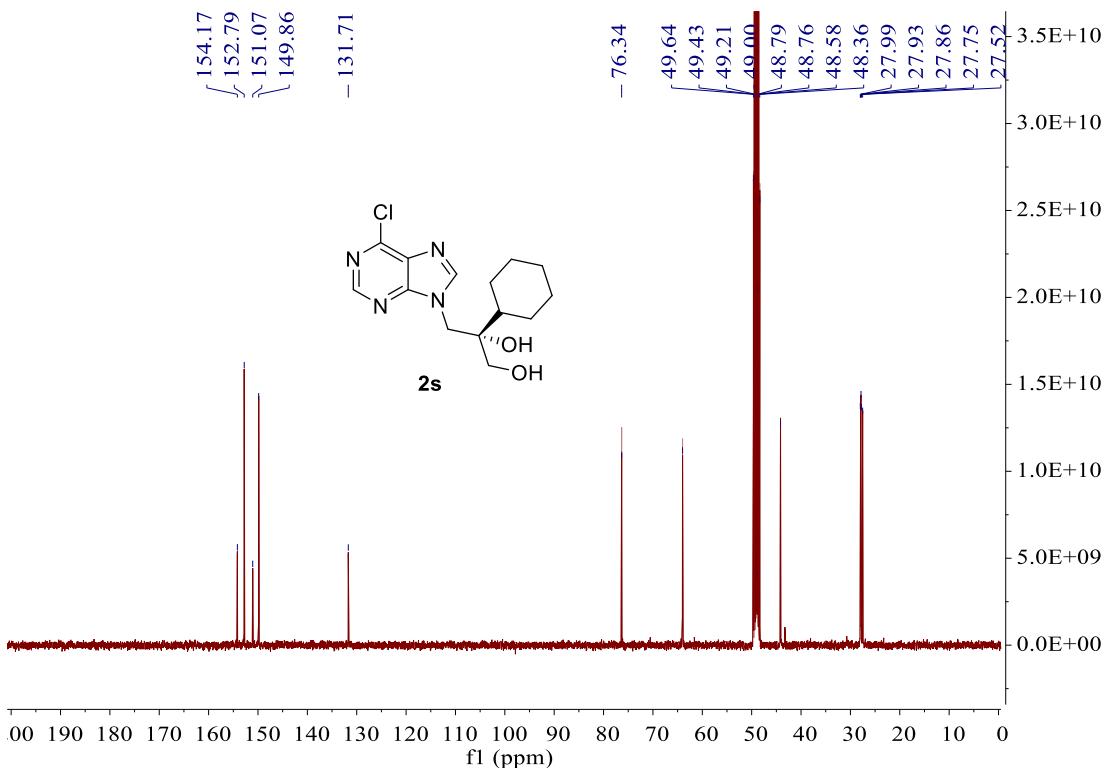
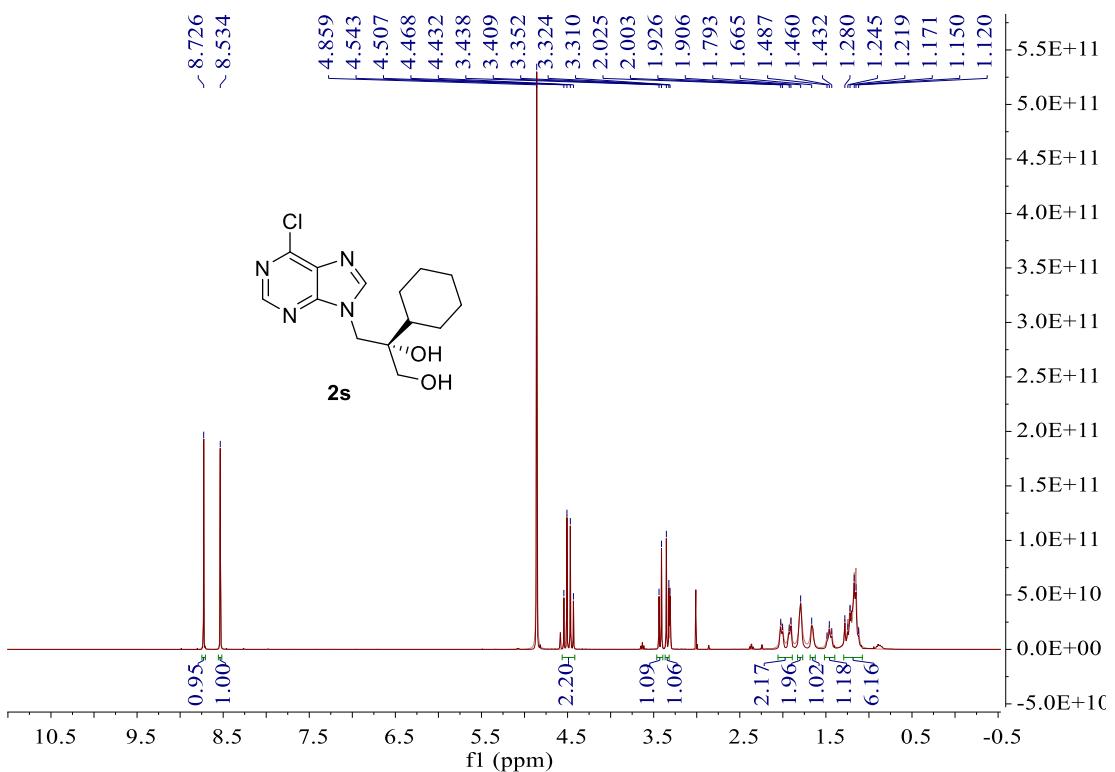


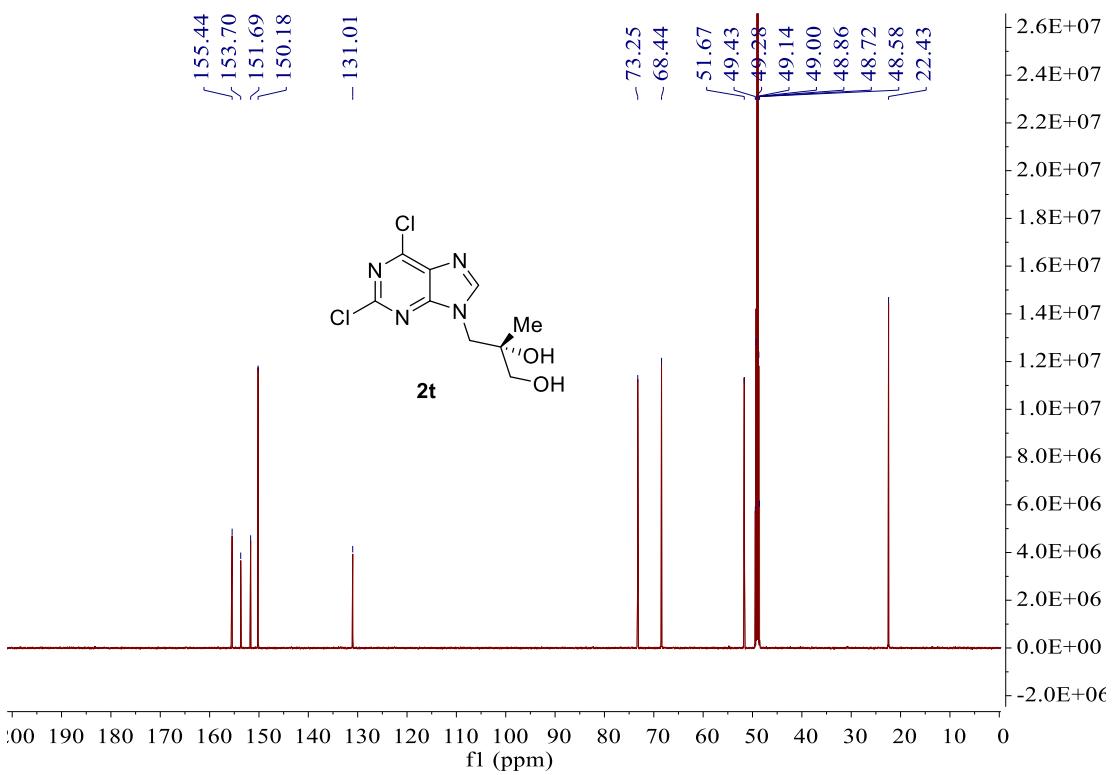
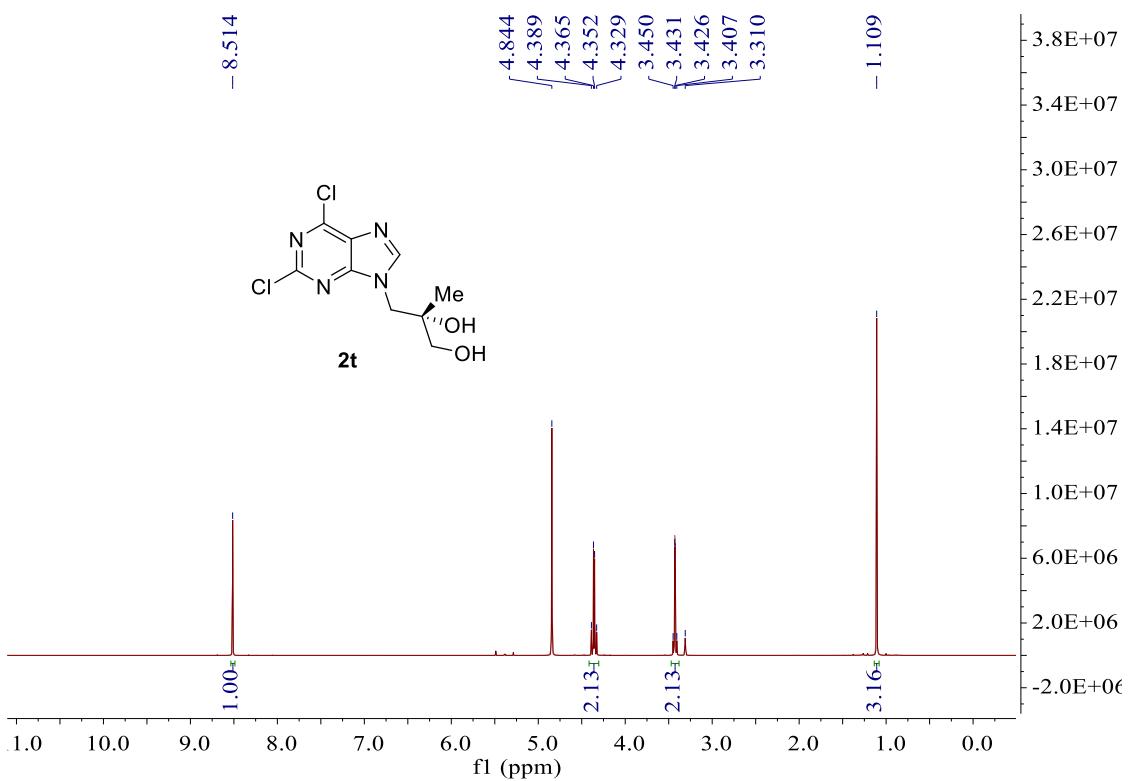


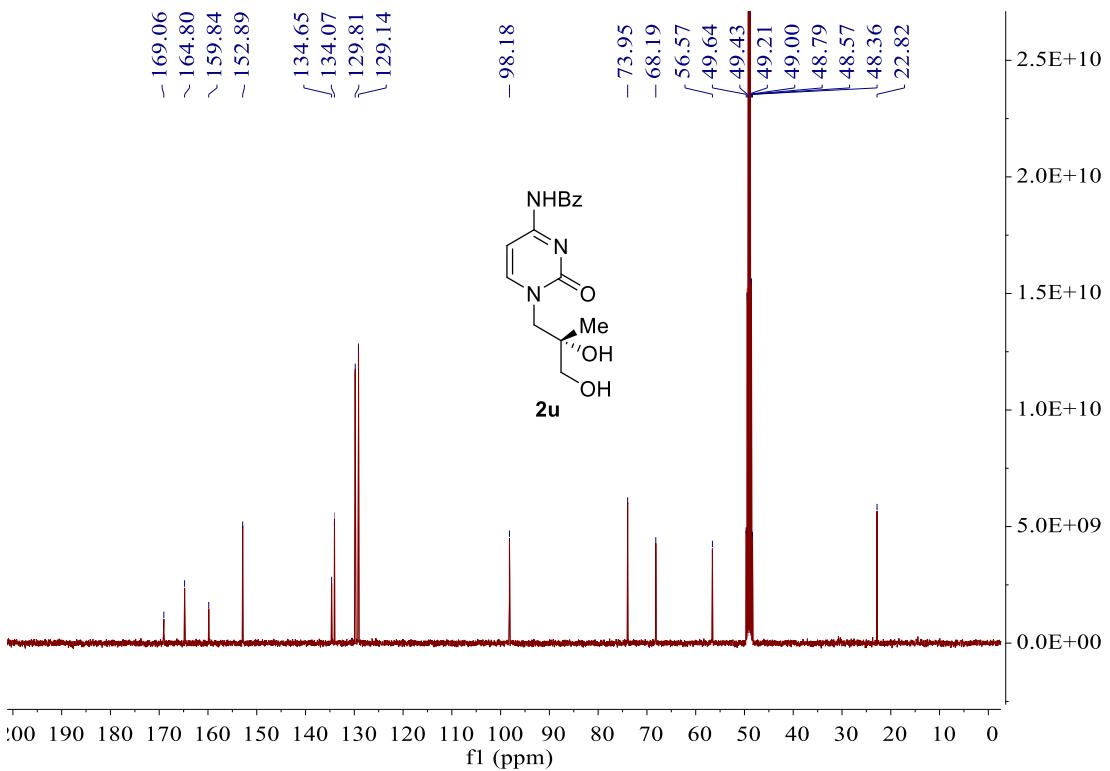
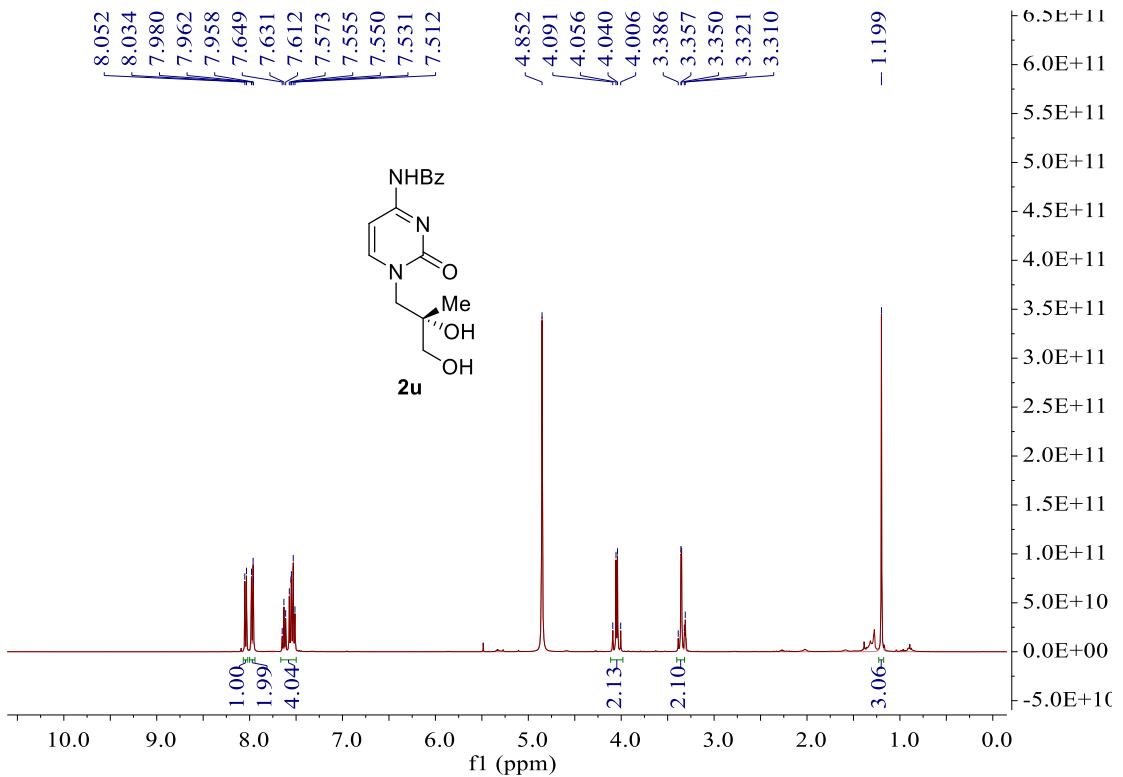


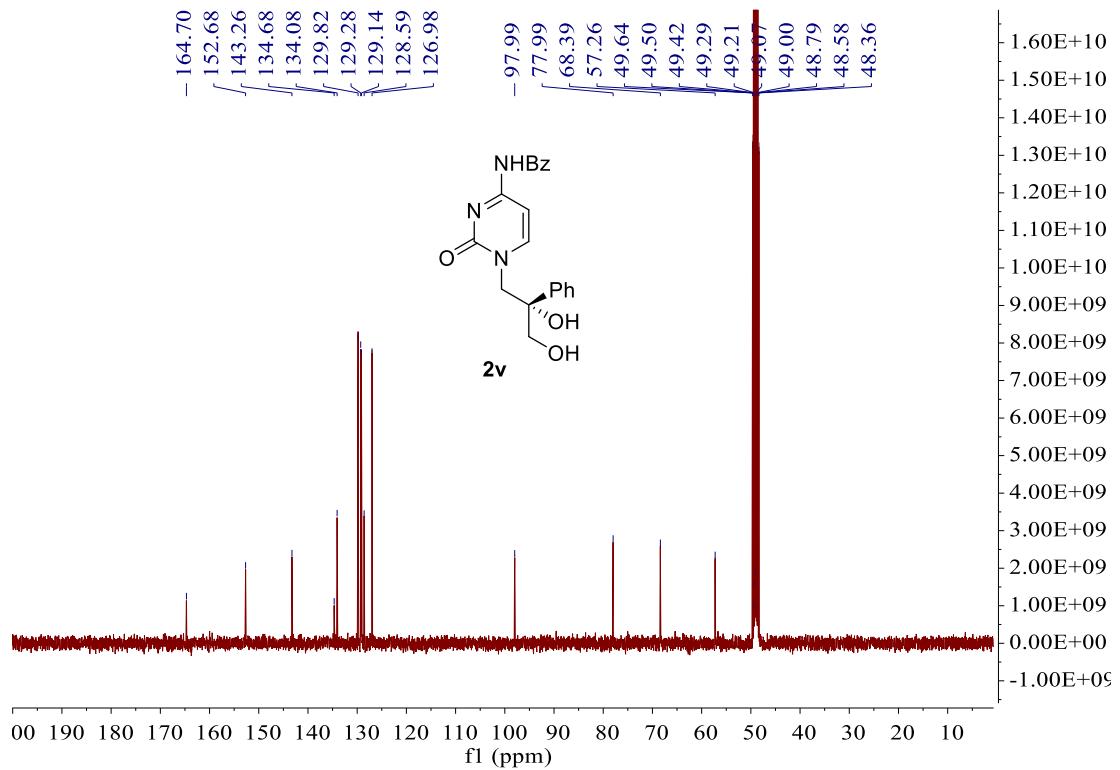
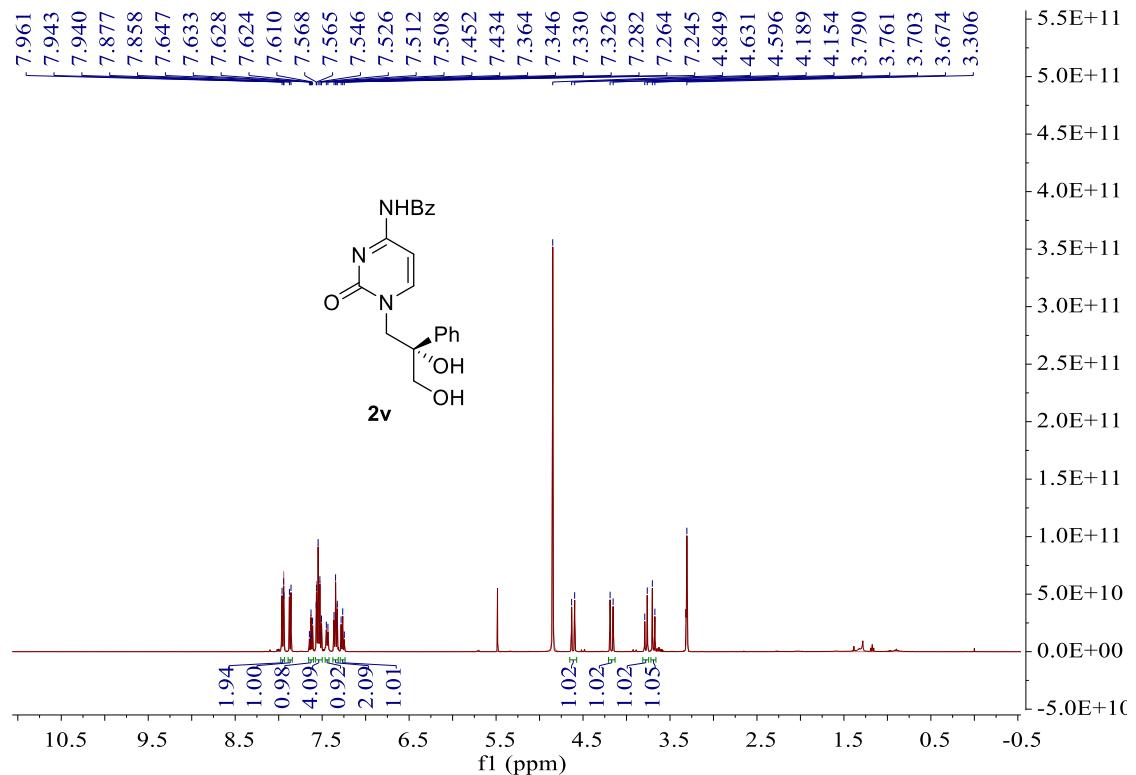


