Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Cross Dehydrogenation Coupling Reaction of Purine Derivatives with Thioethers

Xinjie Li, Peng Qi, and Hongguang Du*

Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology (BUCT), Beijing 100029, China. E-mail: dhg@mail.buct.edu.cn.

Contents

1. Crystal structure of compound 3a

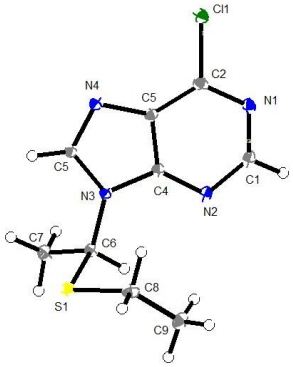


Fig. 1 Crystal structure of compound **3a**.
The thermal ellipsoids are drawn at the 30% probability level

3.1 Sample preparation

3a was dissolved in dichloromethane, and *n*-hexane was subsequently dripped into the system. Then the tube was sealed with parafilm and the system was placed at room temperature to afford the single crystal of **3a**.

3.2 Crystal structure determination of 3a

Crystal Data. $C_9H_{11}ClN_4S$, M =242.73, monoclinic, a = 5.0066(4) Å, b = 12.2115(7) Å, c = 18.0086(15) Å, β = 91.708(9)°, U = 1100.53(14) Å^3, T = 113.60(10), space group $P2_1/n$ (no. 14), Z = 4, μ(Mo Kα) = 0.508, 4424 reflections measured, 2161 unique (R_{int} = 0.0278) which were used in all calculations. The final *wR*(*F2*) was 0.0822 (all data).

Table 1: Crystal data and structure refinement for 3a

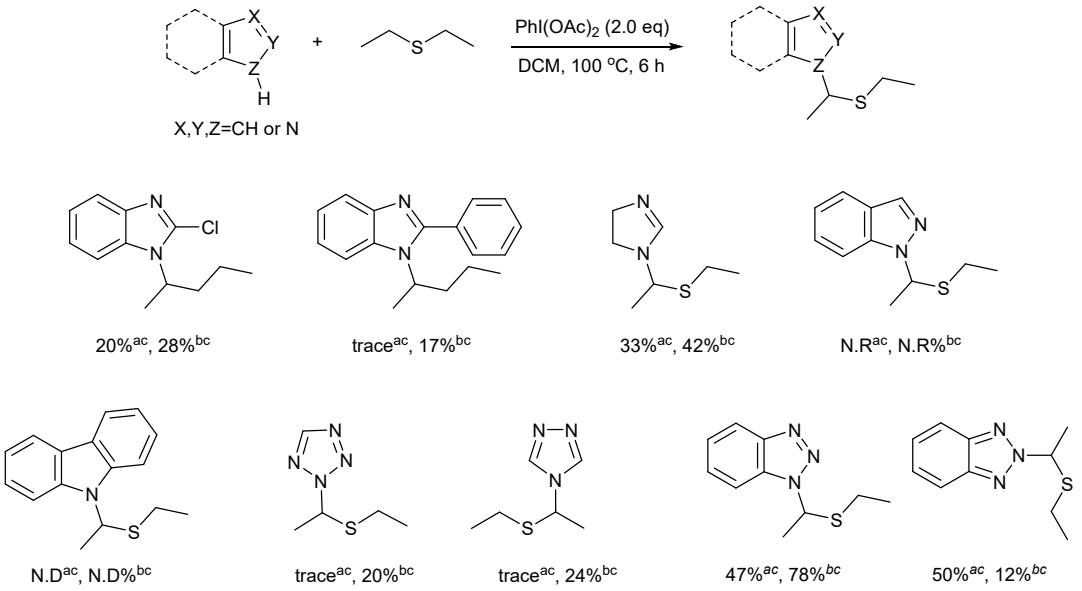
Identification code	3a
Empirical formula	$C_9H_{11}ClN_4S$
Formula weight	242.73
Temperature / K	113.60(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å, b / Å, c / Å	5.0066(4), 12.2115(7), 18.0086(15)
α/°, β/°, γ/°	90.00, 91.708(9), 90.00

Volume / $Å^3$	1100.53(14)
Z	4
ρ_{calc} / mg mm^{-3}	1.465
μ / mm^{-1}	0.508
F(000)	504
Crystal size / mm^3	0.26 × 0.25 × 0.23
2Θ range for data collection	6.68 to 52°
Index ranges	$-6 \le h \le 5$, $-14 \le k \le 15$, $-22 \le l \le 13$
Reflections collected	4424
Independent reflections	2161[R(int) = 0.0278 (inf-0.9Å)]
Data/restraints/parameters	2161/0/138
Goodness-of-fit on F^2	1.053
Final R indexes [$I>2\sigma(I)$ i.e. $F_o>4\sigma(F_o)$]	$R_1 = 0.0353$, $wR_2 = 0.0770$
Final R indexes [all data]	$R_1 = 0.0424$, $wR_2 = 0.0822$
Largest diff. peak/hole / e $Å^{-3}$	0.246/-0.263
Flack Parameters	N
Completeness	0.9975

2. Substrate Scope of the Azoarenes

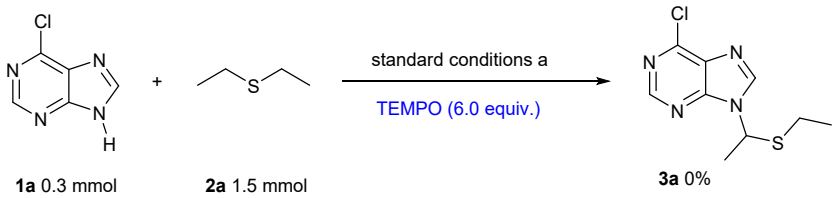
Reaction conditions a: To a 15 mL vial, azoarenes (0.3 mmol), $PhI(OAc)_2$ (0.6 mmol, 2.0 equiv.) were dissolved in DCM (5.0 mL), then **2a** (1.5 mmol, 5.0 equiv.) were added at room temperature. The mixture was stirred in an oil heating bath at 100 °C for 6 hours. The reaction mixture was cooled to room temperature and 10.0 mL water was added, then mixture was extracted with dichloromethane (3×15 mL), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum.

Reaction conditions b: To a 15 mL vial, azoarenes (0.30 mmol), $PhI(OAc)_2$ (0.6 mmol, 2.0 equiv.) were dissolved in DCM (5.0 mL), then sulfide **2** (1.5 mmol, 5.0 equiv.) and TFA (0.45 mmol, 1.5 equiv.) were added at room temperature. The rest of the operation is the same as reaction conditions a.

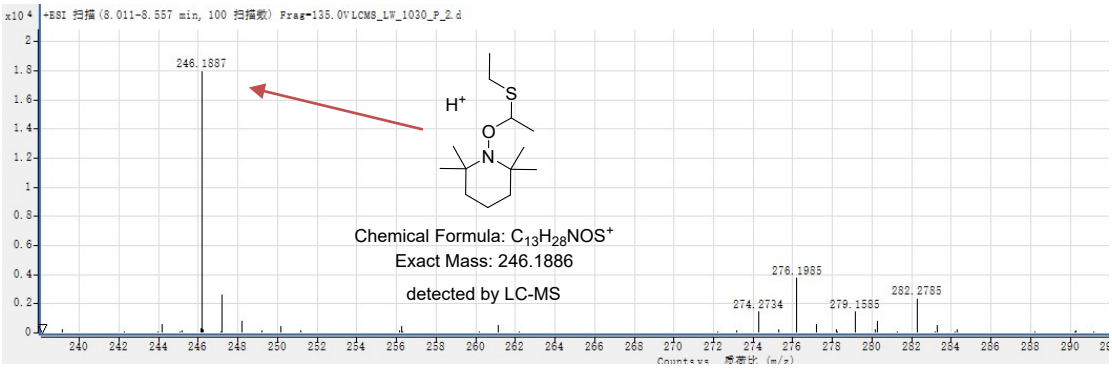


[a]Reaction condition: azoarenes (0.3 mmol), **2a** (1.5 mmol), $PhI(OAc)_2$ (2.0 equiv.), in DCM (5.0 mL) at 100 °C for 6 h. [b]Reaction condition: azoarenes (0.3 mmol), **2a** (1.5 mmol), $PhI(OAc)_2$ (2.0 equiv.), TFA (1.5 equiv.) in DCM (5.0 mL) at 100 °C for 6 h. [c]The yield determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard.

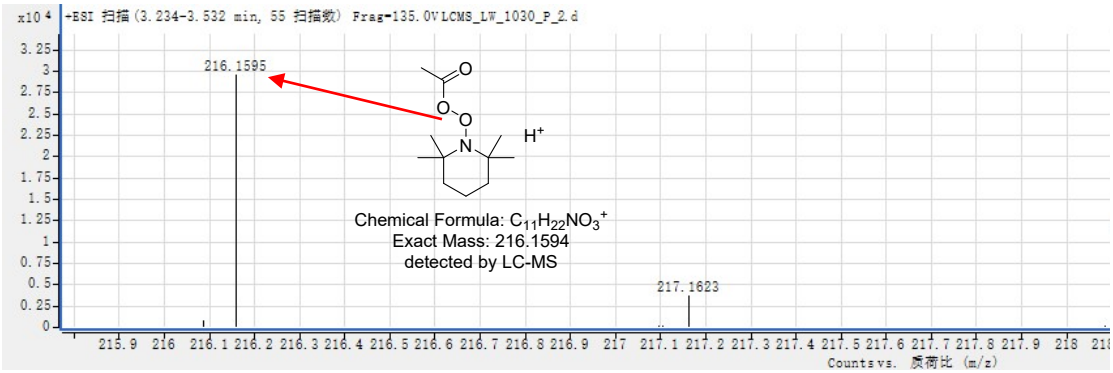
3. Radical Trapping Experiment with TEMPO



To a 15 mL vial, **3a** (0.3 mmol), $PhI(OAc)_2$ (0.6 mmol, 2.0 equiv.) and TEMPO(1.8 mmol, 6.0 equiv.) were dissolved in DCM (5.0 mL), then **2a** (1.5 mmol, 5.0 equiv.) were added at room temperature. The mixture was stirred in an oil heating bath at 100 °C for 6 hours. The reaction mixture was cooled to room temperature and 10.0 mL water was added, then mixture was extracted with dichloromethane (3×15 mL), the combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum.



HRMS (ESI) *m/z* Calcd for $C_{13}H_{28}NOS$ $[M+H]^+$, 246.1886; found : 246.1887.



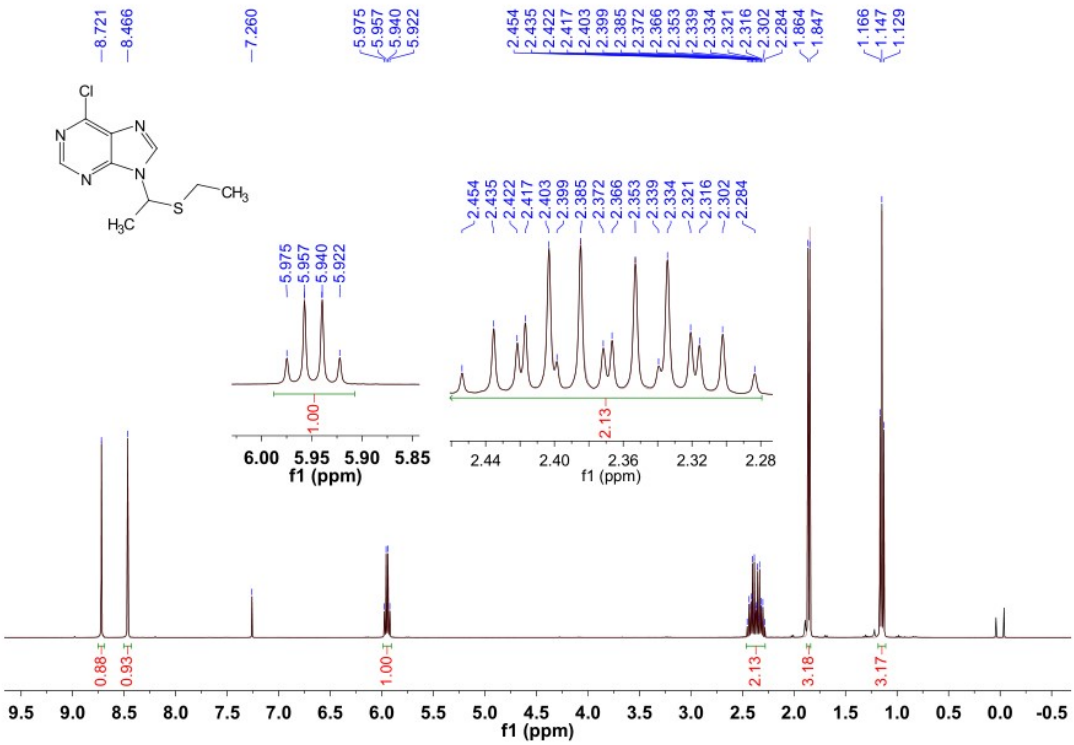
HRMS (ESI) *m/z* Calcd for $C_{11}H_{22}NO_3$ $[M+H]^+$, 216.1594; found : 216.1595

4. References

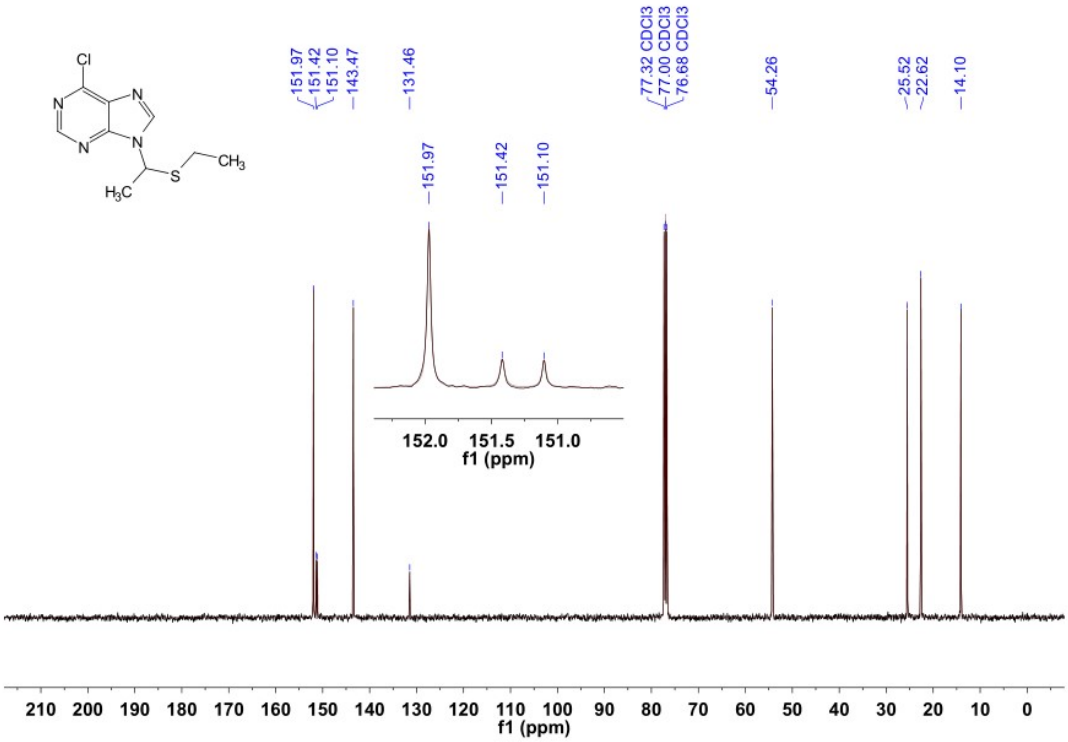
1. M. K. Mohammad Soleiman-Beigi , Reza Aryan b and Lotfi Shiri , *Letters in Organic Chemistry*, 2014, **11**.321-326

5. ^{1}H NMR and ^{13}C NMR Spectra of the Products

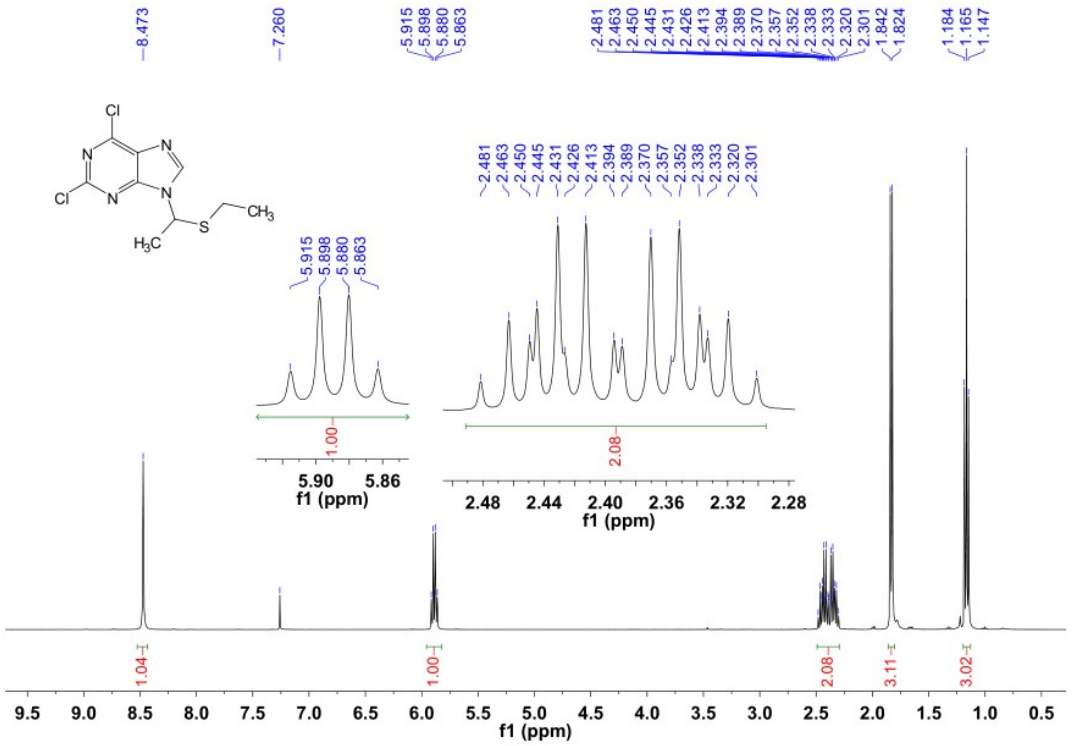
^{1}H NMR Spectrum for **3a** (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR Spectrum for **3a** (100 MHz, $CDCl_3$)

