Synthesis of 3,3-Dihalogenated 2-Aminochromanones via Tandem Dihalogenation and Cyclization of *o*-Hydroxyarylenaminones with NXS (X = Cl or Br)

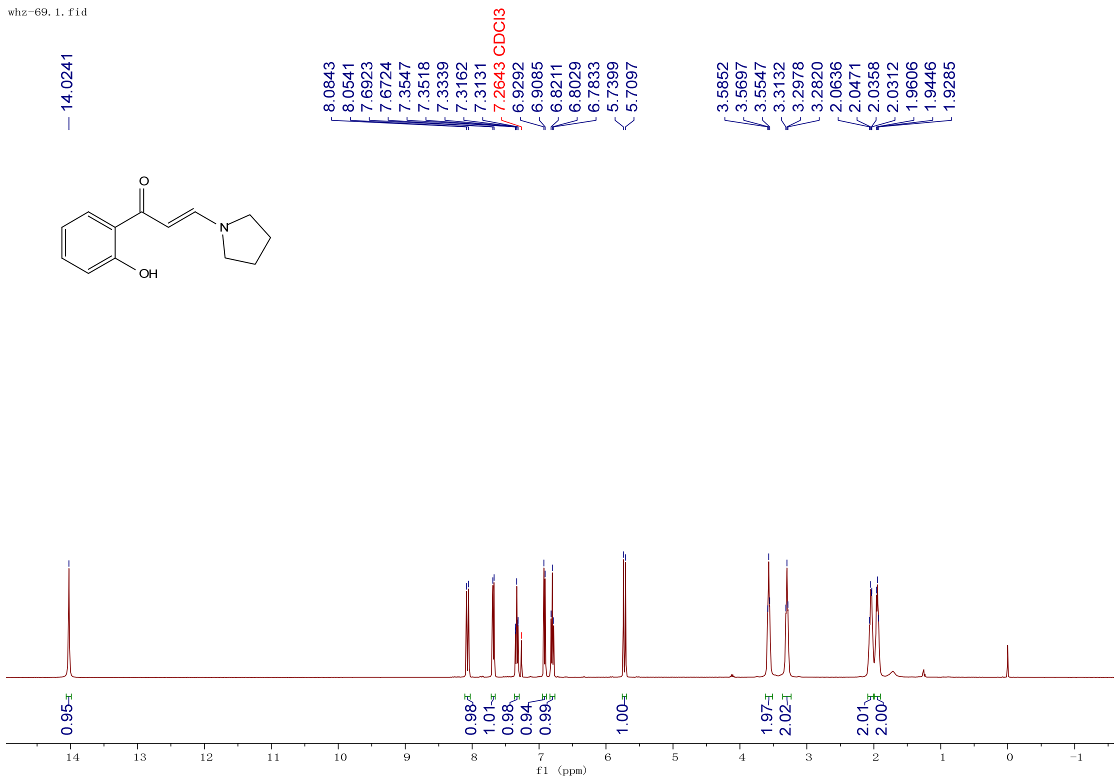
Tian Luo, Haozhi Wu, Li-hua Liao,* Jie-Ping Wan, Yunyun Liu*

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China

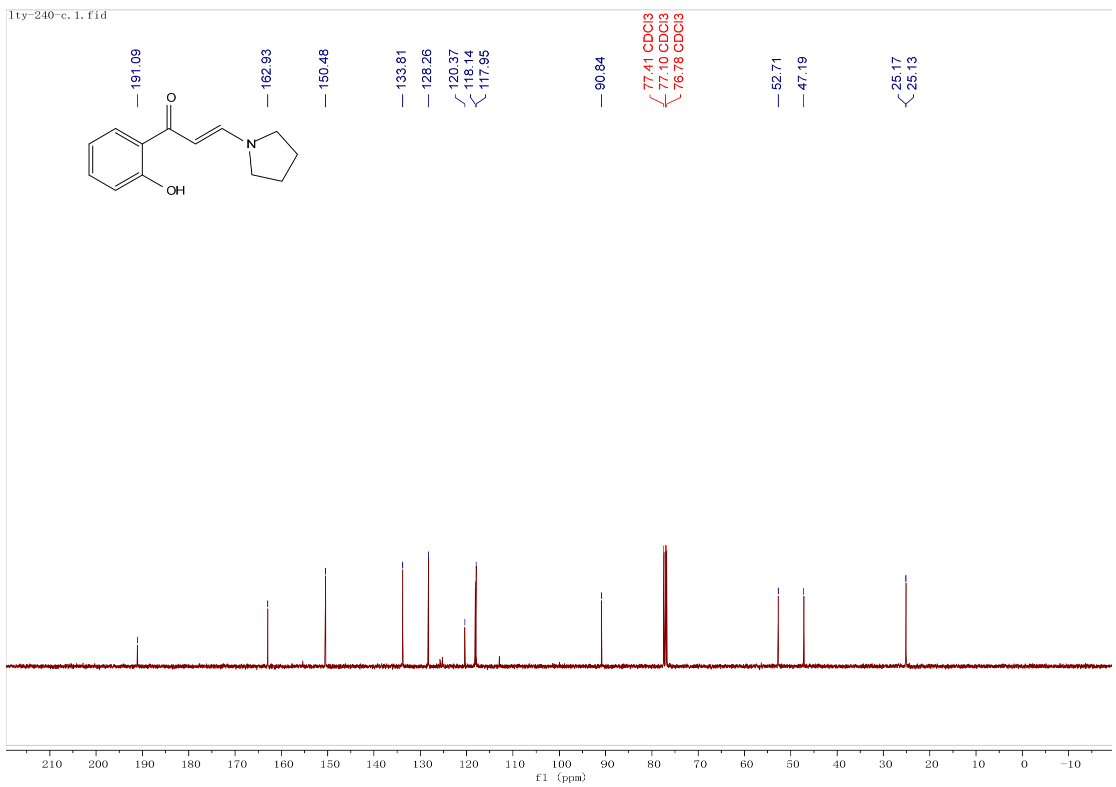
Email: liaolihua@jxnu.edu.cn; chemliuyunyun@jxnu.edu.cn

Contents

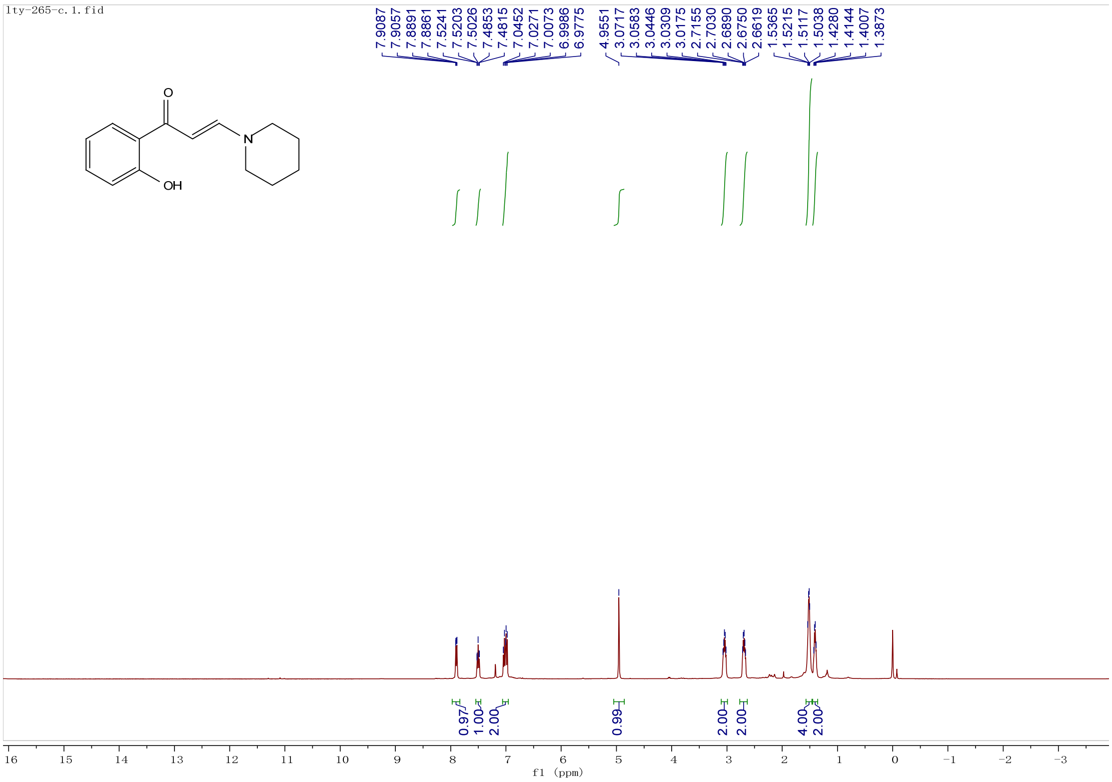
^{1}H and ^{13}C NMR of enaminone substrates and all products



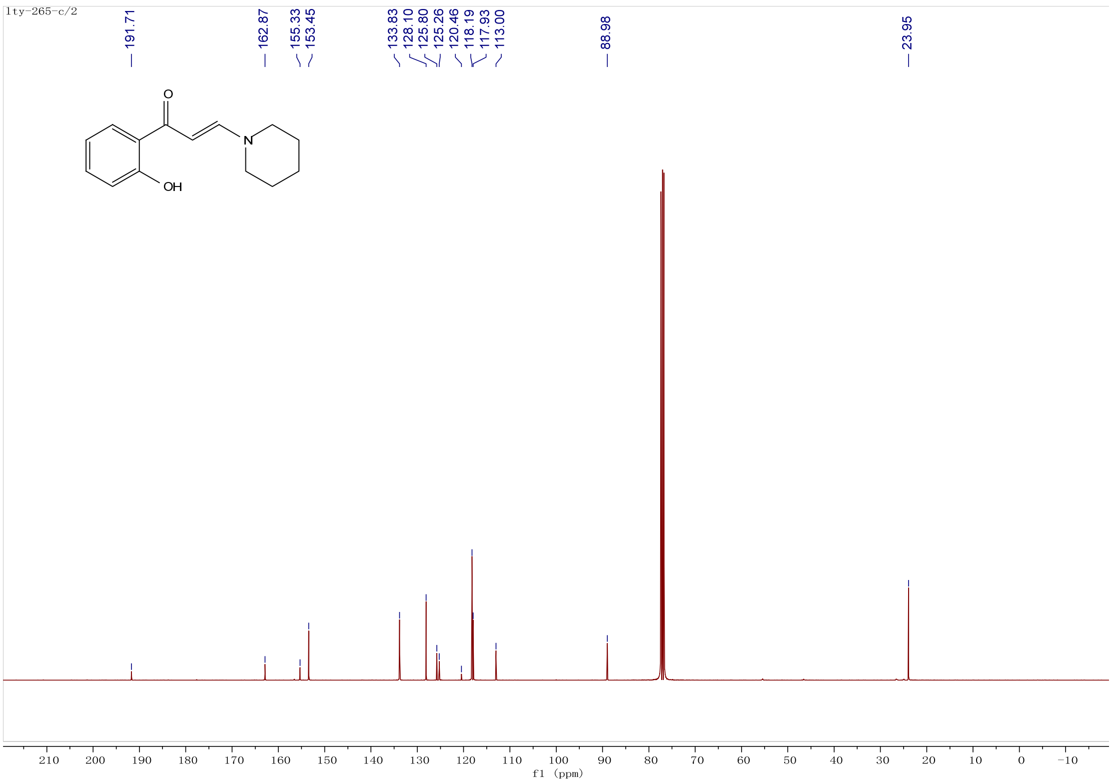
^{1}H NMR spectra of **1q** ($CDCl_3$, 400 MHz)



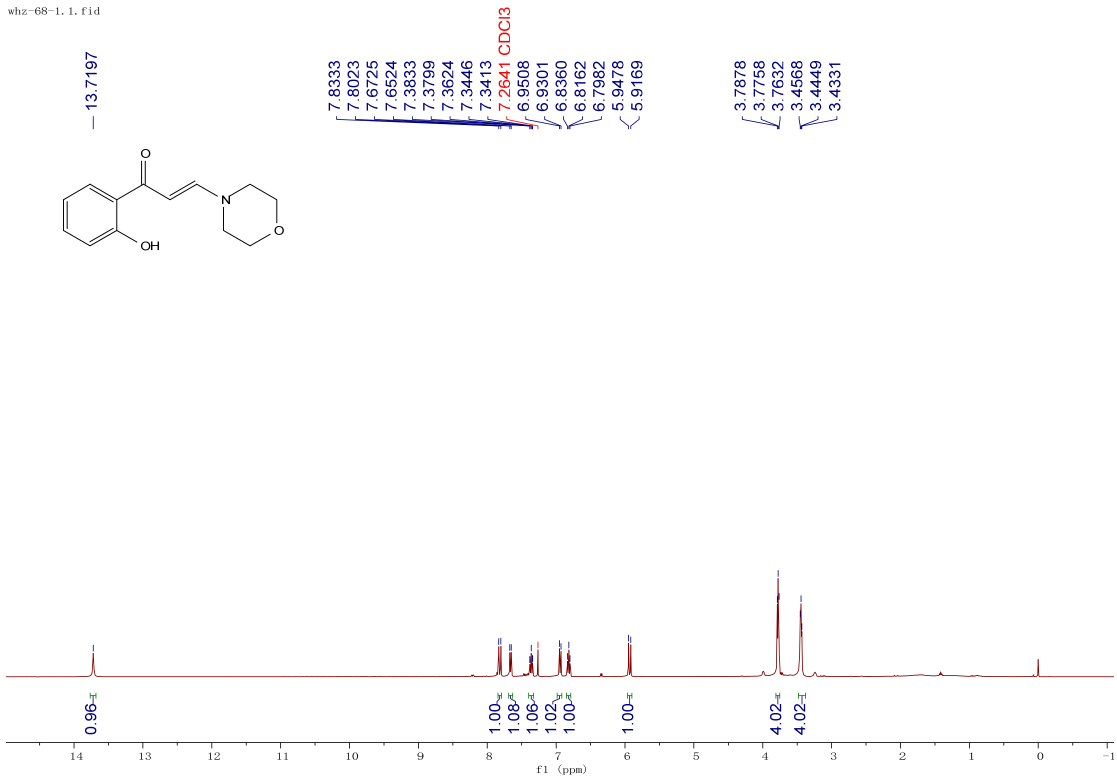
^{13}C{^{1}H} NMR spectra of **1q** ($CDCl_3$, 100 MHz)



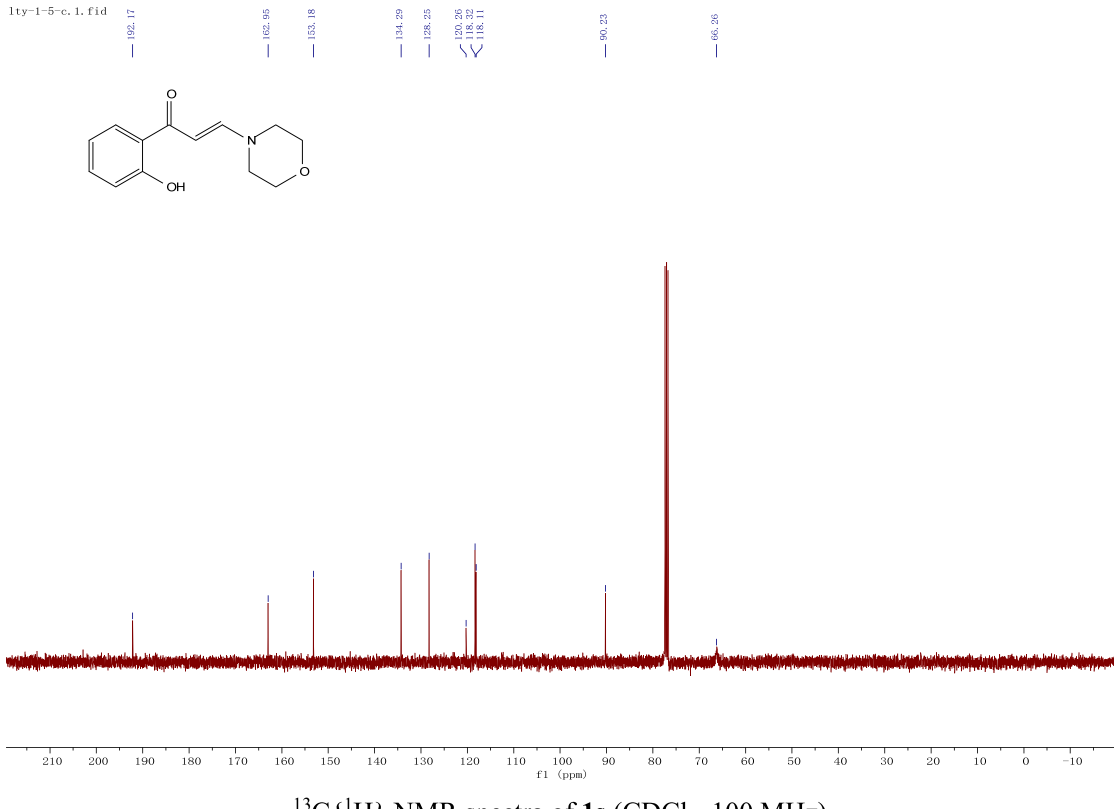
^{1}H NMR spectra of **1r** ($CDCl_3$, 400 MHz)



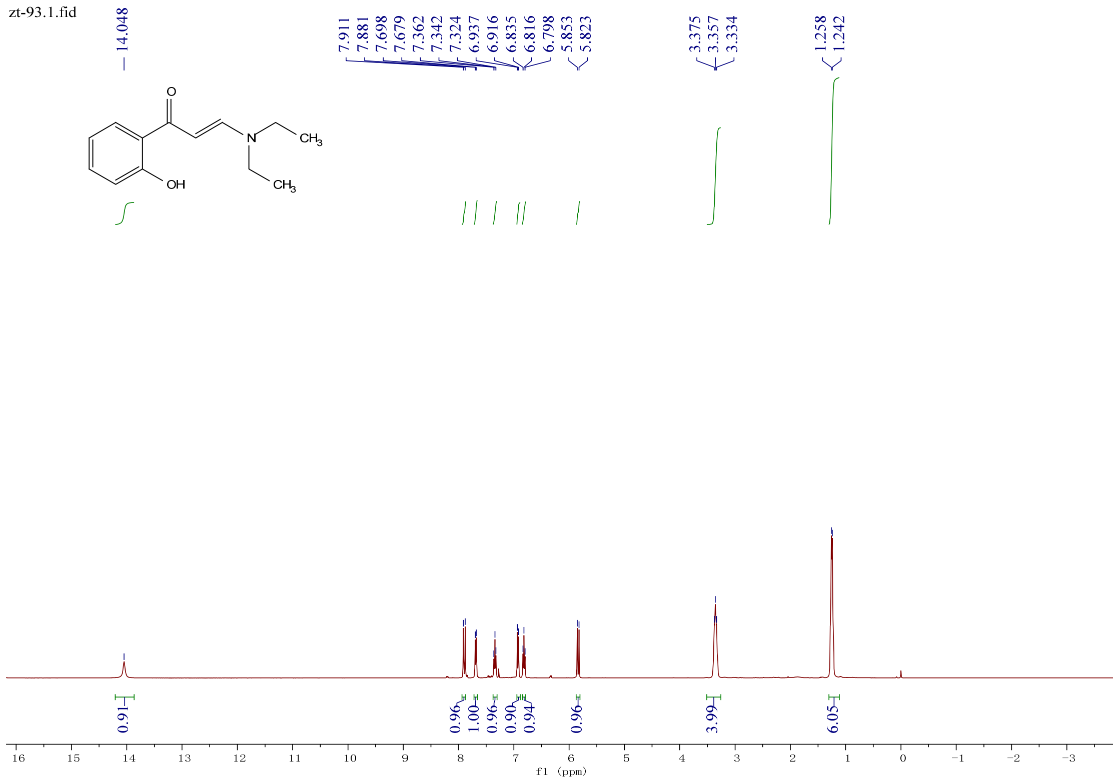
$^{13}C\{^{1}H\}$ NMR spectra of **1r** ($CDCl_3$, 100 MHz)



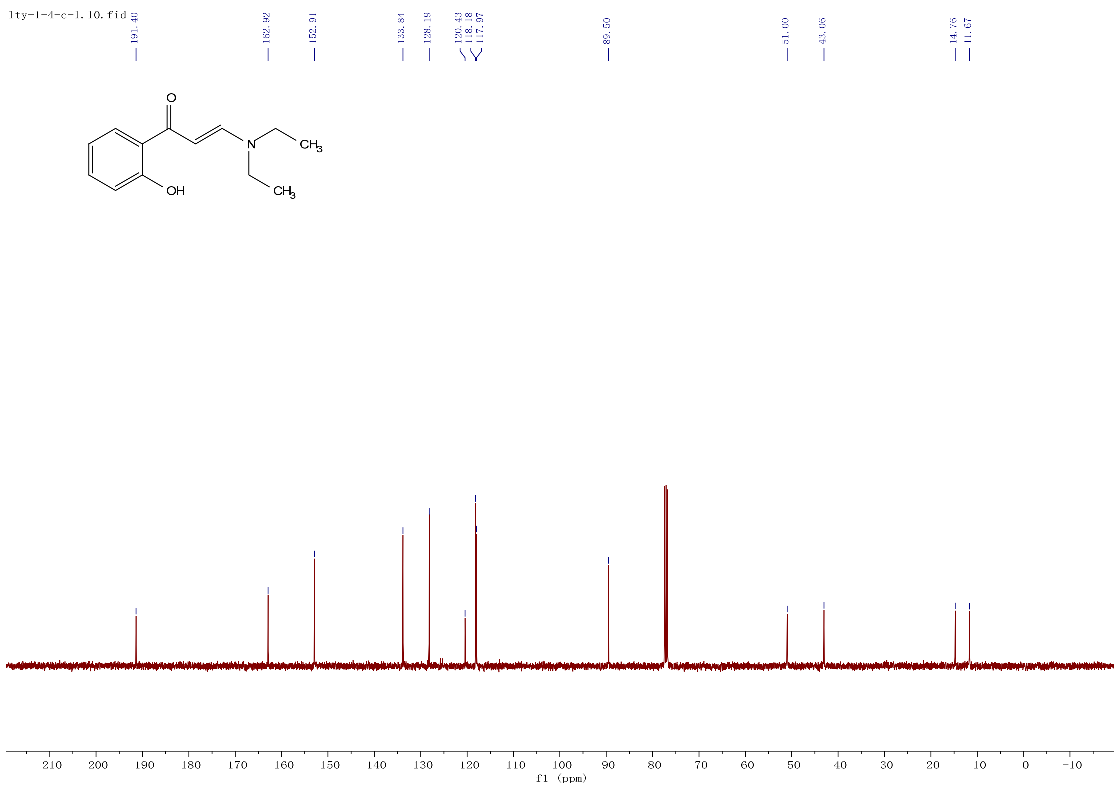
^{1}H NMR spectra of **1s** ($CDCl_3$, 400 MHz)



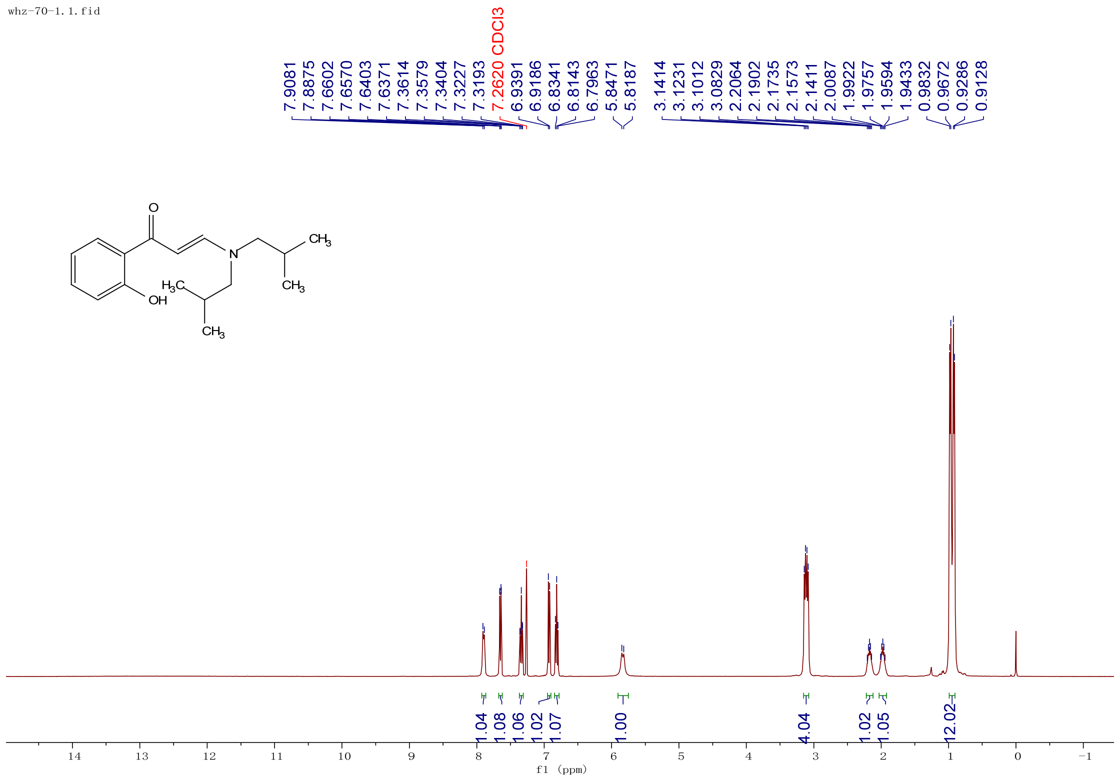
$^{13}C\{^{1}H\}$ NMR spectra of **1s** ($CDCl_3$, 100 MHz)



