Supporting Information

$FeCl_3$-promoted Tandem 1,4-Conjugate Addition/6-*endo-dig* Cyclyzation/Oxidation of Propargylamines and Benzoylacetonitriles/Malononitrile: Direct Access to Functionalized 2-Aryl-4*H*-chromenes

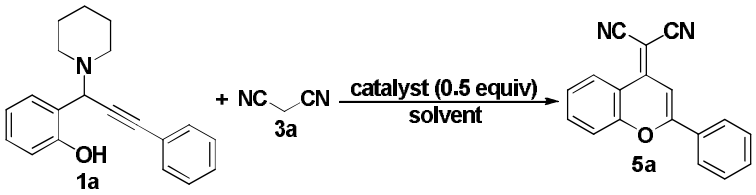
Xinwei He,* Hui Wang, Xiaoting Cai, Qianqian Li, Jiajia Tao, Yongjia Shang*

Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China

* Corresponging author: *xinweihe@mail.ahnu.edu.cn*, *shyj@mail.ahnu.edu.cn*

Table of Contents

Table S1. Optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Temp. (°C)	Yield (%)[b]
1	—	DMF	90	trace
2	HCl	DMF	90	trace
3	$AlCl_3$	DMF	90	15
4	$Sc(OTf)_3$	DMF	90	35
5	$BF_3{\cdot}Et_2O$	DMF	90	10
6	$FeCl_3$	DMF	90	70
7[c]	$FeCl_3$	DMF	90	56
8[d]	$FeCl_3$	DMF	90	72
9	$FeCl_3$	DMSO	90	23
10	$FeCl_3$	THF	90	31
11	$FeCl_3$	MeCN	80	55
12	$FeCl_3$	1, 4-dioxane	90	trace
13	$FeCl_3$	DCE	90	25
14	$FeCl_3$	toluene	90	60
15	$FeCl_3$	EtOH	90	trace
16	$FeCl_3$	DMF	r.t.	trace
17	$FeCl_3$	DMF	60	32
18	$FeCl_3$	DMF	80	58
19	$FeCl_3$	DMF	100	65
20[e]	$FeCl_3$	DMF	90	41

[a] Reaction conditions: 2-(3-phenyl-1-(piperidin-1-yl)prop-2-yn-1-yl)-phenol **1a** (0.50 mmol), propanedinitrile **3a** (0.50 mmol), catalyst (0.25 mmol), solvent (10 mL), in open air for 24 h. [b]Isolated yields. [c]0.2 equiv of catalyst was used. [d]0.8 equiv of catalyst was used. [e] reaction time of 12 h.

X-Ray Crystallography Structures of Compounds **4fa** and **5a**.

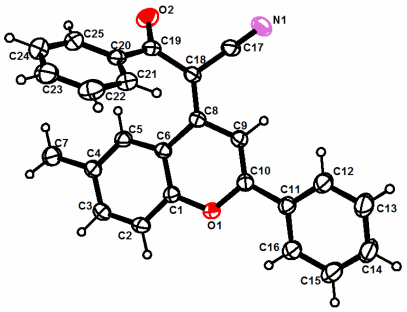


Figure S1. X-ray crystal structure of compound **4fa**.

Crystal data for **4fa**: $C_{25}H_{17}NO_2$, *Mr* = 363.40, Triclinic, *a* = 8.4187 (14) Å, *b* = 9.0328 (14) Å, *c* = 13.363 (2) Å, $\alpha = 104.129(2)^o$, $\beta = 99.655\ (2)^o$, $\gamma = 103.737(2)^o$, *V* = 929.4 (3) $Å^3$, *T* = 293(2) K, space group P-1, *Z* = 2, 9414 reflections collected, 3414 unique (R_{int} = 0.0233) which were used in all calculation. The ellipsoid contour probability level in the caption is 30%.

Crystallographic data for compound **4fa** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC-1841800**.

