The Supporting information for

CuBr Catalyzed C-N Cross Coupling Reaction of Purines and Diaryliodonium Salts to 9-Arylpurines

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General: Melting points were recorded with a micro melting point apparatus and uncorrected. NMR spectra were recorded with a 400 MHz spectrometer for ^{1}H-NMR, 100 MHz for ^{13}C-NMR. Chemical shifts δ were given in ppm relative to the residual proton signals of the deuterated solvent $CDCl_3$ for ^{1}H (7.26 ppm) and ^{13}C NMR (77.0 ppm). High resolution mass spectra were taken with a 3000 mass spectrometer, using Waters Q-TofMS/MS system. Elemental analyses were performed on a PE-2400 elemental analyzer. For column chromatography 200-300 mesh silica gel (GF254) was used as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

Typical Experimental Procedure

Purine **1** (0.5 mmol) was put in a 10 mL glass vial equipped with a small magnetic stirring bar. To this were added 2 mL dichloromethane, 1.5 equiv $Ar_2I^+X^-$, 10 mol% CuBr and 2 equiv K_2CO_3. The mixture was stirred in oil heating bath at reflux temperature under nitrogen for 2.5 h. Then the vial was cooled to room temperature. After evaporation of the solvent, the crude product was purified by column chromatography over silica gel using EtOAc/ petroleum ether (v/v=1:4) as the eluent, to give desired products **3**.

For desired products **3b**, **3d**, **3g** and **3n**, 50 mol% CuBr was needed.

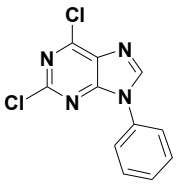
Diaryliodonium Salts were prepared according the reference[1] and cited there.[2]

General procedure to synthesis of diaryliodonium salts

Arene was dissolved or suspended either in concd H_2SO_4 or in a glacial AcOH–concd H_2SO_4 mixture and the resulting mixture was warmed up, with stirring, to 50-55 °C. While keeping the same temperature, $NaIO_4$ (10 mmol) was slowly added portionwise over 1.5 h. The stirring was continued at 50-55 °C for 1.5 h. The cooled final mixtures were poured into stirred ice-H_2O. Any precipitates were filtered off and rejected. The cold filtrates were extracted with Et_2O (4 × 50 mL) and the ethereal extracts (containing the unreacted initial arenes) were discarded. A solution of KBr (2.0 g) in H_2O (10 mL) was added to the vigorously stirred remaining aqueous solutions. The precipitated diaryliodonium bromides were collected by filtration and were washed well with cold H_2O until the filtrates were neutral, dried preliminarily by the suction, and air-dried in the dark to give the crude products.

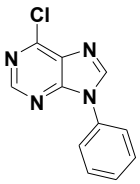
Characterization of compounds

2,6-dichloro-9-phenyl-*9H*-purine (3a)



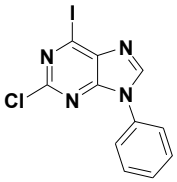
White powder, mp 239-241 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (s, 1H), 7.66 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 6.8 Hz, 2H), 7.51 (t, J = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 152.5, 152.4, 144.8, 133.4, 131.2, 130.2, 129.2, 123.5.

6-chloro-9-phenyl-*9H*-purine (3b)



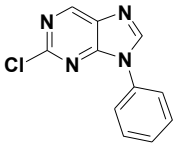
White powder, mp 202-203 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79 (s, 1H), 8.40 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.6, 151.6, 151.4, 144.1, 133.8, 132.1, 130.0, 128.9, 123.5.

2-chloro-6-iodo-9-phenyl-*9H*-purine (3c)



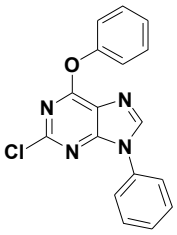
White powder, mp 119-121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (s, 1H), 7.64-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2, 148.6, 144.1, 138.3, 133.4, 130.1, 129.1, 123.5, 123.0. HRMS: calcd for $C_{11}H_6ClIN_4Na$ $[M + Na]^+$ 378.9223, found 378.9222.

2-chloro-9-phenyl-*9H*-purine (3d)



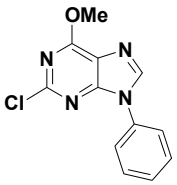
White powder, mp 174-175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.08 (s, 1H), 8.37 (s, 1H), 7.71-7.67 (m, 2H), 7.63-7.59 (m, 2H), 7.53-7.49 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 152.7, 150.8, 145.0, 133.6, 130.1, 128.9, 123.5. HRMS: calcd for $C_{11}H_8ClN_4$ $[M + H]^+$ 231.0437, found 231.0432.

2-chloro-6-phenoxy-9-phenyl-*9H*-purine (3e)



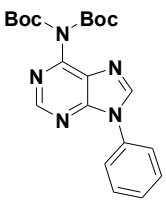
White powder, mp 249-250 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.47 (q, J = 8.0 Hz, 3H), 7.31 (d, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4, 153.6, 152.0, 142.5, 133.9, 130.0, 129.5, 128.7, 125.9, 123.5, 121.4, 121.1. HRMS: calcd for $C_{17}H_{12}ClN_4O$ $[M + H]^+$ 323.0700, found 323.0705.

2-chloro-6-methoxy-9-phenyl-*9H*-purine (3f)



White powder, mp 157-159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (s, 1H), 7.65-7.63 (m, 2H), 7.59-7.49 (m, 2H), 7.45-7.42 (m, 1H), 4.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 153.6, 152.5, 141.6, 134.0, 130.0, 129.9, 128.5, 123.4, 123.3, 120.9, 55.1. HRMS: calcd for $C_{12}H_9ClN_4NaO$ $[M + Na]^+$ 283.0363, found 283.0365.

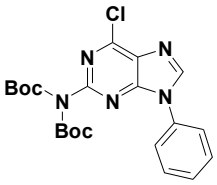
6-(N,N-diterbutoxycarbonyl)-9-phenyl-*9H*-purine (3g)



White powder, mp 129-130 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (s, 1H), 8.35 (s, 1H), 7.73 (d, J

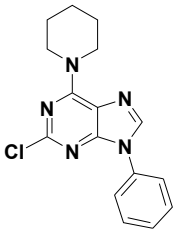
= 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 1.49 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.8, 150.5, 143.6, 134.2, 130.0, 129.3, 128.6, 123.5, 83.9, 27.8.

2-(N,N-diterbutoxycarbonyl)-6-chloro-9-phenyl-*9H*-purine (3h)



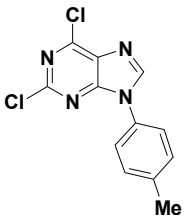
White powder, mp 179-180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.42 (s, 1H),7.69-7.67 (m, 2H), 7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H), 1.42 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 152.0, 151.6, 150.5, 144.7, 133.7, 130.4, 129.9, 128.8, 123.2, 83.6, 27.7.

2-chloro-9-phenyl-6-(piperidin-1-yl)-*9H*-purine (3i)



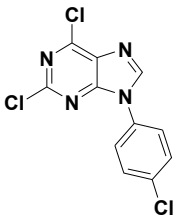
White powder, mp 187-188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (s, 1H),7.62 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.25 (brs, 4H), 1.73 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 154.0, 151.7, 137.3, 134.5, 129.7, 128.1, 123.7, 119.0, 26.1, 24.6. HRMS: calcd for $C_{16}H_{17}ClN_5$ $[M + H]^+$ 314.1172, found 314.1169.

2,6-dichloro-9-*p*-tolyl-*9H*-purine (3k)



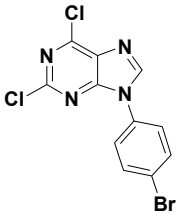
White powder, mp 202-204 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 152.6, 152.2, 144.9, 139.6, 131.1, 130.8, 130.7, 123.5, 21.2.

2,6-dichloro-9-(4-chlorophenyl)-*9H*-purine (3l)



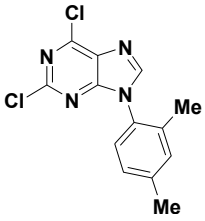
White powder, mp 202-203 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 152.4, 152.3, 144.3, 135.1, 131.8, 131.1, 130.3, 124.6. HRMS: calcd for $C_{11}H_6Cl_3N_4$ $[M + H]^+$ 298.9658, found 298.9653.

9-(4-bromophenyl)-2,6-dichloro-*9H*-purine (3m)



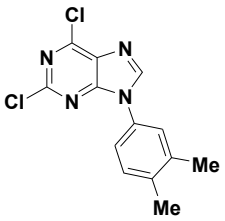
White powder, mp 197-198 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 152.6, 152.4, 144.2, 133.4, 132.4, 131.2, 124.9, 123.1. HRMS: calcd for $C_{11}H_6BrCl_2N_4$ $[M + H]^+$ 342.9153, found 342.9154.

2,6-dichloro-9-(2,4-dimethylphenyl)-*9H*-purine (3n)



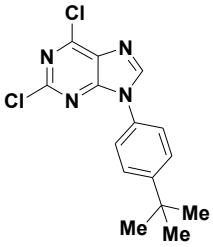
White powder, mp 206-207 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (s, 1H), 7.24 (s, 1H), 7.19-7.14 (m, 2H), 2.42 (s, 3H), 2.09(s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 153.4, 152.2, 146.2, 140.8, 134.7, 132.4, 130.5, 129.2, 128.0, 127.0, 21.2, 17.8. HRMS: calcd for $C_{13}H_{11}Cl_2N_4$ $[M + H]^+$ 293.0361, found 293.0365.

2,6-dichloro-9-(3,4-dimethylphenyl)-*9H*-purine (3o)



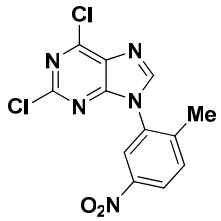
White powder, mp 215-216 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (s, 1H), 7.36-7.30 (m, 3H), 2.35 (s, 3H), 2.33(s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 152.6, 152.1, 145.0, 138.8, 138.2, 131.1, 131.0, 130.9, 124.6, 121.0, 19.9, 19.9. HRMS: calcd for $C_{13}H_{11}Cl_2N_4$ $[M + H]^+$ 293.0361, found 293.0356.

9-(4-tert-butylphenyl)-2,6-dichloro-*9H*-purine (3p)



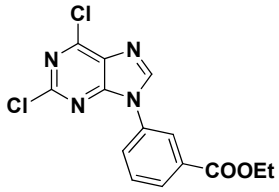
Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (s, 1H), 7.59-7.54 (m, 4H), 1.34 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.4, 152.5, 152.4, 152.1, 144.9, 131.0, 130.6, 127.0, 123.1, 34.7, 31.1. HRMS: calcd for $C_{15}H_{15}Cl_2N_4$ $[M + H]^+$ 321.0674, found 321.0668. Elemental analysis, $C_{15}H_{14}Cl_2N_4$ requires: C, 56.09; H, 4.39; Cl, 22.08; N, 17.44; Found: C, 56.10; H, 4.38; Cl, 22.09, N, 17.43.

2,6-dichloro-9-(2-methyl-5-nitrophenyl)-9*H*-purine (3r)



White powder, mp 212-214 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (dd, J_1 = 8.4 Hz, J_2 = 2 Hz, 1H), 8.22 (d, J = 2.4 Hz, 1H), 8.21 (s, 1H), 7.67 (d, J = Hz, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.2, 153.1, 152.9, 146.9, 145.0, 143.1, 132.8, 132.6, 130.6, 125.2, 122.9, 18.5. HRMS: calcd for $C_{12}H_8Cl_2N_5O_2$ $[M + H^+]$ 324.0055, found 324.0053.

ethyl 3-(2,6-dichloro-9*H*-purin-9-yl)benzoate (3s)



White powder, mp 156-158 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (s, 1H), 8.28 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 4.43 (q, *J* = 4.0 Hz, 2H), 1.42 (t, *J* = 4.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.0, 153.9, 152.5, 152.5, 144.5, 133.6, 132.7, 131.1, 130.3, 130.1, 127.7, 124.3, 61.8, 14.2. HRMS: calcd for $C_{14}H_{11}Cl_2N_4O_2$ [M + H^+] 337.0259, found 337.0255.