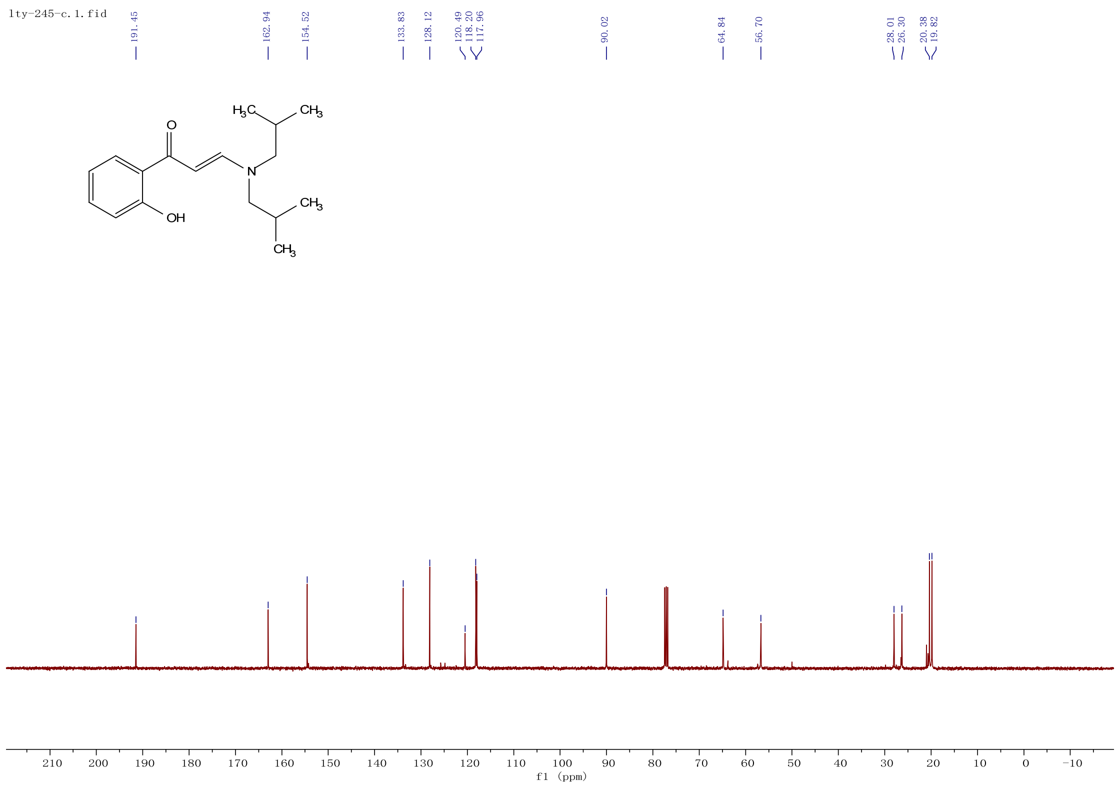
^{1}H NMR spectra of **1t** ($CDCl_3$, 400 MHz)



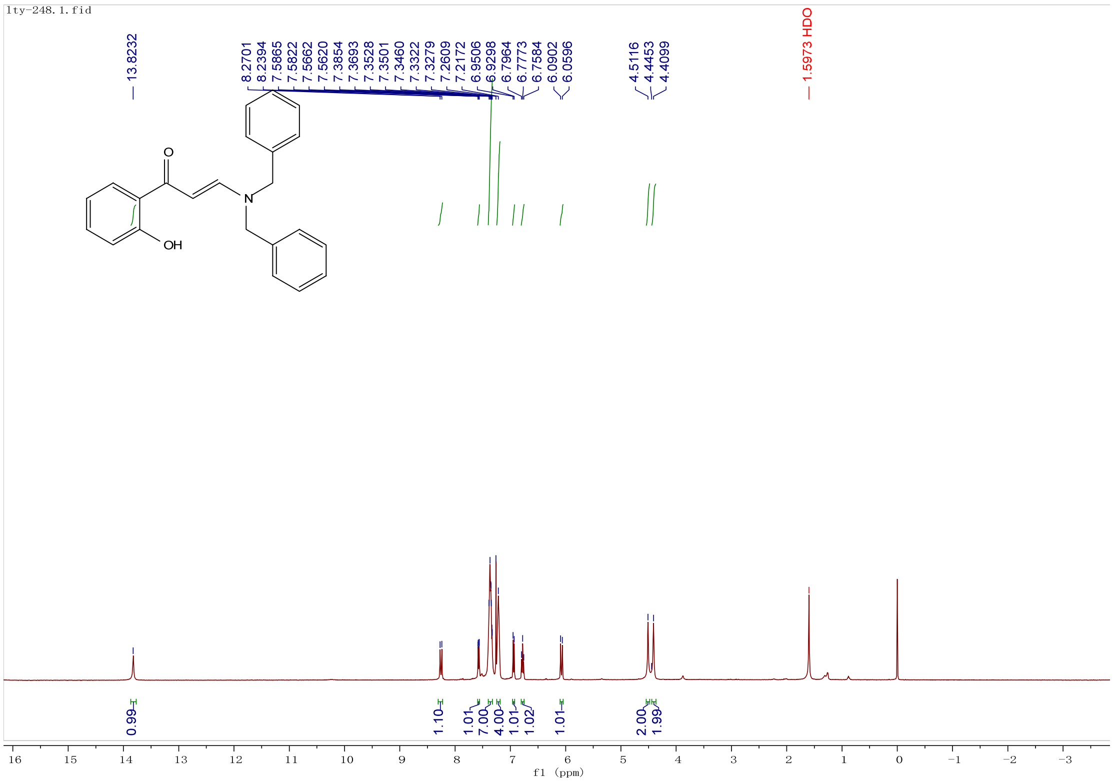
^{13}C{^{1}H} NMR spectra of **1t** ($CDCl_3$, 100 MHz)



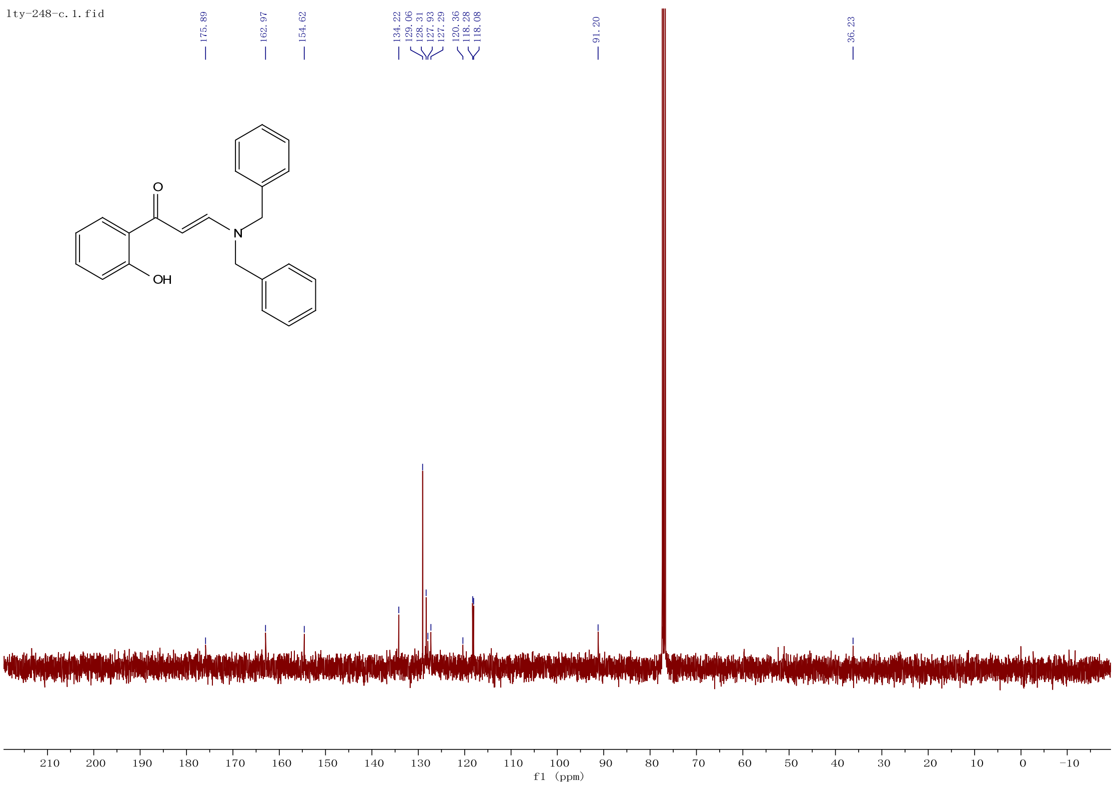
^{1}H NMR spectra of **1u** ($CDCl_3$, 400 MHz)



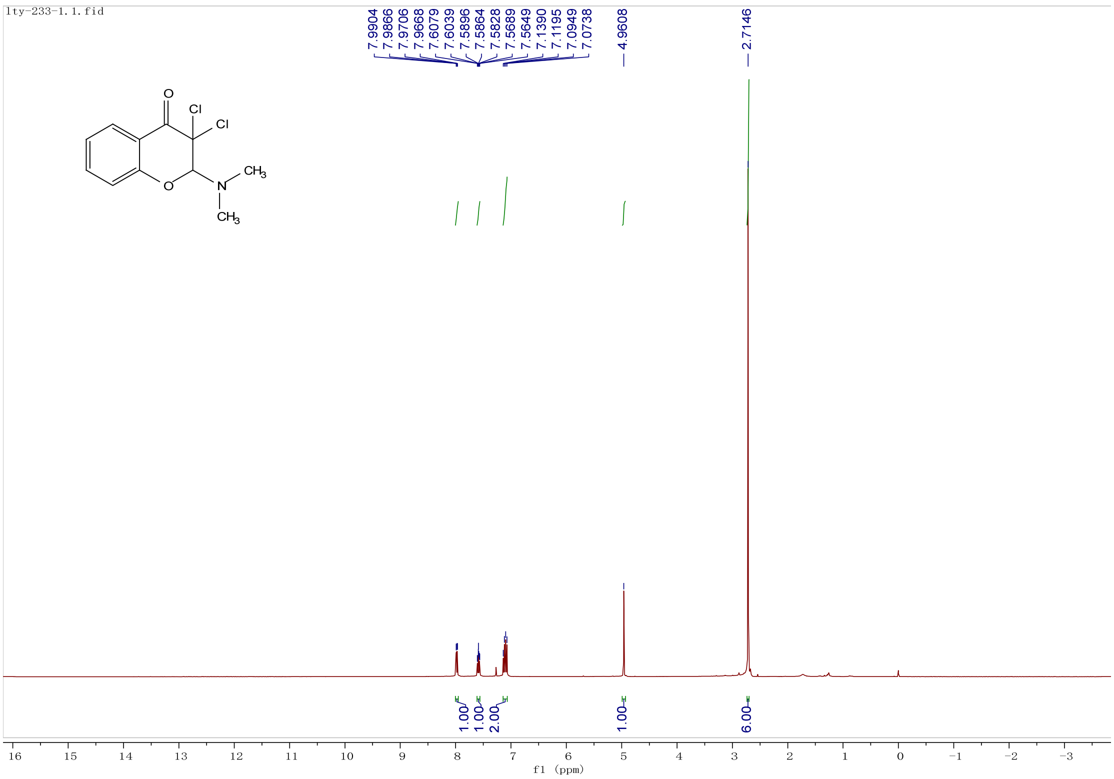
$^{13}C\{^{1}H\}$ NMR spectra of **1u** ($CDCl_3$, 100 MHz)



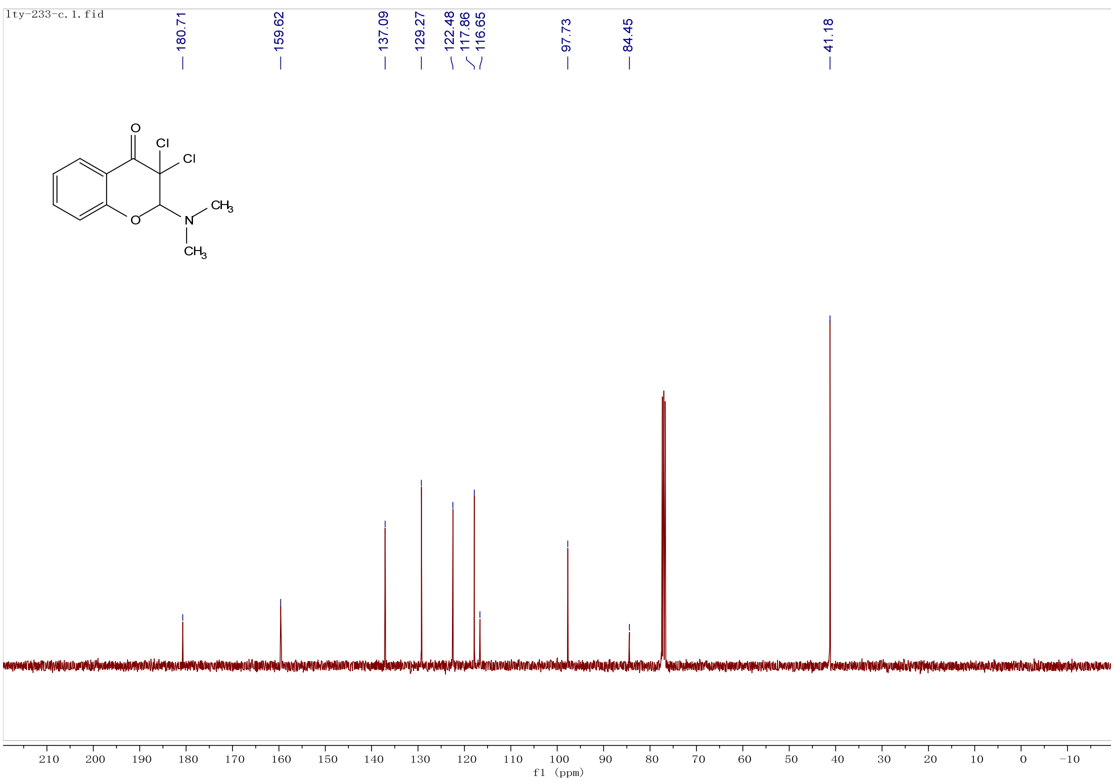
^{1}H NMR spectra of **1v** ($CDCl_3$, 400 MHz)



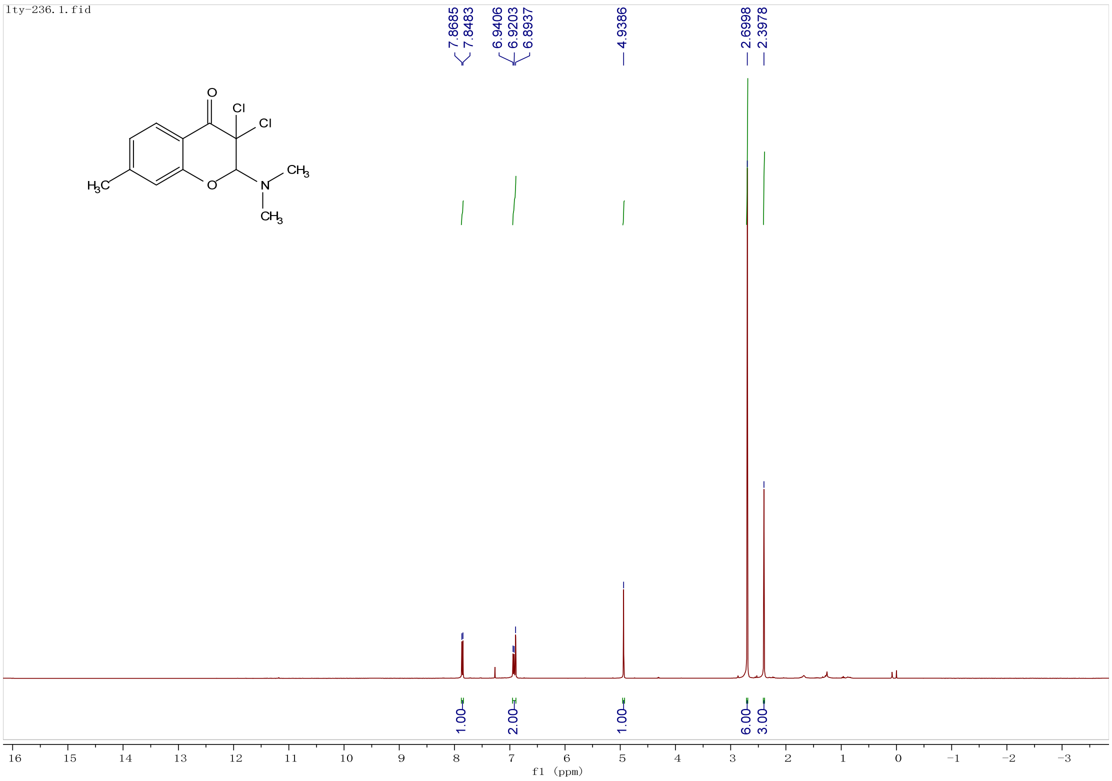
^{13}C{^{1}H} NMR spectra of **1v** ($CDCl_3$, 100 MHz)



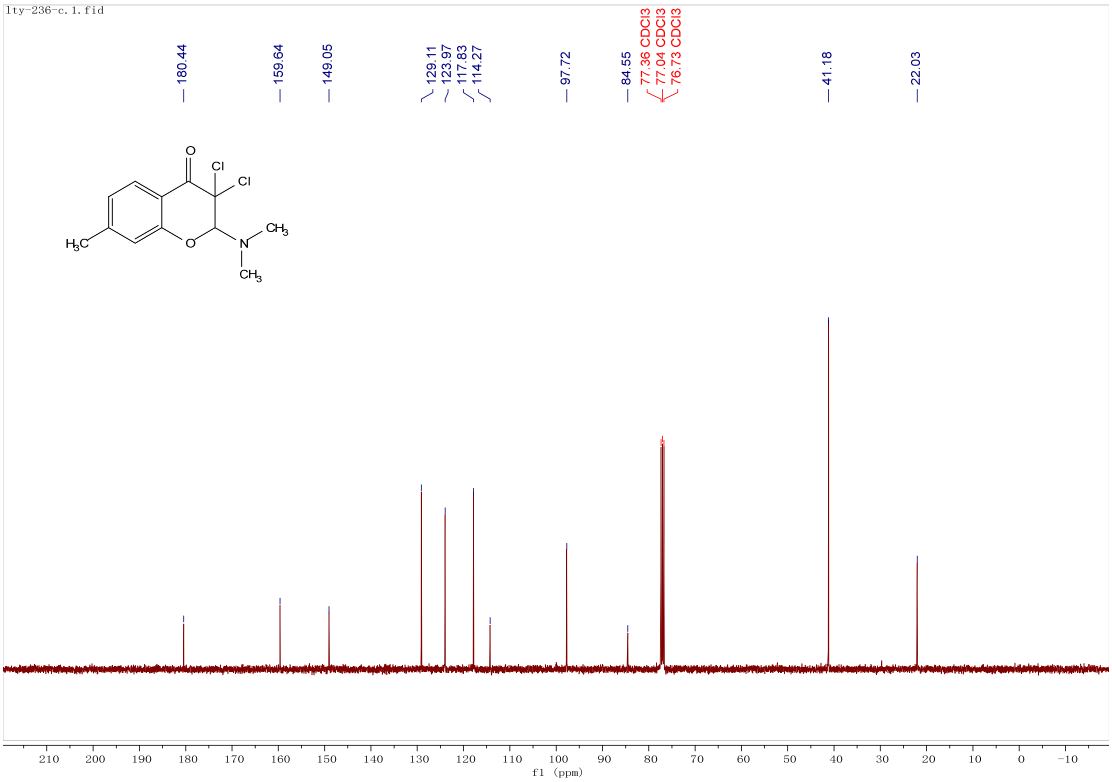
^{1}H NMR spectra of **3a** ($CDCl_3$, 400 MHz)



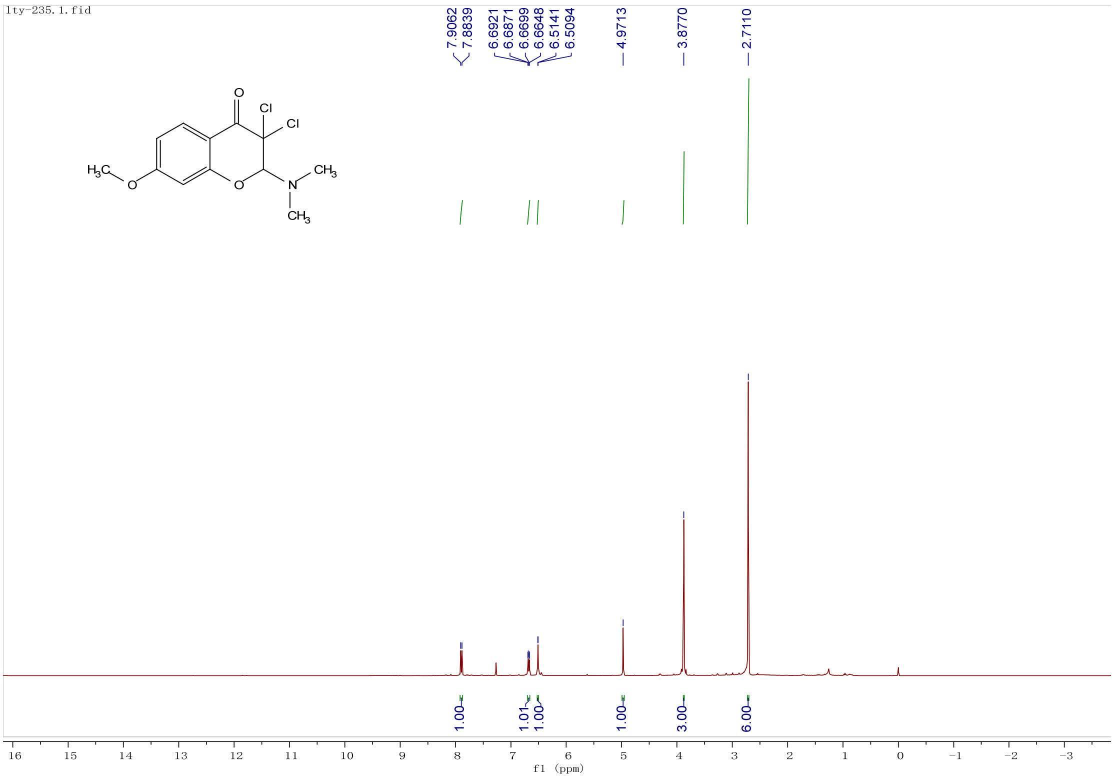
$^{13}C\{^{1}H\}$ NMR spectra of **3a** ($CDCl_3$, 100 MHz)



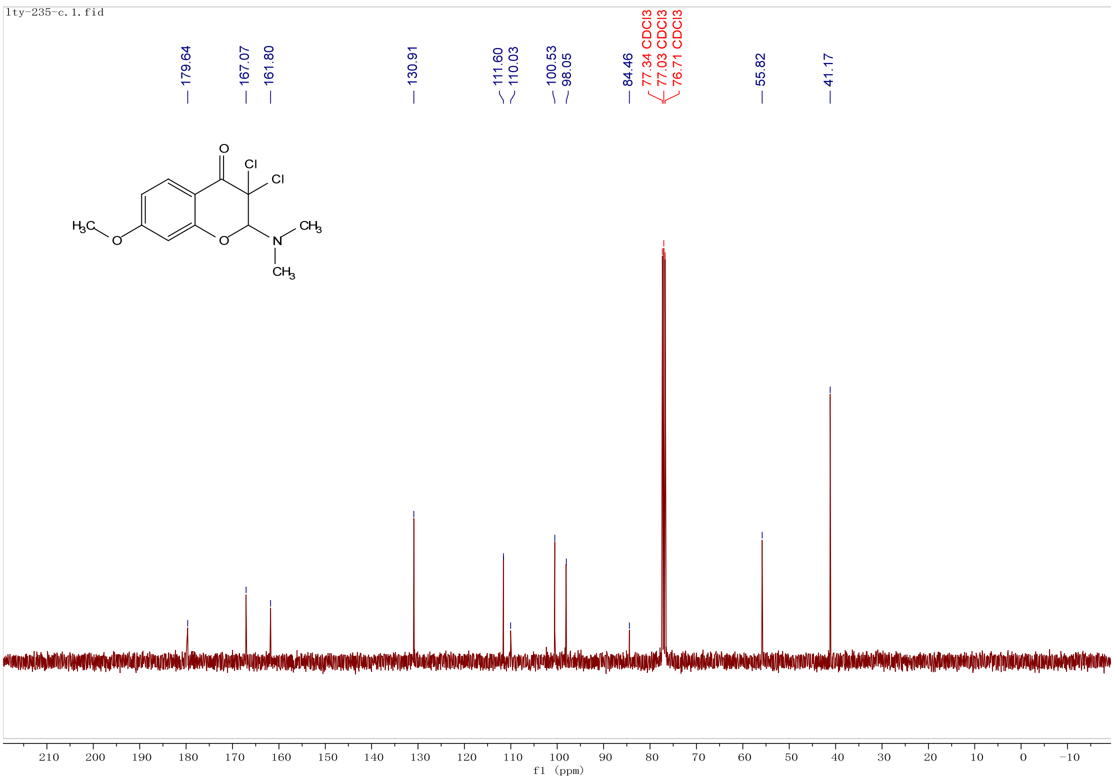
^{1}H NMR spectra of **3b** ($CDCl_3$, 400 MHz)