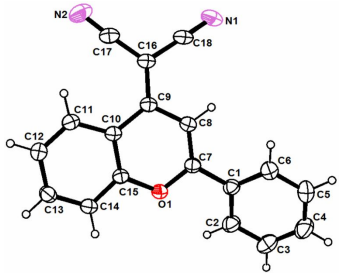
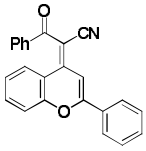


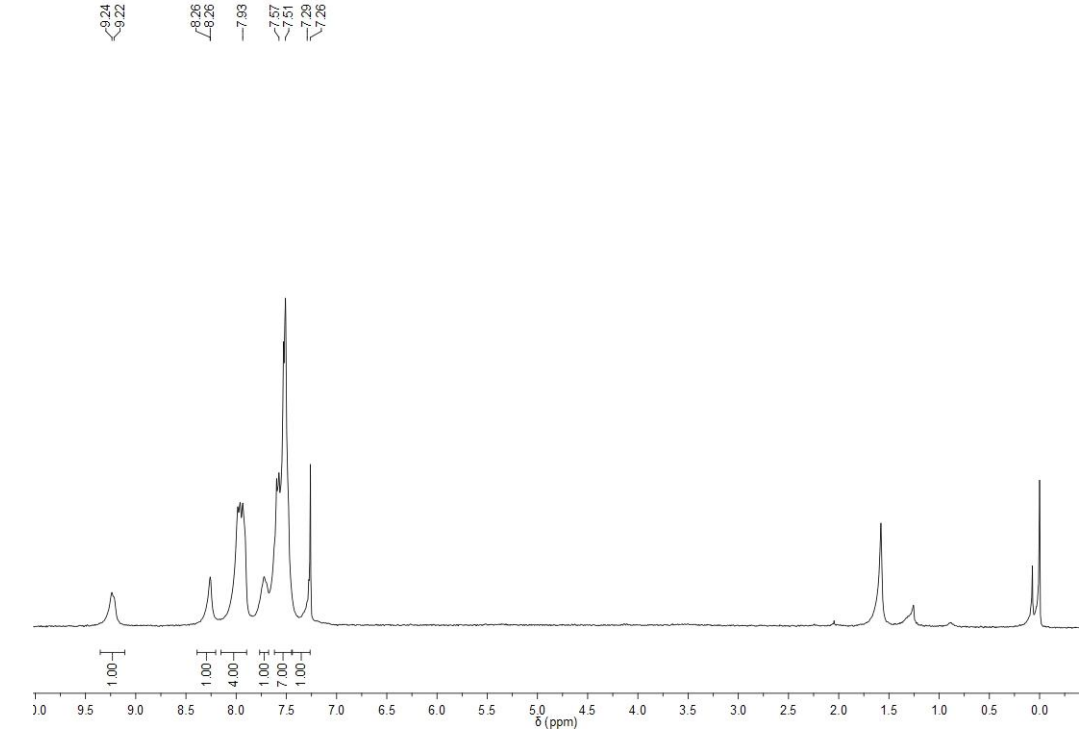
Figure S2. X-ray crystal structure of compound **5a**.

