

## Supporting Information

### **Cobalt(III)-Catalyzed C–H Halogenation of 6-Arylpurines: Facile Entry into Arylated, Sulfenylated and Alkoxyated 6-Arylpurines**

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<sup>†</sup>Division of Natural Product Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India

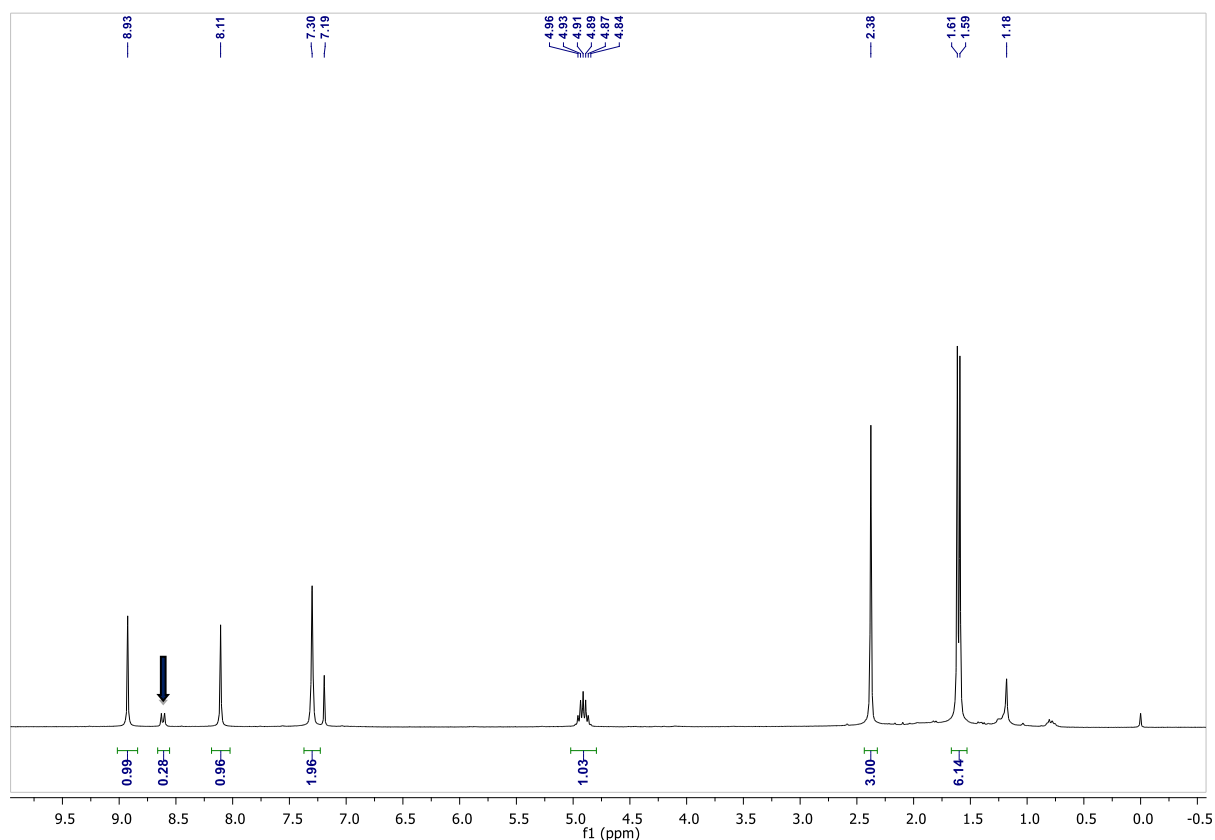
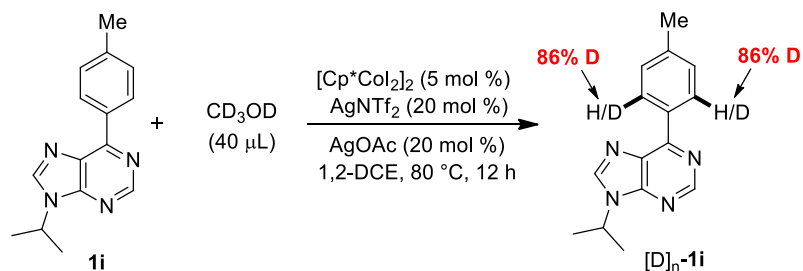
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	<b>Table of Content</b>	S-1
<b>1</b>	<b>H/D Exchange Experiment</b>	S-2
<b>2</b>	<b>Intermolecular Competitive Experiment</b>	S-3
<b>3</b>	<b>Spectral Copies of <sup>1</sup>H and <sup>13</sup>C NMR of Compounds Obtained in this Study</b>	S-4

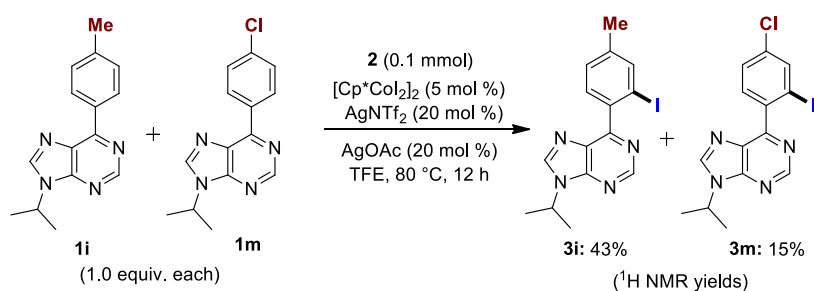
## 1. H/D Exchange Experiment (Scheme 3 a)

To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1ba** (18.5 mg, 0.10 mmol), [Cp\*CoI<sub>2</sub>]<sub>2</sub> (4.8 mg, 10 mol %), AgNTf<sub>2</sub> (7.8 mg, 20 mol %) AgOAc (3.3 mg, 20 mol%), CD<sub>3</sub>OD (40 μL) and 1,2-dichloroethane (0.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h, cooled to room temperature, filtered through a pad of celite and then washed with EtOAc (10 mL × 3). The solvent was removed under reduced pressure and the extents of deuterium incorporation was measured by <sup>1</sup>H NMR analysis of the crude mixture.



**Figure S1.** Crude <sup>1</sup>H NMR for H/D exchange experiment of **1i** with CD<sub>3</sub>OD.

## 2. Intermolecular competitive Experiment (Scheme 3 b)



To a dried screw capped vial with a spinvane triangular-shaped Teflon stirbar were added **1i** (18.5 mg, 0.10 mmol), **1m** (18.5 mg, 0.10 mmol), *N*-iodosuccinimide (18.5 mg, 0.10 mmol),  $[\text{Cp}^*\text{CoI}_2]_2$  (4.8 mg, 10 mol %),  $\text{AgNTf}_2$  (7.8 mg, 20 mol %),  $\text{AgOAc}$  (3.3 mg, 20 mol %), TFE (0.5 mL) under argon atmosphere. The reaction mixture was stirred at 80 °C for 12 h, cooled to room temperature, poured into water (20 mL) and then washed with EtOAc (15 mL  $\times$  2). The organic layer was washed with 1N NaOH (15 mL), dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was evaporated under reduced pressure. The conversions of **3i** and **3m** was determined by  $^1\text{H}$  NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as an internal standard.

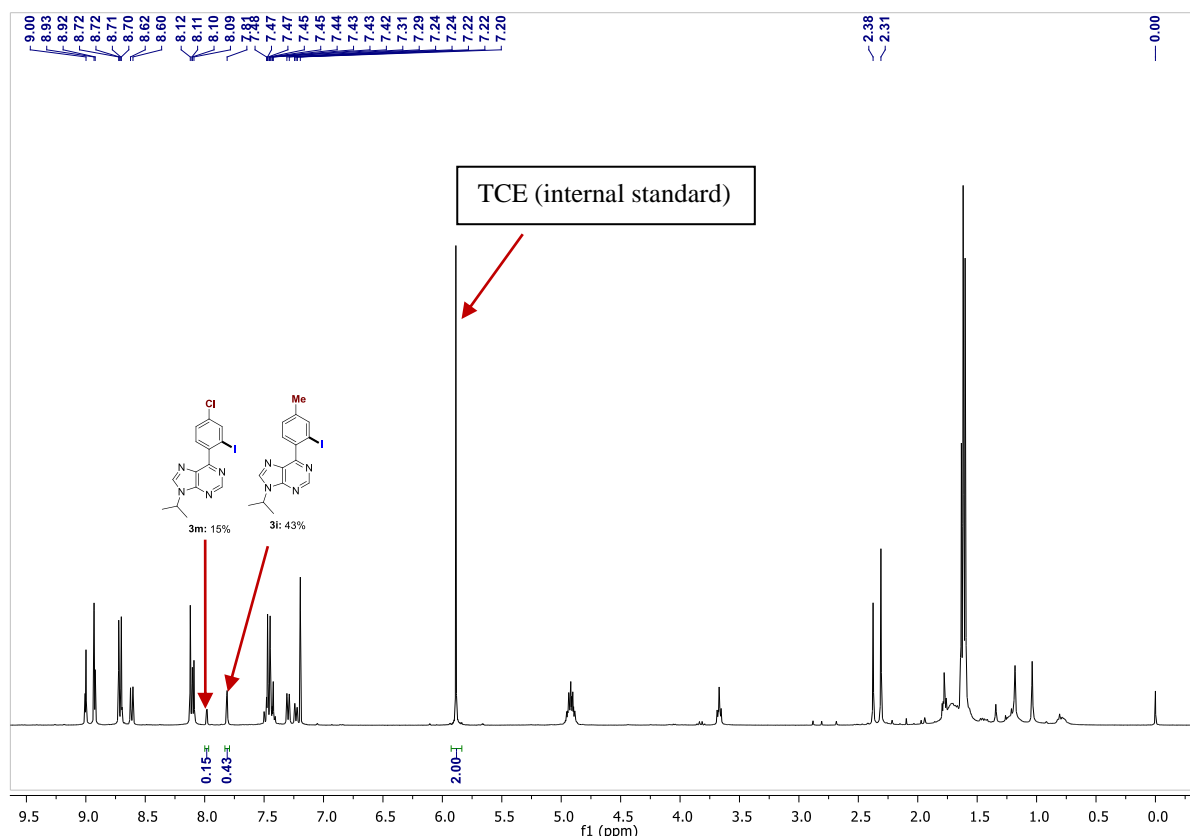
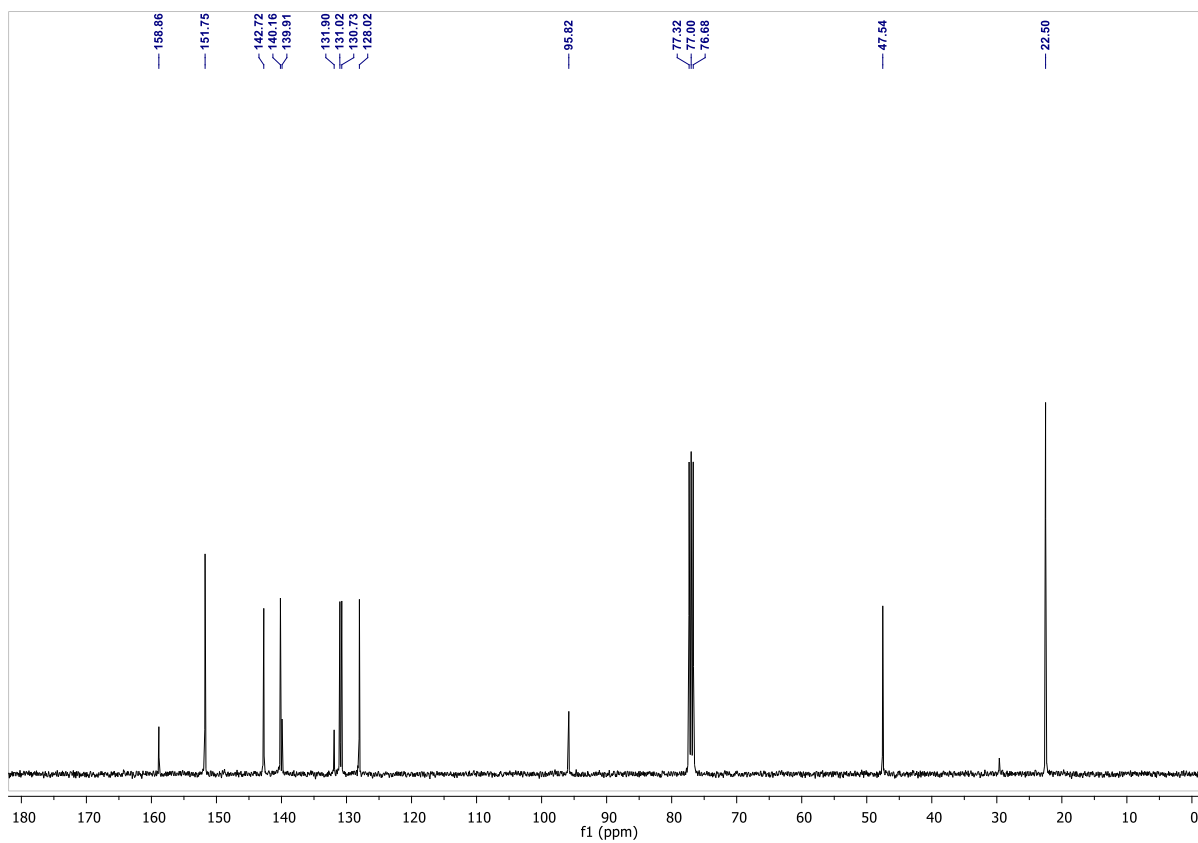
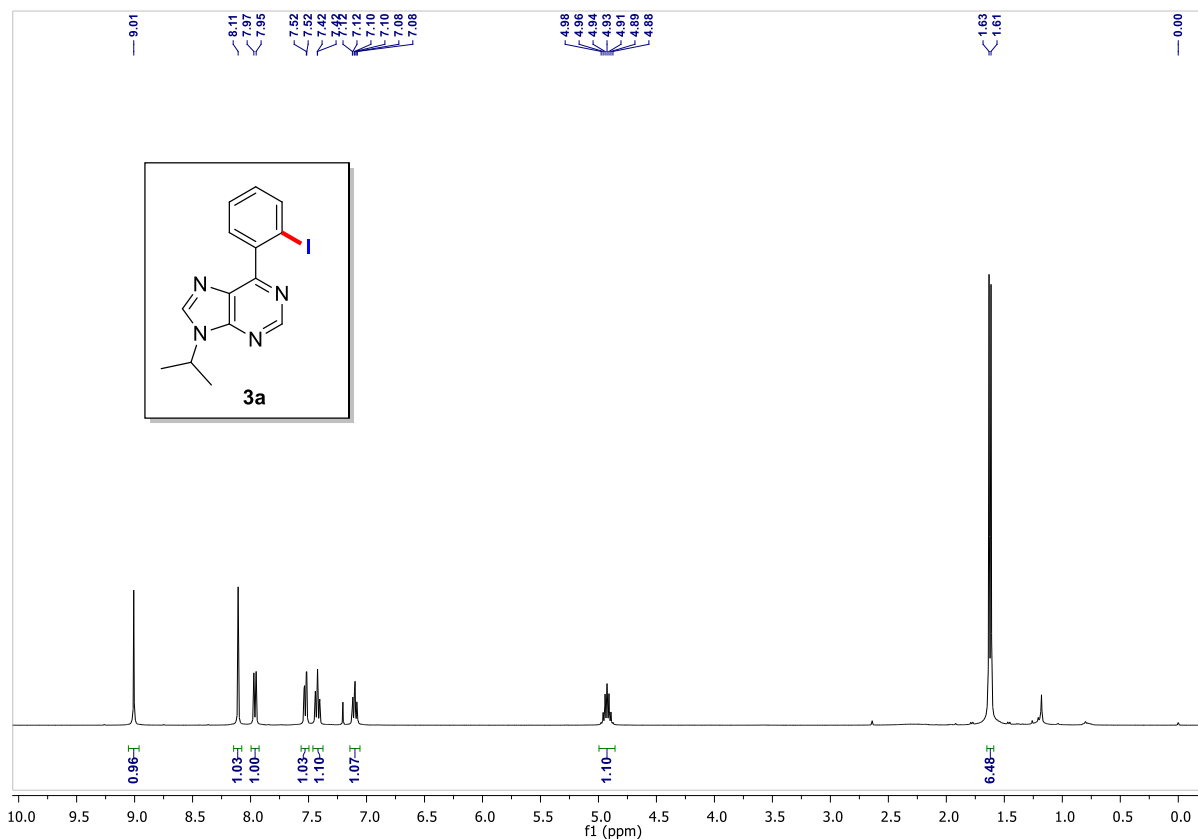


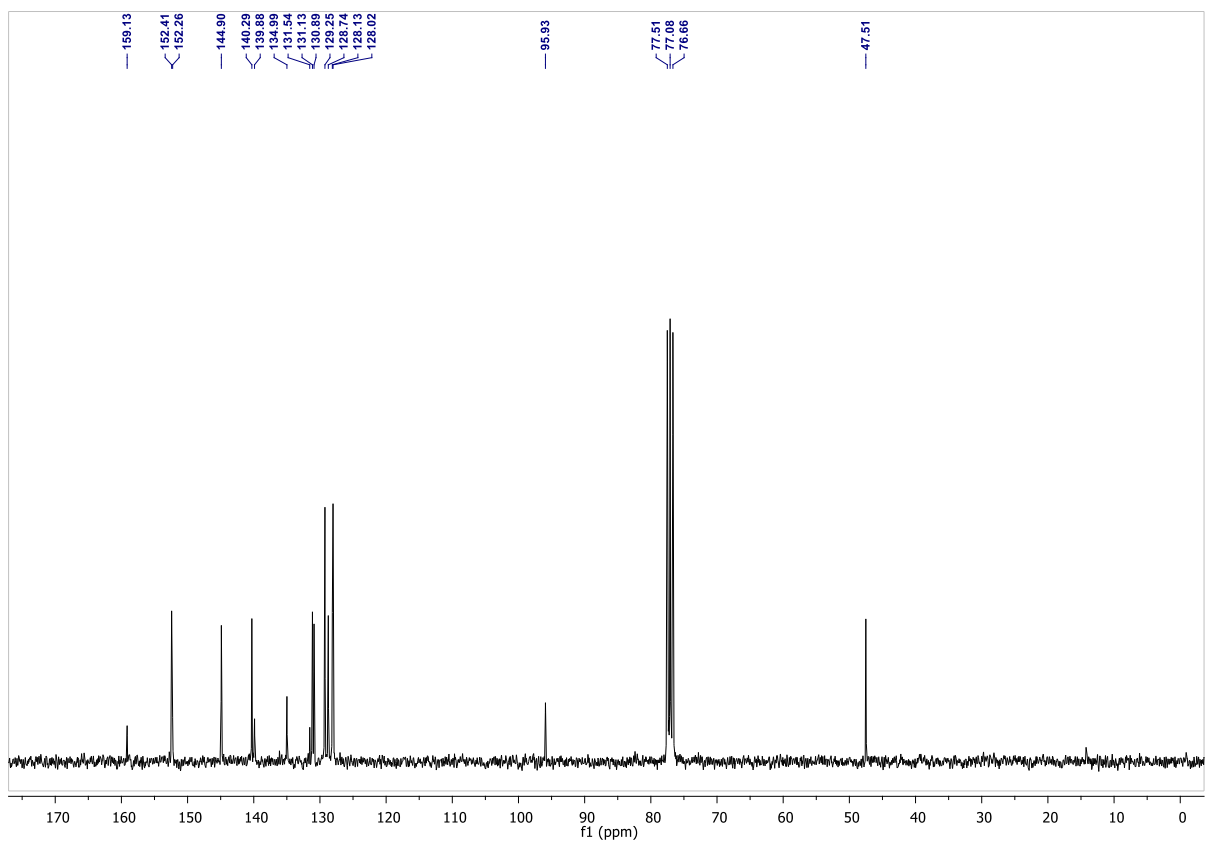
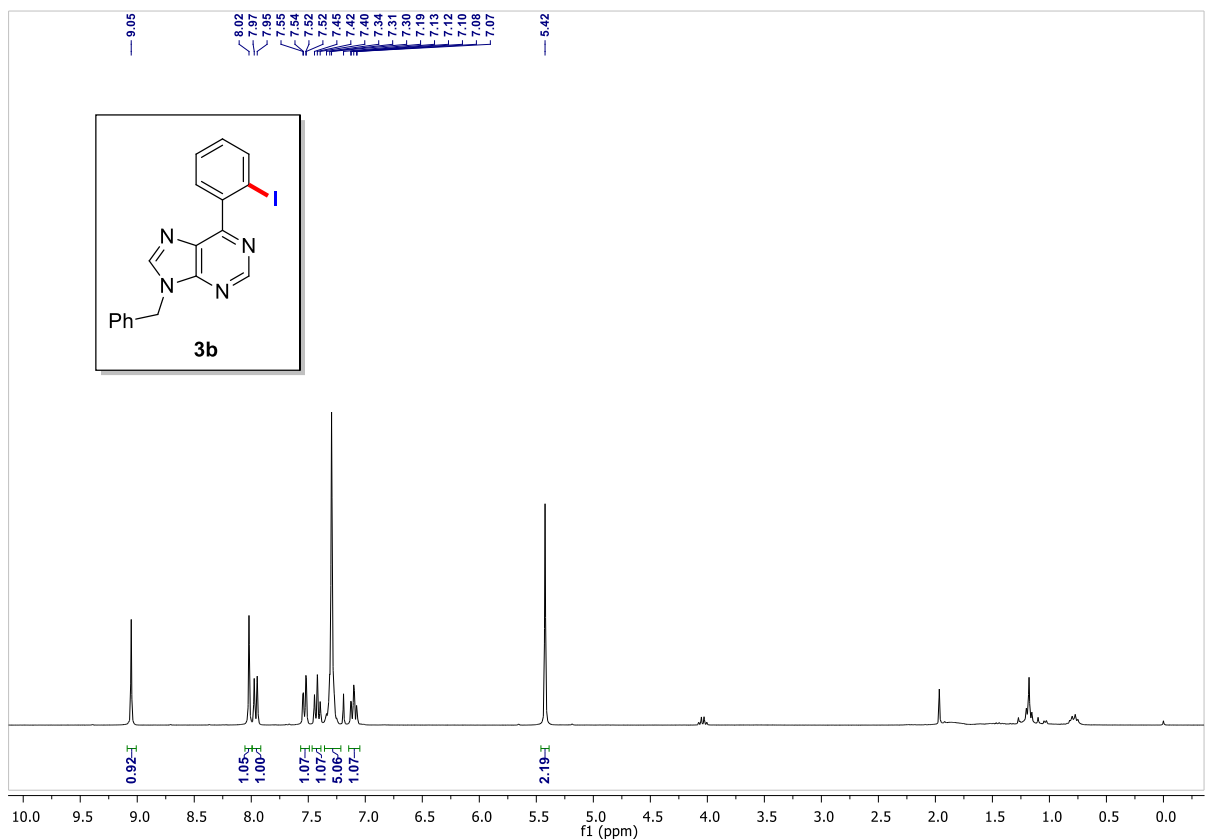
Figure S2. Crude  $^1\text{H}$  NMR for intermolecular competitive experiment between **1i** and **1m**.