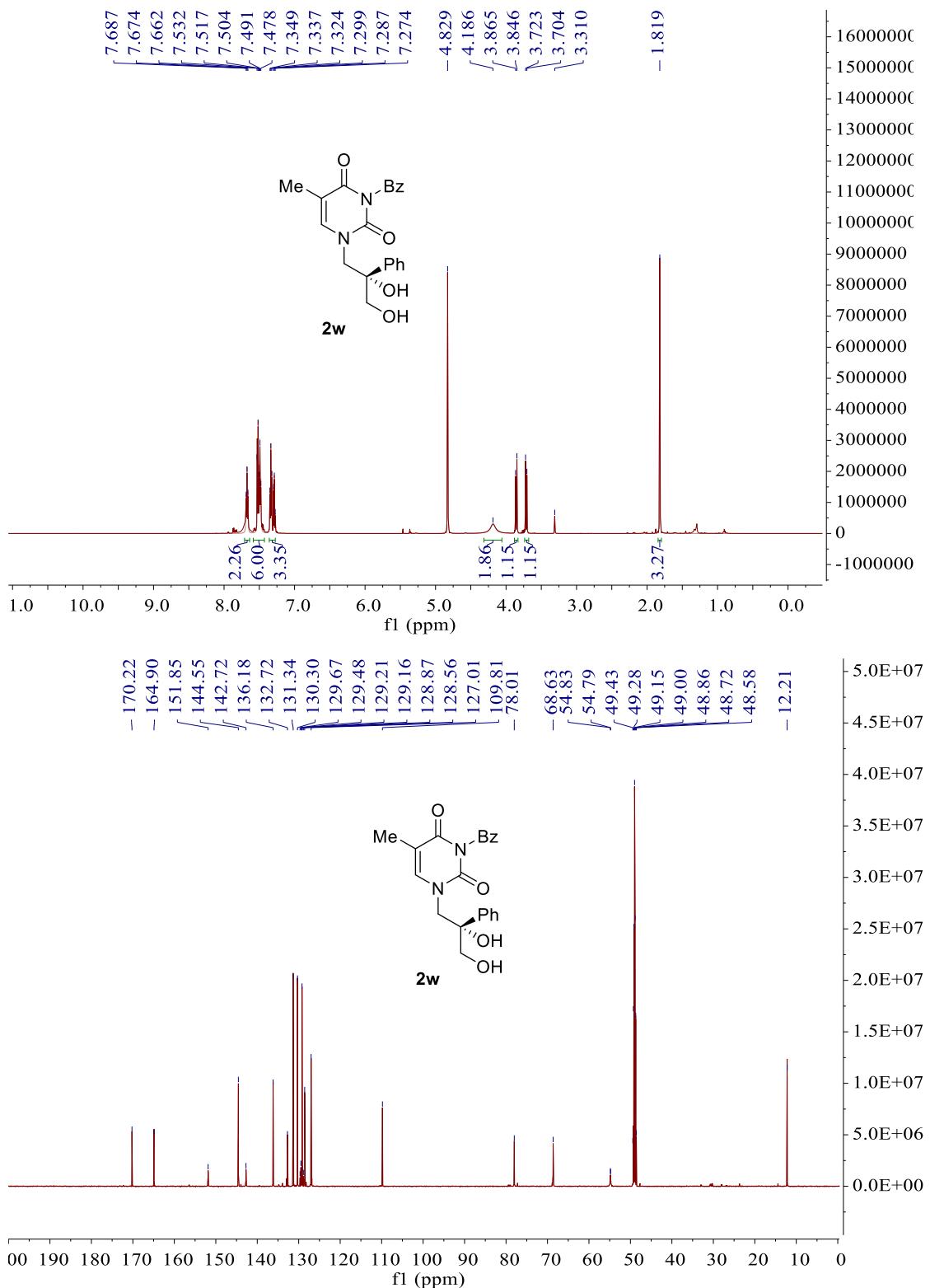


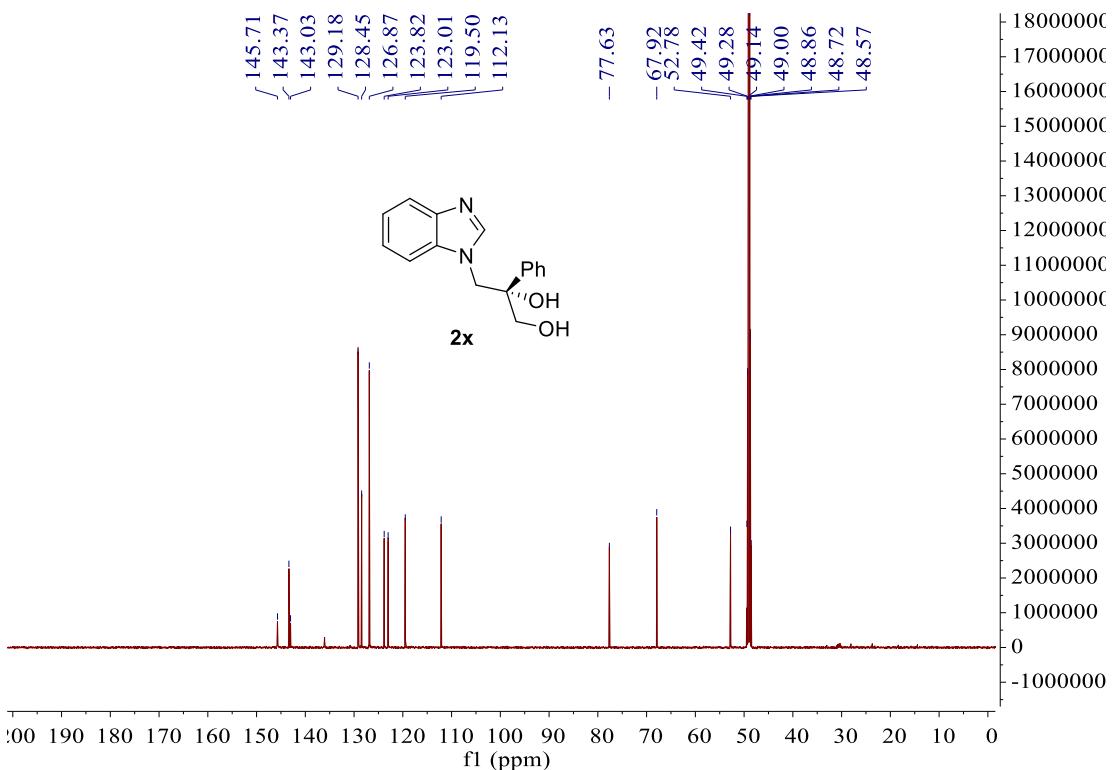
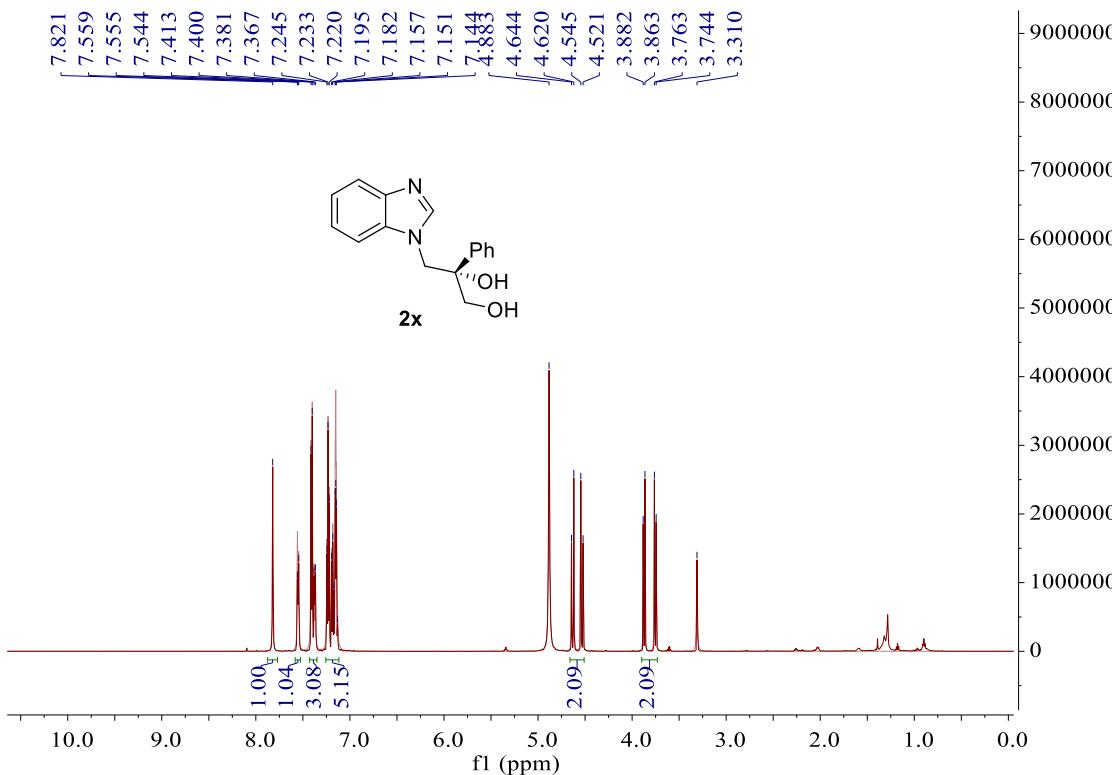


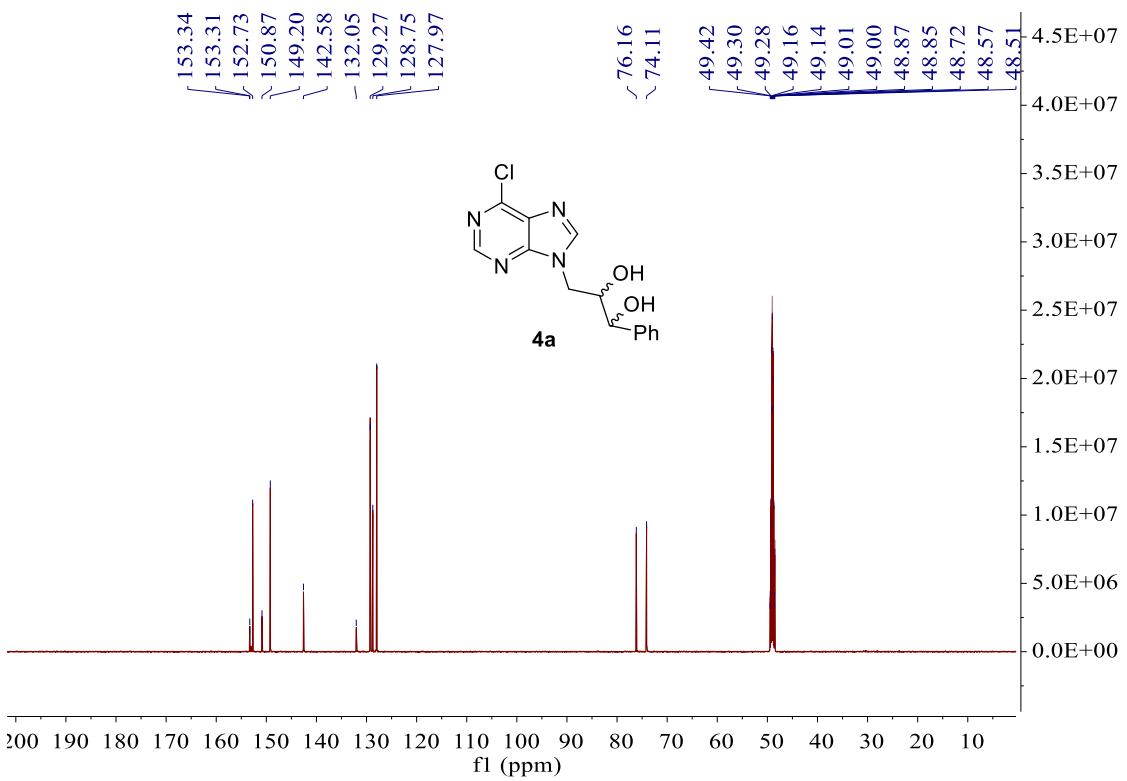
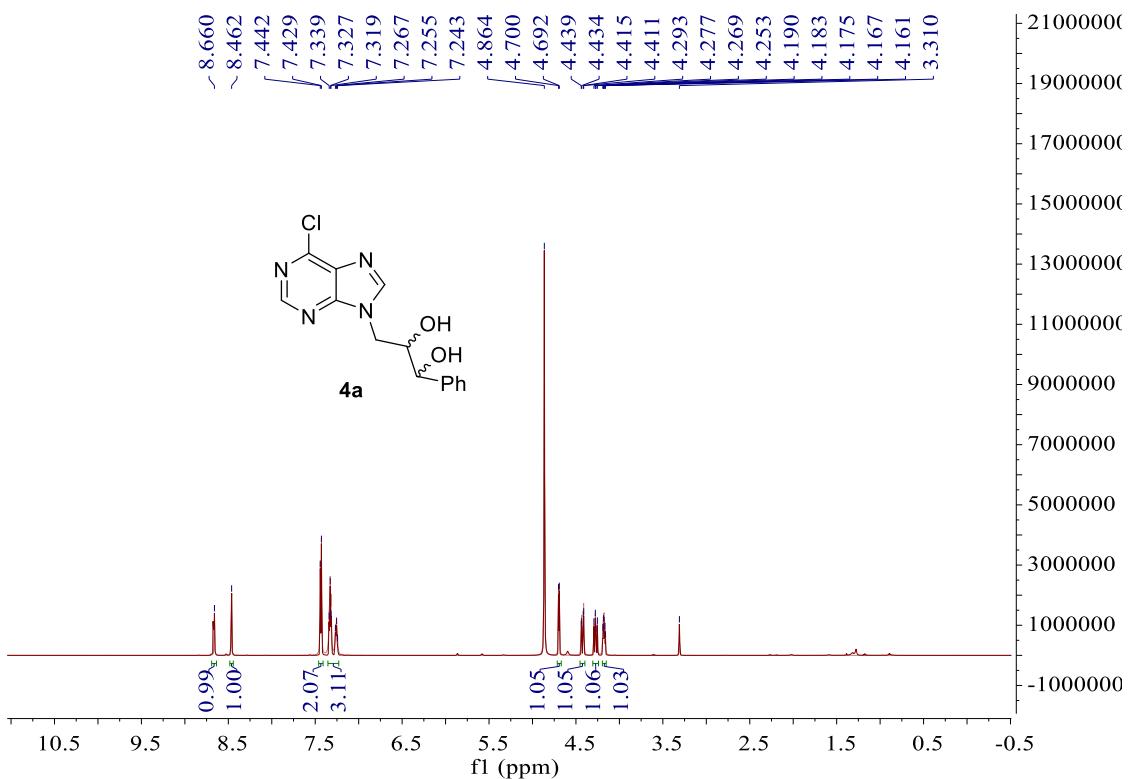


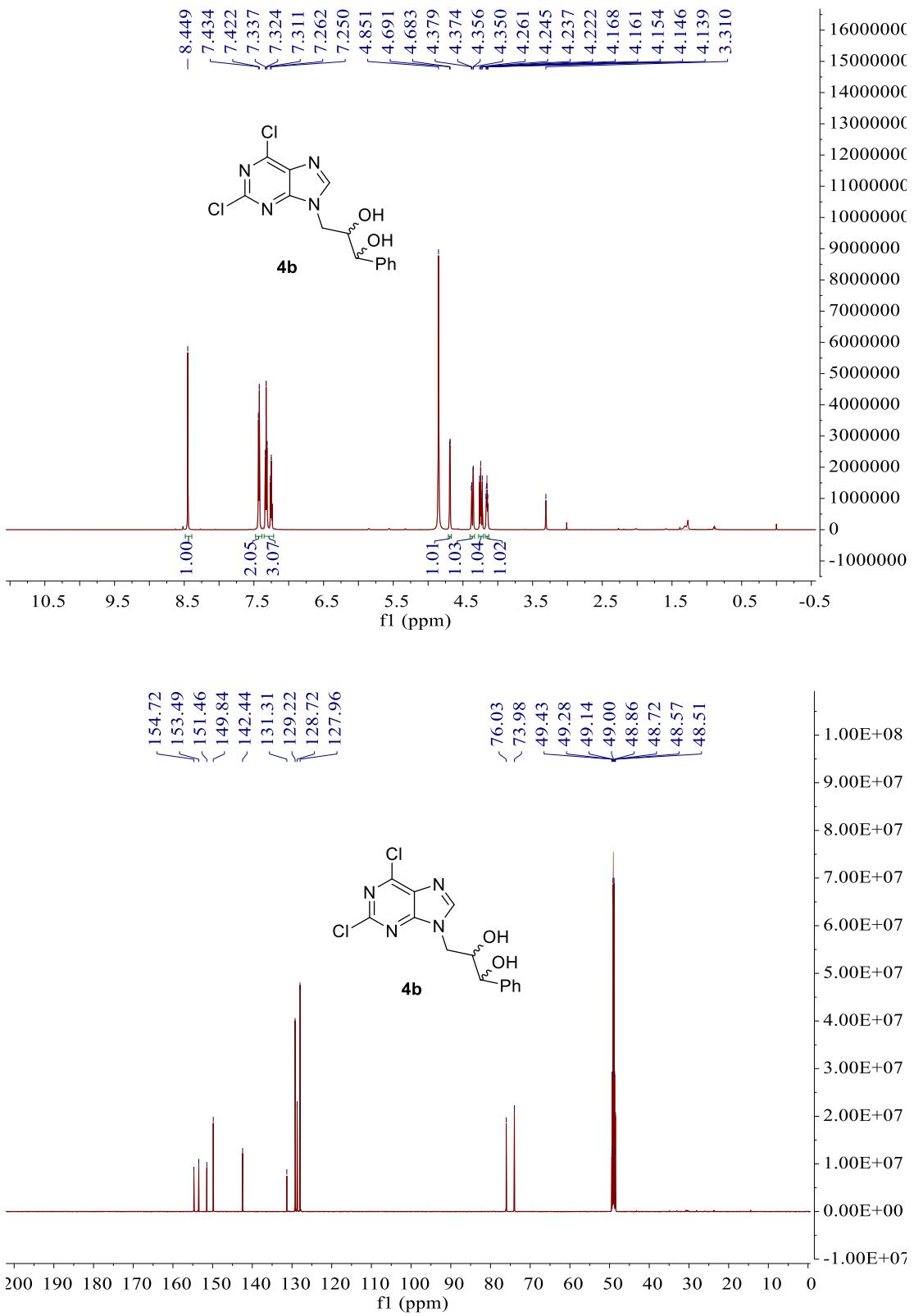


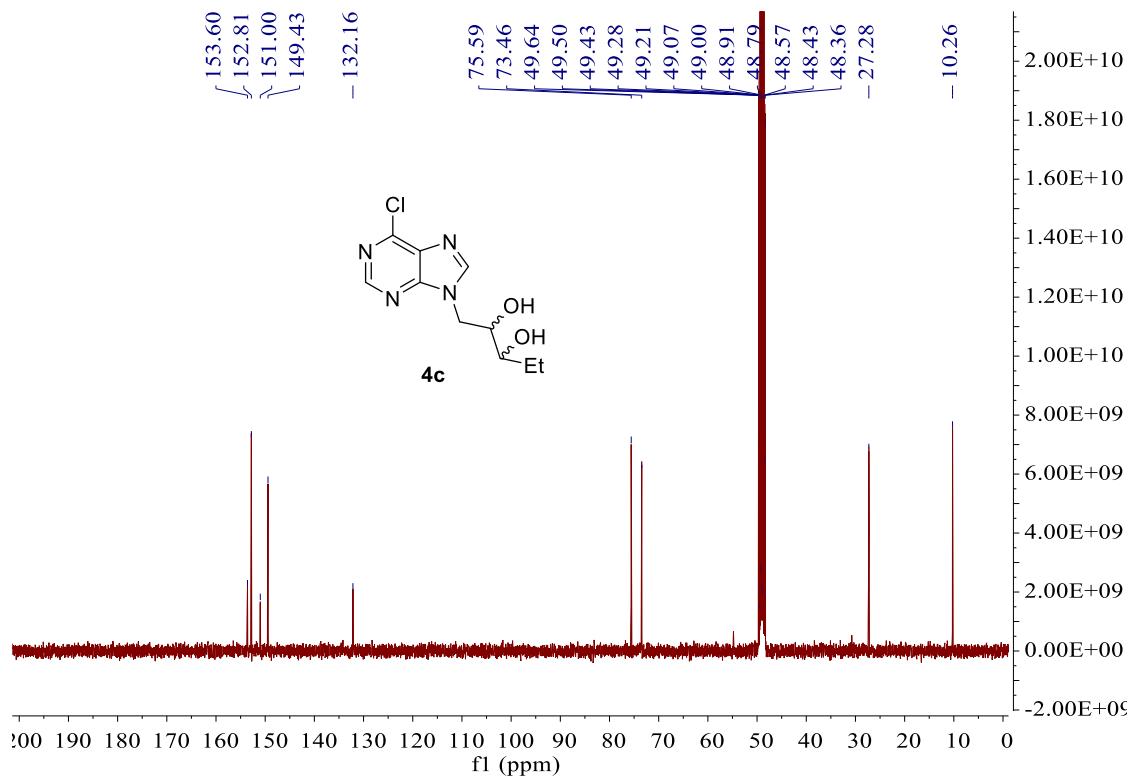
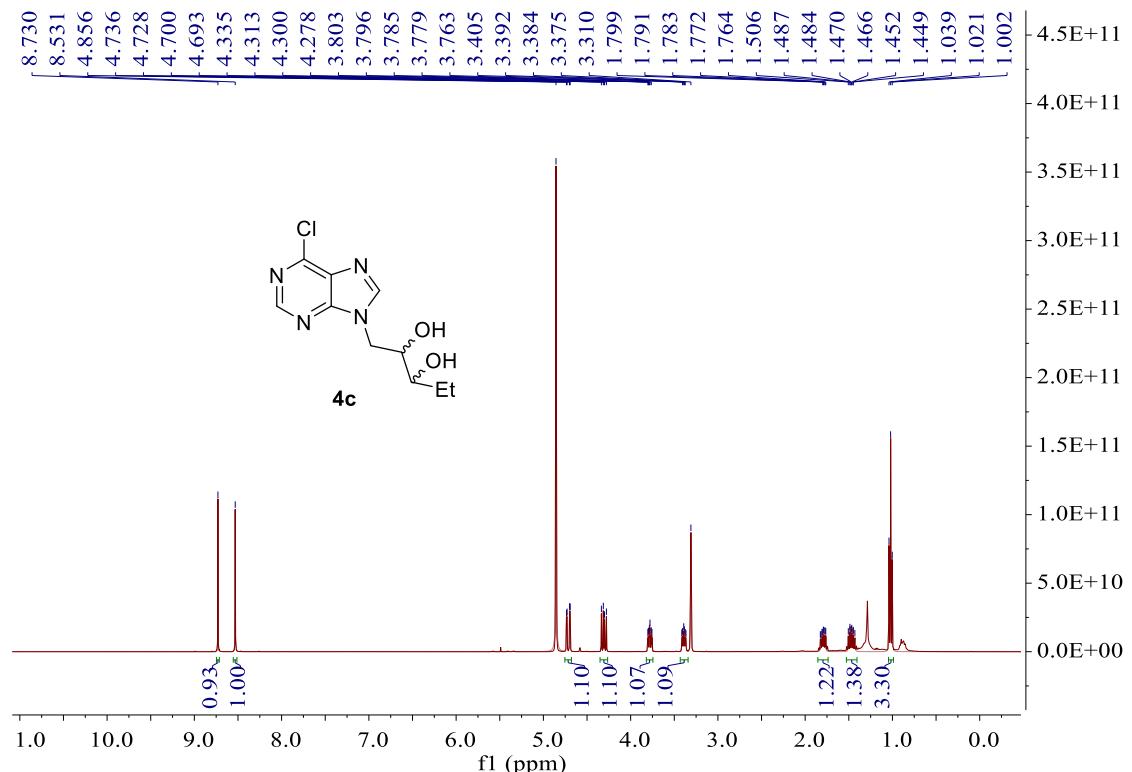