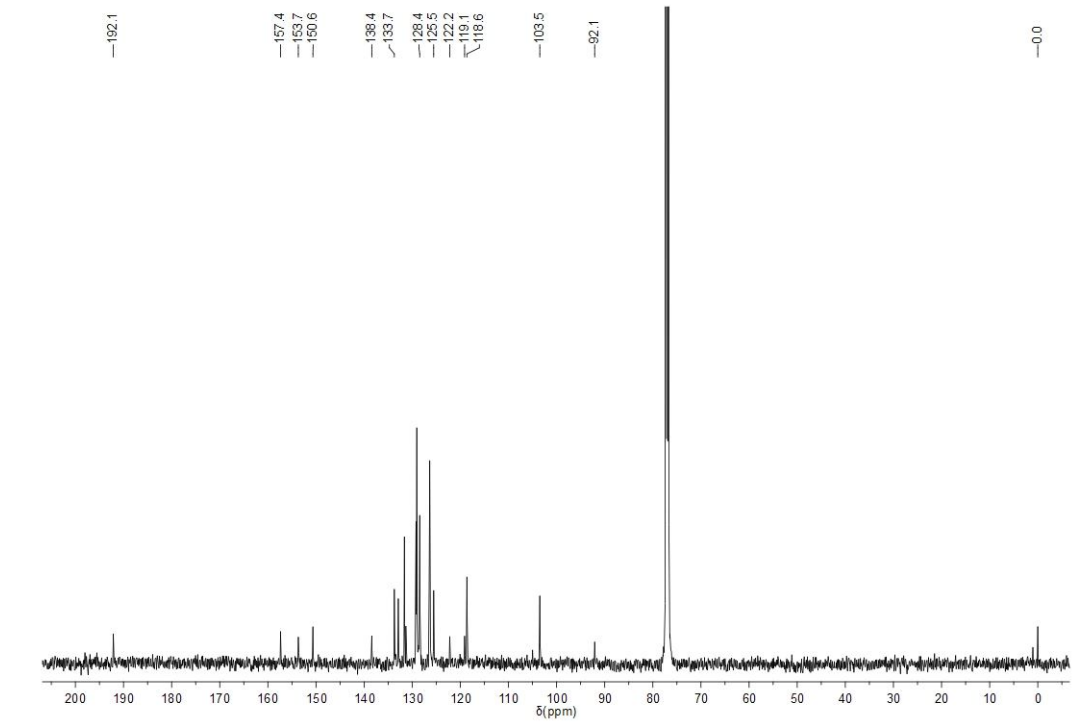
Crystal data for **5a**: $C_{18}H_{10}N_2O$, *Mr* = 270.28, Triclinic, *a* = 7.4925 (4) Å, *b* = 9.5061 (5) Å, *c* = 10.1328 (6) Å, $\alpha = 76.219\ (3)^o$, $\beta = 73.540\ (3)^o$, $\gamma = 83.242\ (3)^o$, *V* = 671.23 (6) $Å^3$, *T* = 293(2) K, space group P-1, *Z* = 2, 12108 reflections collected, 3001 unique (R_{int} = 0.0349) which were used in all calculation. The ellipsoid contour probability level in the caption is 30%.

Crystallographic data for compound **5a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC-1841801**.

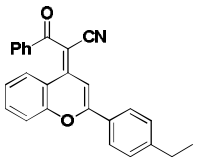
^{1}H NMR and ^{13}C NMR Spectra of Compound 4aa