### **3. Spectral Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR of Compounds Obtained in this Study**

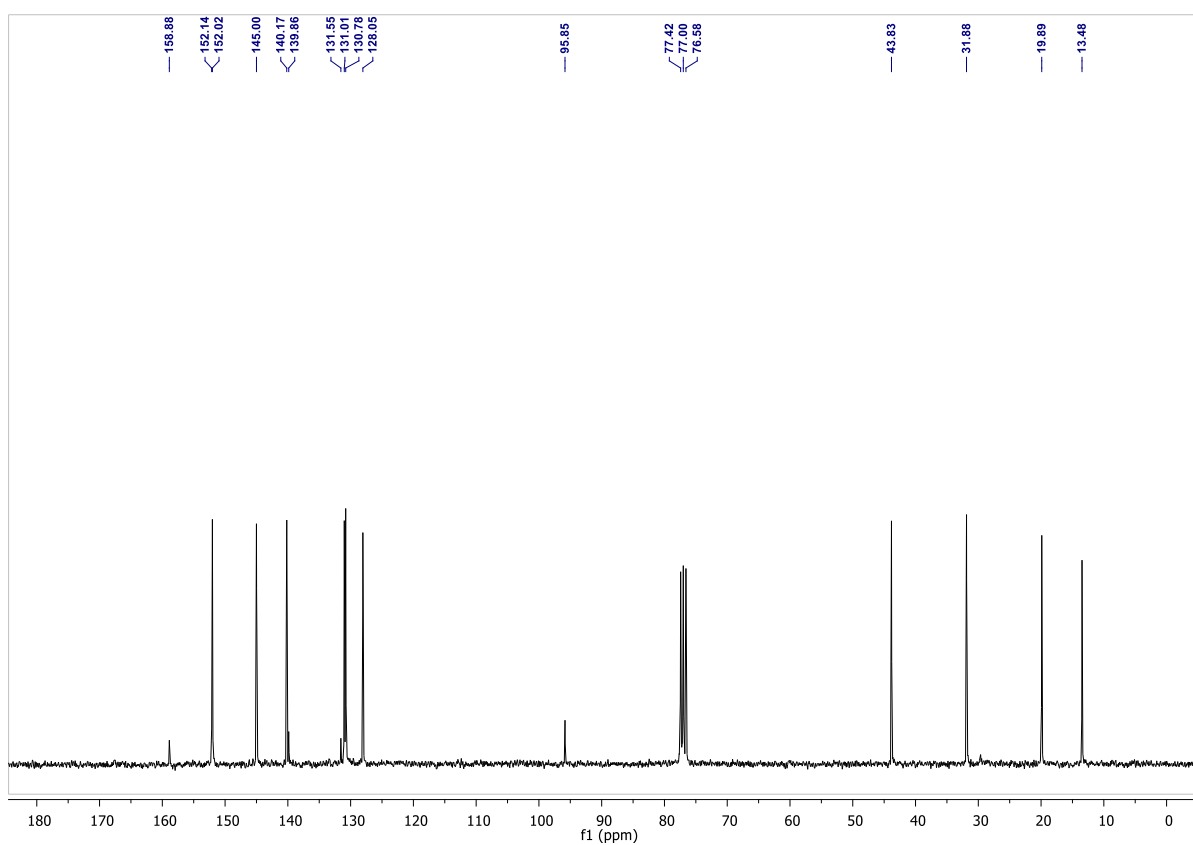
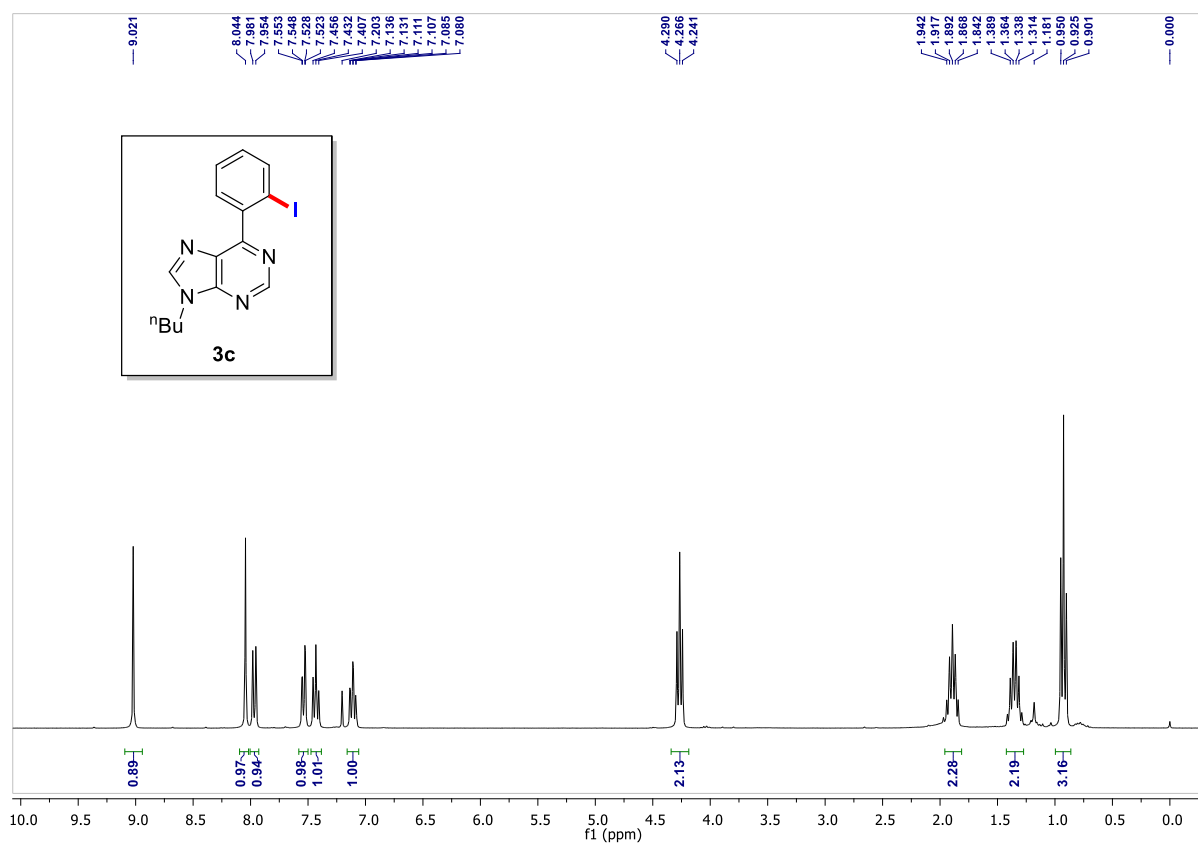
# 6-(2-Iodophenyl)-9-isopropyl-9H-purine (3a)



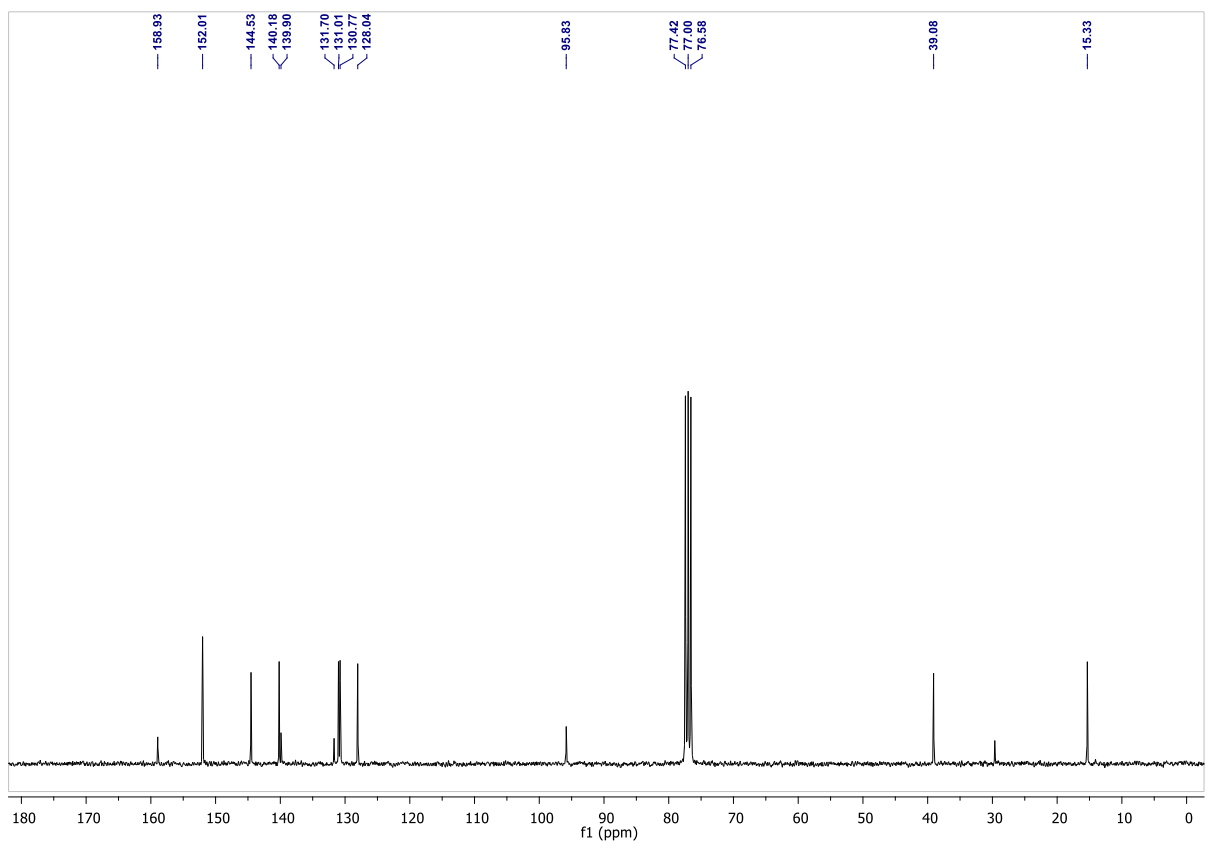
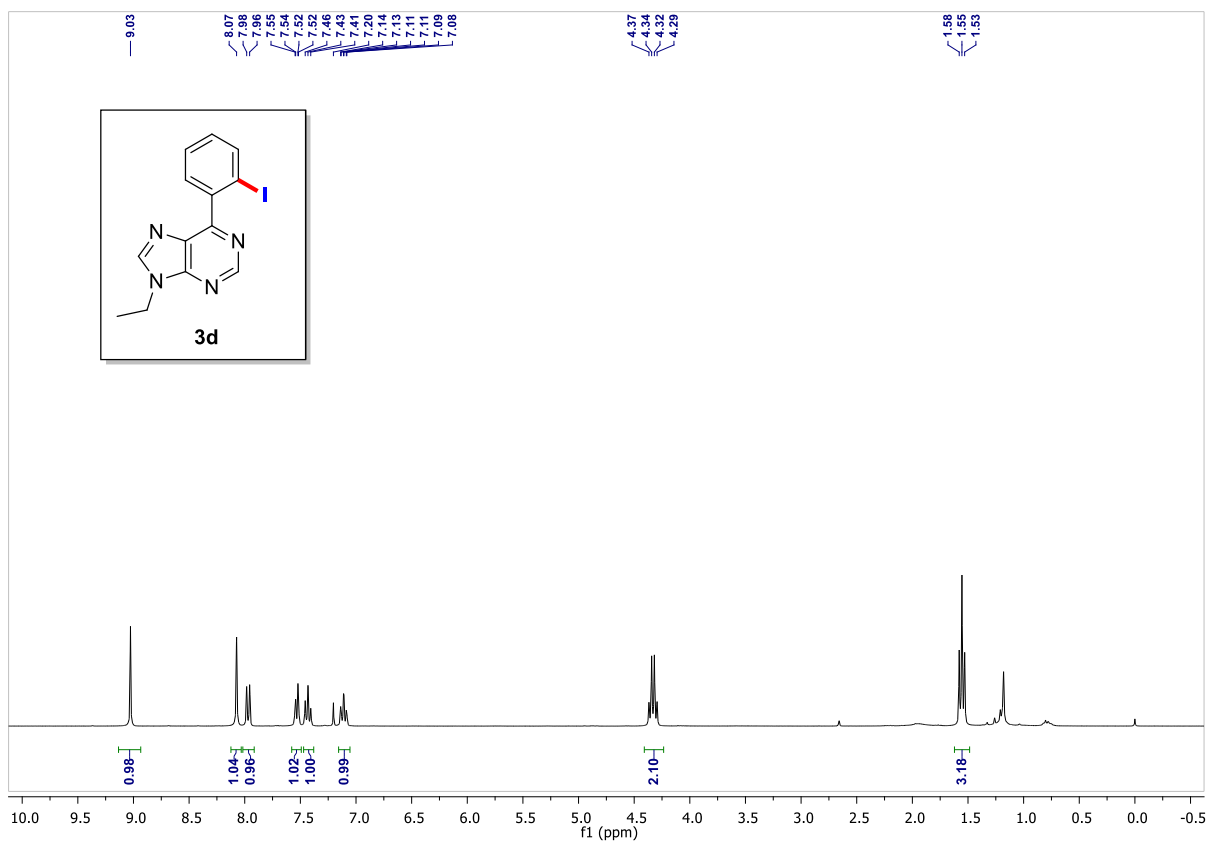
### 9-Benzyl-6-(2-iodophenyl)-9H-purine (3b)



# 9-Butyl-6-(2-iodophenyl)-9H-purine (3c)

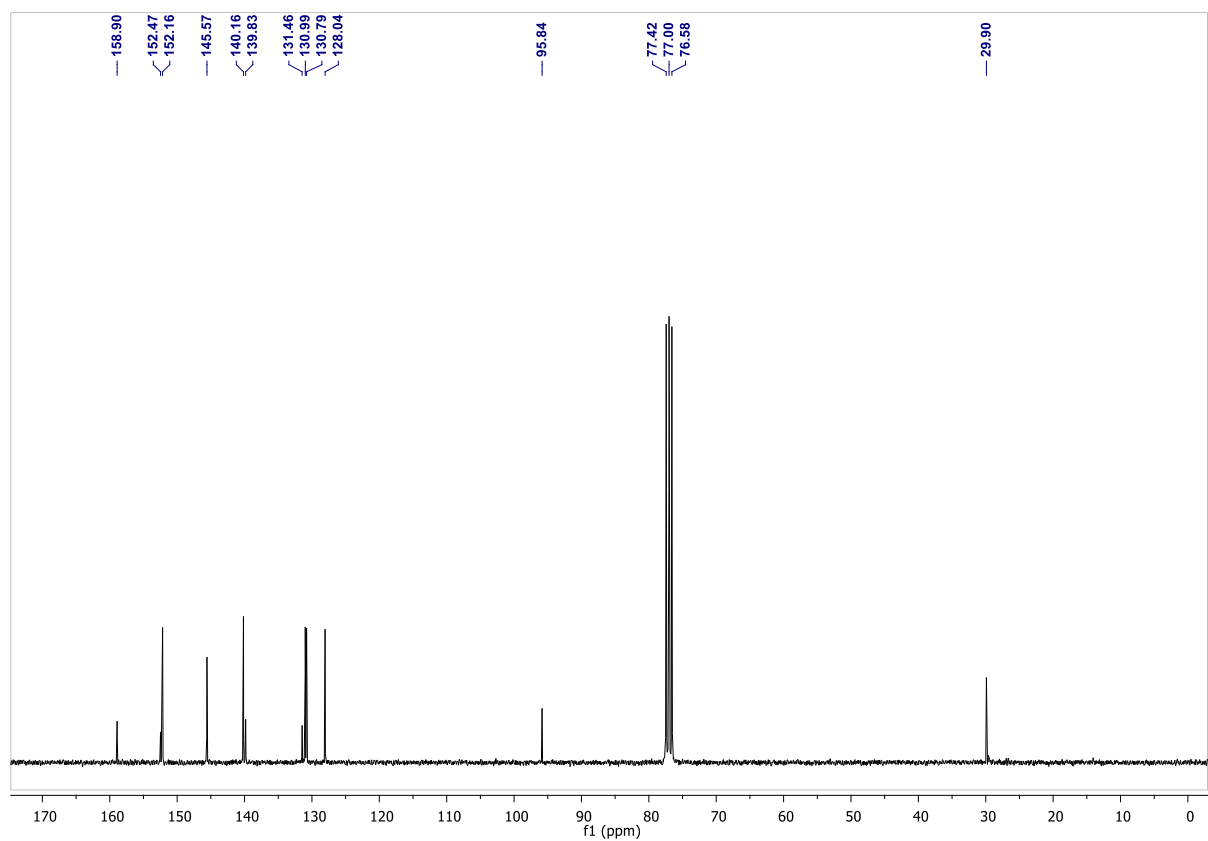
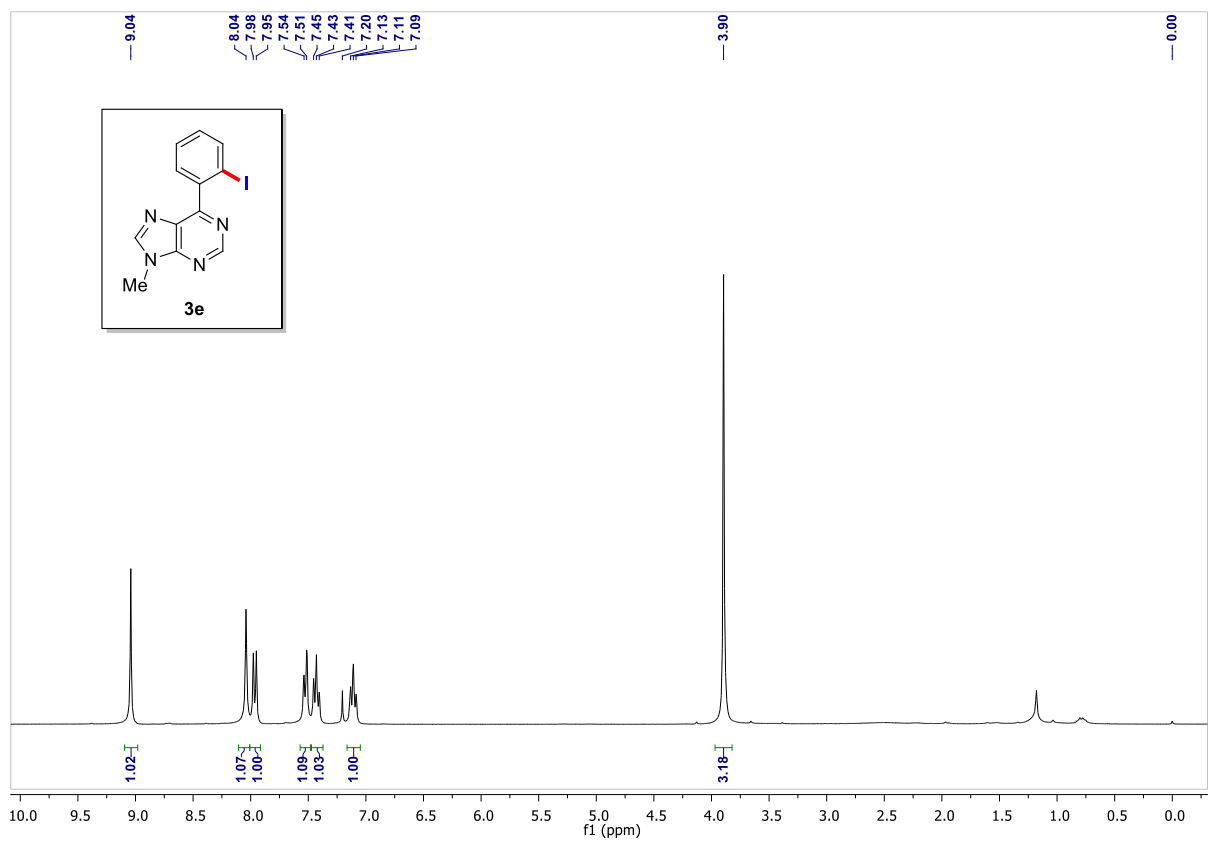


# 9-Ethyl-6-(2-iodophenyl)-9H-purine (3d)

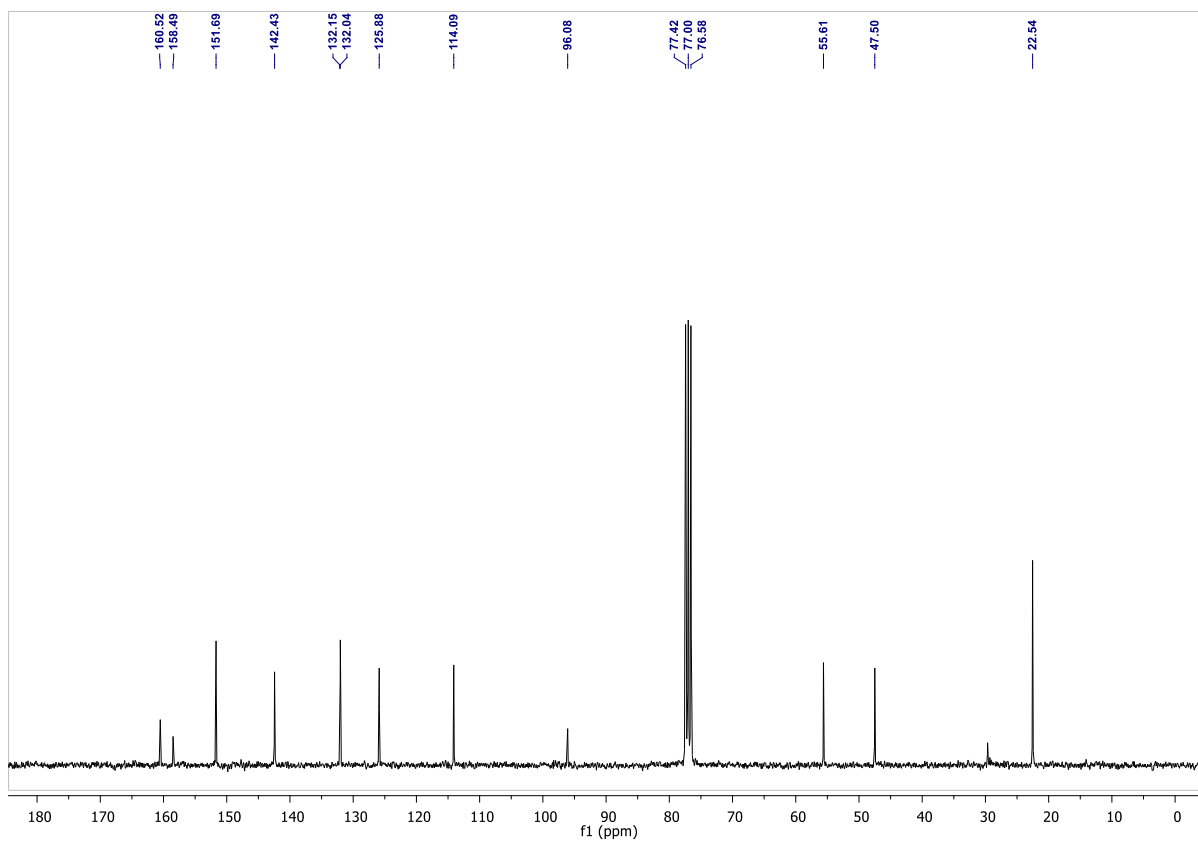
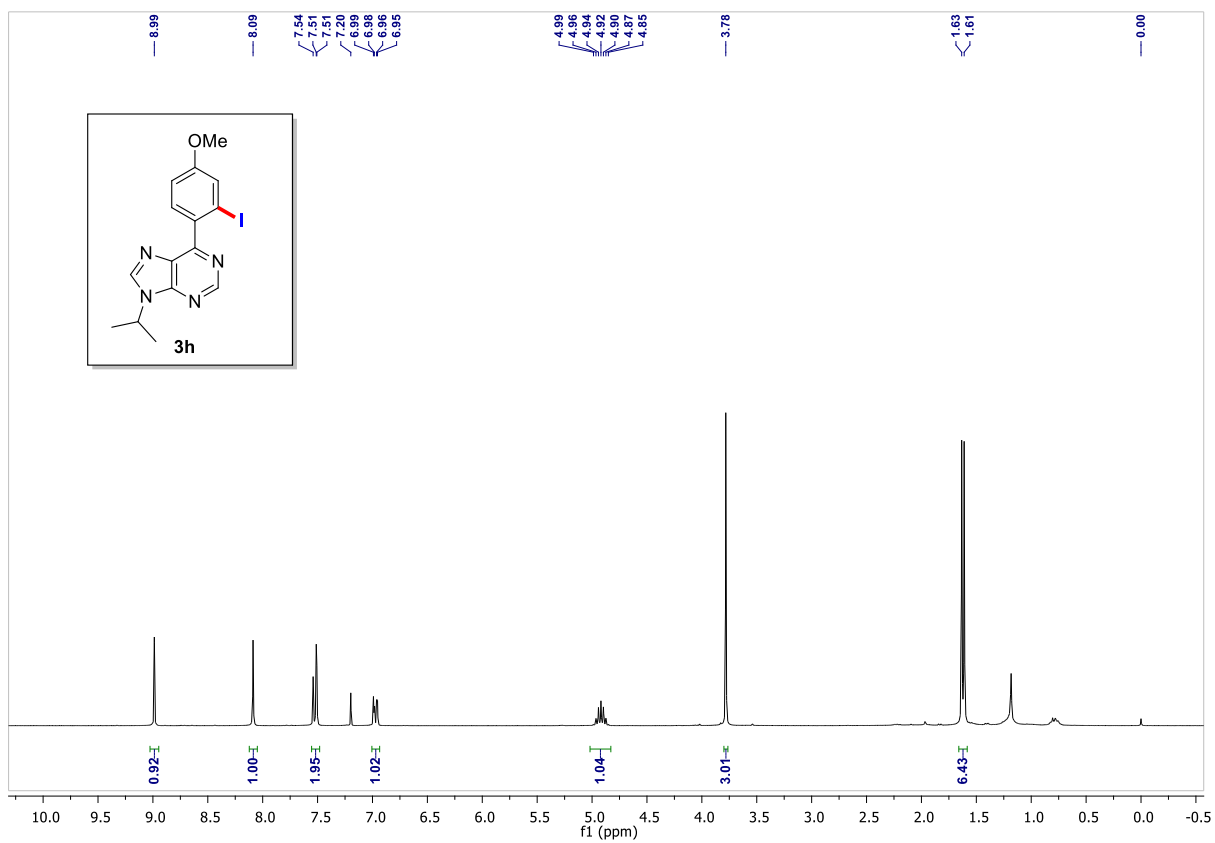




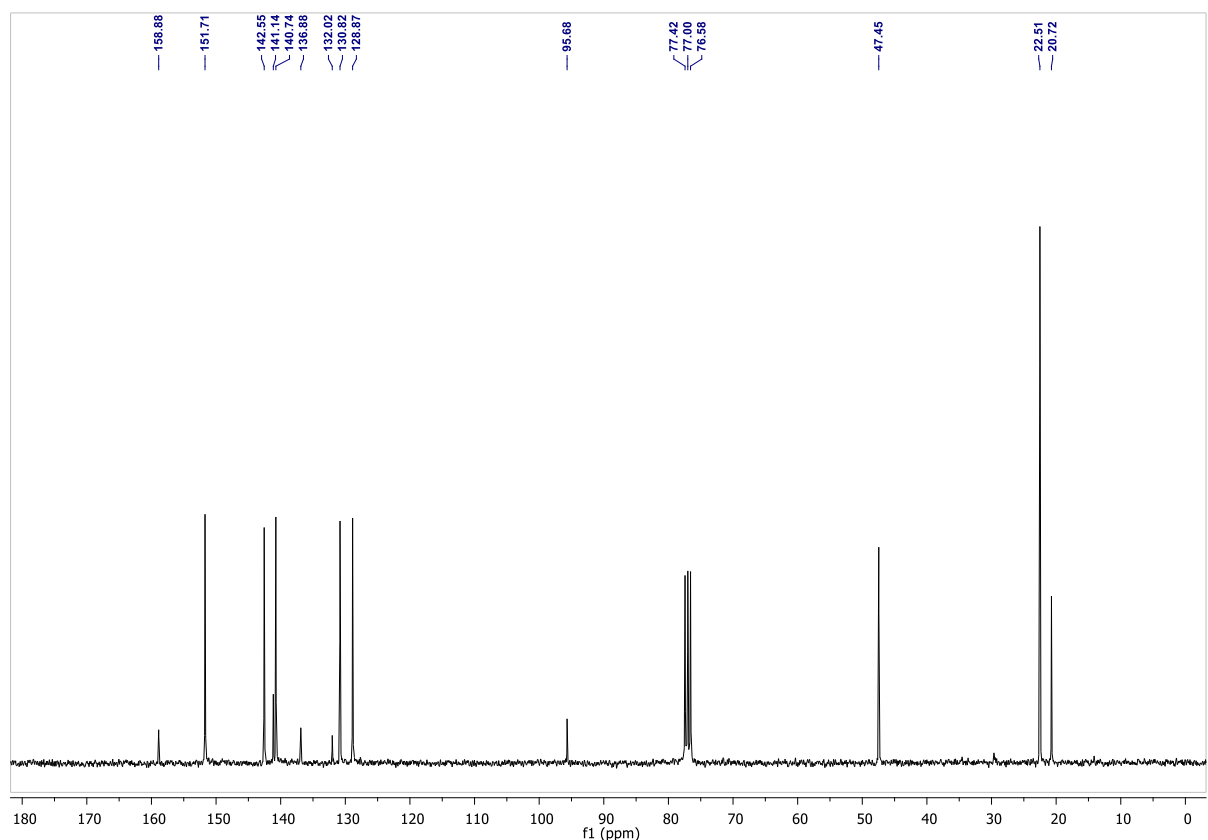
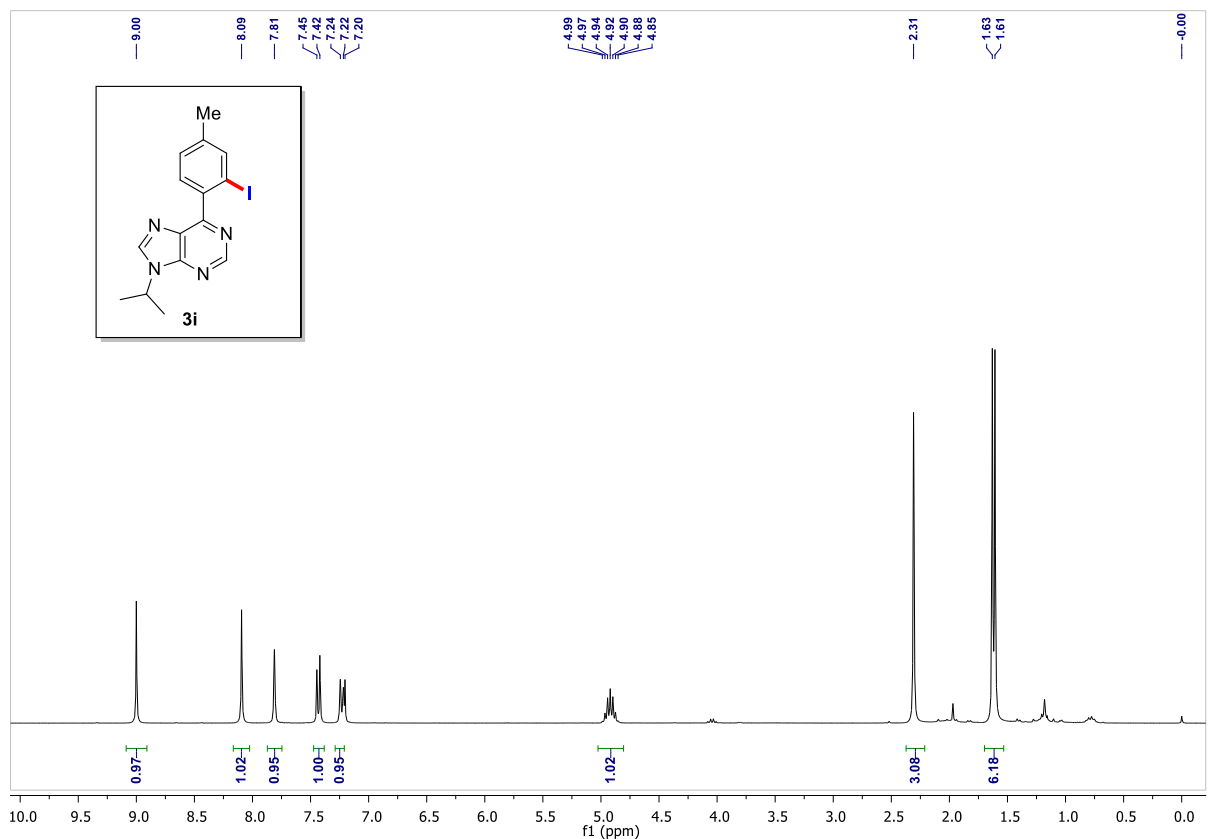
### 6-(2-Iodophenyl)-9-methyl-9H-purine (3e)