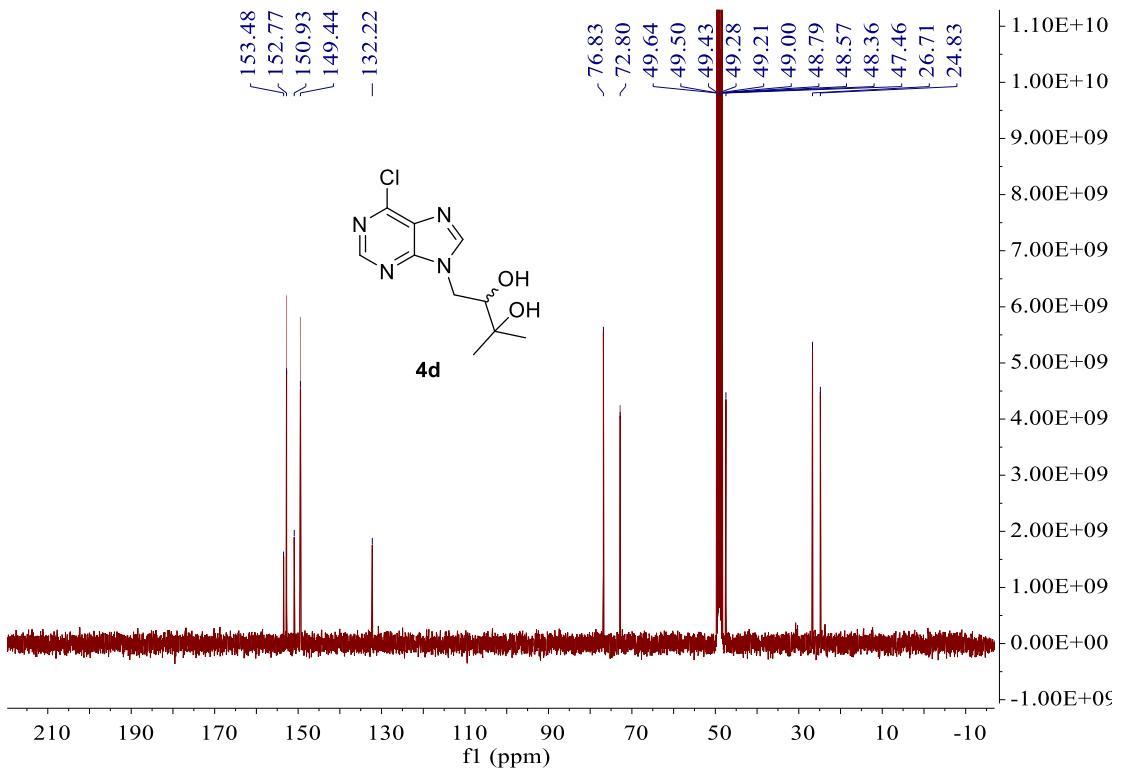
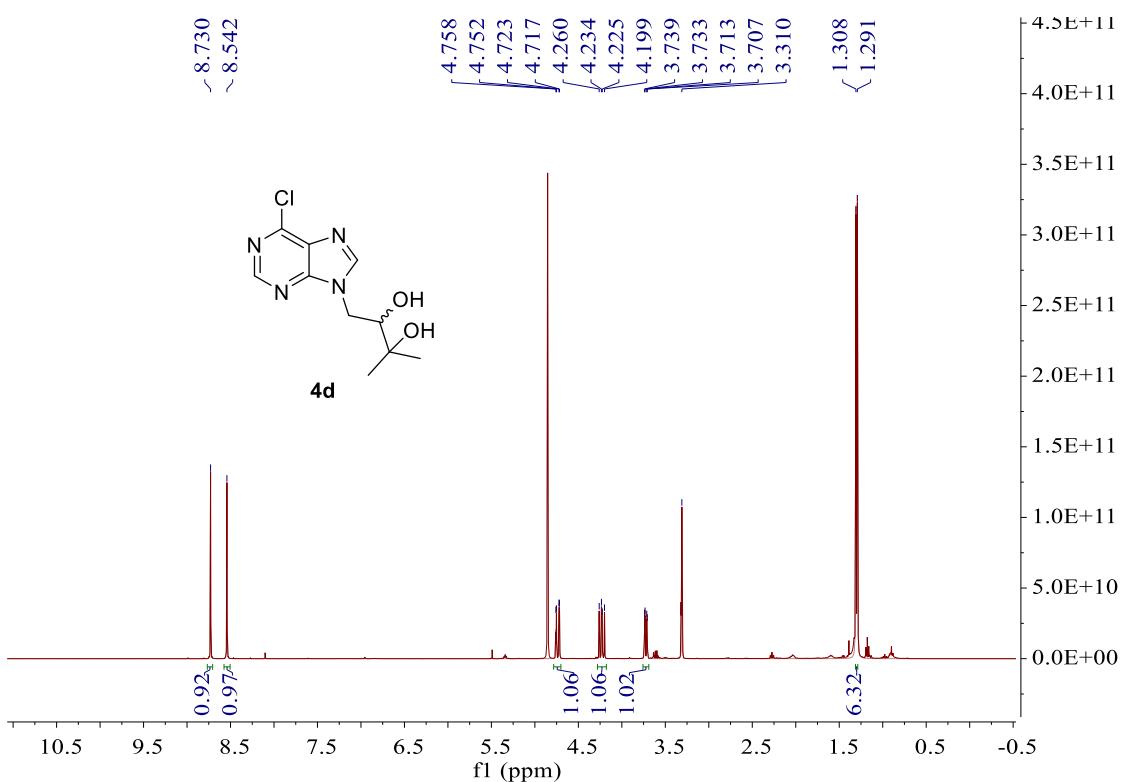




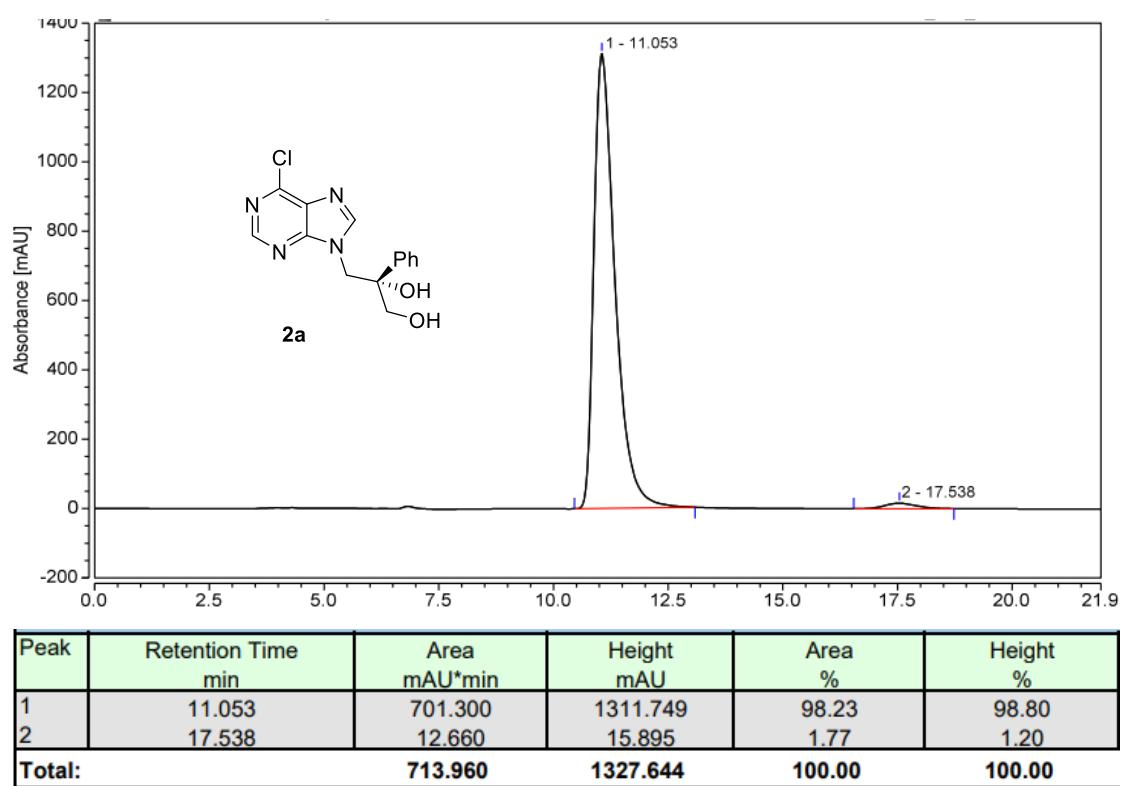
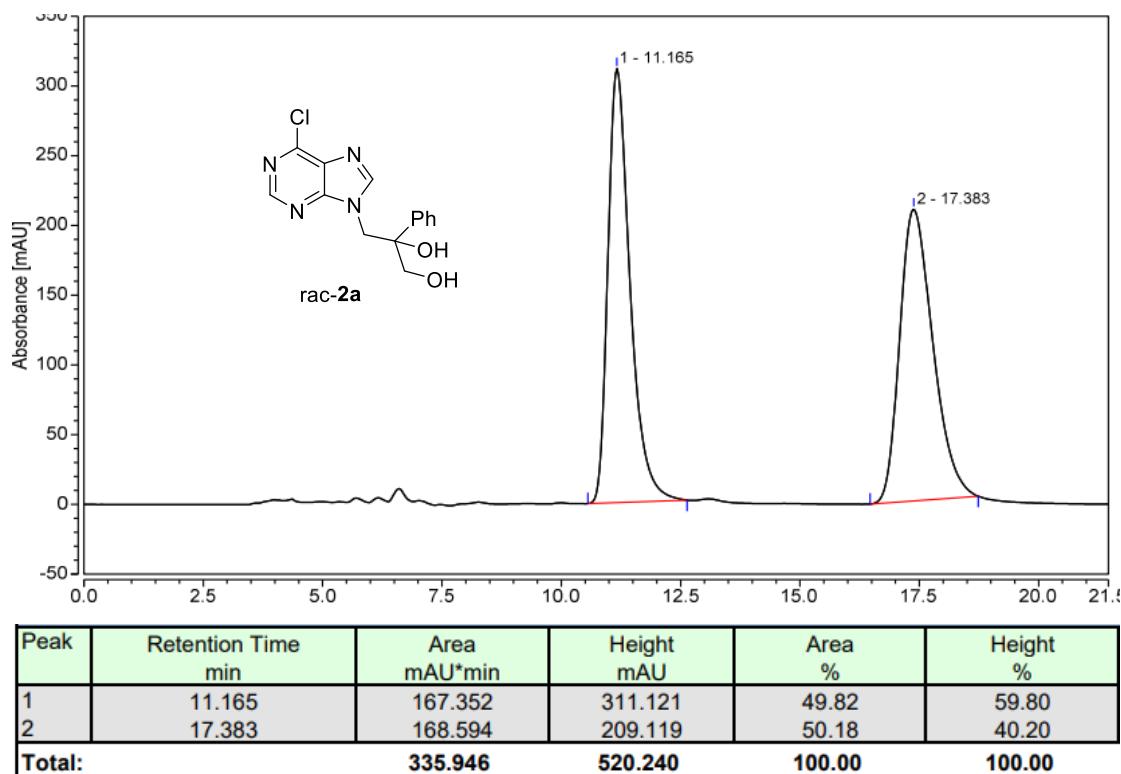


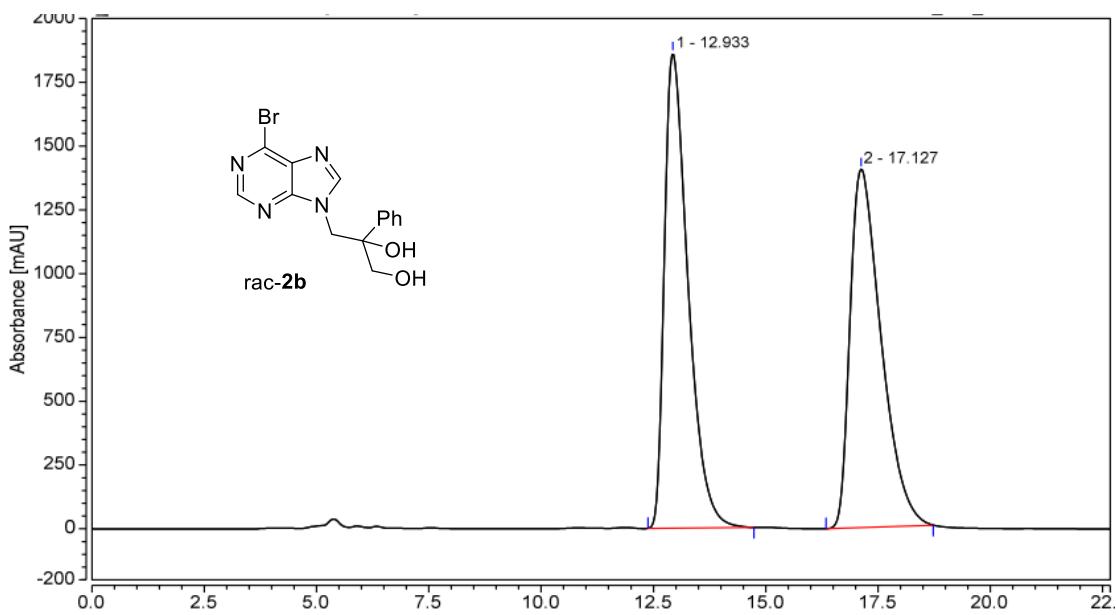




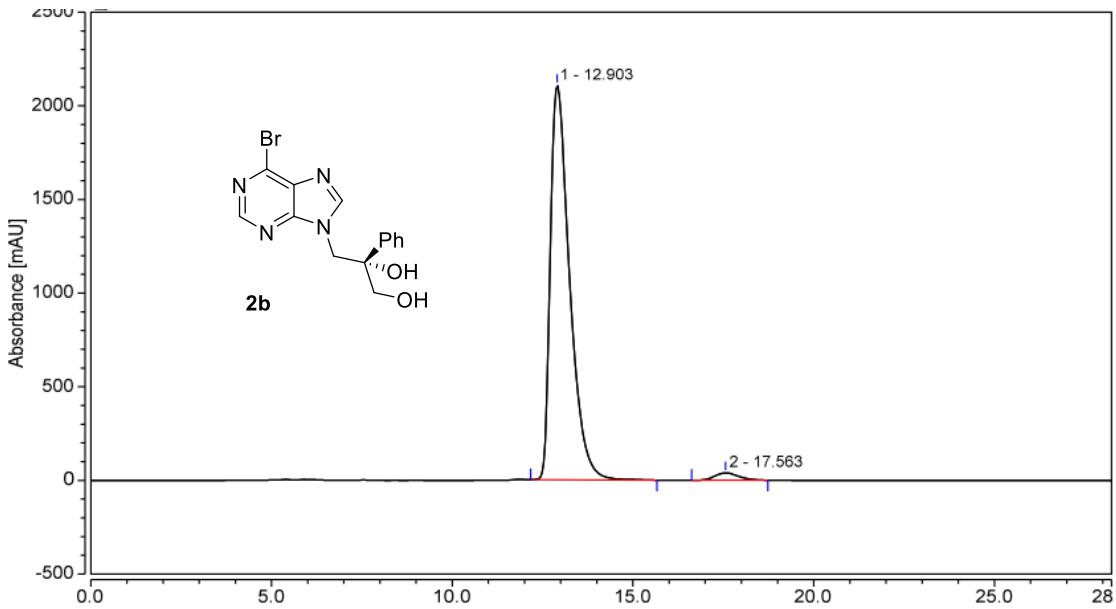


## 6. Copies of HPLC spectra for racemic and chiral products

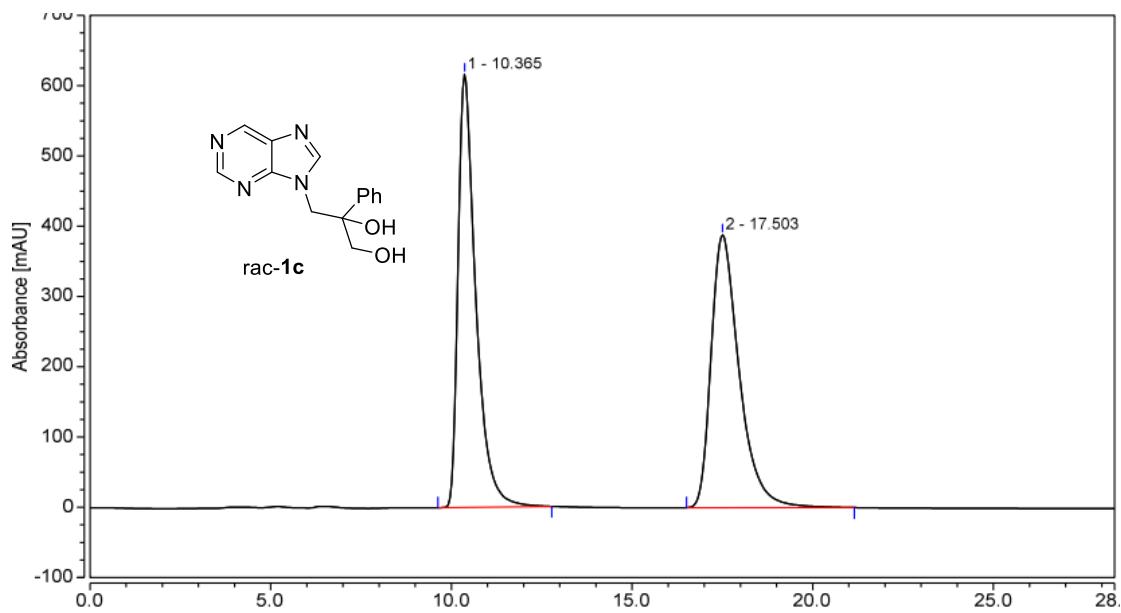




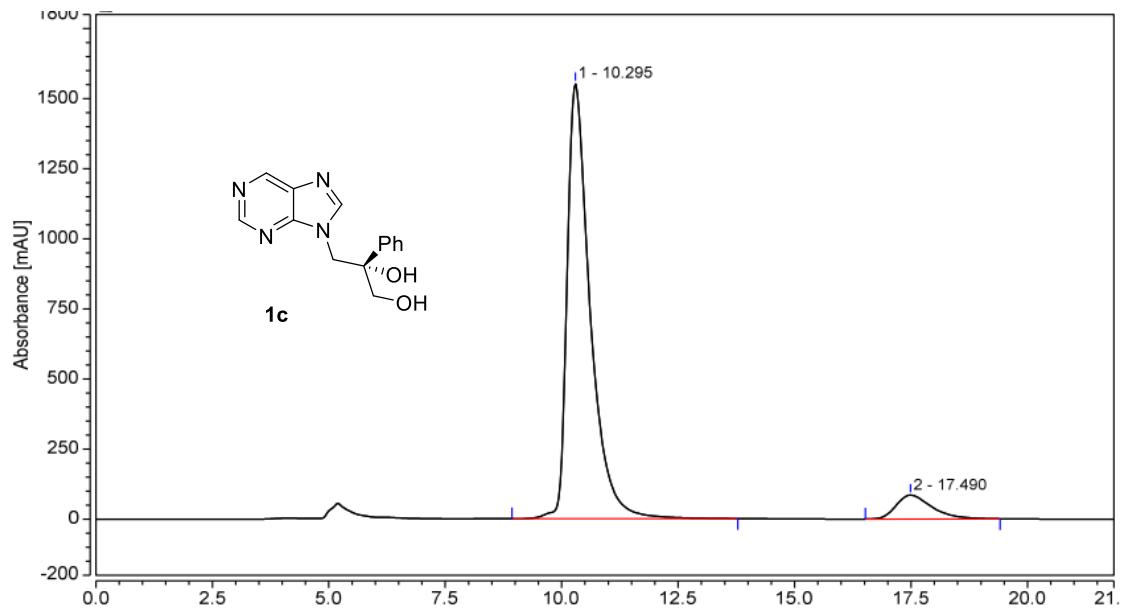
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.933	1136.935	1862.039	50.26	56.99
2	17.127	1125.214	1405.105	49.74	43.01
<b>Total:</b>		<b>2262.149</b>	<b>3267.144</b>	<b>100.00</b>	<b>100.00</b>



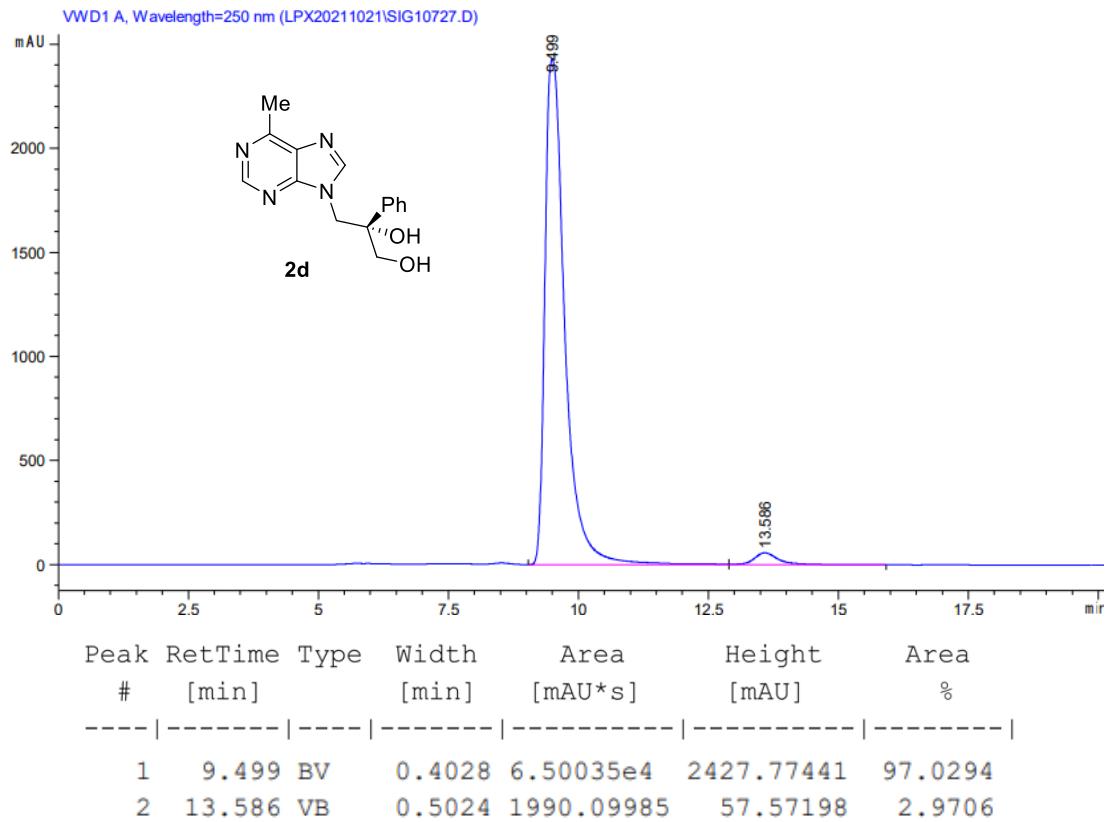
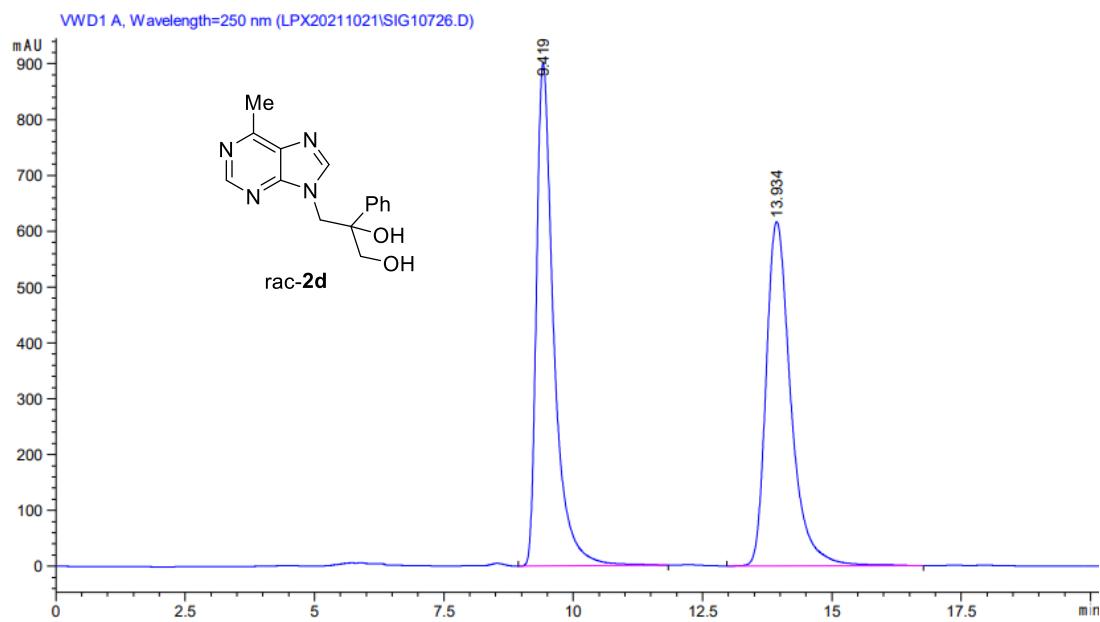
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.903	1299.200	2106.591	97.74	98.18
2	17.563	30.009	39.047	2.26	1.82
<b>Total:</b>		<b>1329.210</b>	<b>2145.638</b>	<b>100.00</b>	<b>100.00</b>