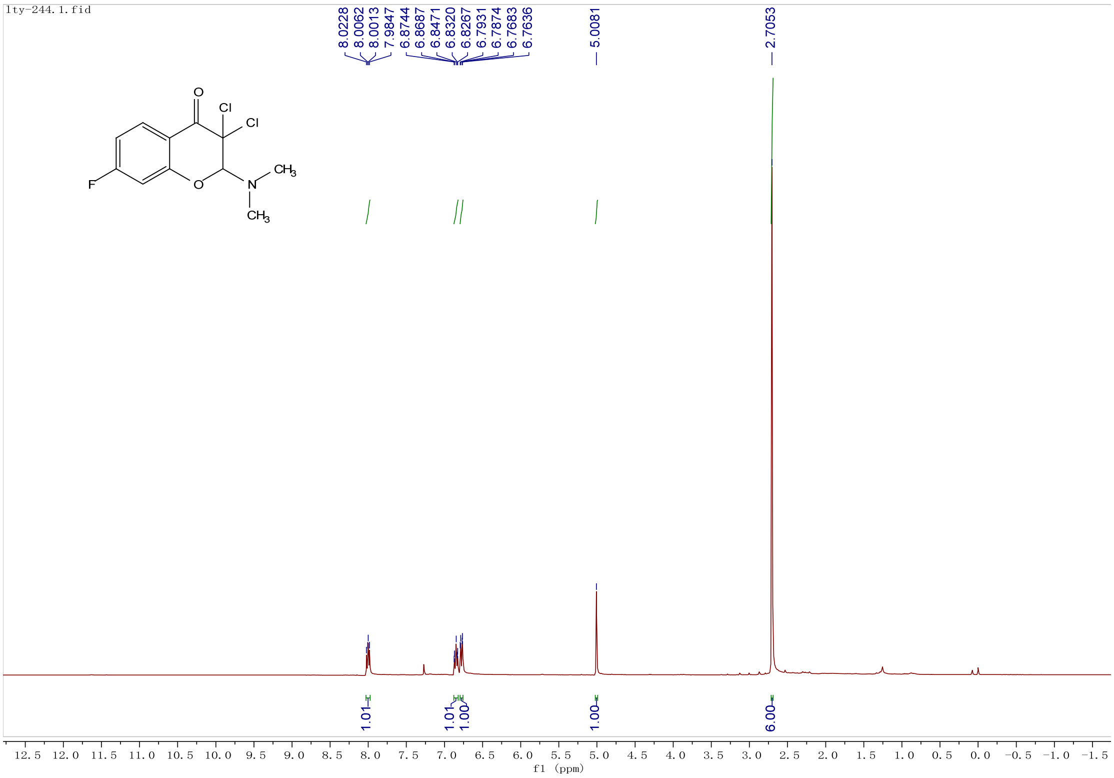
$^{13}C\{^{1}H\}$ NMR spectra of **3b** ($CDCl_3$, 100 MHz)



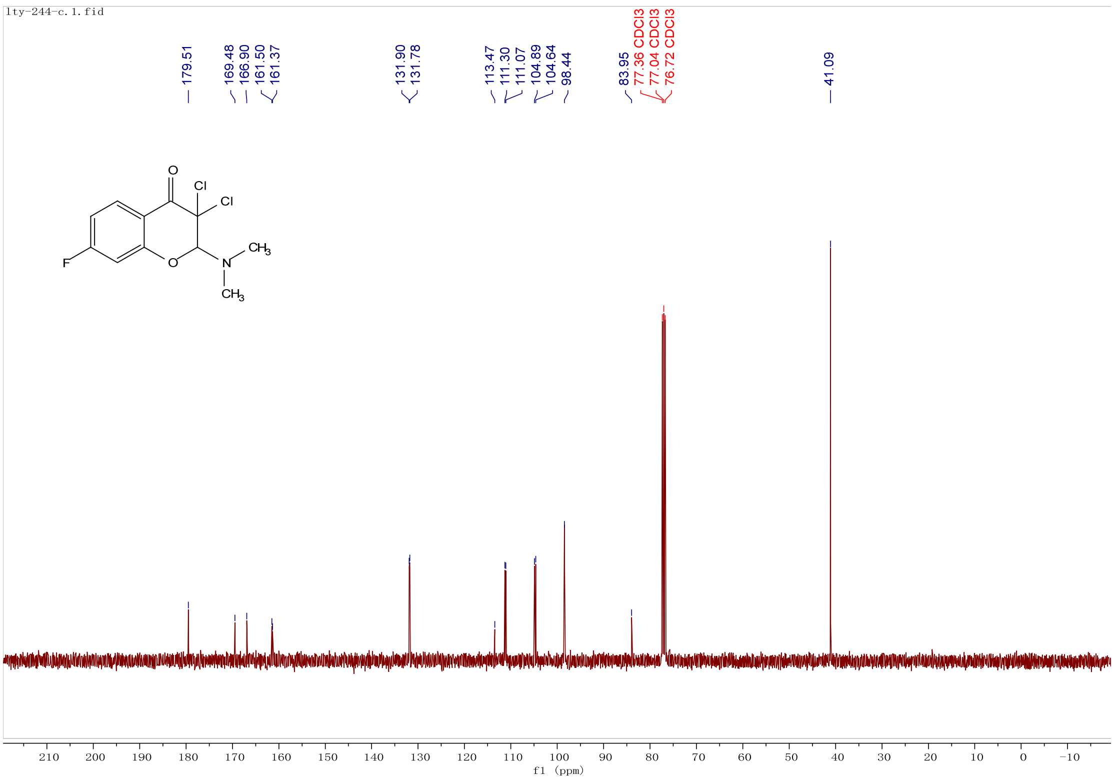
^{1}H NMR spectra of **3c** ($CDCl_3$, 400 MHz)



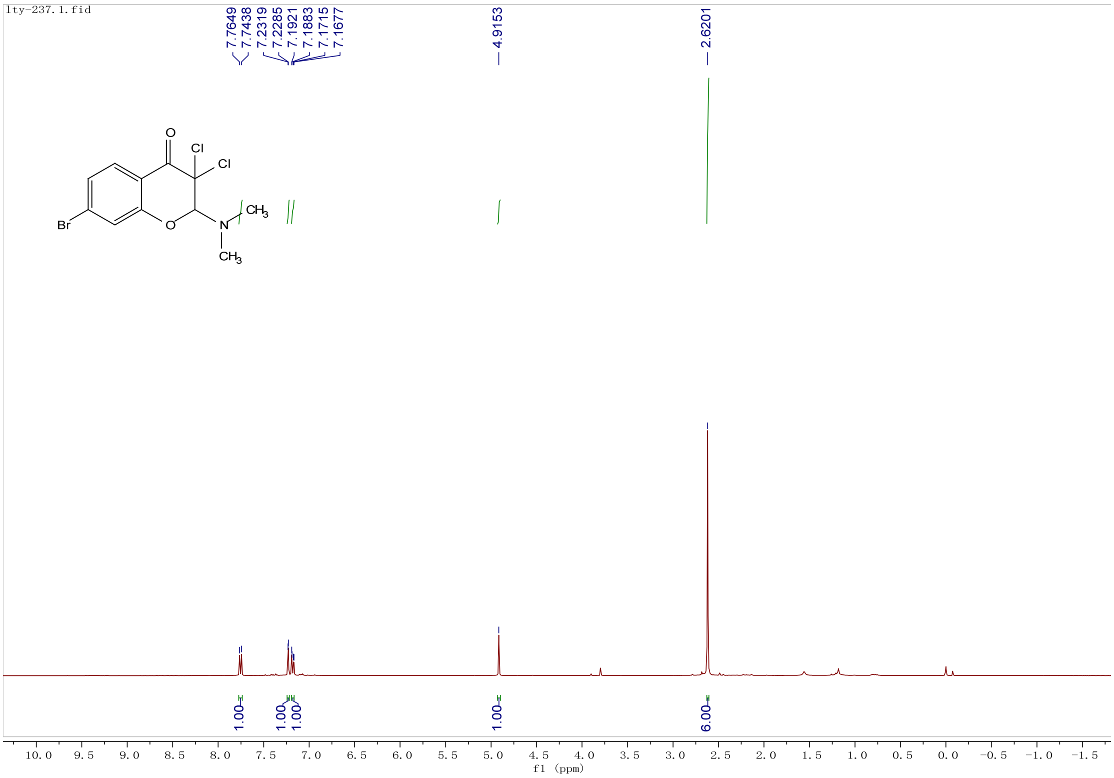
$^{13}C\{^{1}H\}$ NMR spectra of **3c** ($CDCl_3$, 100 MHz)



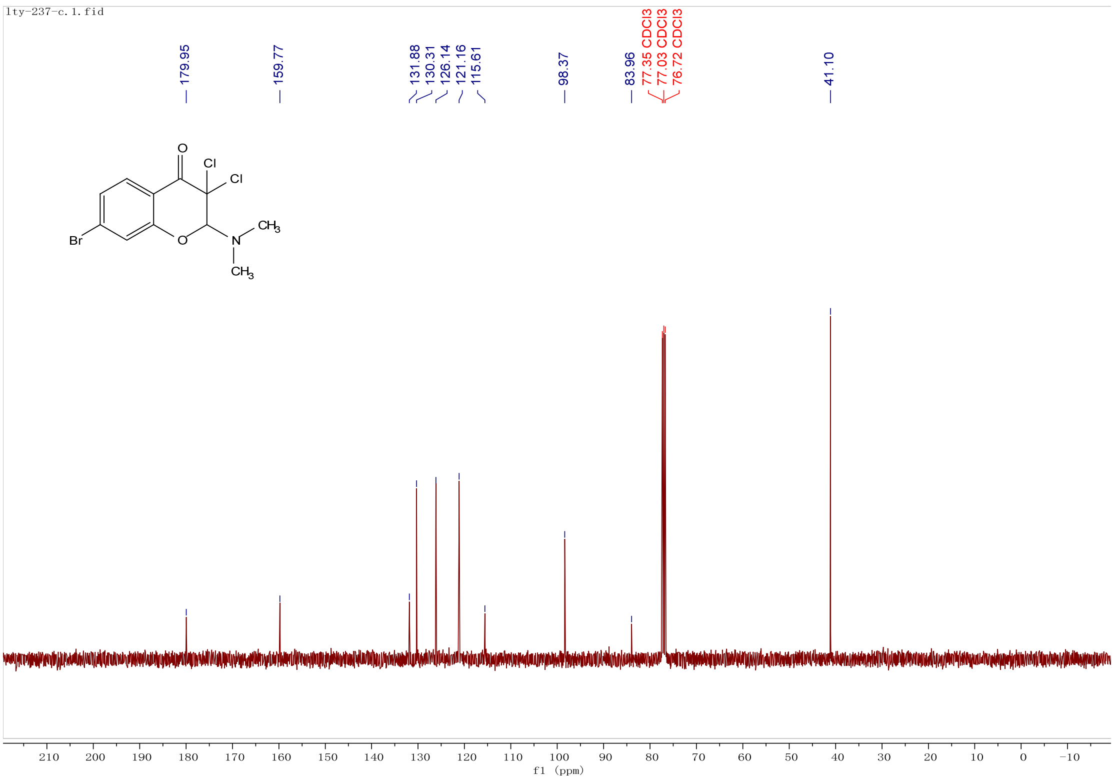
^{1}H NMR spectra of **3d** ($CDCl_3$, 400 MHz)



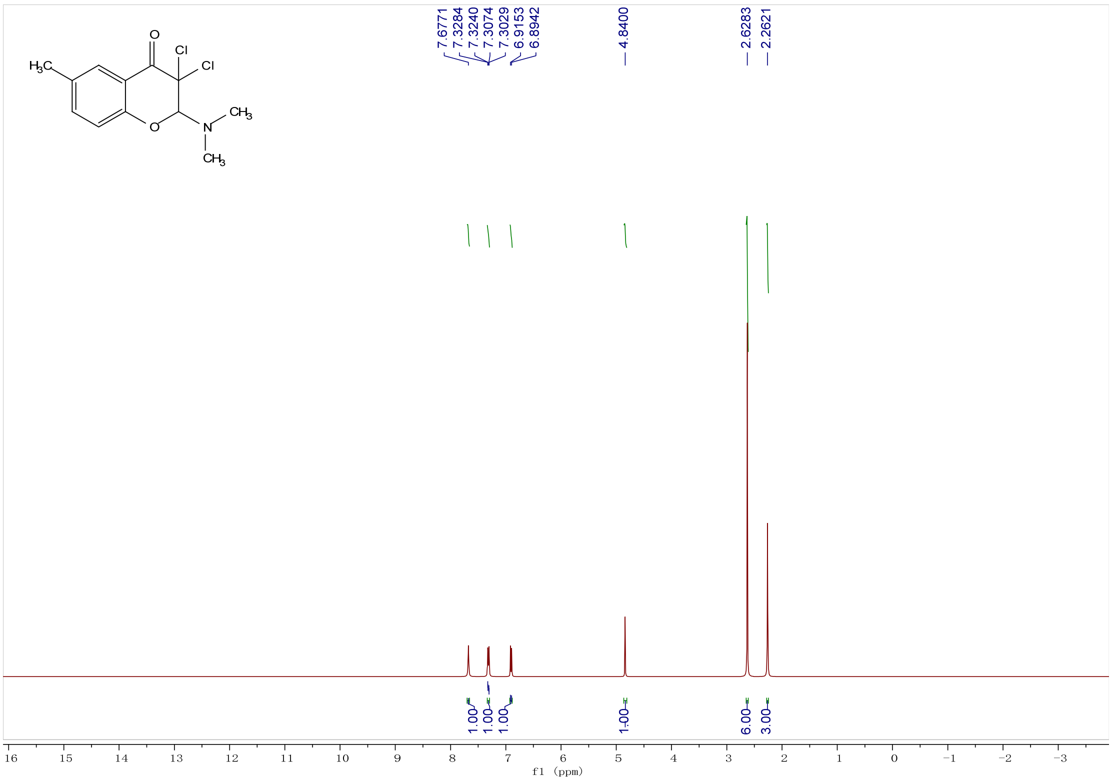
$^{13}C\{^{1}H\}$ NMR spectra of **3d** ($CDCl_3$, 100 MHz)



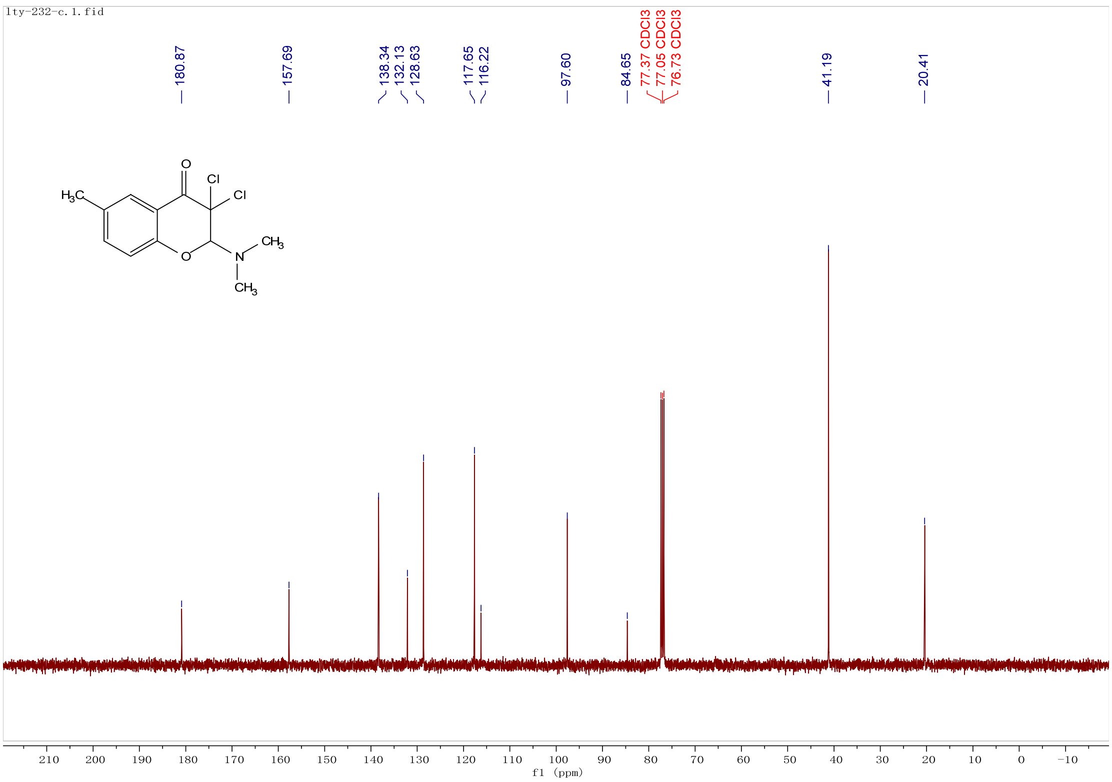
^{1}H NMR spectra of **3e** ($CDCl_3$, 400 MHz)



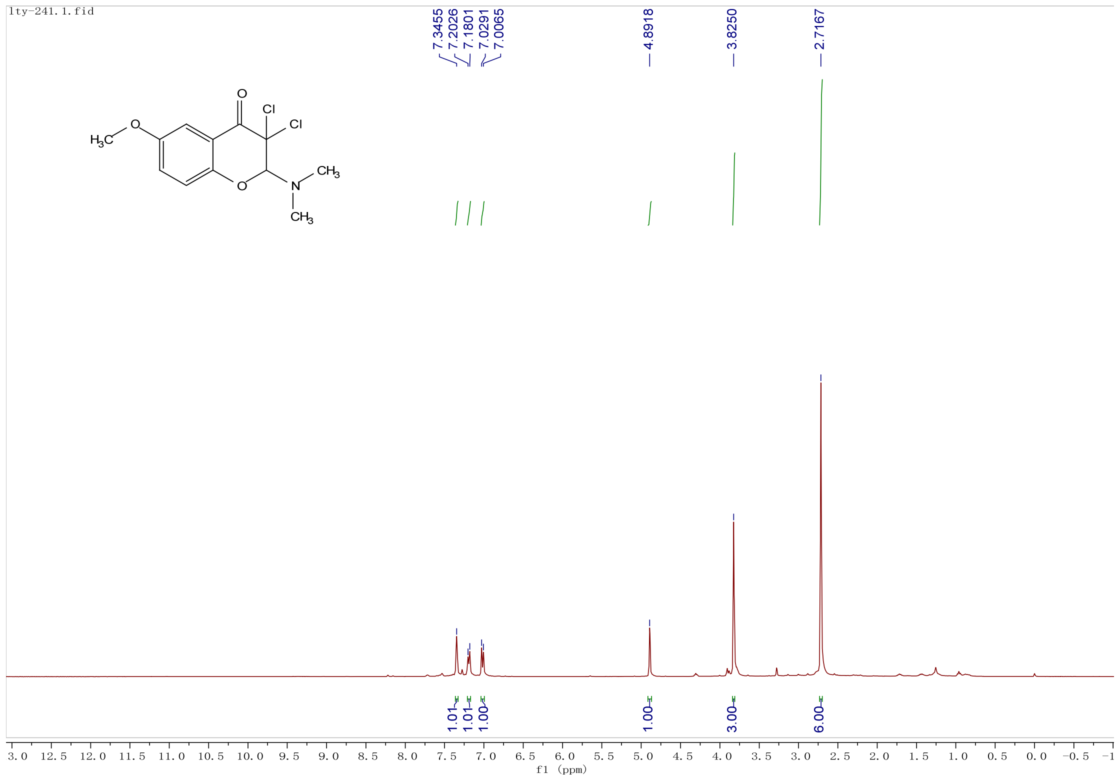
$^{13}C\{^{1}H\}$ NMR spectra of **3e** ($CDCl_3$, 100 MHz)



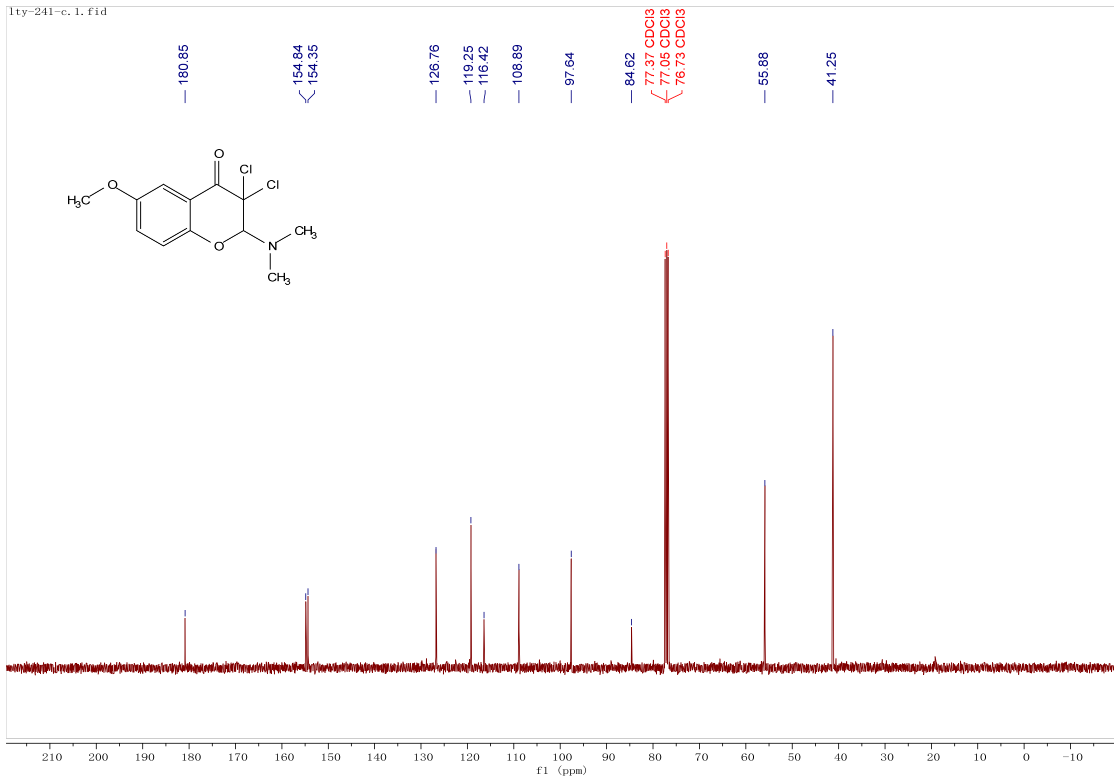
^{1}H NMR spectra of **3f** ($CDCl_3$, 400 MHz)



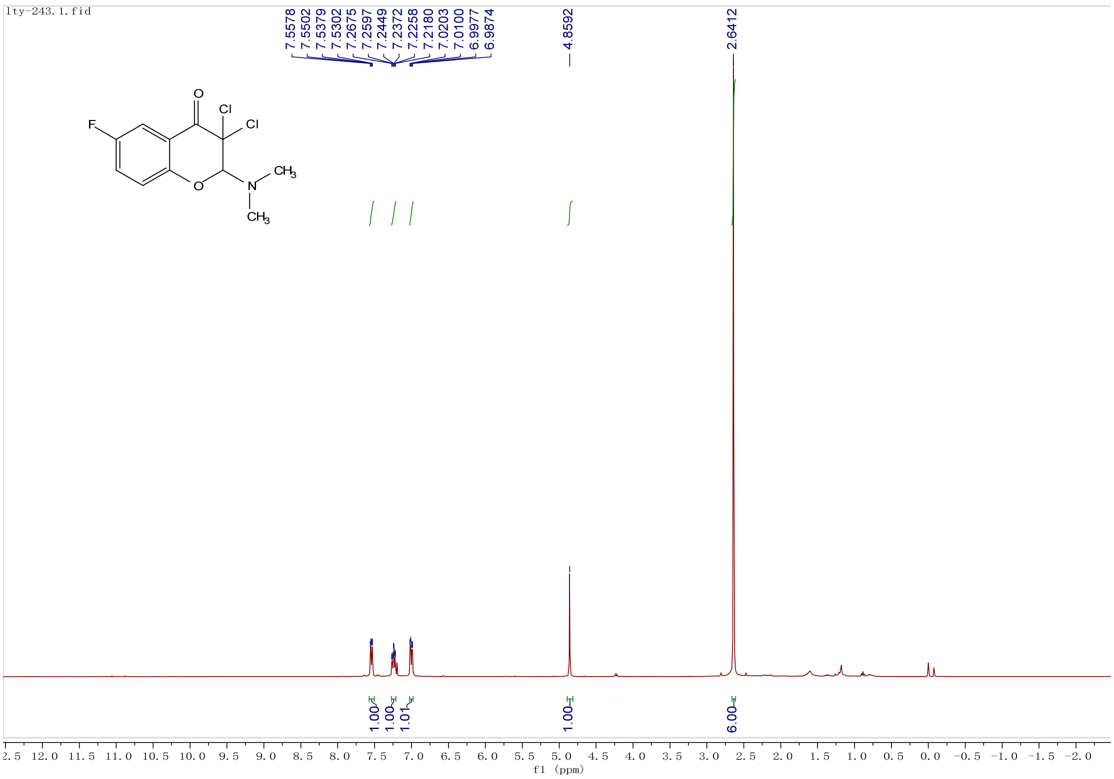
^{13}C{^{1}H} NMR spectra of **3f** ($CDCl_3$, 100 MHz)