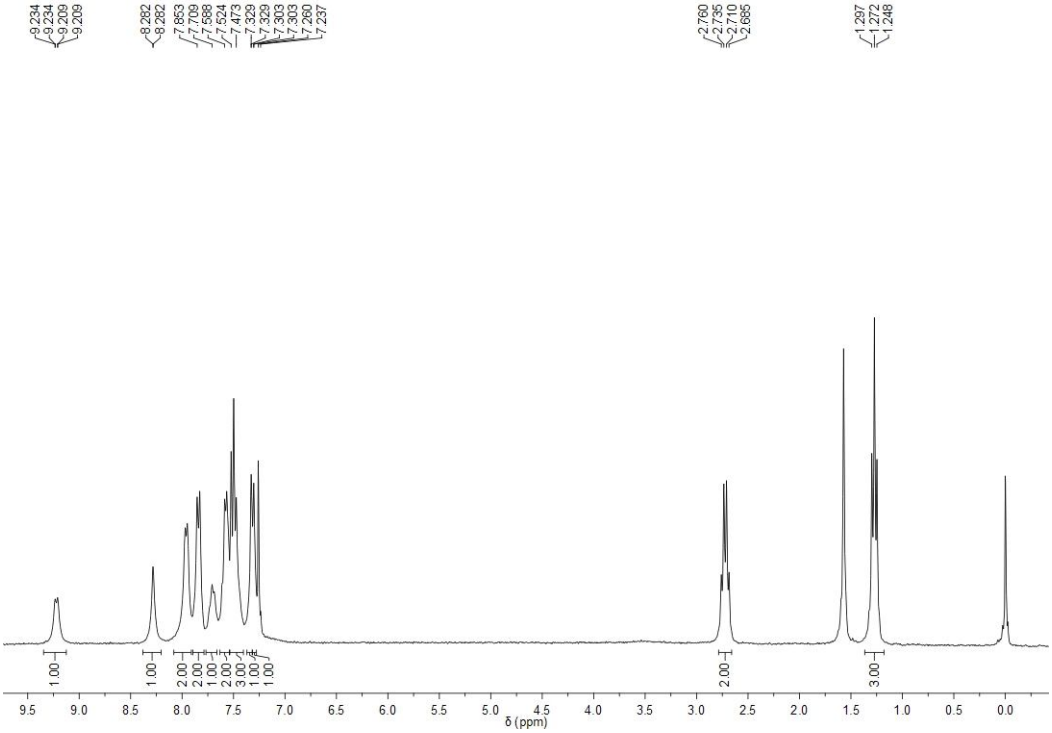


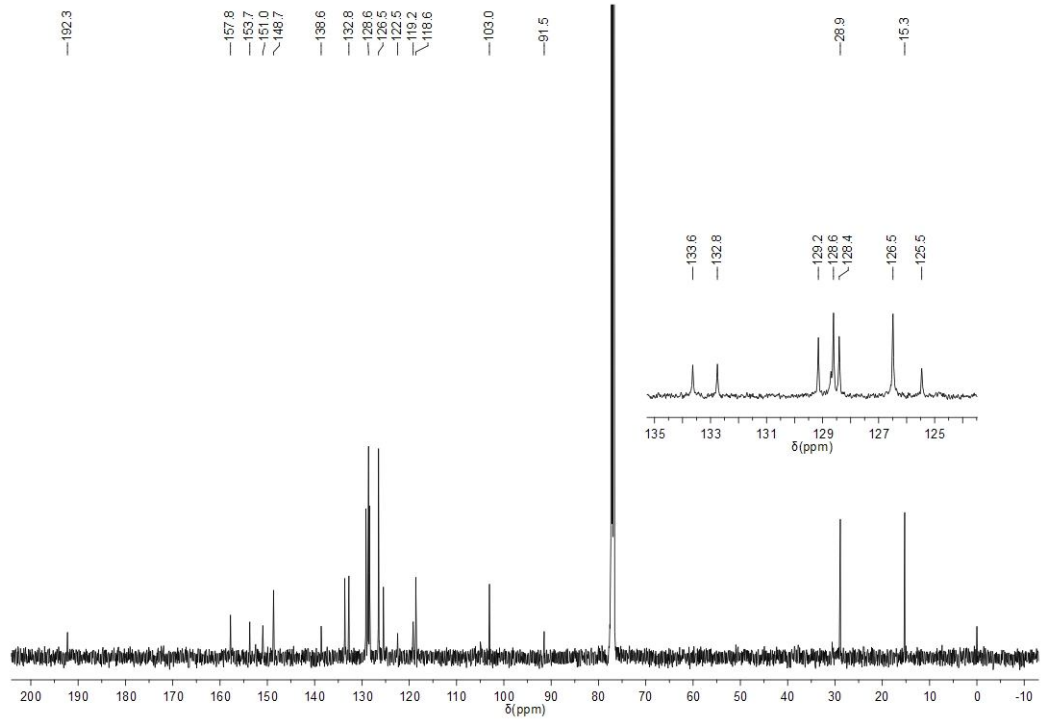




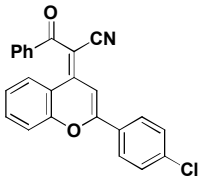
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ba