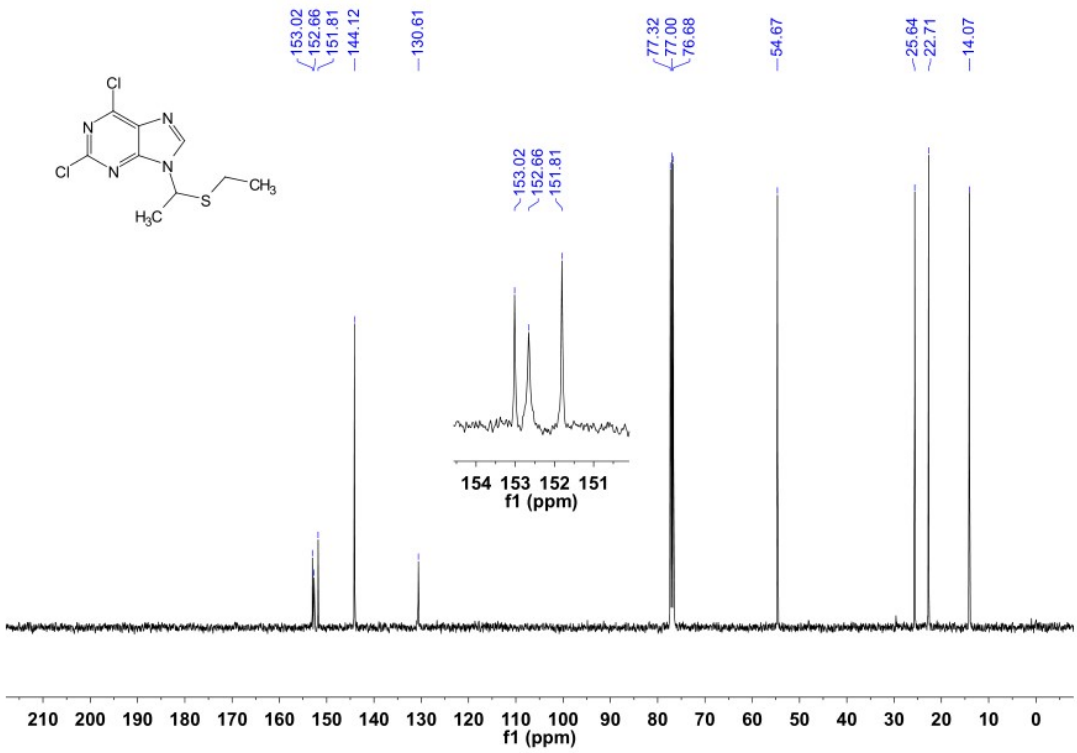


^{1}H NMR Spectrum for **3b** (400 MHz, $CDCl_3$)

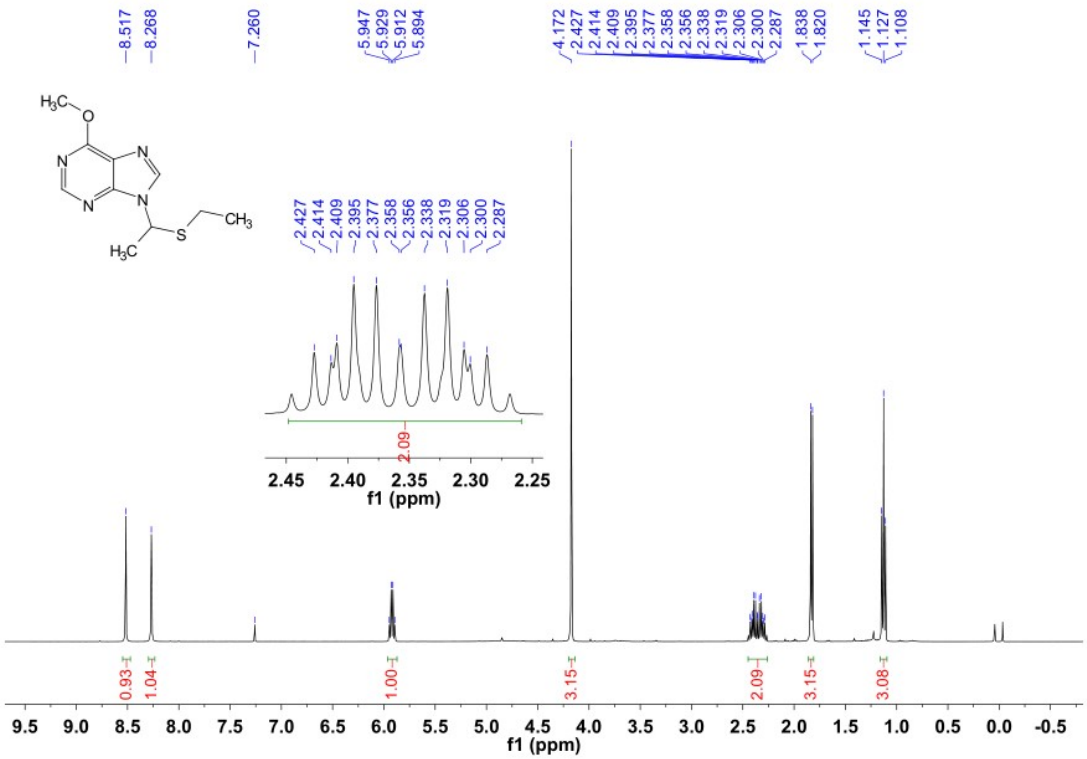


13

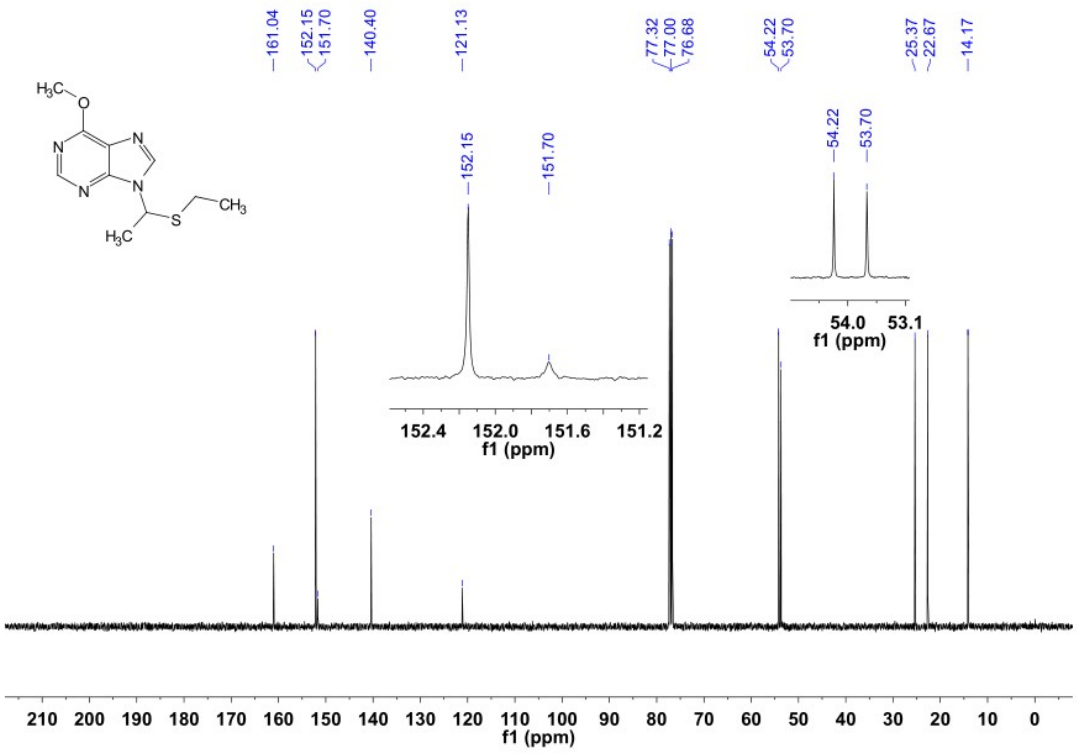
C {^{1}H} NMR Spectrum for **3b** (100 MHz, $CDCl_3$)



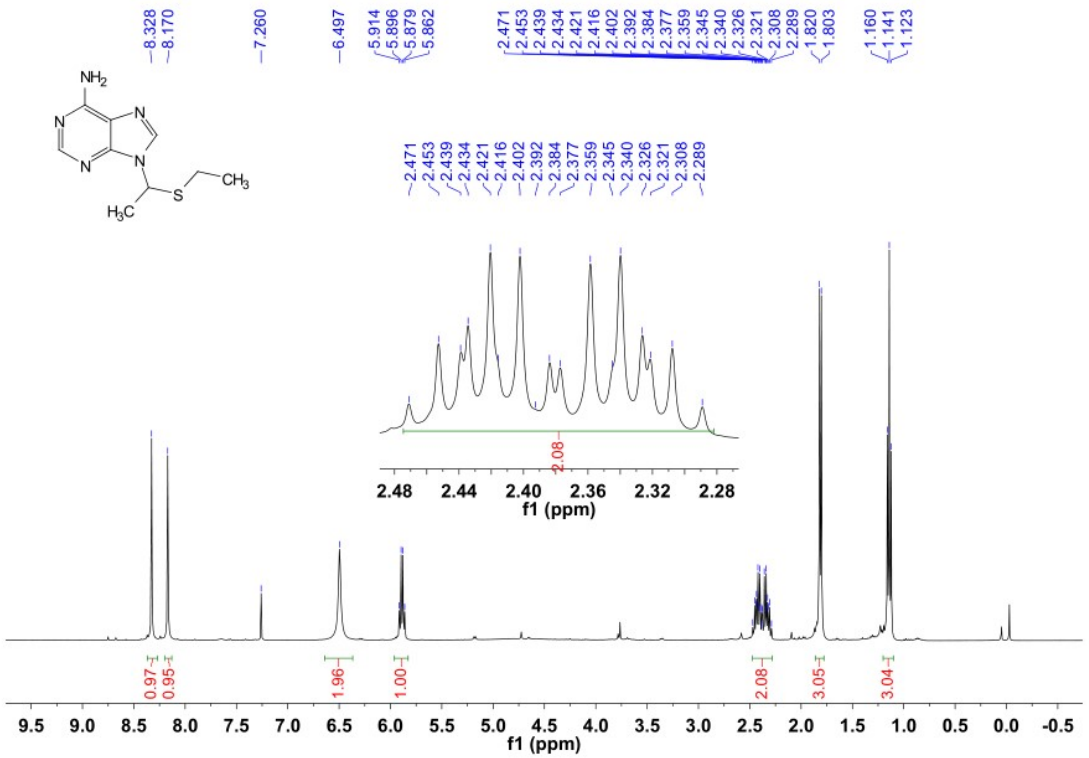
^{1}H NMR Spectrum for **3c** (400 MHz, $CDCl_3$)



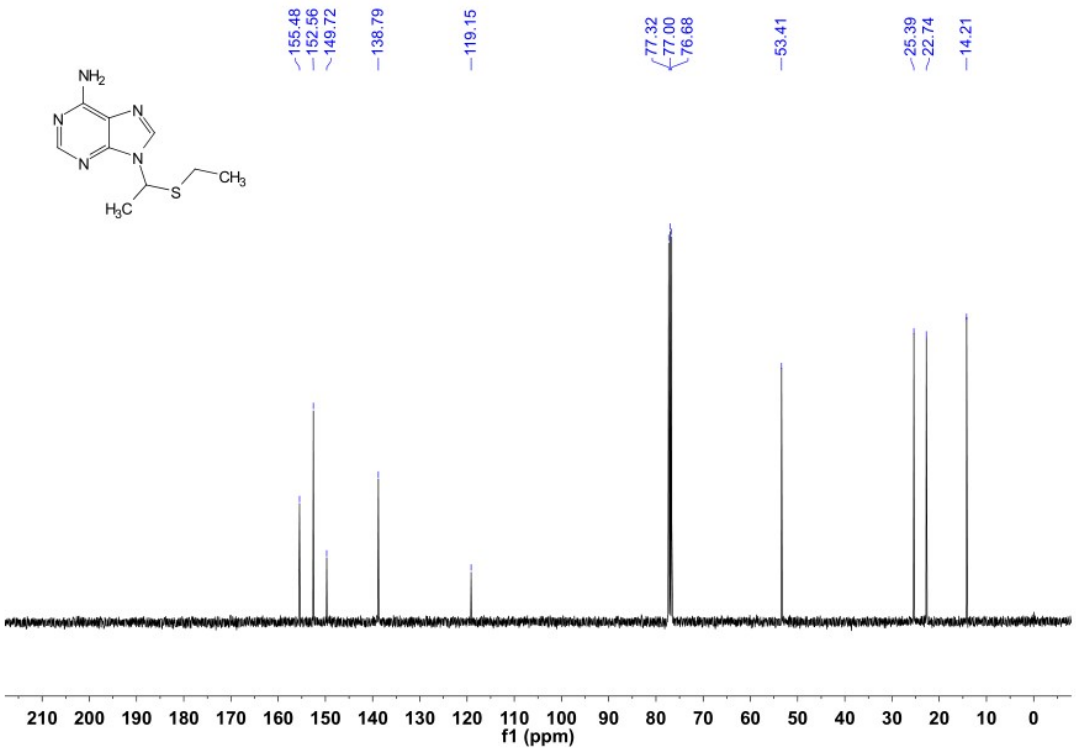
^{13}C {^{1}H} NMR Spectrum for **3c** (100 MHz, $CDCl_3$)



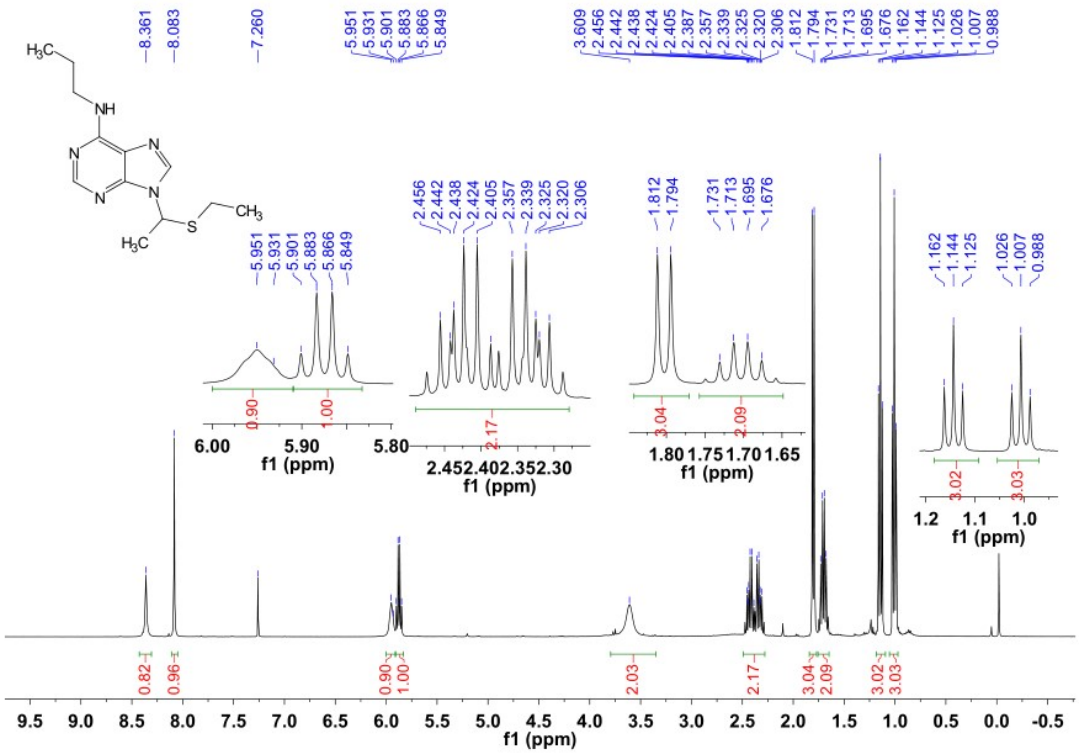
^{1}H NMR Spectrum for **3d** (400 MHz, $CDCl_3$)



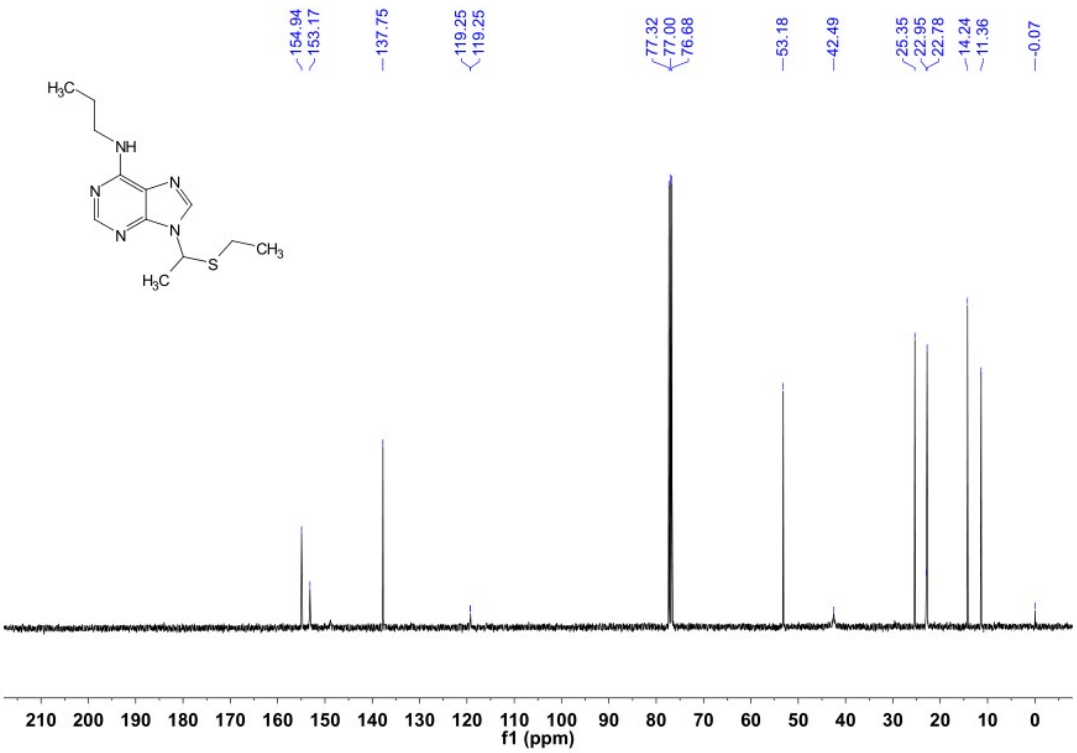
^{13}C {^{1}H} NMR Spectrum for **3d** (100 MHz, $CDCl_3$)