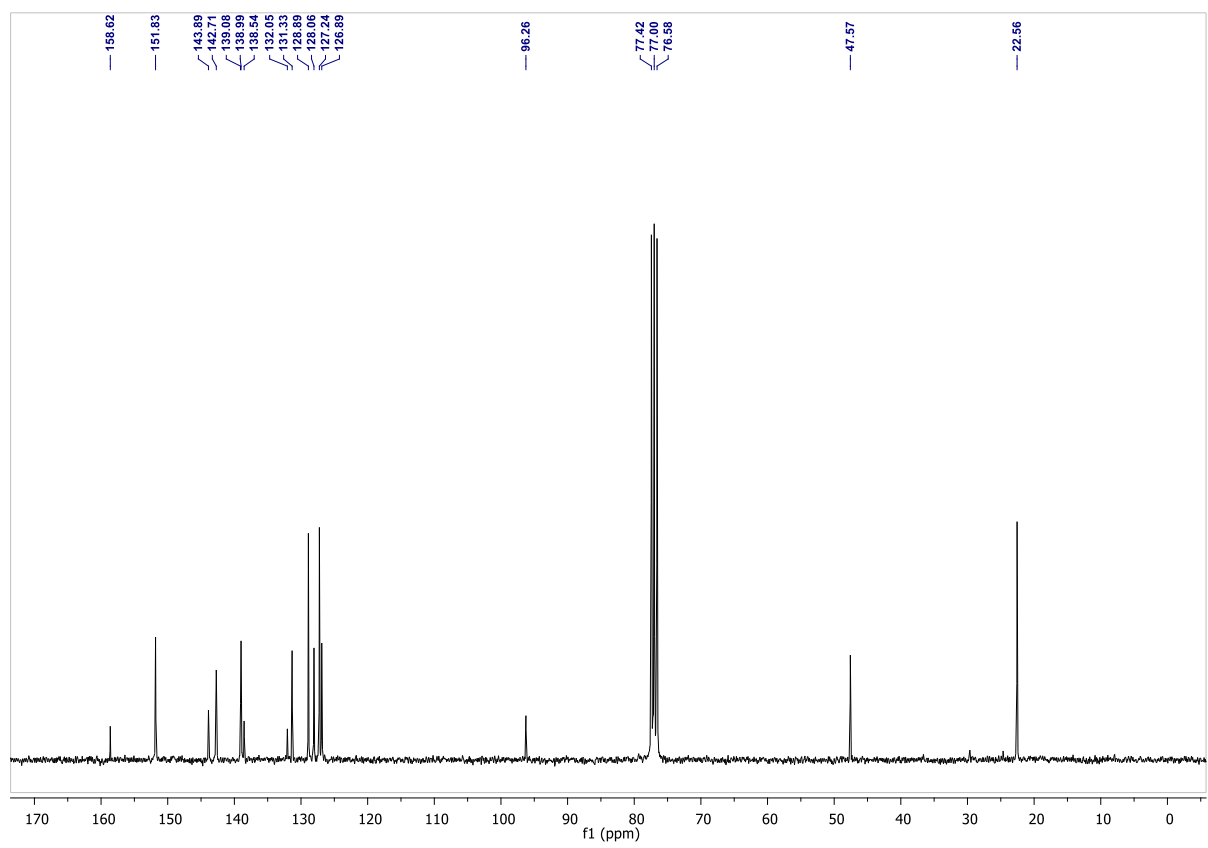
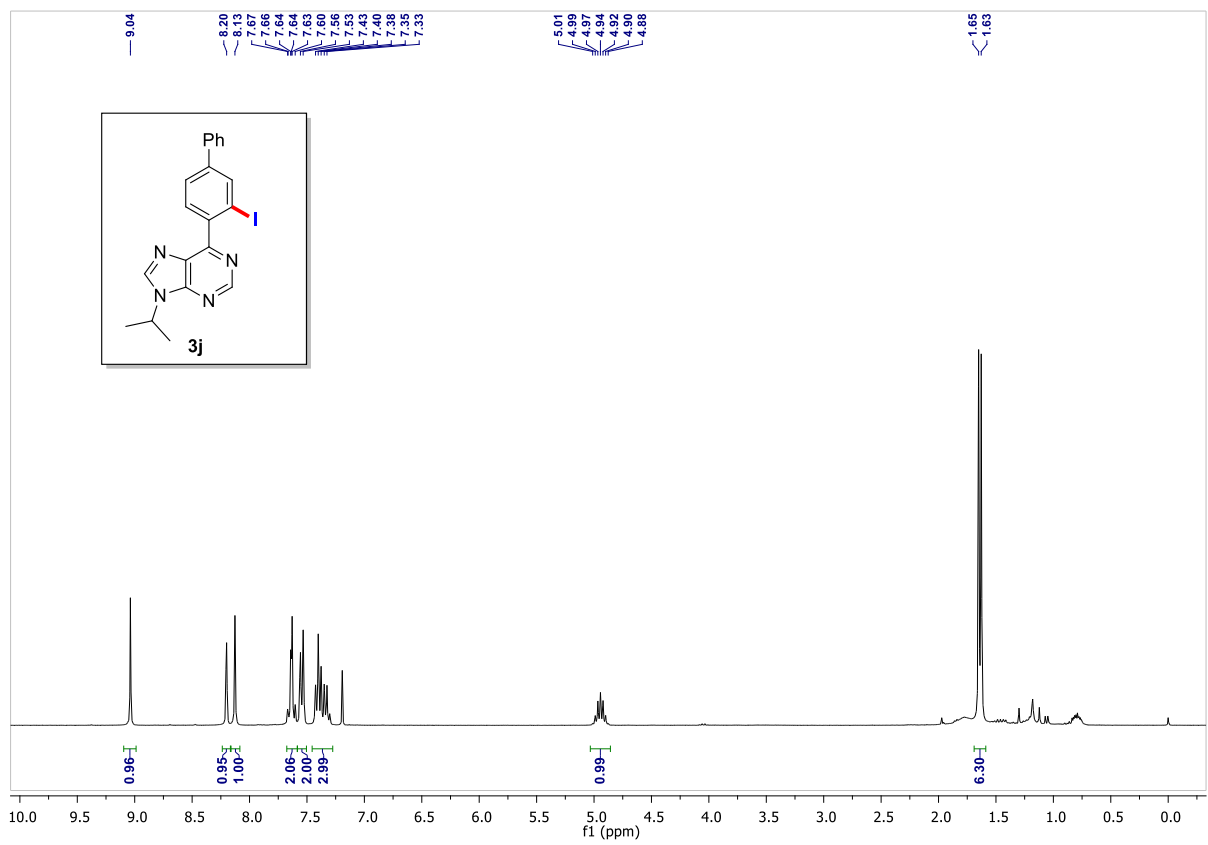
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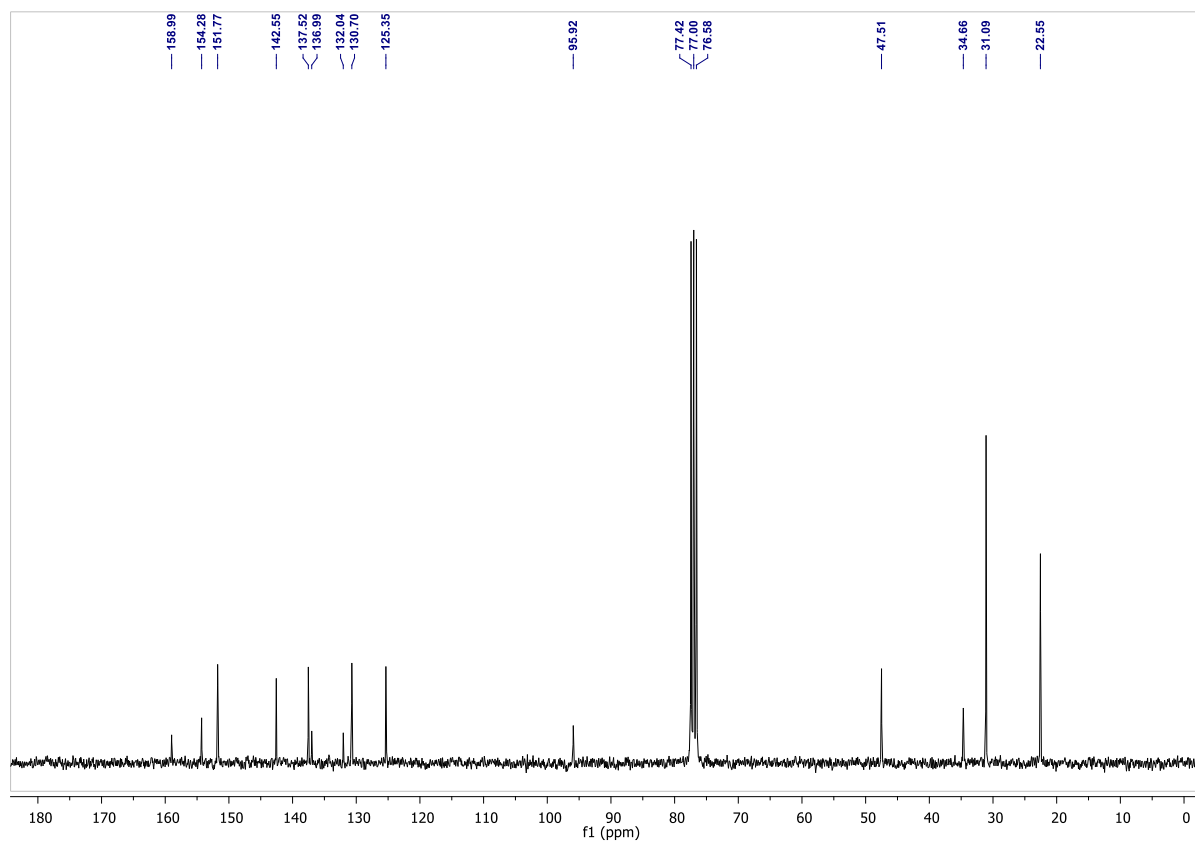
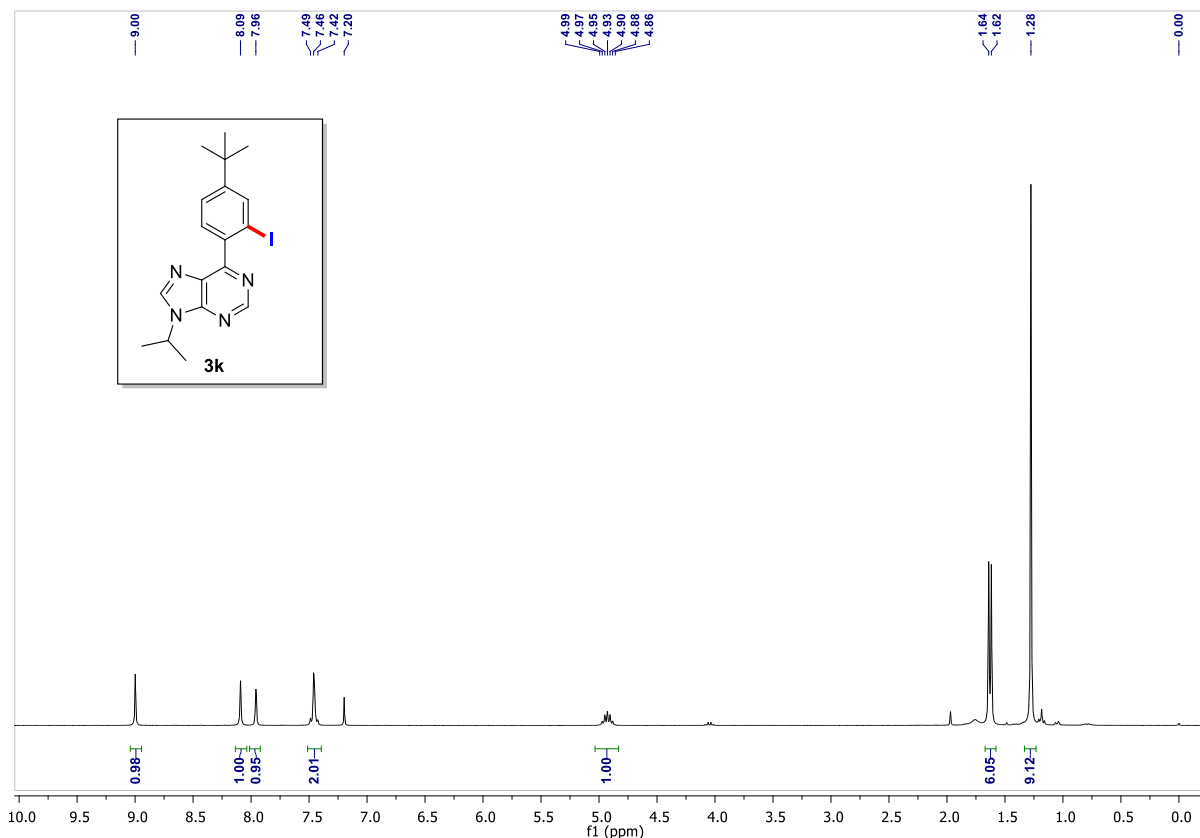
### 6-(2-Iodo-4-methylphenyl)-9-isopropyl-9H-purine (3i)



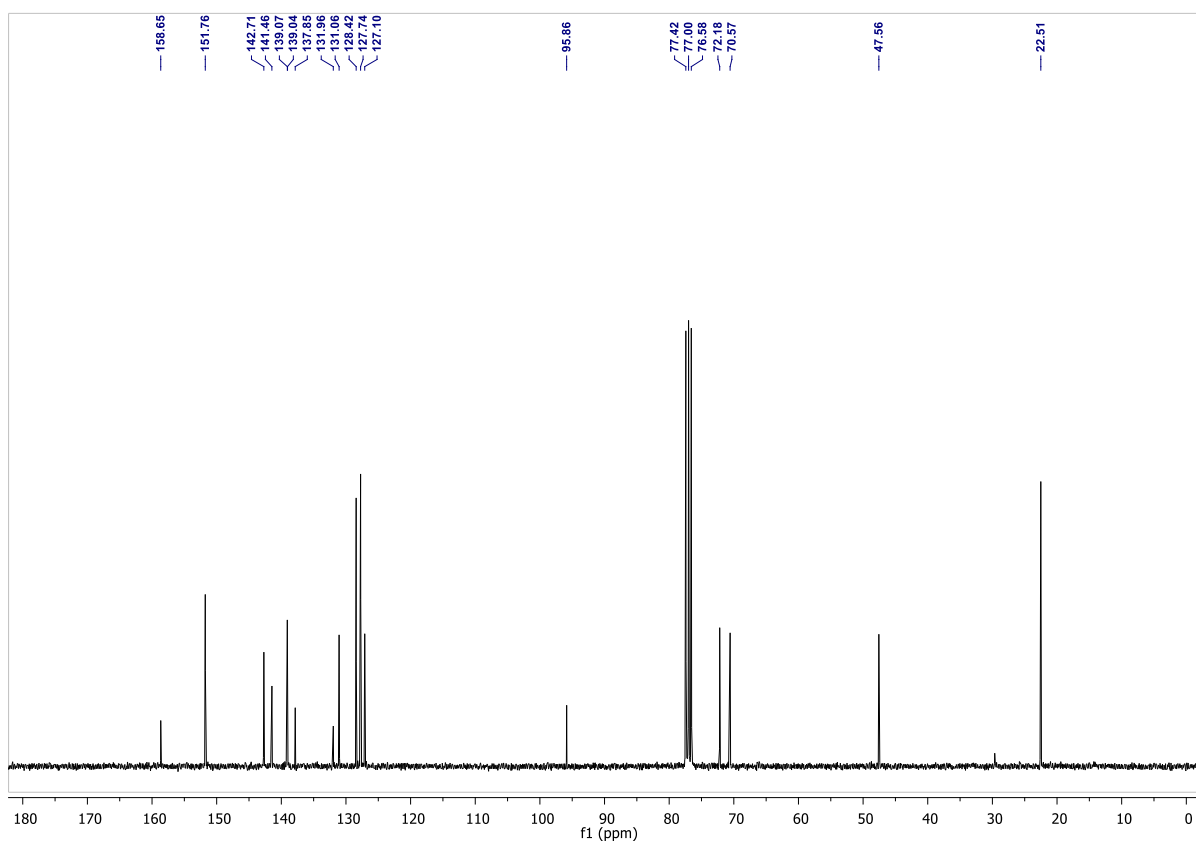
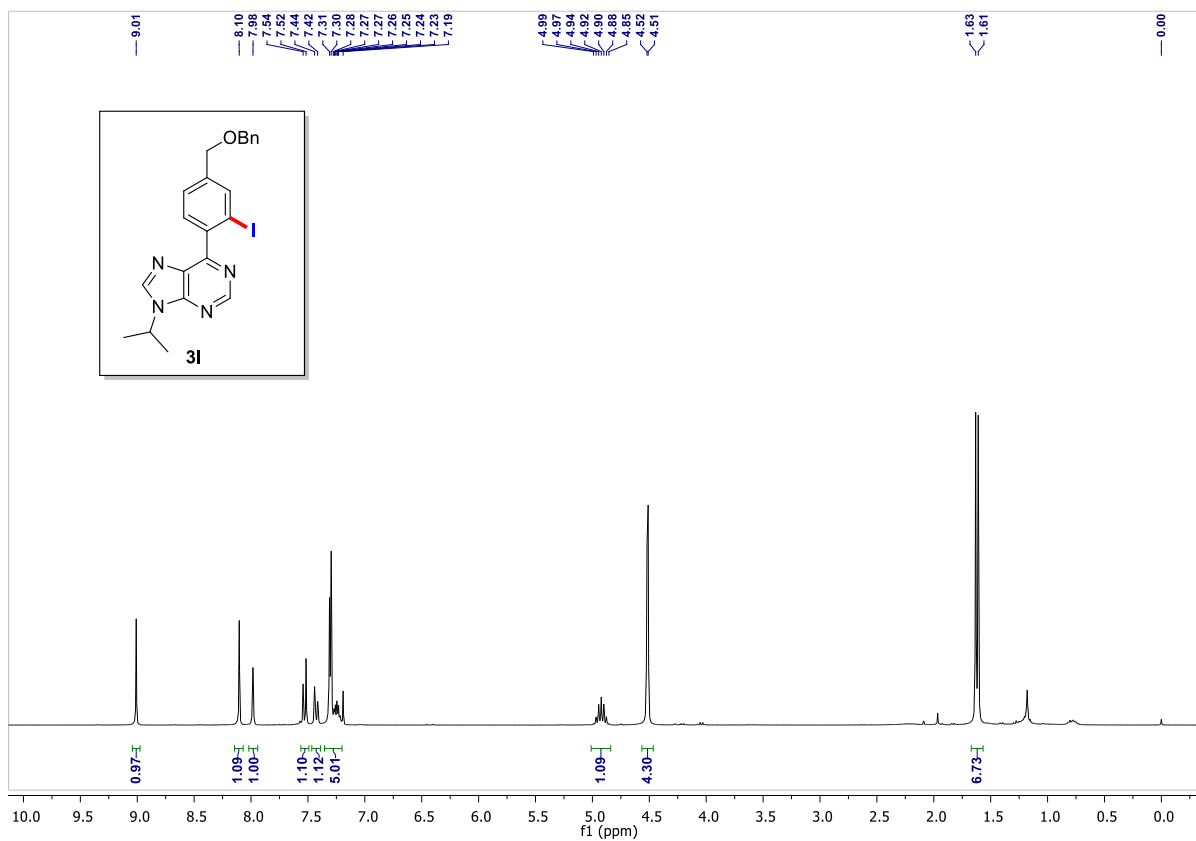
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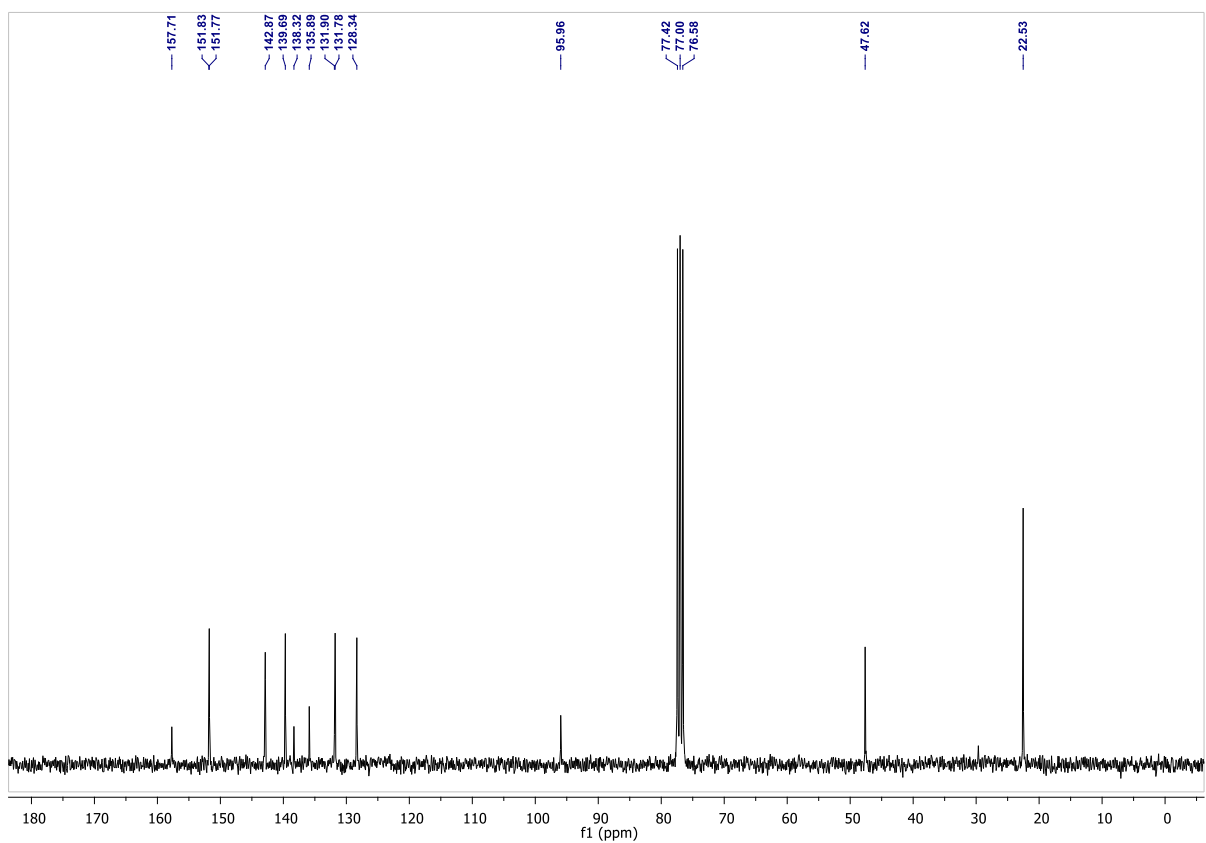
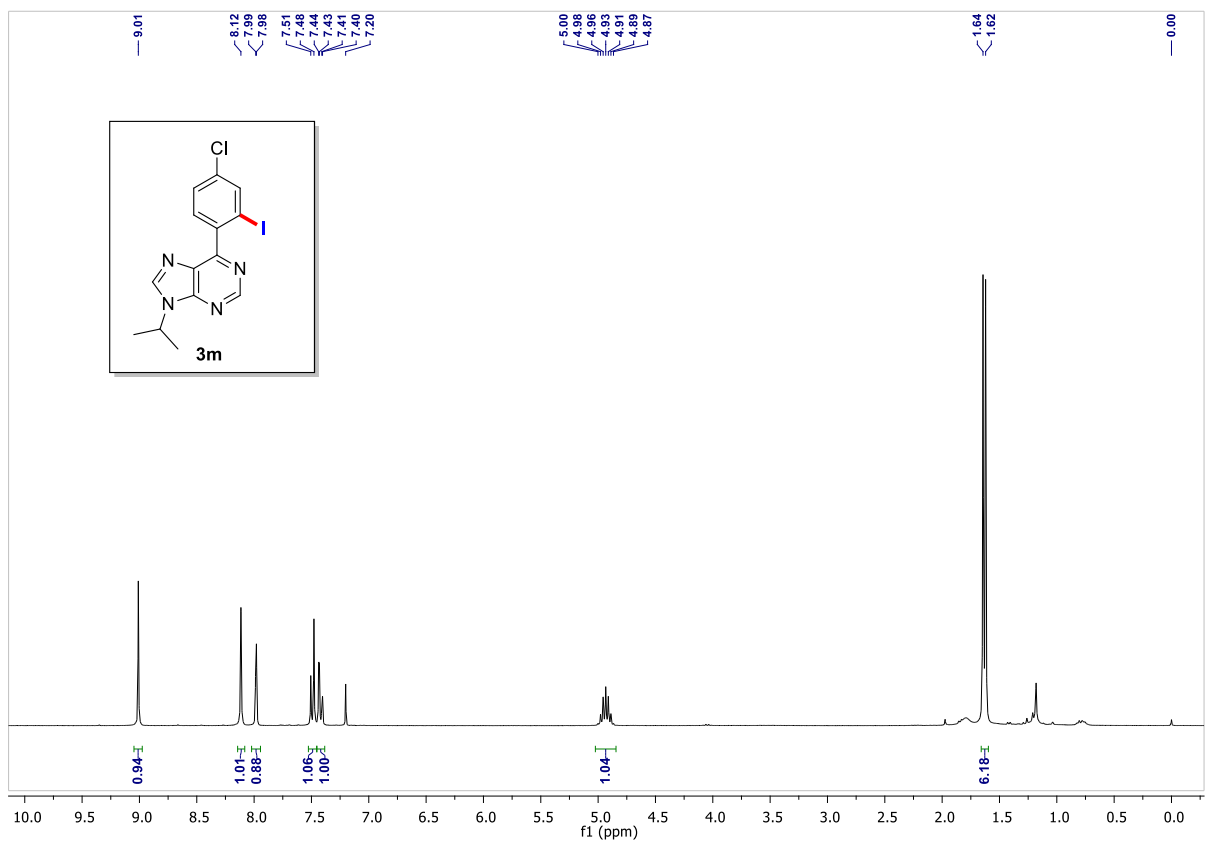
# 6-[4-(*tert*-Butyl)-2-iodophenyl]-9-isopropyl-9*H*-purine (3k)