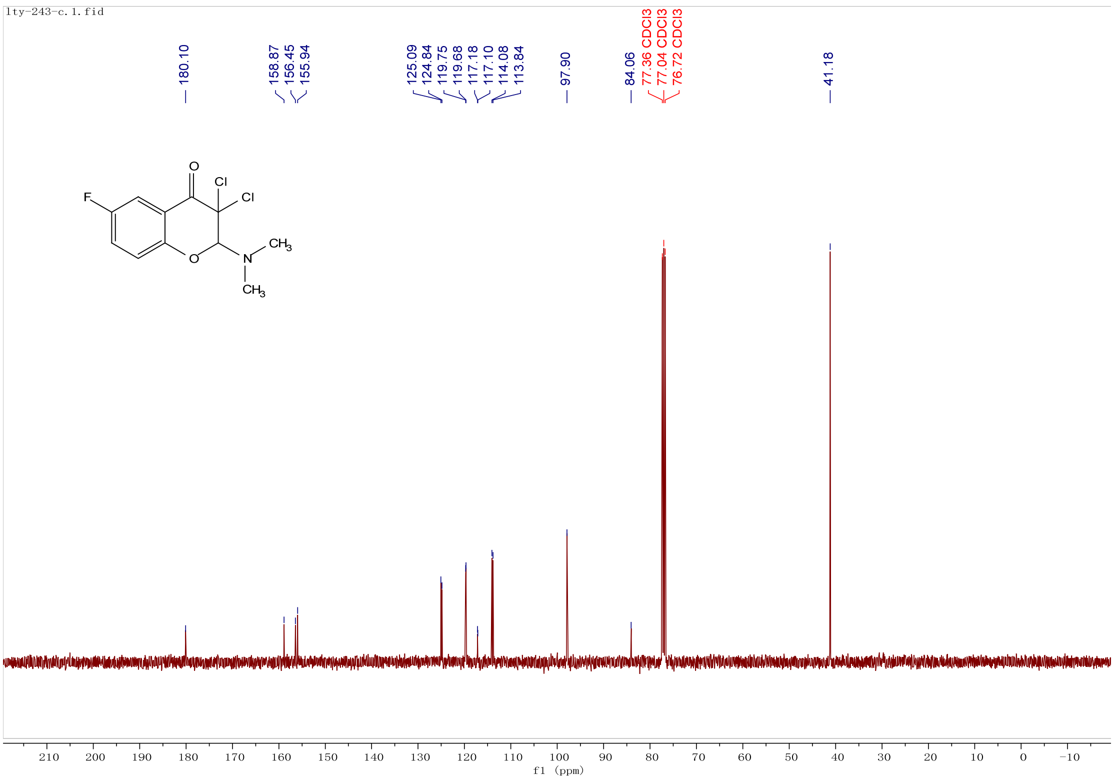
^1H NMR spectra of **3g** ($CDCl_3$, 400 MHz)



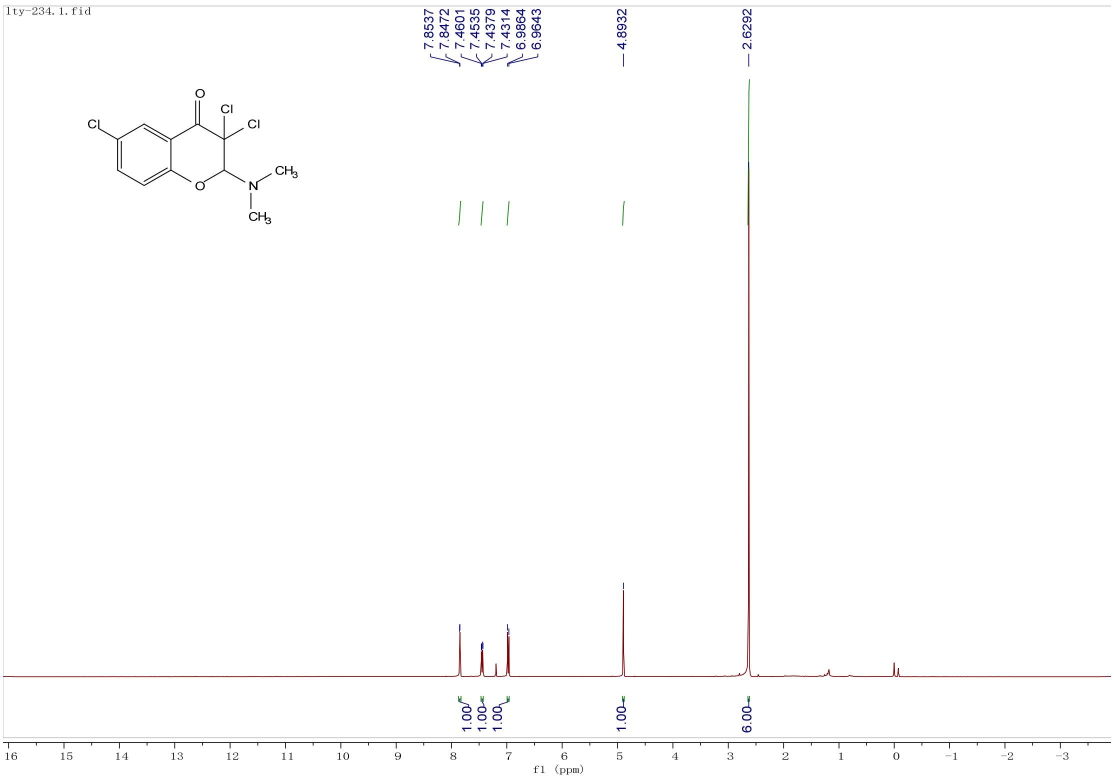
$^{13}C\{^1H\}$ NMR spectra of **3g** ($CDCl_3$, 100 MHz)



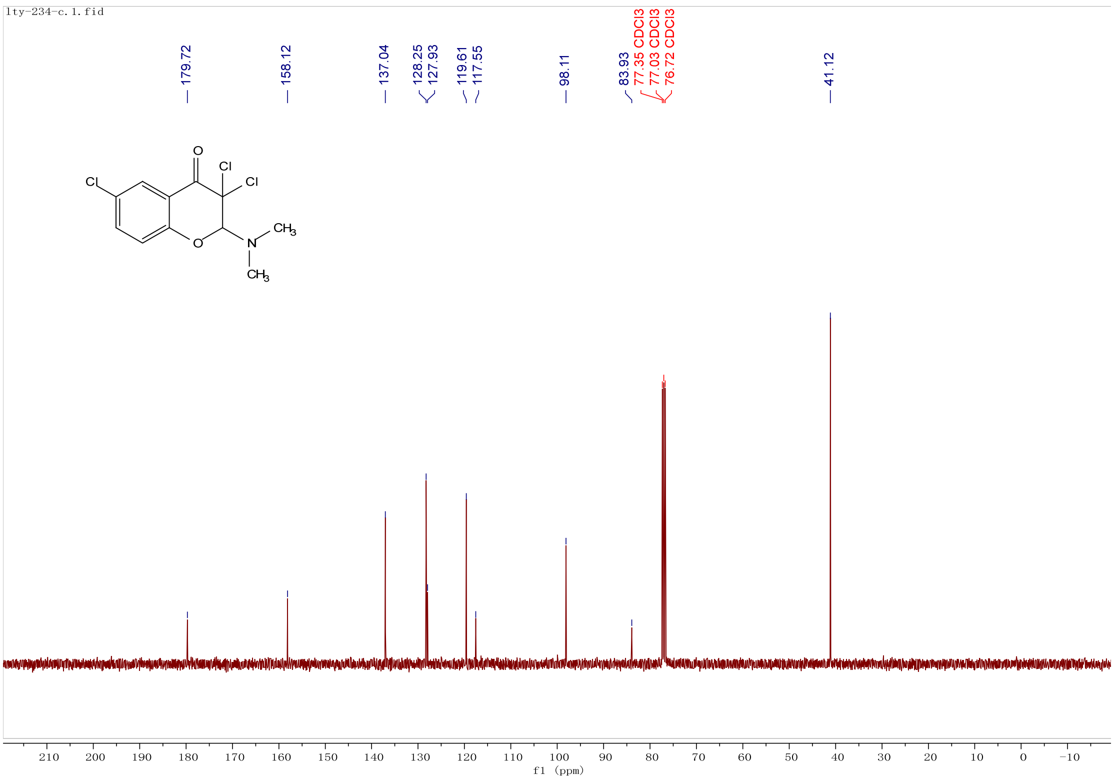
^{1}H NMR spectra of **3h** ($CDCl_3$, 400 MHz)



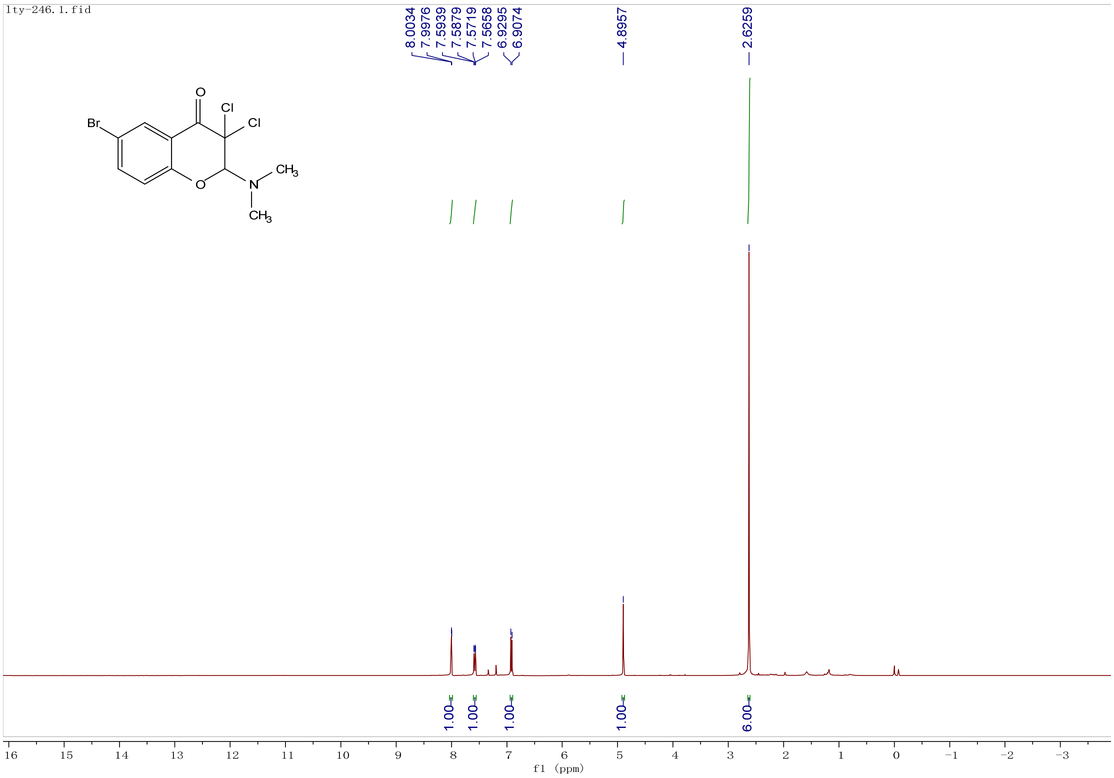
$^{13}C\{^1H\}$ NMR spectra of **3h** ($CDCl_3$, 100 MHz)



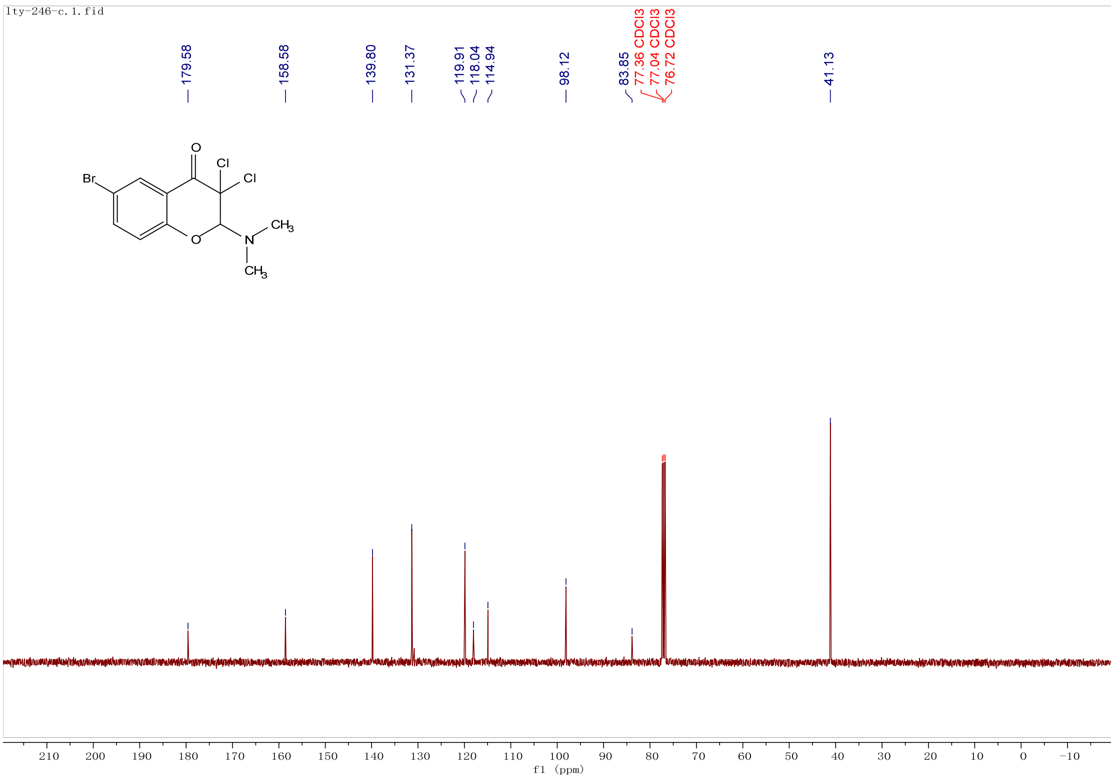
^{1}H NMR spectra of **3i** ($CDCl_3$, 400 MHz)



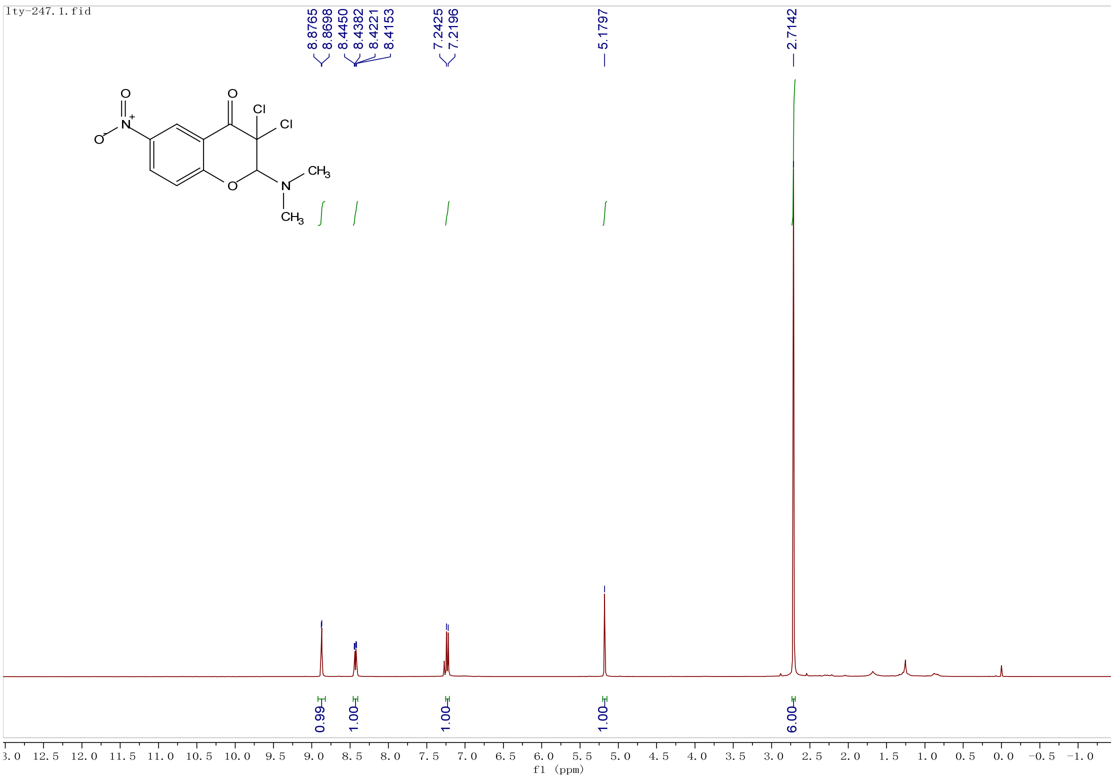
$^{13}C\{^{1}H\}$ NMR spectra of **3i** ($CDCl_3$, 100 MHz)



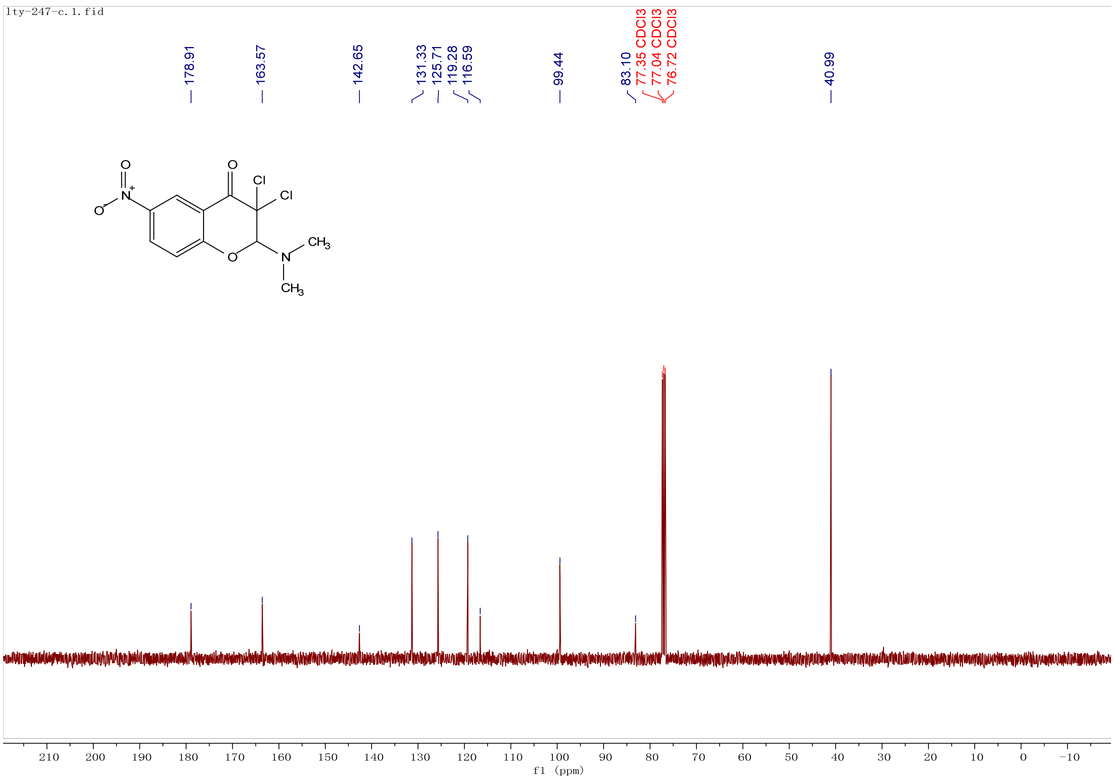
[1]H NMR spectra of **3j** ($CDCl_3$, 400 MHz)



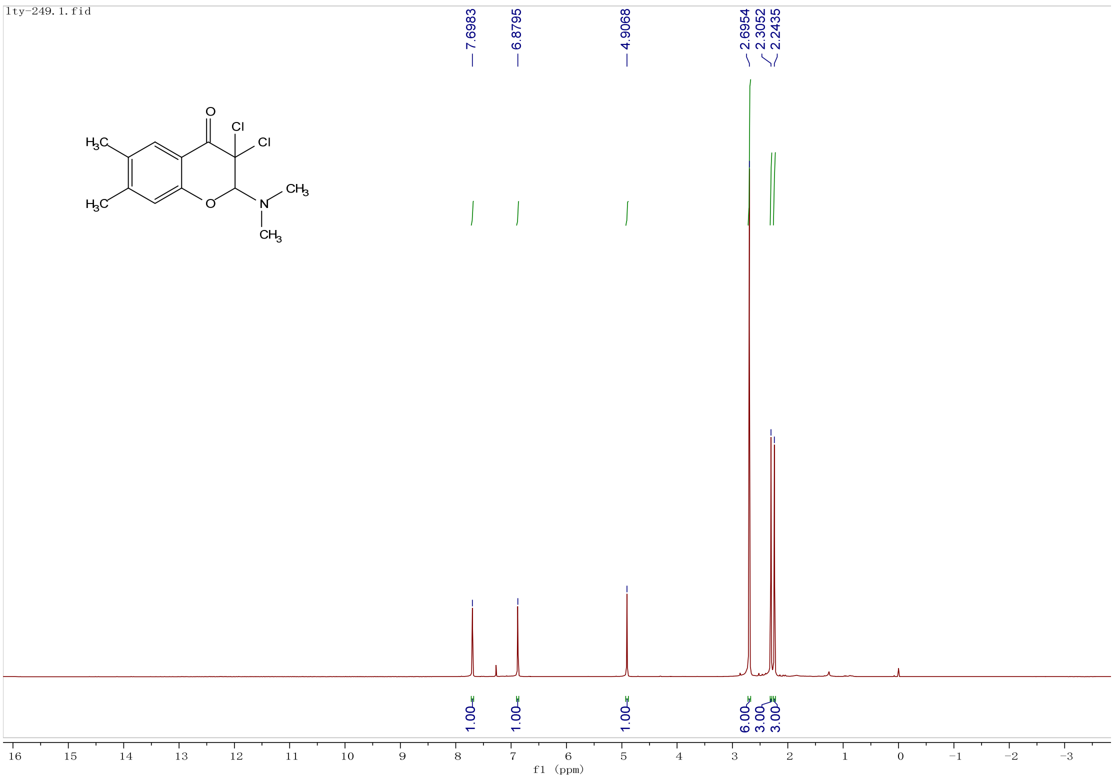
[13]C{[1]H} NMR spectra of **3j** ($CDCl_3$, 100 MHz)



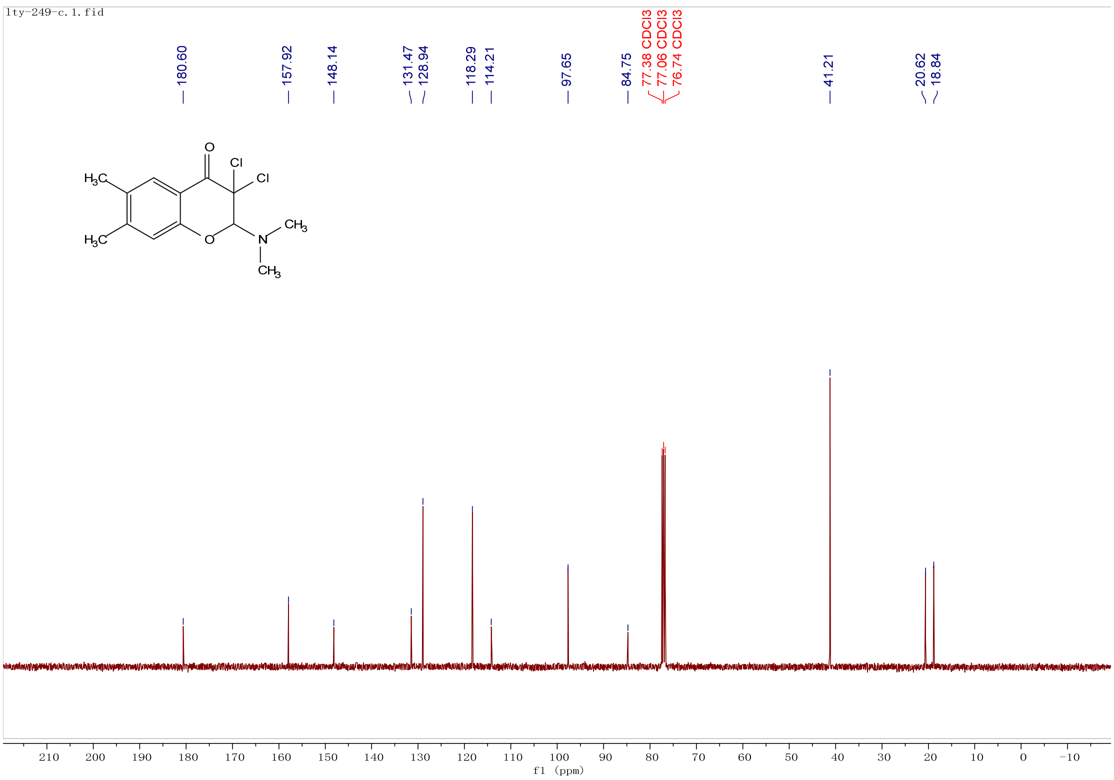
^{1}H NMR spectra of **3k** ($CDCl_3$, 400 MHz)