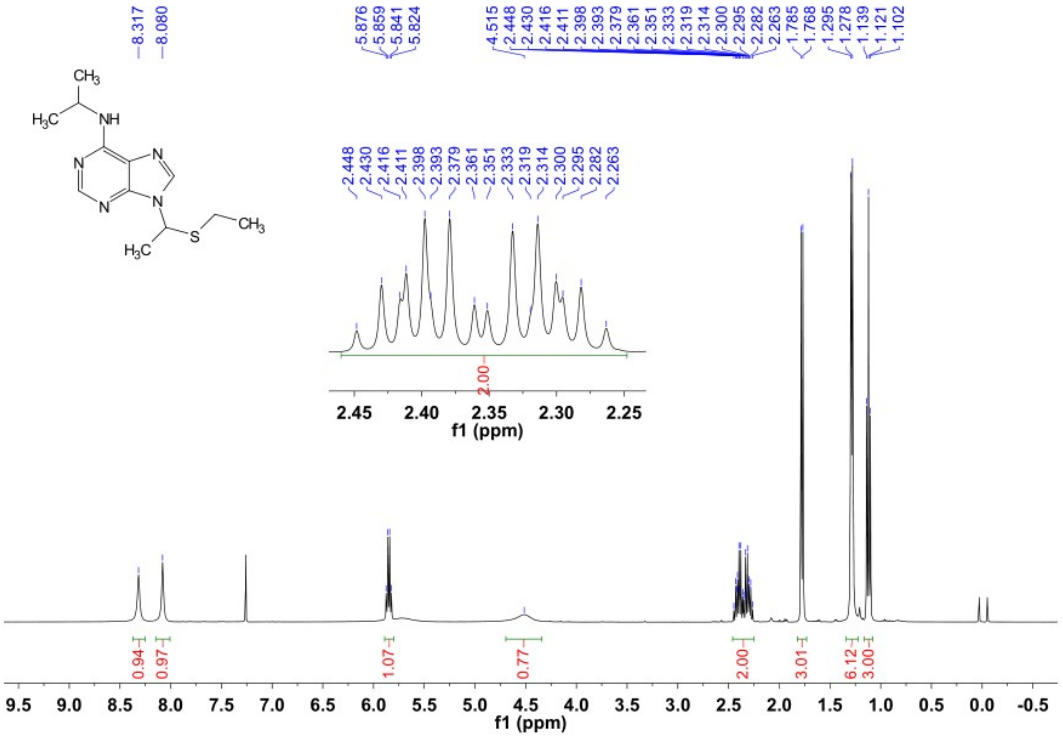
^{1}H NMR Spectrum for **3e** (400 MHz, $CDCl_3$)



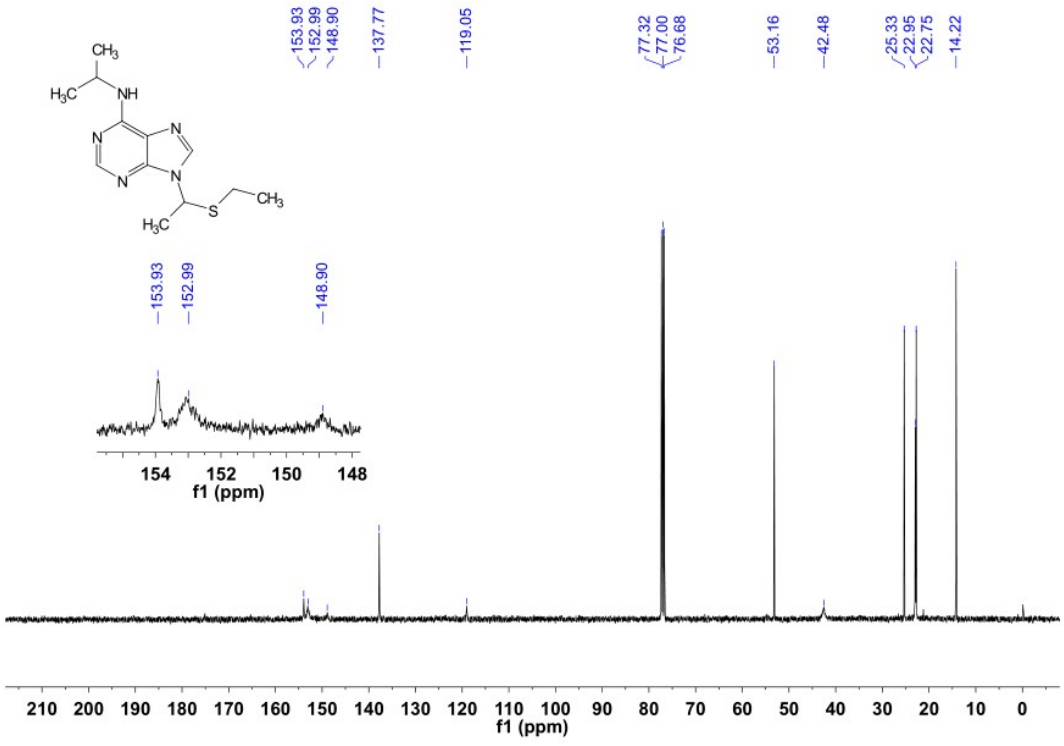
^{13}C {^{1}H} NMR Spectrum for **3e** (100 MHz, $CDCl_3$)



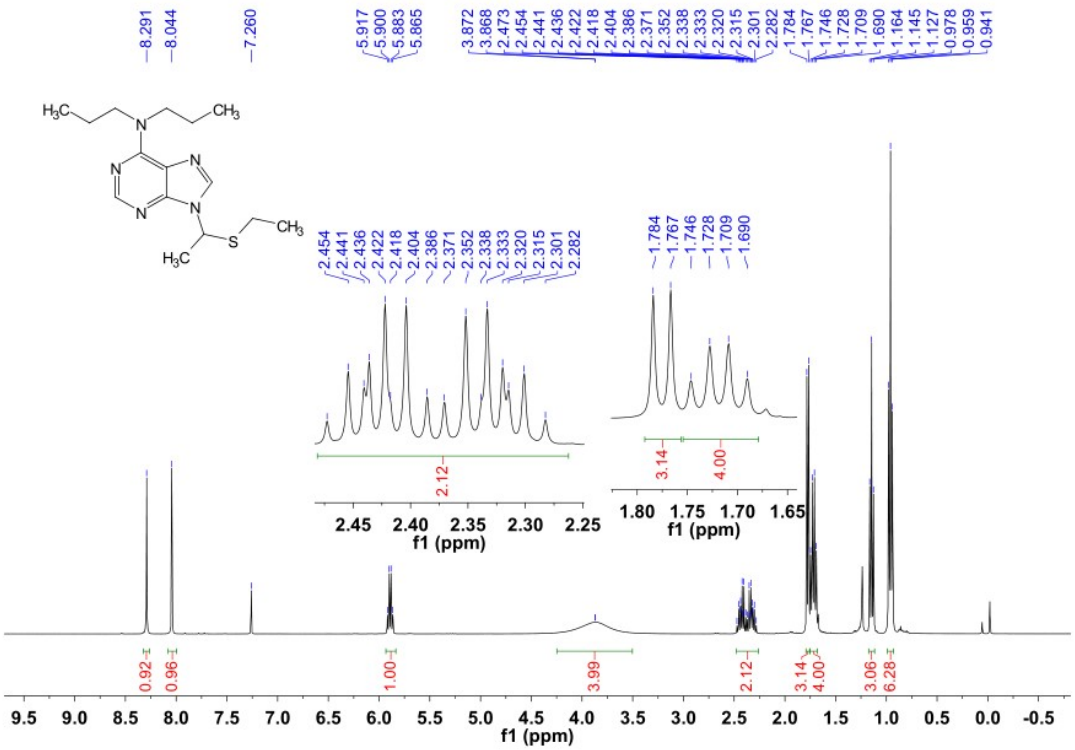
^{1}H NMR Spectrum for **3f** (400 MHz, $CDCl_3$)



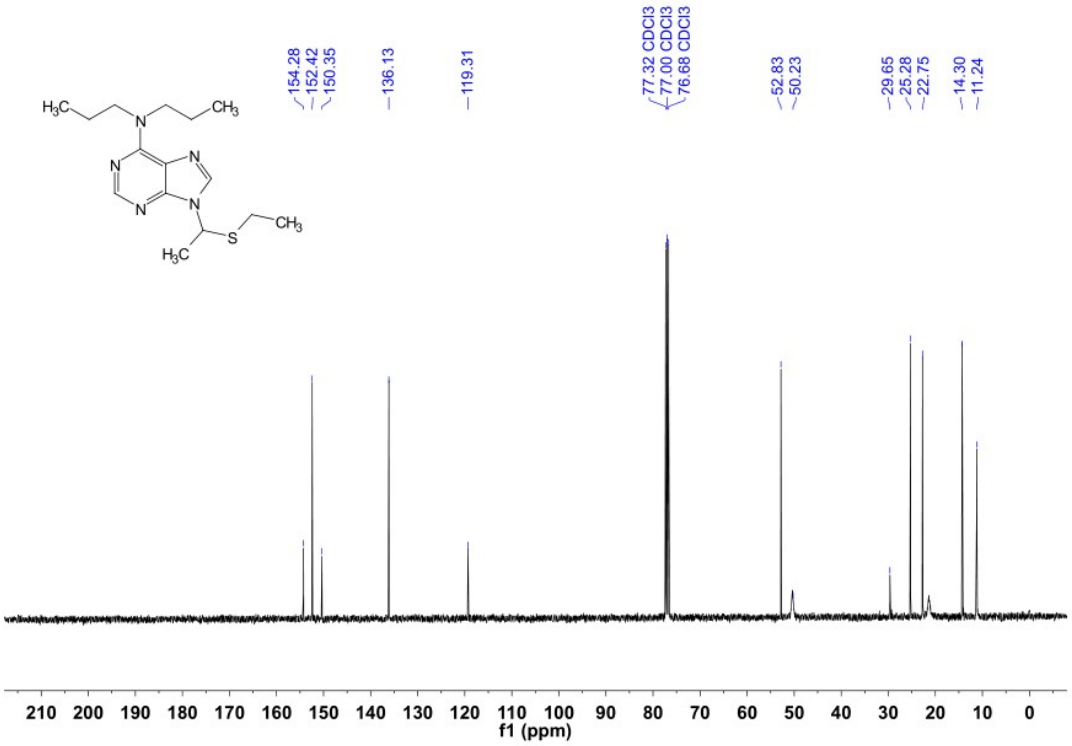
^{13}C {^{1}H} NMR Spectrum for **3f**(100 MHz, $CDCl_3$)



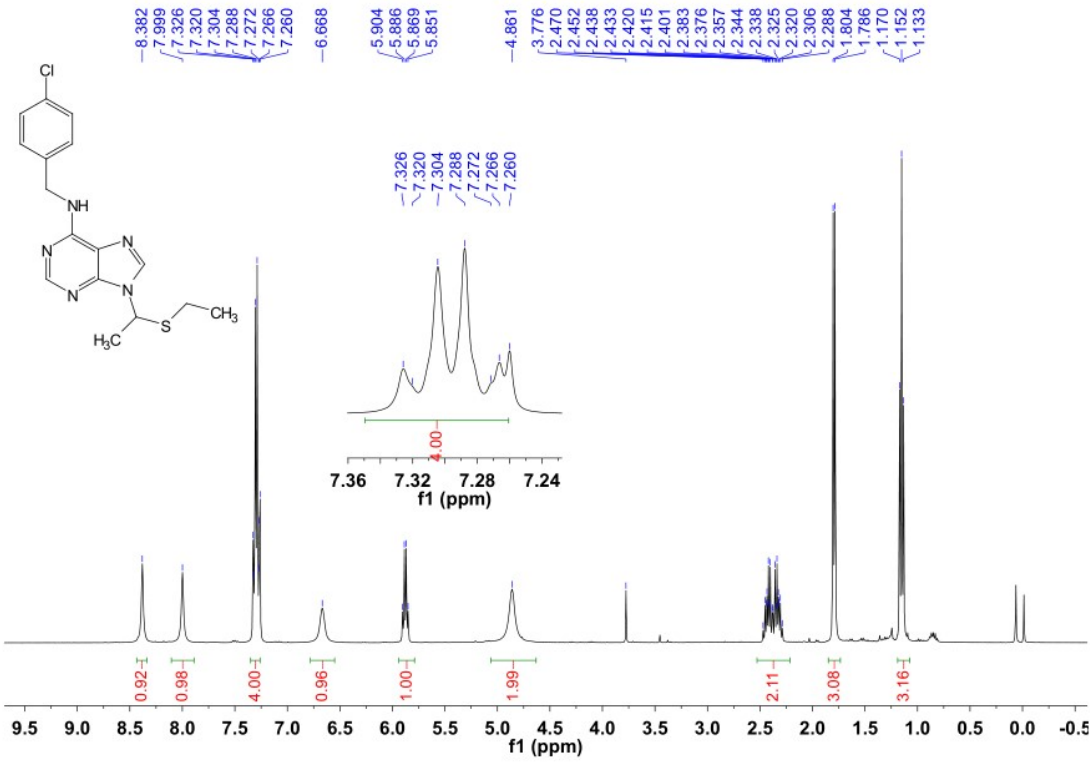
^{1}H NMR Spectrum for **3g** (400 MHz, $CDCl_3$)



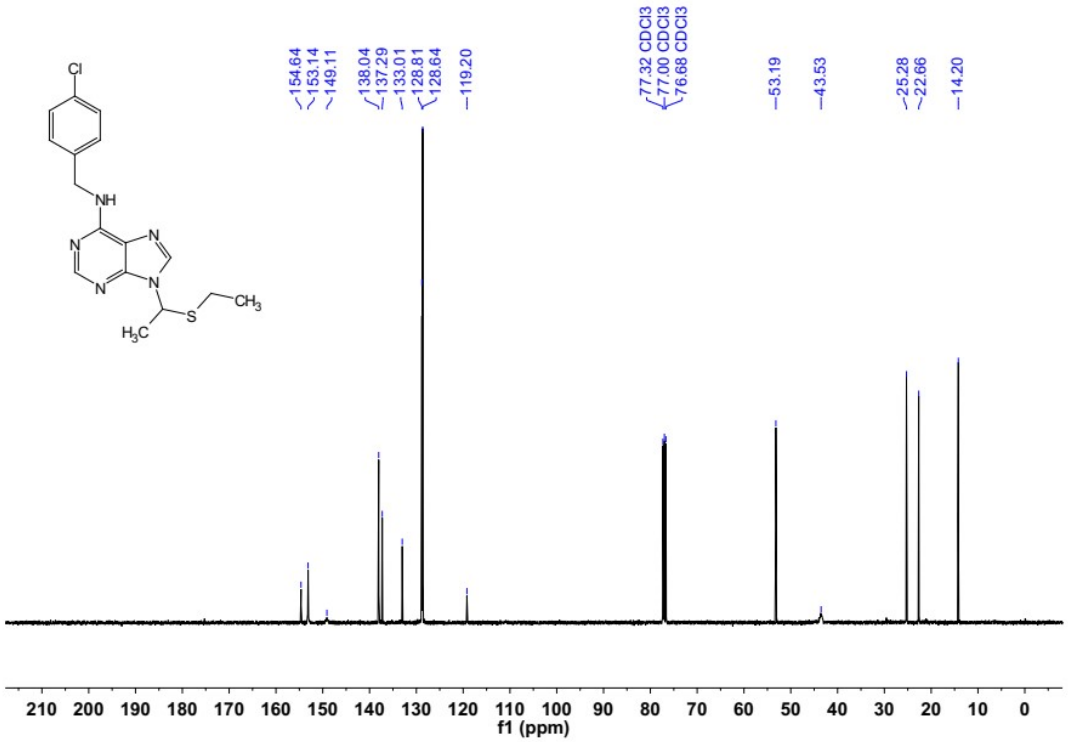
^{13}C {^{1}H} NMR Spectrum for **3g** (100 MHz, $CDCl_3$)



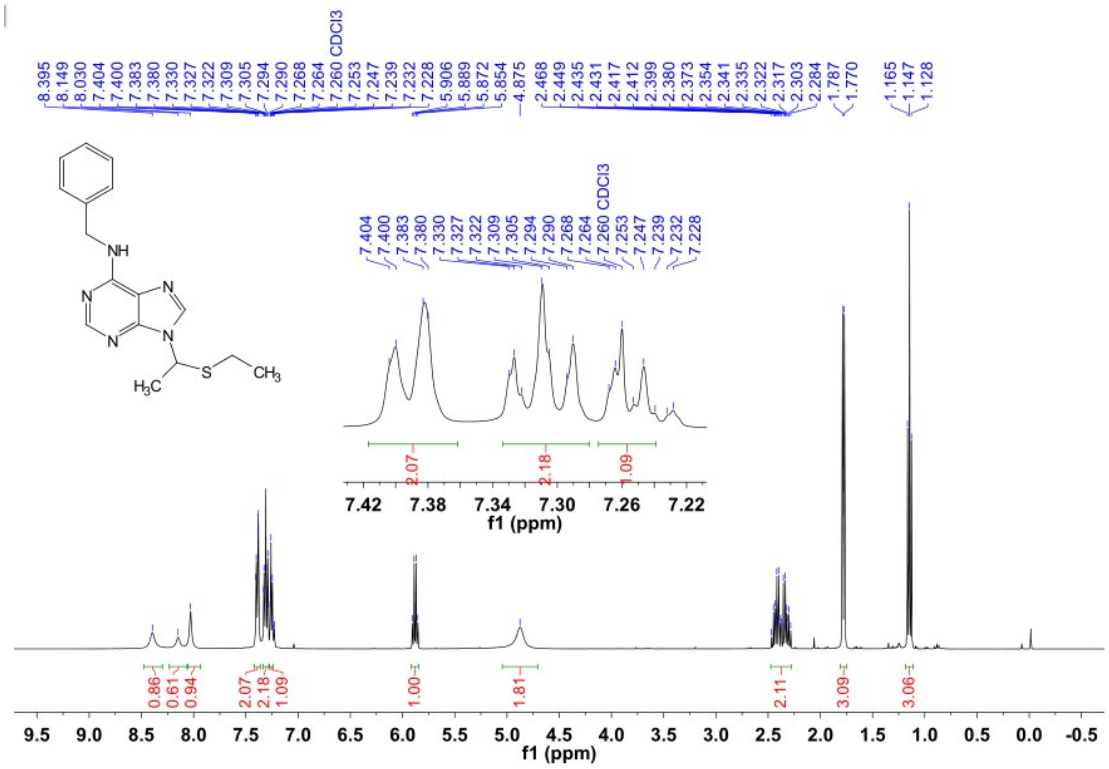
^{1}H NMR Spectrum for **3h** (400 MHz, $CDCl_3$)