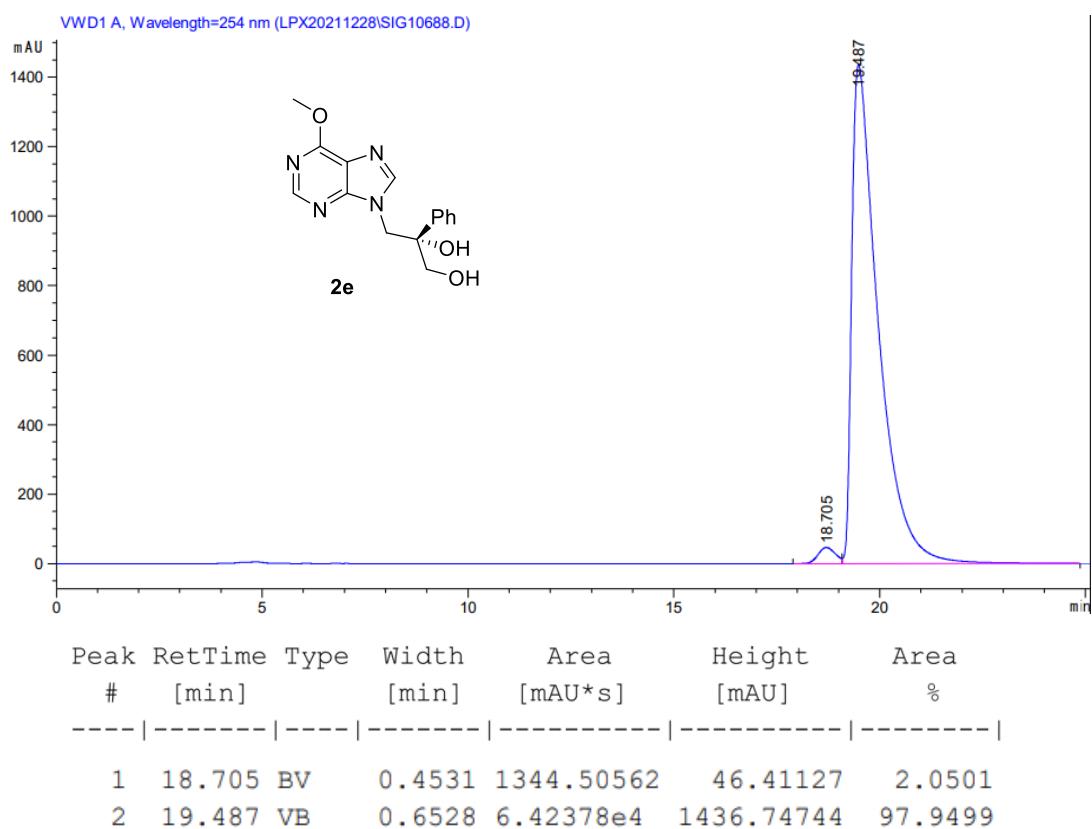
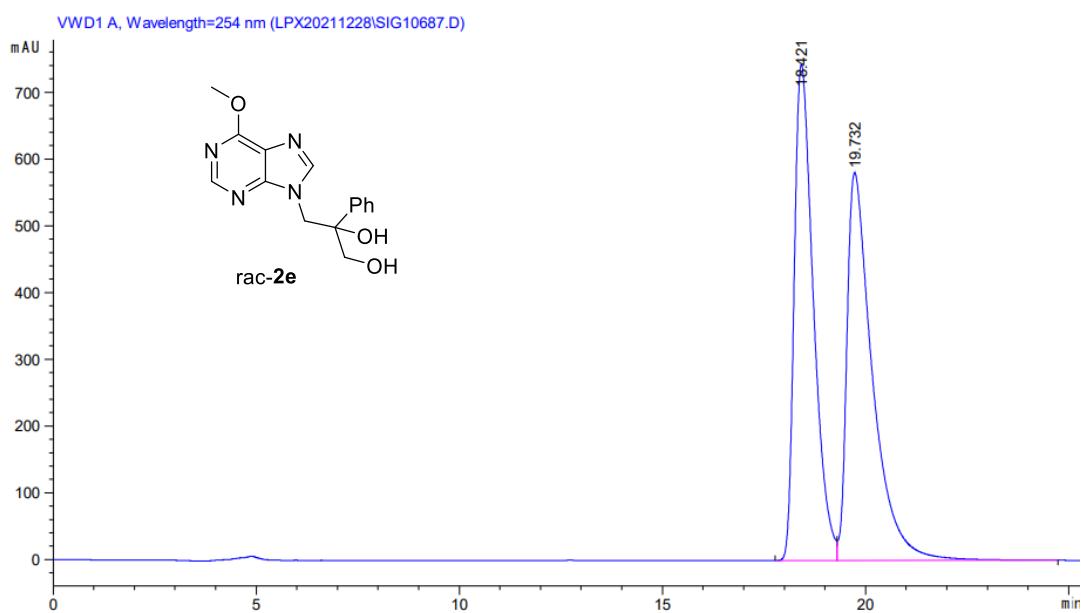


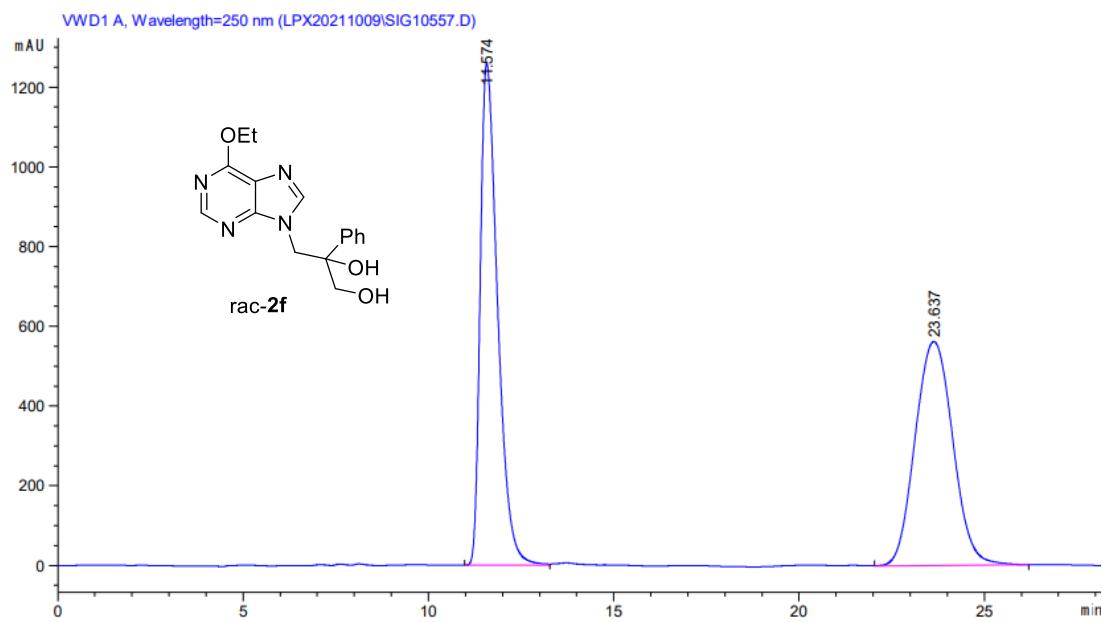
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.365	350.900	616.267	50.01	61.36
2	17.503	350.772	388.160	49.99	38.64
<b>Total:</b>		<b>701.672</b>	<b>1004.427</b>	<b>100.00</b>	<b>100.00</b>



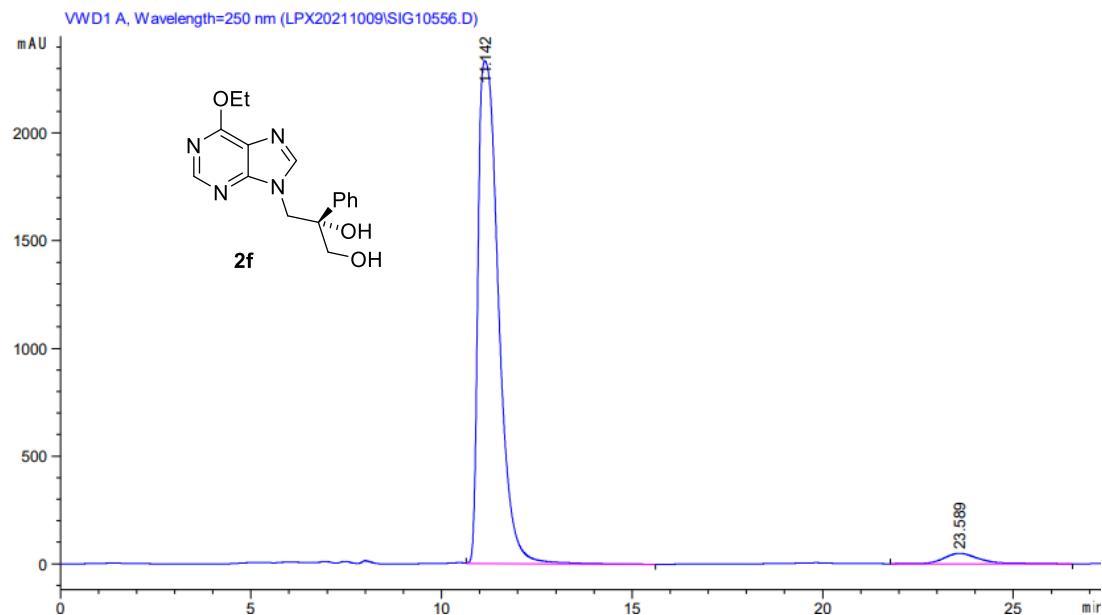
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.295	890.426	1552.128	92.17	94.80
2	17.490	75.681	85.071	7.83	5.20
<b>Total:</b>		<b>966.107</b>	<b>1637.199</b>	<b>100.00</b>	<b>100.00</b>



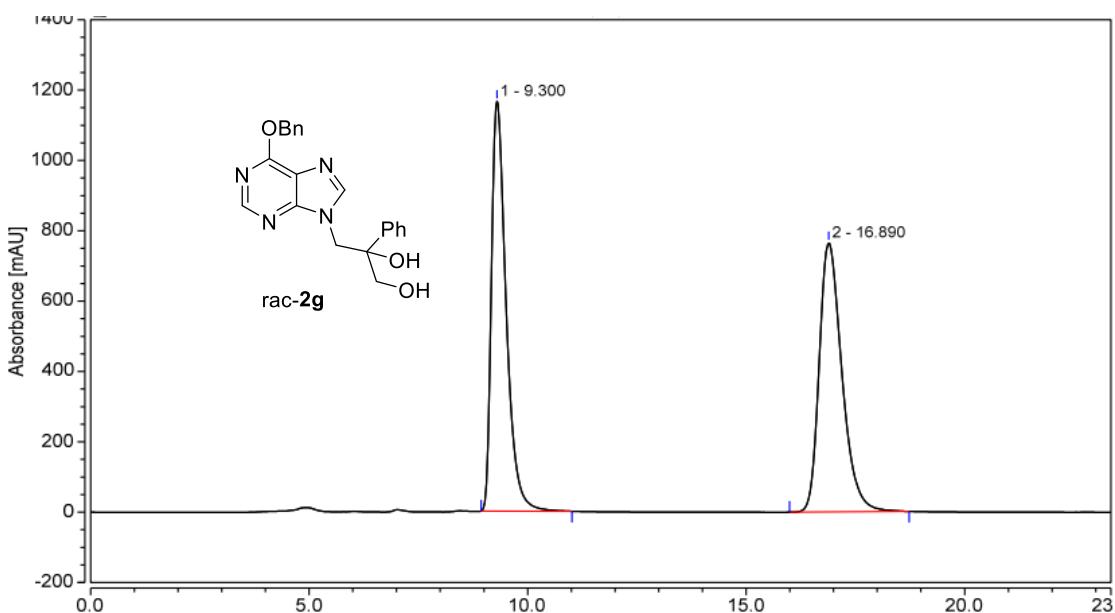




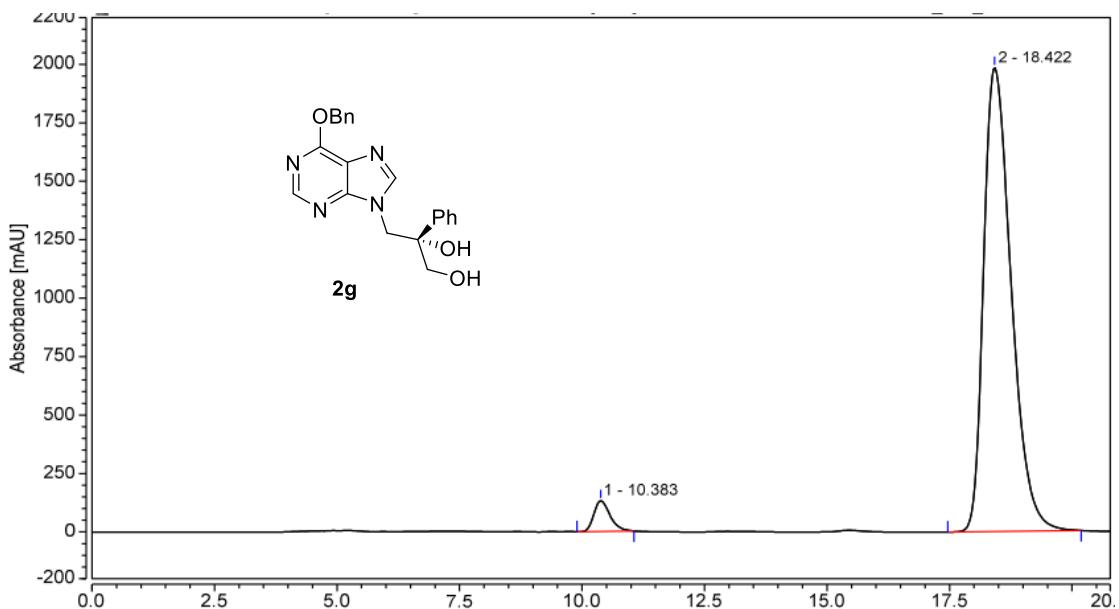
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.574	BV	0.4934	4.09975e4	1259.80493	50.7454
2	23.637	VB	1.0798	3.97931e4	561.97565	49.2546



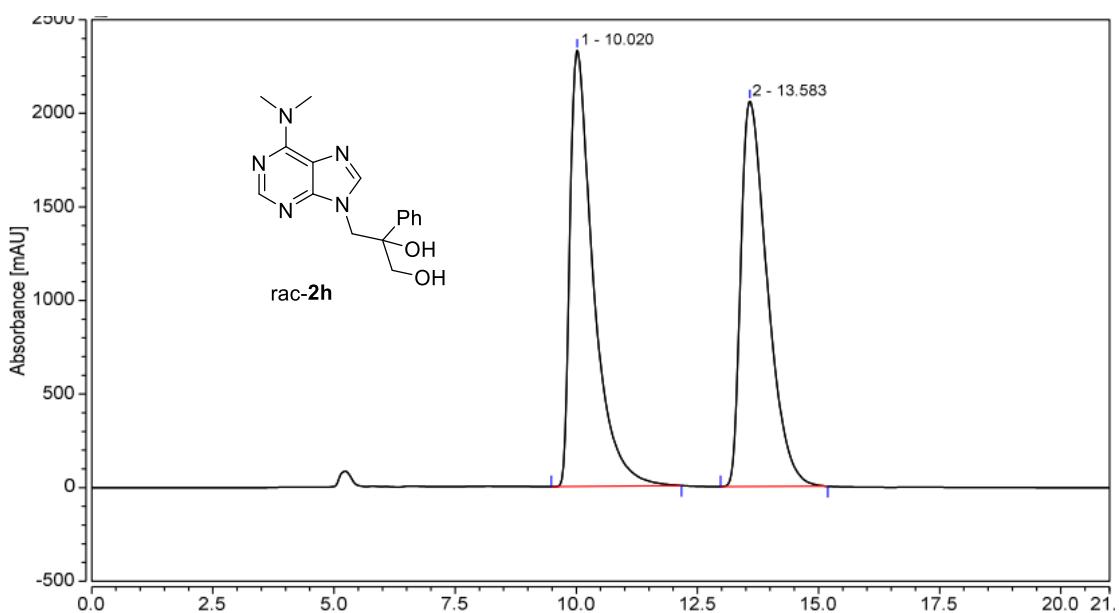
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.142	BV	0.5744	8.66354e4	2334.20801	96.4463
2	23.589	BB	0.9708	3192.19116	48.38729	3.5537



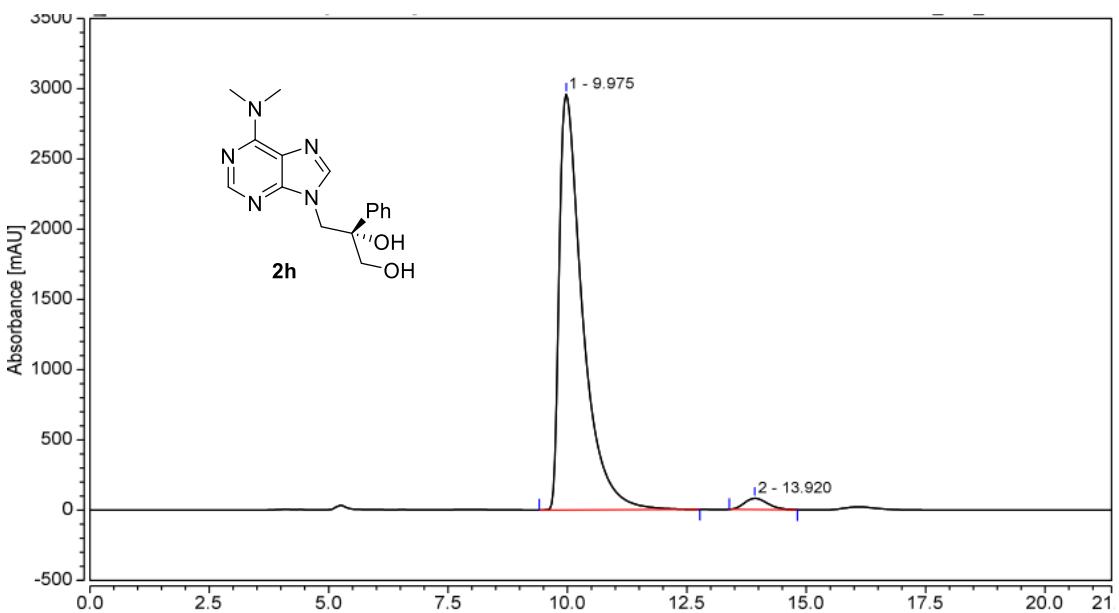
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.300	450.531	1165.175	49.51	60.35
2	16.890	459.428	765.490	50.49	39.65
<b>Total:</b>		<b>909.960</b>	<b>1930.665</b>	<b>100.00</b>	<b>100.00</b>



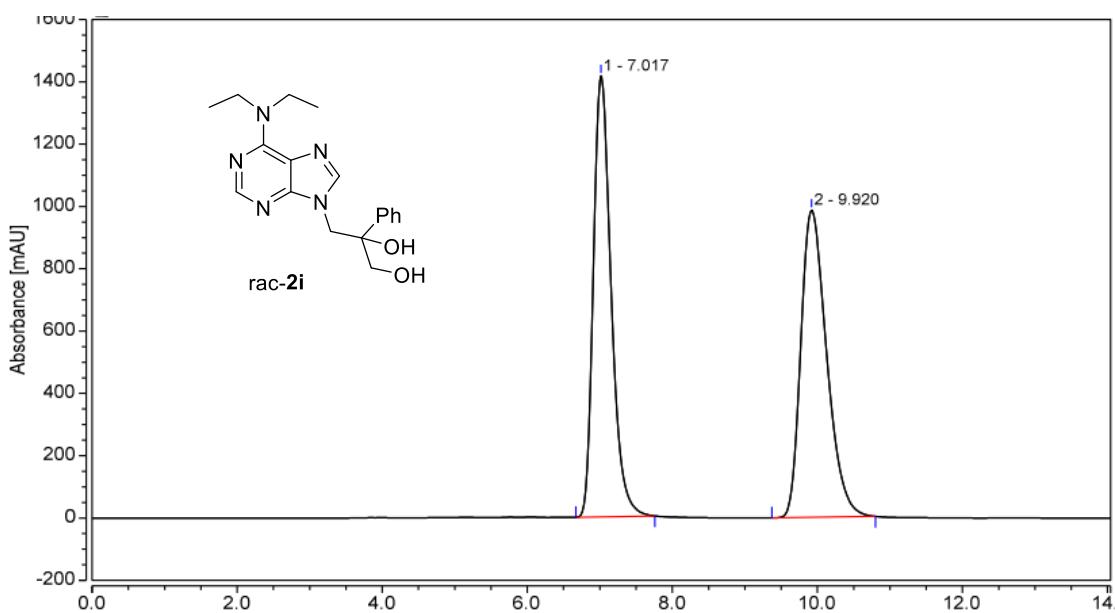
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.383	50.304	131.164	3.74	6.20
2	18.422	1293.865	1983.993	96.26	93.80
<b>Total:</b>		<b>1344.168</b>	<b>2115.157</b>	<b>100.00</b>	<b>100.00</b>



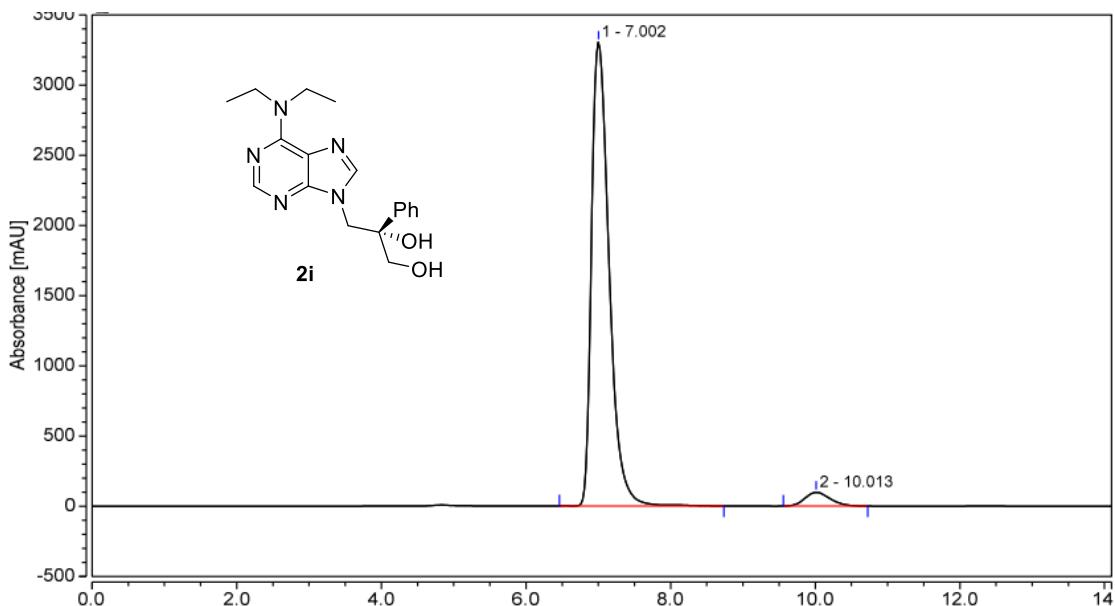
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.020	1303.164	2330.252	49.93	53.08
2	13.583	1307.052	2060.051	50.07	46.92
<b>Total:</b>		<b>2610.216</b>	<b>4390.303</b>	<b>100.00</b>	<b>100.00</b>