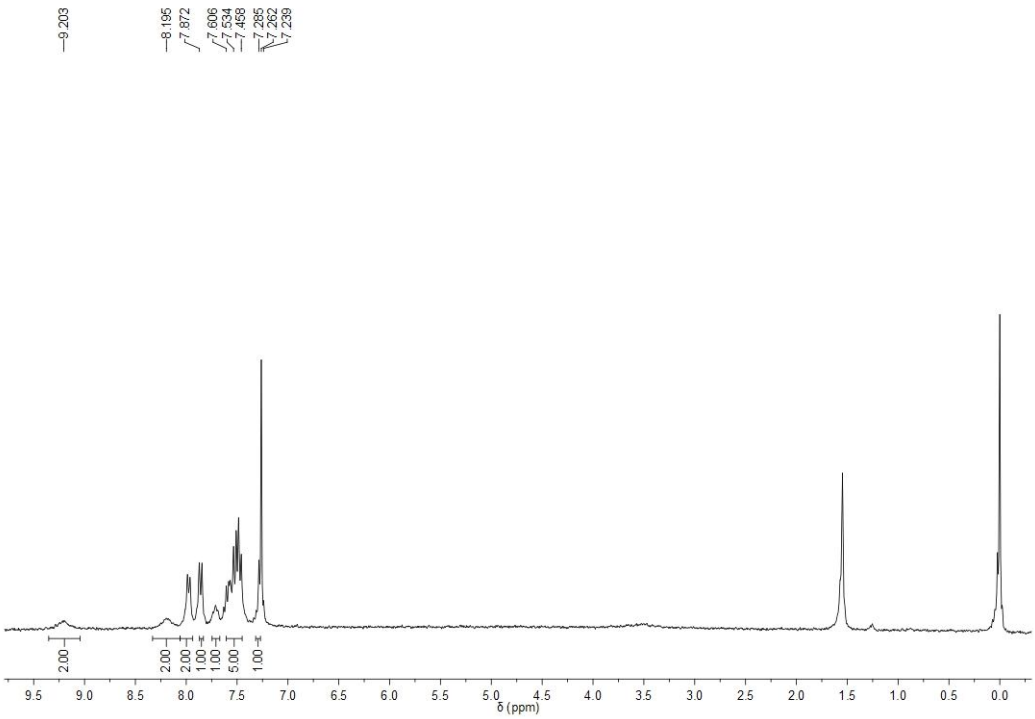


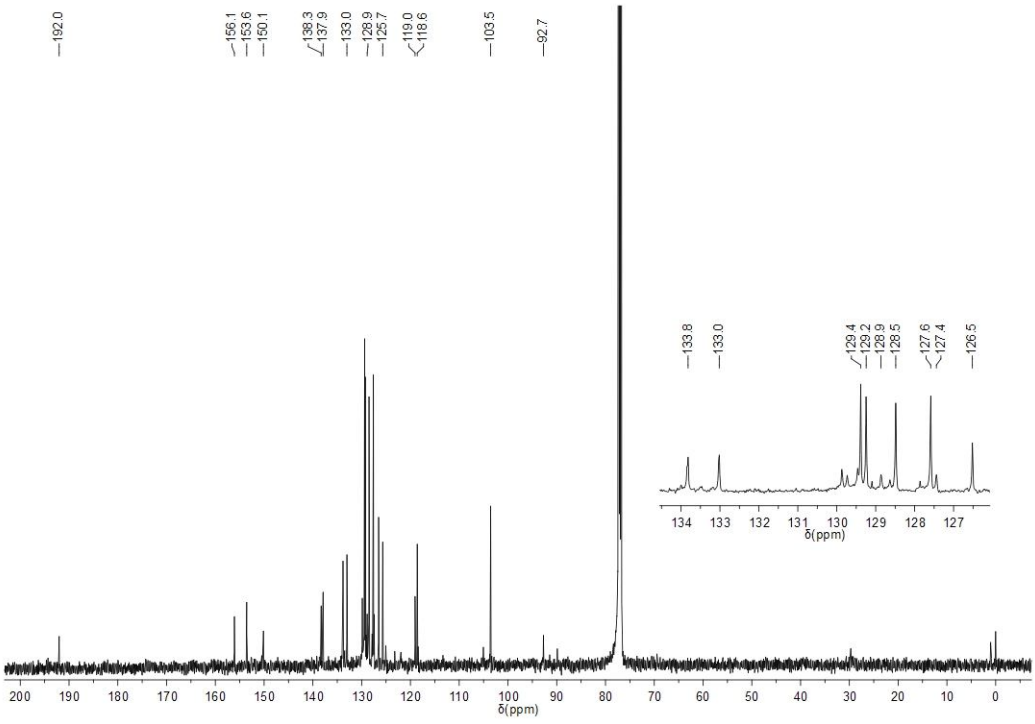




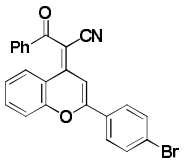
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ca