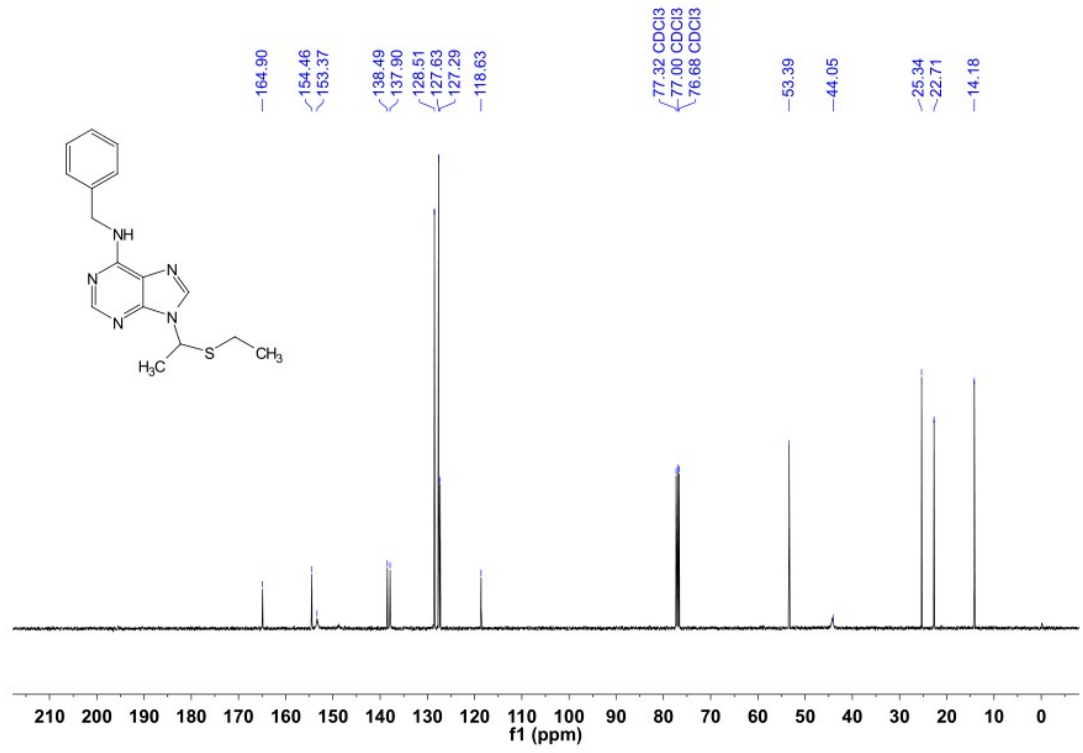
^{13}C {^{1}H} NMR Spectrum for **3h** (100 MHz, $CDCl_3$)



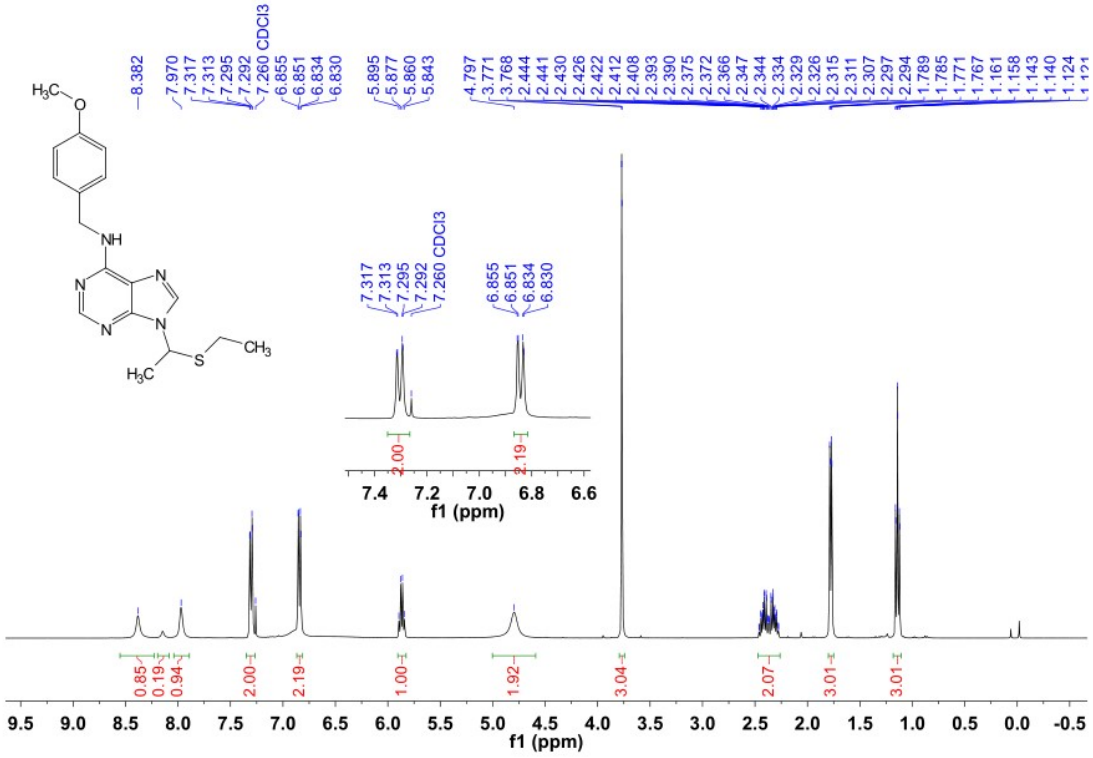
^{1}H NMR Spectrum for **3i** (400 MHz, $CDCl_3$)



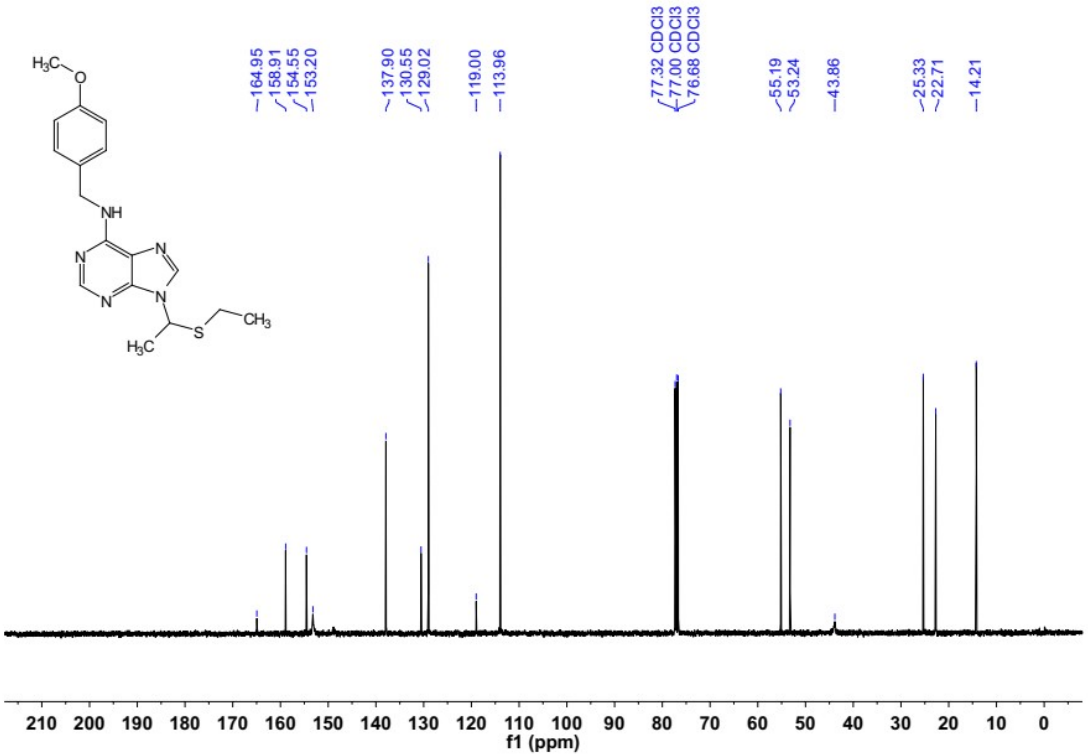
^{13}C {^{1}H} NMR Spectrum for **3i** (100 MHz, $CDCl_3$)



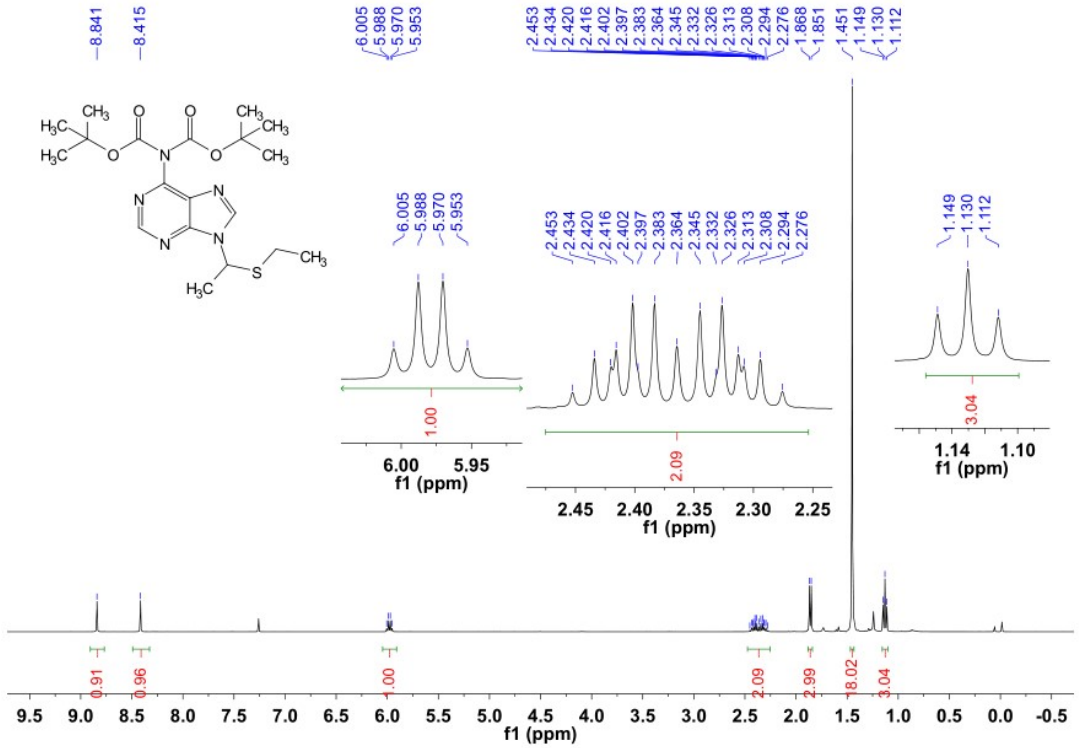
^{1}H NMR Spectrum for **3j** (400 MHz, $CDCl_3$)



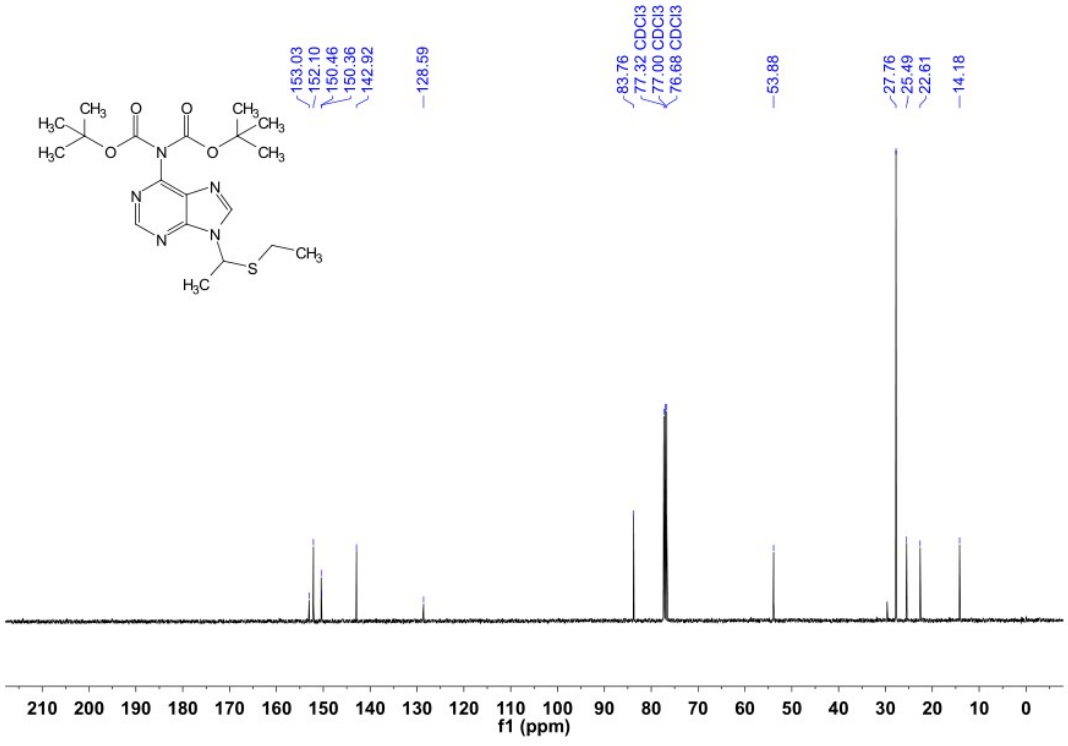
^{13}C {^{1}H} NMR Spectrum for **3j** (100 MHz, $CDCl_3$)



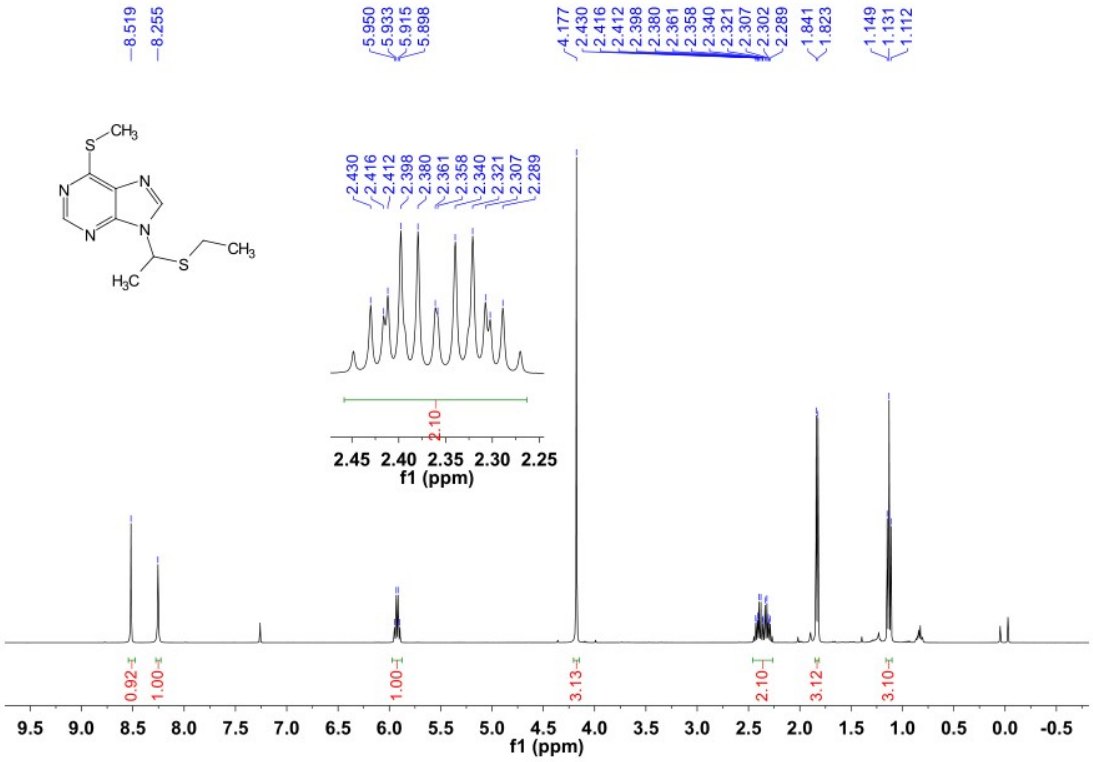
^{1}H NMR Spectrum for **3k** (400 MHz, $CDCl_3$)



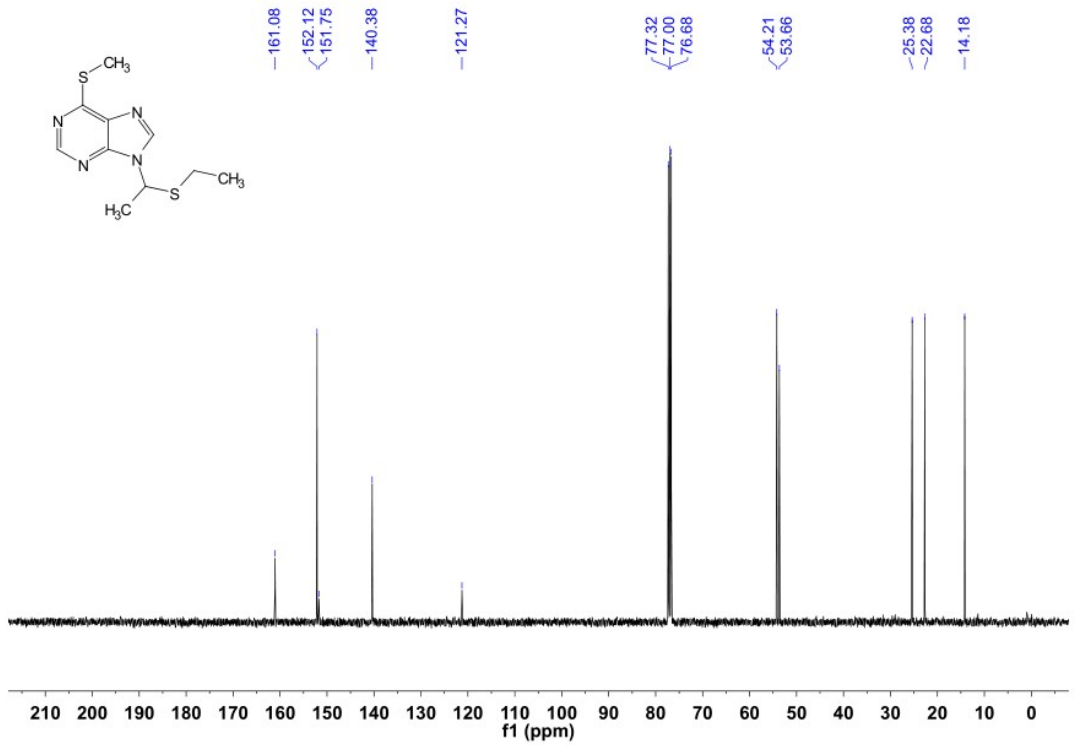
^{13}C {^{1}H} NMR Spectrum for **3k** (100 MHz, $CDCl_3$)