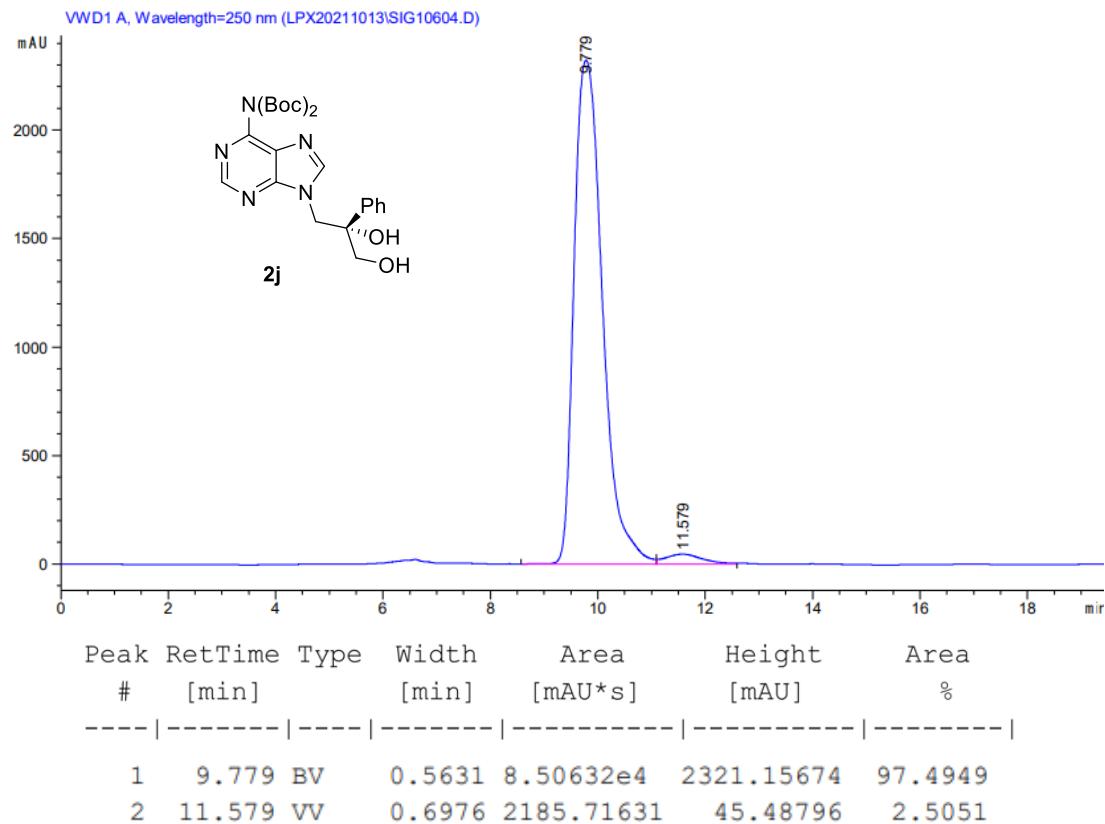
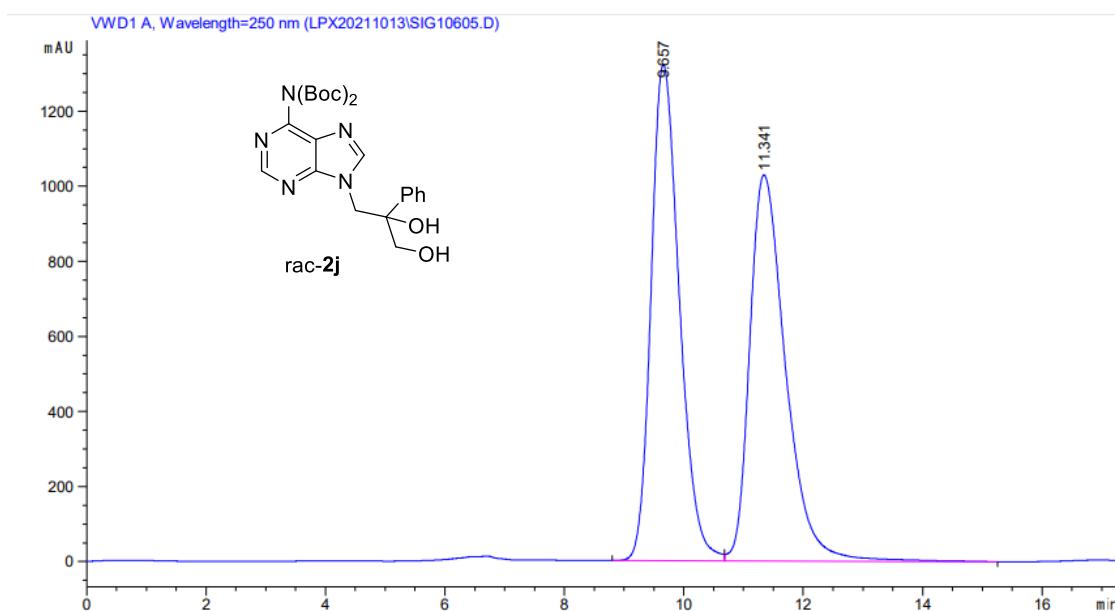
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.975	1671.614	2959.782	97.39	97.38
2	13.920	44.731	79.707	2.61	2.62
<b>Total:</b>		<b>1716.345</b>	<b>3039.489</b>	<b>100.00</b>	<b>100.00</b>

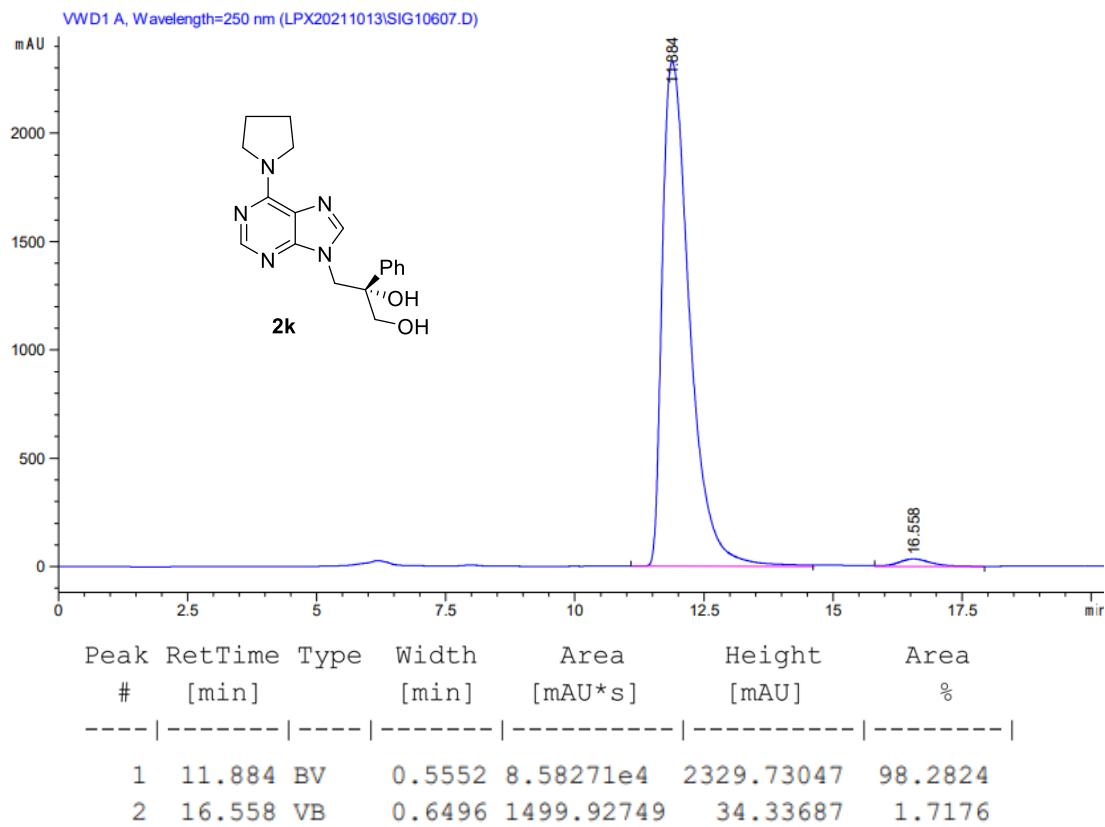
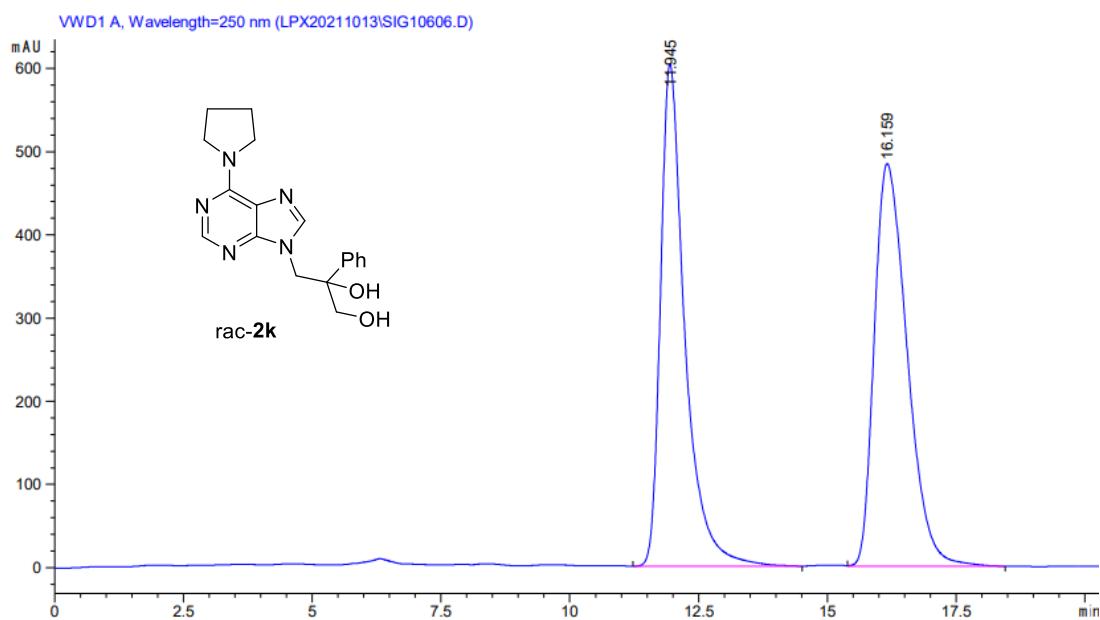


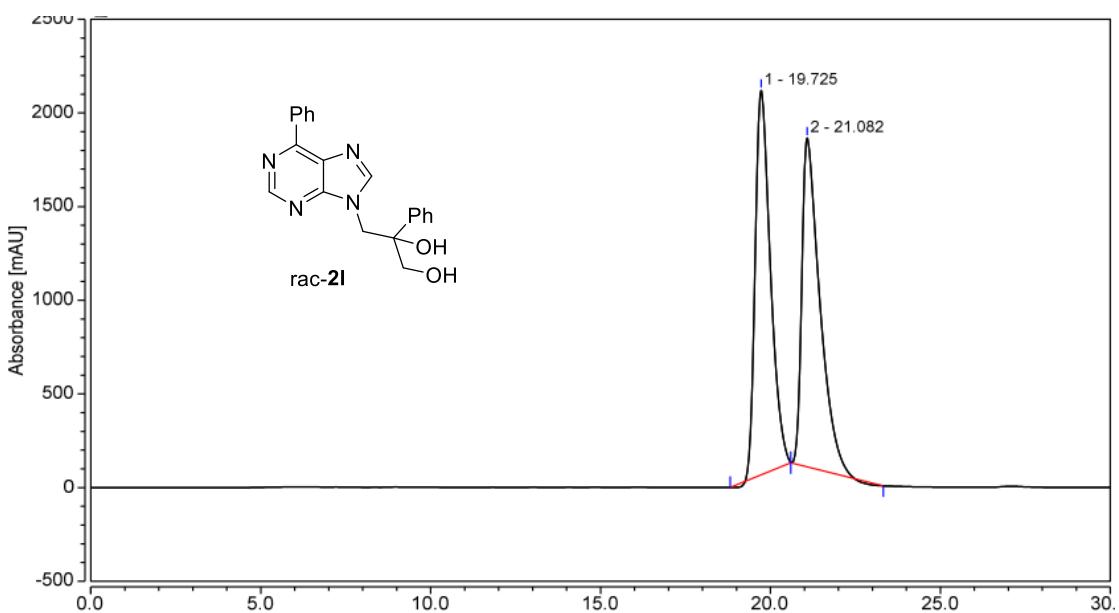
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.017	401.605	1415.680	49.72	58.95
2	9.920	406.101	985.818	50.28	41.05
<b>Total:</b>		<b>807.706</b>	<b>2401.498</b>	<b>100.00</b>	<b>100.00</b>



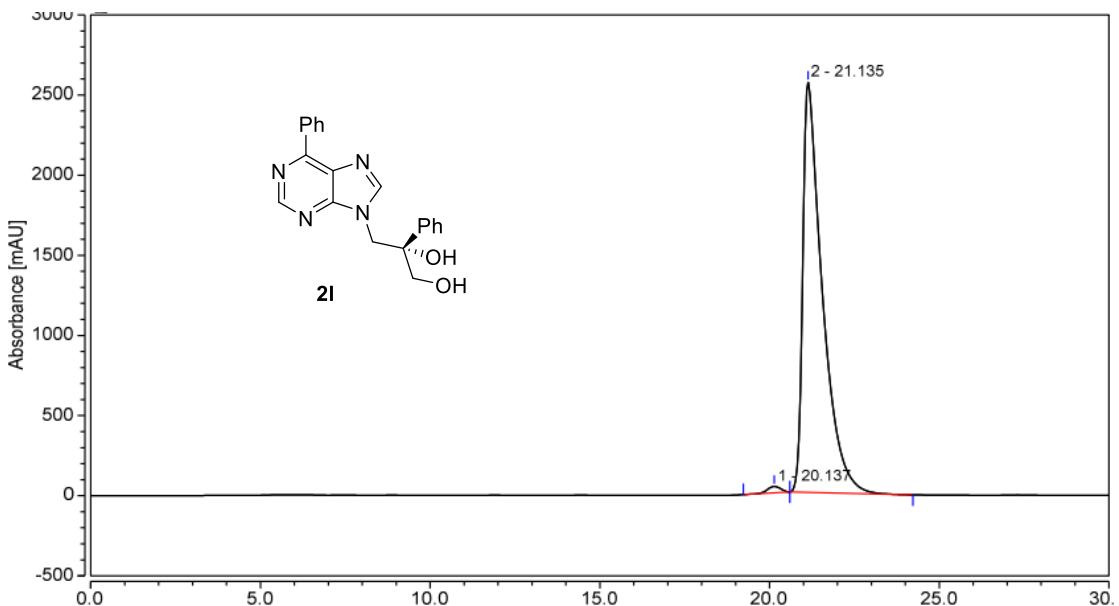
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.002	929.340	3303.169	95.90	97.13
2	10.013	39.770	97.676	4.10	2.87
<b>Total:</b>		<b>969.110</b>	<b>3400.845</b>	<b>100.00</b>	<b>100.00</b>



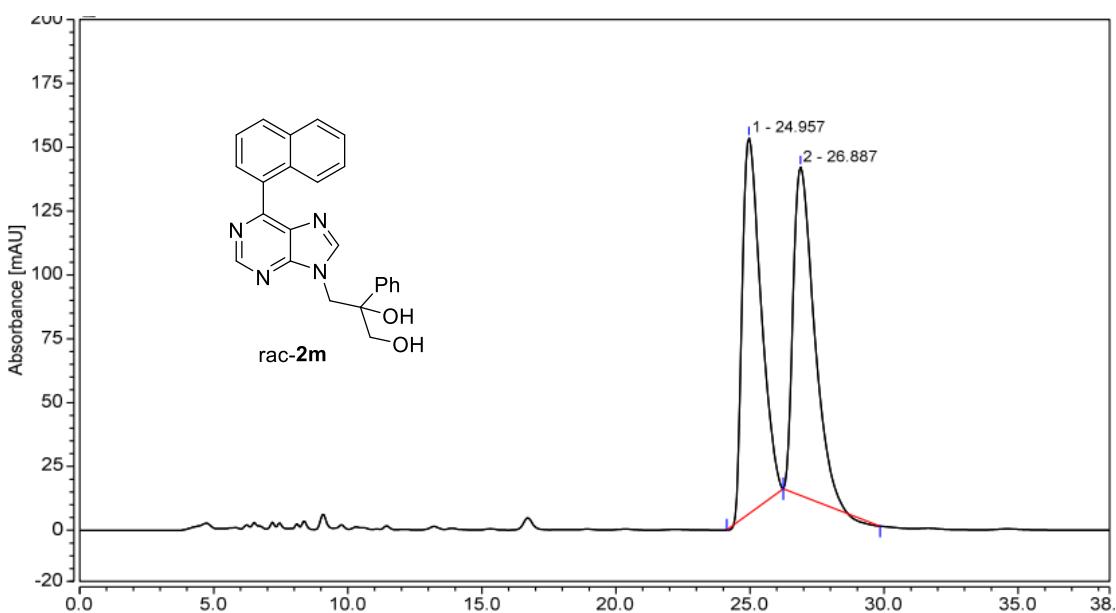




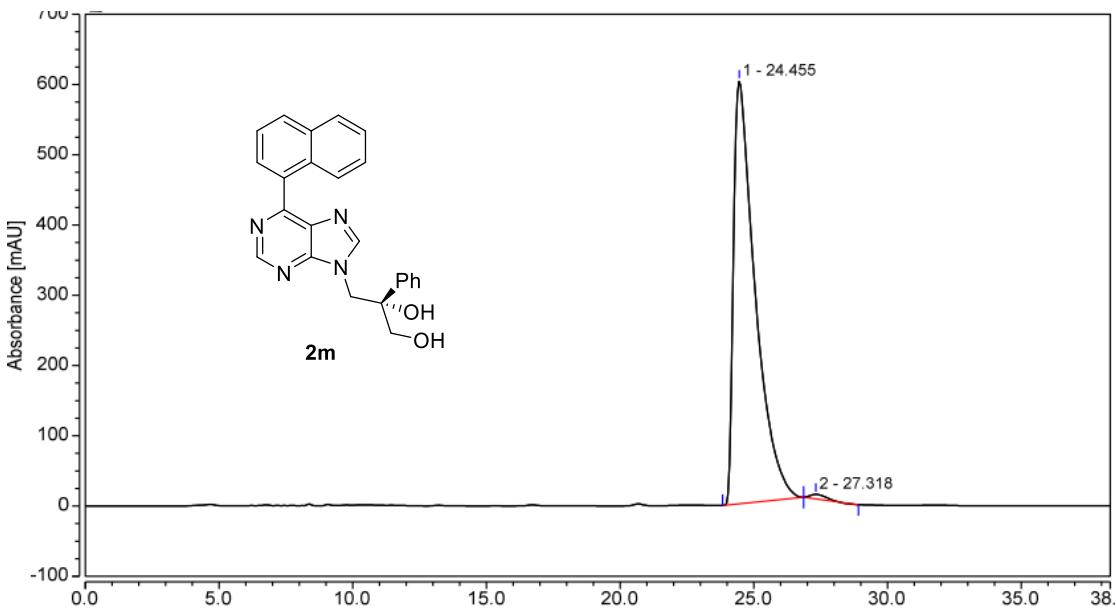
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.725	1061.623	2052.494	49.69	53.91
2	21.082	1074.802	1754.904	50.31	46.09
<b>Total:</b>		<b>2136.425</b>	<b>3807.398</b>	<b>100.00</b>	<b>100.00</b>



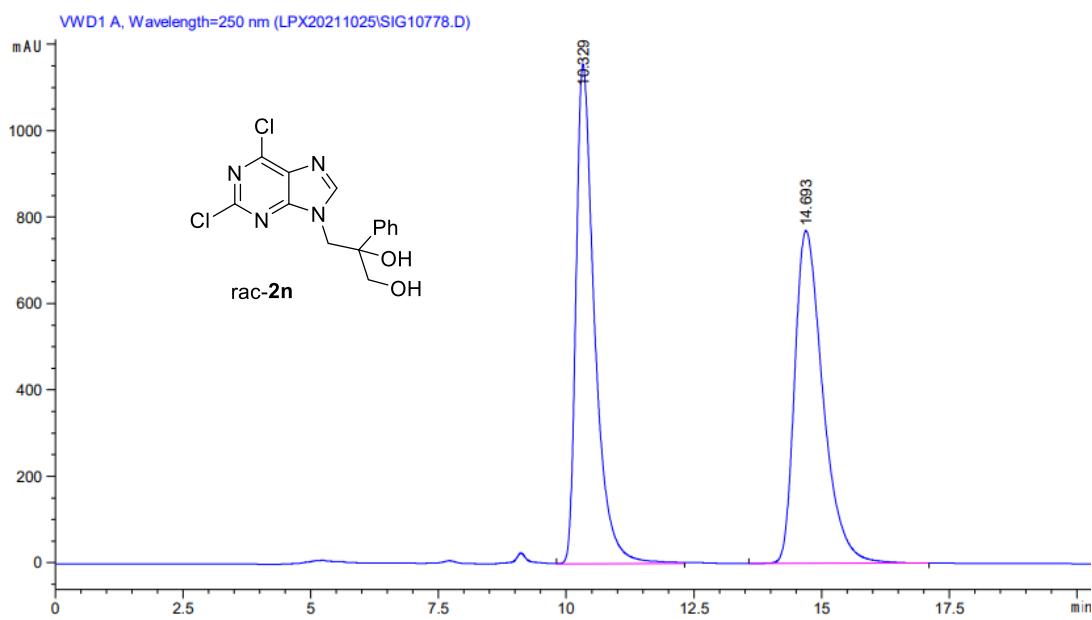
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.137	18.209	40.109	1.06	1.54
2	21.135	1705.939	2559.155	98.94	98.46
<b>Total:</b>		<b>1724.148</b>	<b>2599.264</b>	<b>100.00</b>	<b>100.00</b>



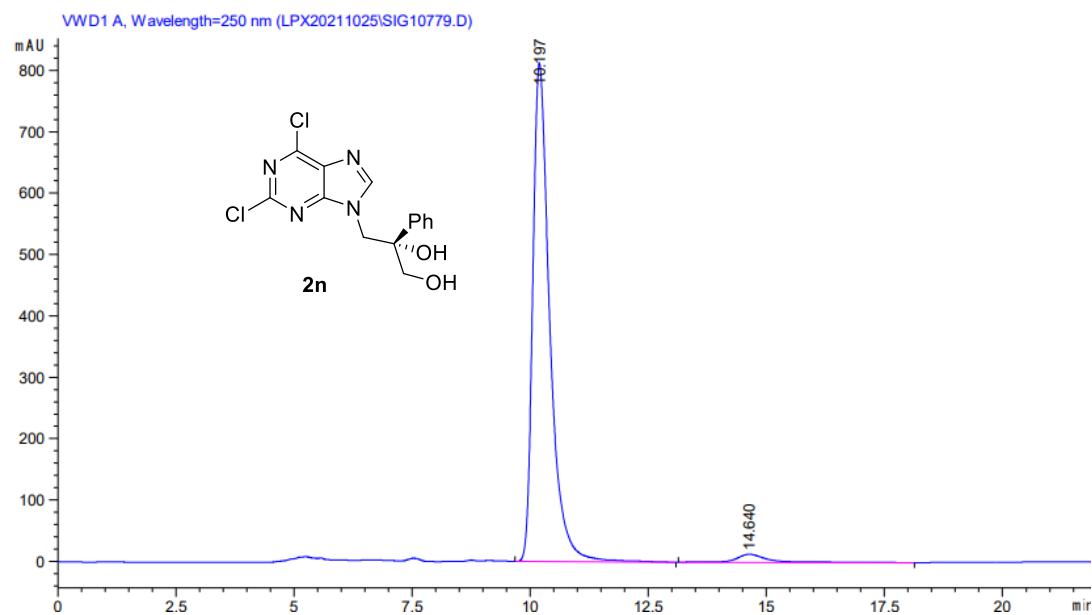
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.957	118.682	147.294	50.40	53.39
2	26.887	116.793	128.605	49.60	46.61
<b>Total:</b>		<b>235.475</b>	<b>275.899</b>	<b>100.00</b>	<b>100.00</b>