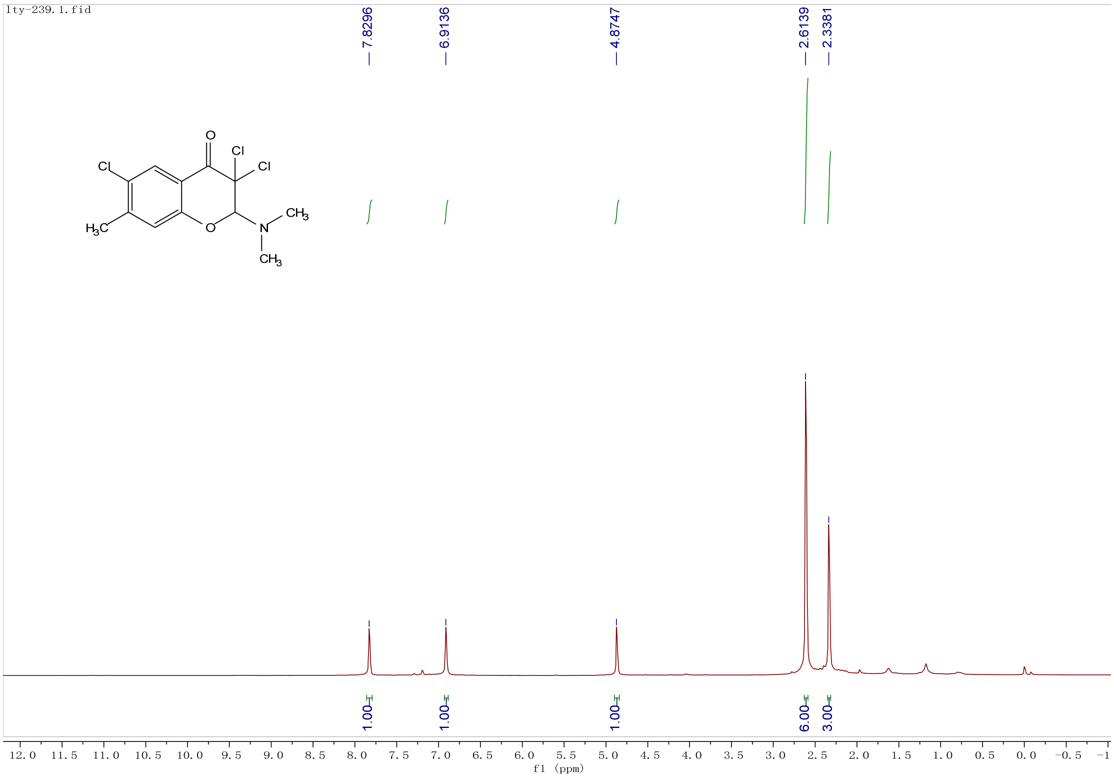
$^{13}C\{^{1}H\}$ NMR spectra of **3k** ($CDCl_3$, 100 MHz)



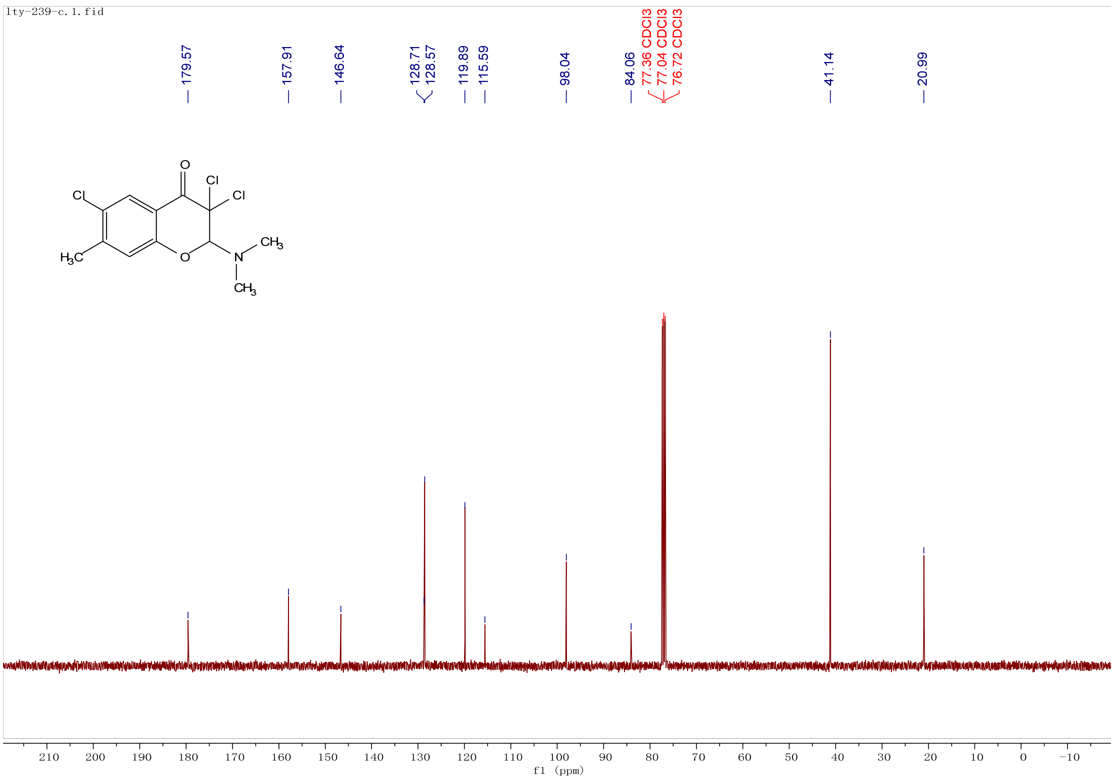
^{1}H NMR spectra of **3l** ($CDCl_3$, 400 MHz)



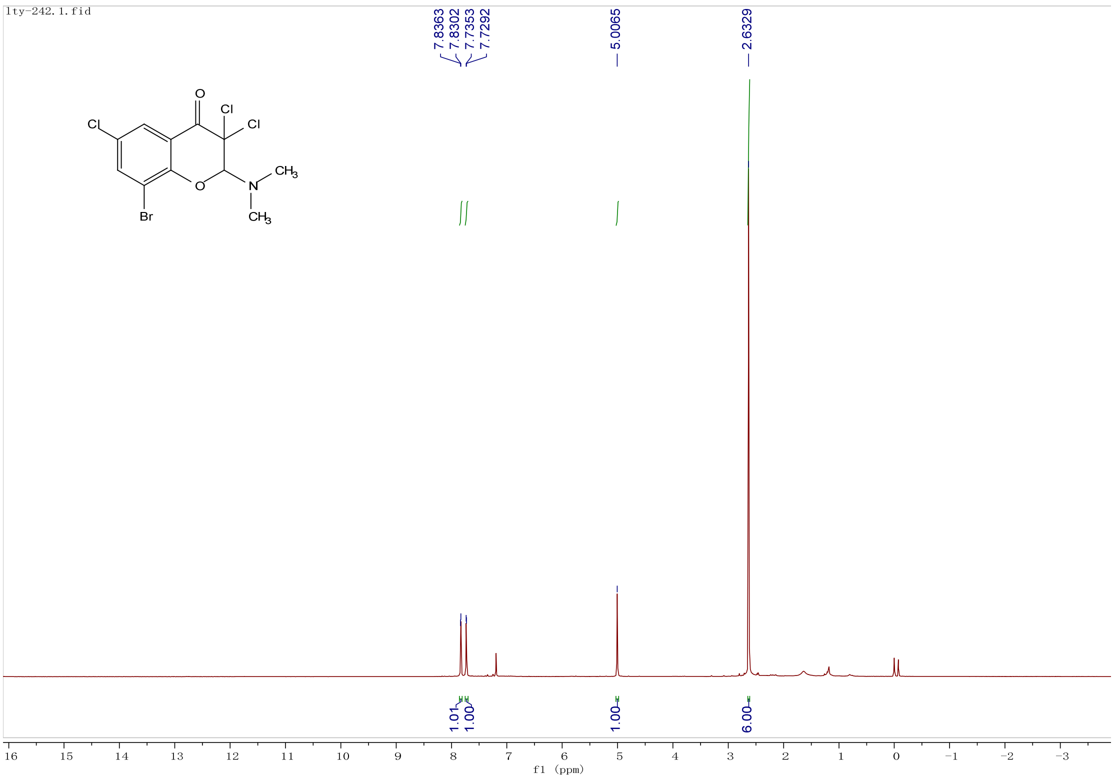
^{13}C{^{1}H} NMR spectra of **3l** ($CDCl_3$, 100 MHz)



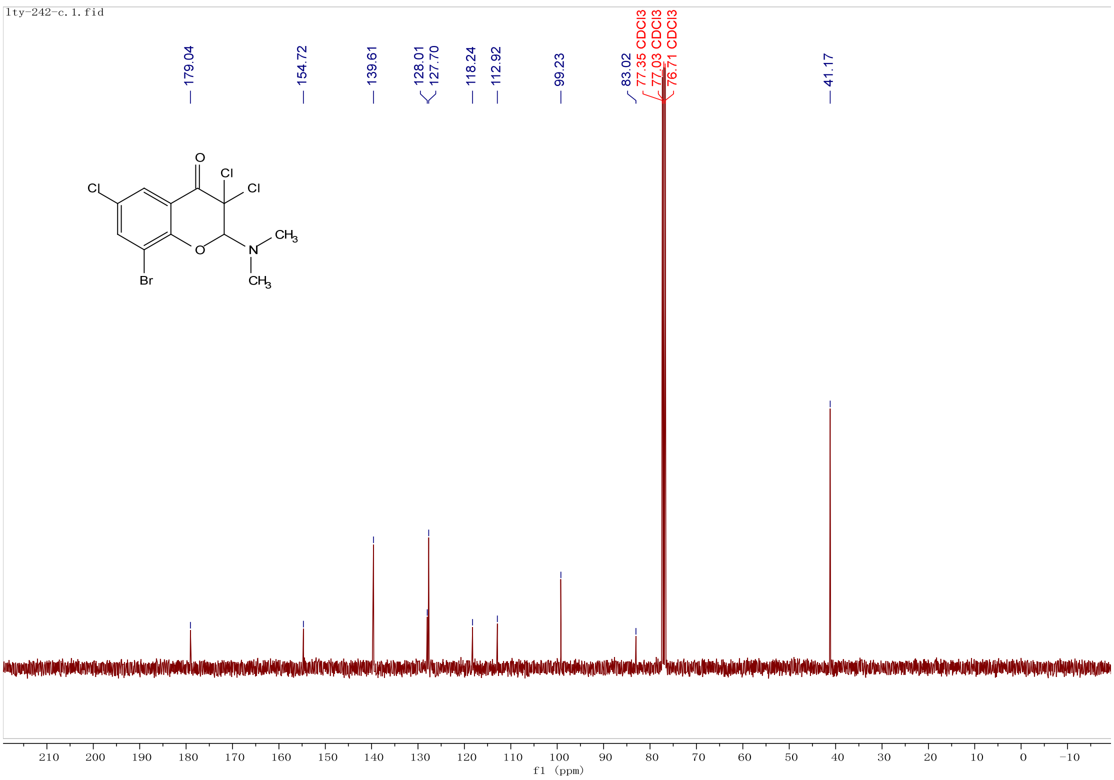
^{1}H NMR spectra of **3m** (CDCl$_3$, 400 MHz)



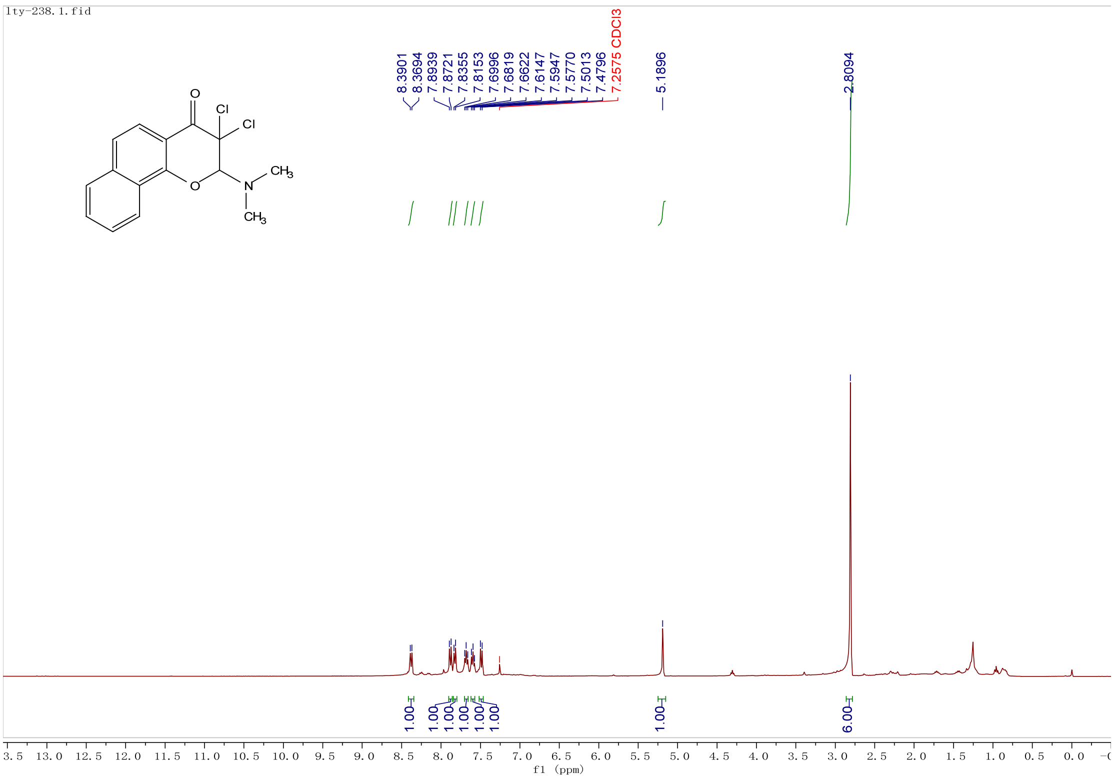
^{13}C{^{1}H} NMR spectra of **3m** (CDCl$_3$, 100 MHz)



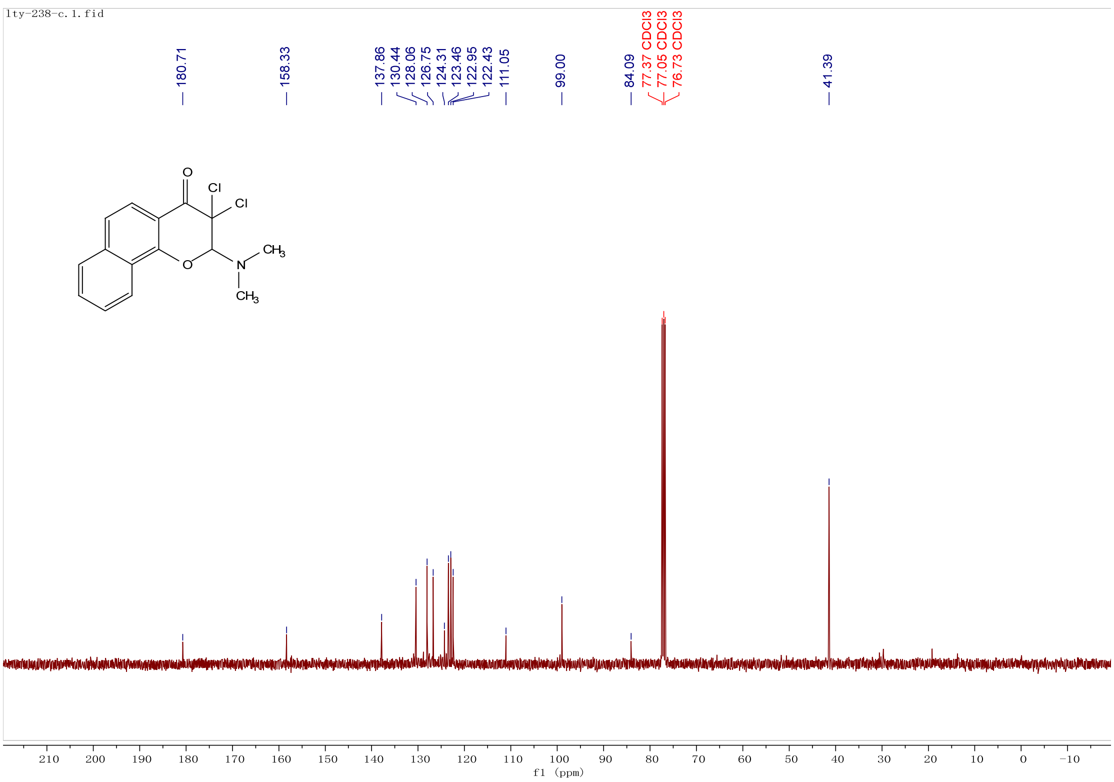
^{1}H NMR spectra of **3n** ($CDCl_3$, 400 MHz)



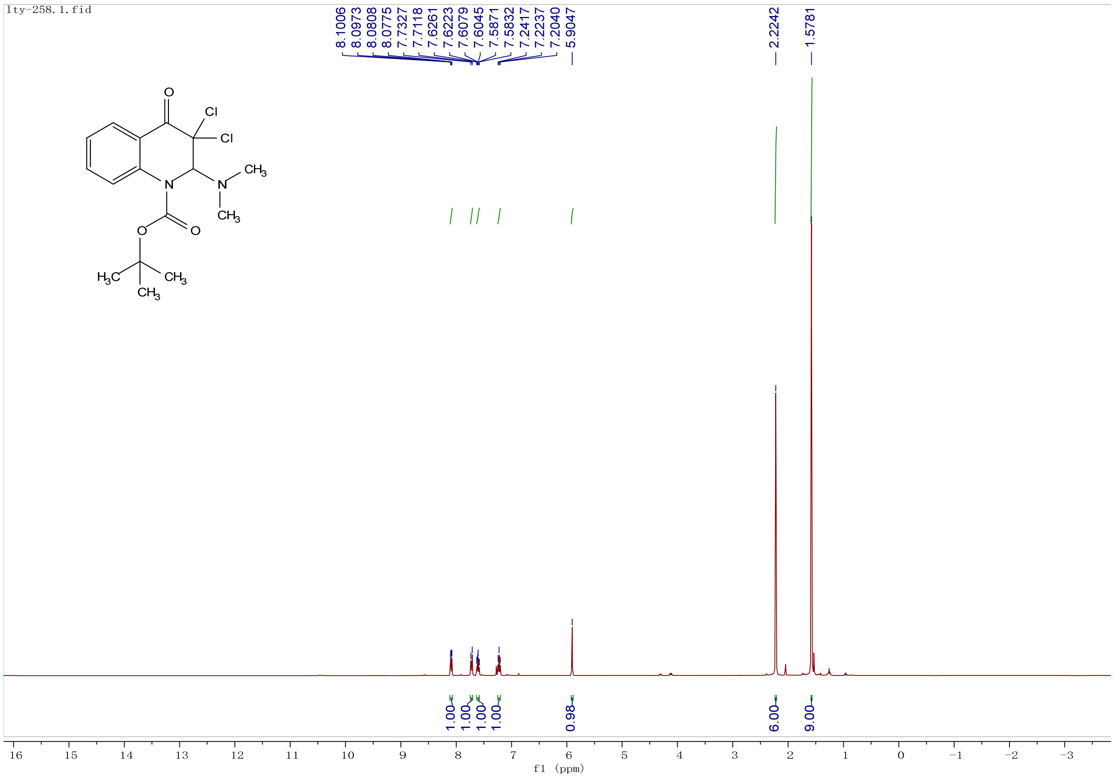
$^{13}C\{^{1}H\}$ NMR spectra of **3n** ($CDCl_3$, 100 MHz)



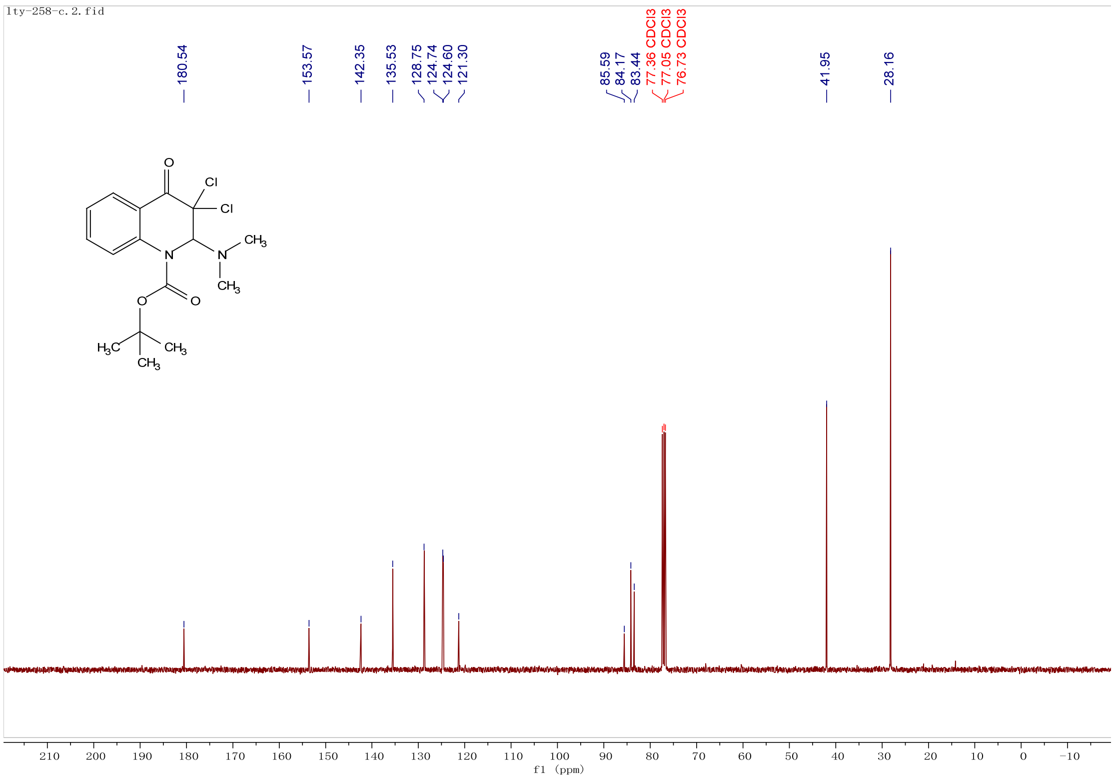
^{1}H NMR spectra of **3o** ($CDCl_3$, 400 MHz)



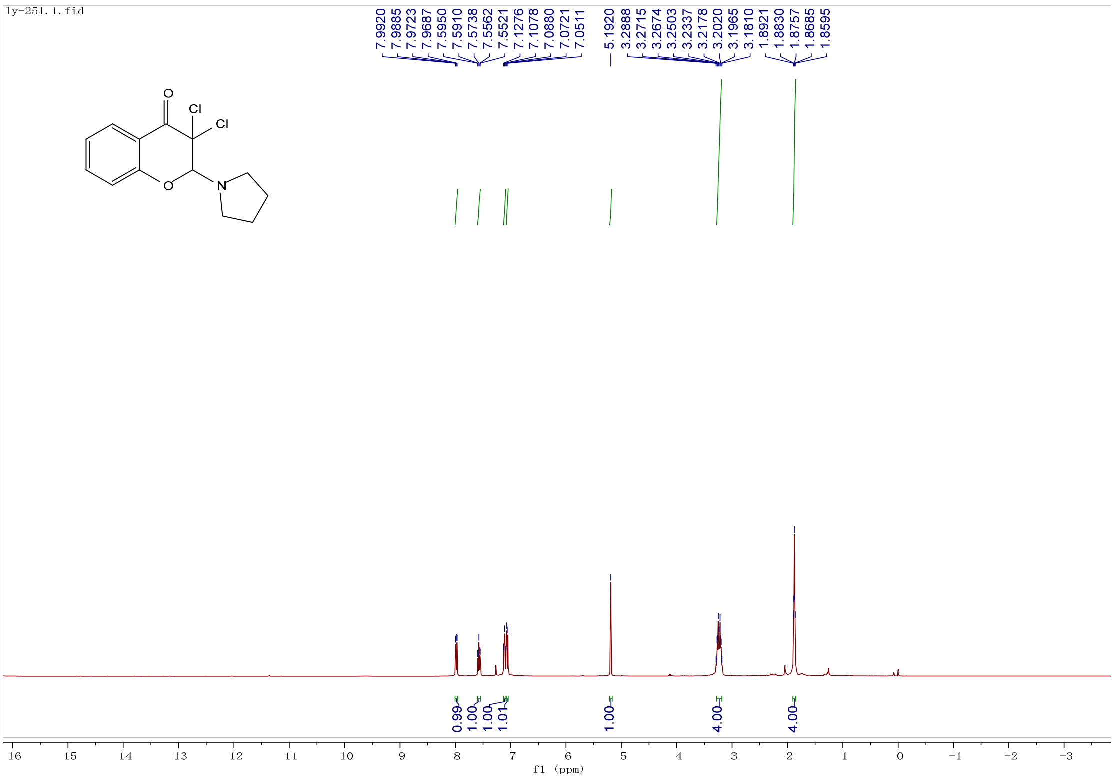
$^{13}C\{^1H\}$ NMR spectra of **3o** ($CDCl_3$, 100 MHz)