X-ray Crystal Structural

X-ray Crystal Structural of 2,6-dichloro-9-(4-chlorophenyl)-9*H*-purine (3l)

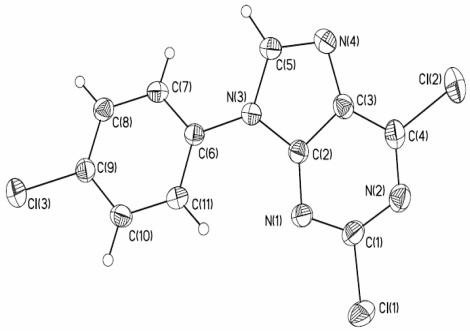
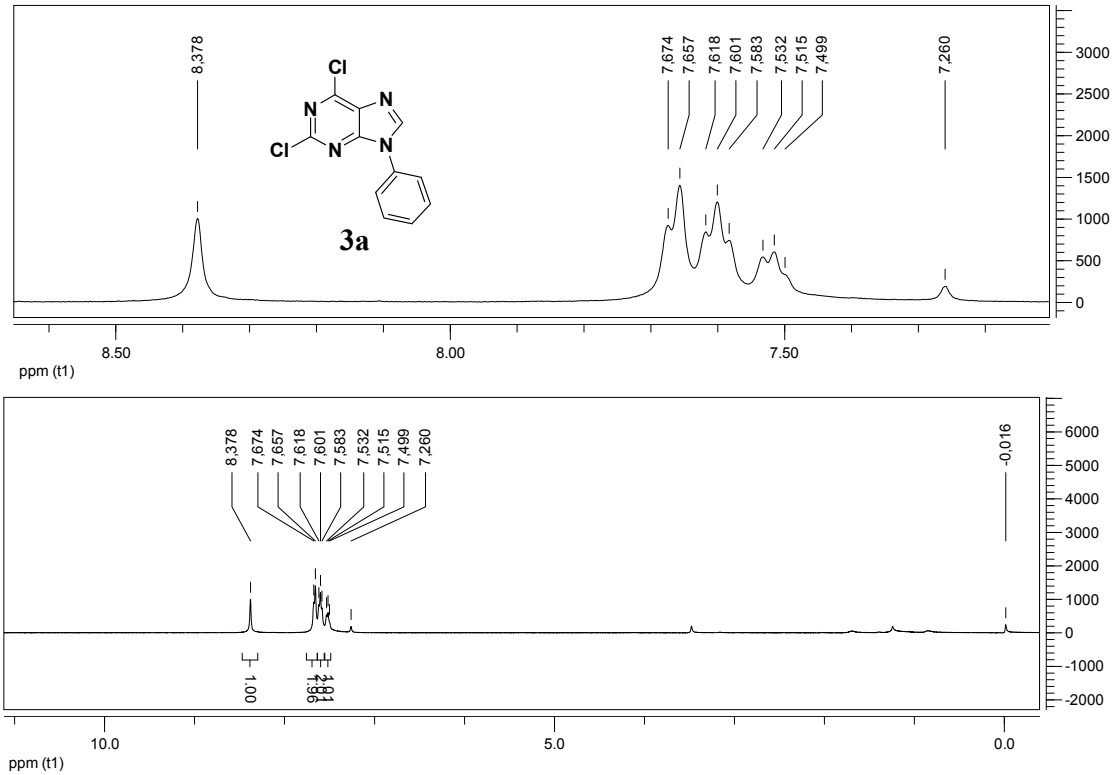


Figure 1. The molecular structure of 3l

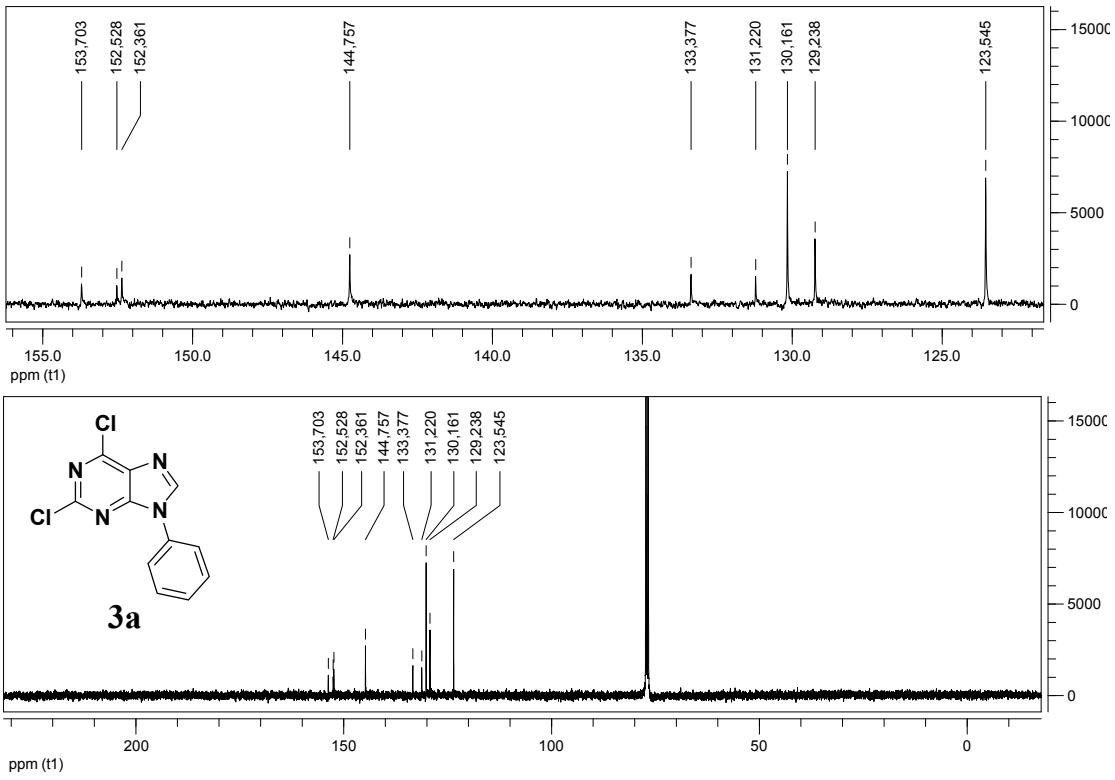
References

1. a) E. A. Merritt, B. Olofsson, *Angew. Chem., Int. Ed.* **2009**, *48*, 9052; b) B. Wang, J. W. Graskemper, L. Qin, S. G. DiMagno, *Angew. Chem., Int. Ed.* **2010**, *49*, 4079.
2. a) L. Kraszkiewicz, L. Skulski, *Synthesis* **2008**, *15*, 2373. b) J. V. Crivello, J. H. W. Lam, *Macromolecules* **1977**, *10,* 1307.