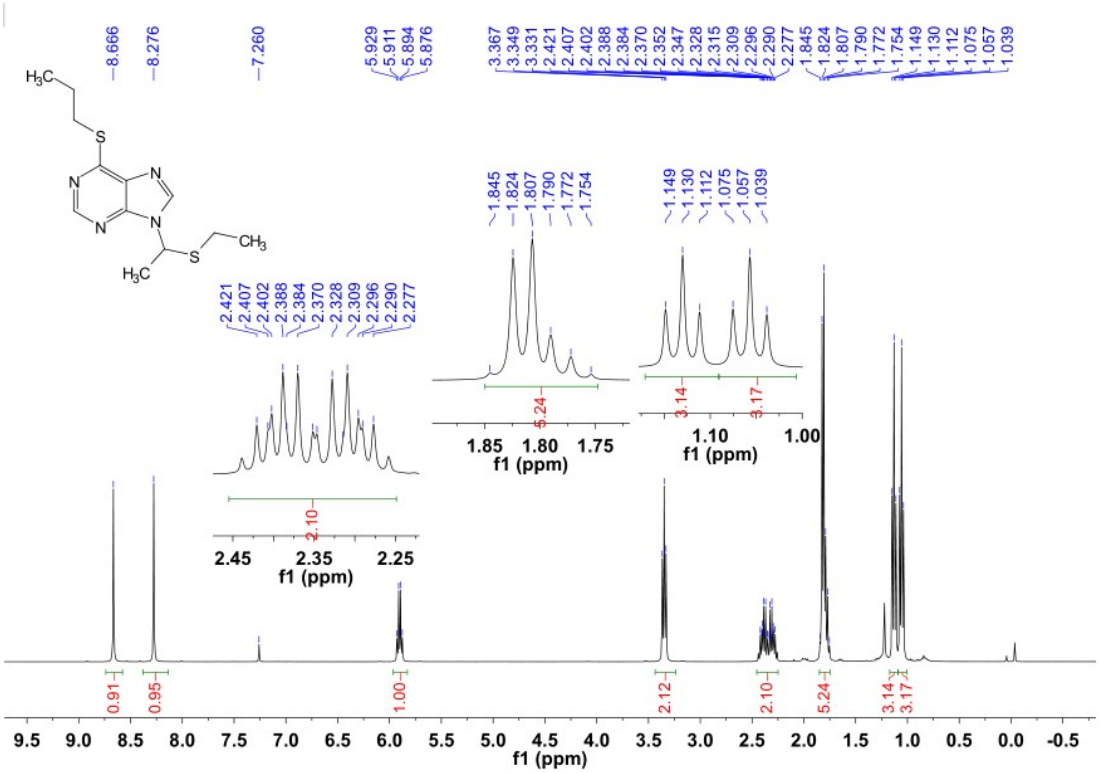
^{1}H NMR Spectrum for **3l** (400 MHz, $CDCl_3$)



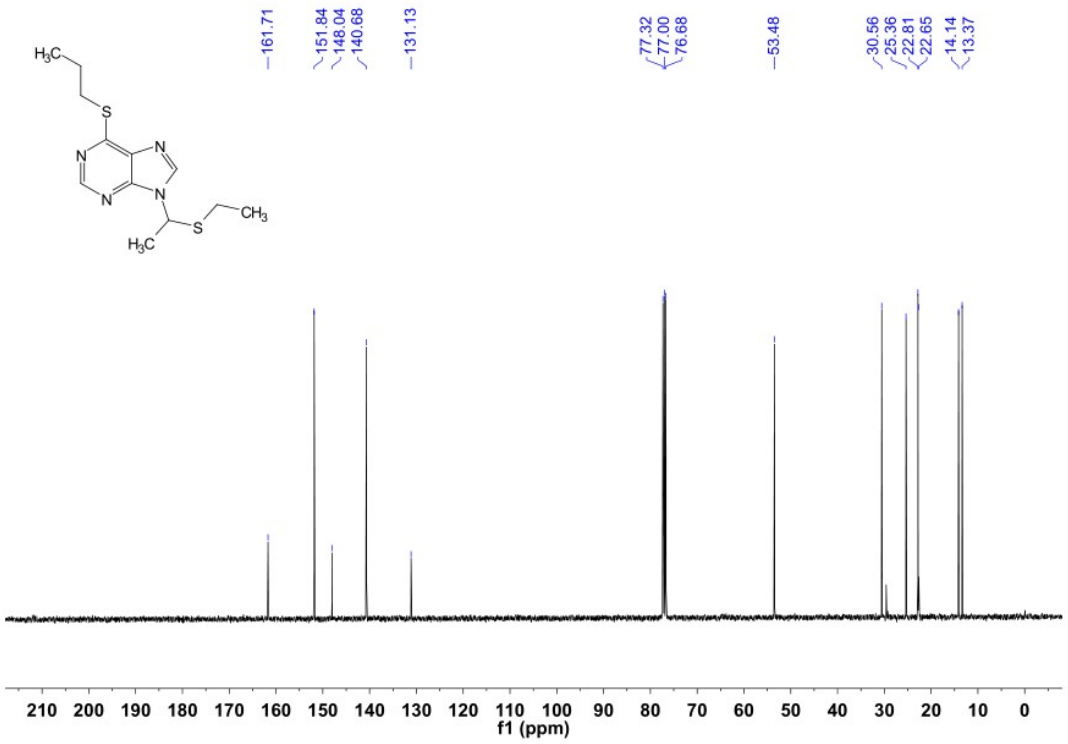
^{13}C {^{1}H} NMR Spectrum for **3l** (100 MHz, $CDCl_3$)



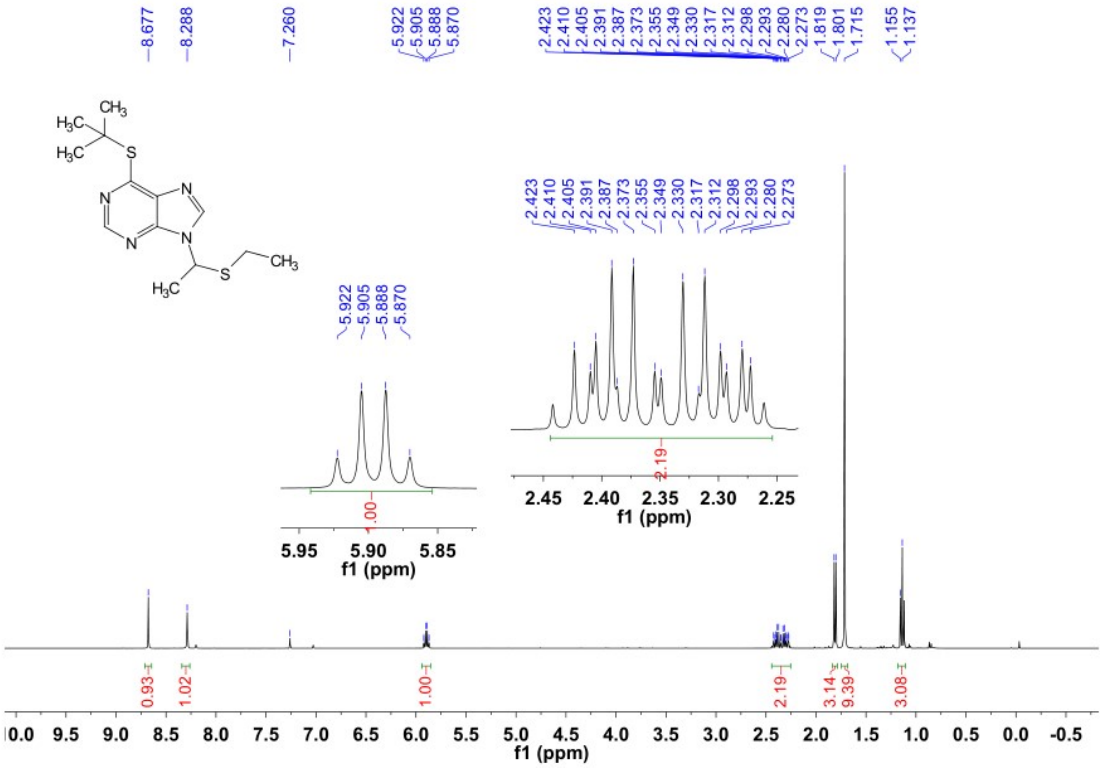
^{1}H NMR Spectrum for **3m** (400 MHz, $CDCl_3$)



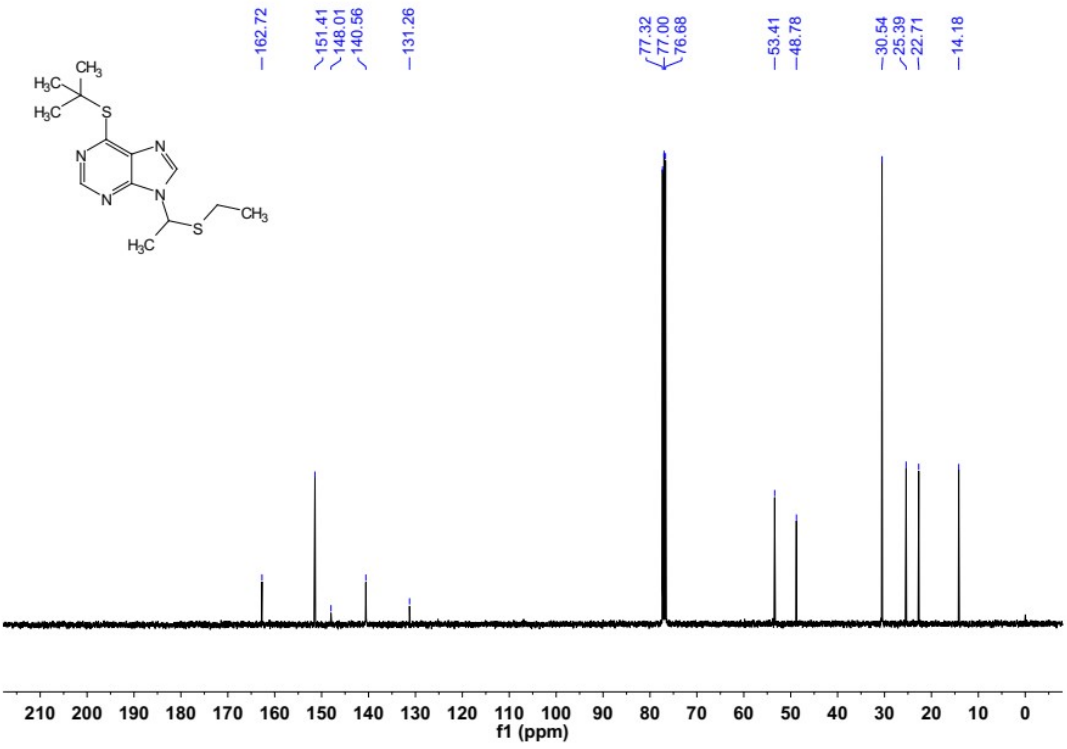
^{13}C {^{1}H} NMR Spectrum for **3m** (100 MHz, $CDCl_3$)



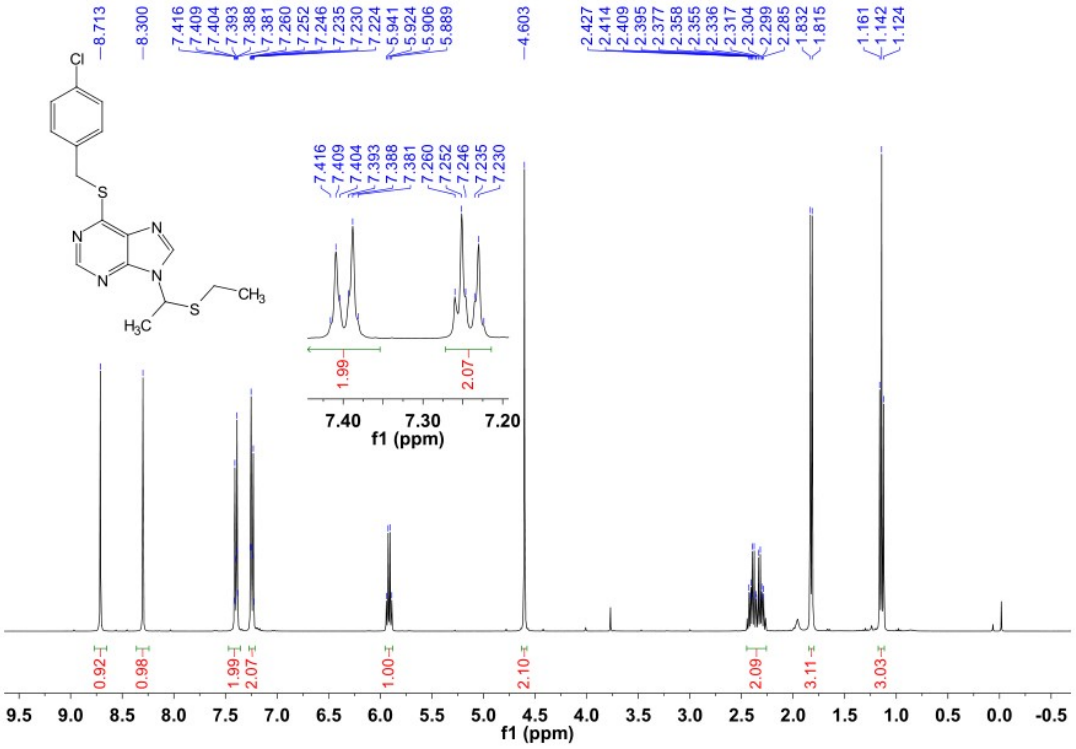
^{1}H NMR Spectrum for **3n** (400 MHz, $CDCl_3$)



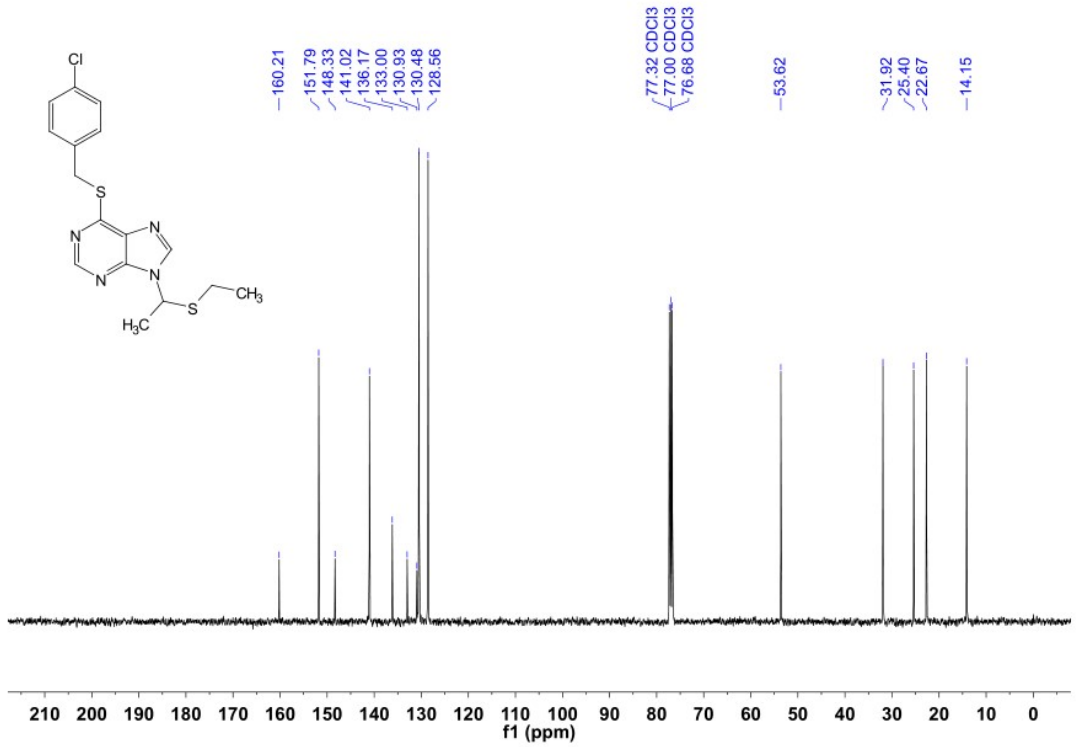
^{13}C {^{1}H} NMR Spectrum for **3n** (100 MHz, $CDCl_3$)



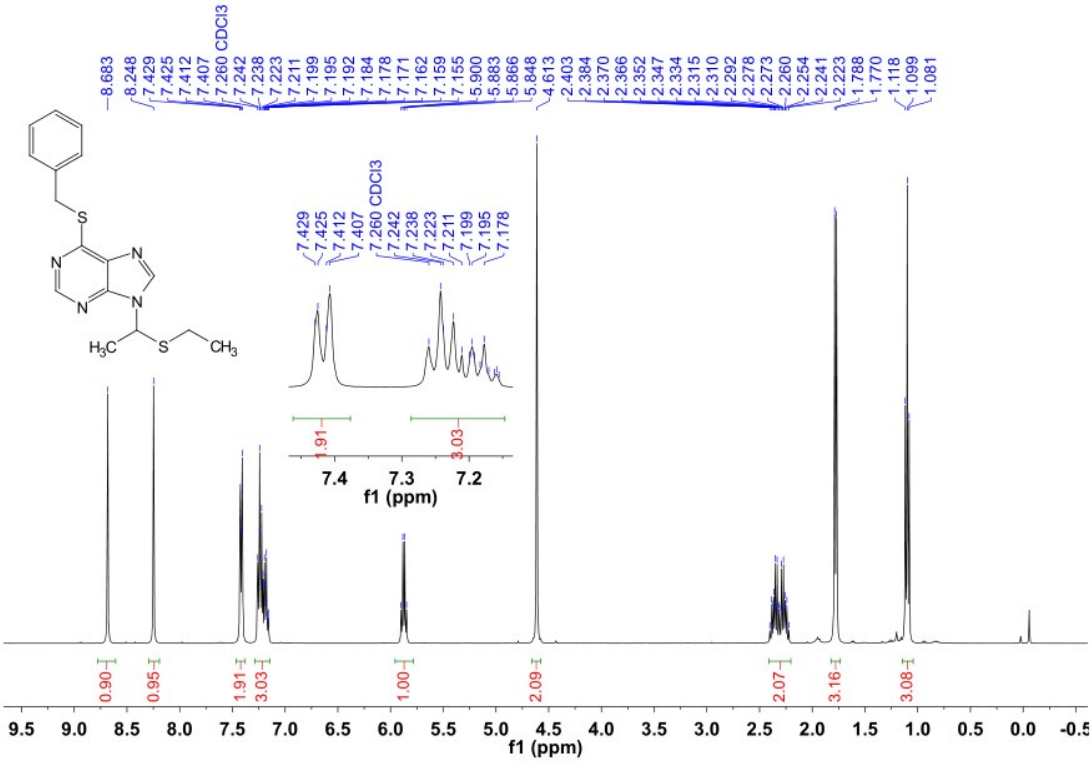
^{1}H NMR Spectrum for **3o** (400 MHz, $CDCl_3$)