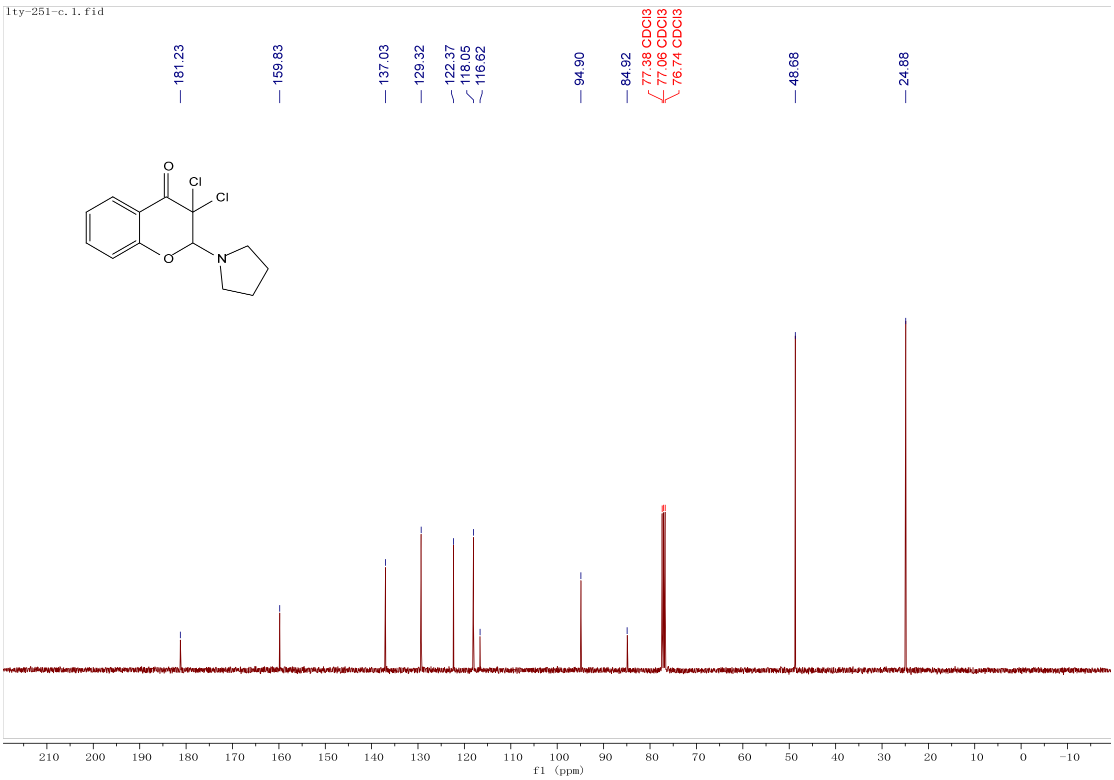
^{1}H NMR spectra of **3p** ($CDCl_3$, 400 MHz)



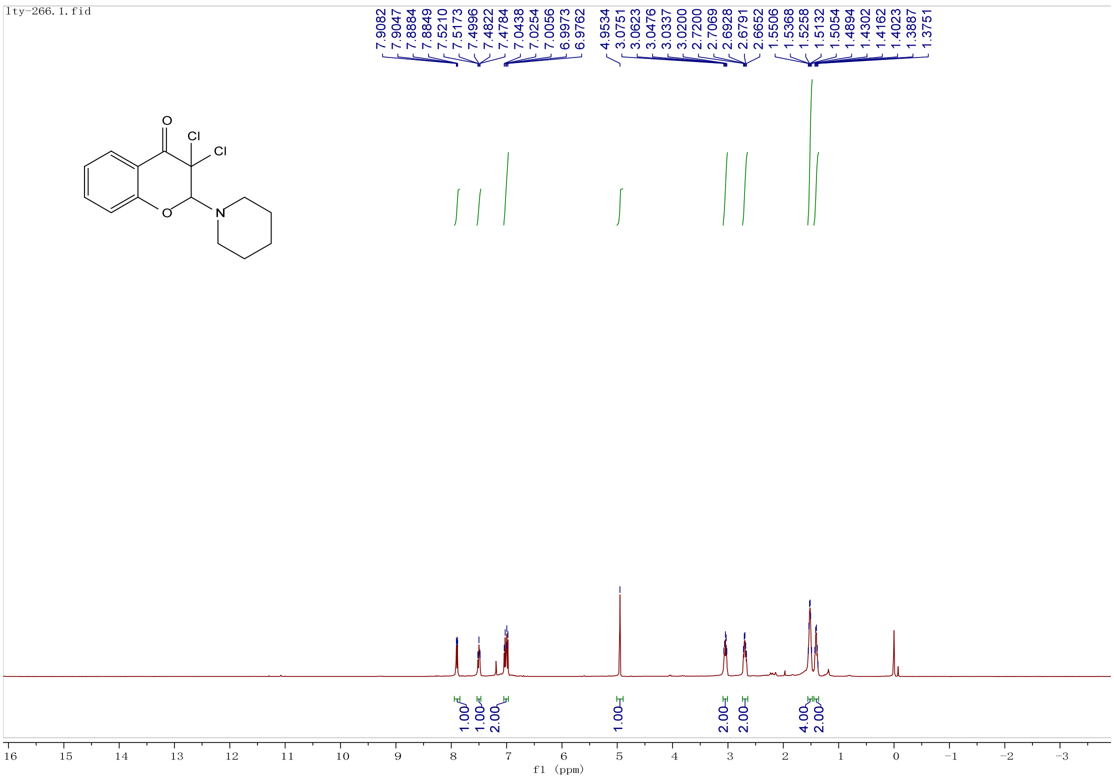
$^{13}C\{^1H\}$ NMR spectra of **3p** ($CDCl_3$, 100 MHz)



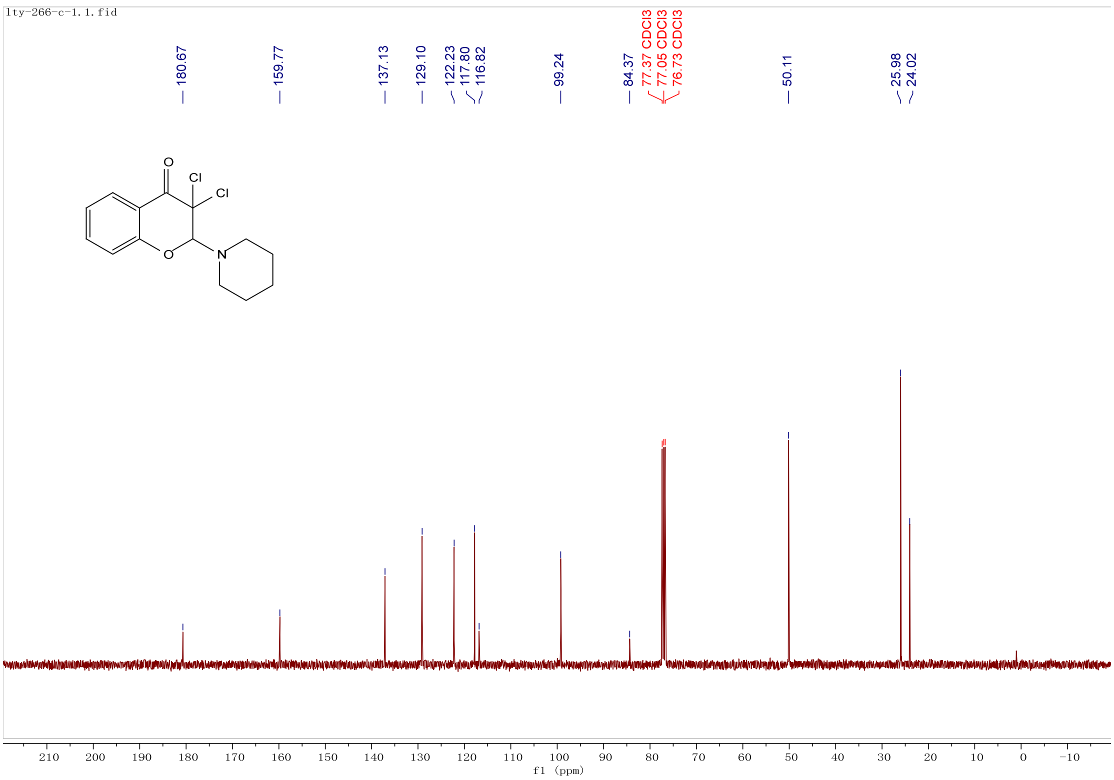
^{1}H NMR spectra of **3q** ($CDCl_3$, 400 MHz)



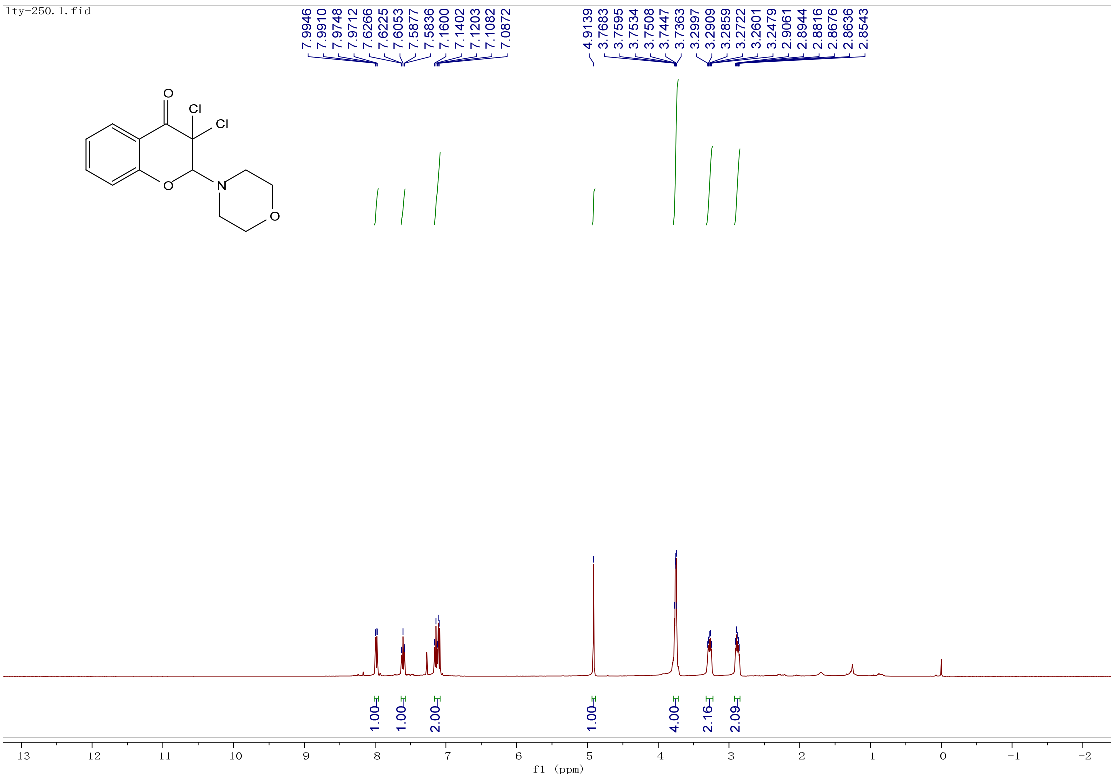
$^{13}C\{^{1}H\}$ NMR spectra of **3q** ($CDCl_3$, 100 MHz)



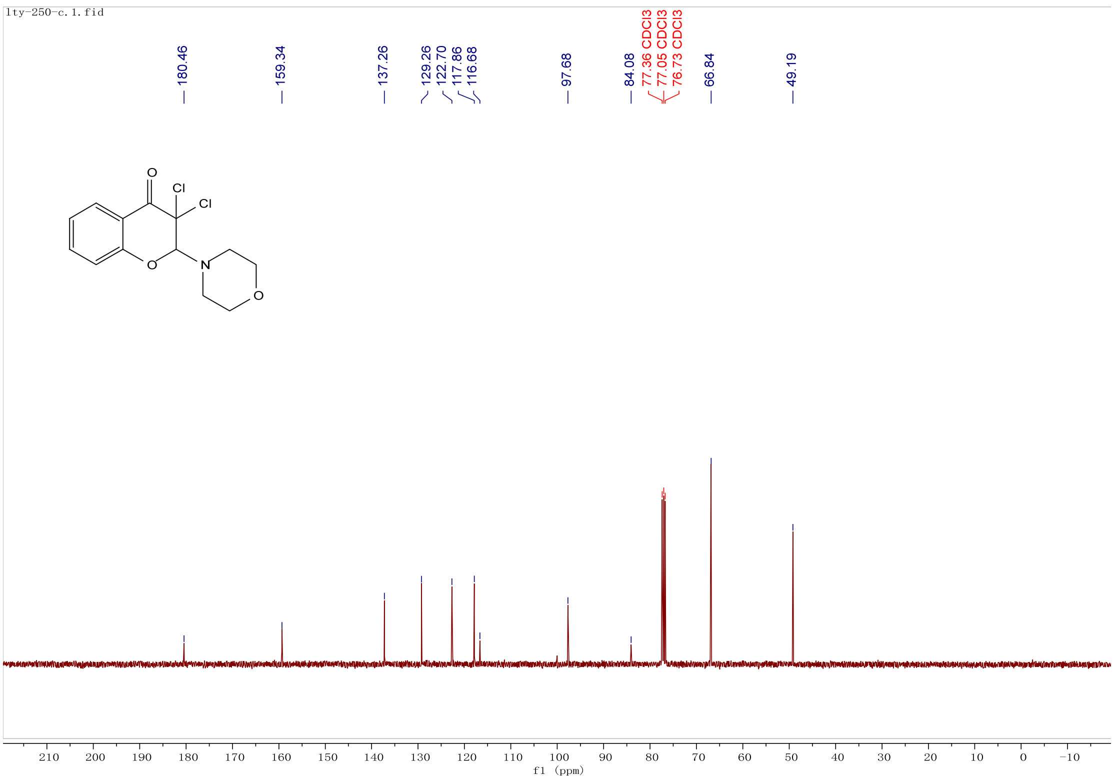
^{1}H NMR spectra of **3r** ($CDCl_3$, 400 MHz)



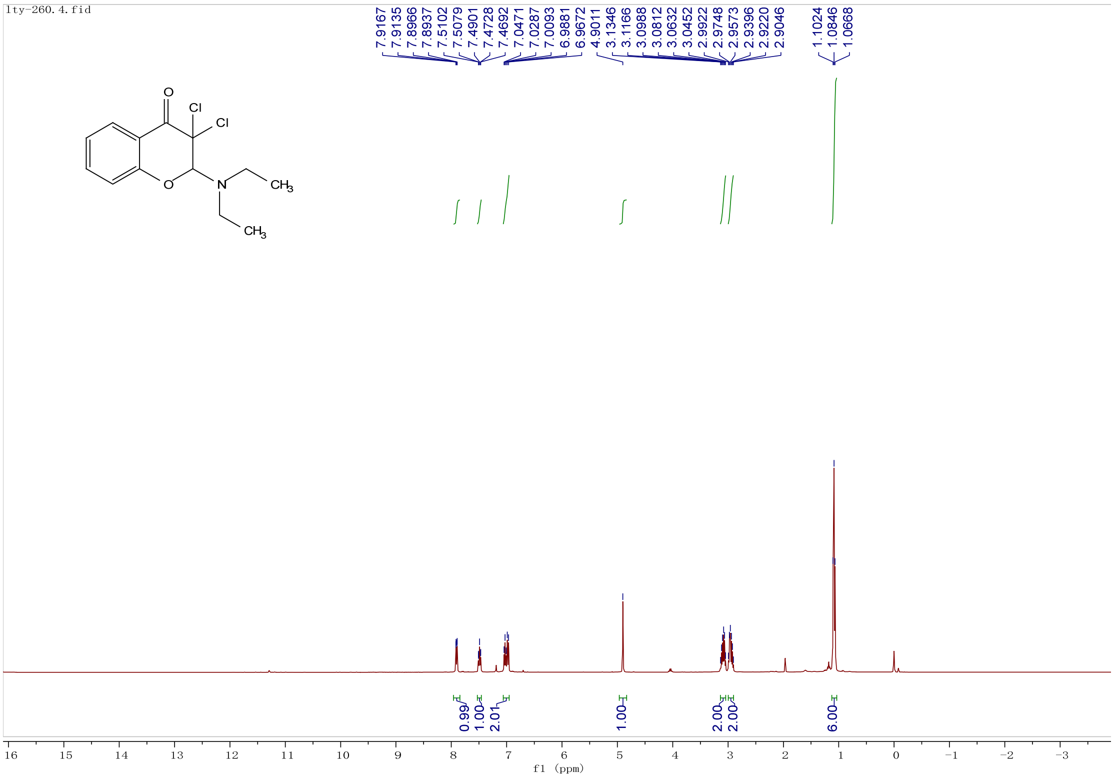
^{13}C{^{1}H} NMR spectra of **3r** ($CDCl_3$, 100 MHz)



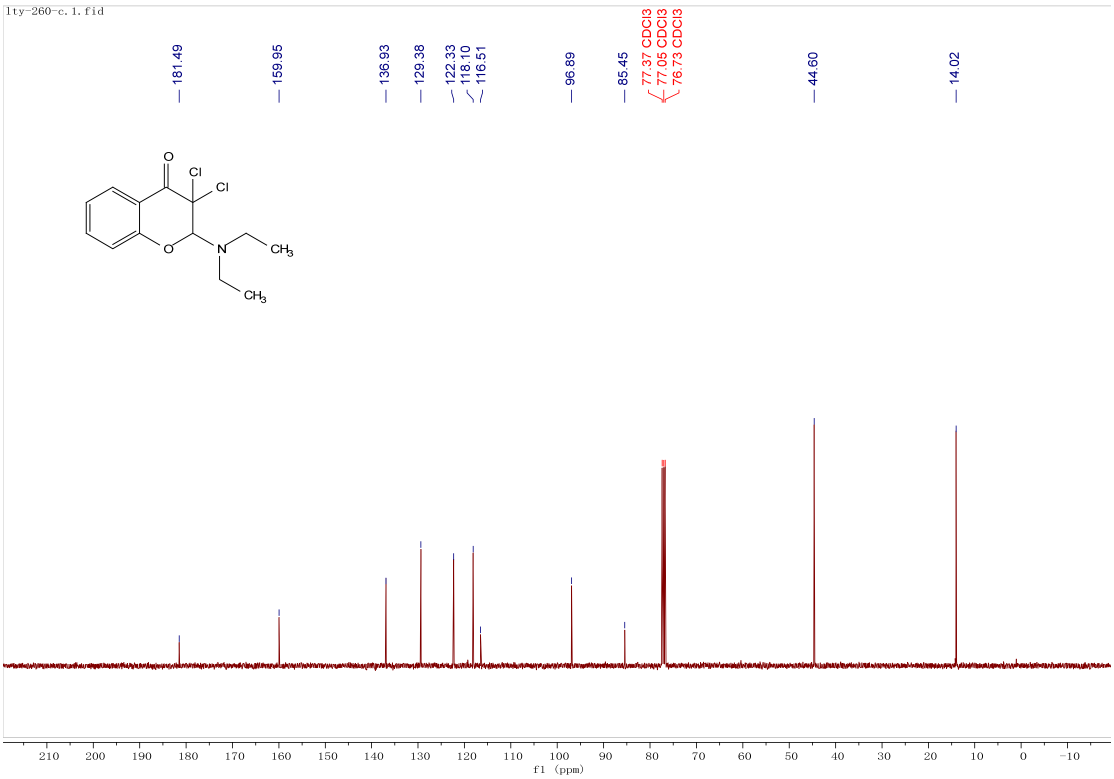
[1]H NMR spectra of **3s** ($CDCl_3$, 400 MHz)



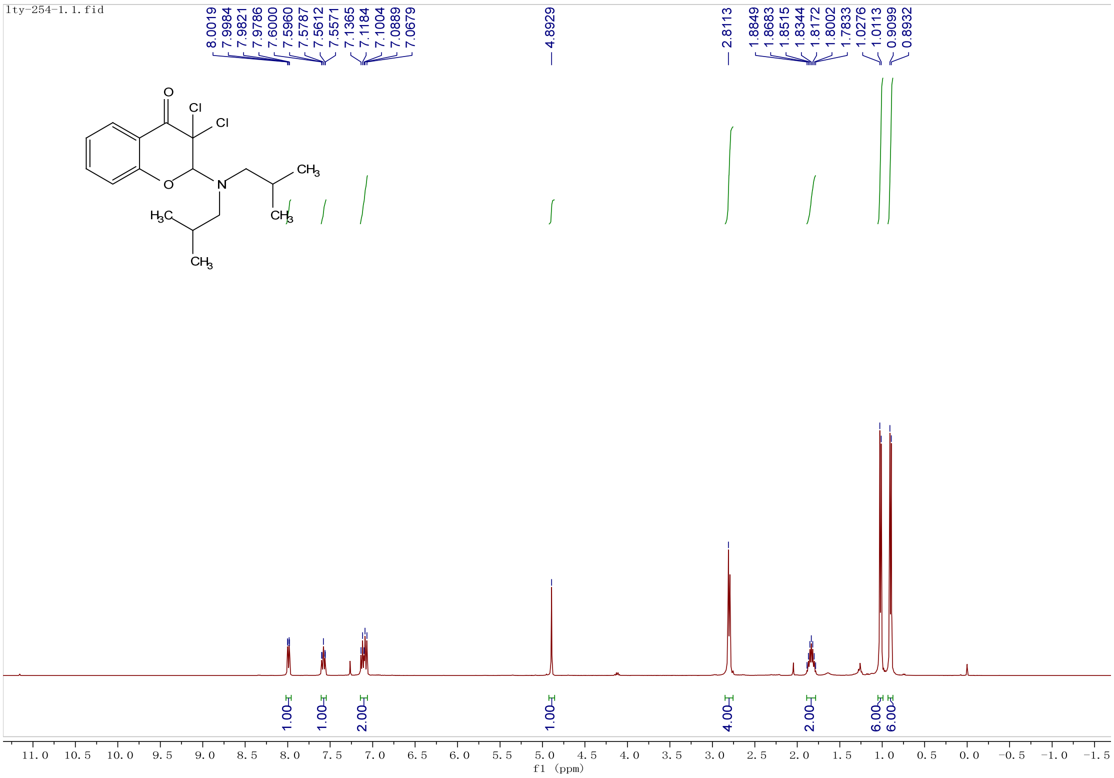
[13]C{[1]H} NMR spectra of **3s** ($CDCl_3$, 100 MHz)



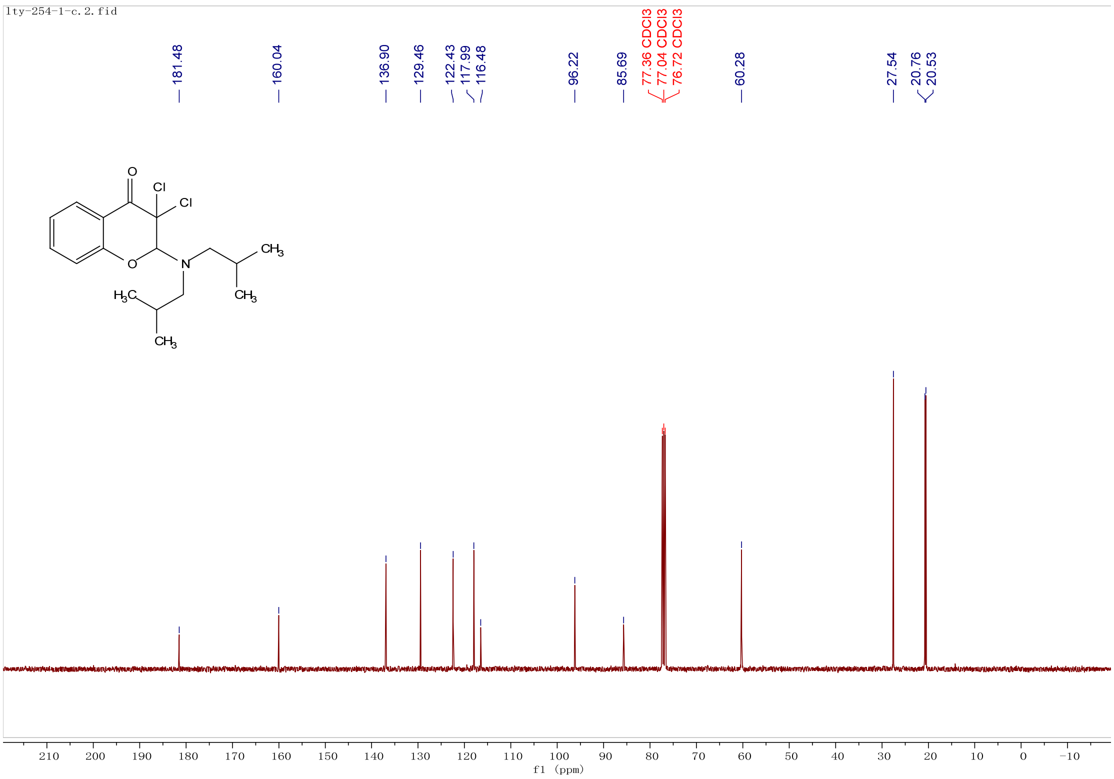
^{1}H NMR spectra of **3t** ($CDCl_3$, 400 MHz)