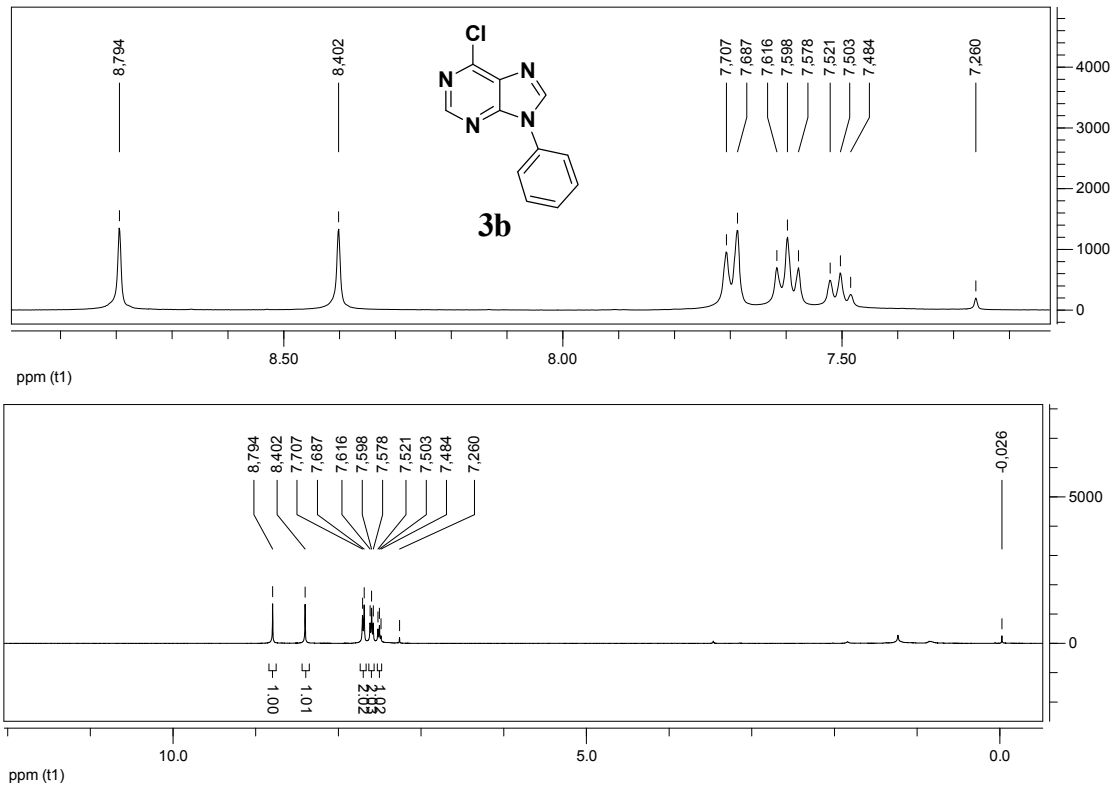
^{1}H NMR of compound **3a**



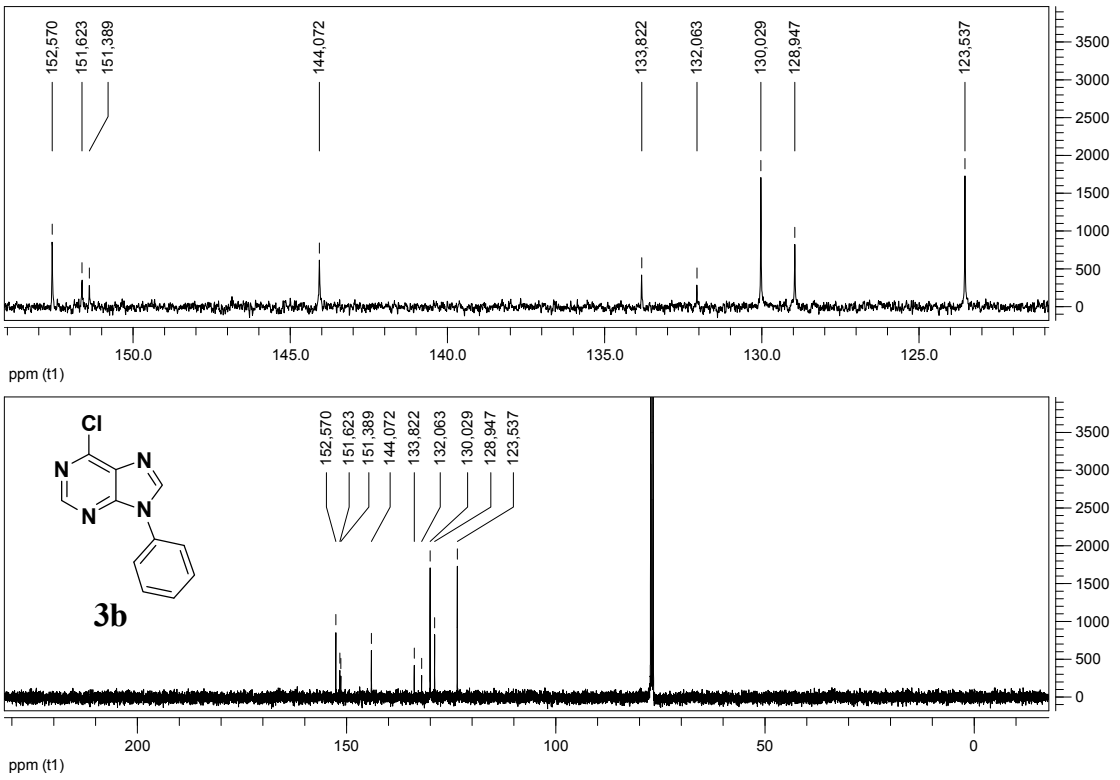
^{13}C NMR of compound **3a**



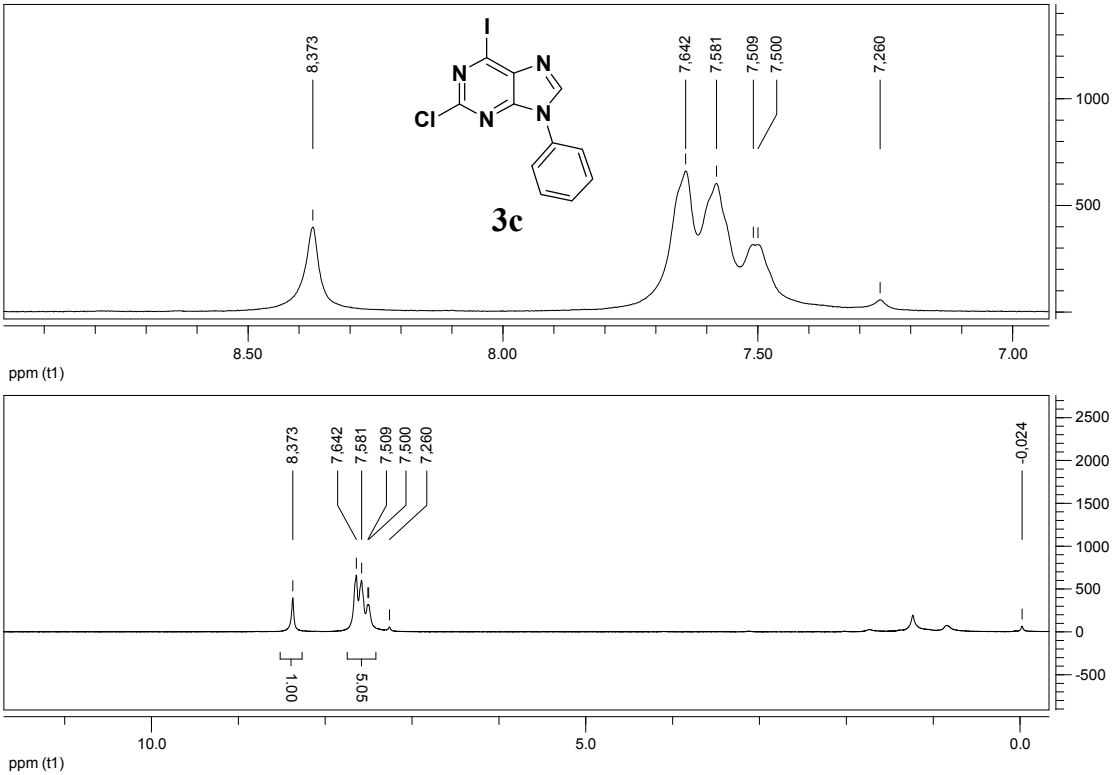
^{1}H NMR of compound **3b**



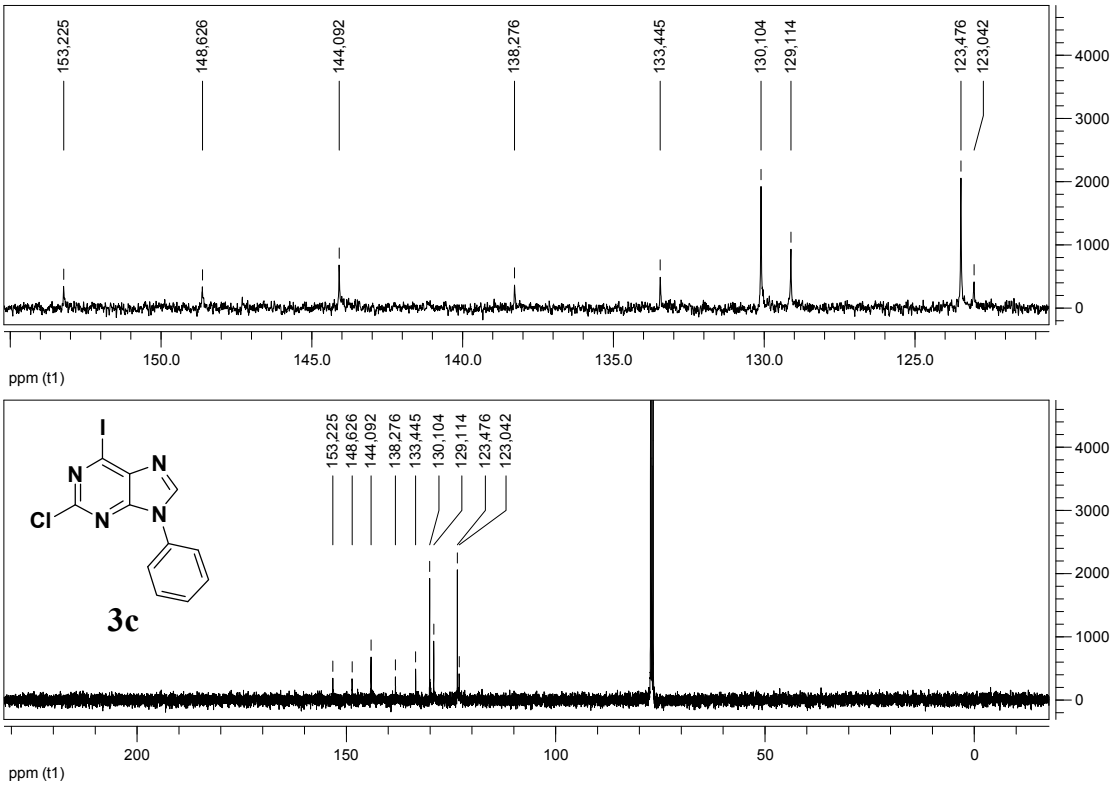
^{13}C NMR of compound **3b**



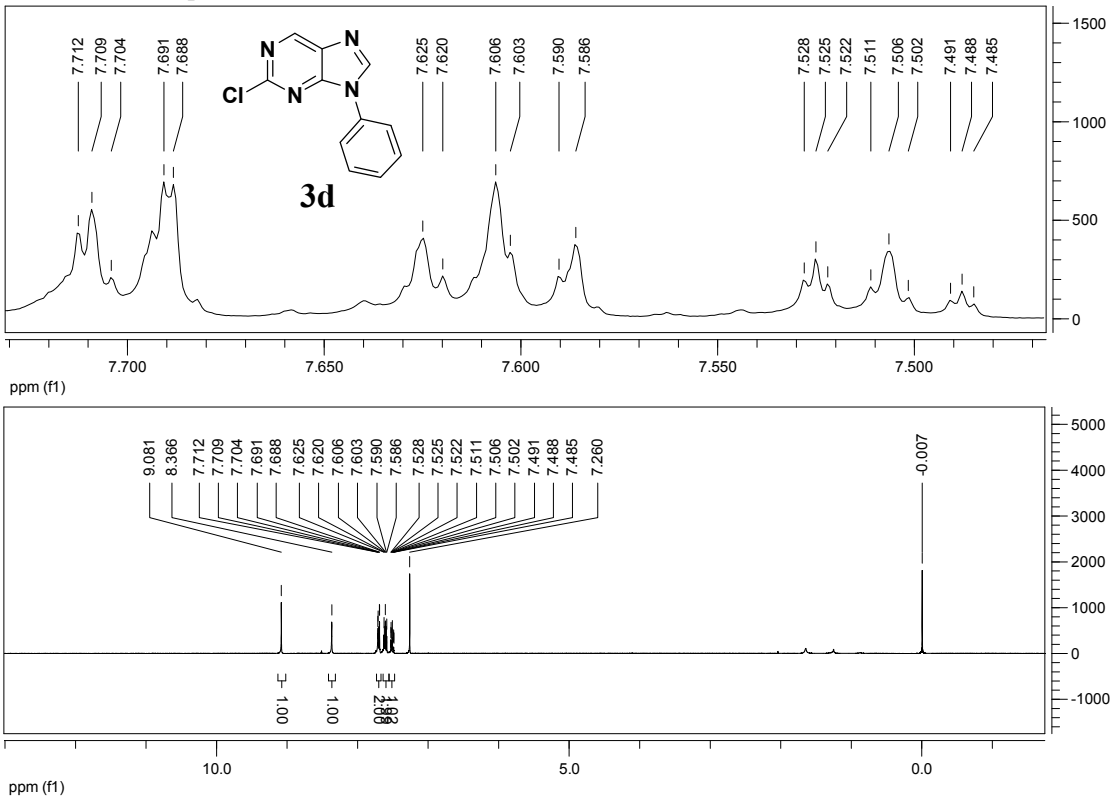
^{1}H NMR of compound **3c**



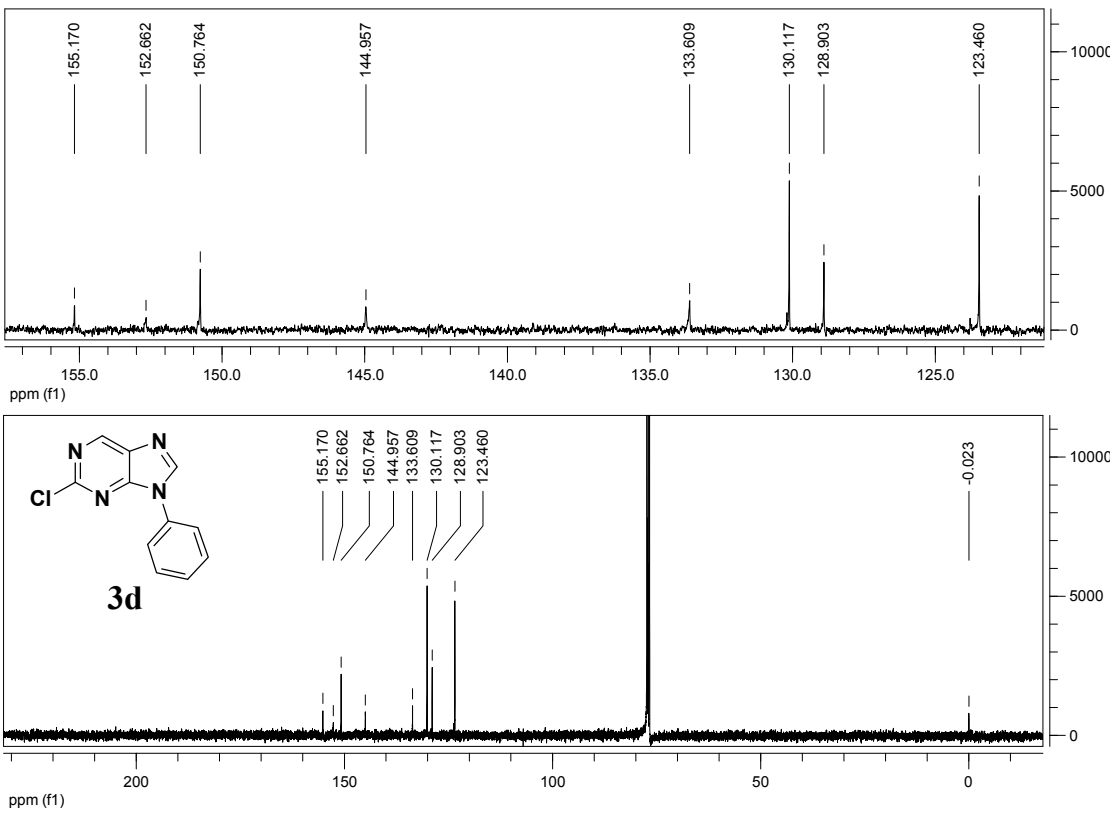