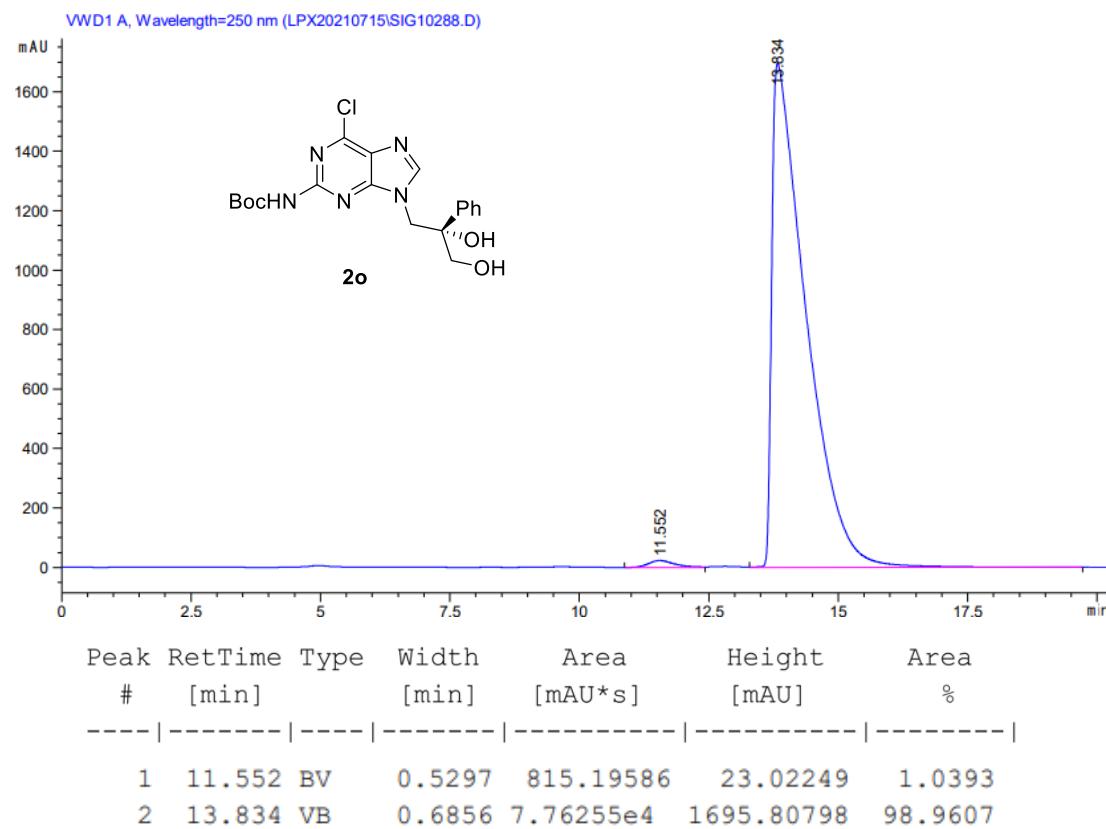
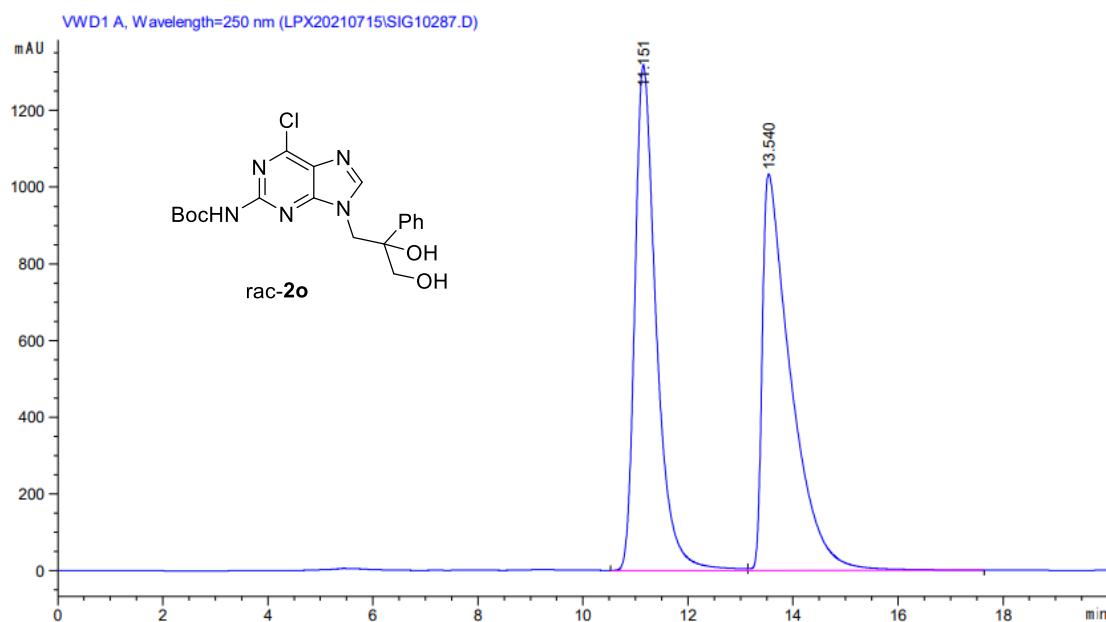
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.455	563.081	601.969	99.25	98.93
2	27.318	4.277	6.500	0.75	1.07
<b>Total:</b>		<b>567.358</b>	<b>608.469</b>	<b>100.00</b>	<b>100.00</b>

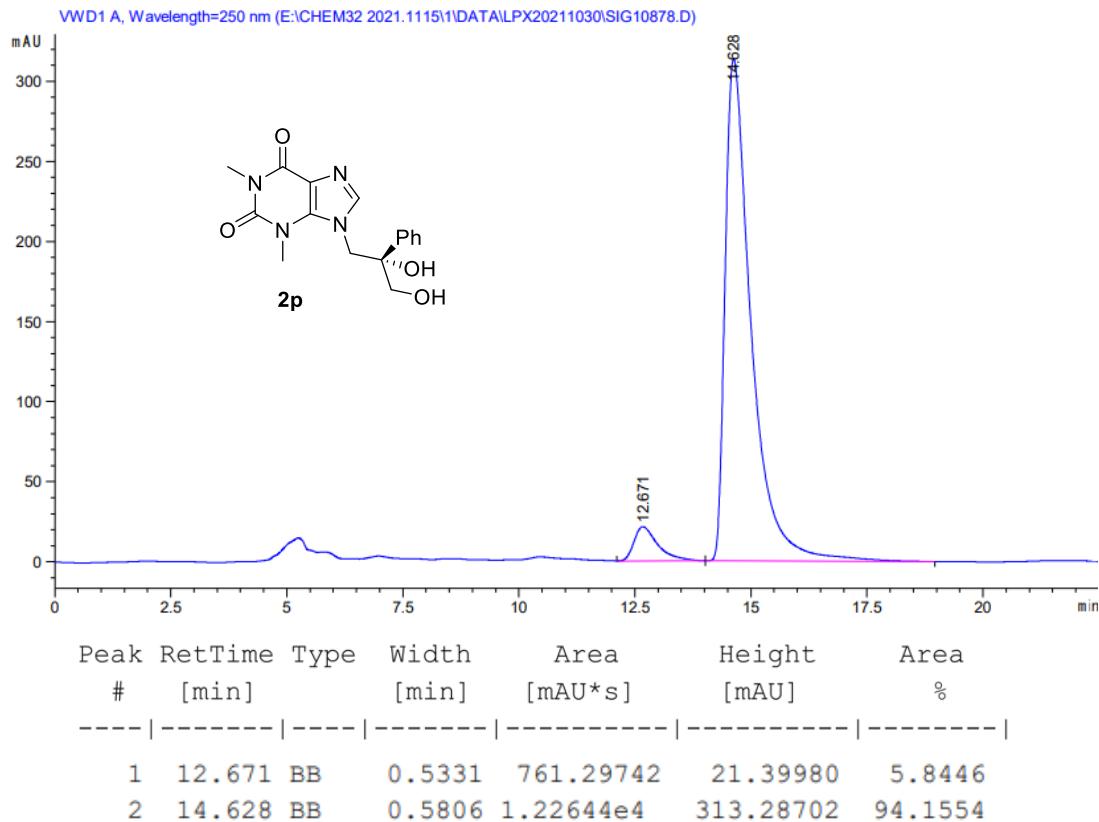
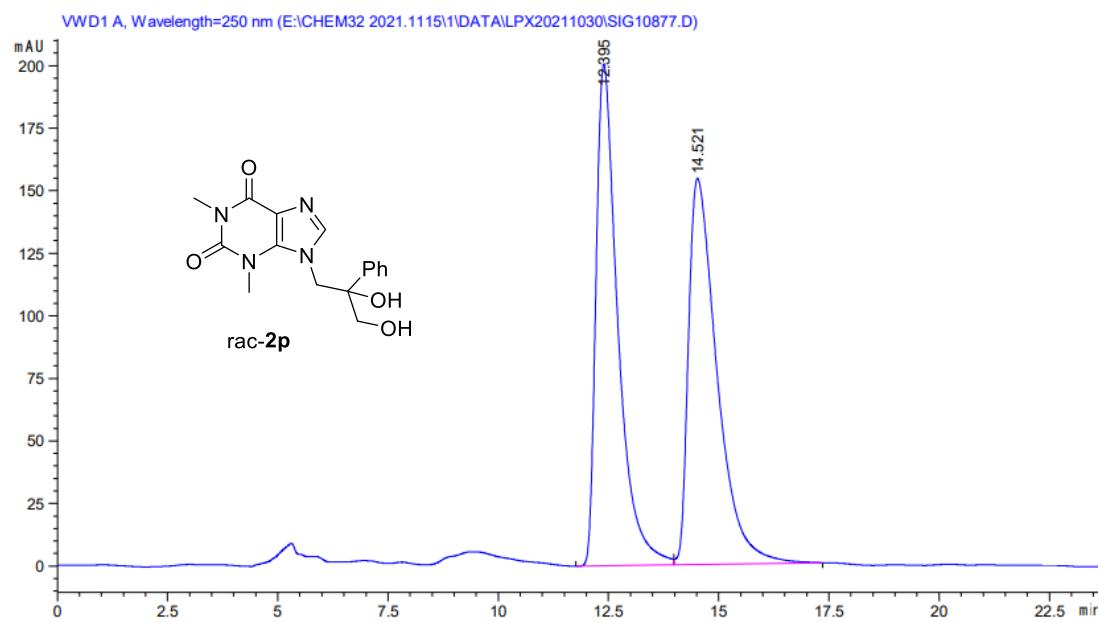


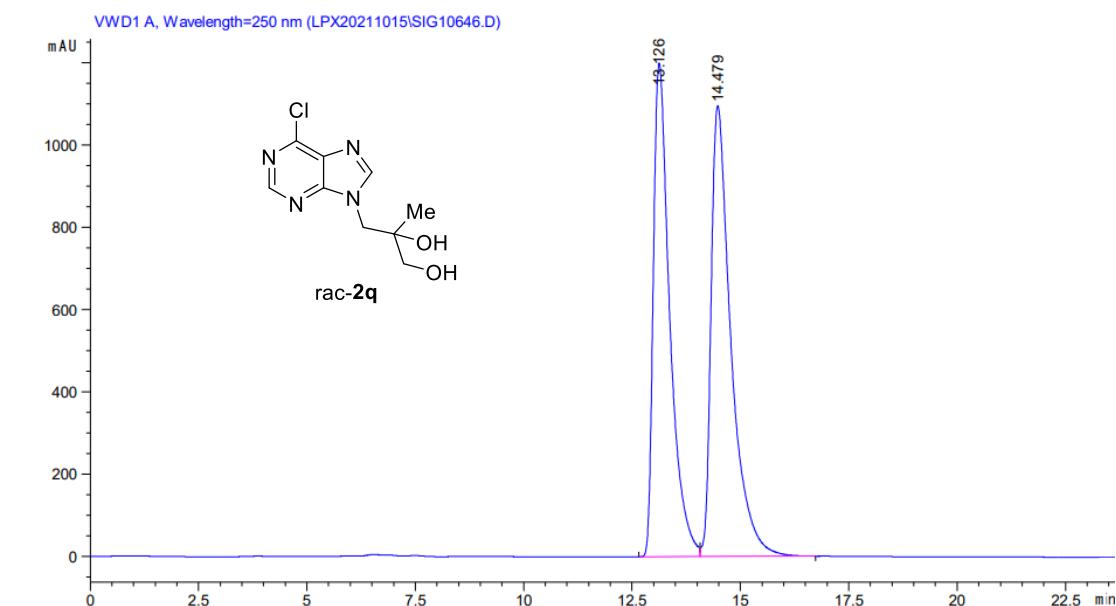
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.329	VV	0.3740	2.92691e4	1156.42456	49.7311
2	14.693	BB	0.5897	2.95857e4	770.00256	50.2689



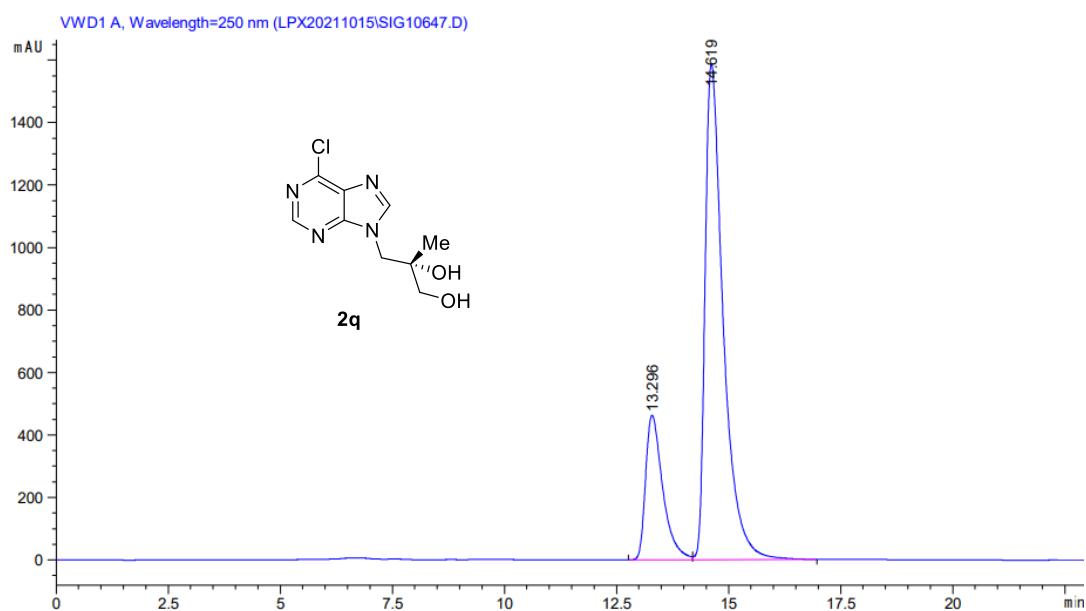
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.197	BB	0.3807	2.03163e4	812.36597	96.9384
2	14.640	BB	0.6606	641.63995	13.19451	3.0616



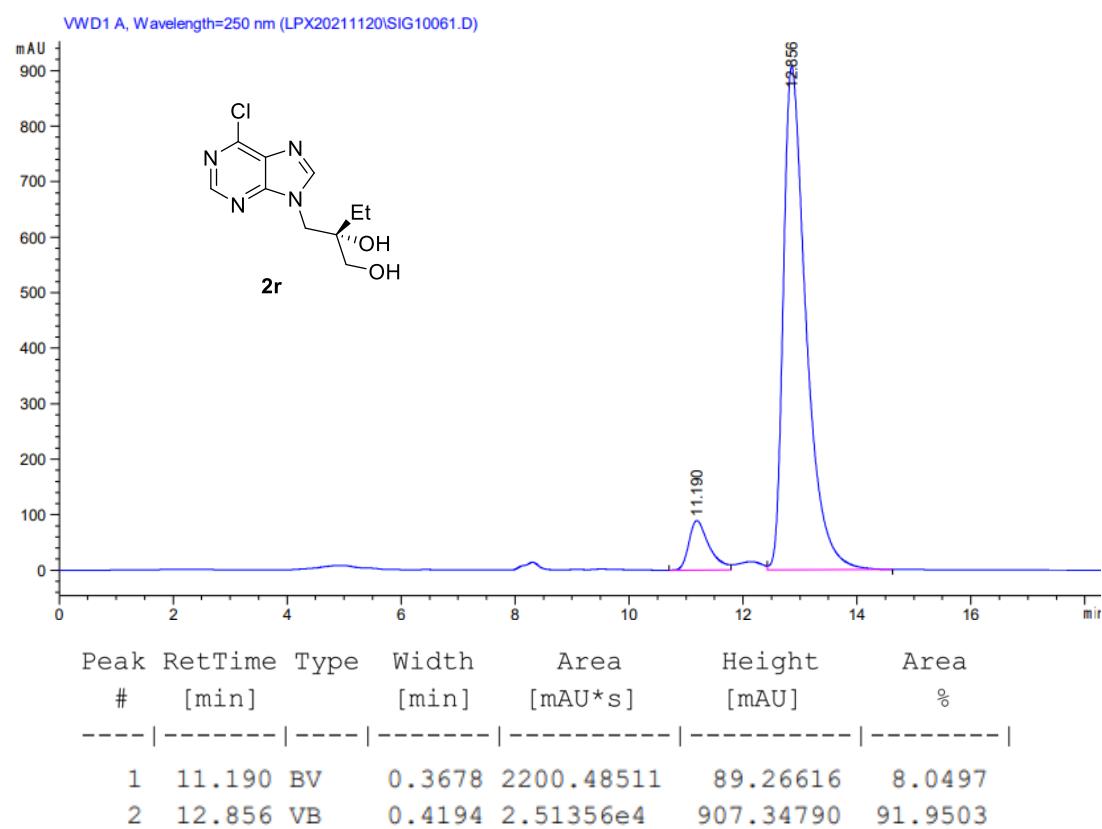
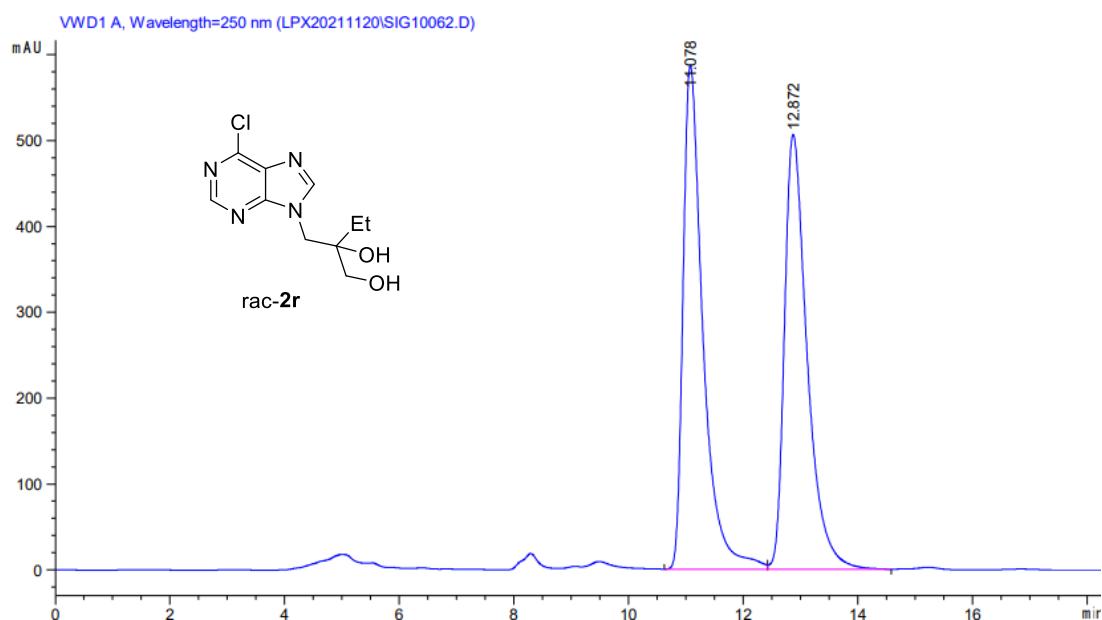


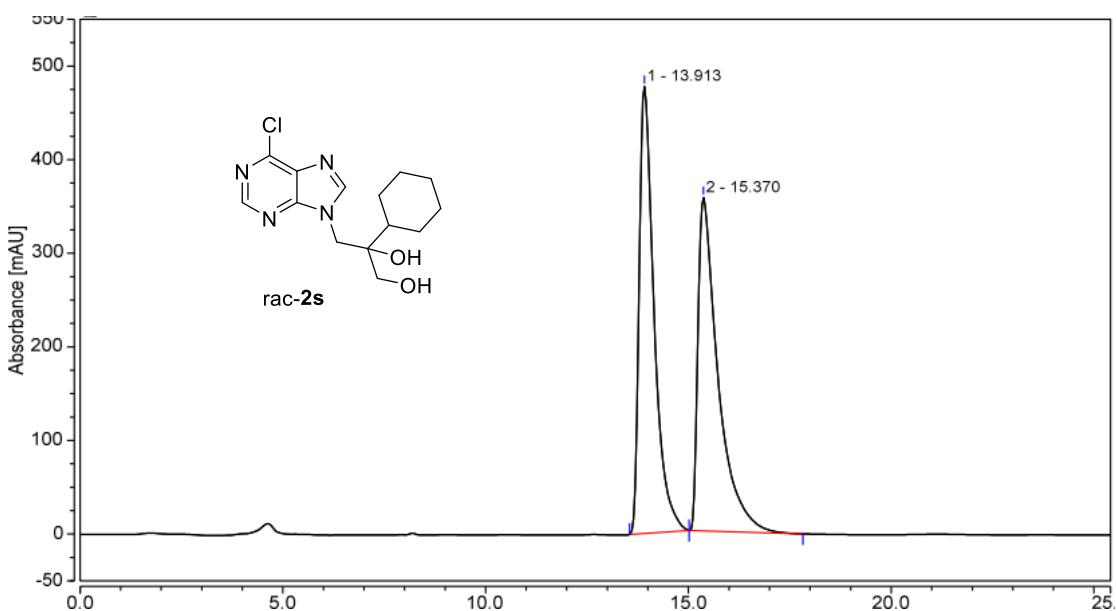


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.126	BV	0.3895	3.16624e4	1199.65710	47.5489
2	14.479	VB	0.4737	3.49267e4	1096.47461	52.4511

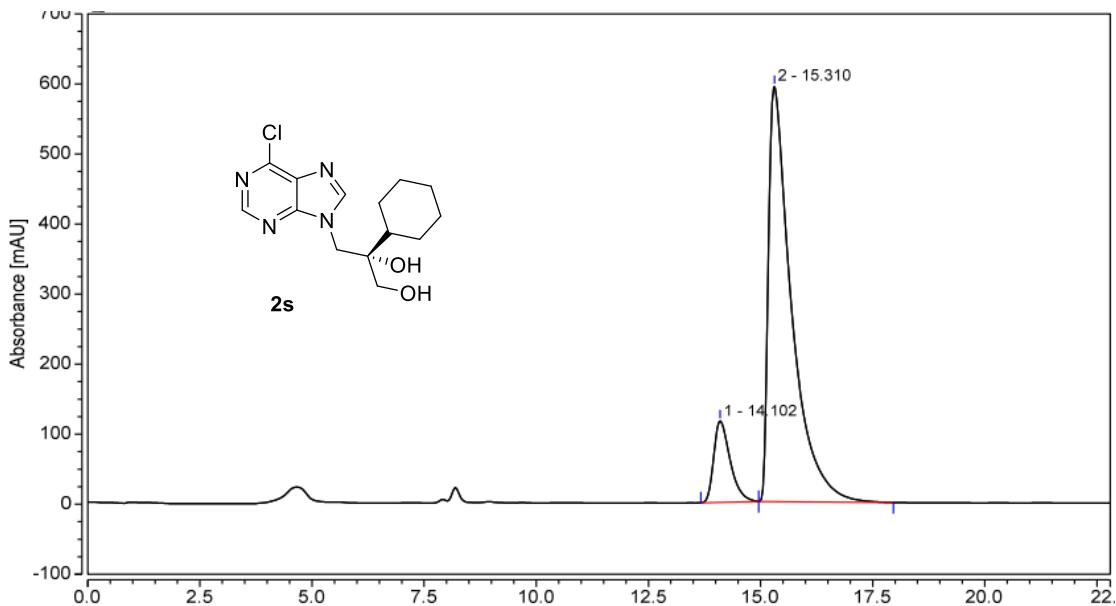


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.296	BV	0.4033	1.23562e4	462.89117	21.6555
2	14.619	VB	0.4236	4.47018e4	1585.82190	78.3445