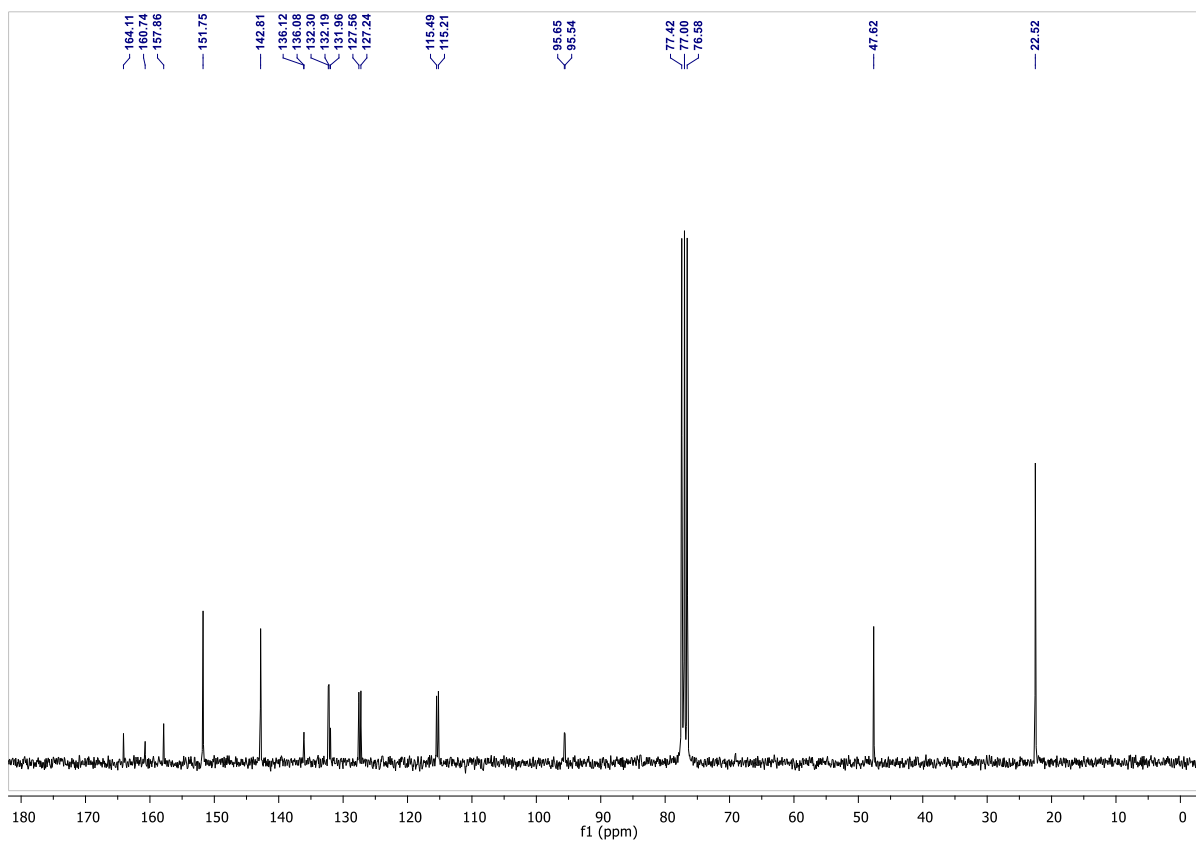
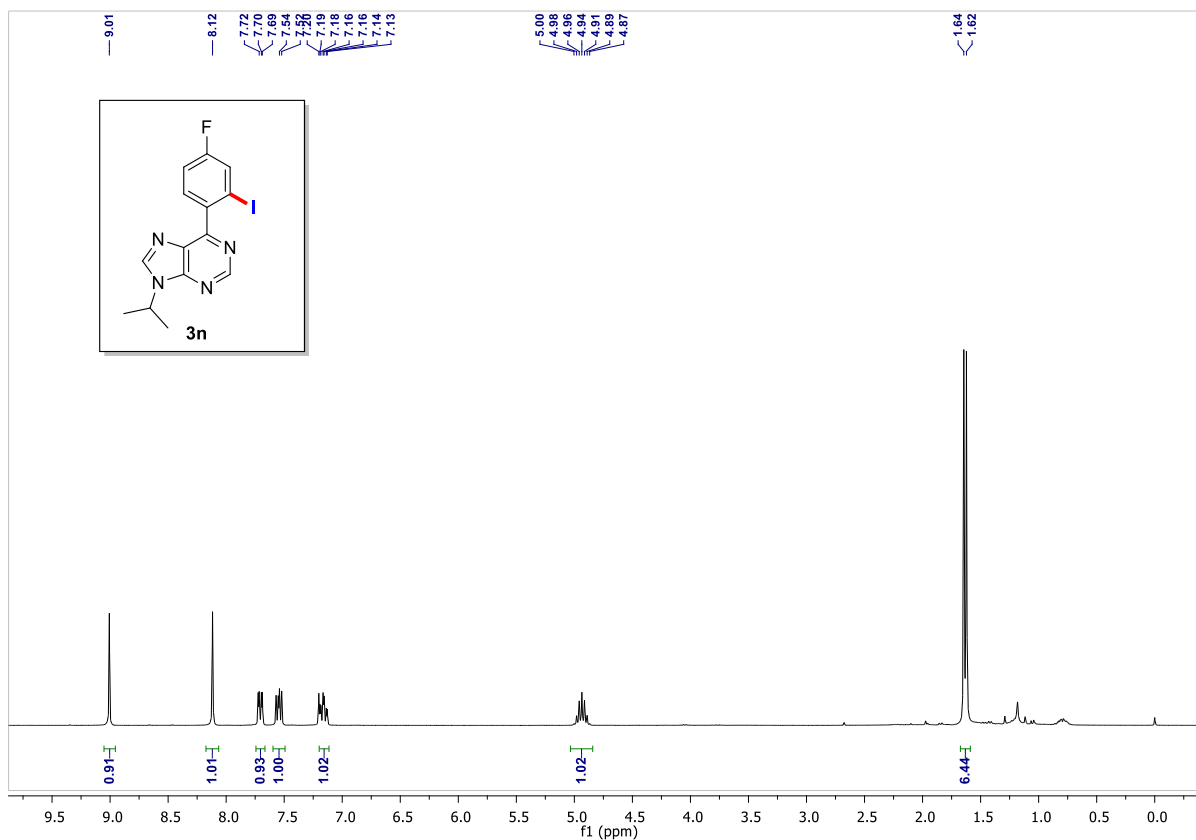
# 6-[4-(Benzyloxy)methyl-2-iodophenyl]-9-isopropyl-9H-purine (3I)



# 6-(4-Chloro-2-iodophenyl)-9-isopropyl-9H-purine (3m)

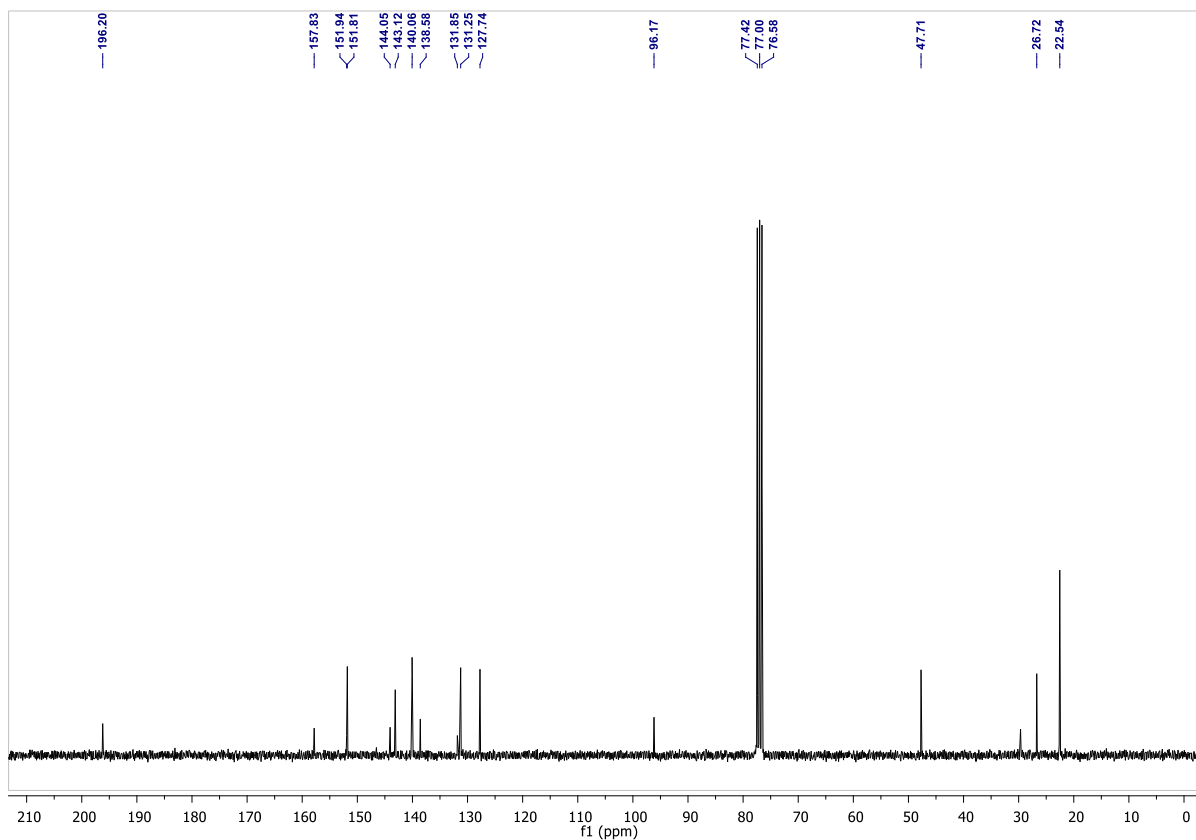
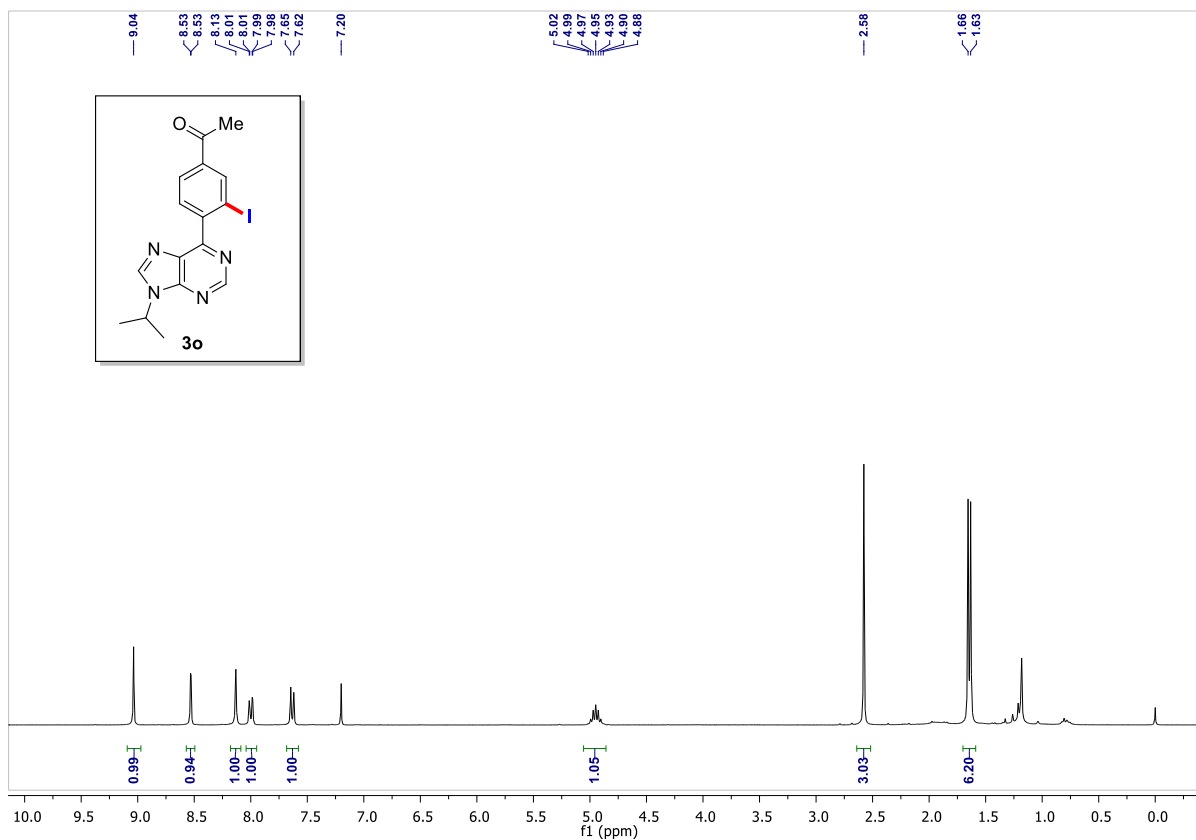


# 6-(4-Fluoro-2-iodophenyl)-9-isopropyl-9H-purine (3n)

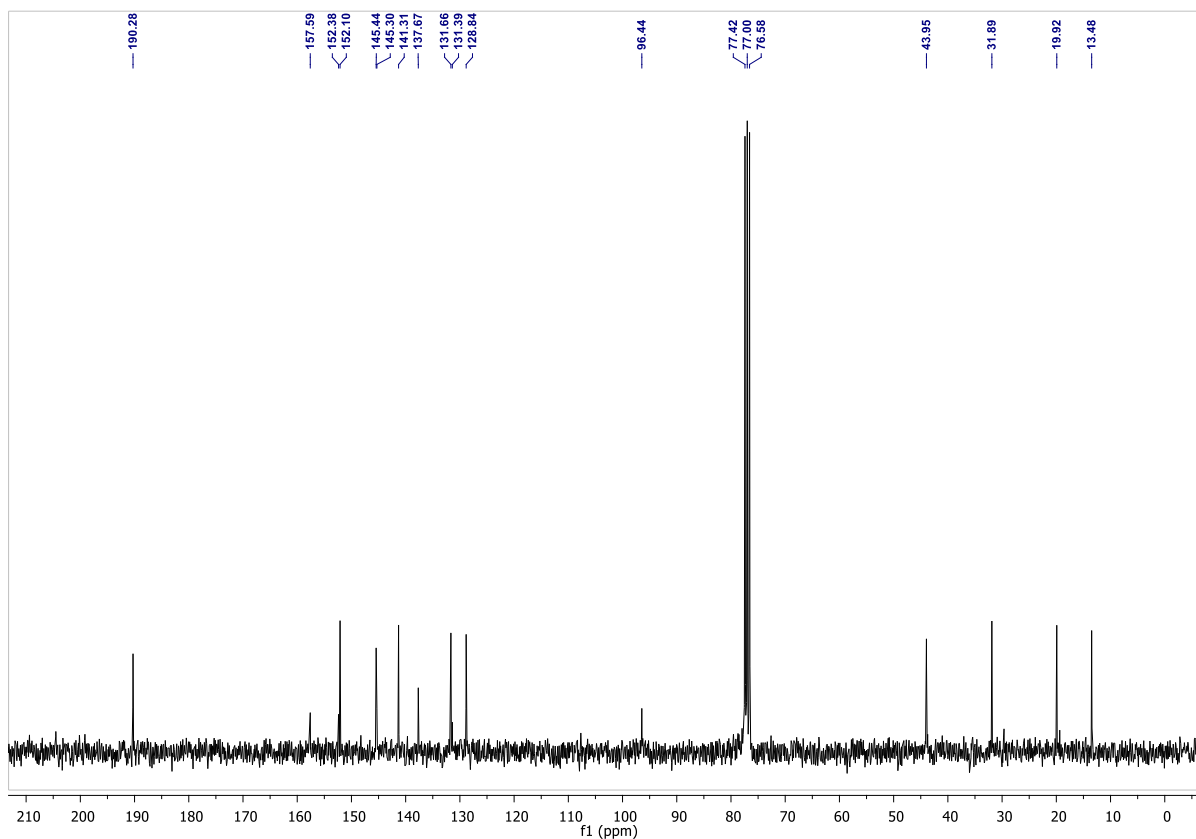
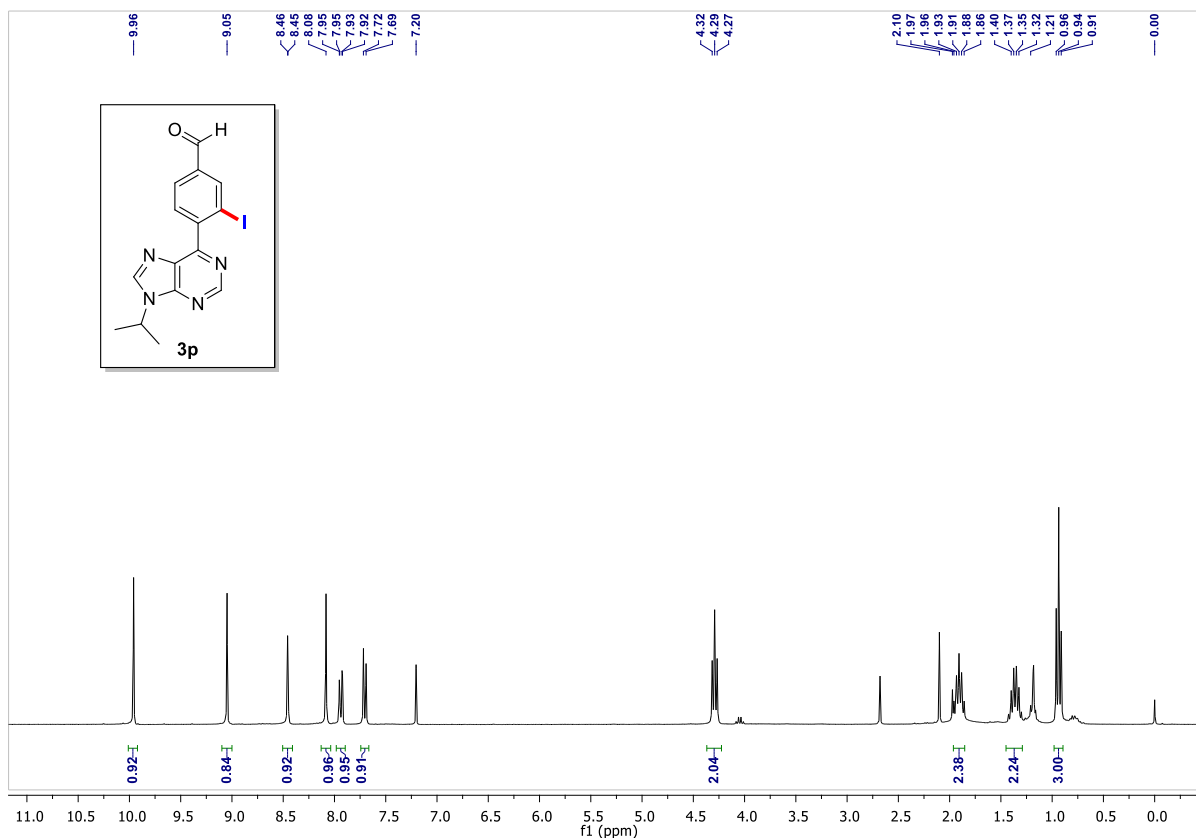




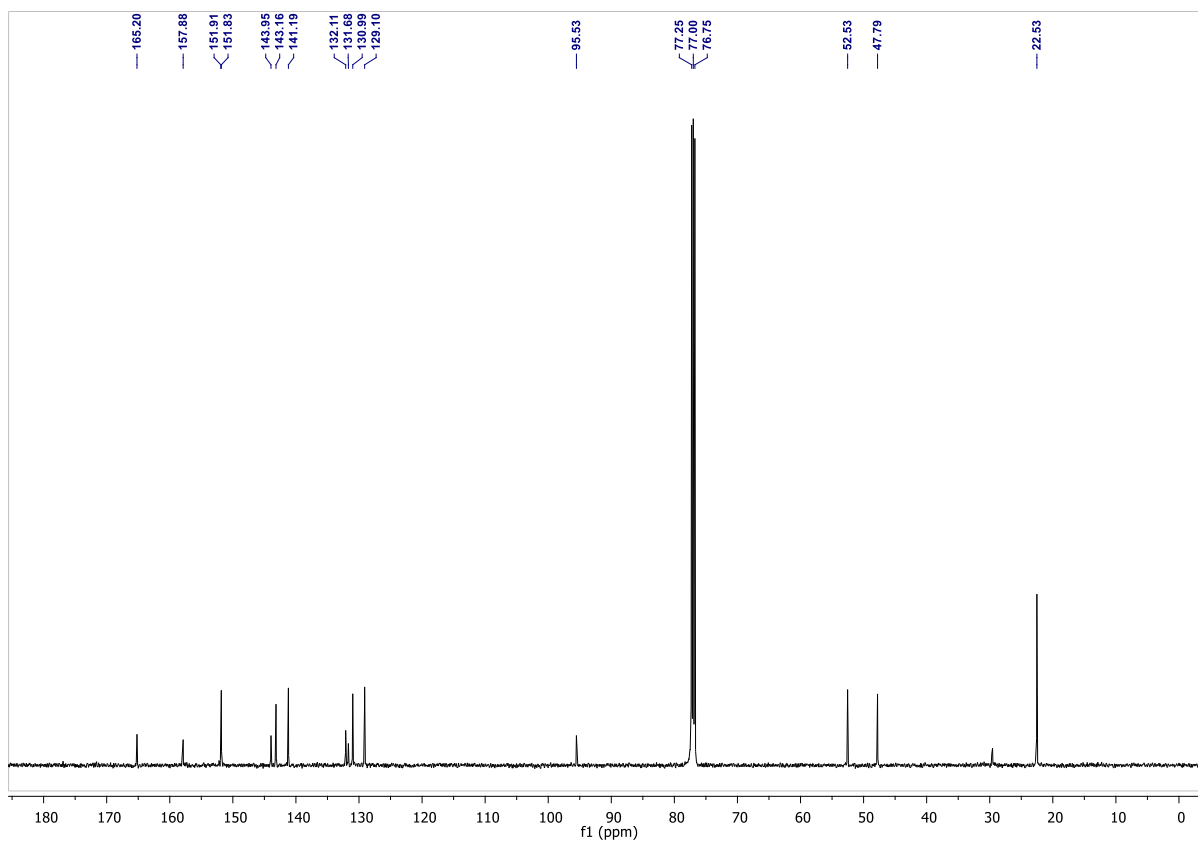
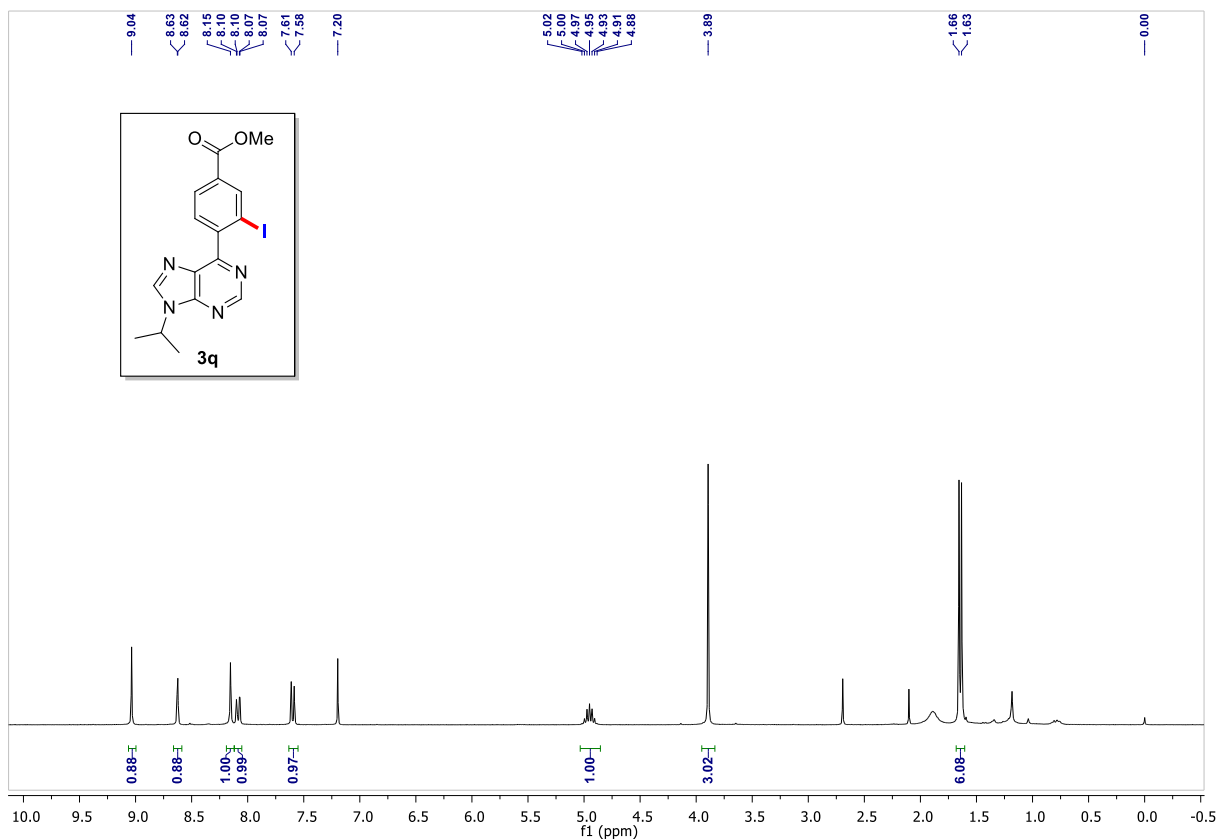
# 1-[3-iodo-4-(9-isopropyl-9H-purin-6-yl)phenyl]ethanone (3o)