^{13}C NMR of compound **3c**



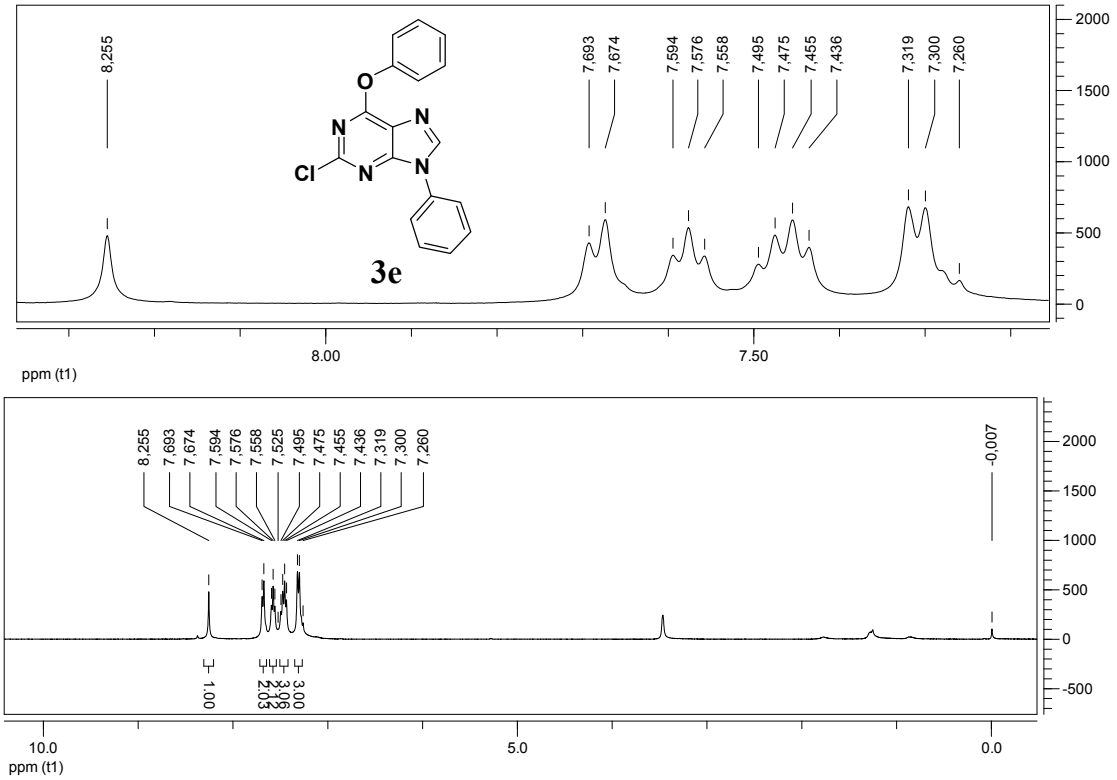
^{1}H NMR of compound **3d**



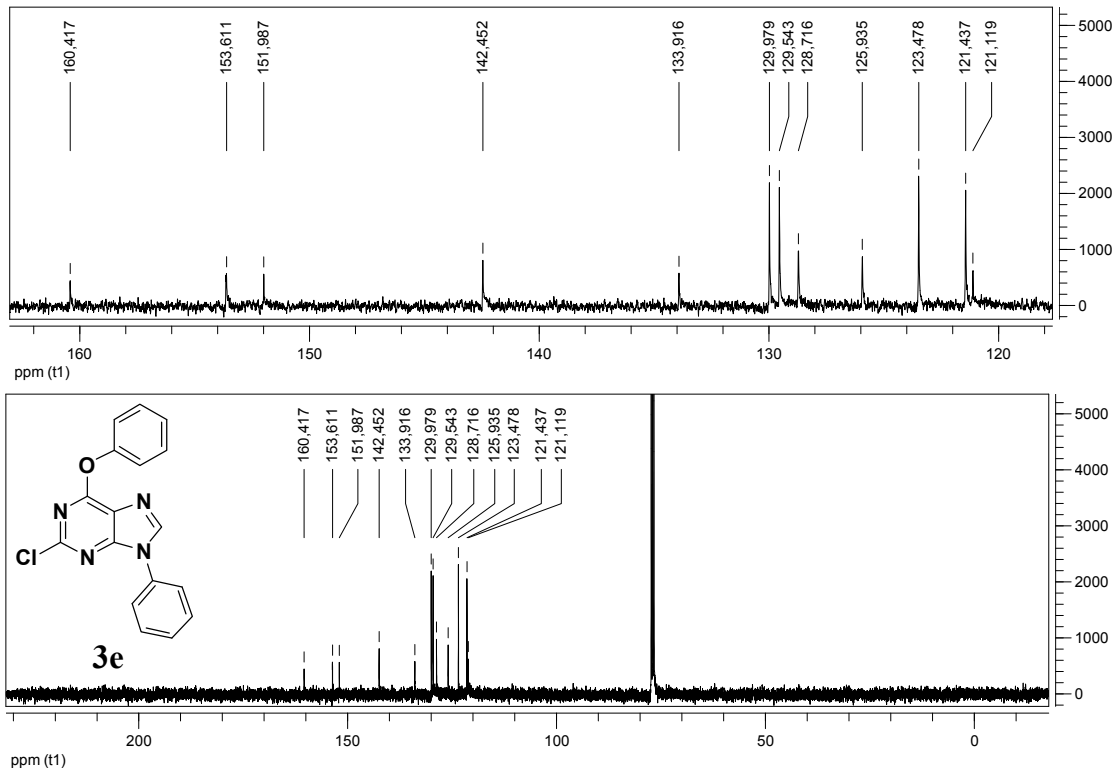
^{13}C NMR of compound **3d**



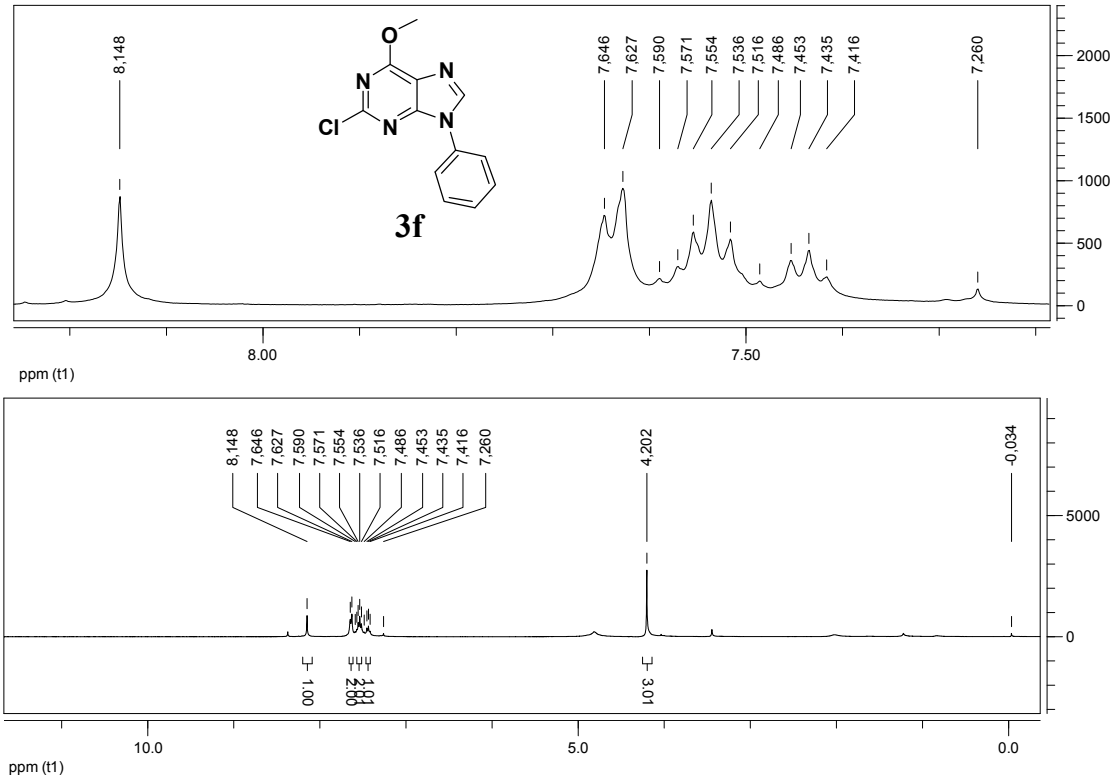
^{1}H NMR of compound **3e**



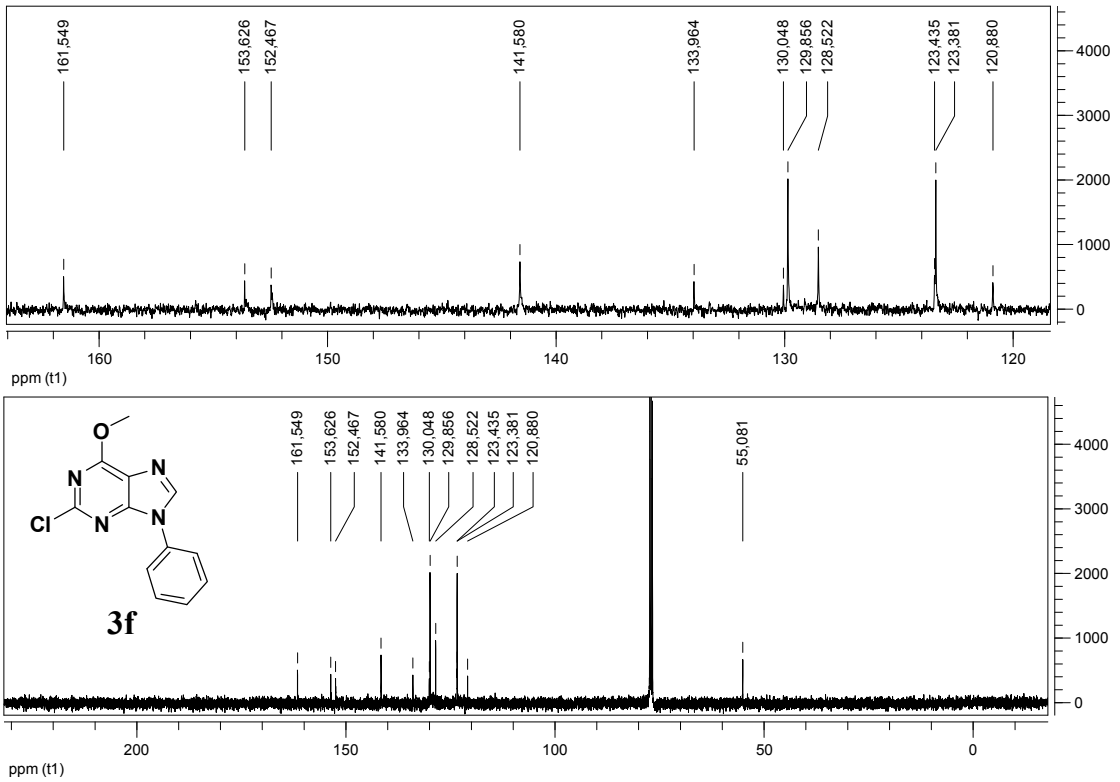
^{13}C NMR of compound **3e**



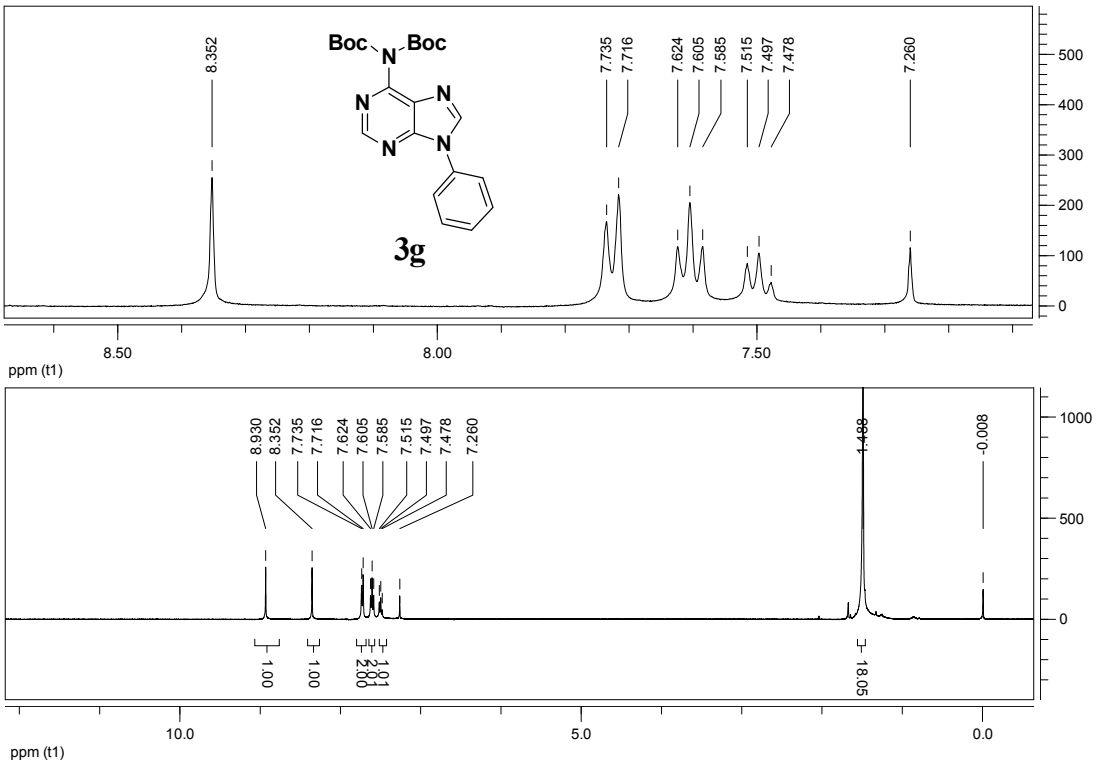