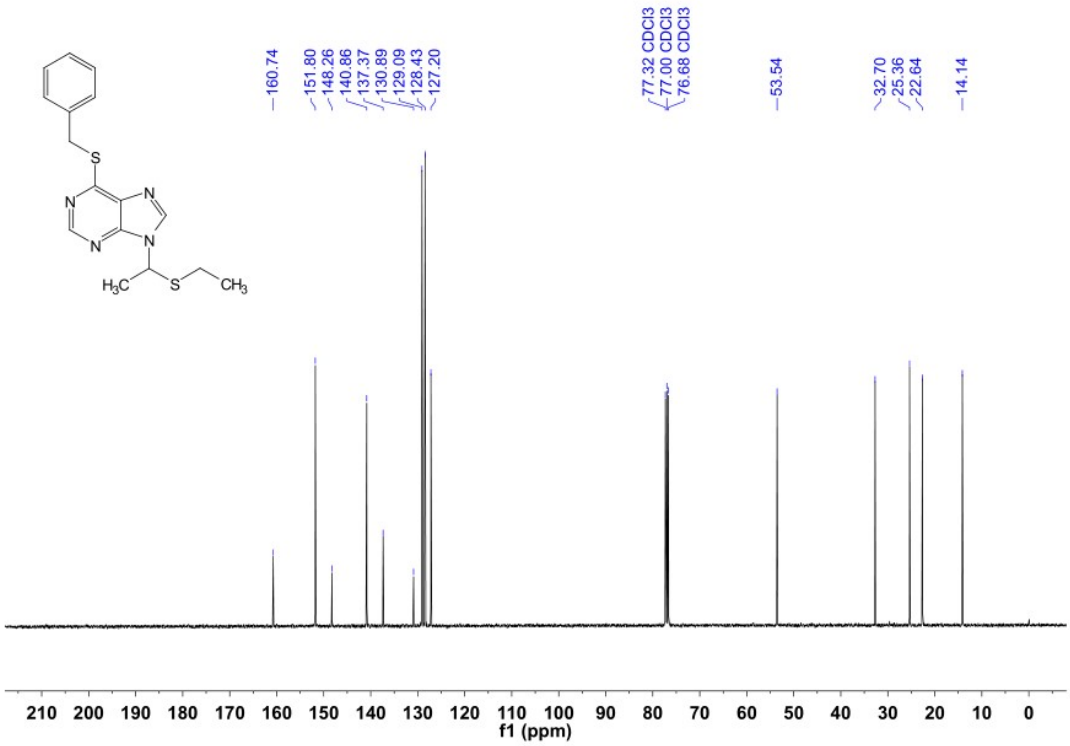
^{13}C {^{1}H} NMR Spectrum for **3o** (100 MHz, $CDCl_3$)



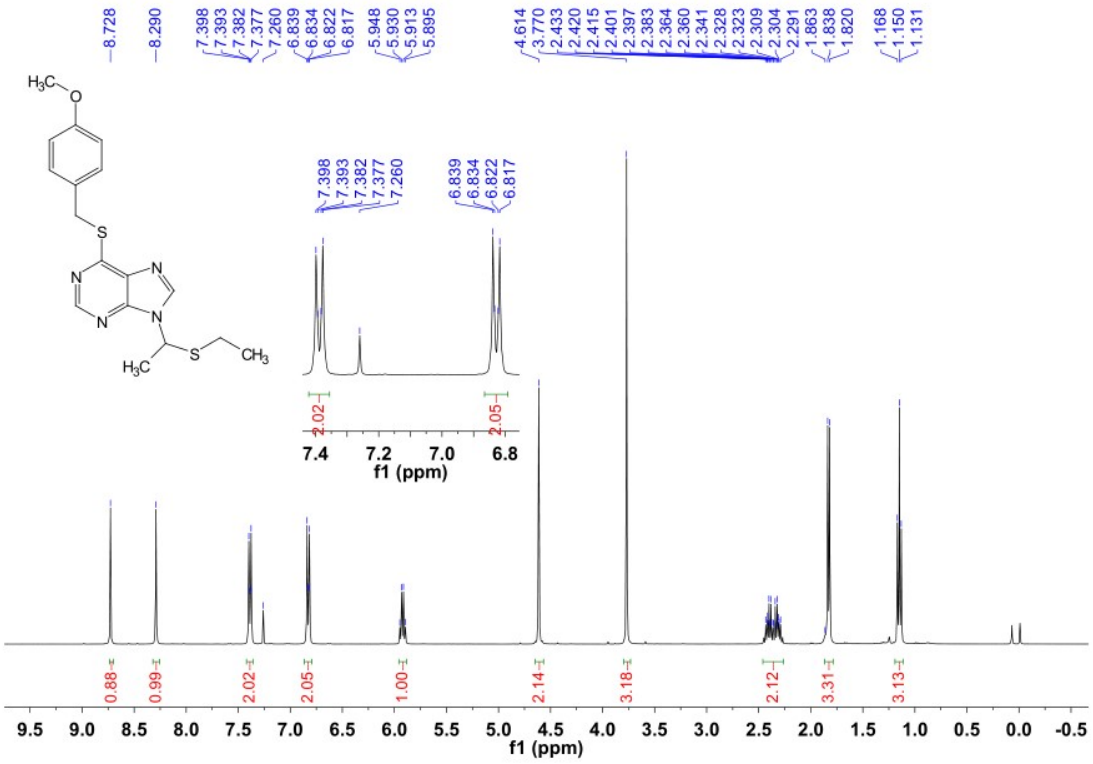
^{1}H NMR Spectrum for **3p** (400 MHz, $CDCl_3$)



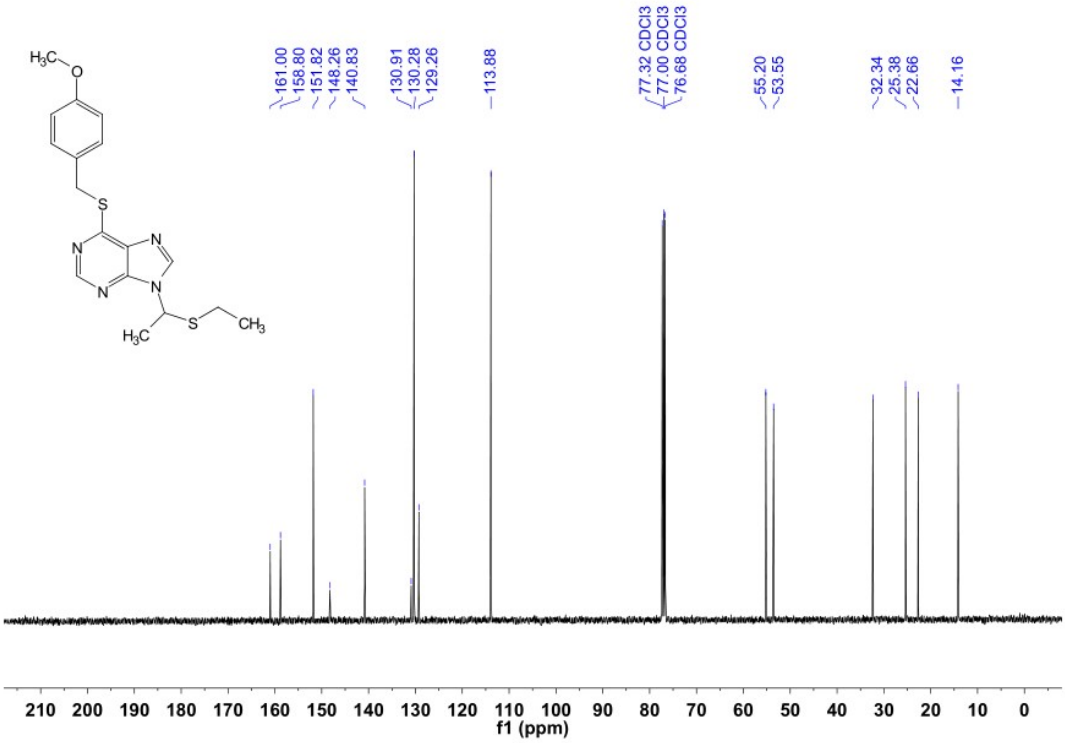
^{13}C {^{1}H} NMR Spectrum for **3p** (100 MHz, $CDCl_3$)



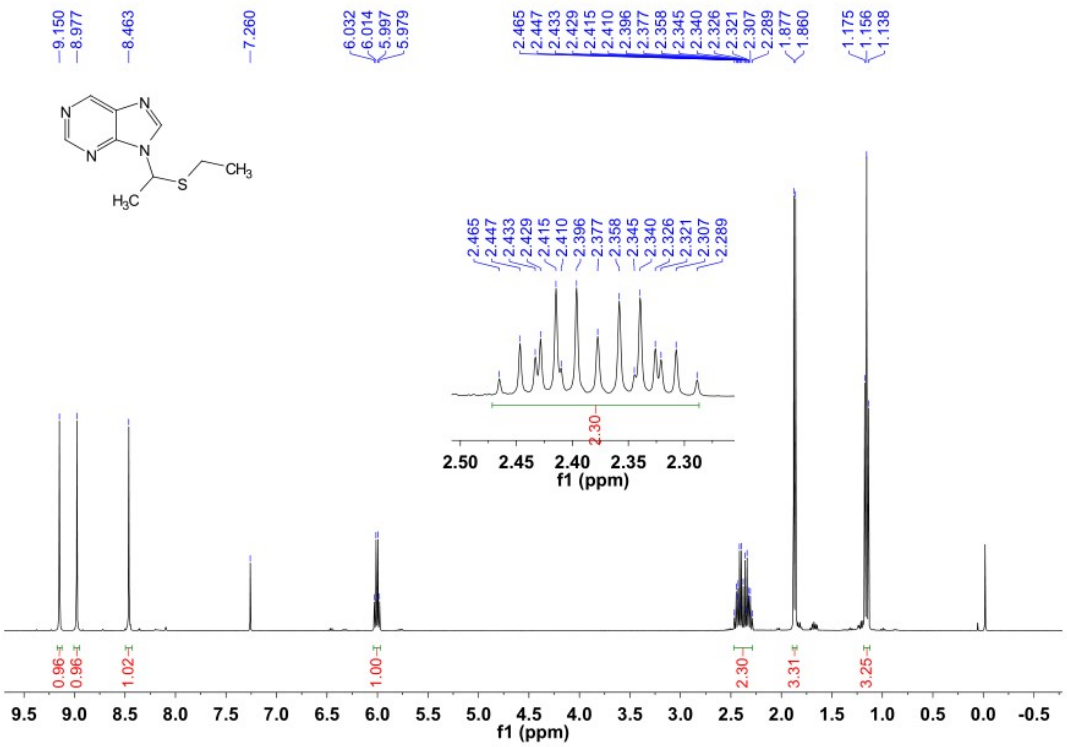
^{1}H NMR Spectrum for **3q** (400 MHz, $CDCl_3$)



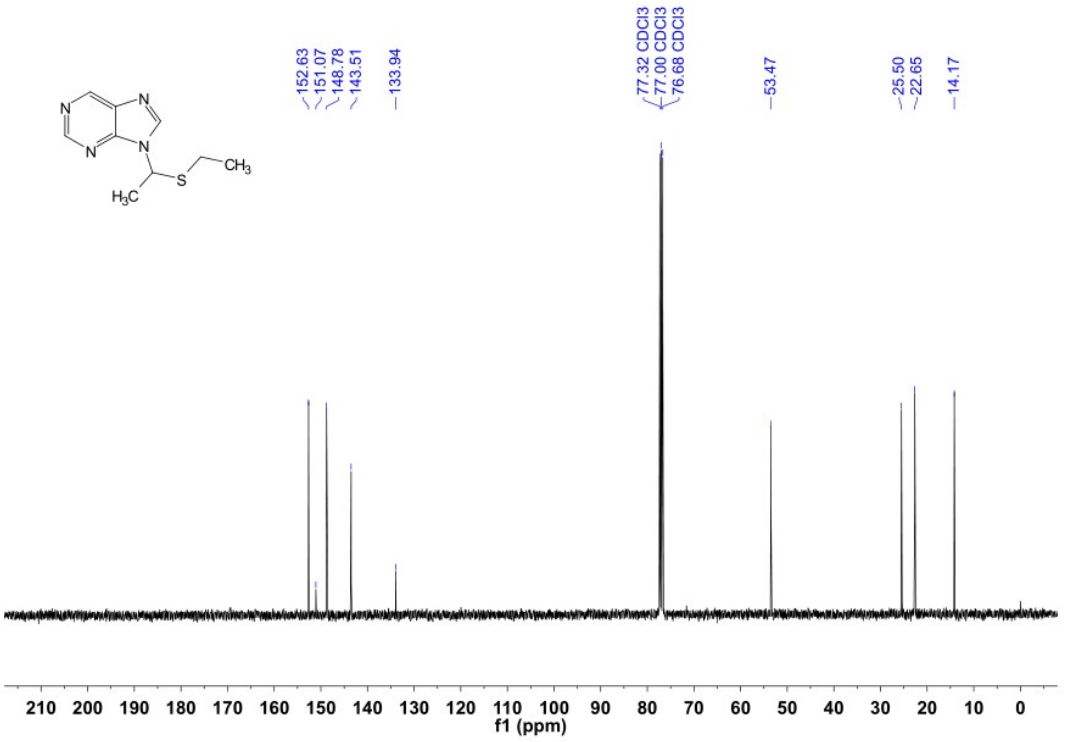
^{13}C {^{1}H} NMR Spectrum for **3q** (100 MHz, $CDCl_3$)



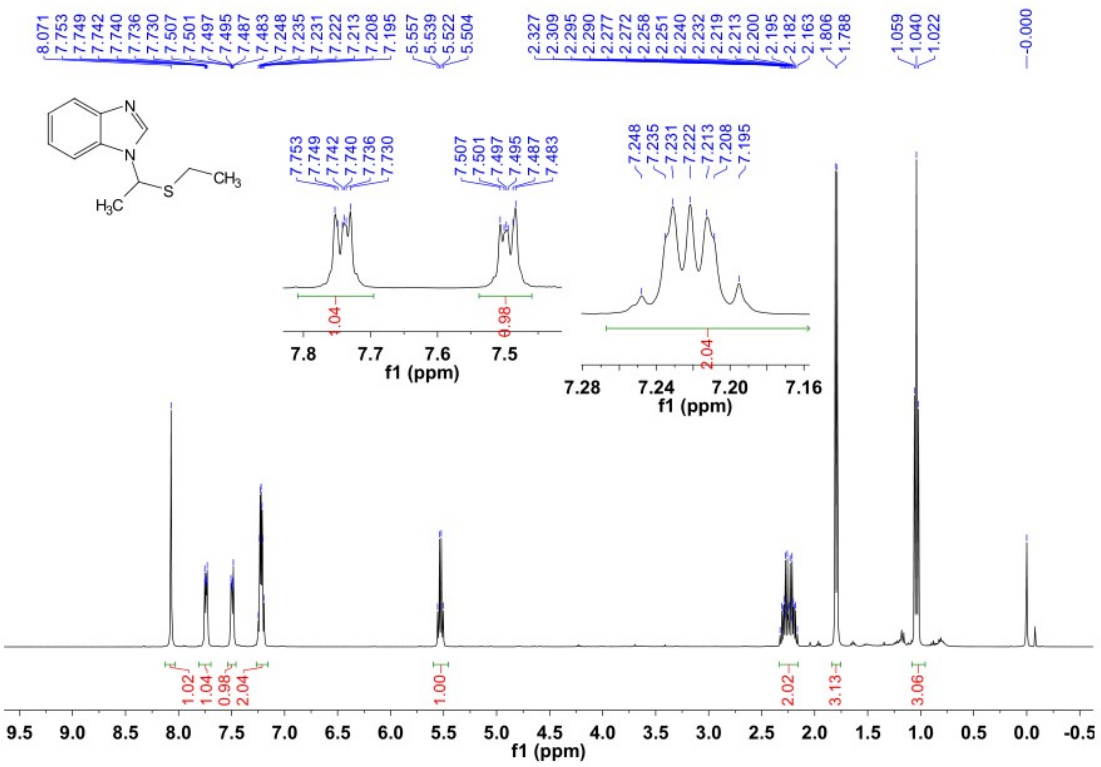
^{1}H NMR Spectrum for **3r** (400 MHz, $CDCl_3$)