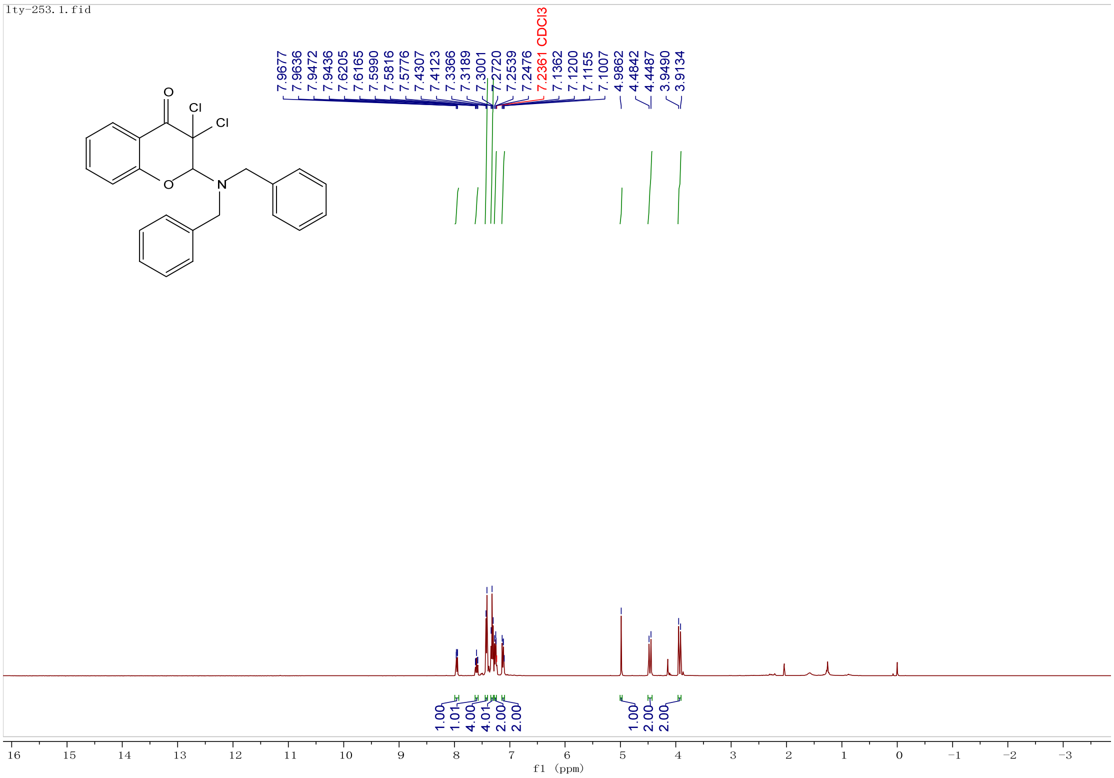
^{13}C{^{1}H} NMR spectra of **3t** ($CDCl_3$, 100 MHz)



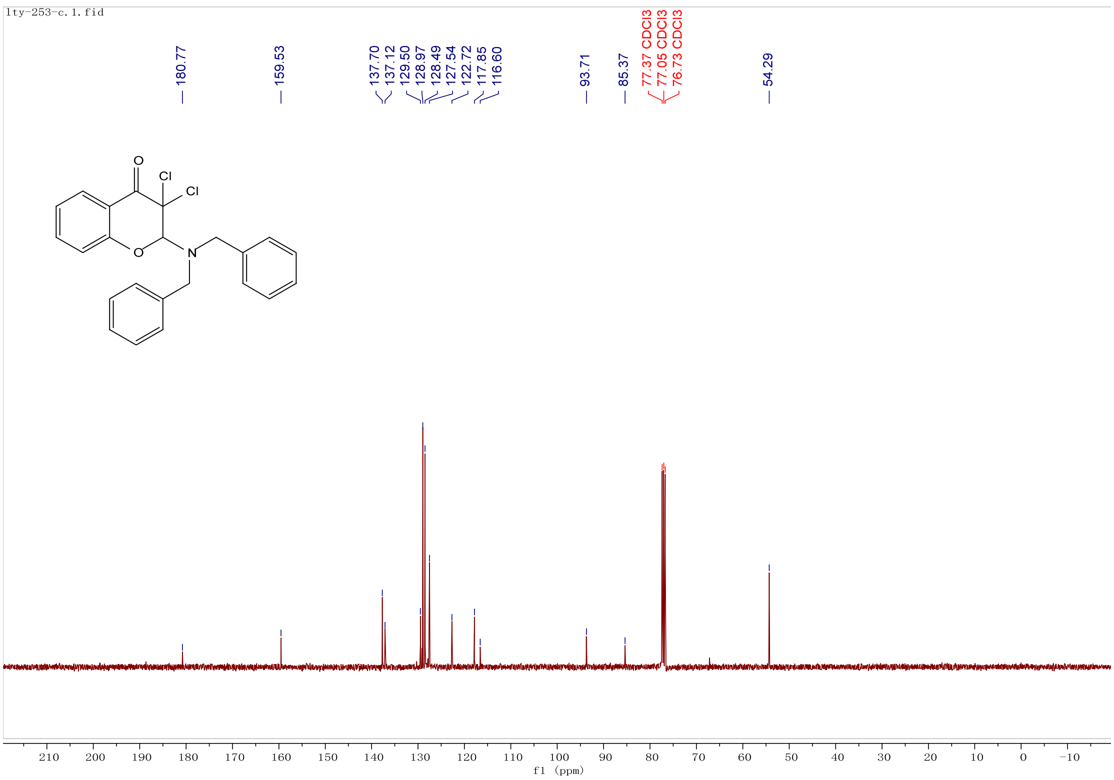
^{1}H NMR spectra of **3u** ($CDCl_3$, 400 MHz)



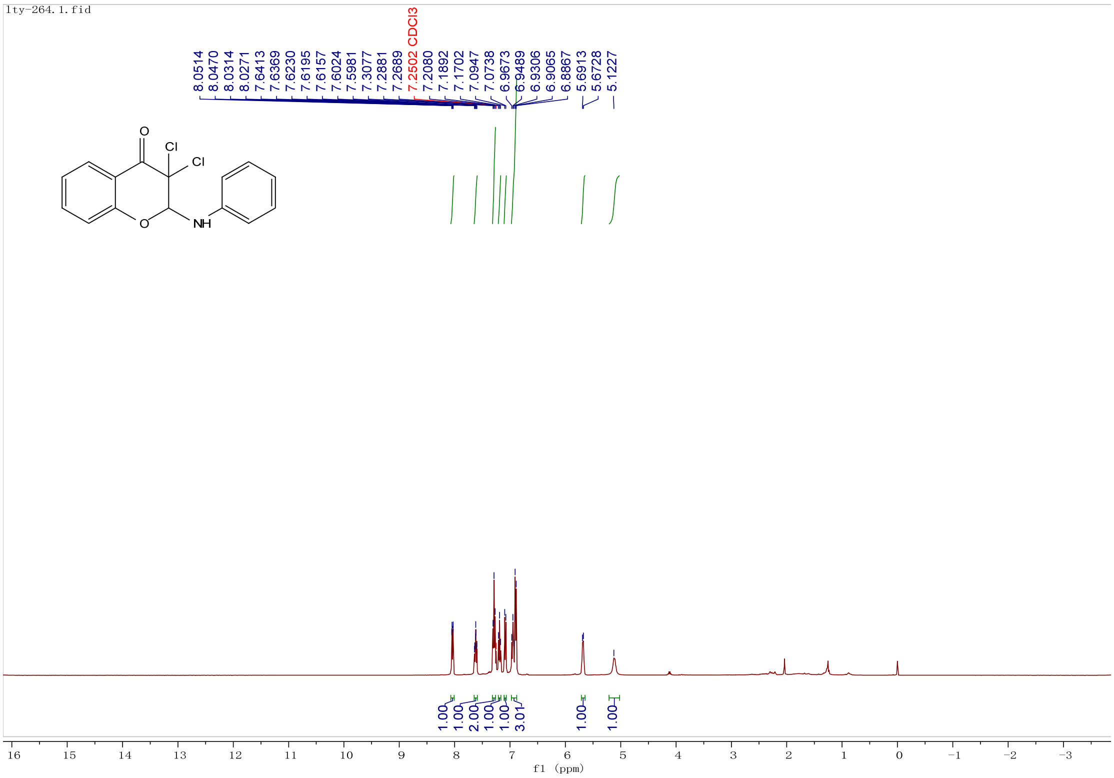
$^{13}C\{^1H\}$ NMR spectra of **3u** ($CDCl_3$, 100 MHz)



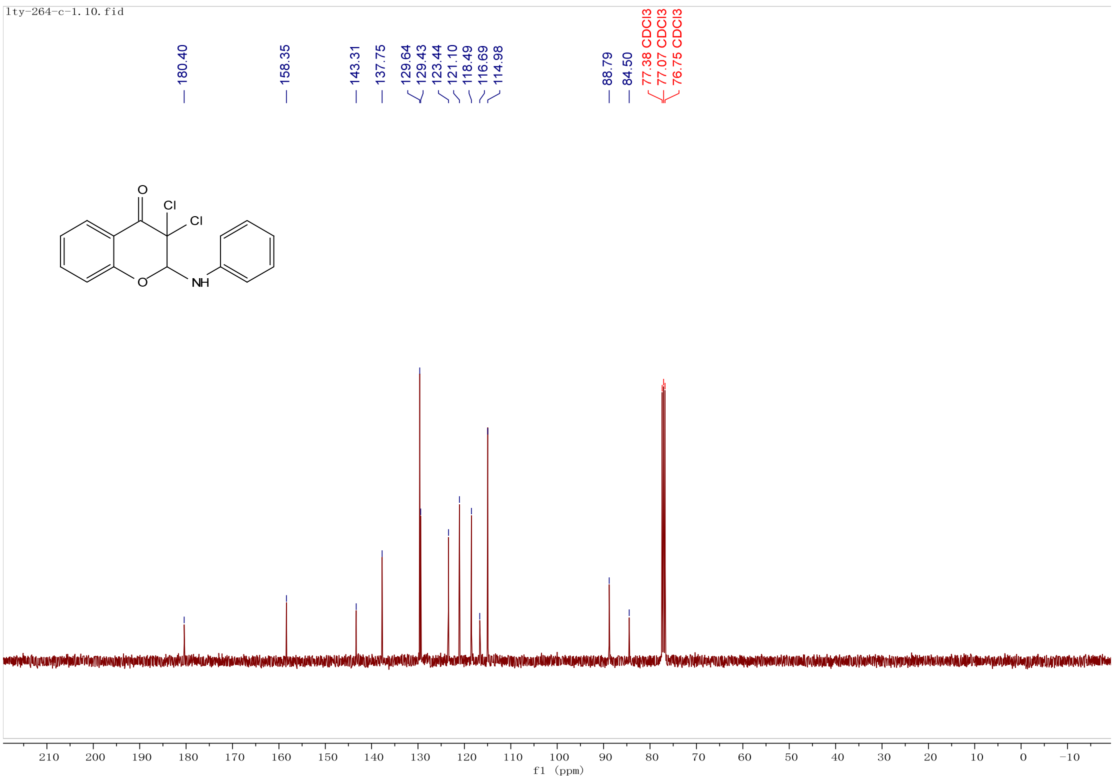
^{1}H NMR spectra of **3v** ($CDCl_3$, 400 MHz)



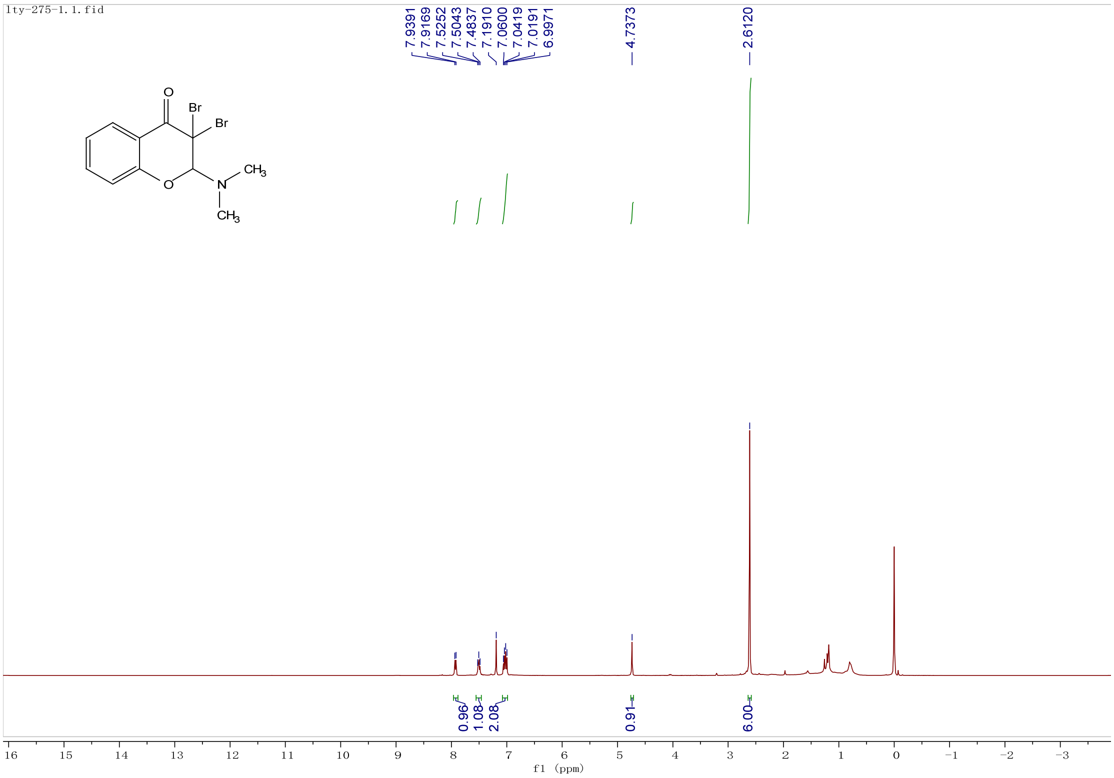
^{13}C{^{1}H} NMR spectra of **3v** ($CDCl_3$, 100 MHz)



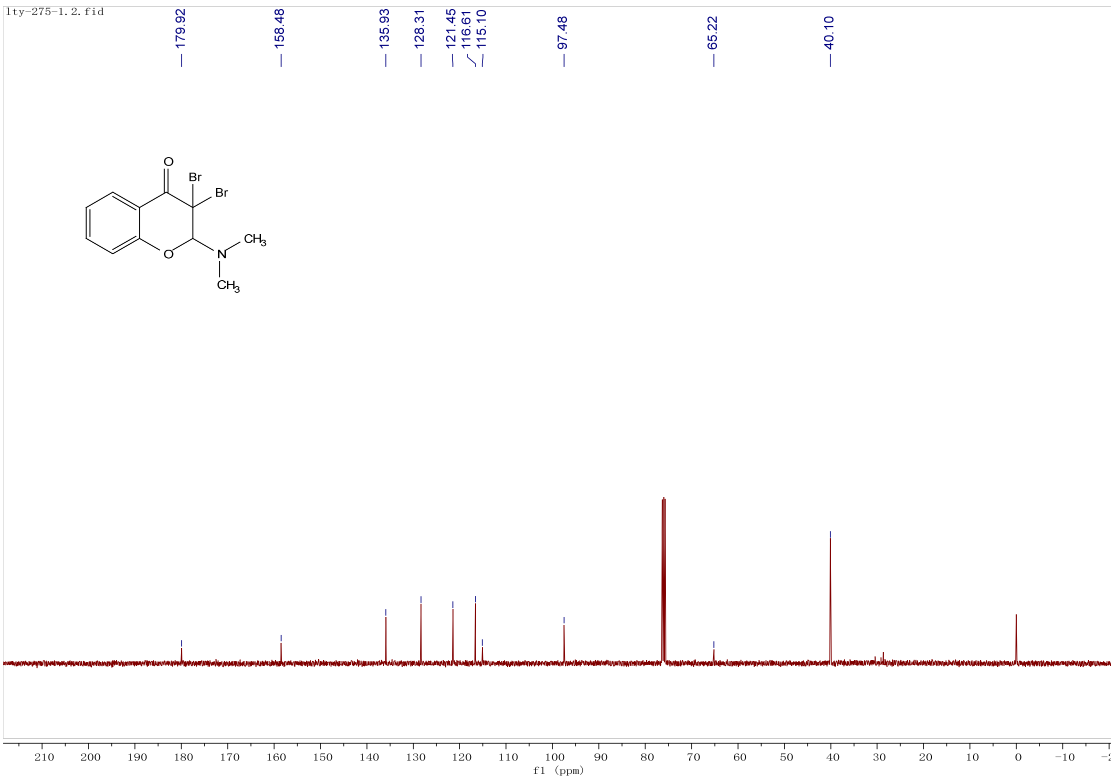
^{1}H NMR spectra of **3w** ($CDCl_3$, 400 MHz)



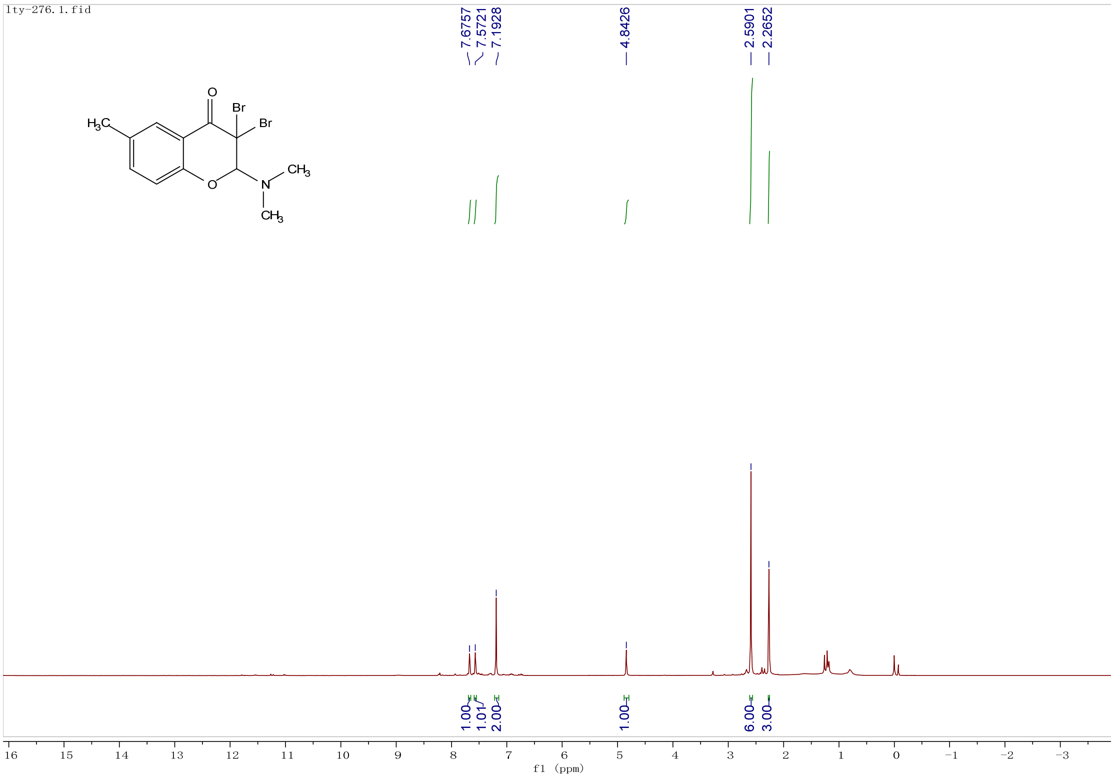
$^{13}C\{^1H\}$ NMR spectra of **3w** ($CDCl_3$, 100 MHz)



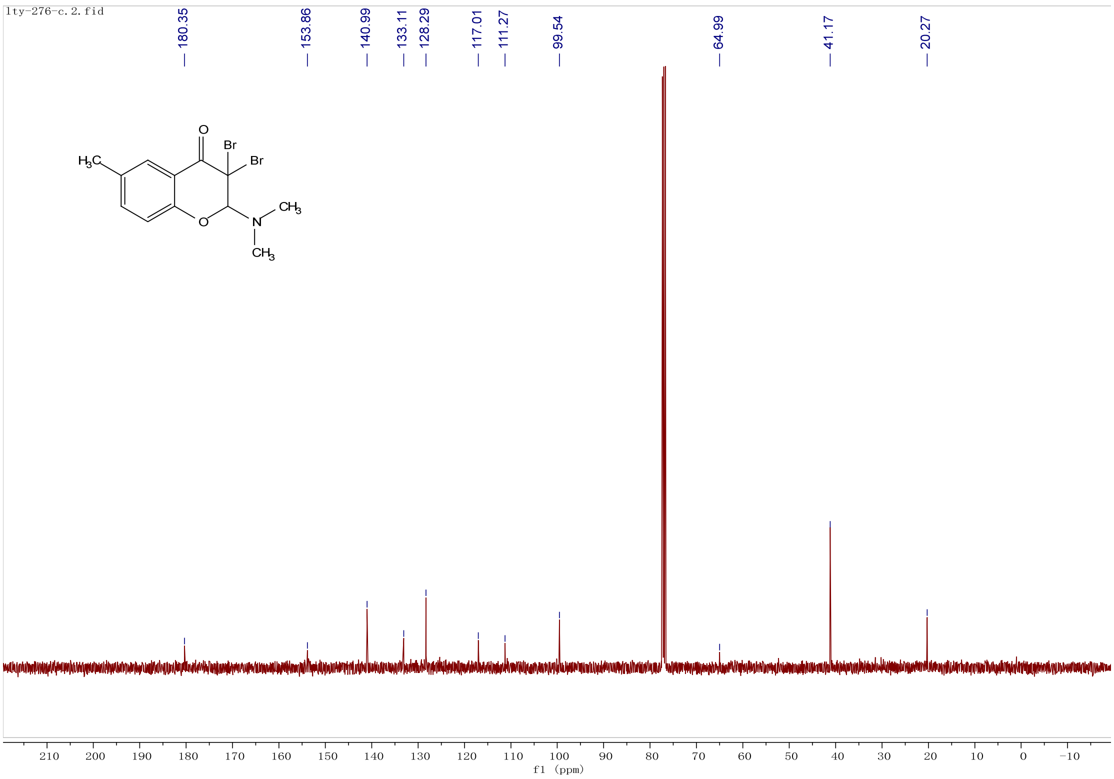
[1]H NMR spectra of **4a** ($CDCl_3$, 400 MHz)



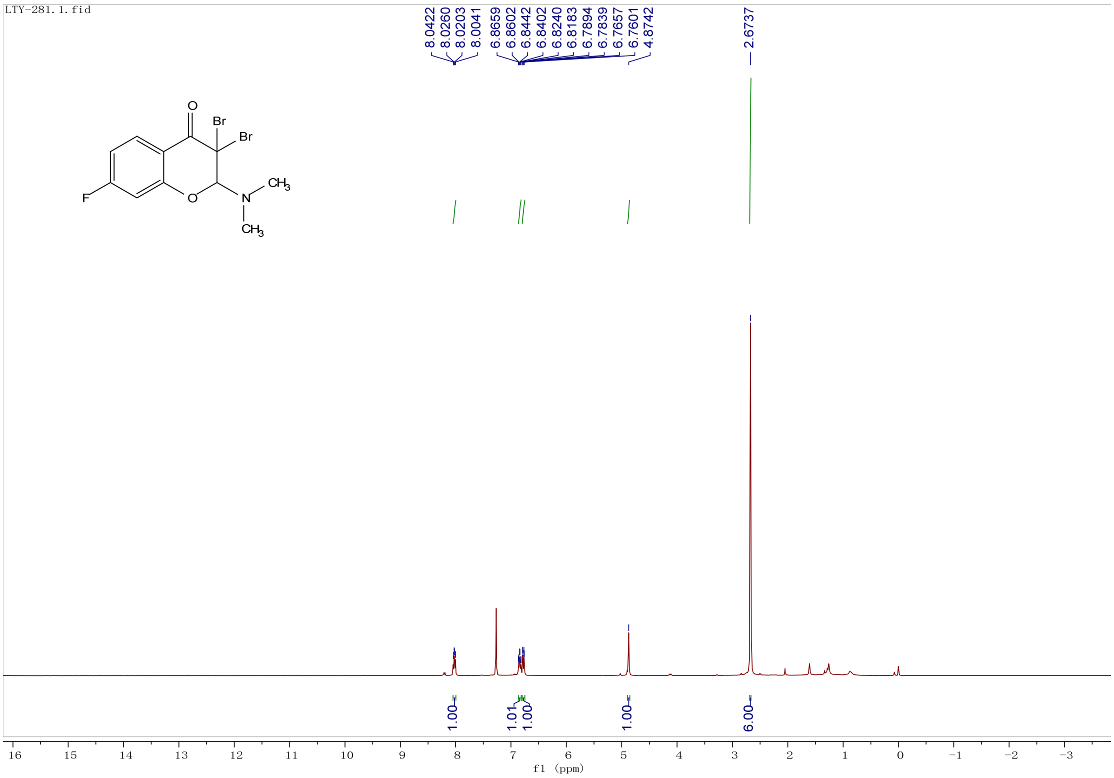
[13]C{[1]H} NMR spectra of **4a** ($CDCl_3$, 100 MHz)