^{1}H NMR of compound **3f**



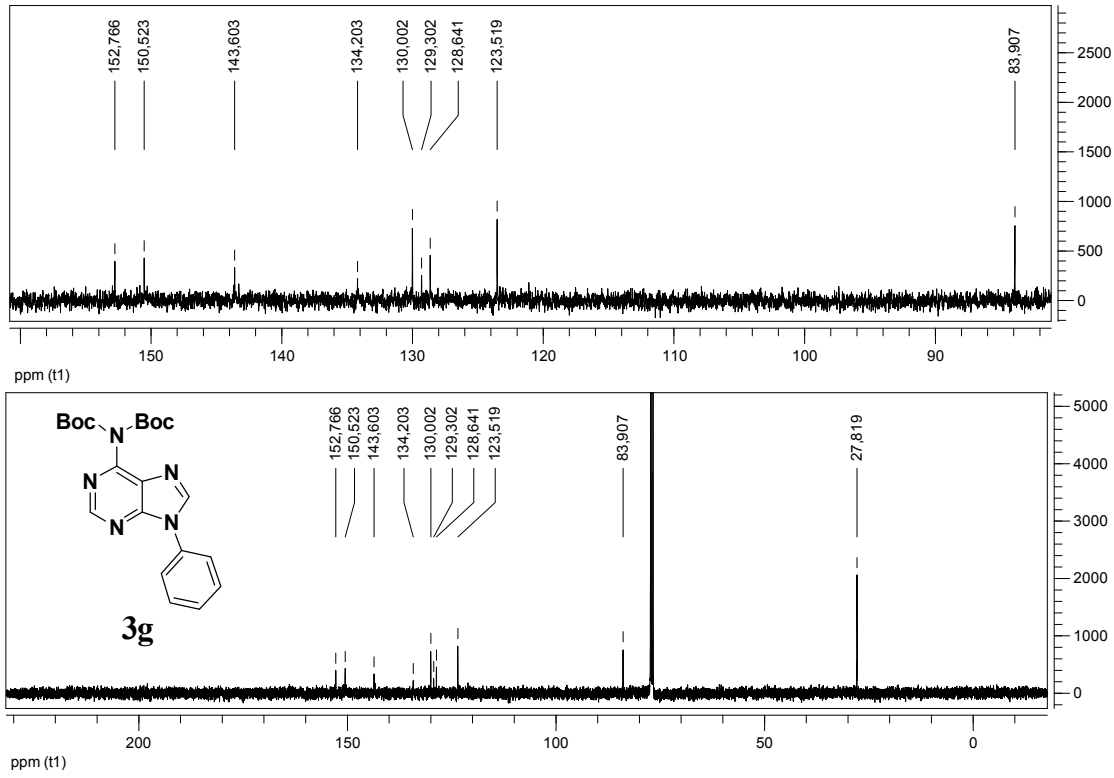
^{13}C NMR of compound **3f**



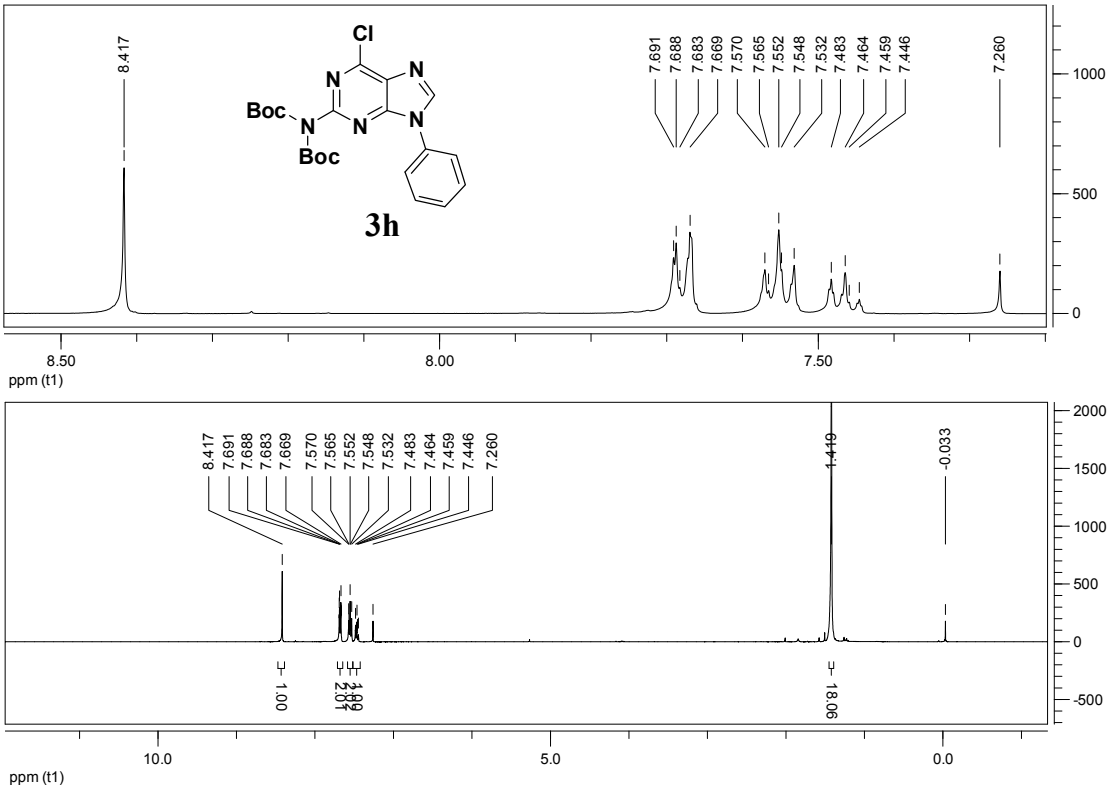
^{1}H NMR of compound **3g**



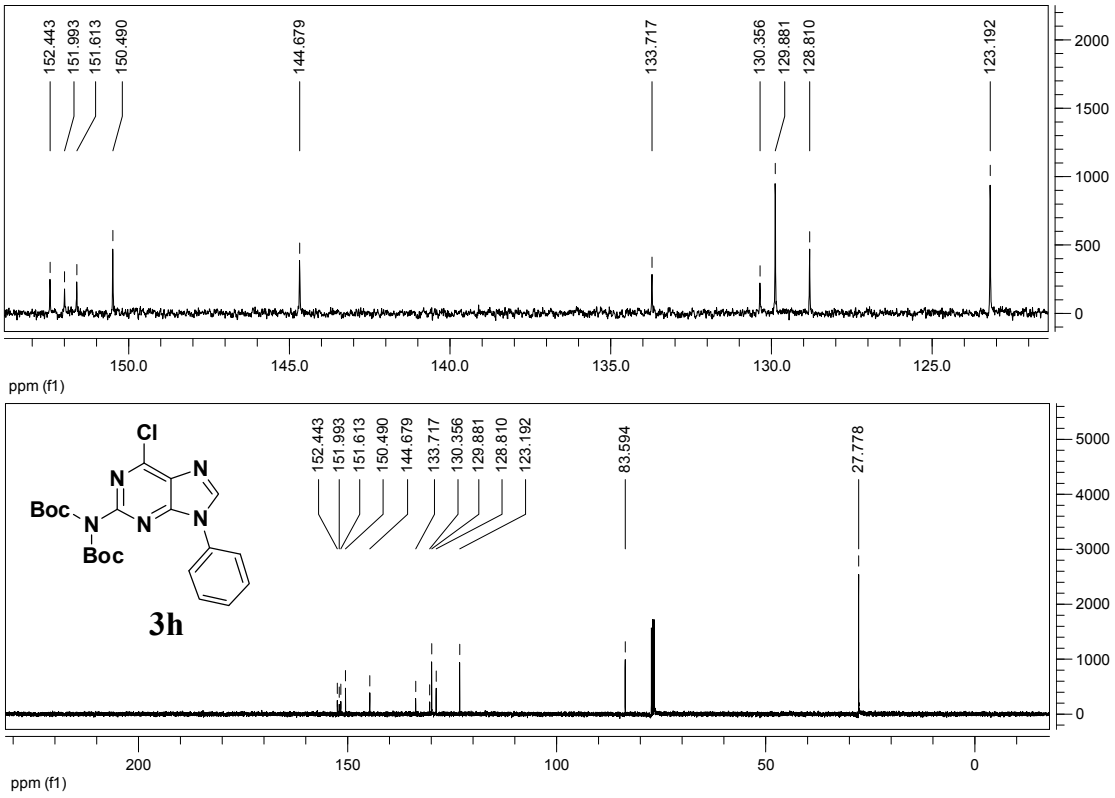
^{13}C NMR of compound **3g**



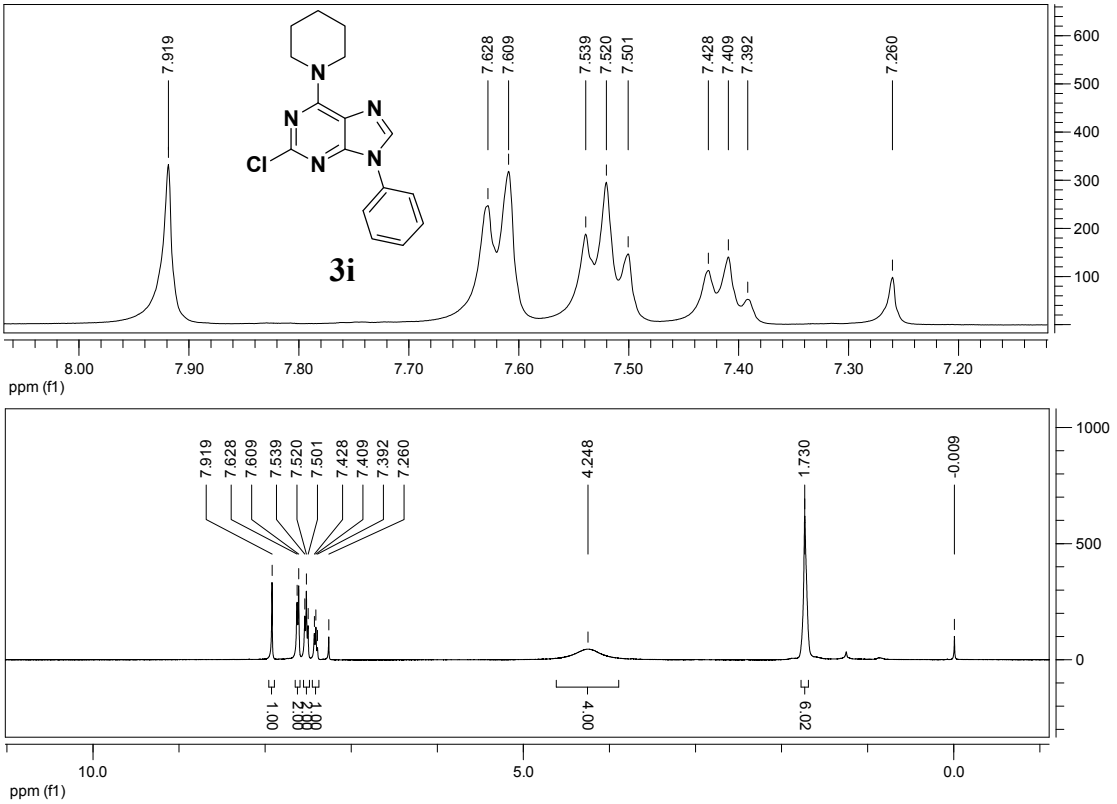
^{1}H NMR of compound **3h**



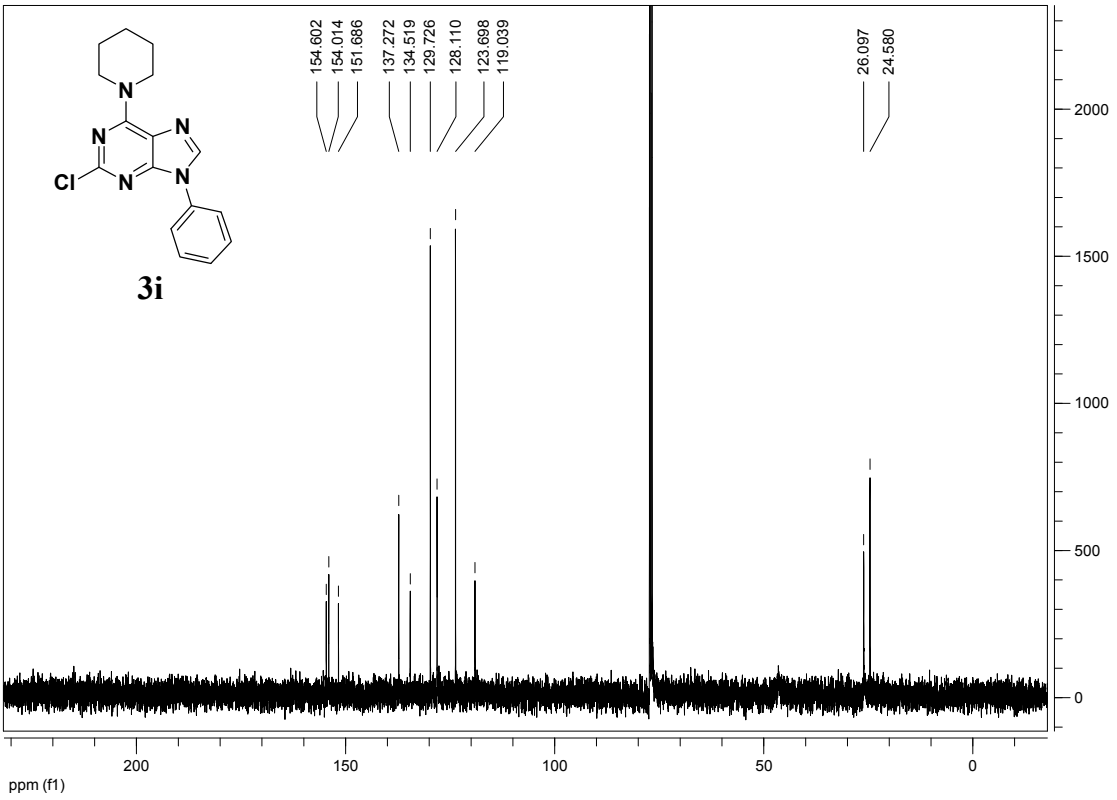
^{13}C NMR of compound **3h**