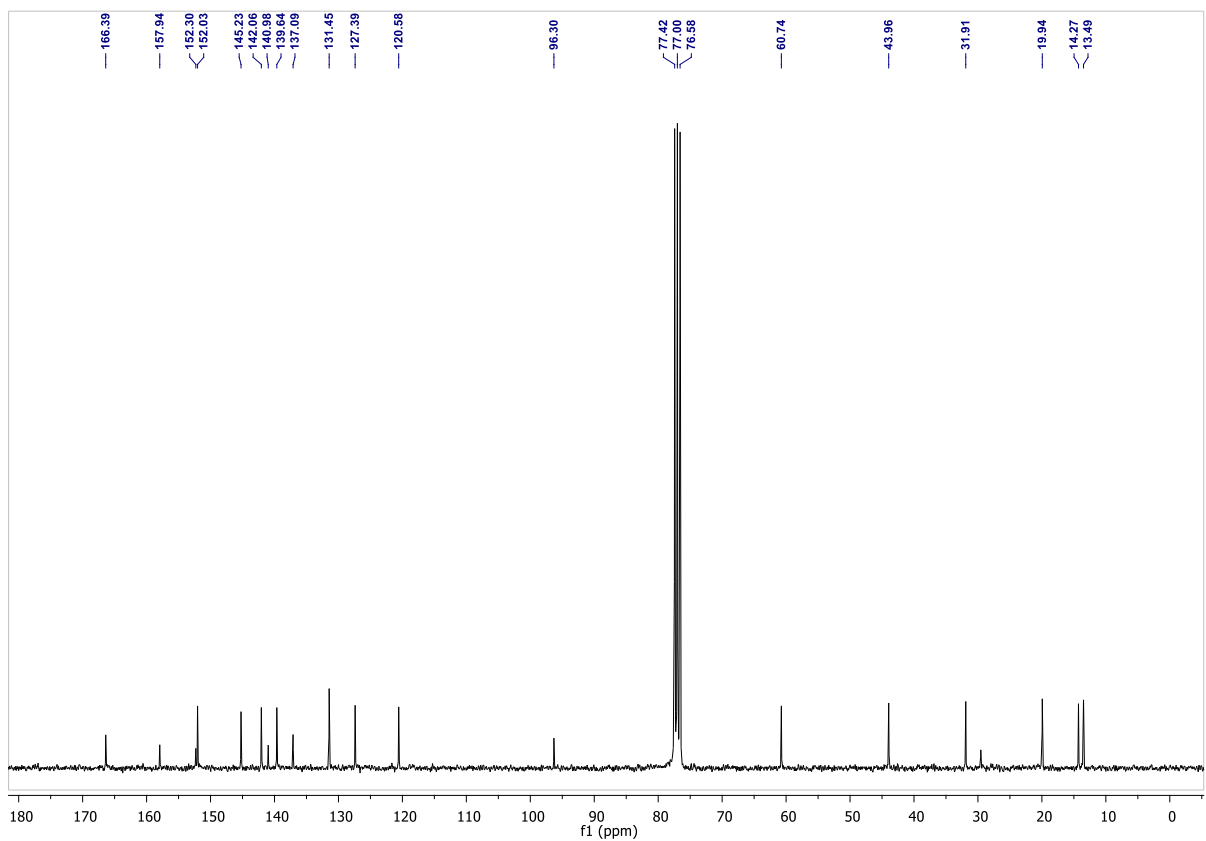
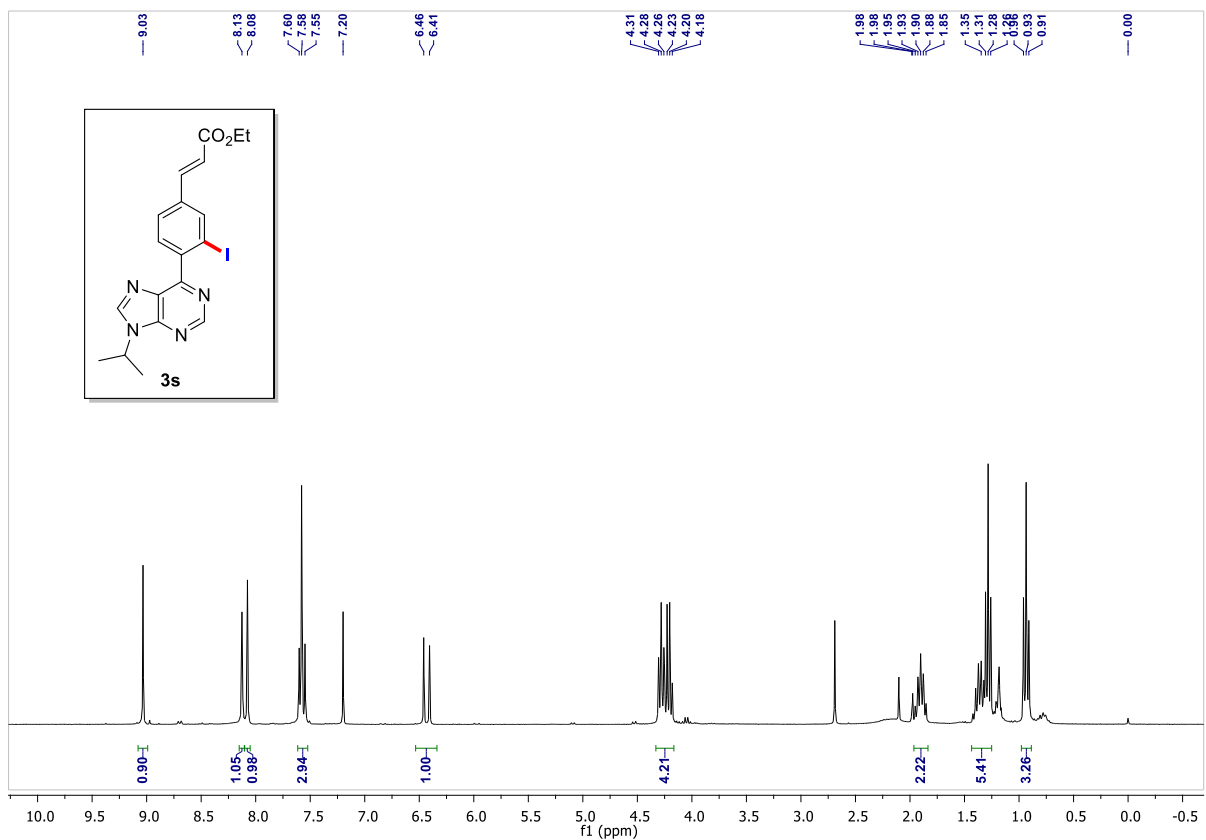
# 4-(9-Butyl-9H-purin-6-yl)-3-iodobenzaldehyde (3p)



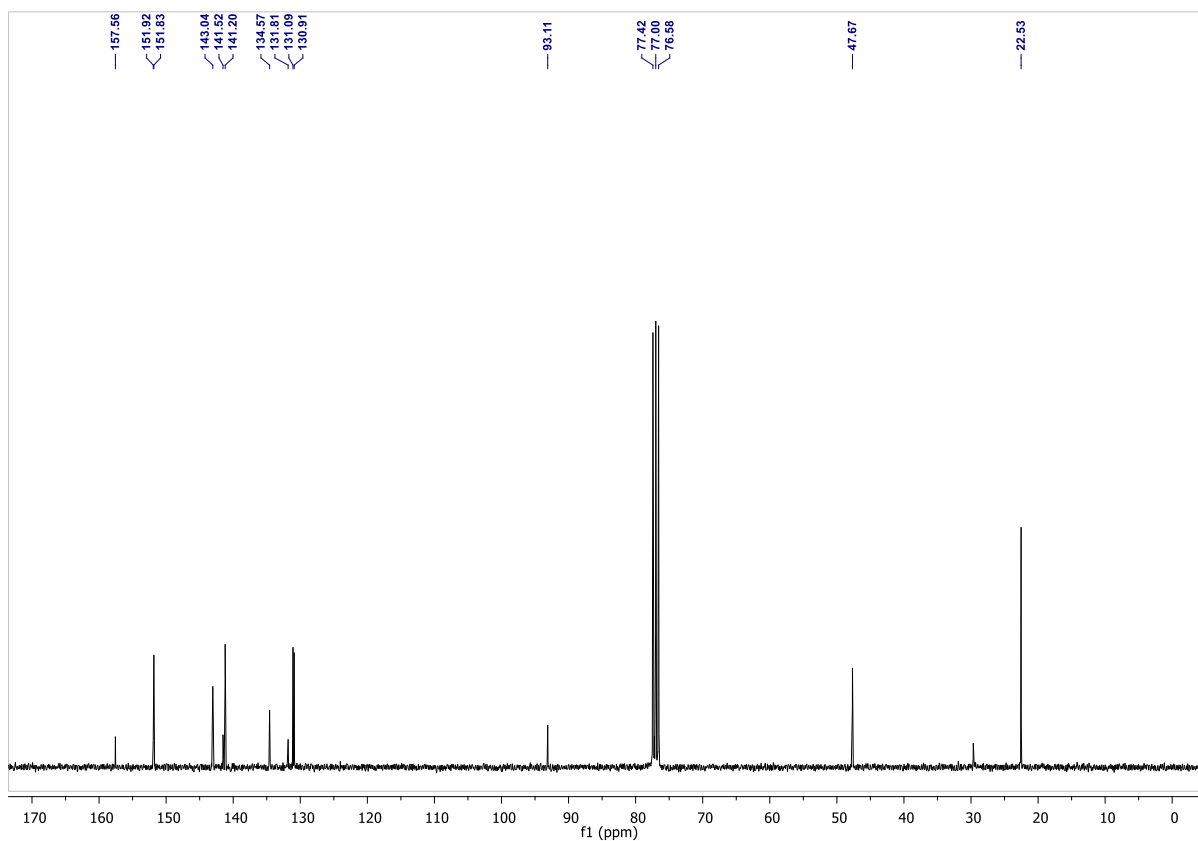
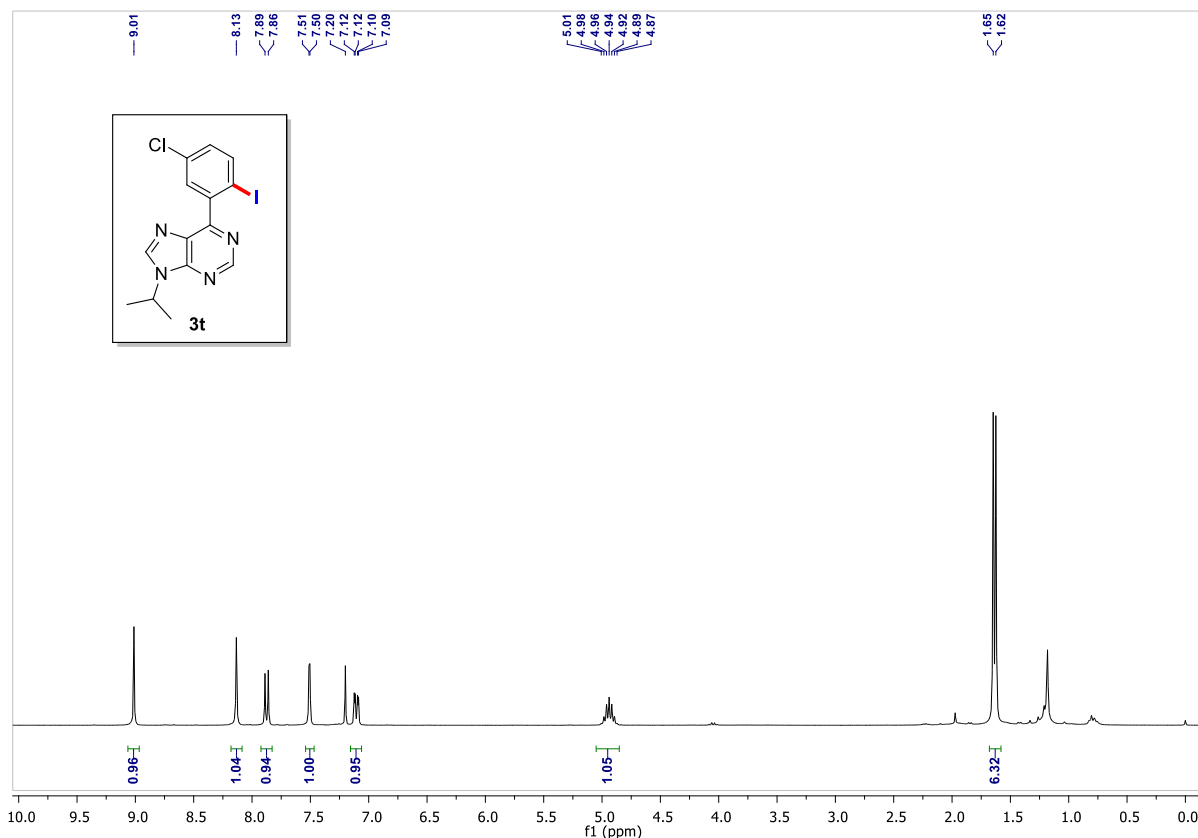
# Methyl 3-iodo-4-(9-isopropyl-9H-purin-6-yl)benzoate (3q)



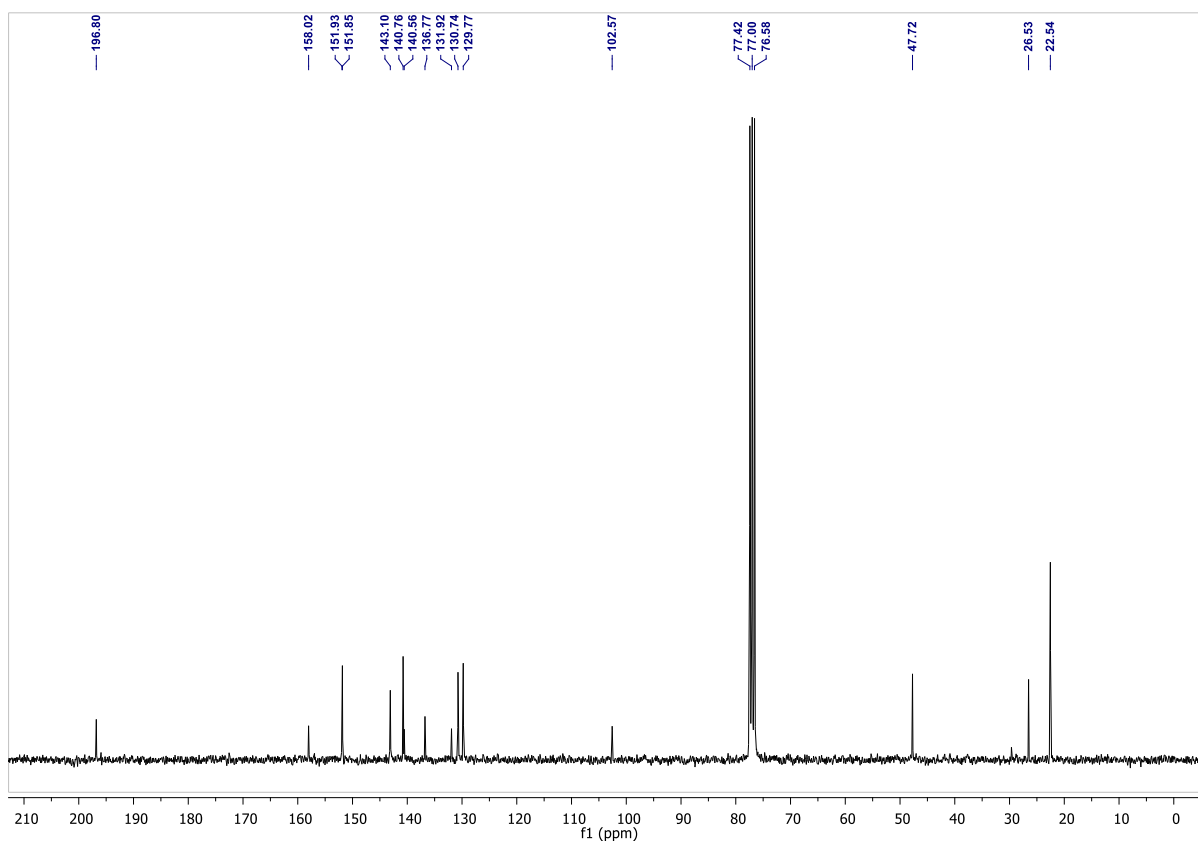
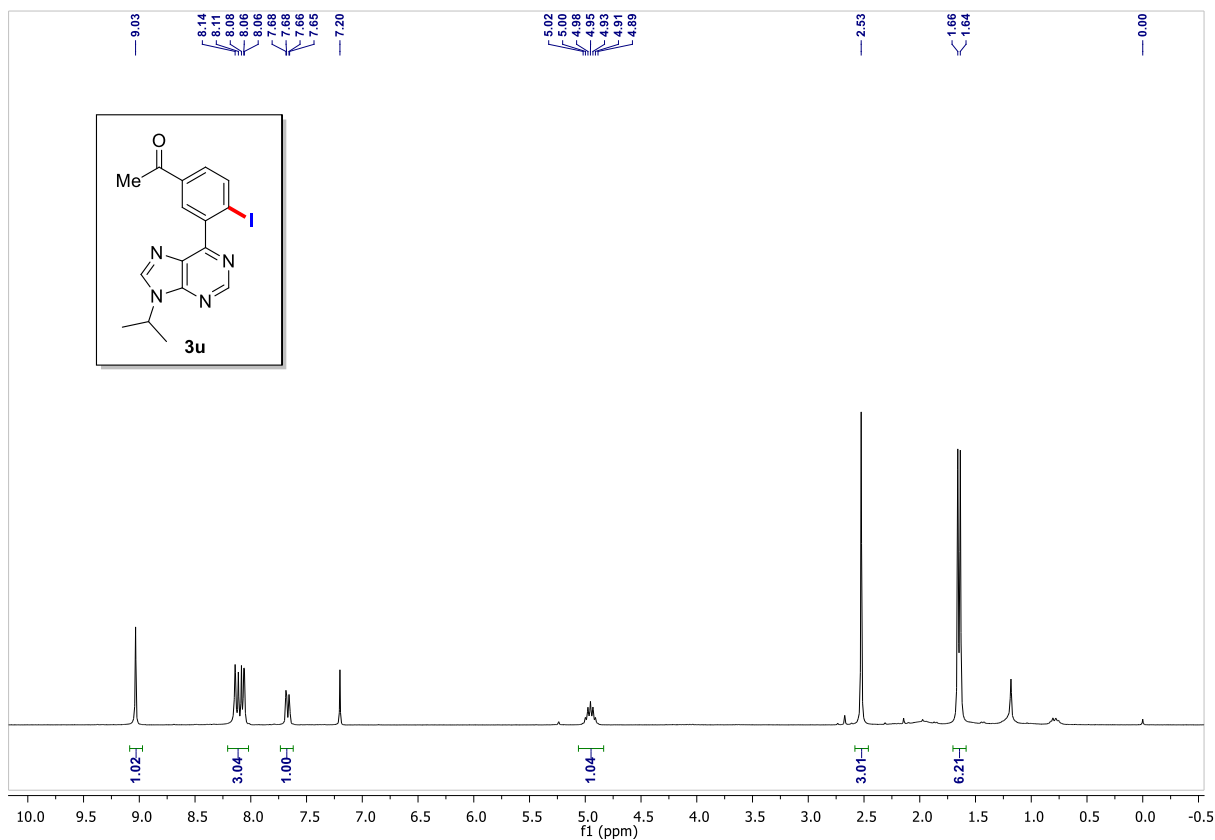
**(E)-Ethyl 3-(4-(9-butyl-9H-purin-6-yl)-3-iodophenyl)acrylate (3s)**



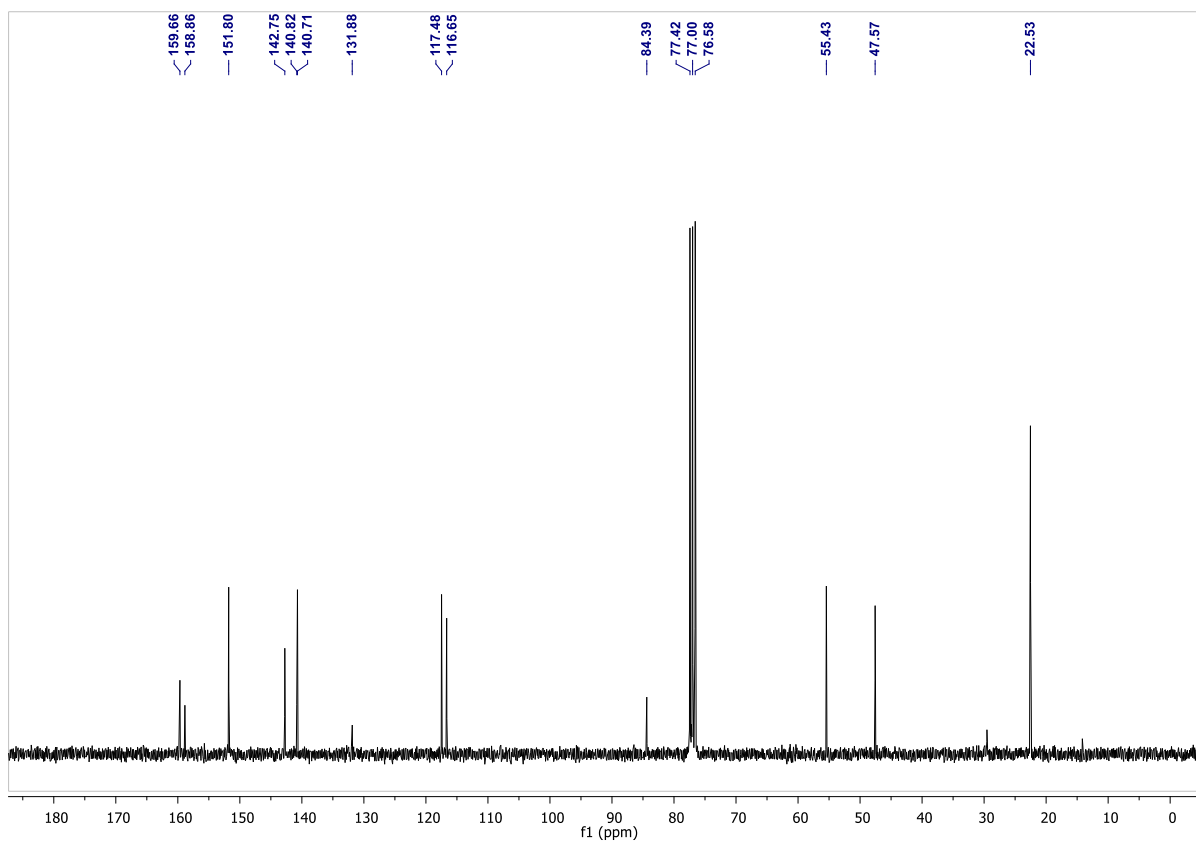
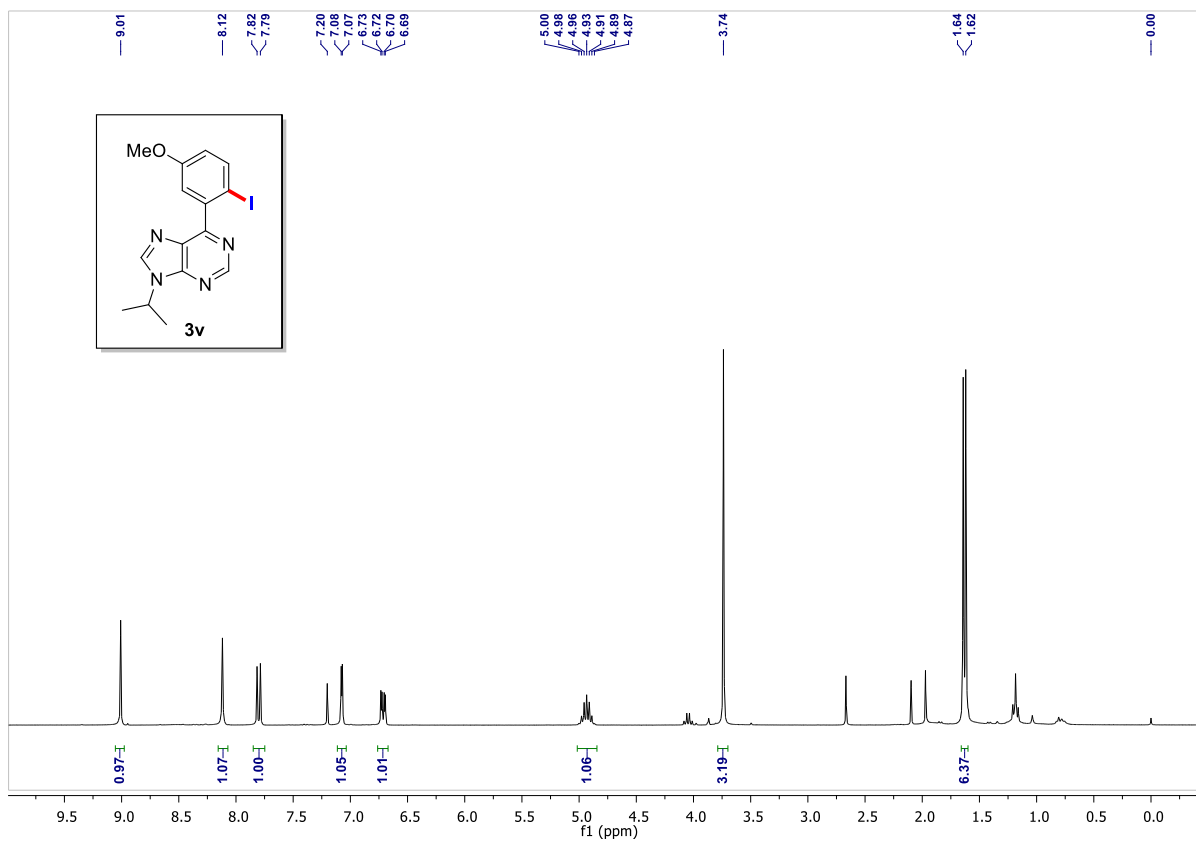
# 6-(5-Chloro-2-iodophenyl)-9-isopropyl-9H-purine (3t)