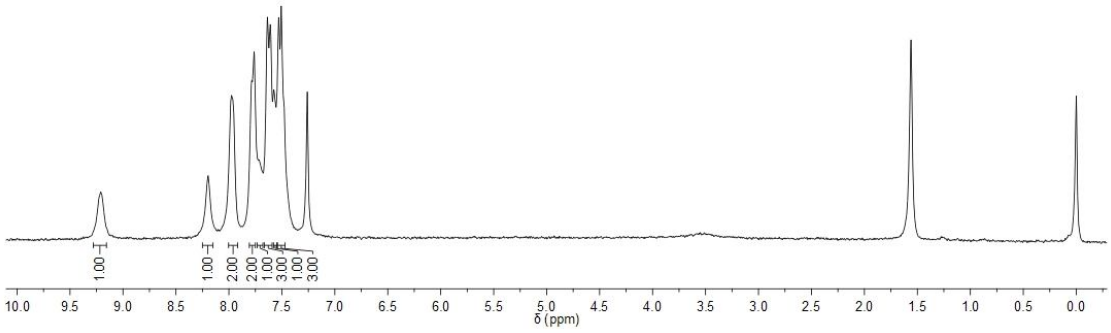


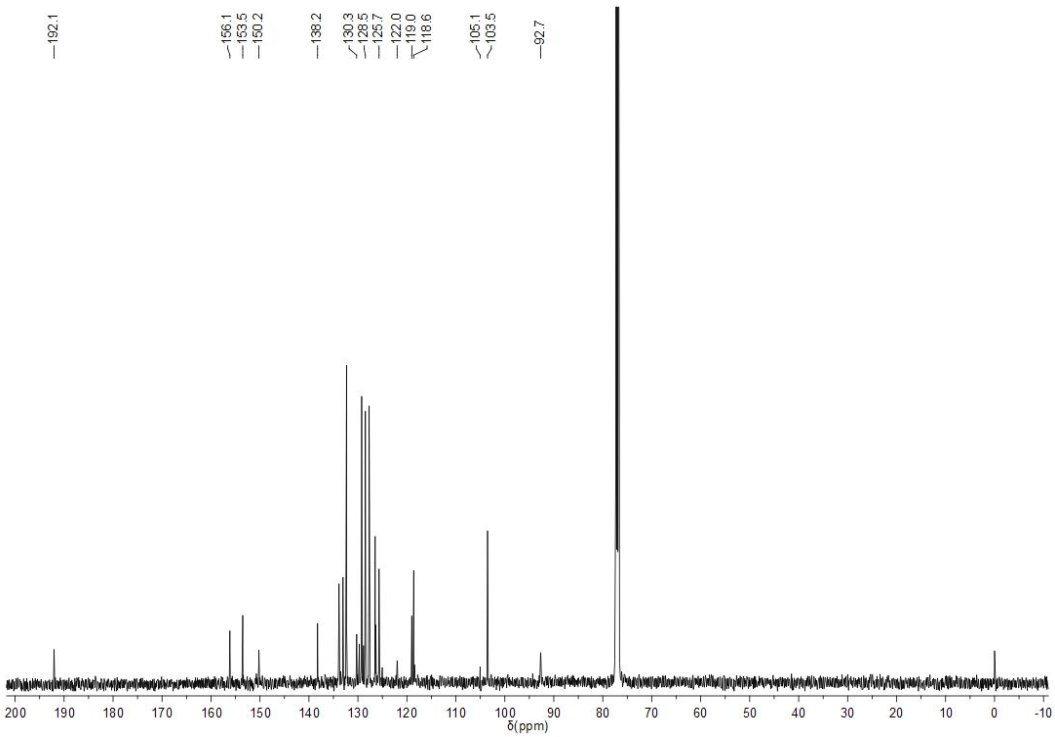




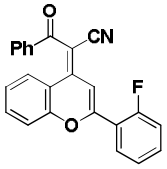
^{1}H NMR and ^{13}C NMR Spectra of Compound 4da