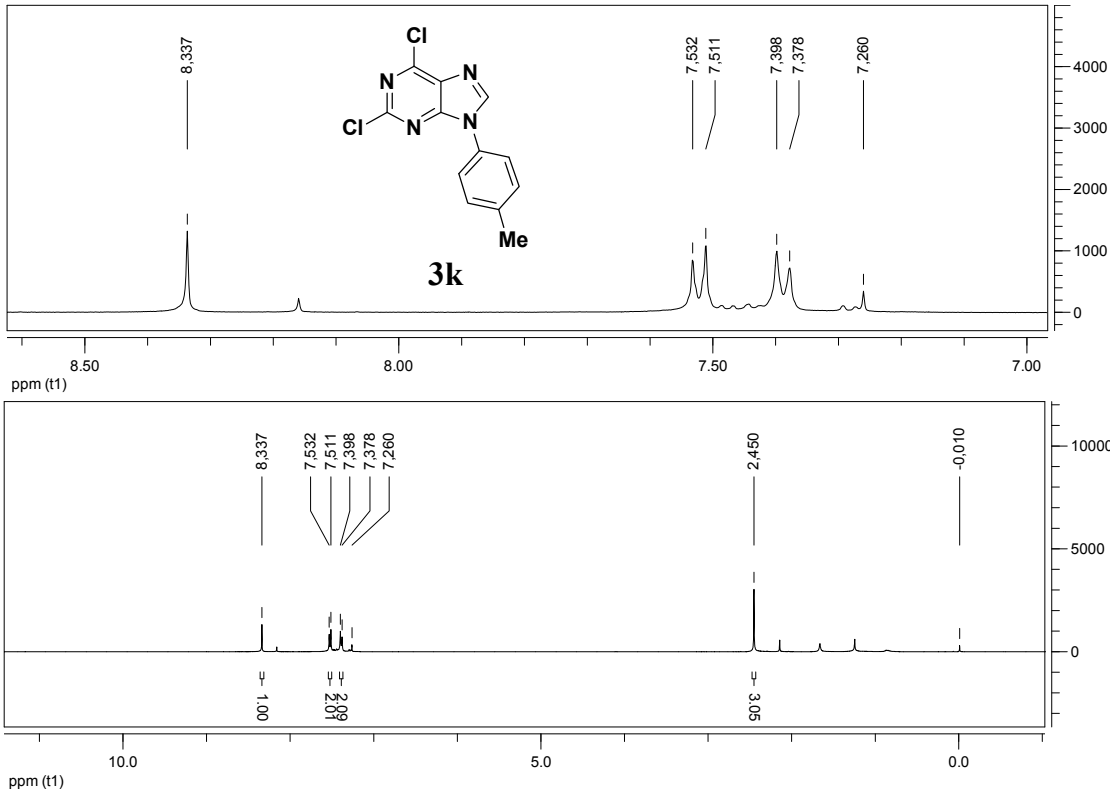
^{1}H NMR of compound **3i**



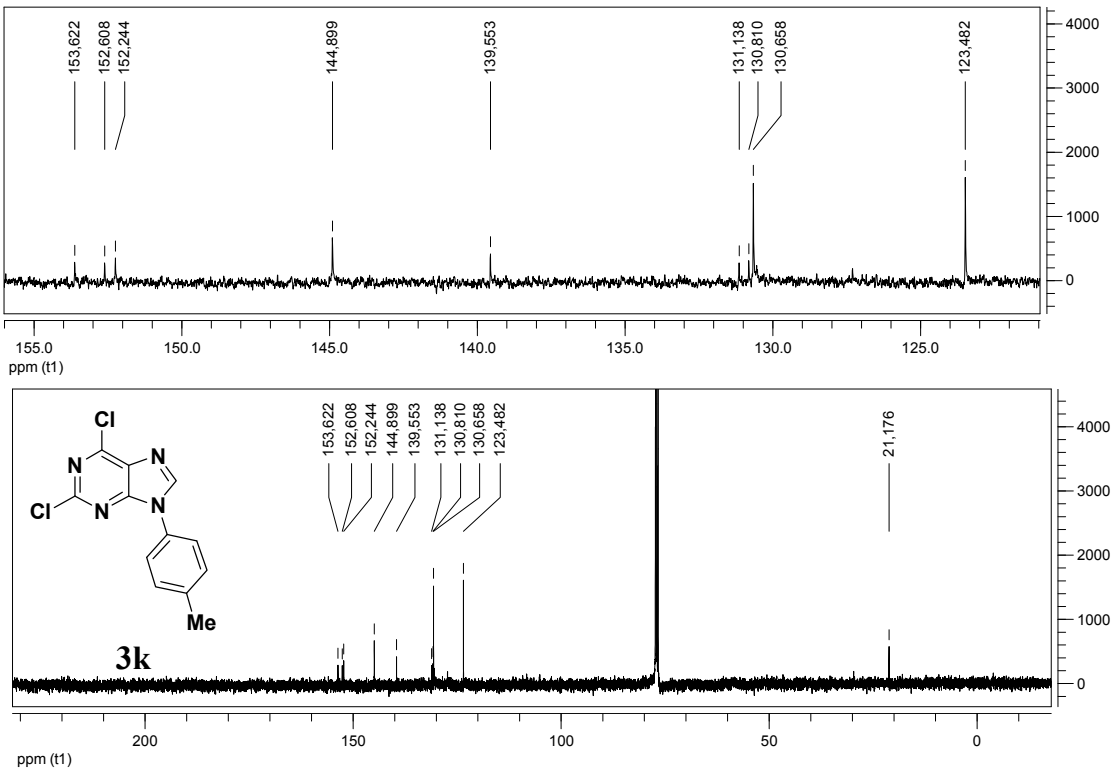
^{13}C NMR of compound **3i**



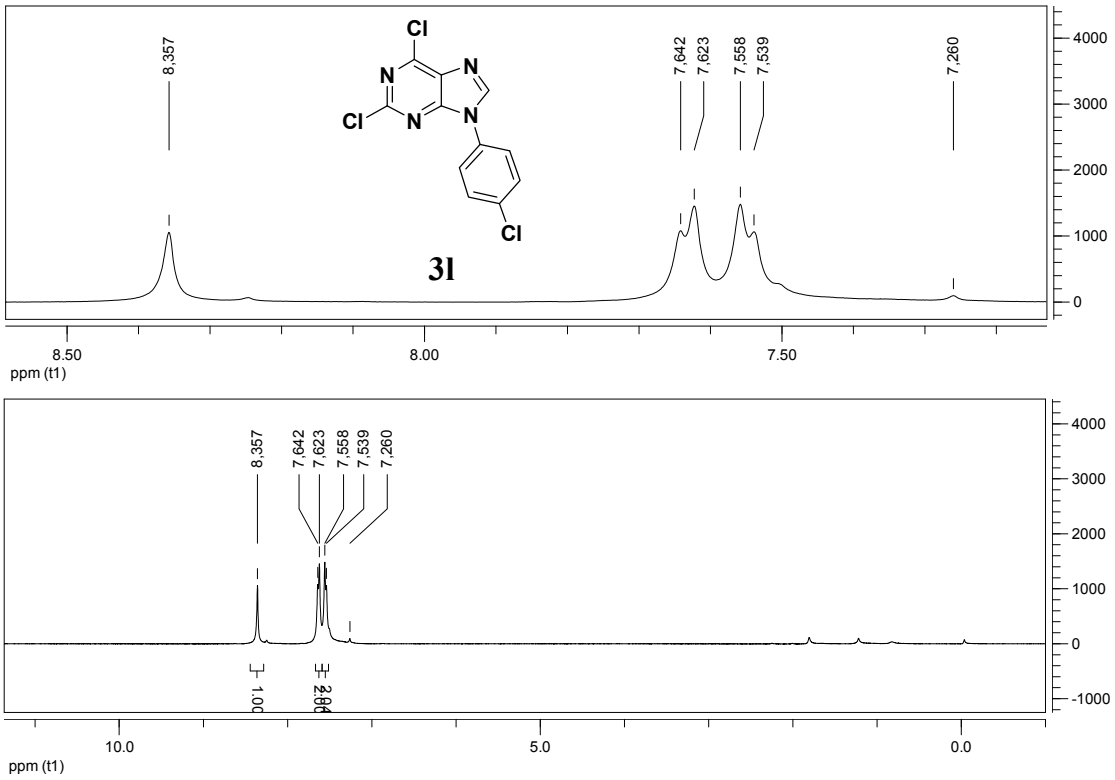
^{1}H NMR of compound **3k**



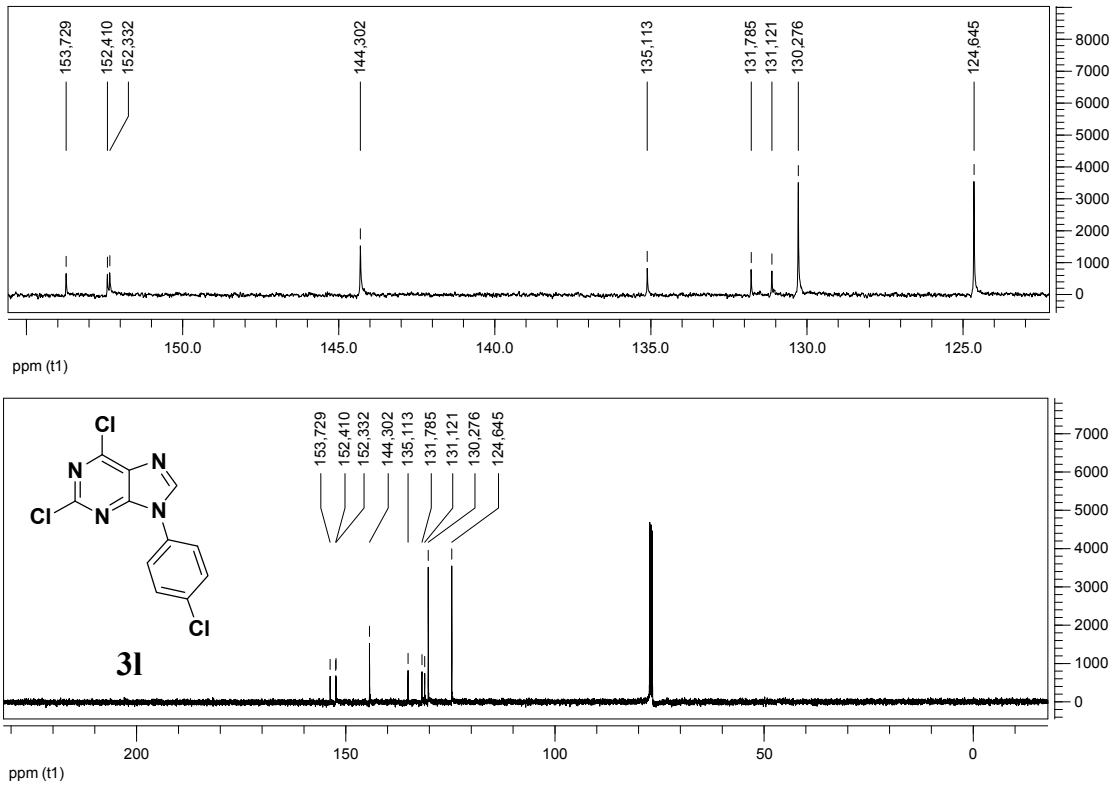
^{13}C NMR of compound **3k**



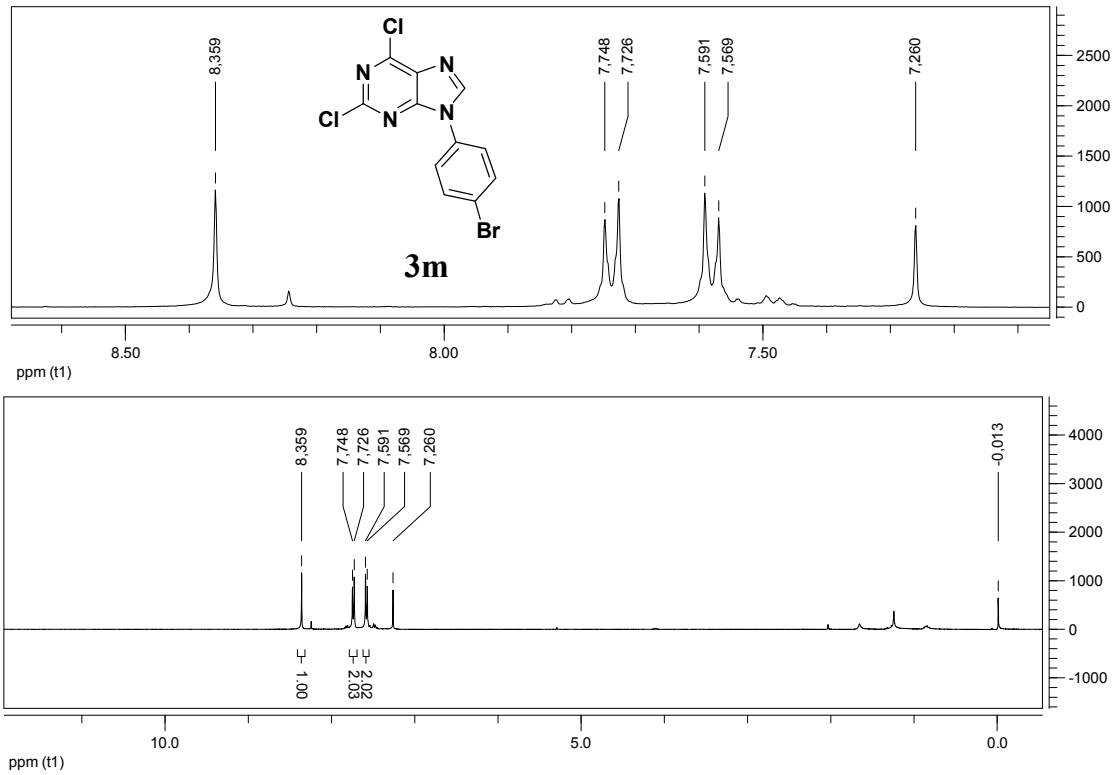
^{1}H NMR of compound **3l**



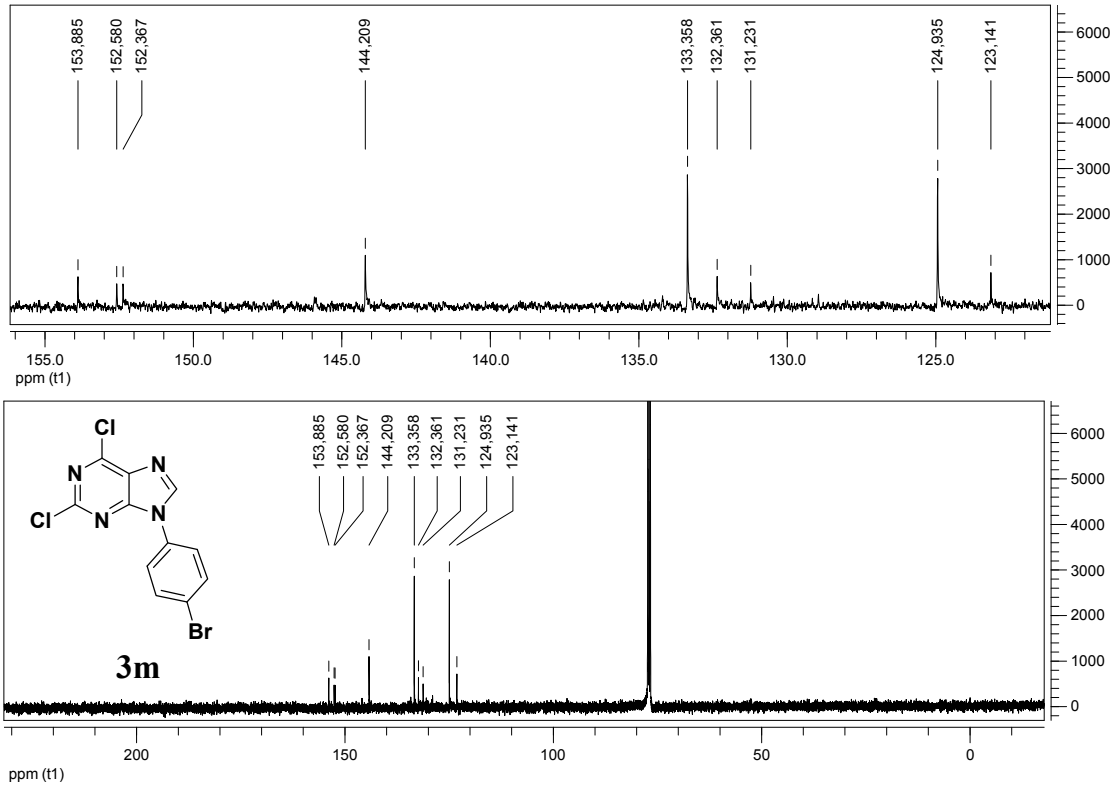