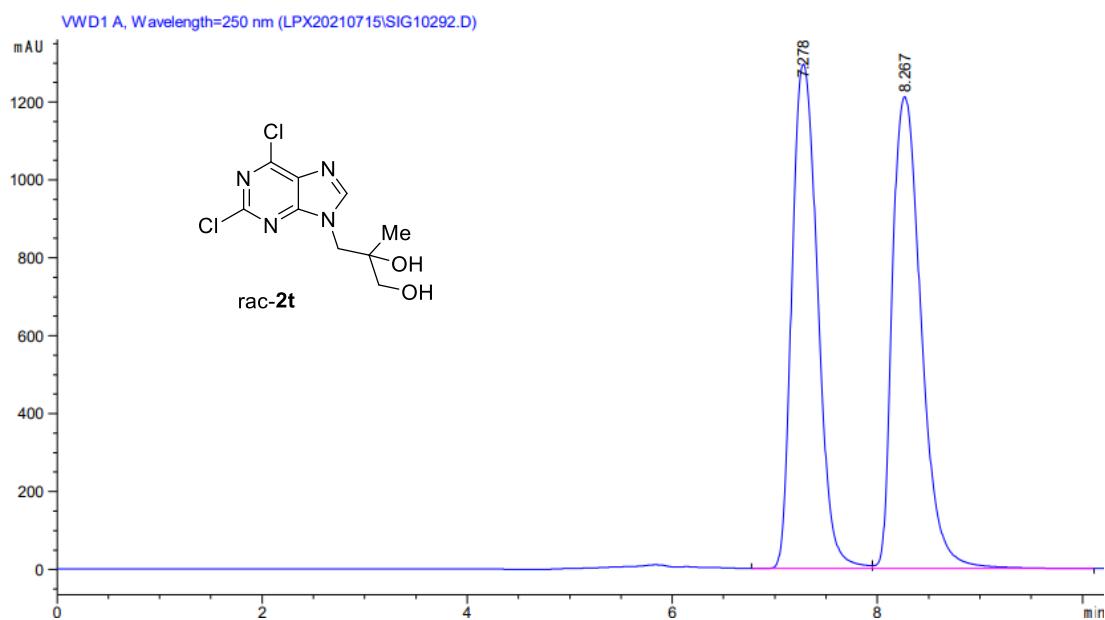




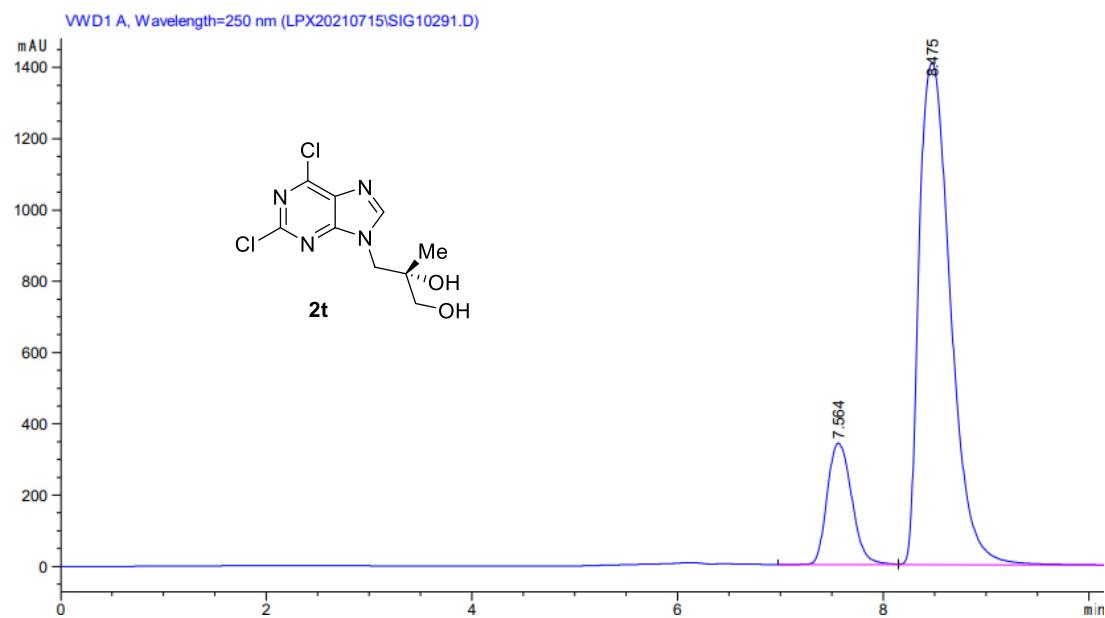
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.913	203.332	477.435	49.94	57.27
2	15.370	203.801	356.205	50.06	42.73
<b>Total:</b>		<b>407.130</b>	<b>833.640</b>	<b>100.00</b>	<b>100.00</b>



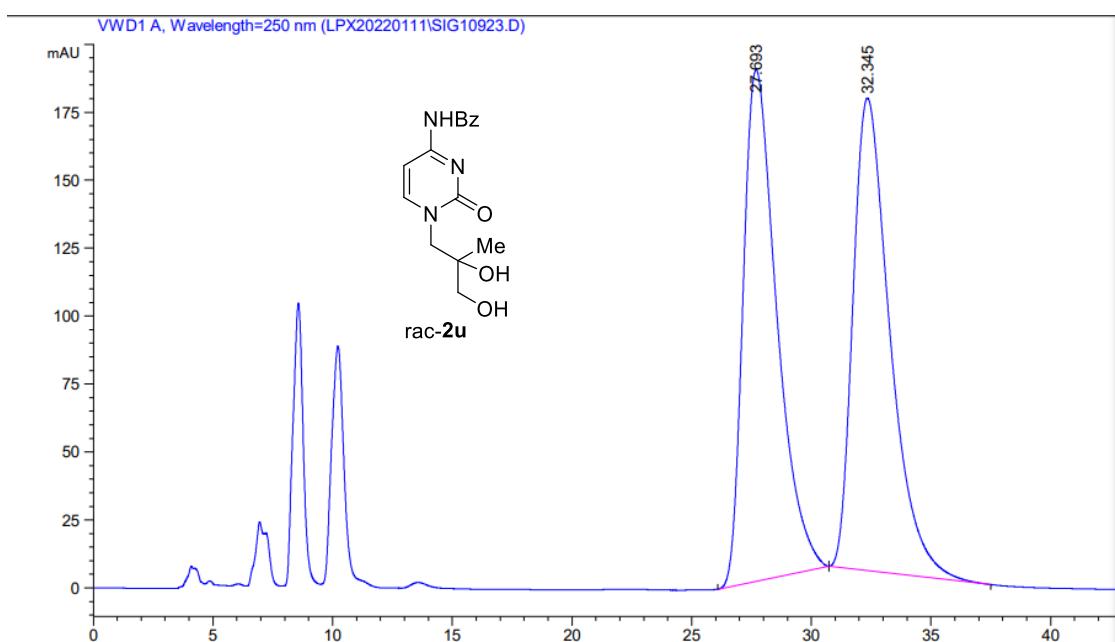
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.102	49.529	116.176	12.26	16.39
2	15.310	354.383	592.584	87.74	83.61
<b>Total:</b>		<b>403.911</b>	<b>708.760</b>	<b>100.00</b>	<b>100.00</b>



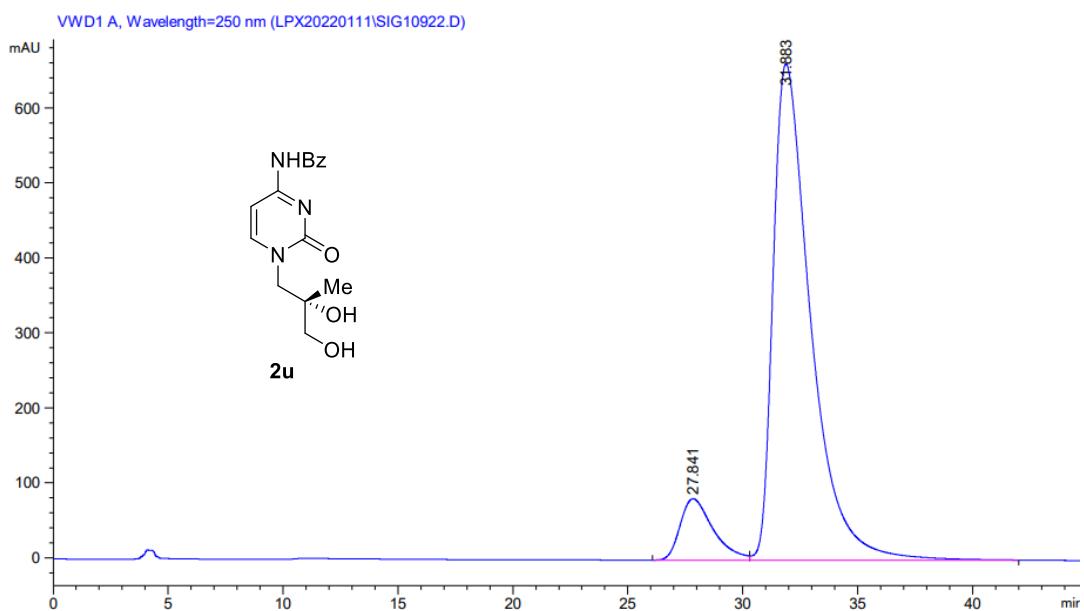
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.278	BV	0.2794	2.24277e4	1294.50317	48.6813
2	8.267	VB	0.3093	2.36428e4	1211.66931	51.3187



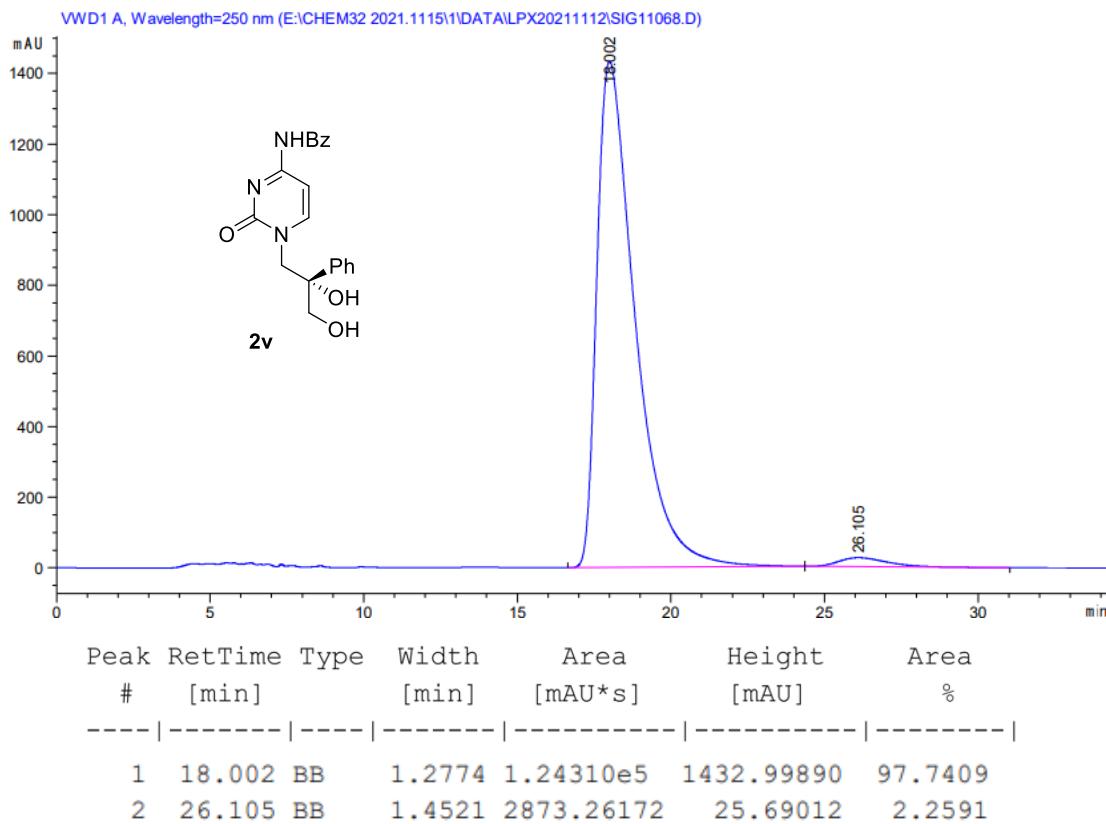
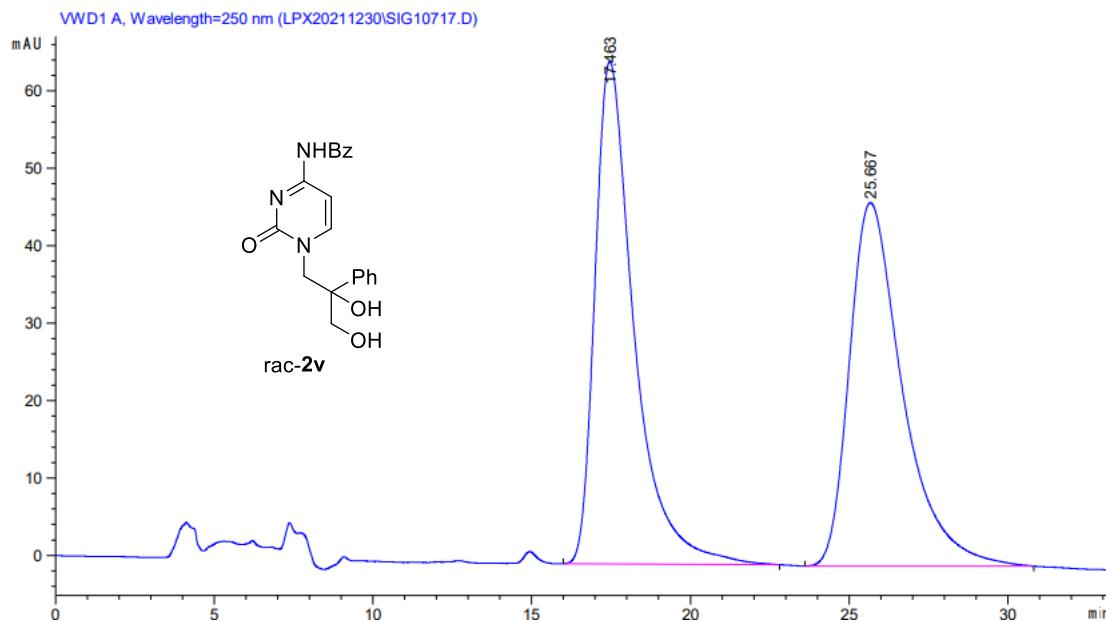
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.564	BV	0.2688	5682.79639	340.98703	16.0153
2	8.475	VBA	0.3388	2.98007e4	1407.68237	83.9847

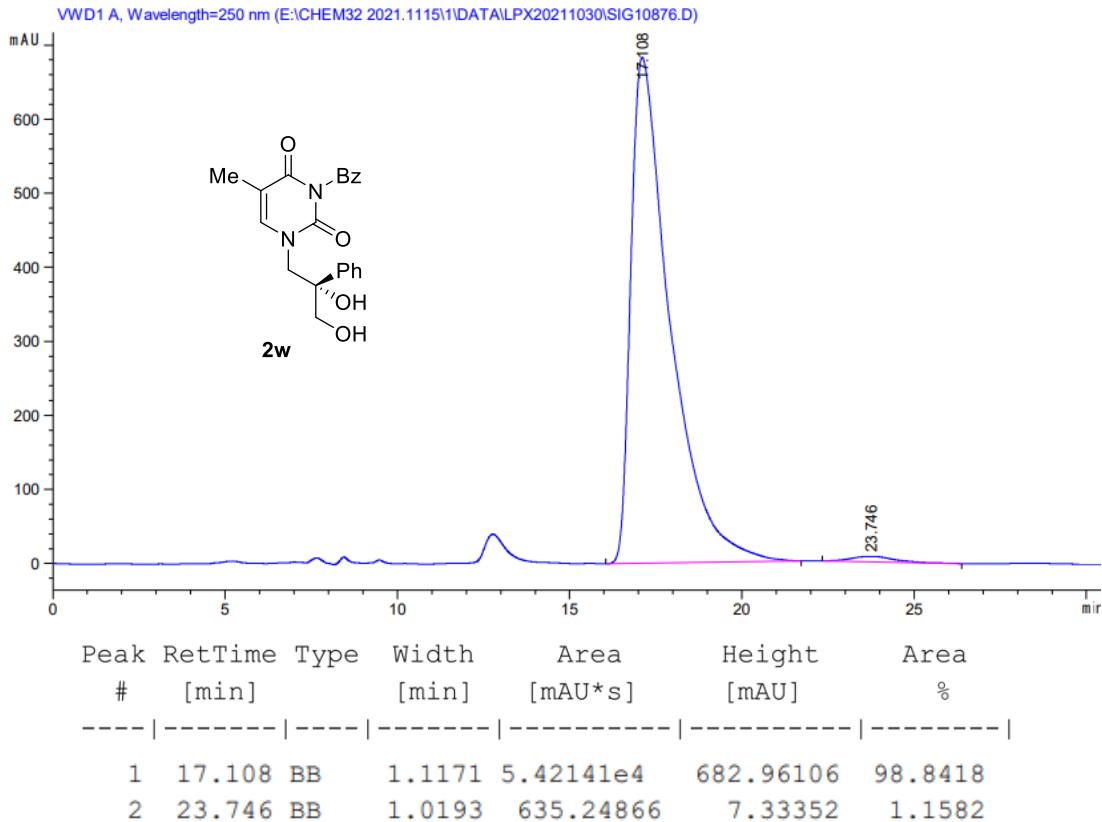
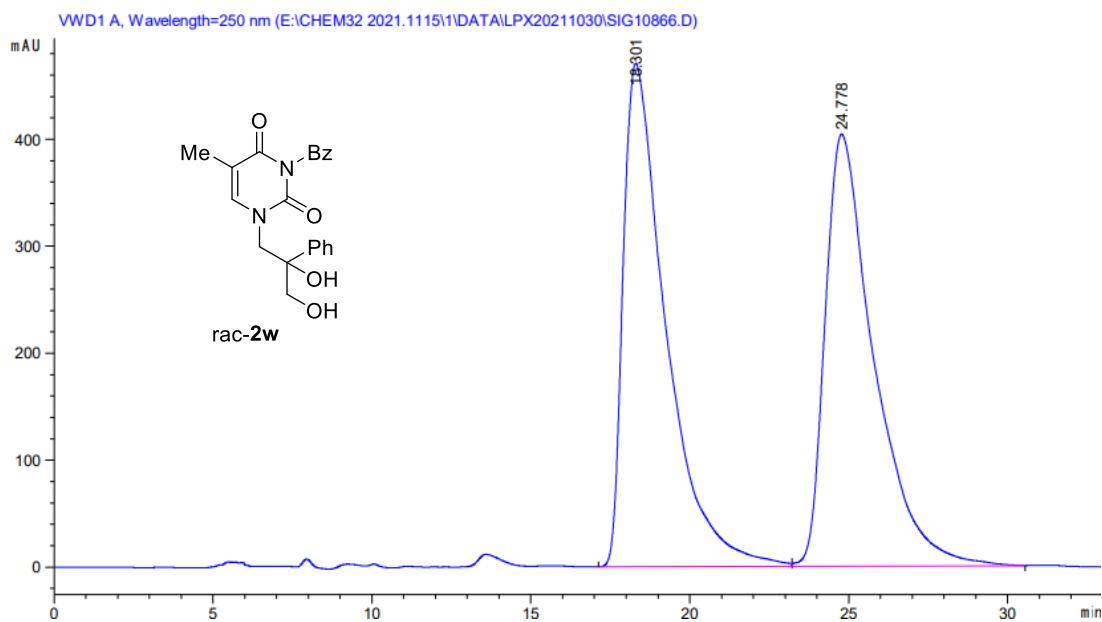


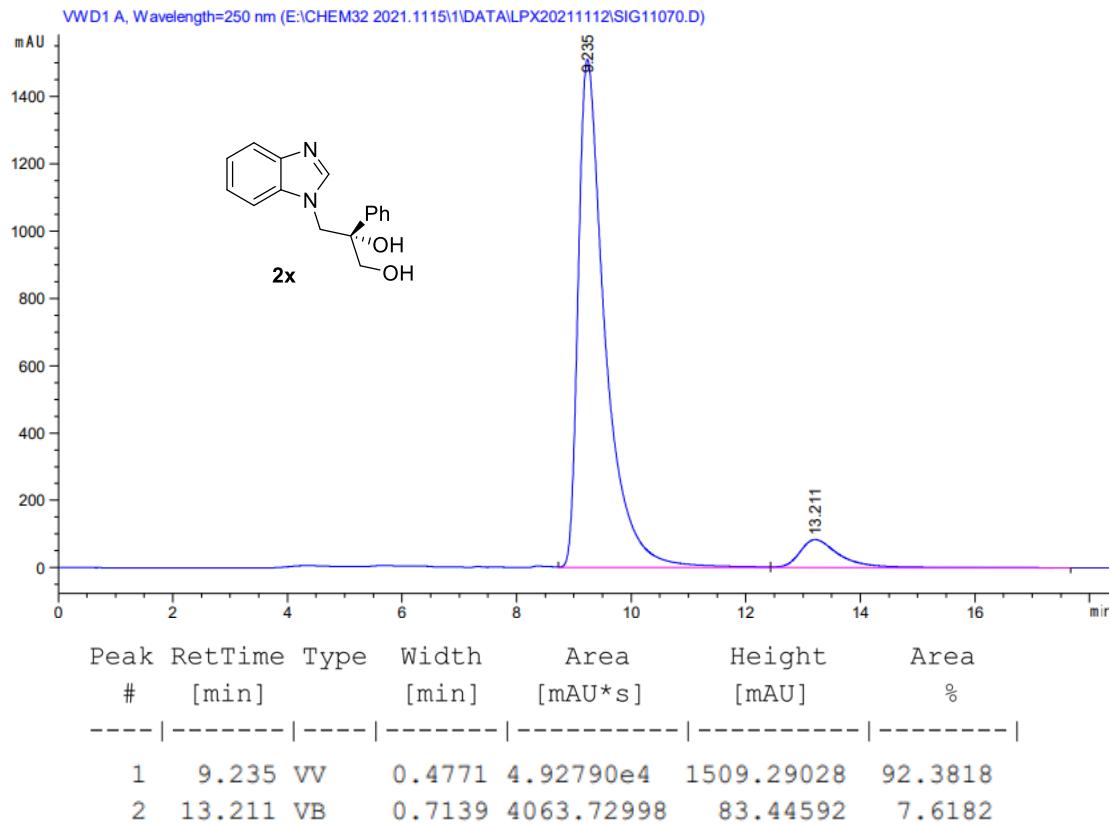
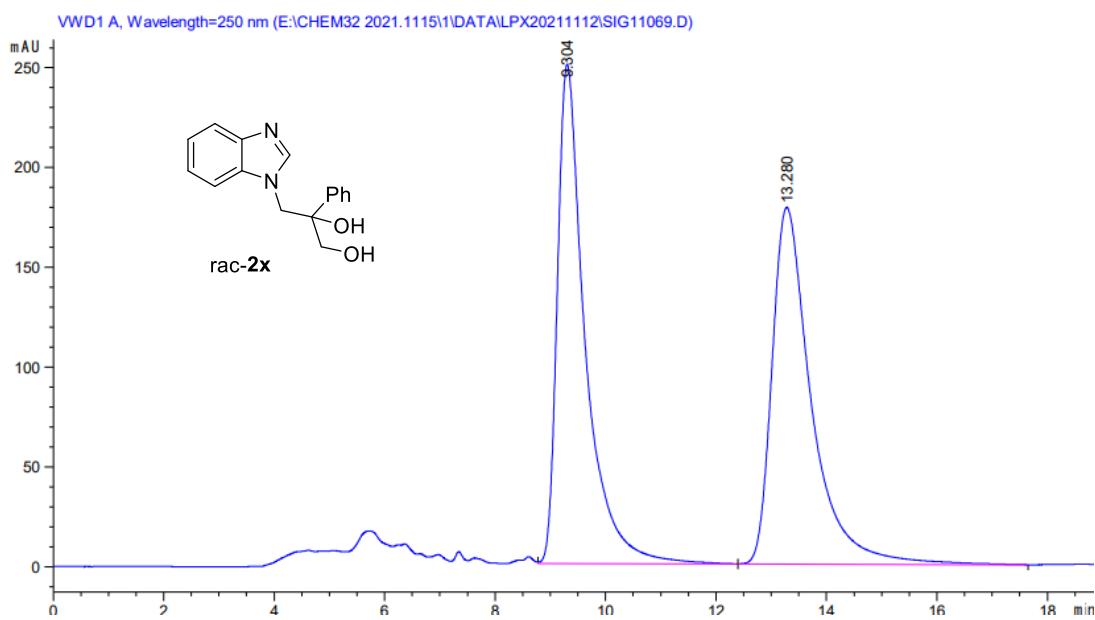
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.693	BB	1.4536	1.83490e4	188.22507	49.5682
2	32.345	BB	1.6094	1.86686e4	173.92896	50.4318