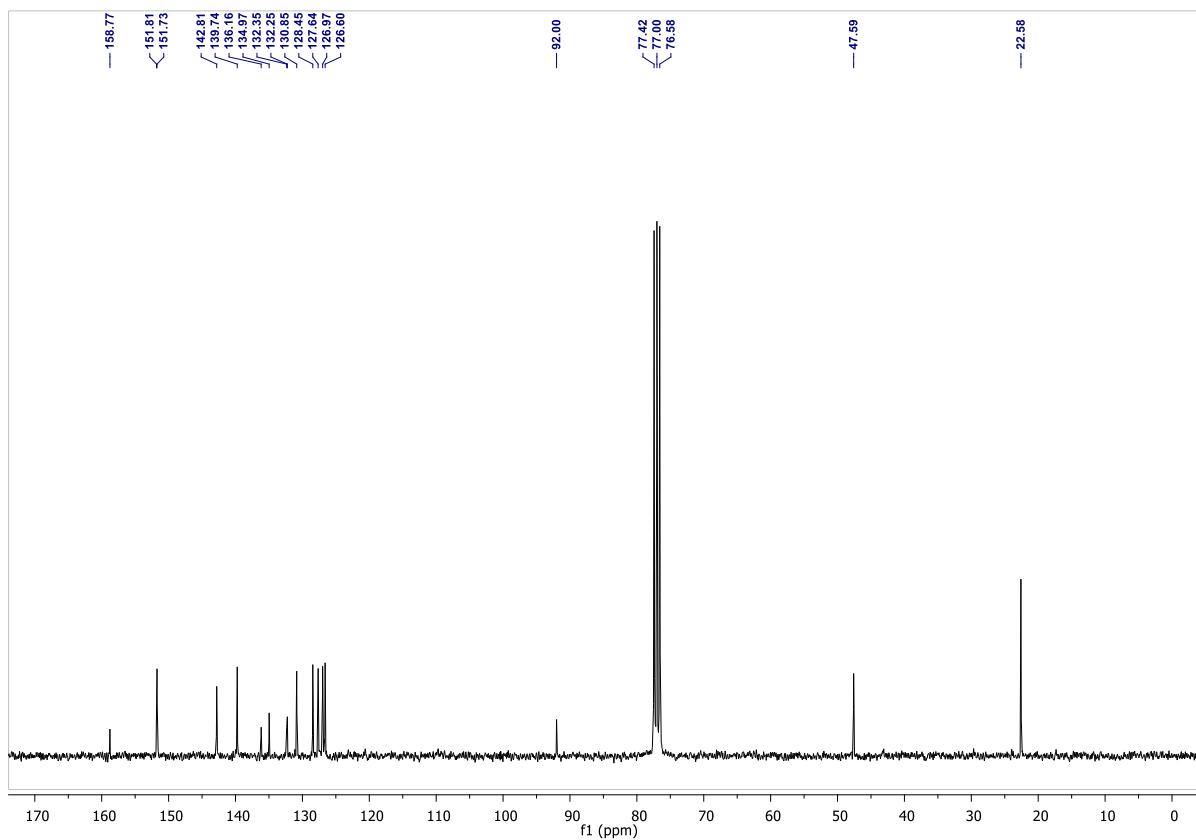
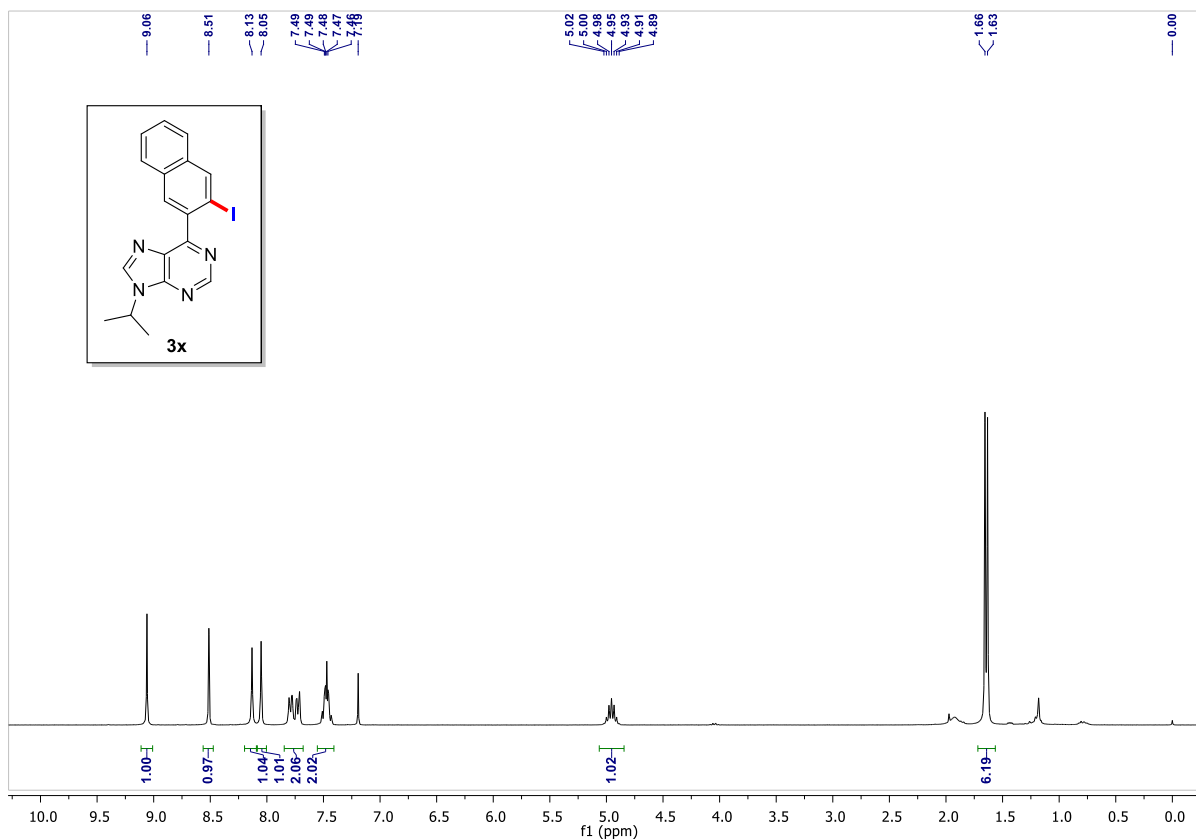
# 1-[4-Iodo-3-(9-isopropyl-9H-purin-6-yl)phenyl]ethanone (3u)



# 6-(2-Iodo-5-methoxyphenyl)-9-isopropyl-9H-purine (3v)

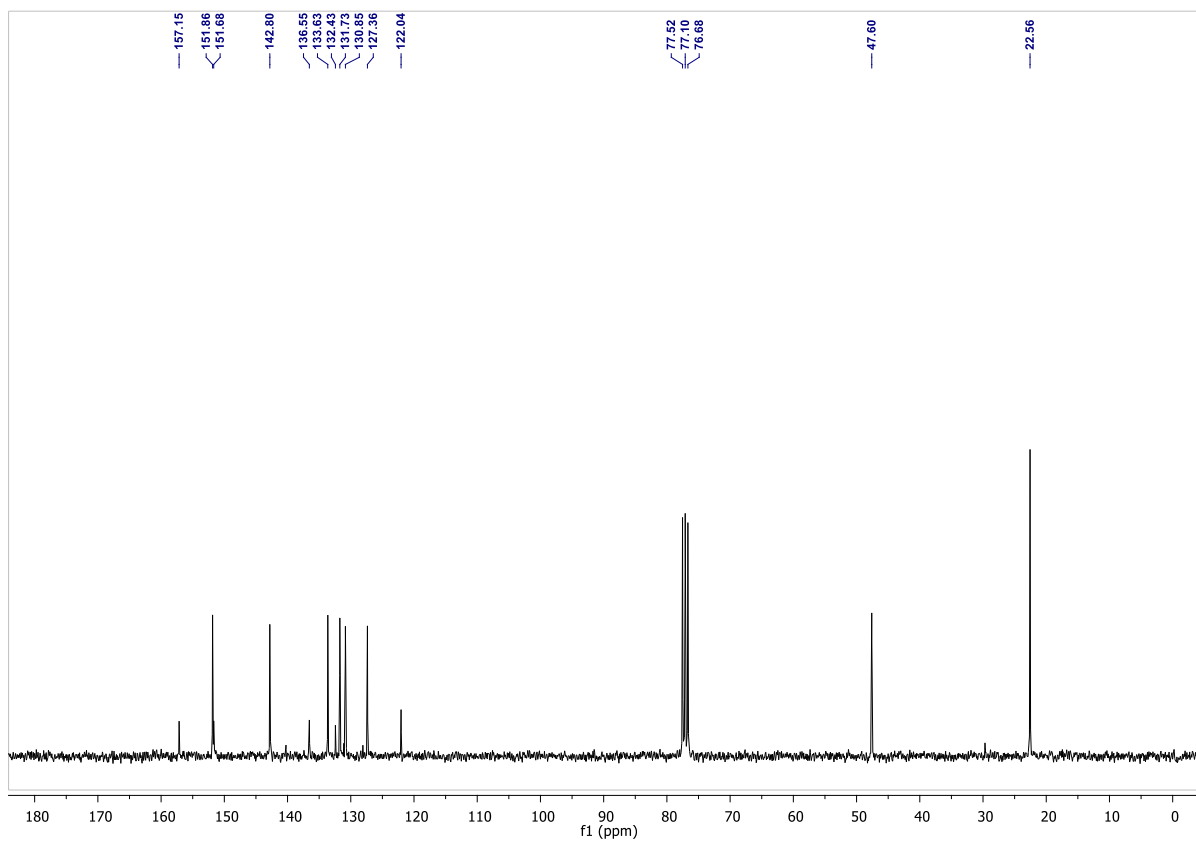
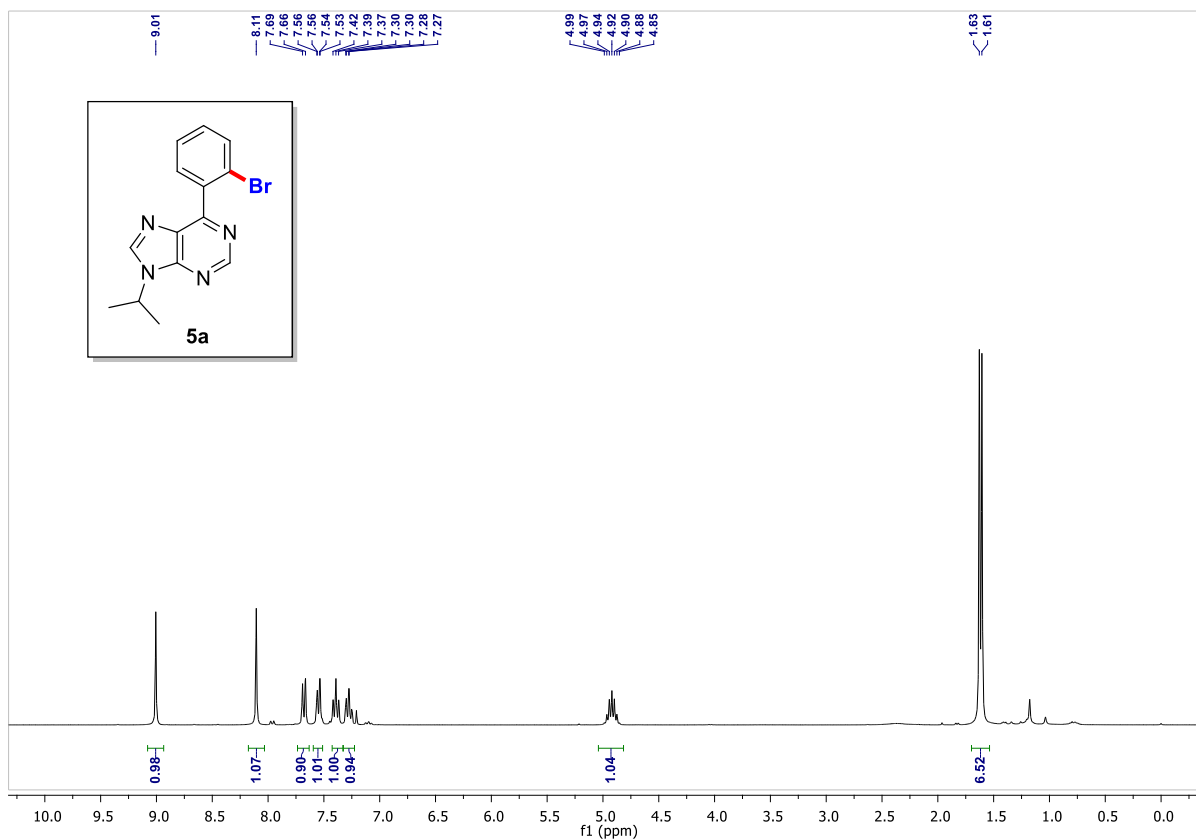


# 6-(3-Iodonaphthalen-2-yl)-9-isopropyl-9H-purine (3x)

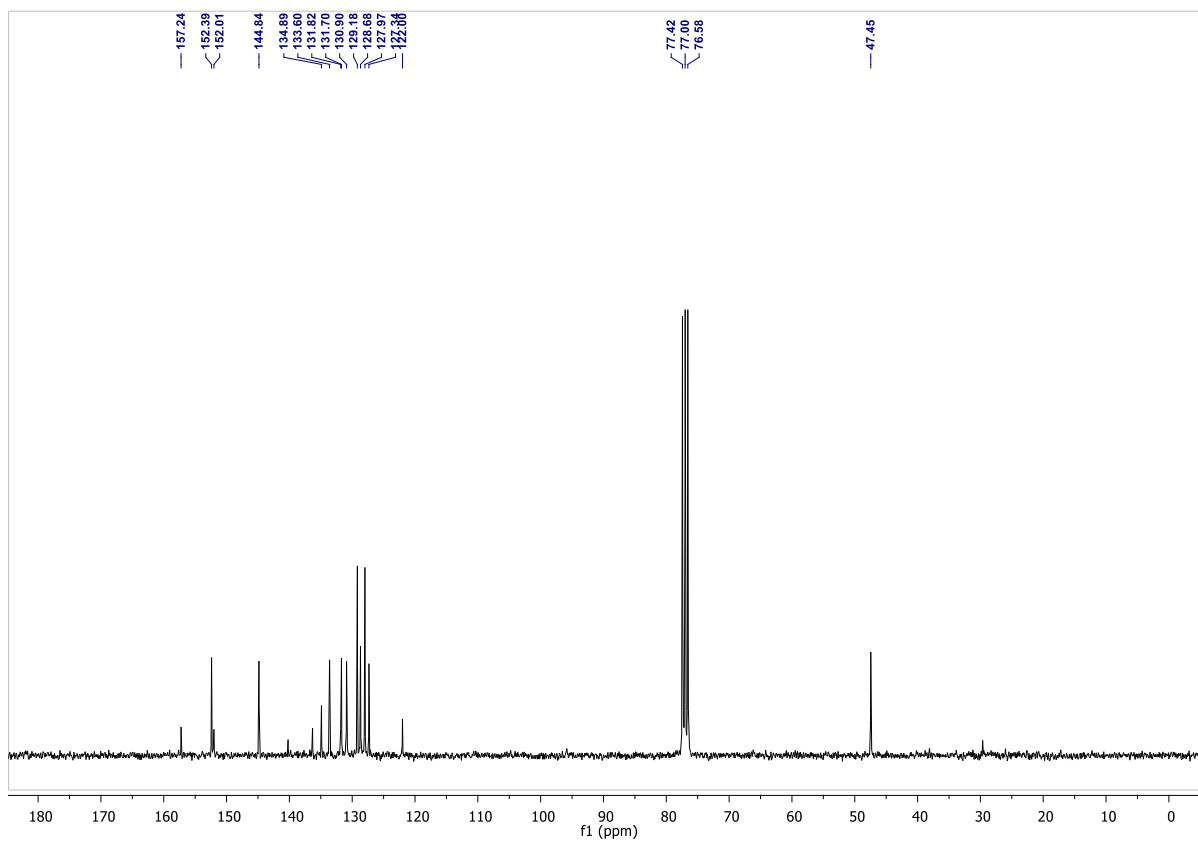
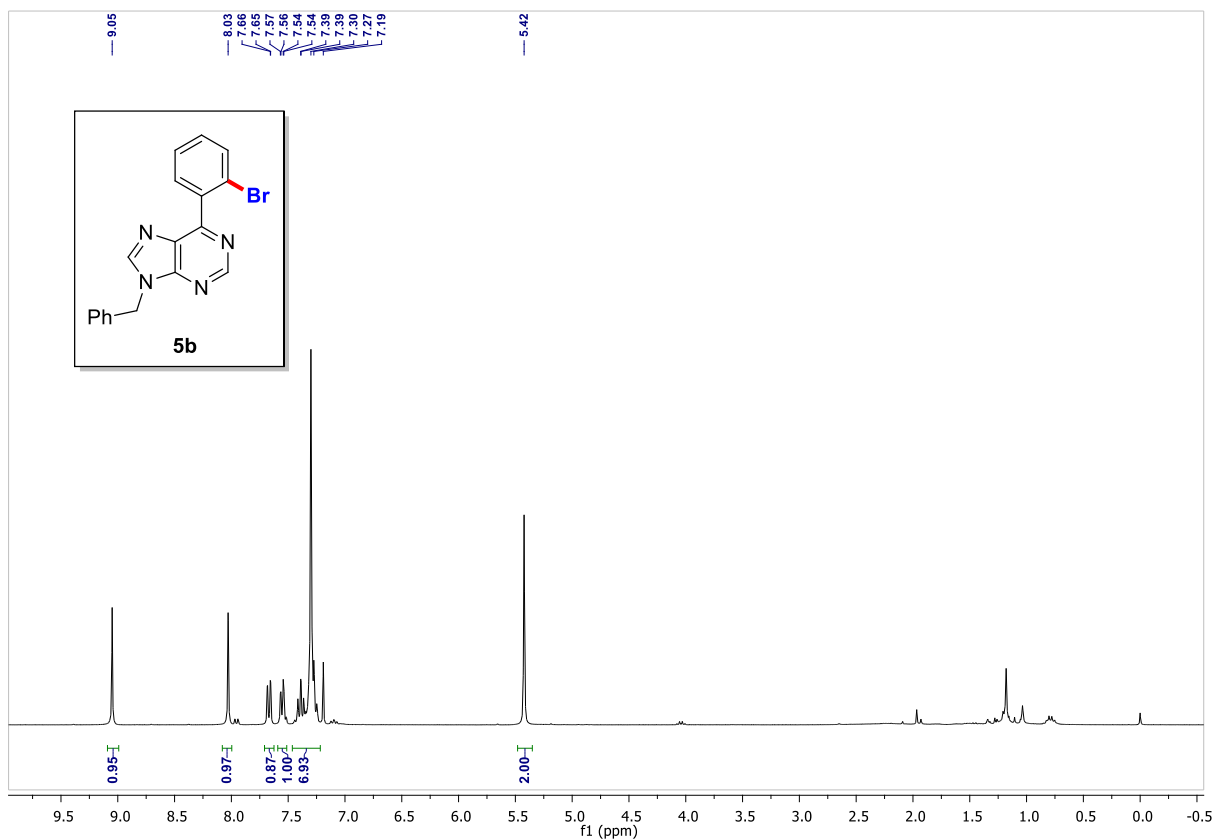




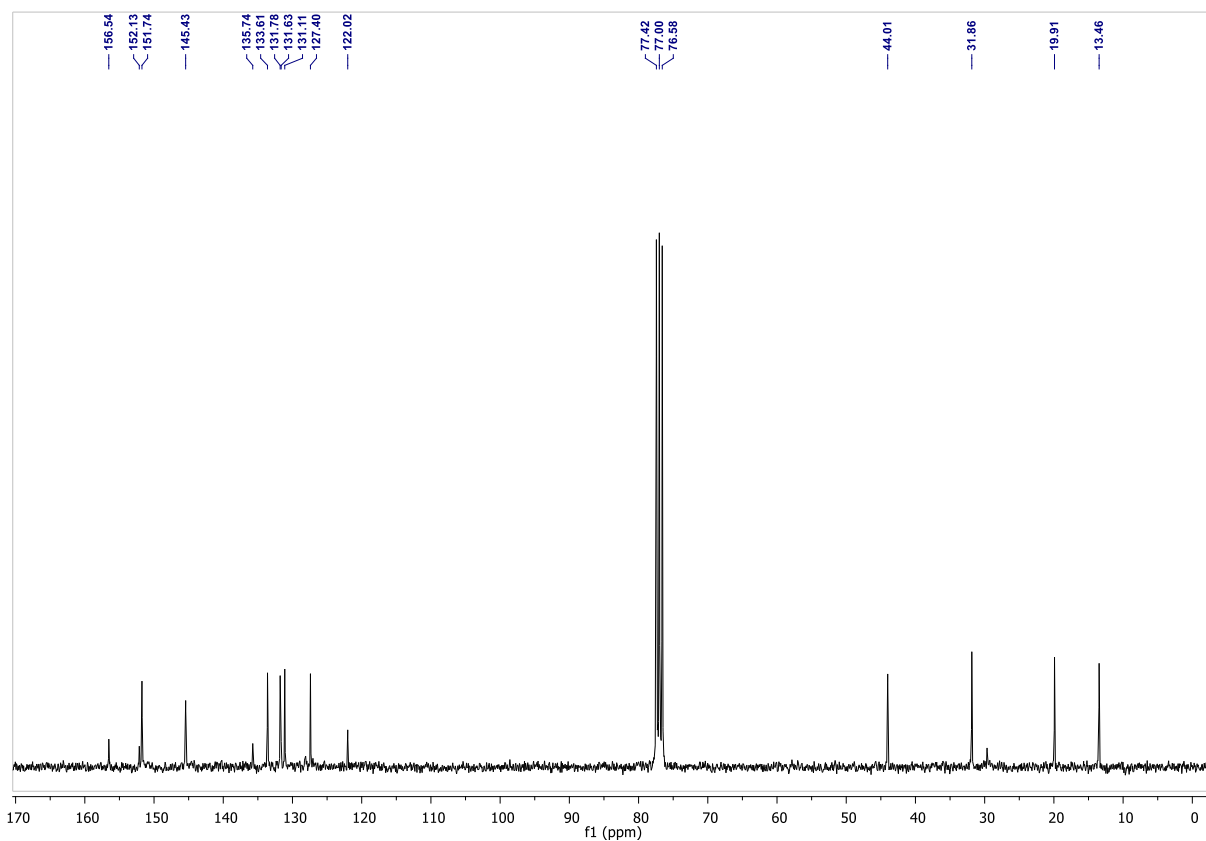
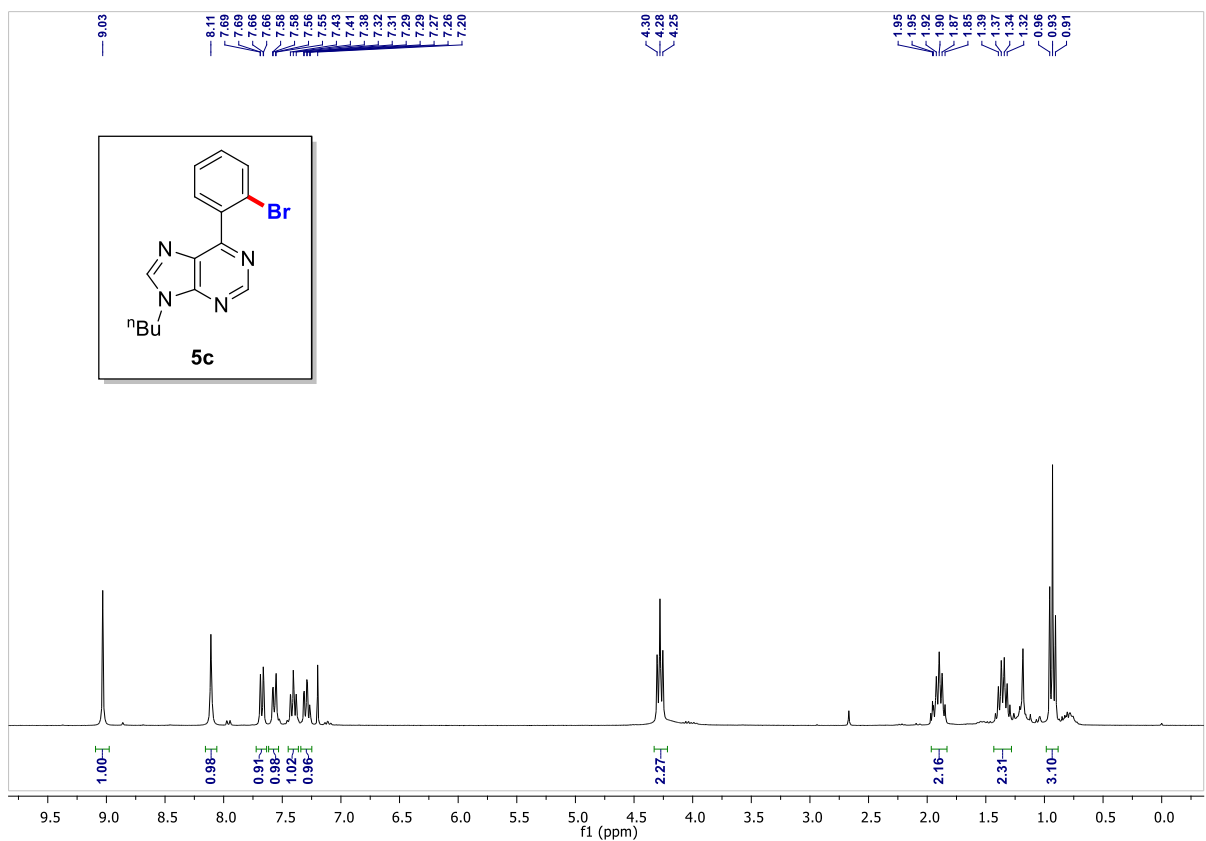
# 6-(2-Bromophenyl)-9-isopropyl-9H-purine (5a)