^{13}C NMR of compound **3l**



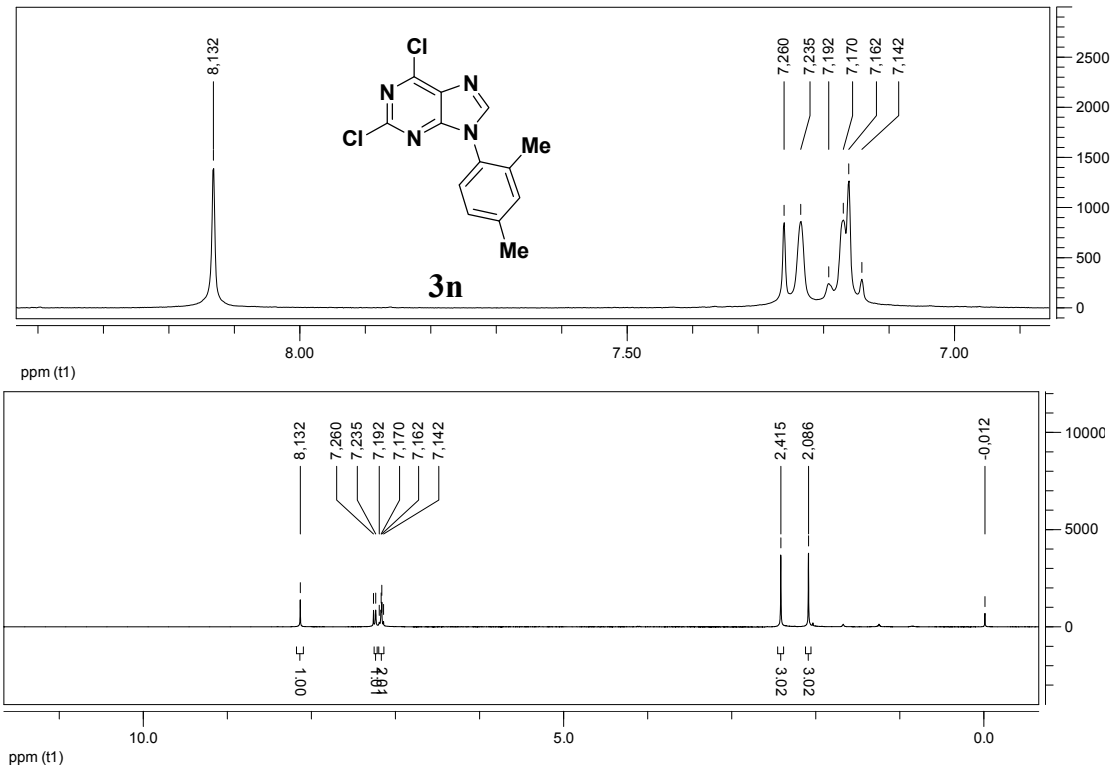
^{1}H NMR of compound **3m**



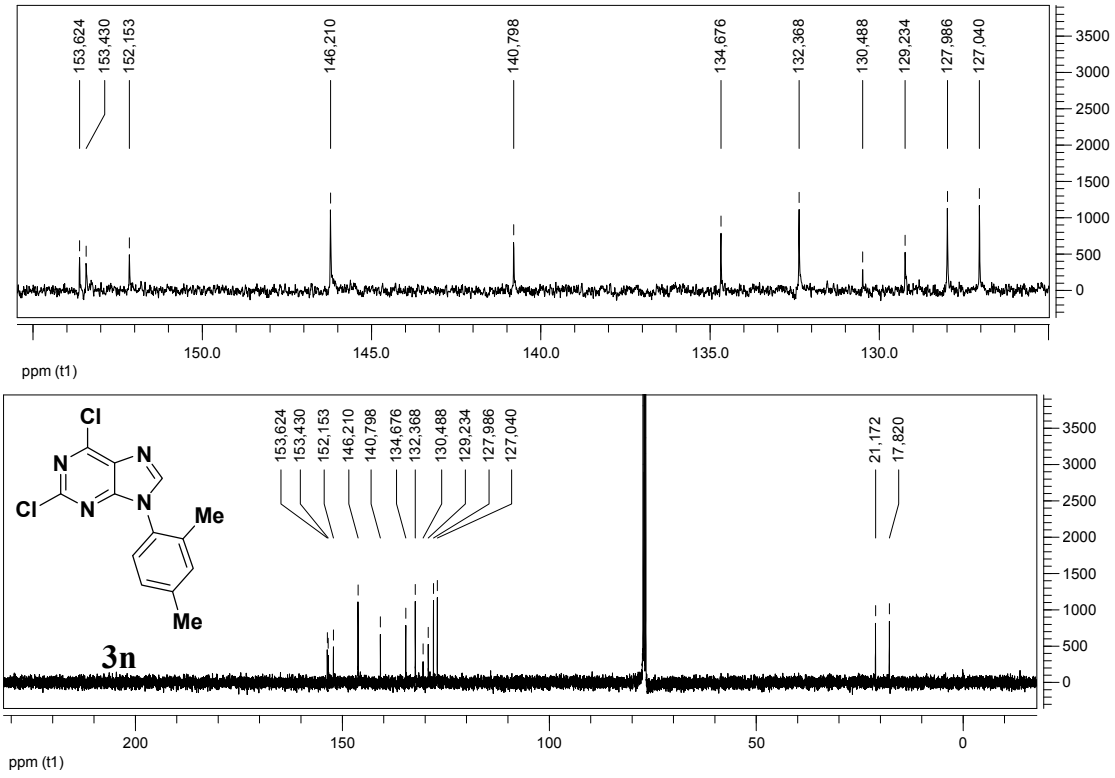
^{13}C NMR of compound **3m**



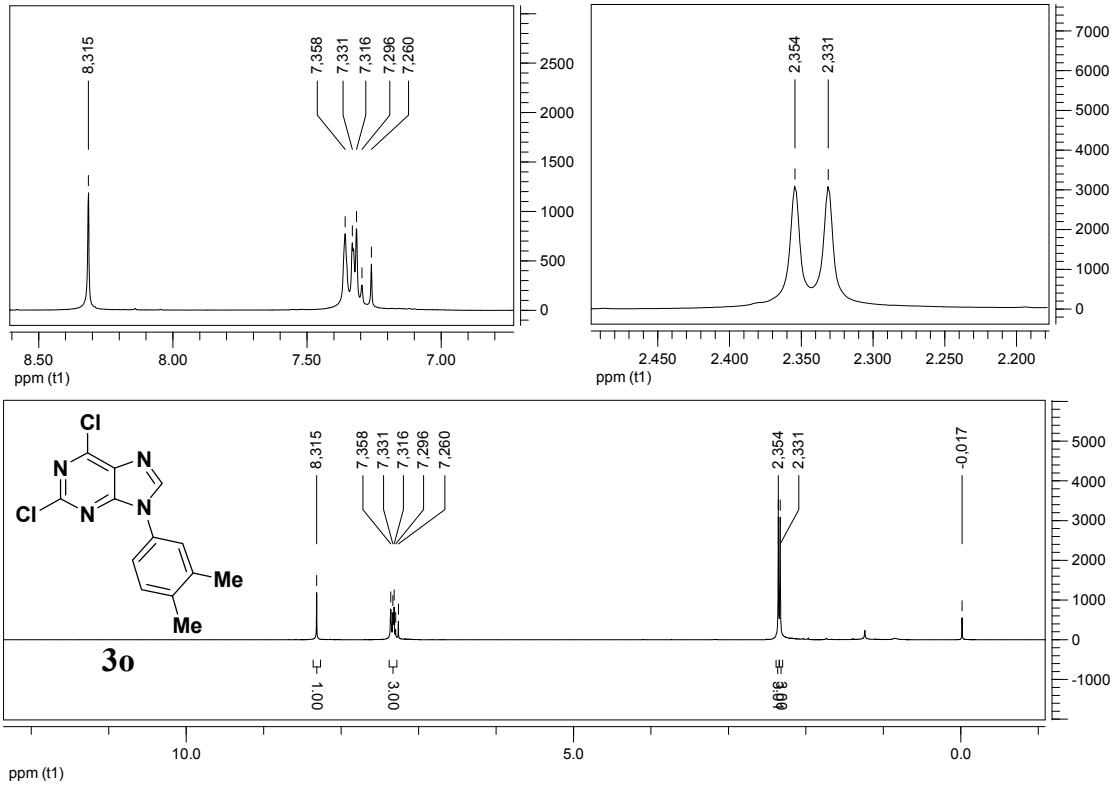
^{1}H NMR of compound **3n**



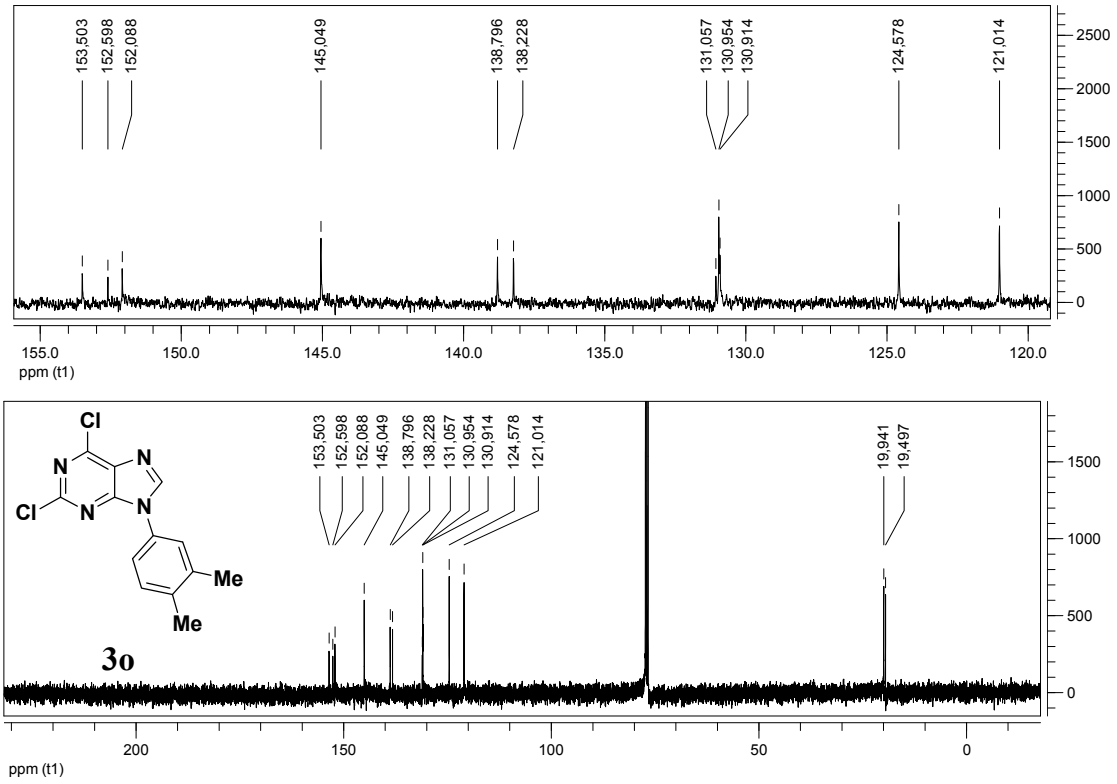
^{13}C NMR of compound **3n**



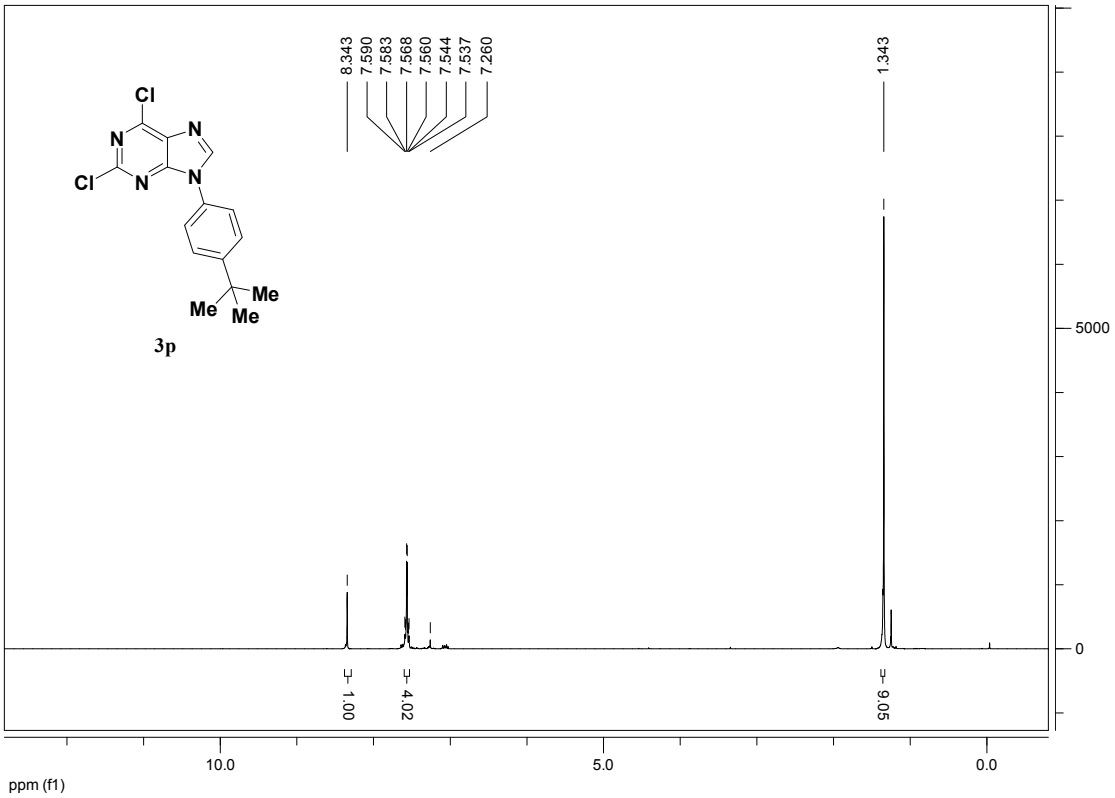
^{1}H NMR of compound **3o**