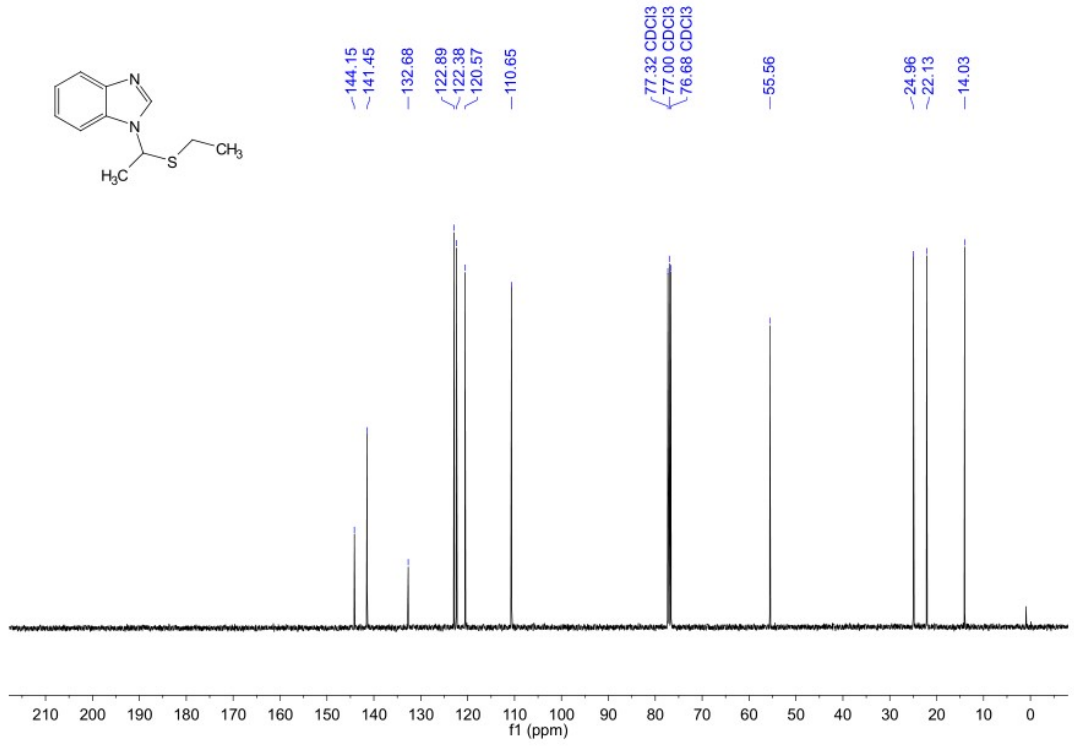
^{13}C {^{1}H} NMR Spectrum for **3r** (100 MHz, $CDCl_3$)



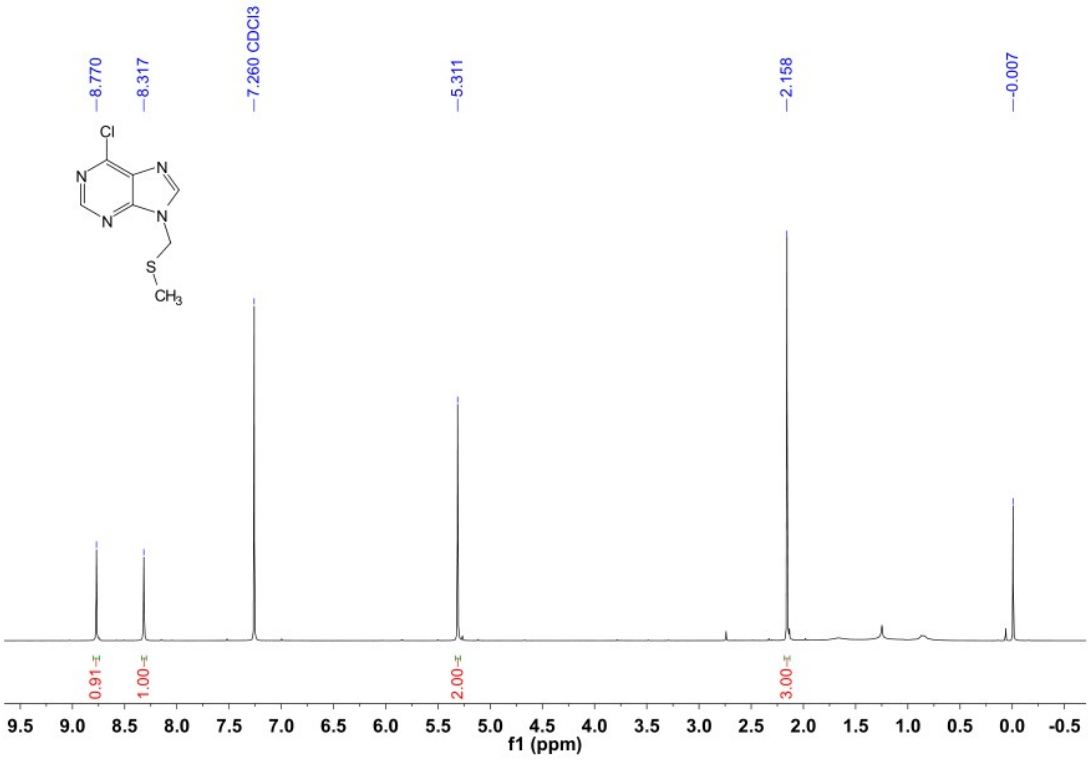
^{1}H NMR Spectrum for **3w** (400 MHz, $CDCl_3$)



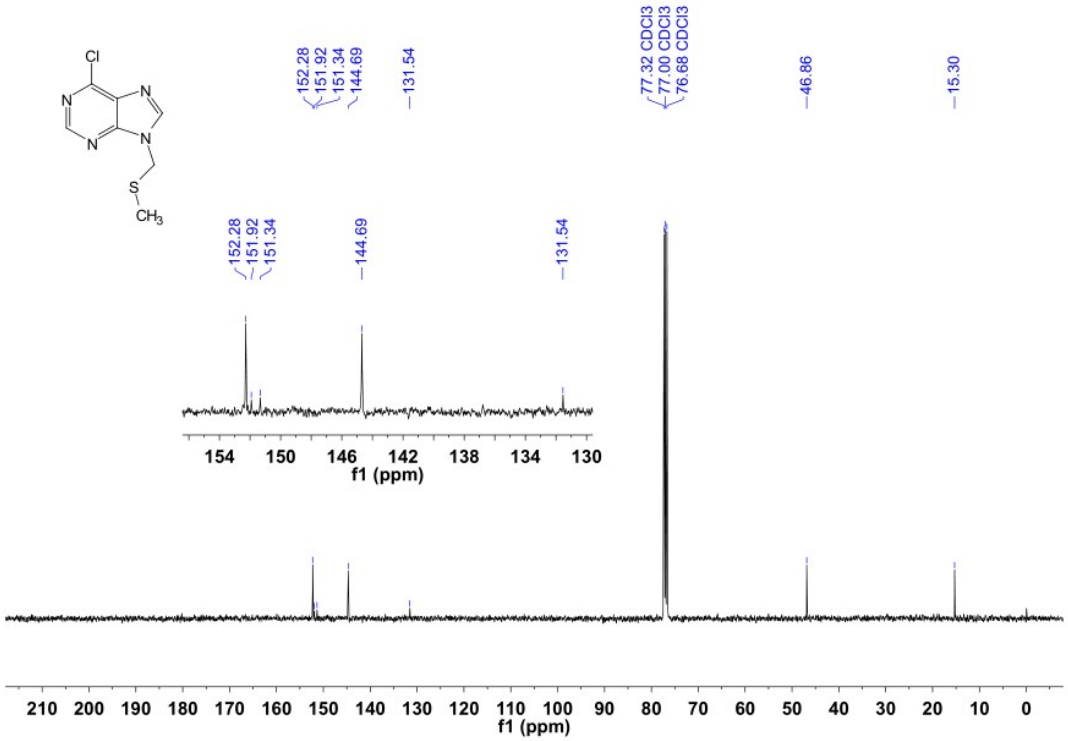
^{13}C {^{1}H} NMR Spectrum for **3w** (100 MHz, $CDCl_3$)



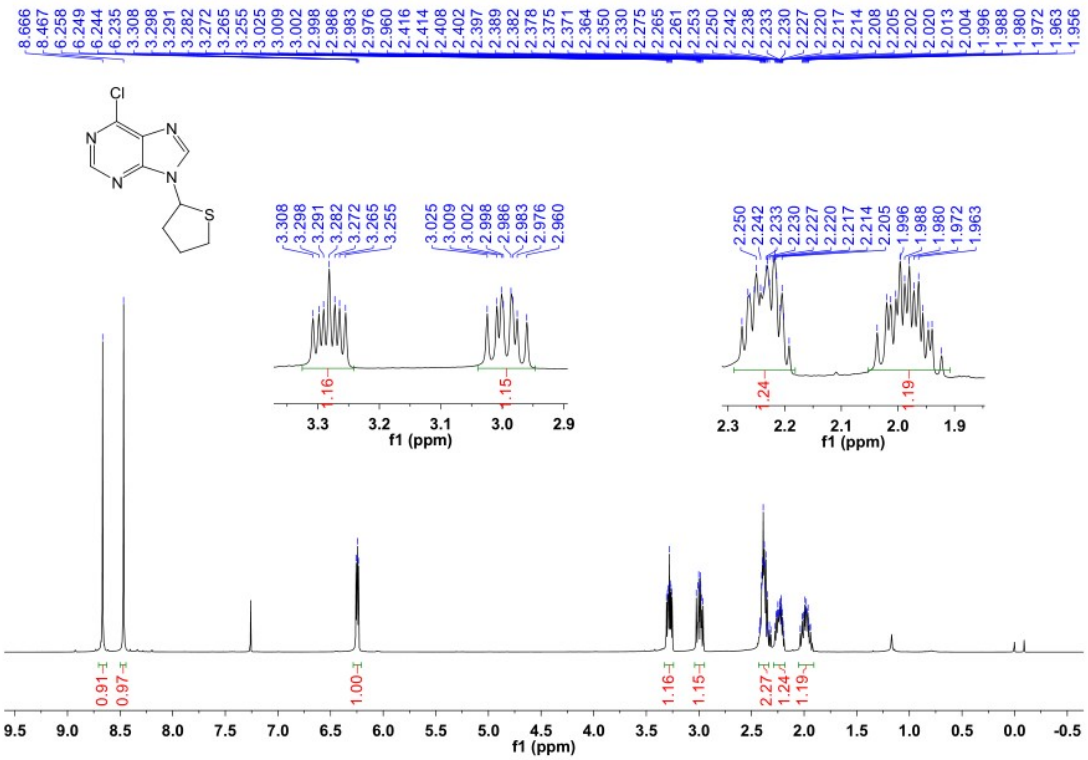
^{1}H NMR Spectrum for **4a** (400 MHz, $CDCl_3$)



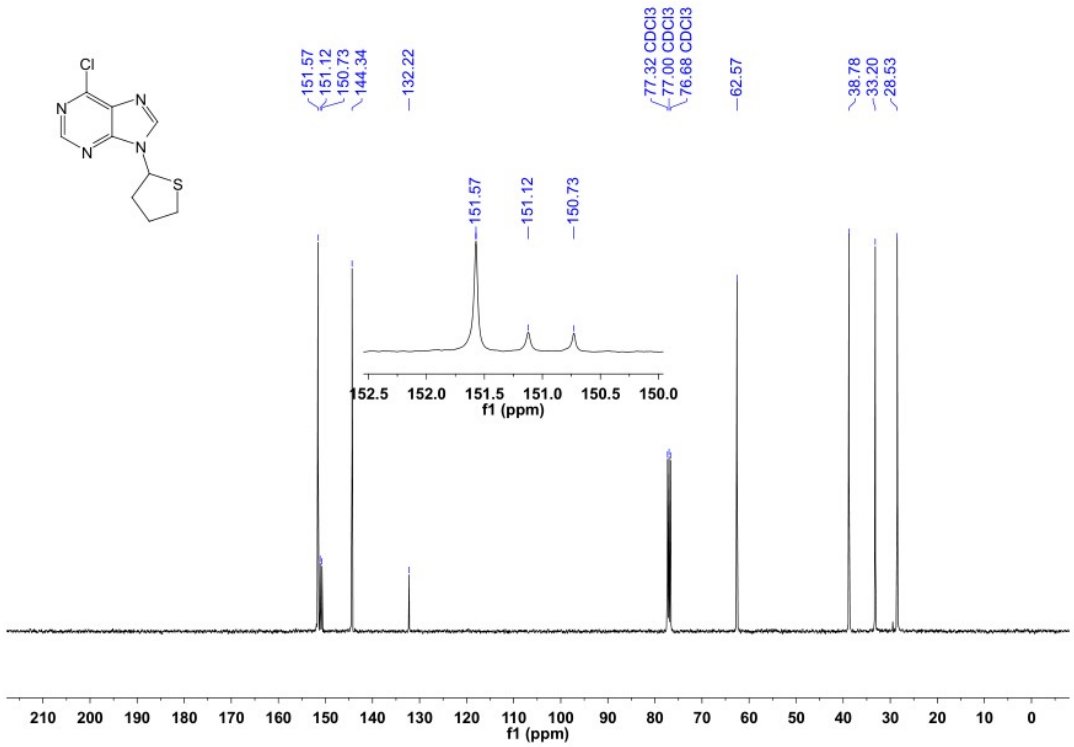
^{13}C {^{1}H} NMR Spectrum for **4a** (100 MHz, $CDCl_3$)



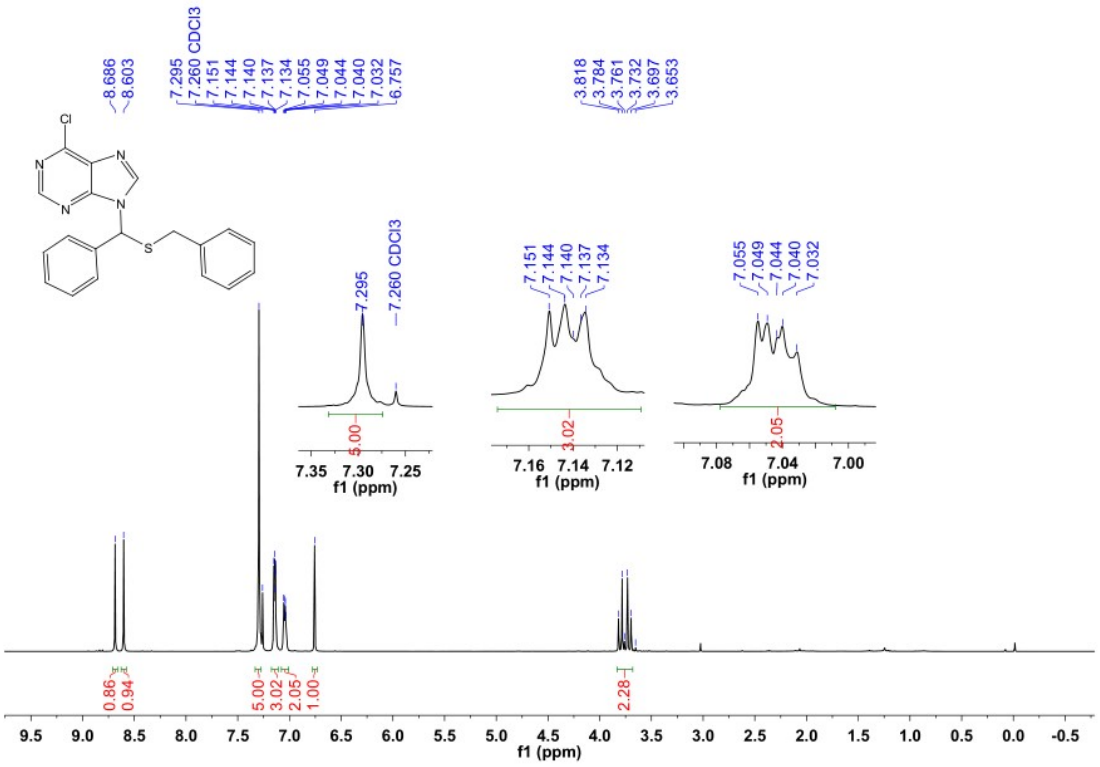
^{1}H NMR Spectrum for **4b** (400 MHz, $CDCl_3$)



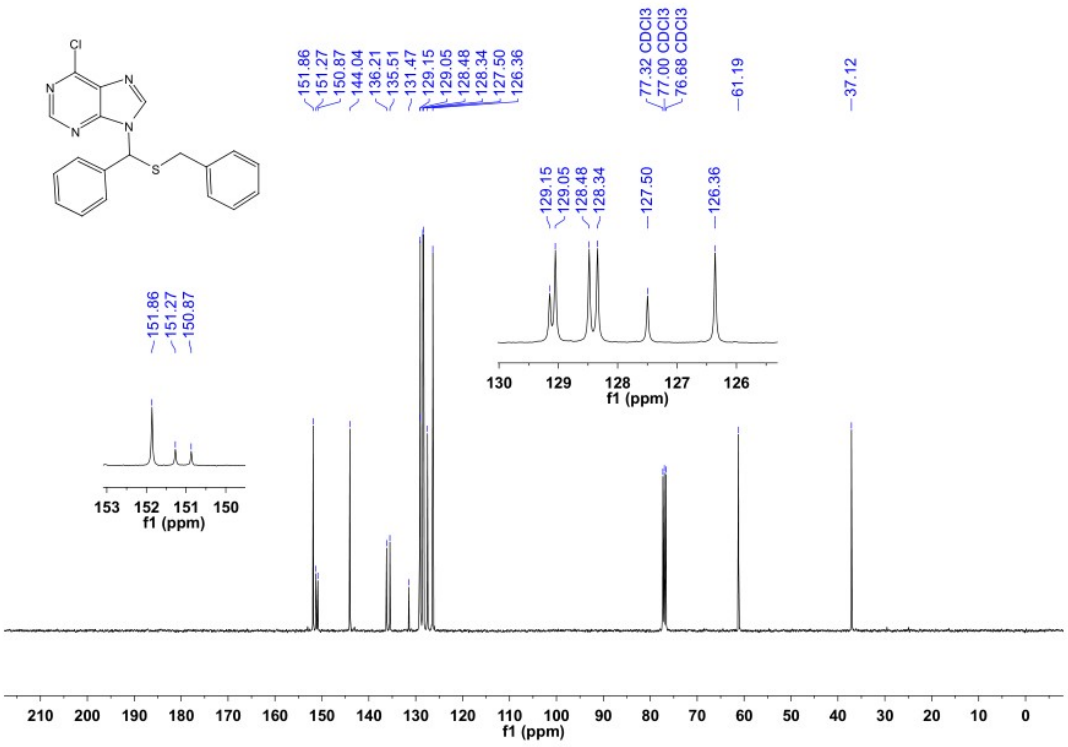
^{13}C {^{1}H} NMR Spectrum for **4b** (100 MHz, $CDCl_3$)