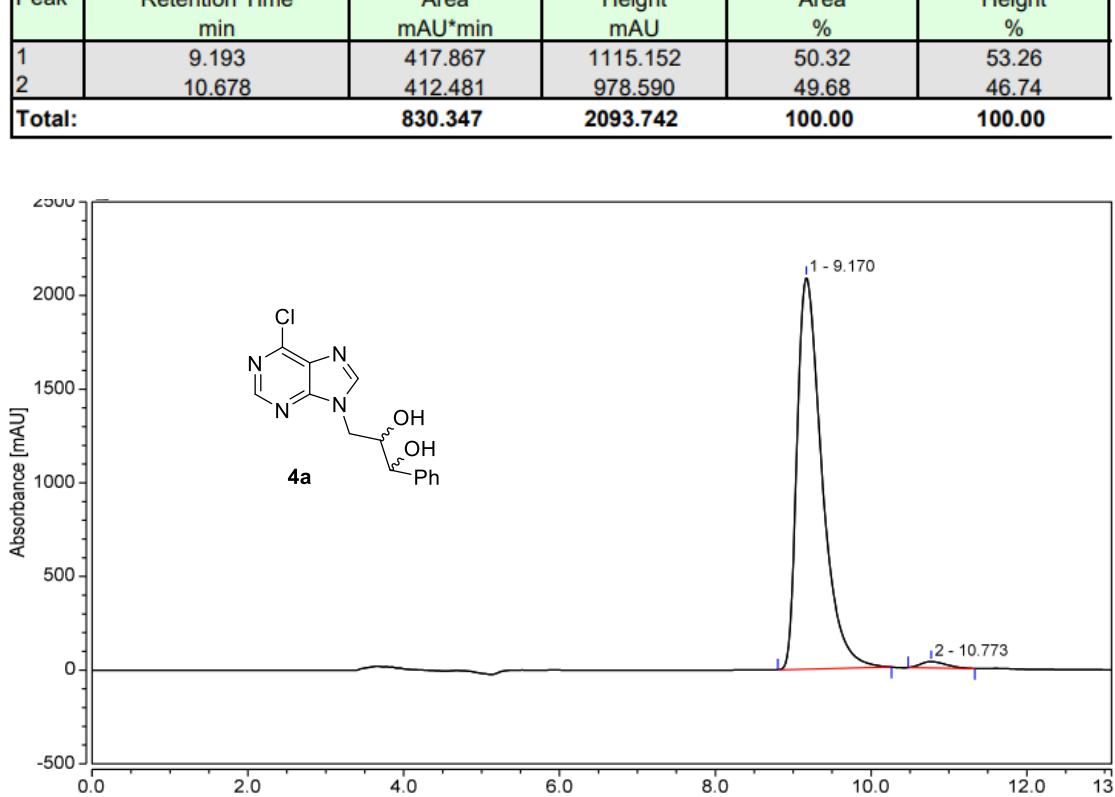
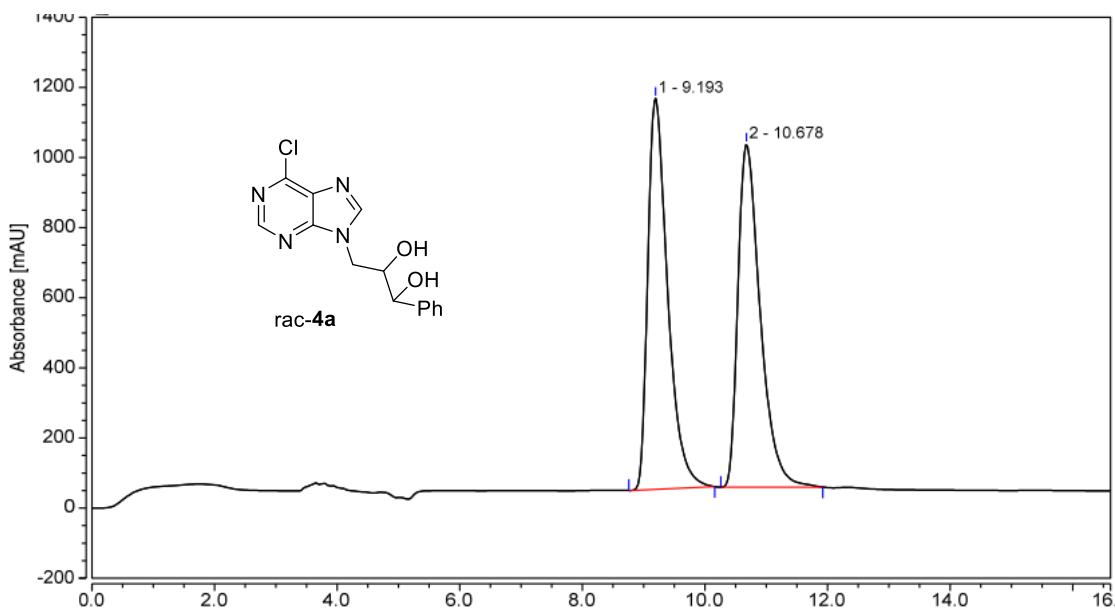


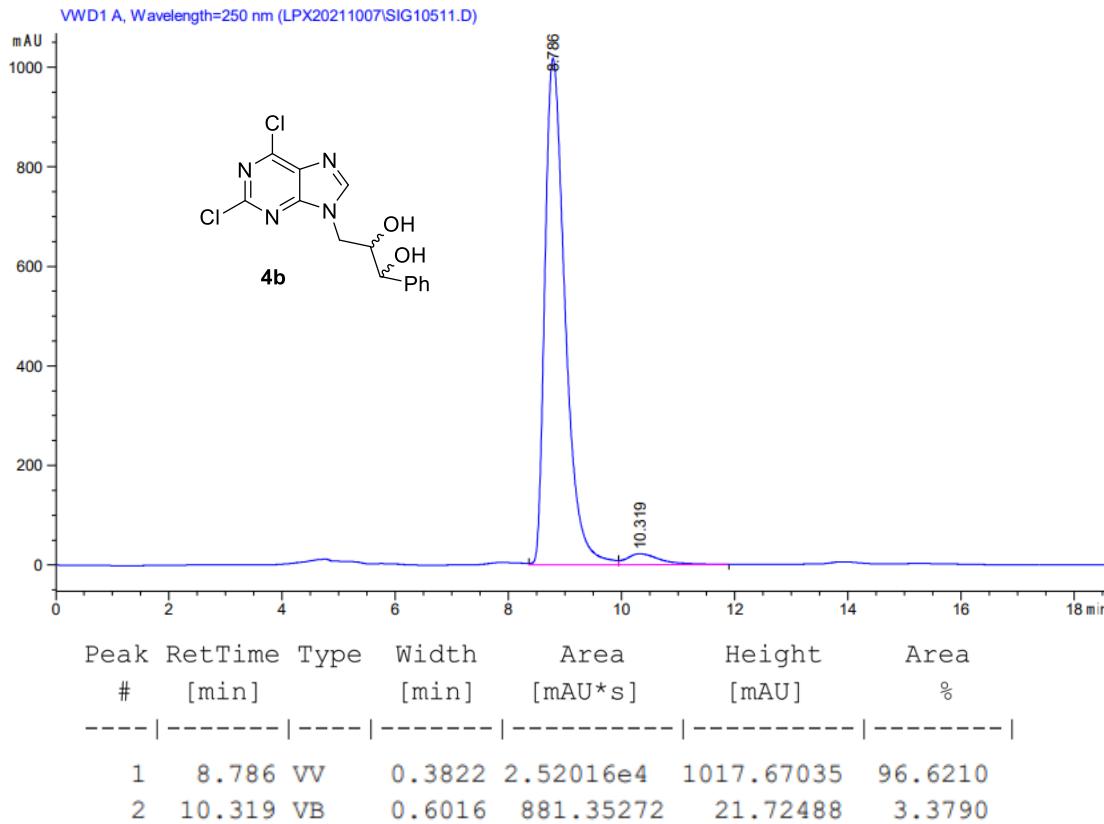
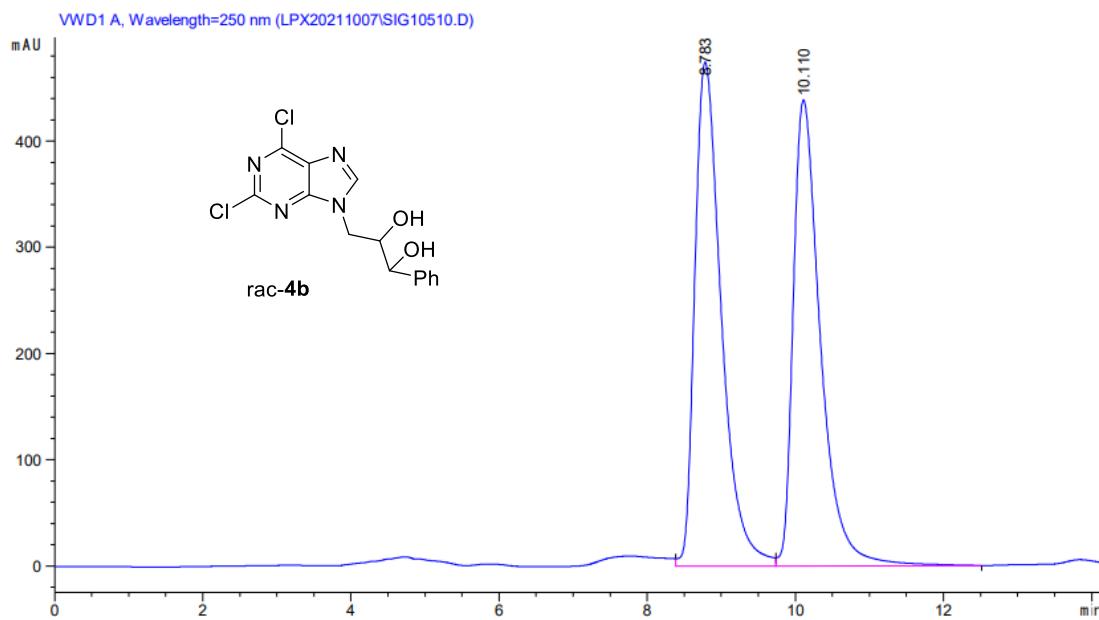
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.841	BV	1.4463	8154.69824	81.76841	9.7952
2	31.883	VB	1.6846	7.50977e4	661.45398	90.2048

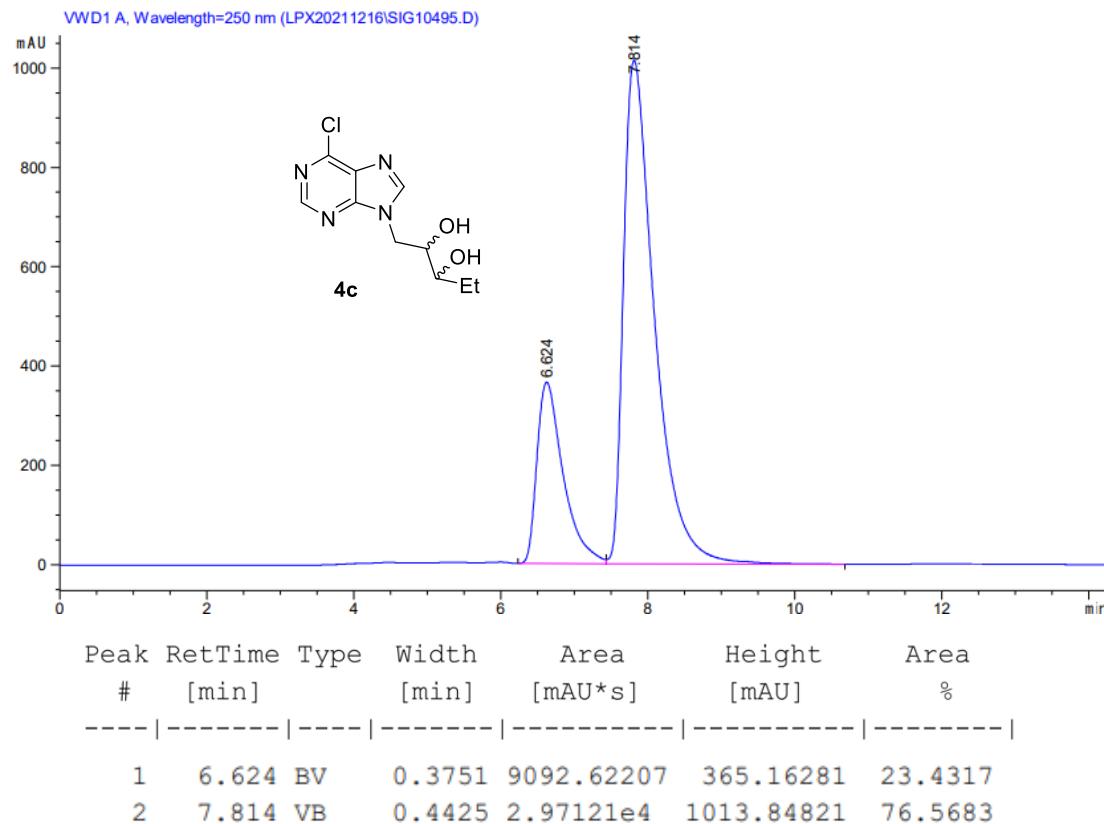
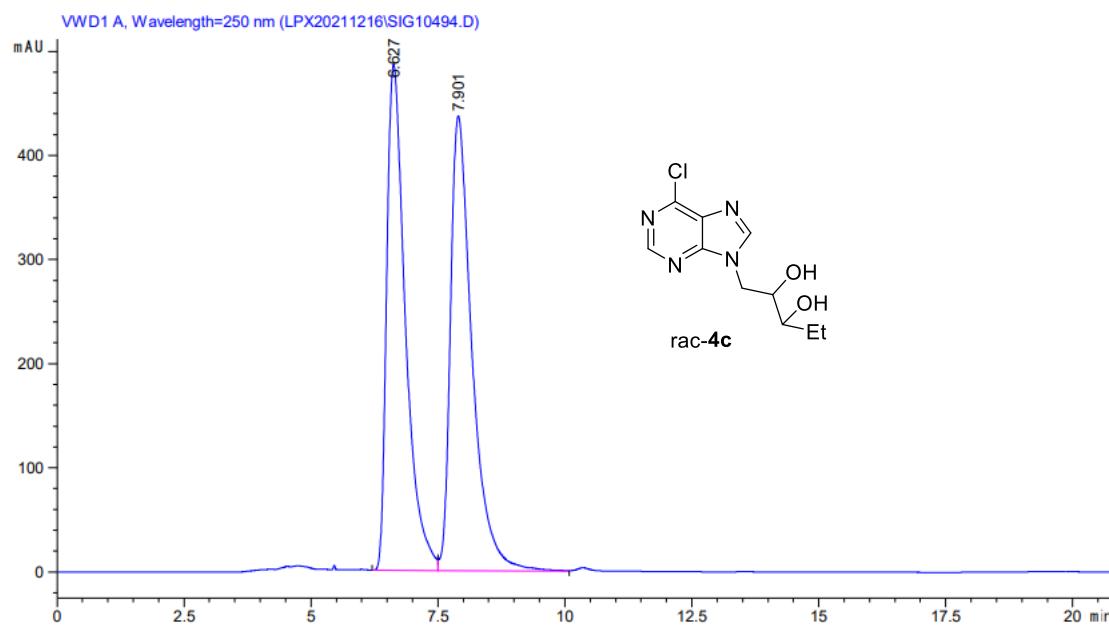


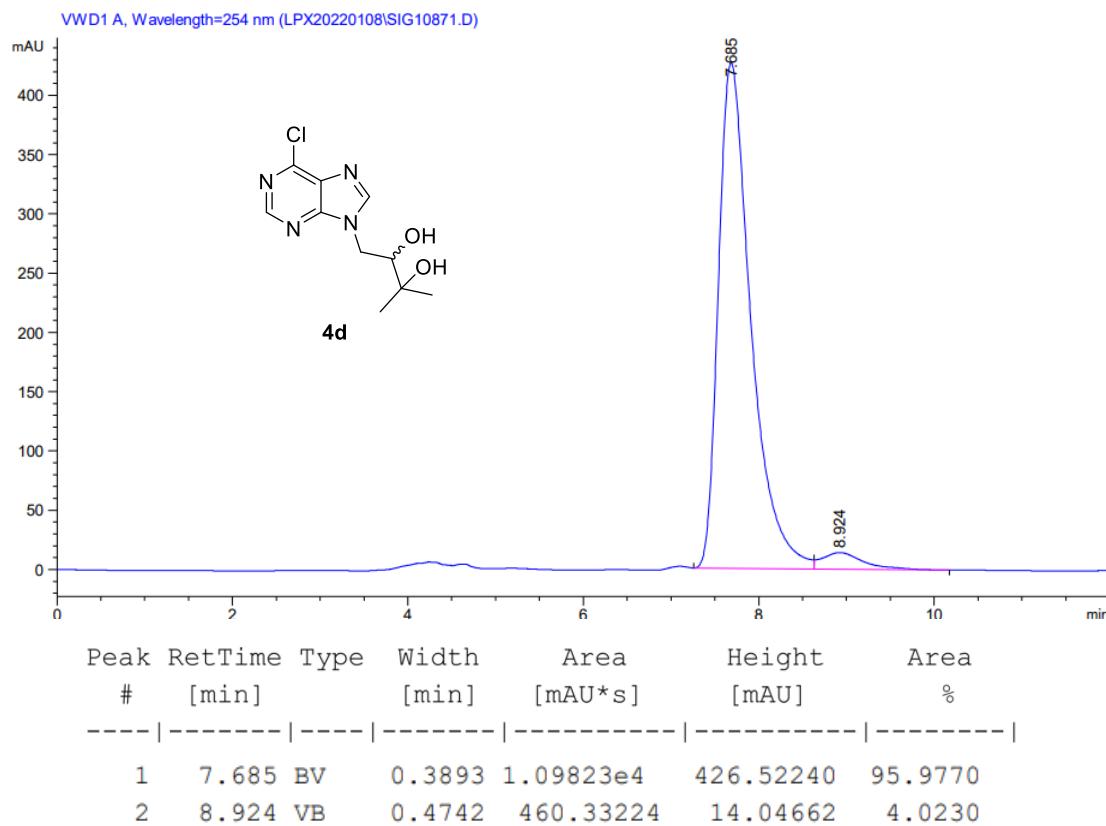
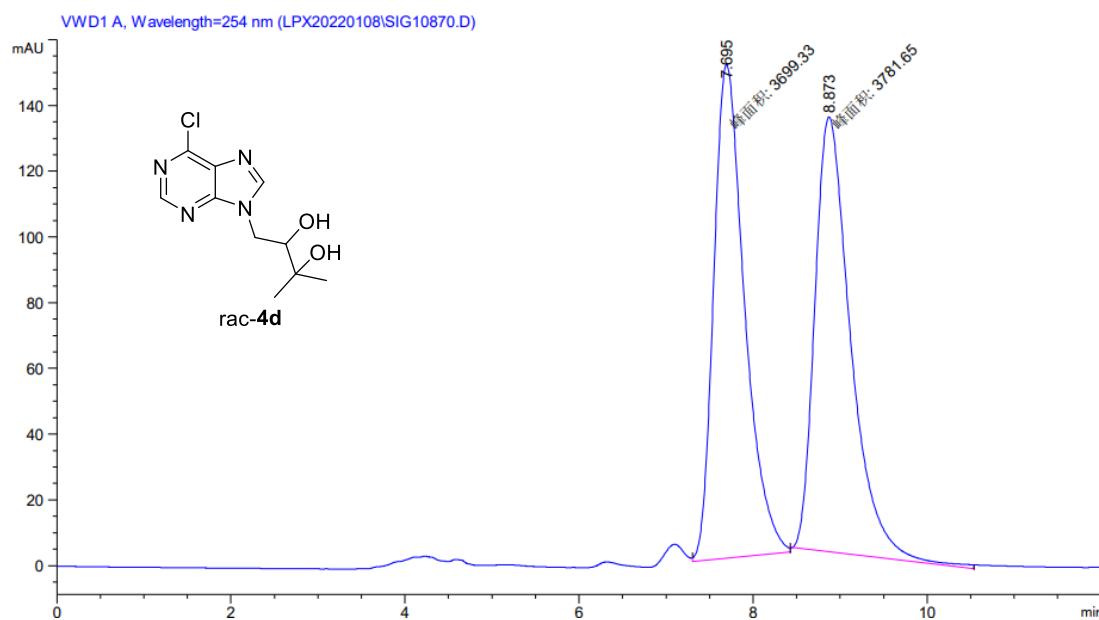












## 7. References

1. M. Kim, B. Park, M. Shin, S. Kim, J. Kim, M. H. Baik and S. H. Cho, Copper-catalyzed enantiotopic-group-selective allylation of *gem*-diborylalkanes, *J. Am. Chem. Soc.*, **2021**, *143*, 1069-1077.
2. J. Y. See, H. Yang, Y. Zhao, M. W Wong, Z. Ke and Y. Y. Yeung, Desymmetrizing enantio-and diastereoselective selenoetherification through supramolecular catalysis, *ACS Catal.*, **2018**, *8*, 850-858.
3. J. Chen and T. Hayashi, Asymmetric synthesis of alkylzincs by rhodium-catalyzed enantioselective arylative cyclization of 1, 6-enynes with arylzincs, *Angew. Chem. Int. Ed.*, **2020**, *59*, 18510-18514.
4. K. Jindrich, L.-L. Gundersen, Synthesis of N-alkenylpurines by rearrangements of the corresponding N-allyl isomers: scopes and limitations, *Eur. J. Org. Chem.* **2013**, *10*, 2008-2019.