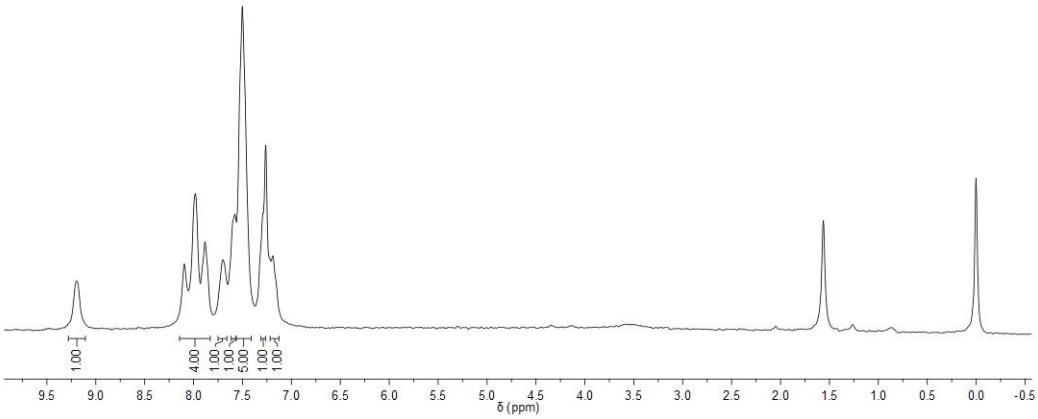


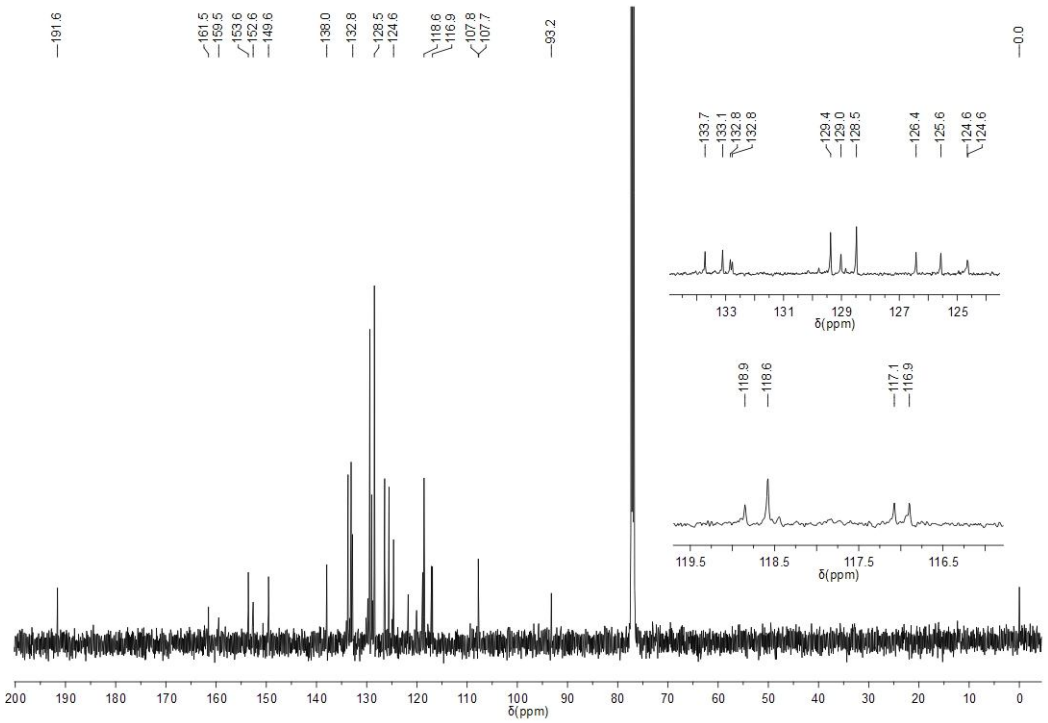




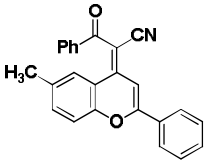
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ea