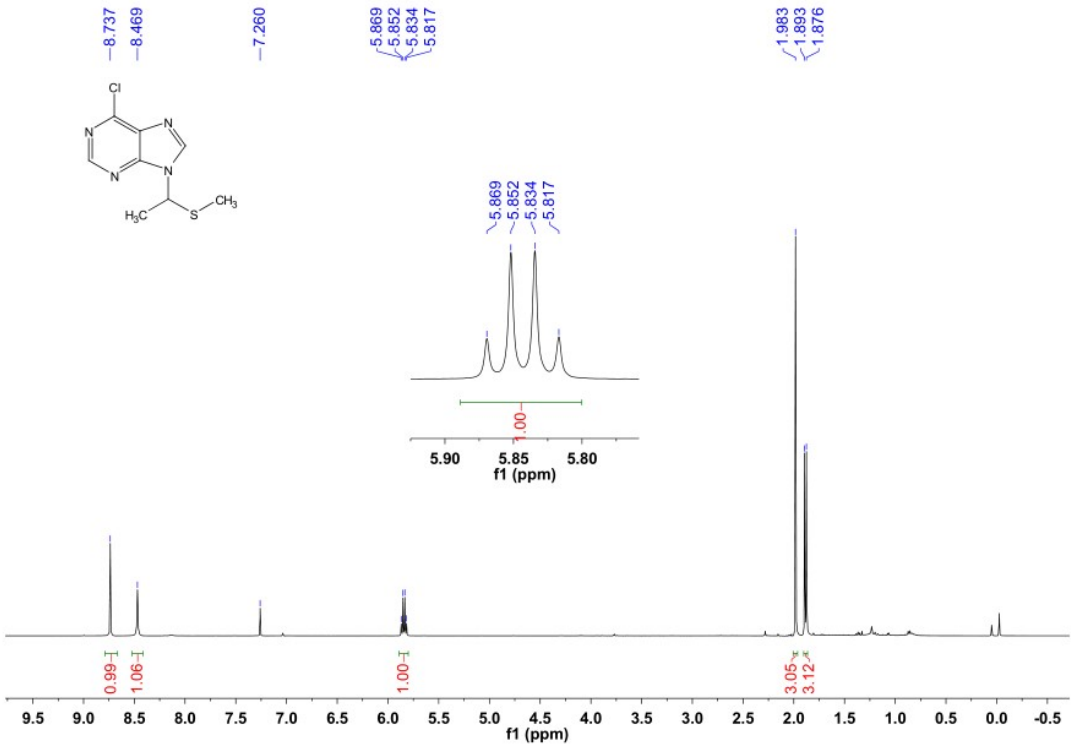
^{1}H NMR Spectrum for **4d** (400 MHz, $CDCl_3$)



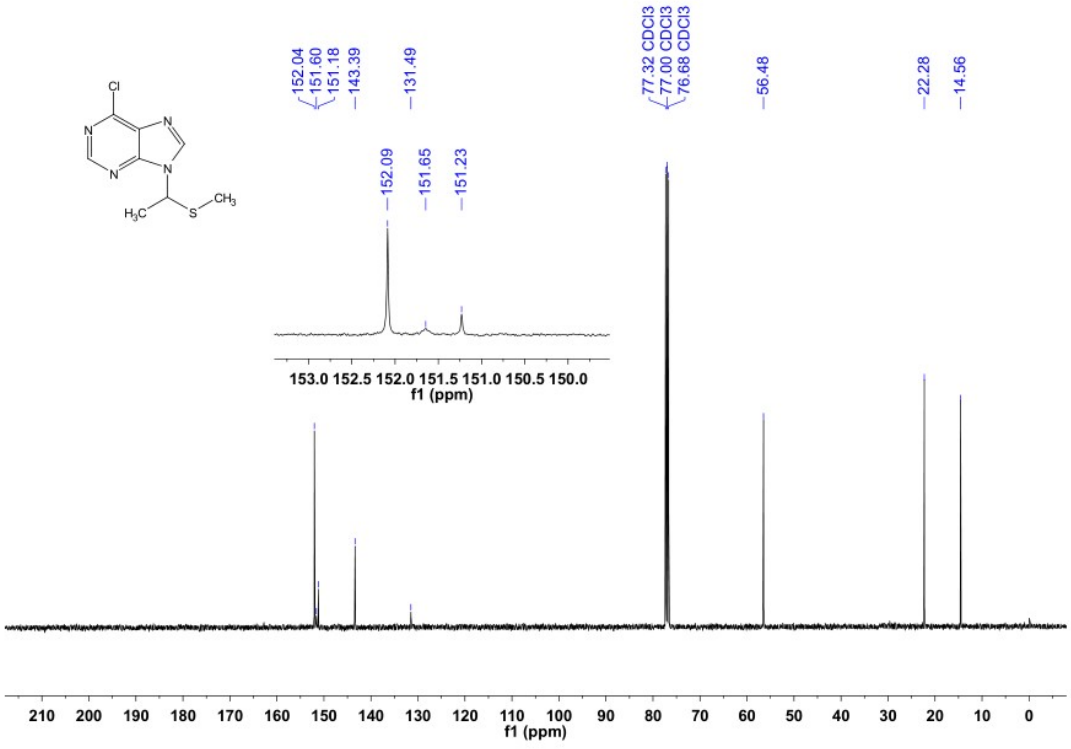
^{13}C {^{1}H} NMR Spectrum for **4d** (100 MHz, $CDCl_3$)



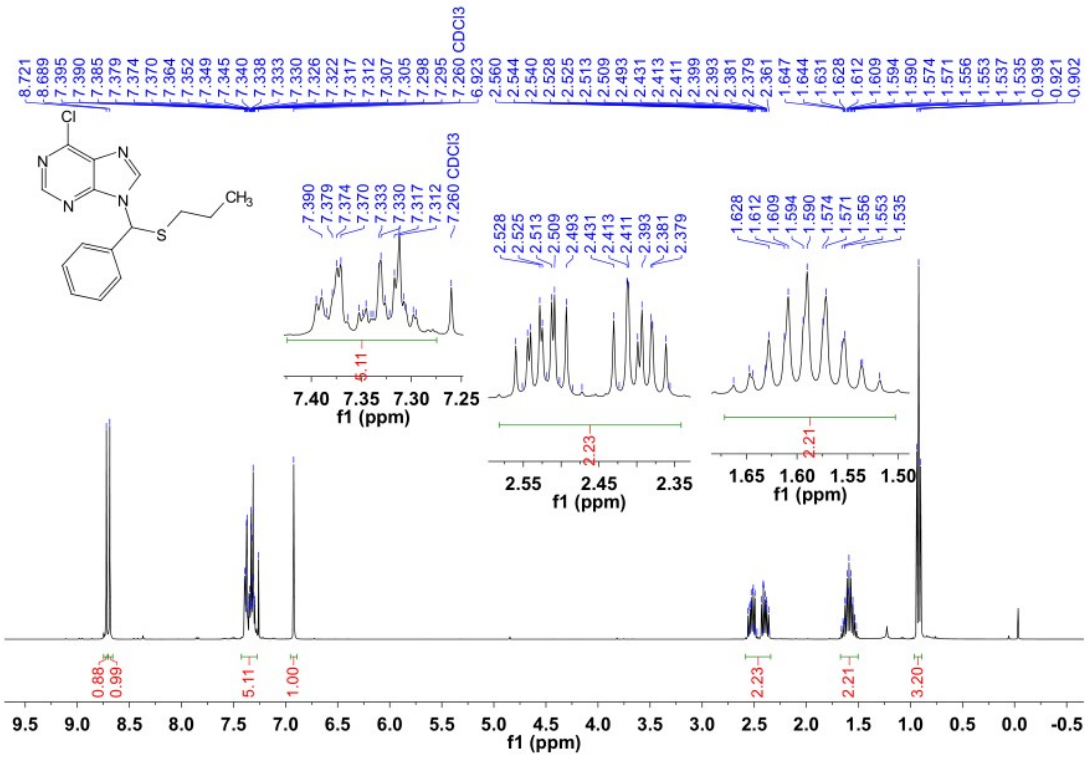
^{1}H NMR Spectrum for **4f** (400 MHz, $CDCl_3$)



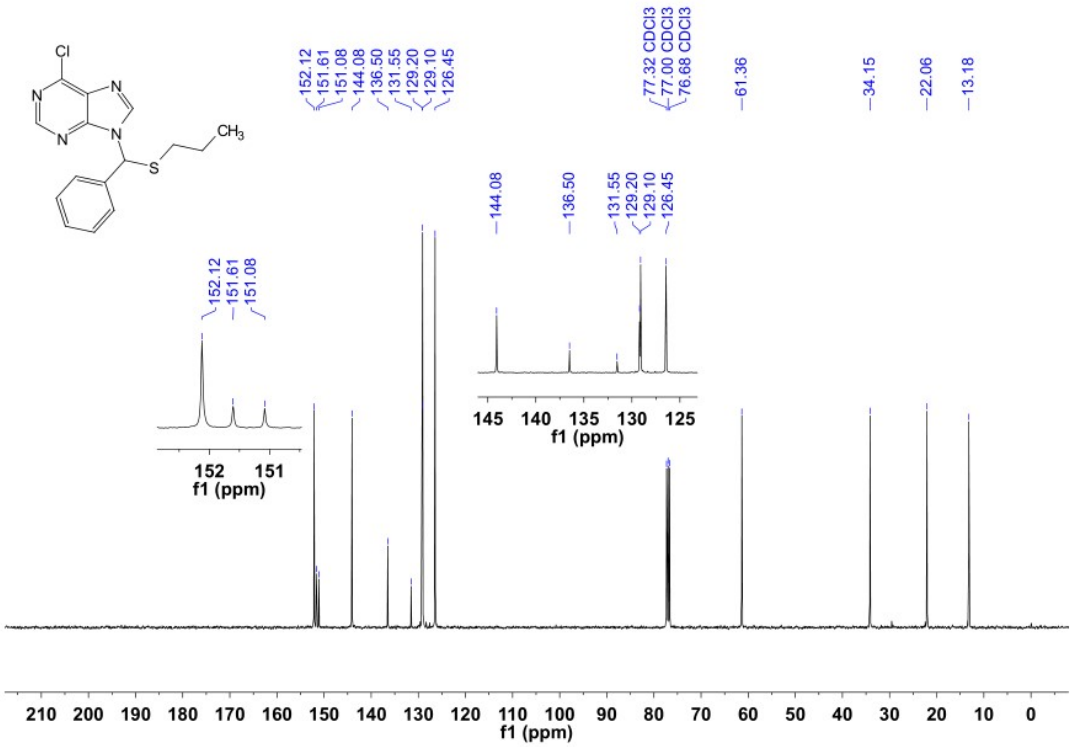
^{13}C {^{1}H} NMR Spectrum for **4f** (100 MHz, $CDCl_3$)



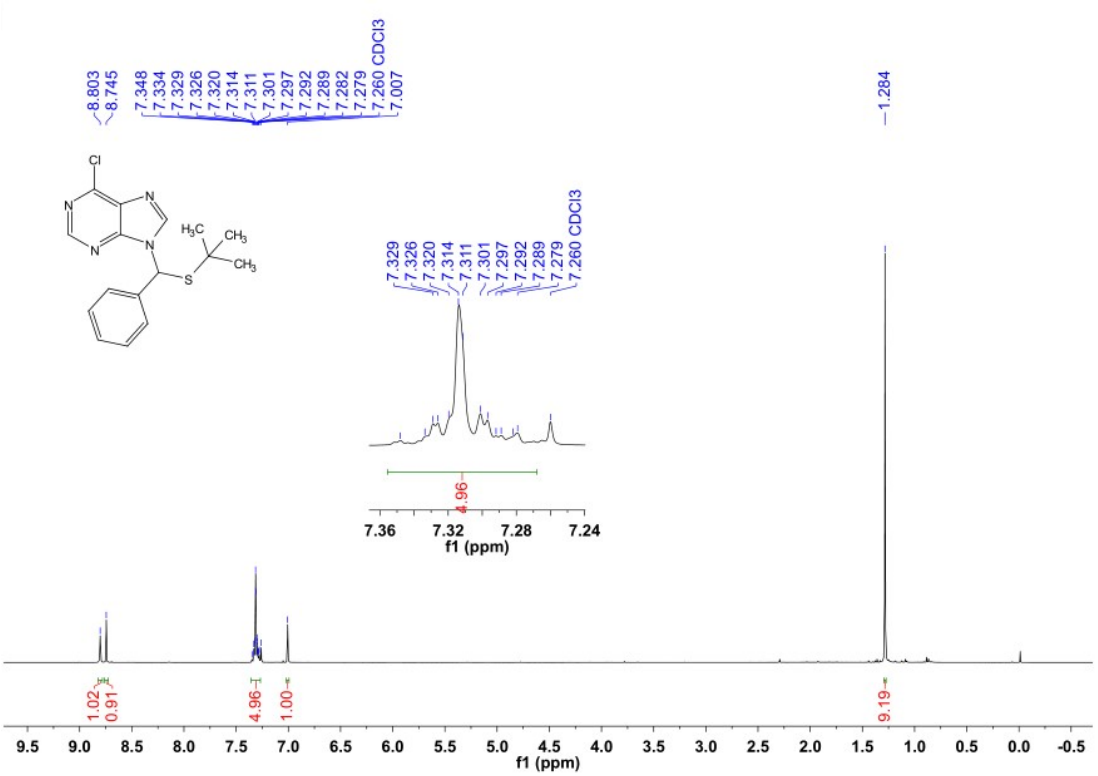
^{1}H NMR Spectrum for **4g** (400 MHz, $CDCl_3$)



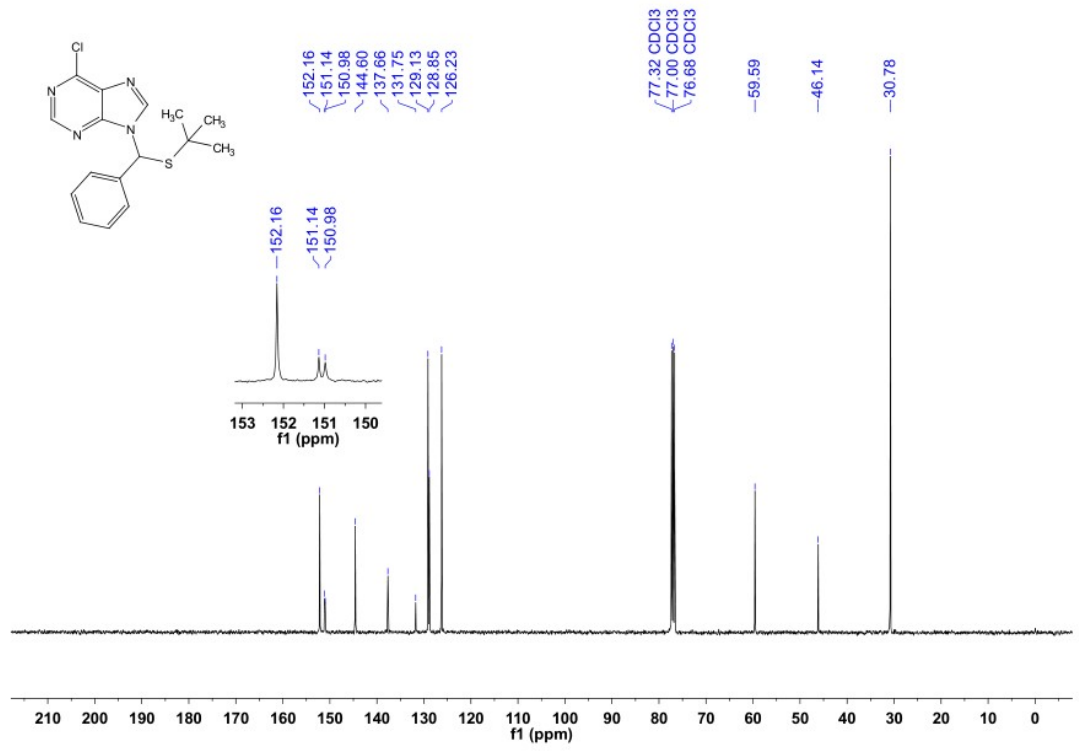
^{13}C {^{1}H} NMR Spectrum for **4g** (100 MHz, $CDCl_3$)



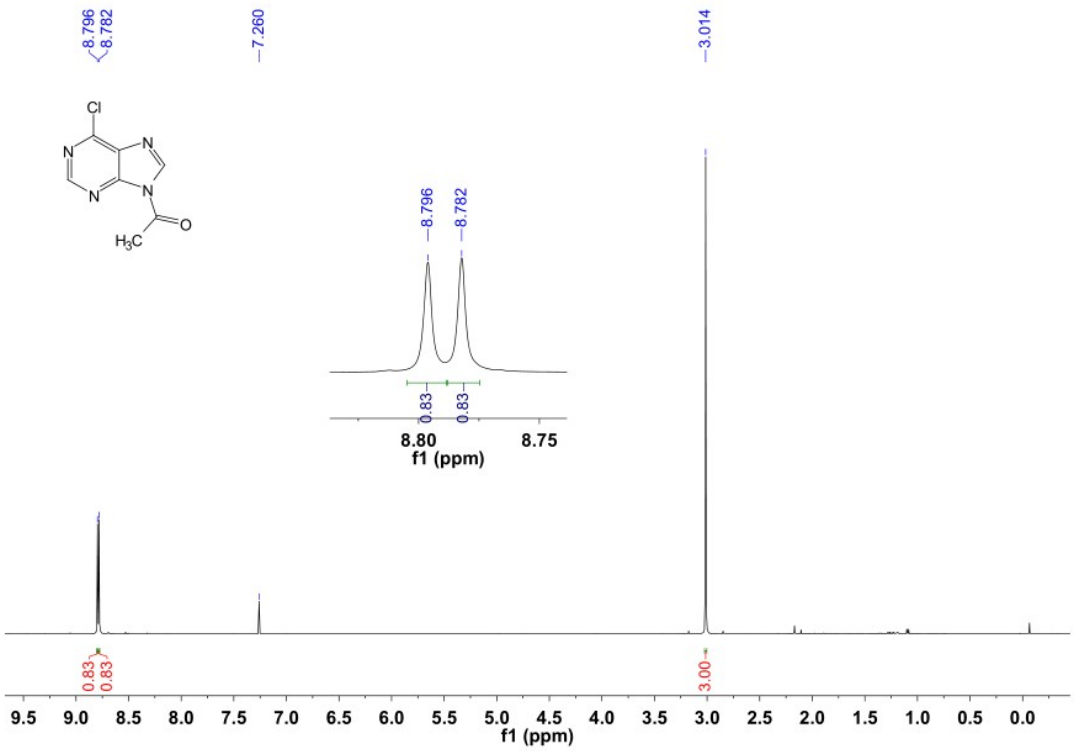
^{1}H NMR Spectrum for **4h** (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR Spectrum for **4h** (100 MHz, $CDCl_3$)



^{1}H NMR Spectrum for **5**(400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR Spectrum for **5** (100 MHz, $CDCl_3$)