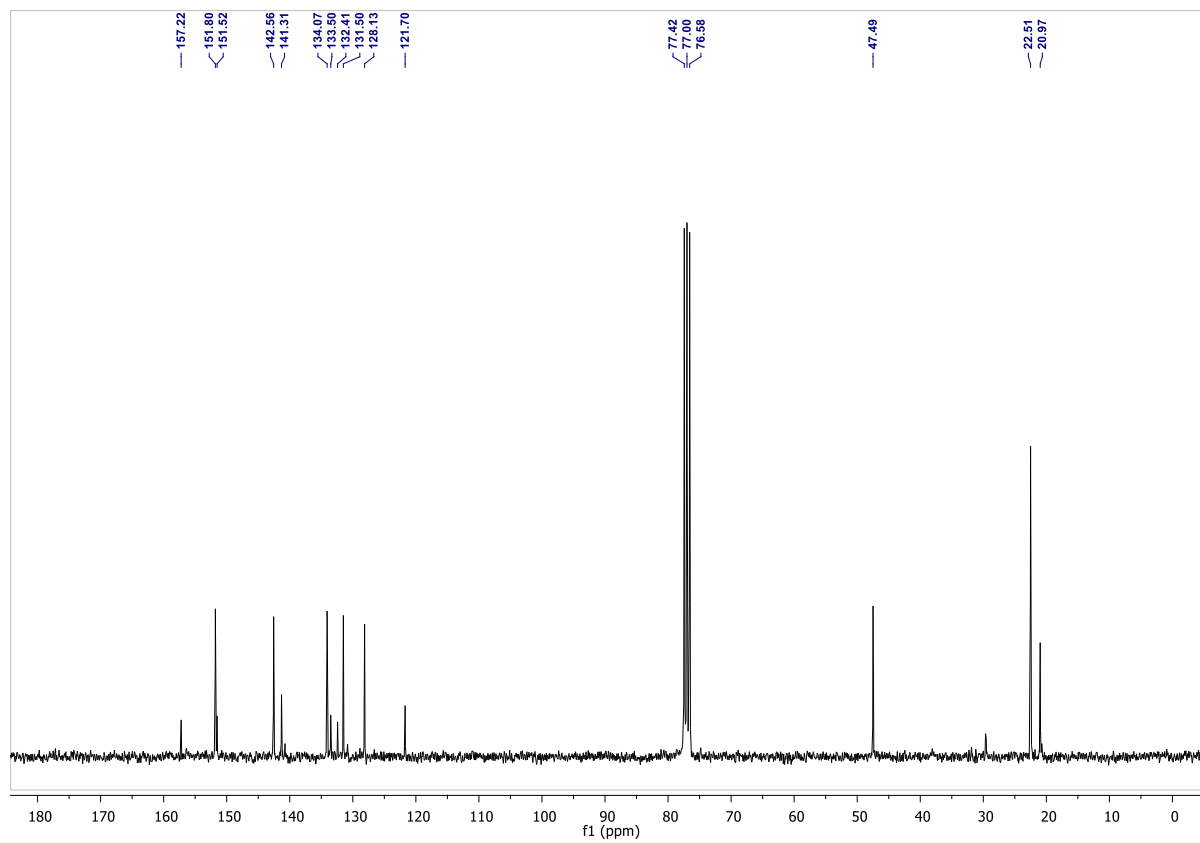
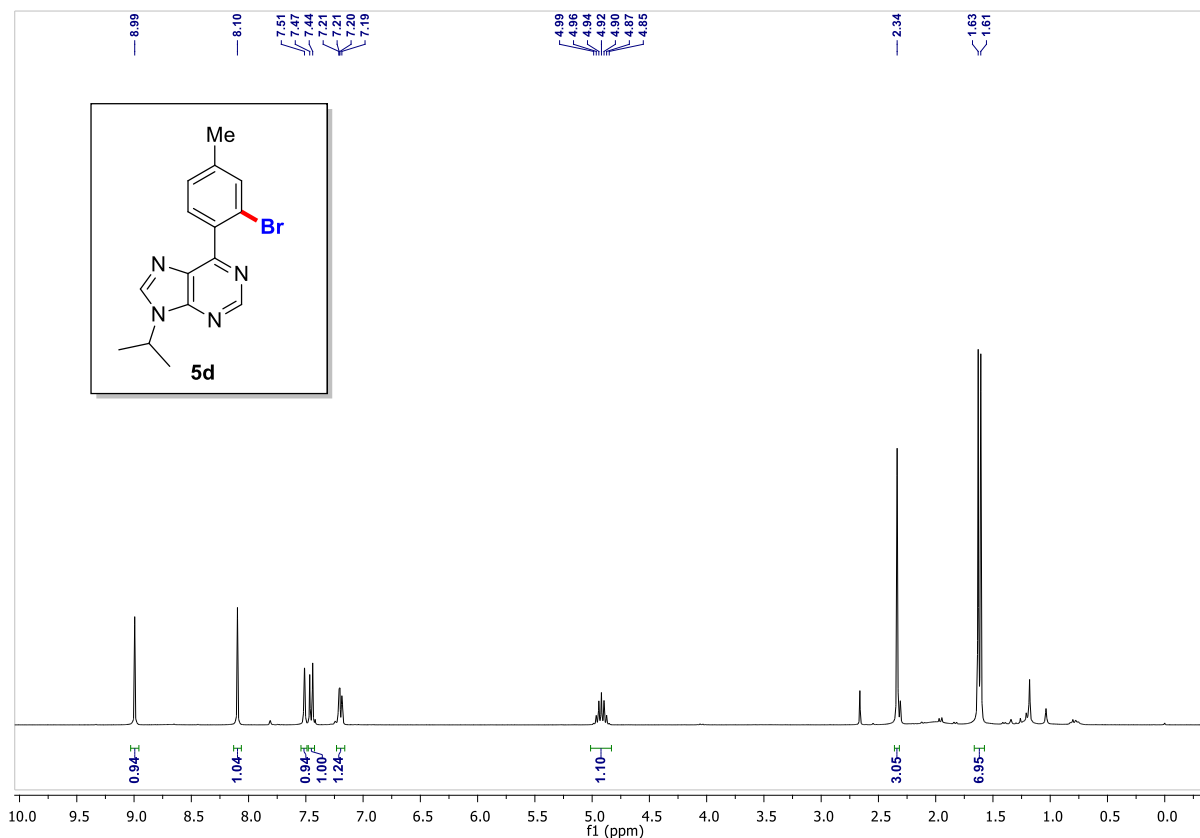
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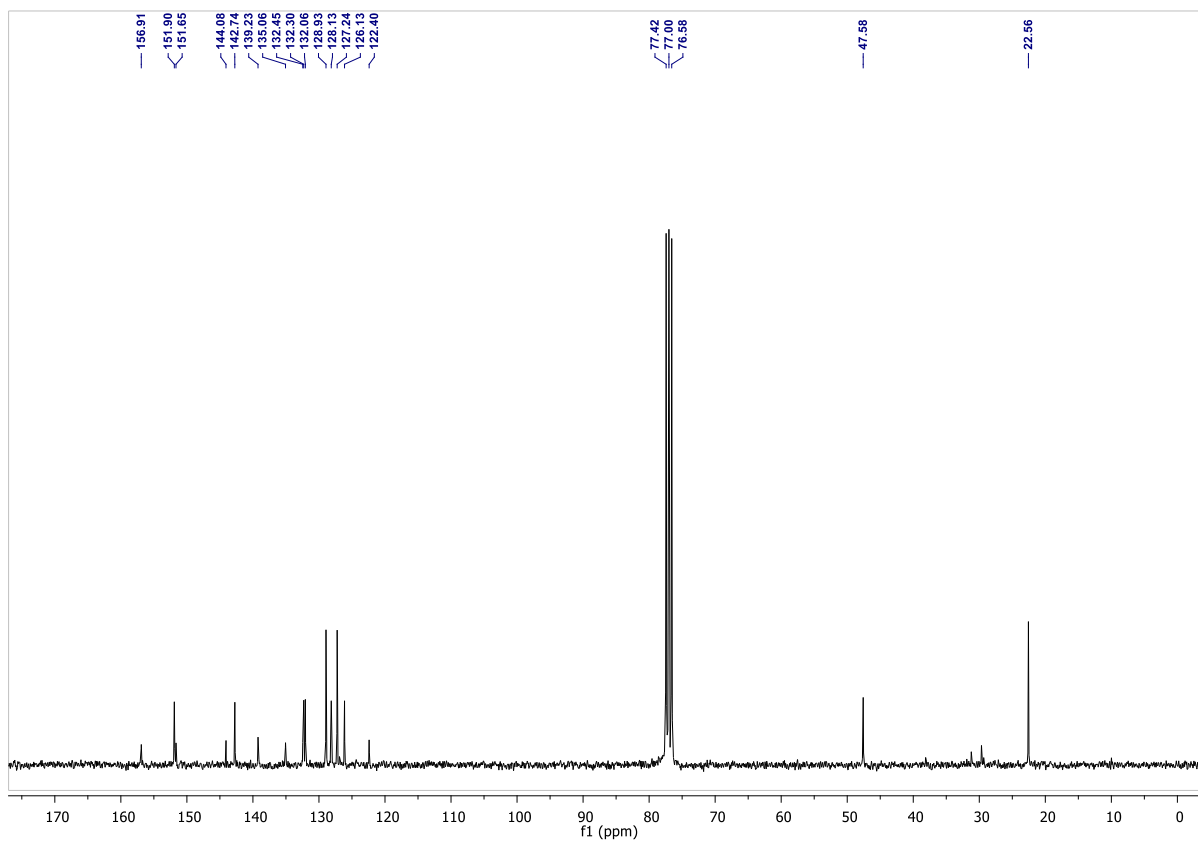
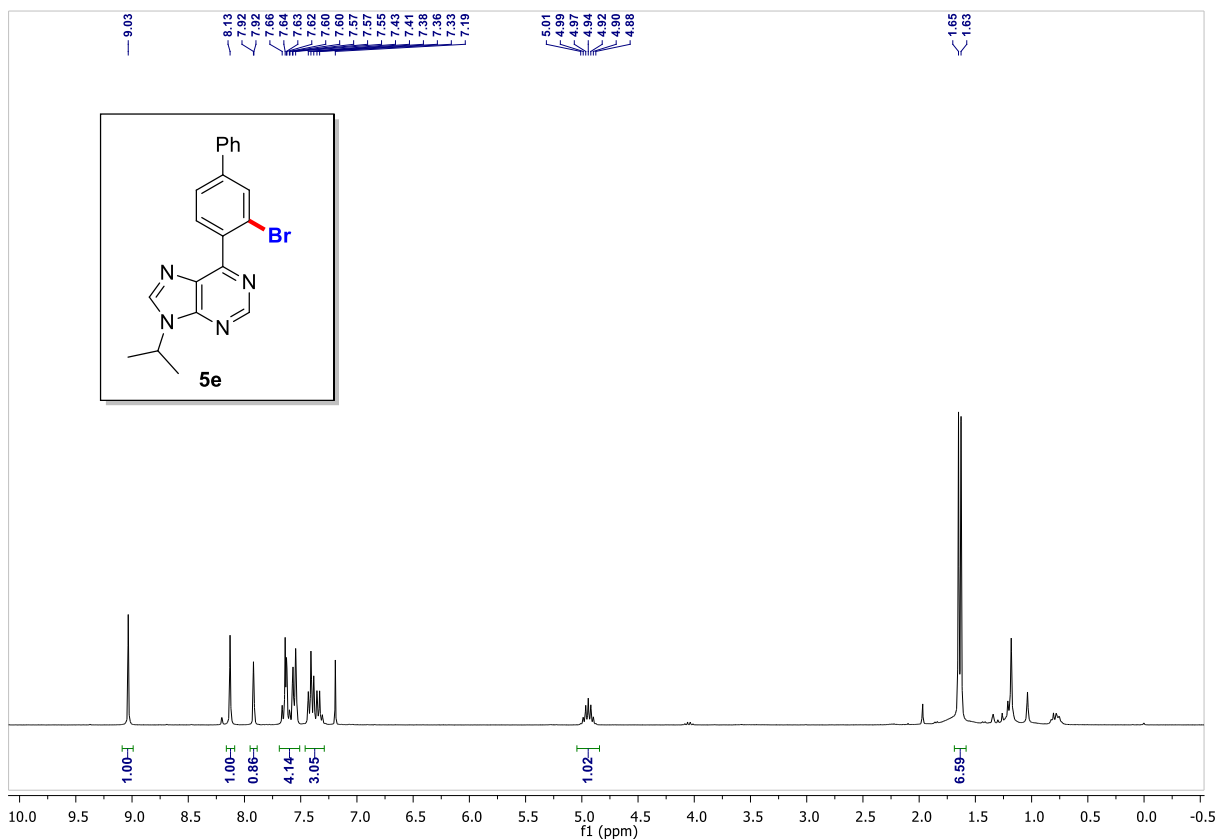
# 9-Butyl-6-(2-bromophenyl)-9H-purine (5c)



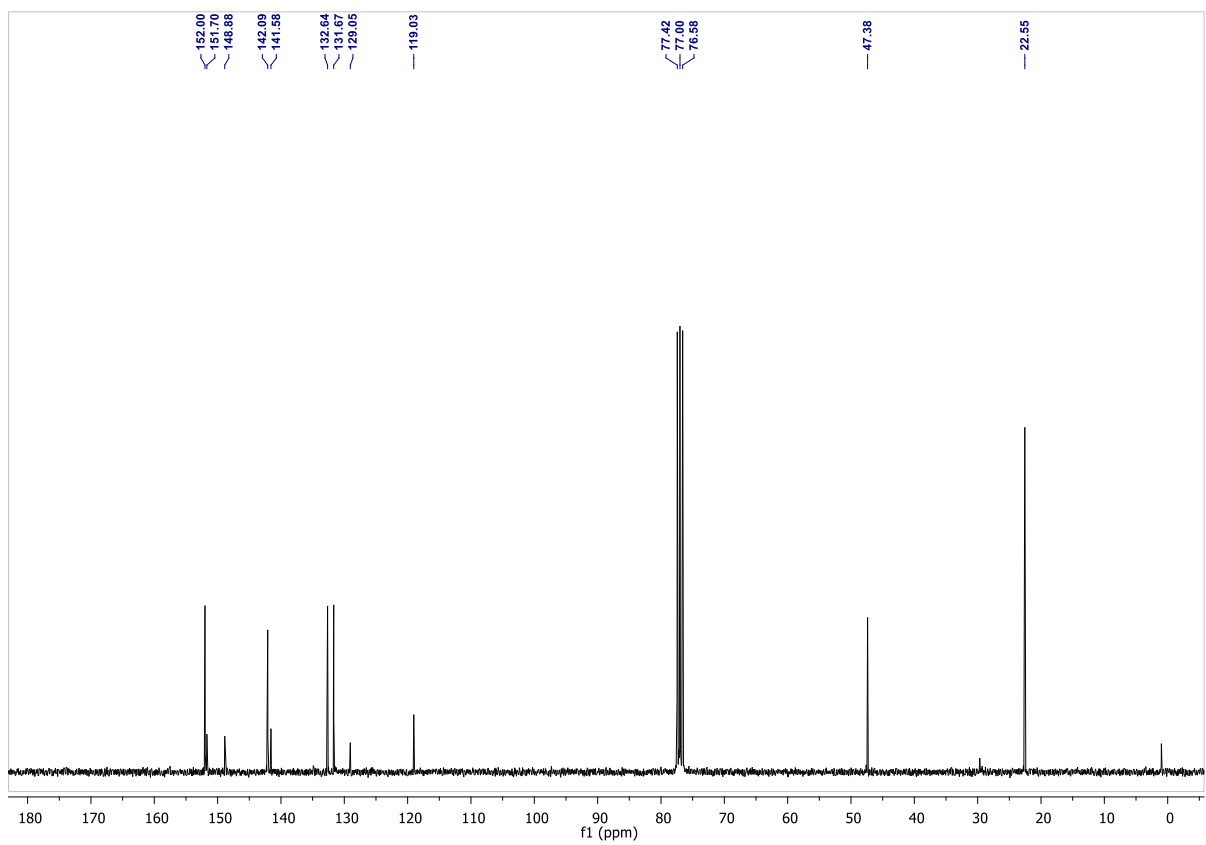
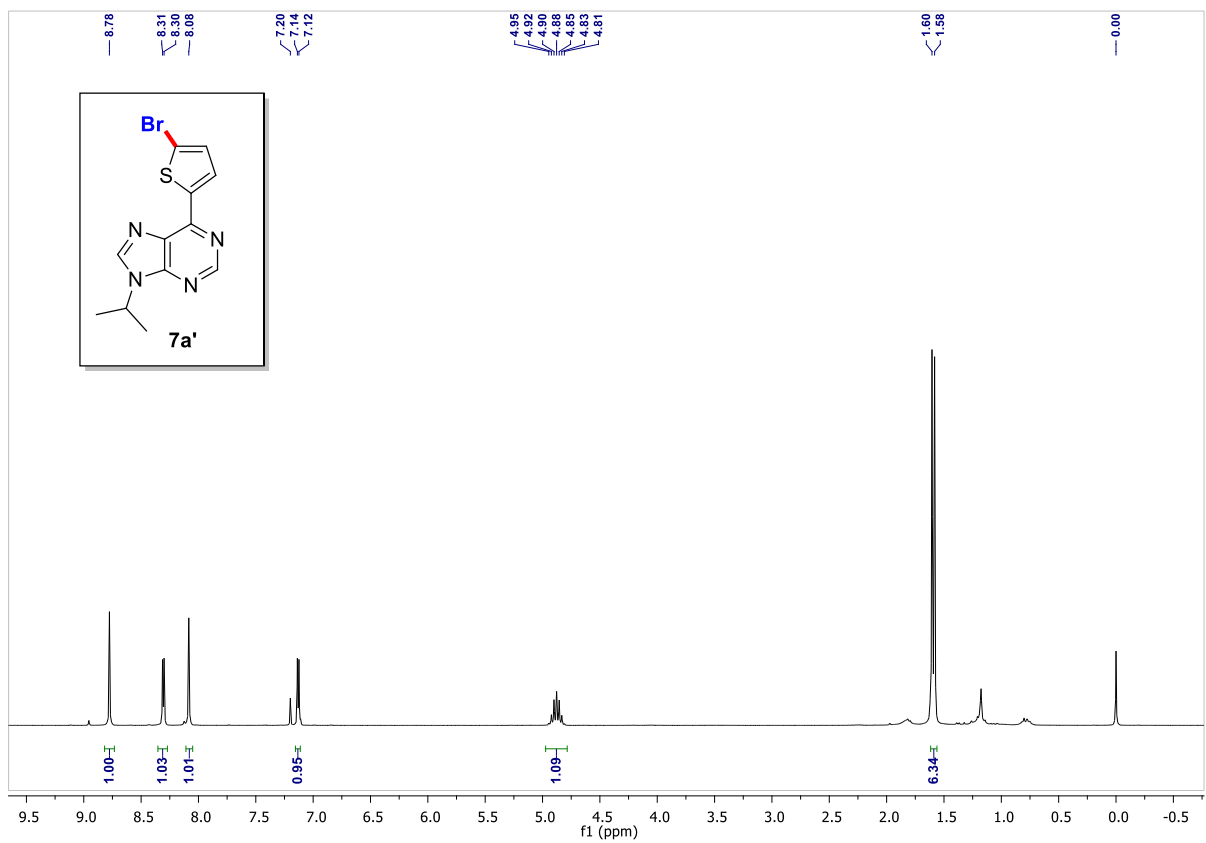
# 6-(2-Bromo-4-methylphenyl)-9-isopropyl-9H-purine (5d)