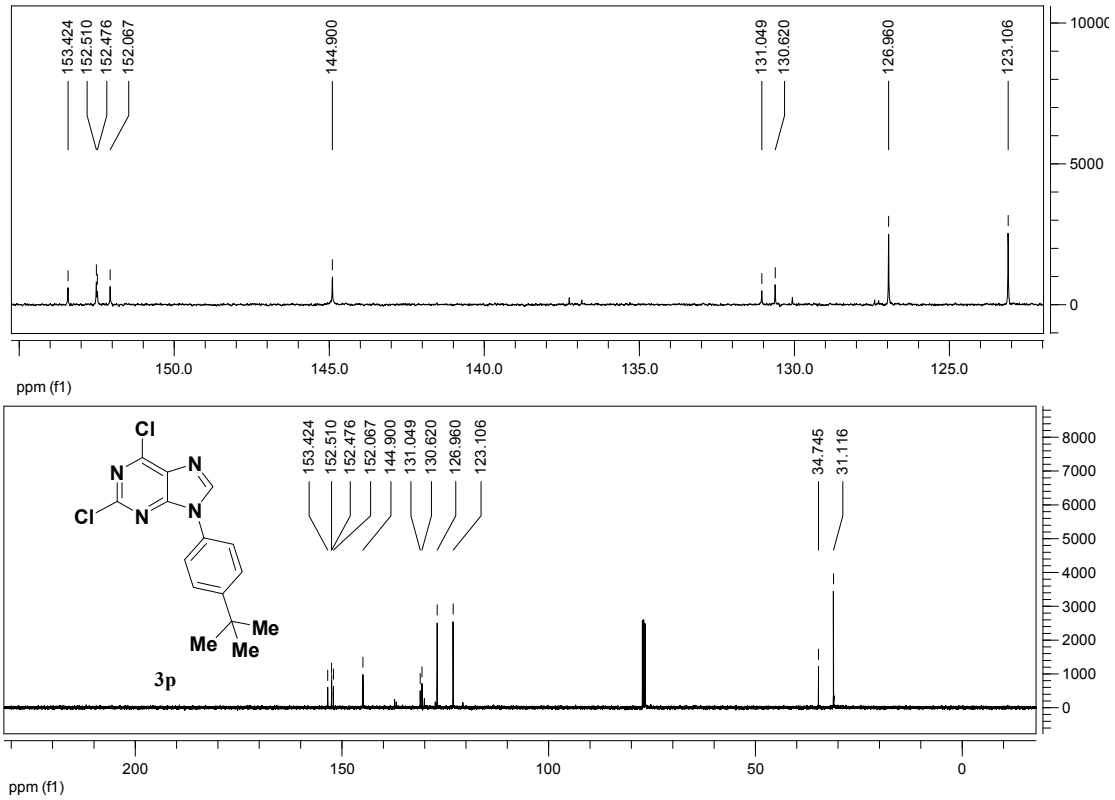
^{13}C NMR of compound **3o**



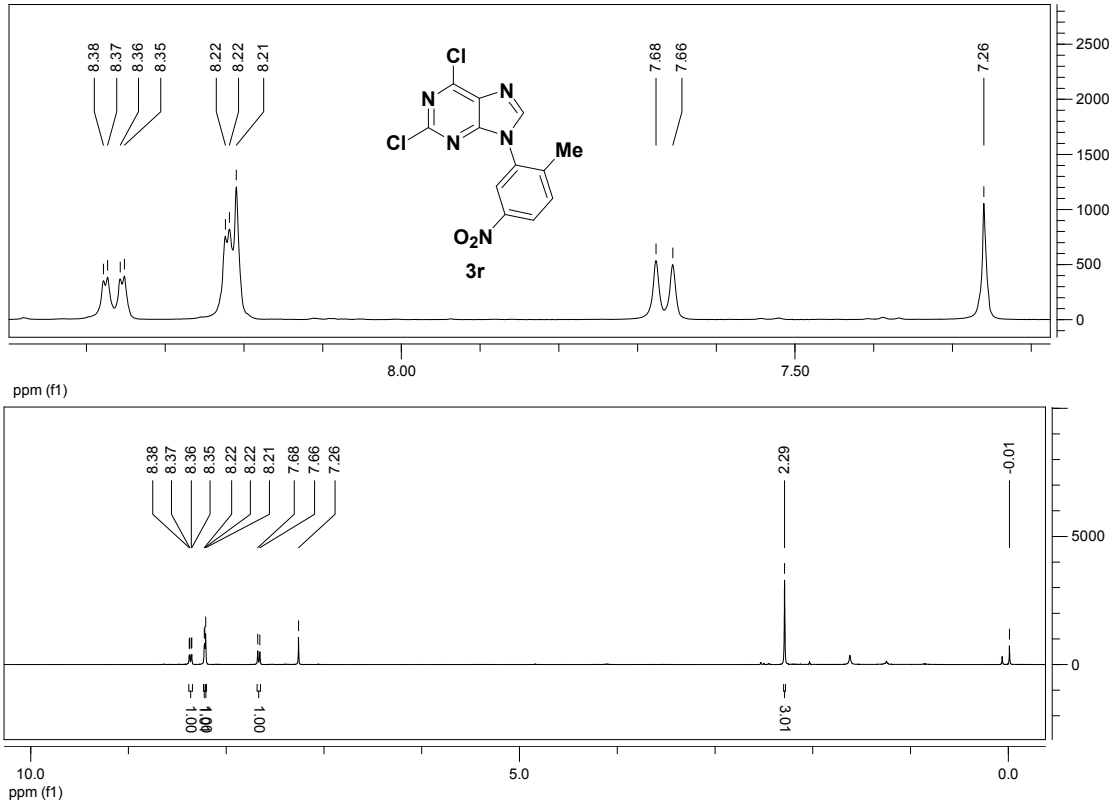
^{1}H NMR of compound **3p**



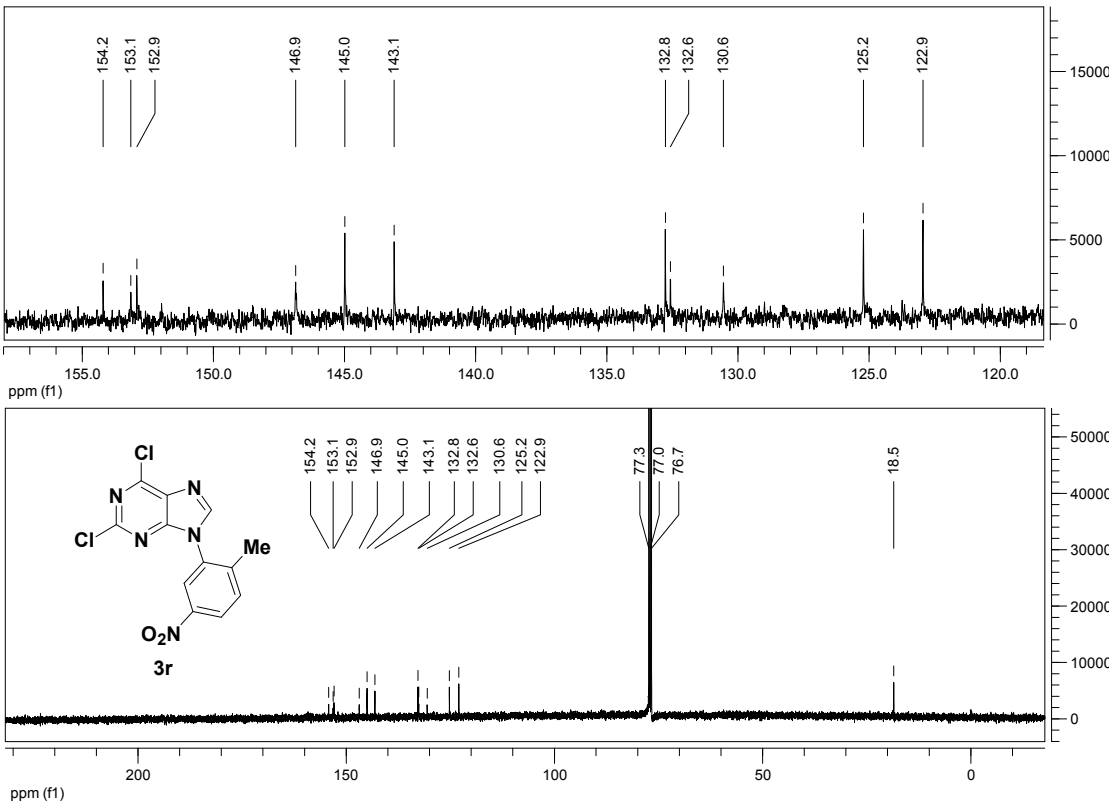
^{13}C NMR of compound **3p**



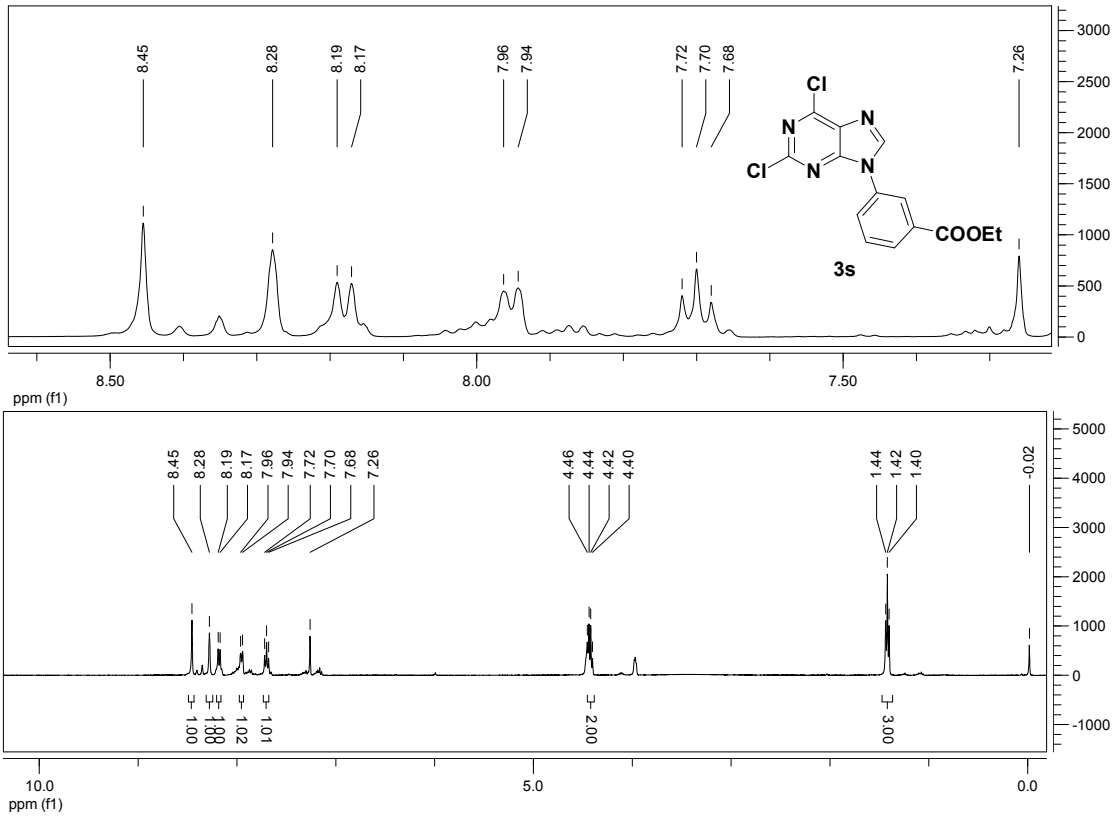
^{1}H NMR of compound **3r**



^{13}C NMR of compound **3r**



^{1}H NMR of compound **3s**



^{13}C NMR of compound **3s**