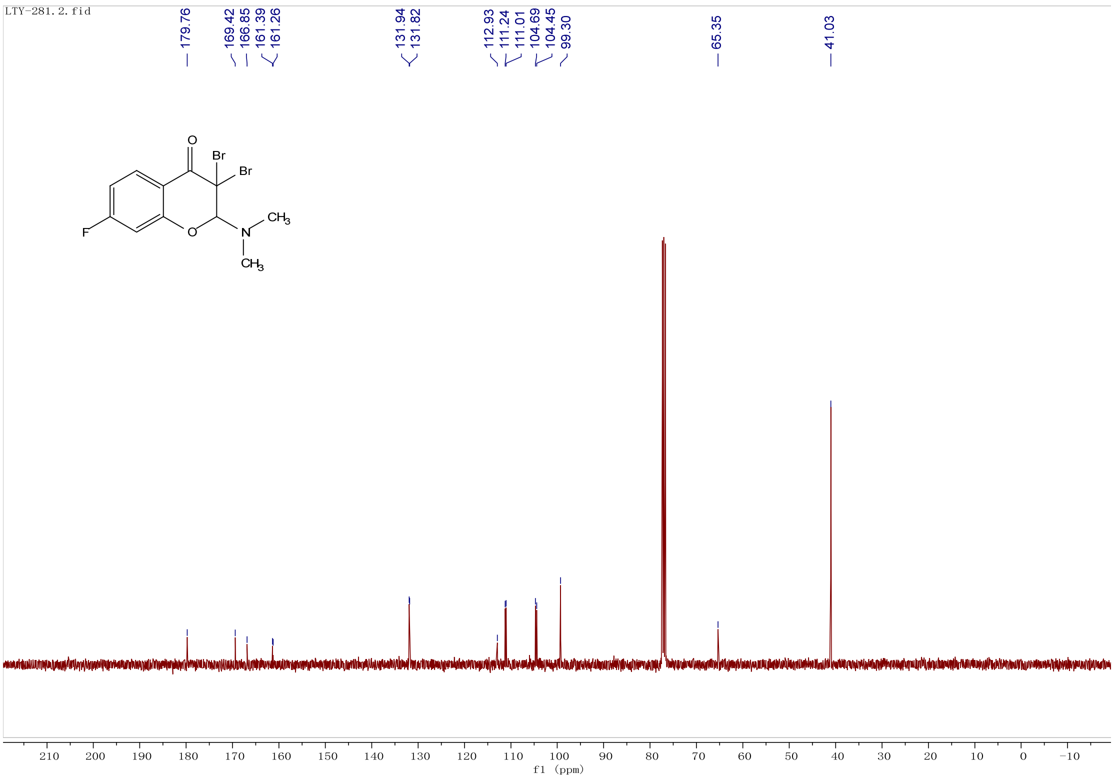
^{1}H NMR spectra of **4b** ($CDCl_3$, 400 MHz)



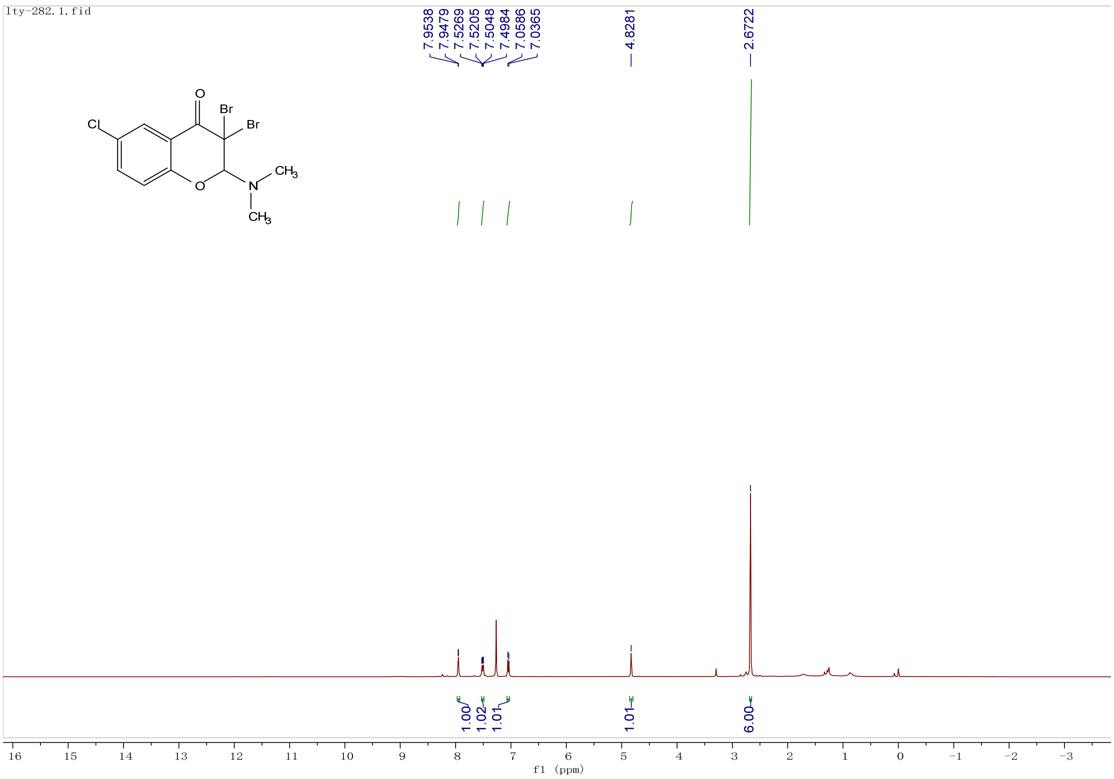
$^{13}C\{^{1}H\}$ NMR spectra of **4b** ($CDCl_3$, 100 MHz)



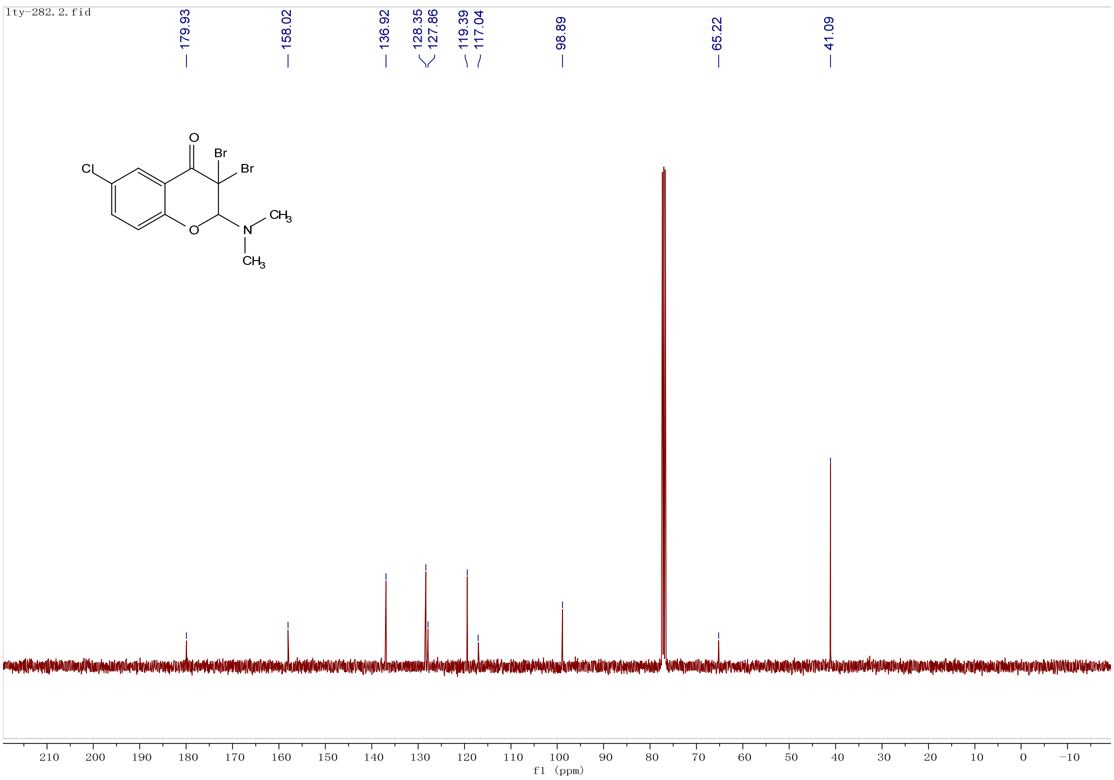
^{1}H NMR spectra of **4c** ($CDCl_3$, 400 MHz)



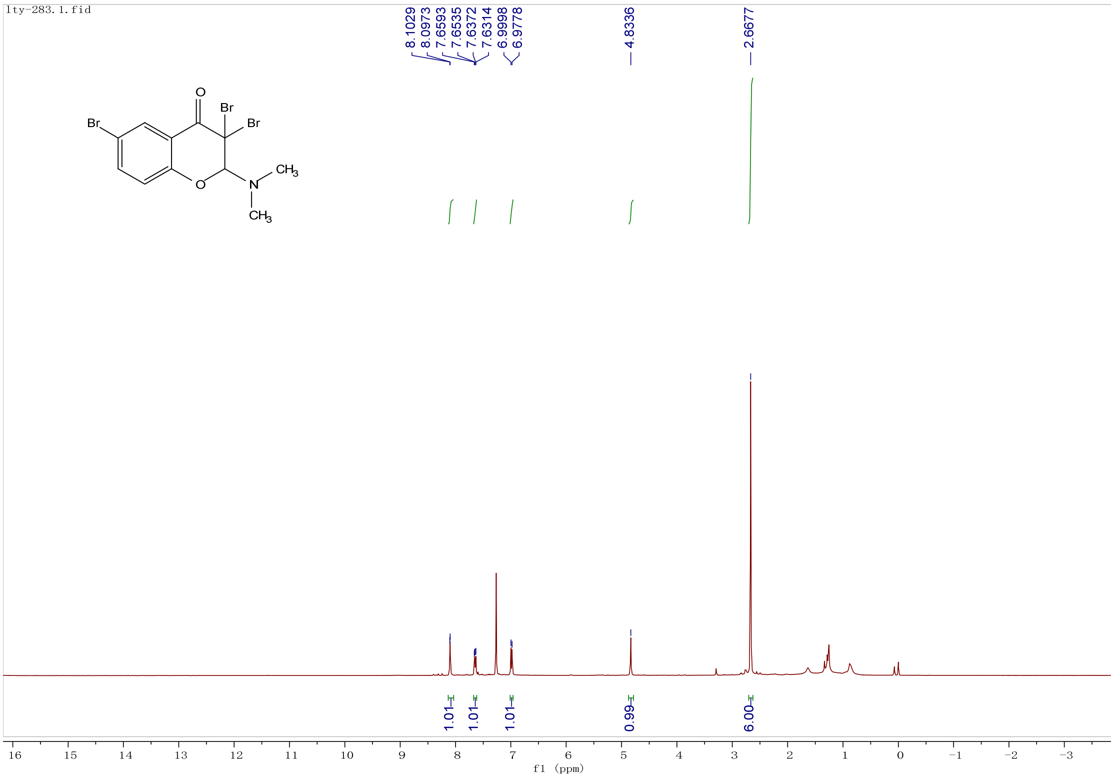
$^{13}C\{^{1}H\}$ NMR spectra of **4c** ($CDCl_3$, 100 MHz)



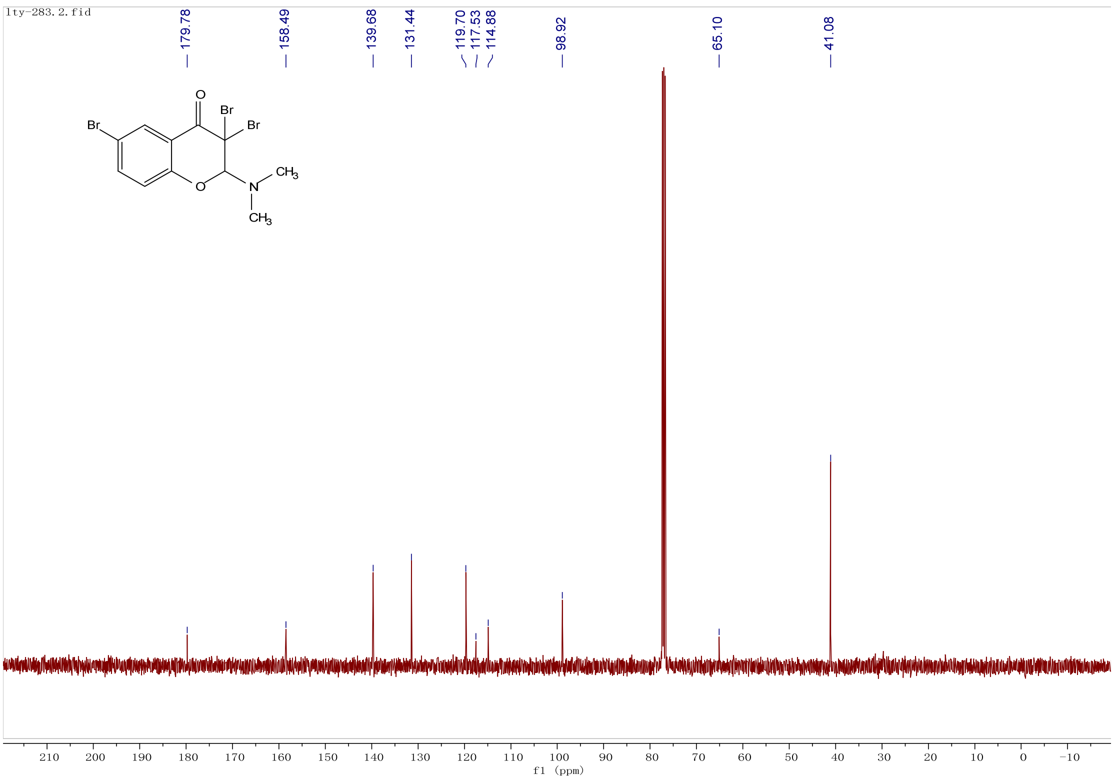
^{1}H NMR spectra of **4d** ($CDCl_3$, 400 MHz)



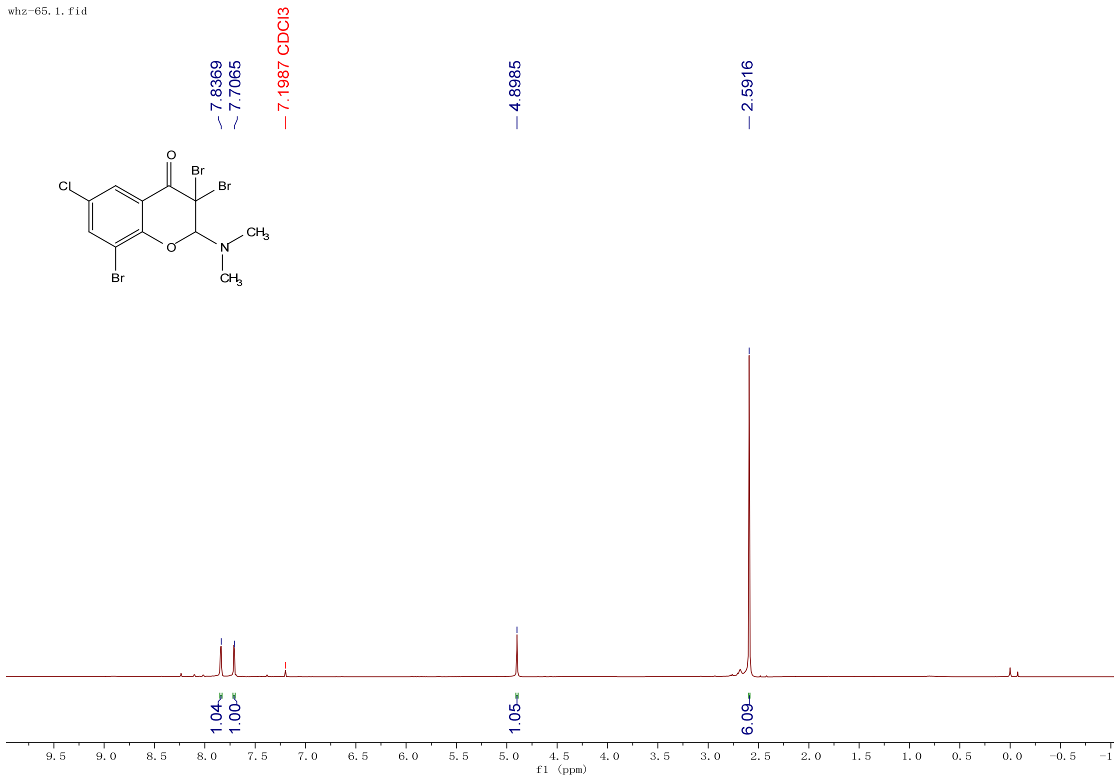
$^{13}C\{^{1}H\}$ NMR spectra of **4d** ($CDCl_3$, 100 MHz)



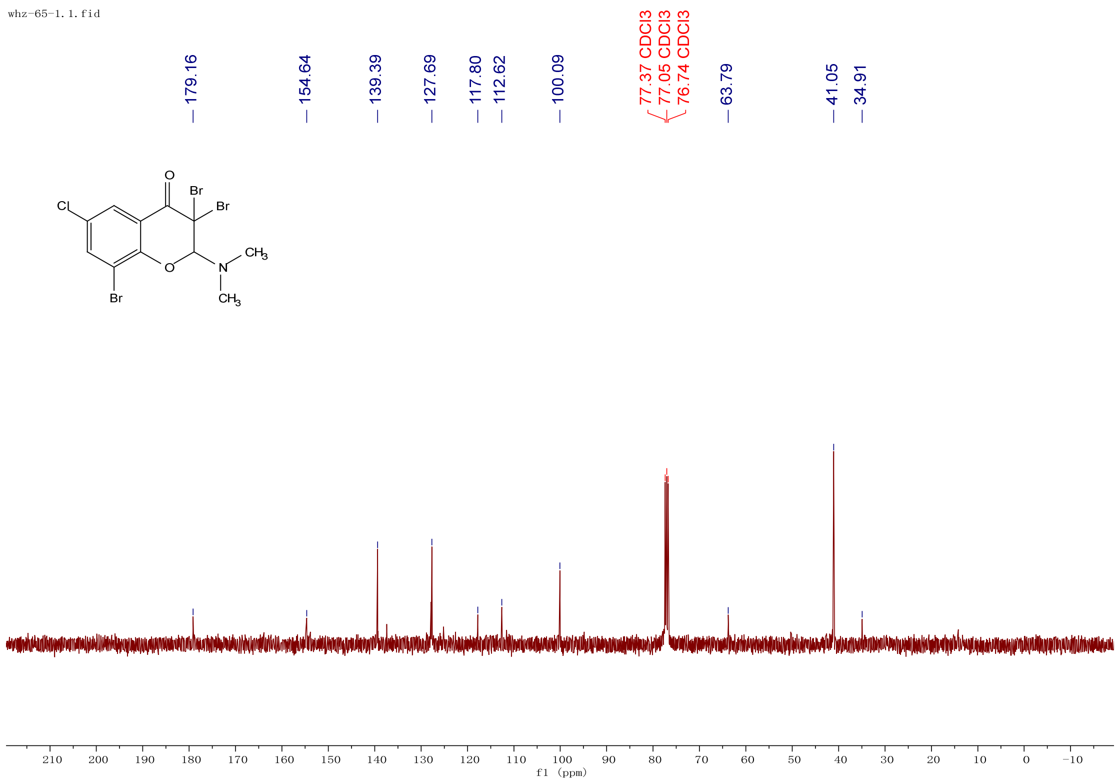
^{1}H NMR spectra of **4e** ($CDCl_3$, 400 MHz)



$^{13}C\{^{1}H\}$ NMR spectra of **4e** ($CDCl_3$, 100 MHz)



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



$^{13}C\{^{1}H\}$ NMR spectra of **4f** ($CDCl_3$, 100 MHz)

Procedure for the single crystal preparation

Pure product **3k** was dissolved in dichloromethane, and filtered to removed any unsolved solid. The solution was then moved to a test tube. Afterwards, petroleum ether was added slowly to the tube and led to the formation of two-phase liquid mixture. Subsequently, the tube was then sealed with plastic membrane in the head. After digging some hole in the membrane with needle, the tube was then located in restful atmosphere. The slow evaporation of the solvent at room temperature provided the single crystal sample proper for analysis.

Information of X–ray crystallography analysis

Suitable single crystal of **3k** was selected under a stereo microscope and fixed with epoxy cement on respective fine glass fiber, and the structure of single crystal was determined by X-ray single crystal diffraction with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The reflection intensity in the θ range 3.1–25.1° for **1** was collected at 295(2) K using the ω scans technique. The employed single crystal exhibits no detectable decay during the data collection. The data were corrected for Lp and absorption effects. The direct method employing the SHELXS-2016 program gave the initial positions for part of non-hydrogen atoms, and the subsequent difference Fourier syntheses using SHELXL-2016 program resulted in initial positions for the rest non-hydrogen atoms. The hydrogen atoms on the organic ligands were geometrically generated. The full-matrix least-squares technique was applied for refinement of positions and anisotropic displacement parameters of all the non-hydrogen atoms, as well as the positions of the hydrogen atoms using riding mode with isotropic displacement parameters set to 1.2 or 1.5 times of the values for C atoms. Detailed information about the crystal data and structure determination is summarized in Table S1.

Figure S1 X-ray crystal structure of **3k** (with thermal ellipsoids at 45 % probability)

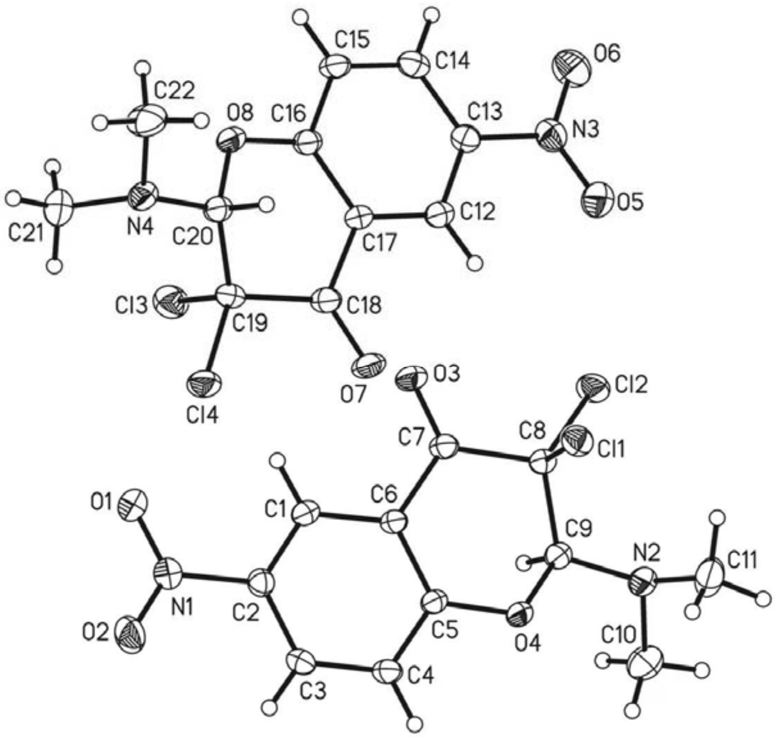


Table S1 Typical crystal structure data for **3k**

Compounds	**3k**
Empirical formula	$C_{11}H_{10}Cl_2N_2O_4$
Formula weight	305.11
Description	colorless, platelet
Crystal size (mm)	0.49 × 0.38 × 0.15
Temperature (K)	295(2)
Crystal system	Triclinic
Space group	P–1
a (Å)	12.349(2)
b (Å)	24.445(5)
c (Å)	8.811(2)
α(°)	90
β(°)	101.89(3)
γ(°)	90
Volume (Å^3)	2602.5(1)
Z	8
D_{calc} (g cm^{-3})	1.557
F(000)	1248
μ (mm^{-1})	0.510
θ range (deg)	3.1–25.1
Reflections collected	20281
Unique reflections (R_{int})	4588 (0.050)
Data,restraints, parameters	2737, 0, 0.051
Goodness of fit on F^2	1.171
hkl range	±14, ±28, ±10
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0405, 0.0869
R_1, wR_2 (all data)[a]	0.0728, 0.1277
A, B values in w [b)]	0.0354, 2.3886
$\delta\rho_{max}$, $\delta\rho_{min}$ (e·Å^{-3})	0.319, -0.476

[a)] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

[b)] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$