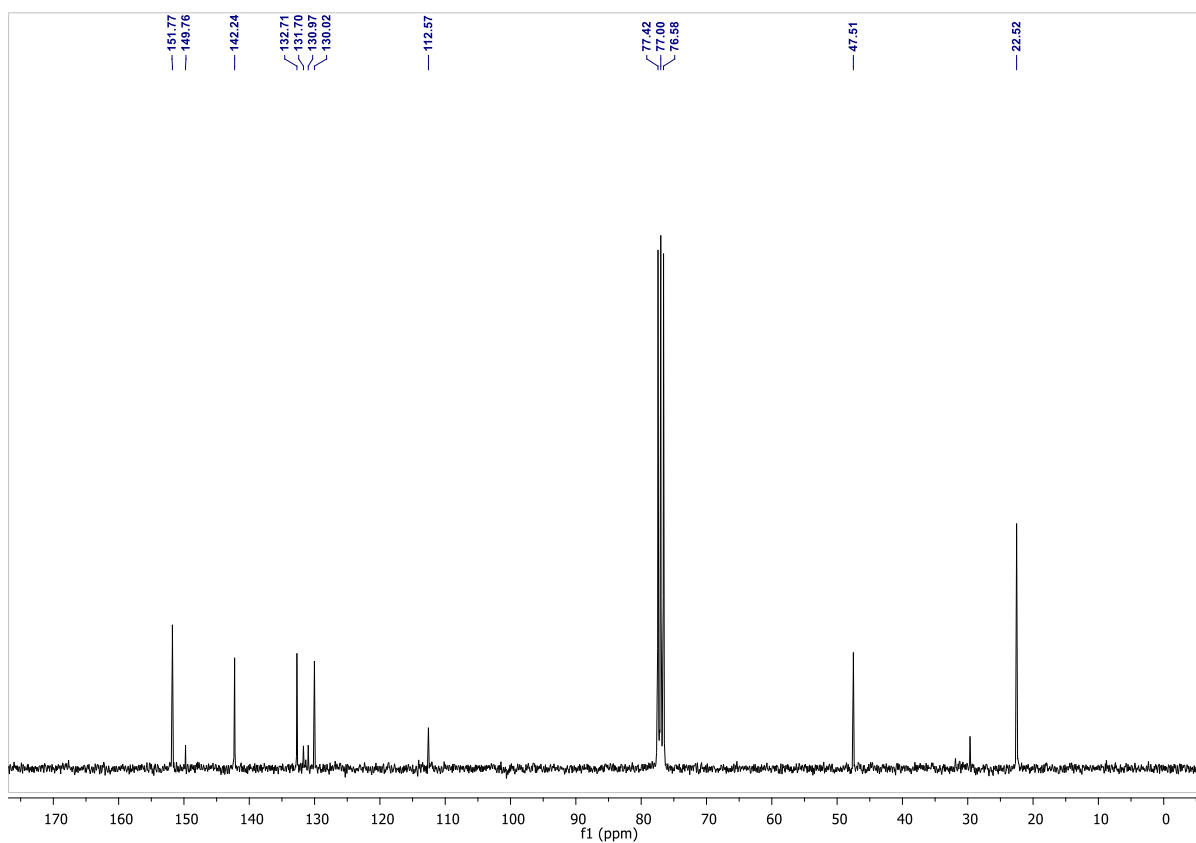
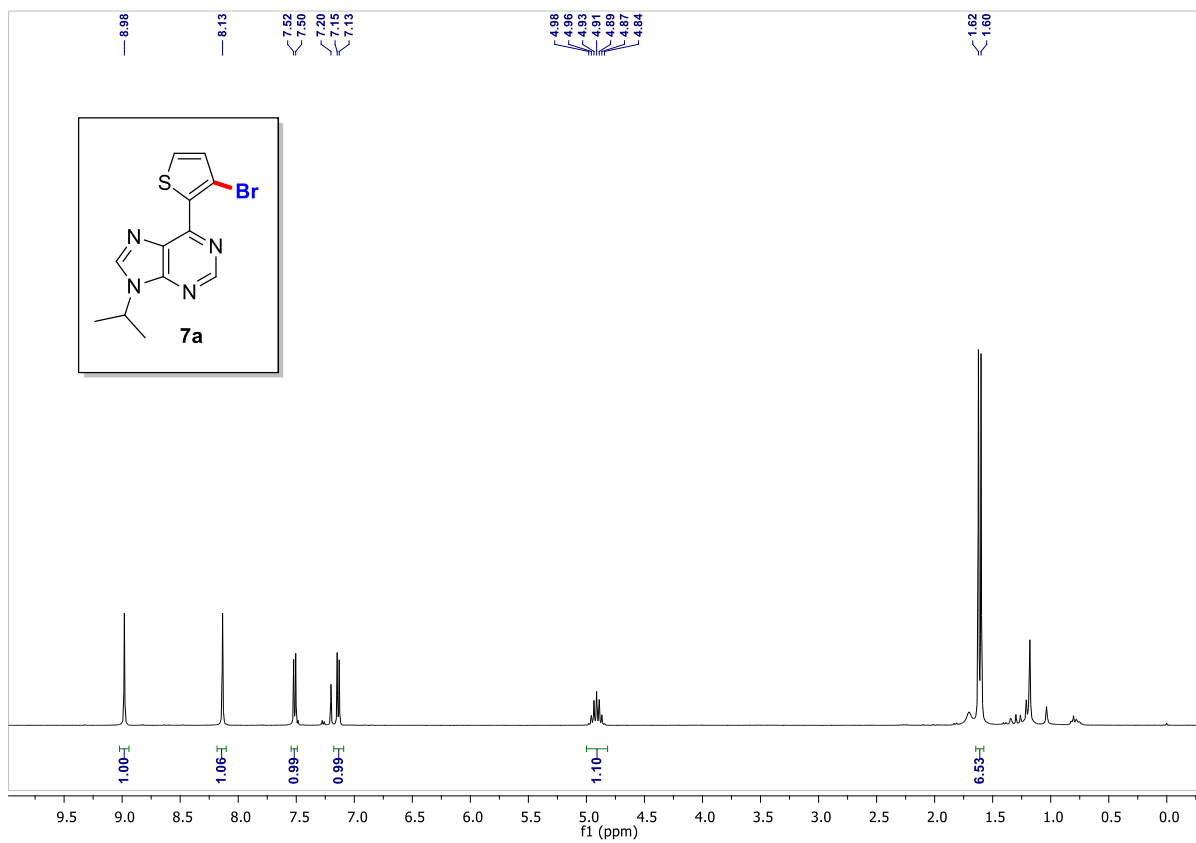
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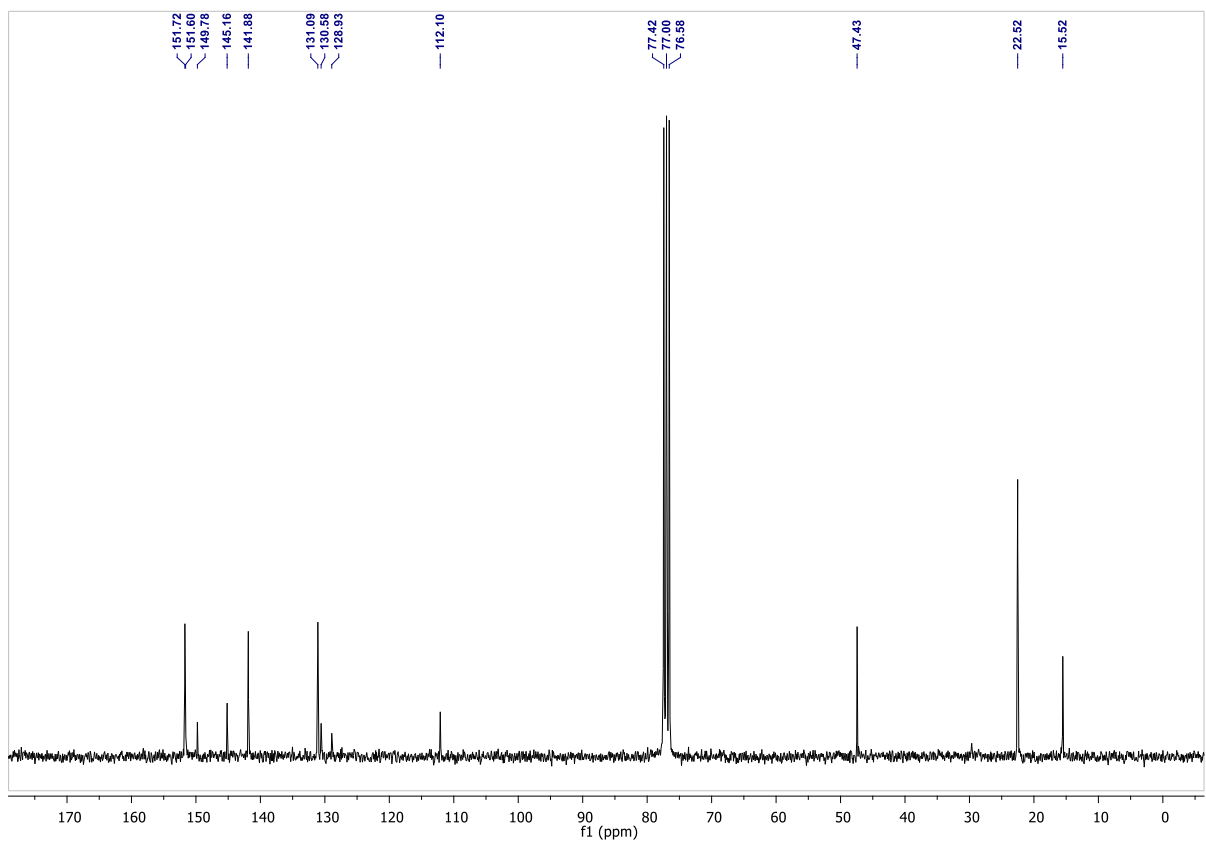
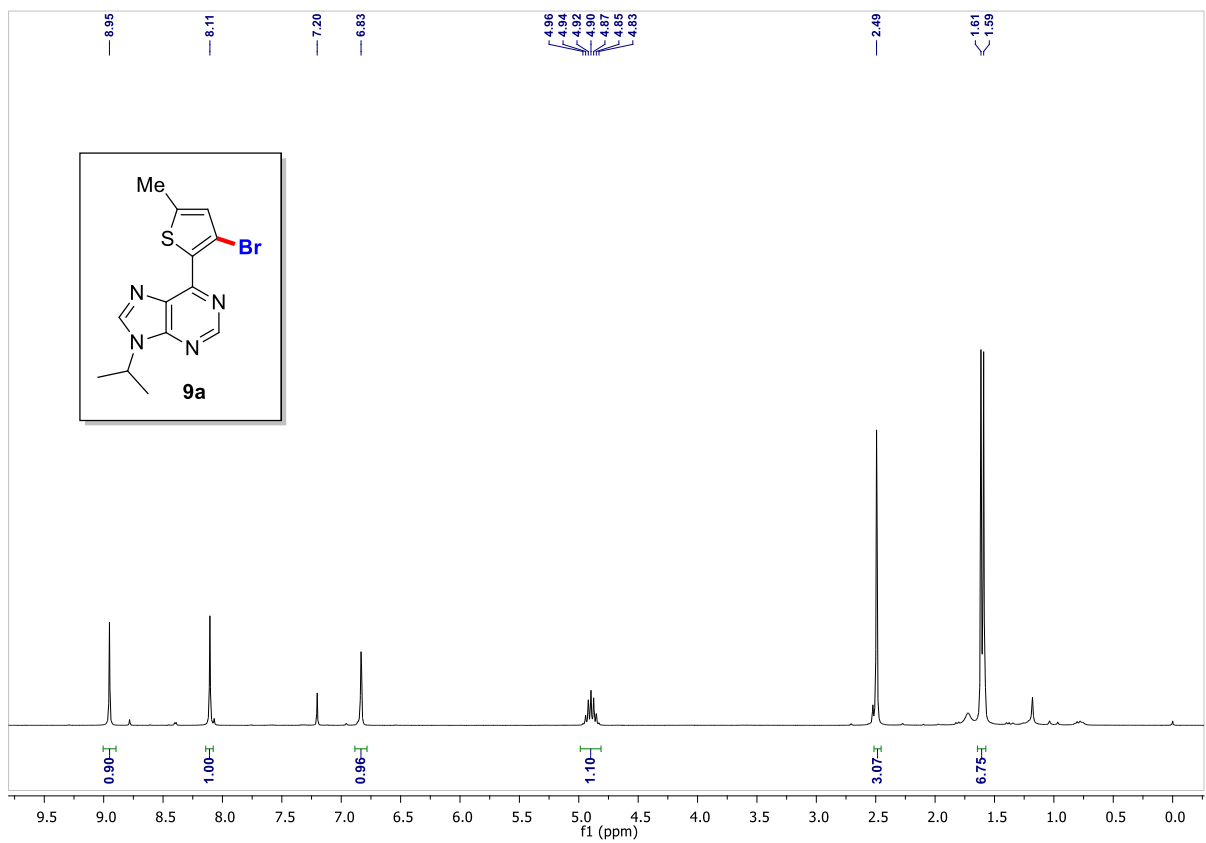
# 6-(5-Bromothiophen-2-yl)-9-isopropyl-9H-purine (7a')



### 6-(3-Bromothiophen-2-yl)-9-isopropyl-9H-purine (7a)

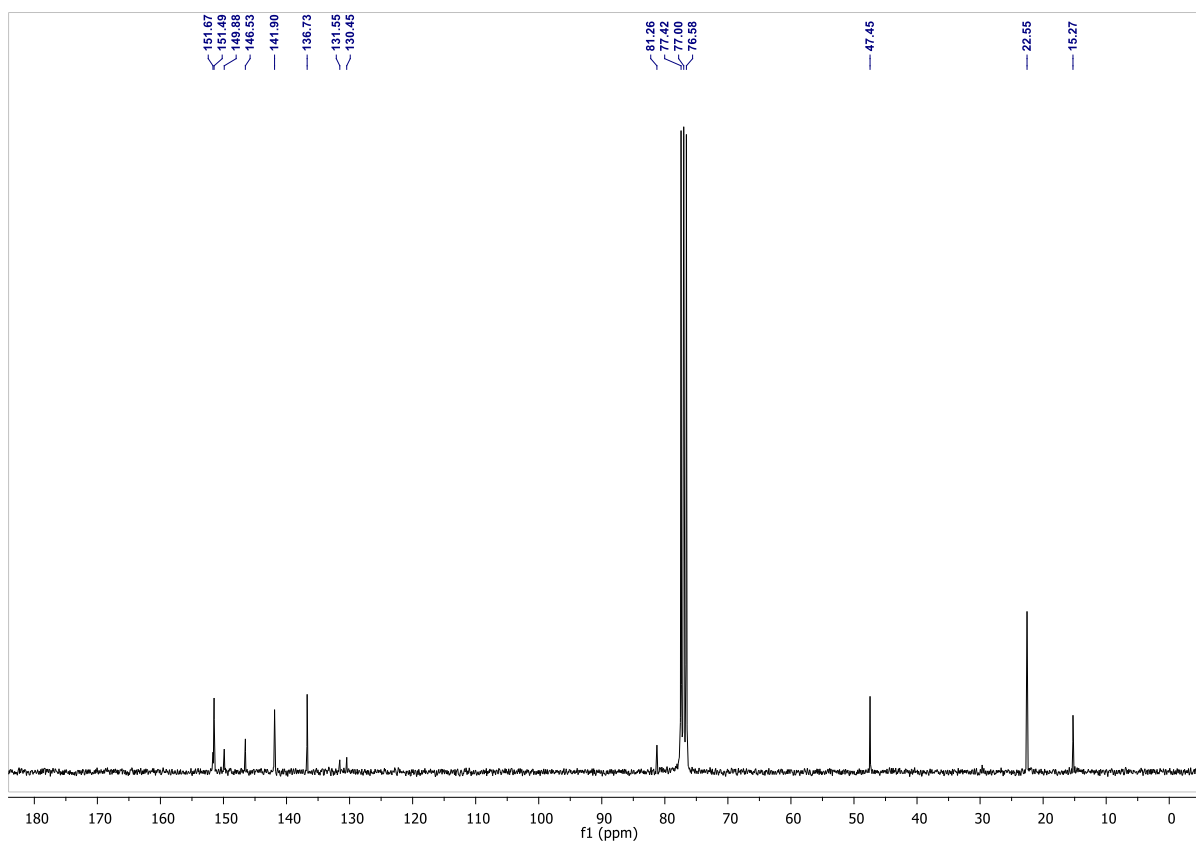
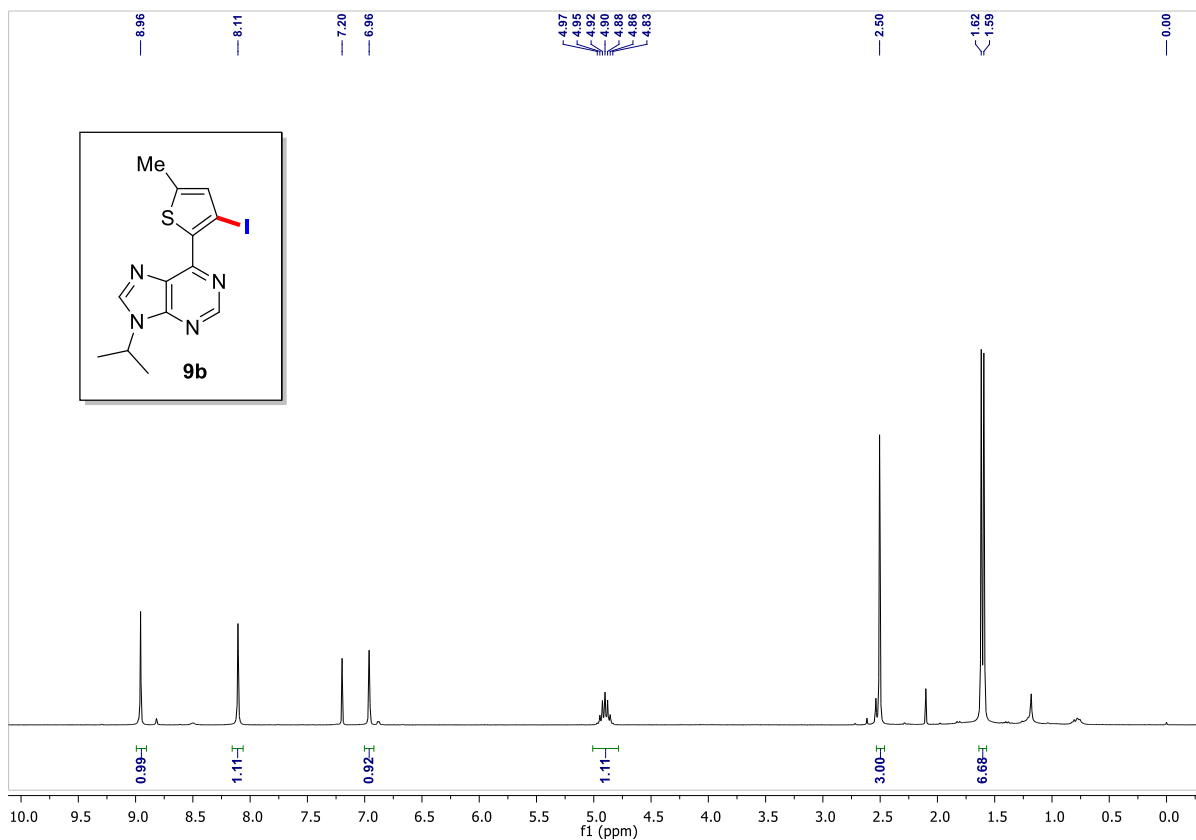


### 6-(3-Bromo-5-methylthiophen-2-yl)-9-isopropyl-9H-purine (9a)

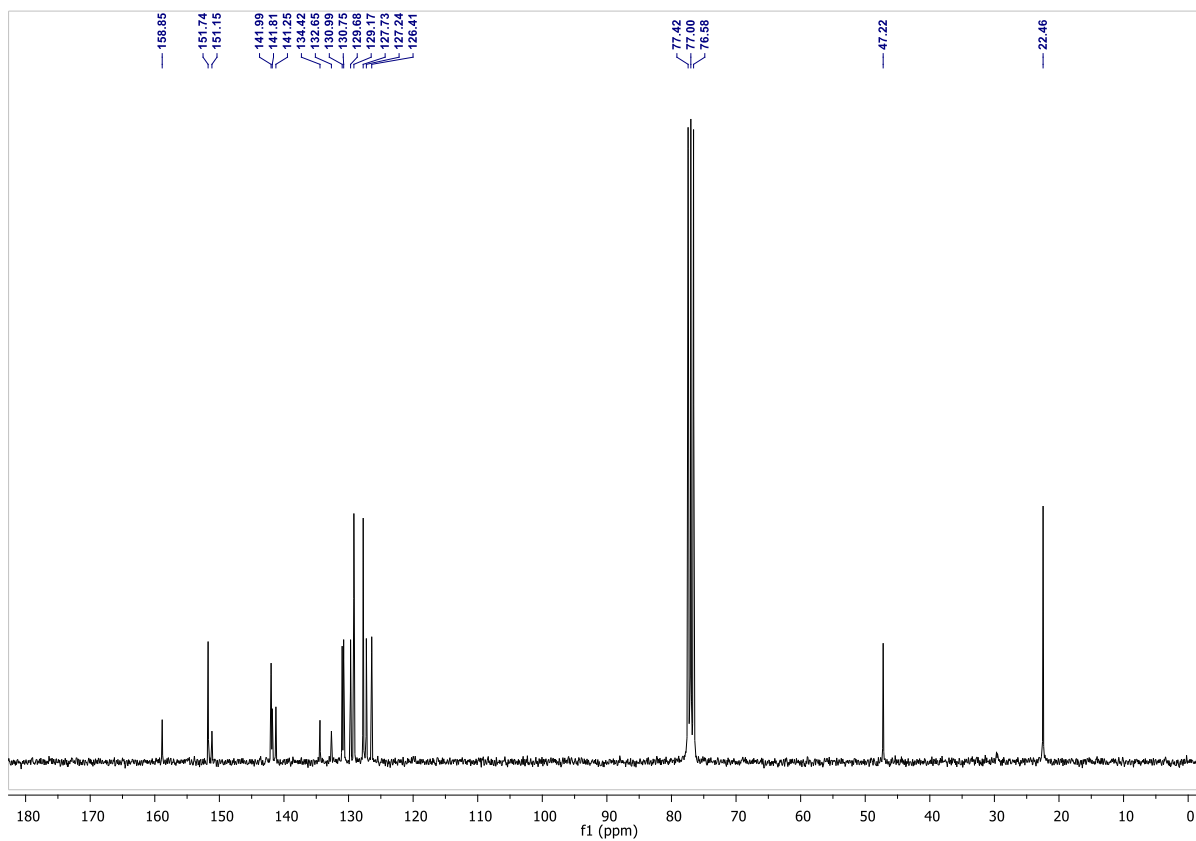
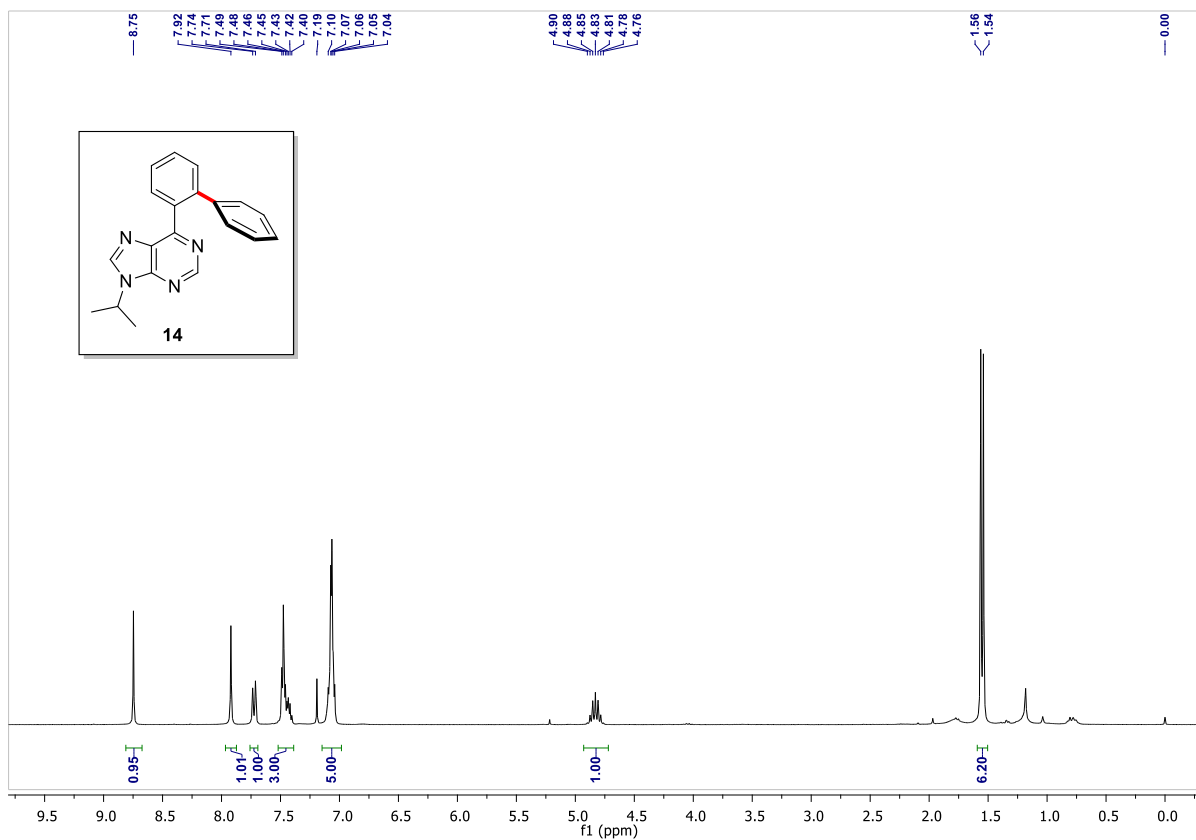




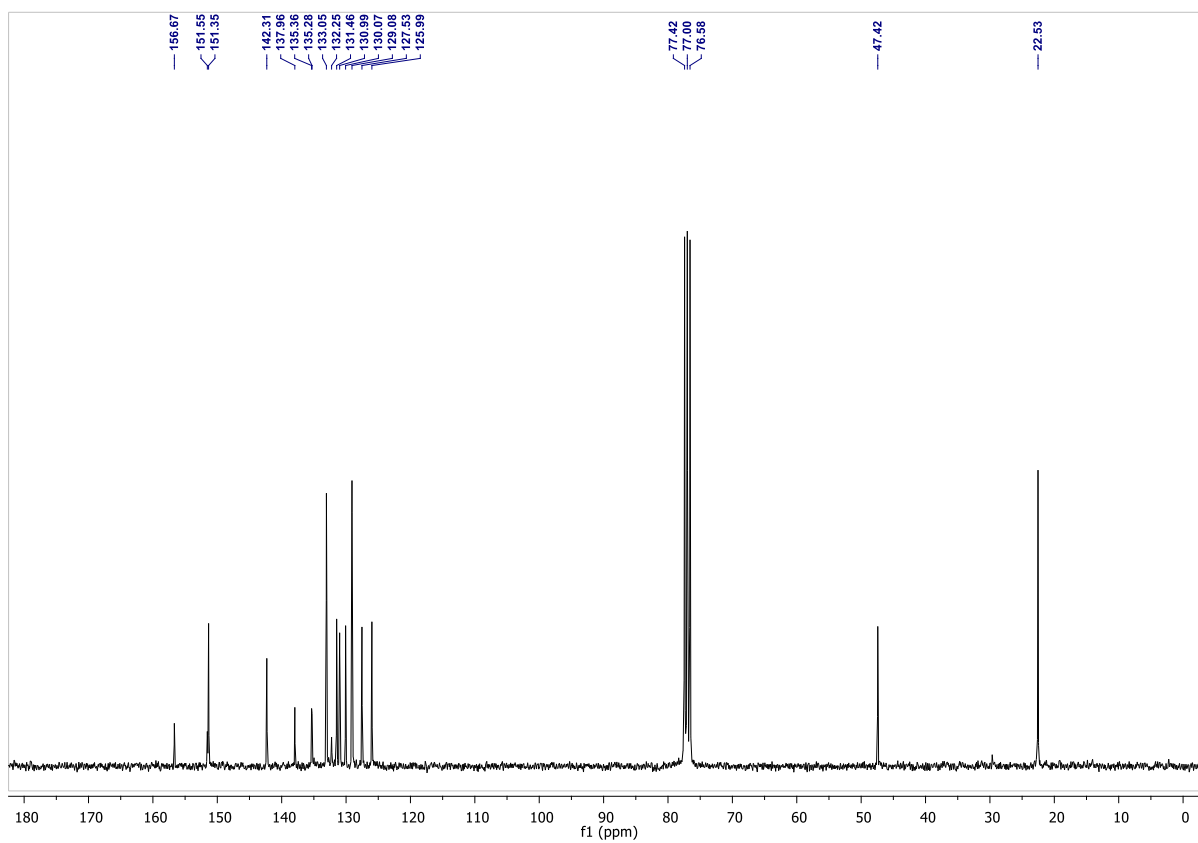
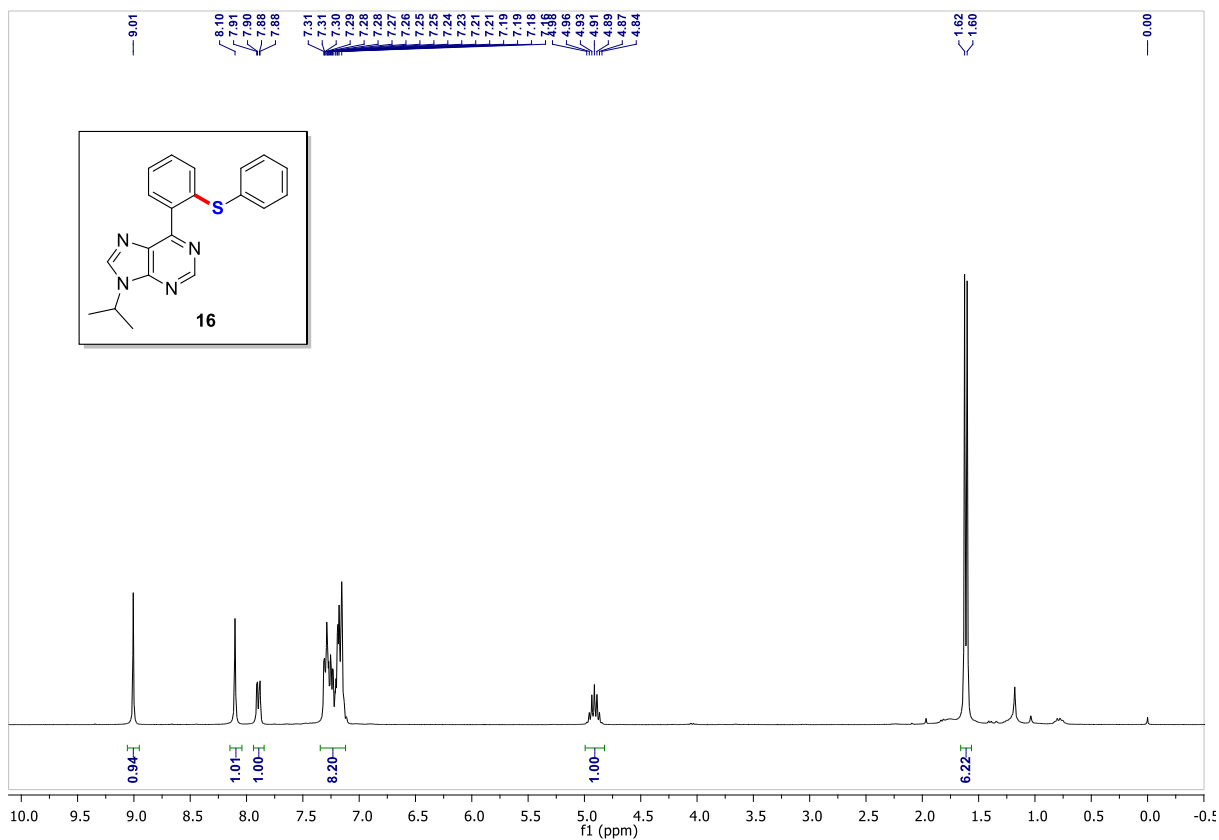
# 6-(3-Iodo-5-methylthiophen-2-yl)-9-isopropyl-9H-purine (9b)



# 6-([1,1'-Biphenyl]-2-yl)-9-isopropyl-9H-purine (14)



# 9-Isopropyl-6-(2-(phenylthio)phenyl)-9H-purine (16)



### 6-(2-Butoxyphenyl)-9-isopropyl-9H-purine (17)