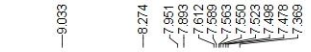


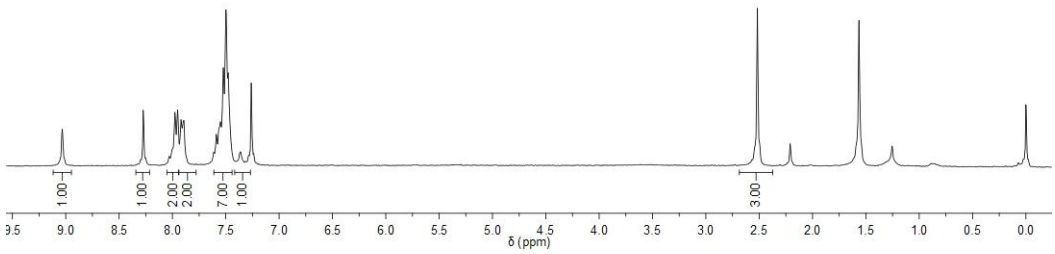


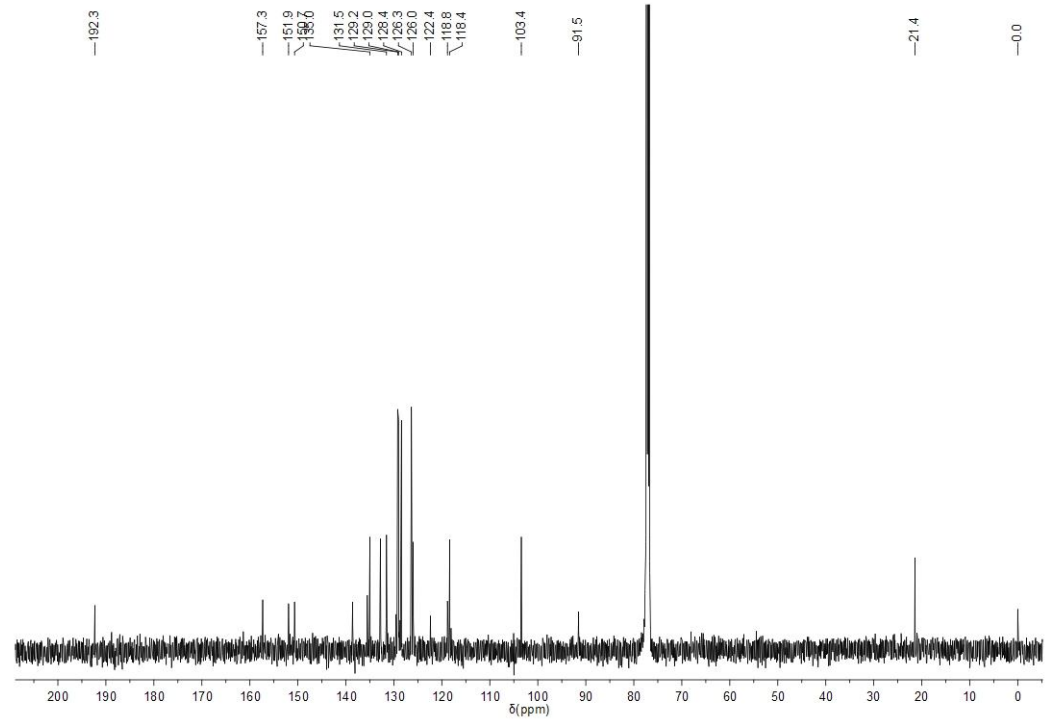


^{1}H NMR and ^{13}C NMR Spectra of Compound 4fa

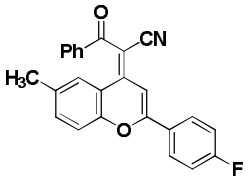


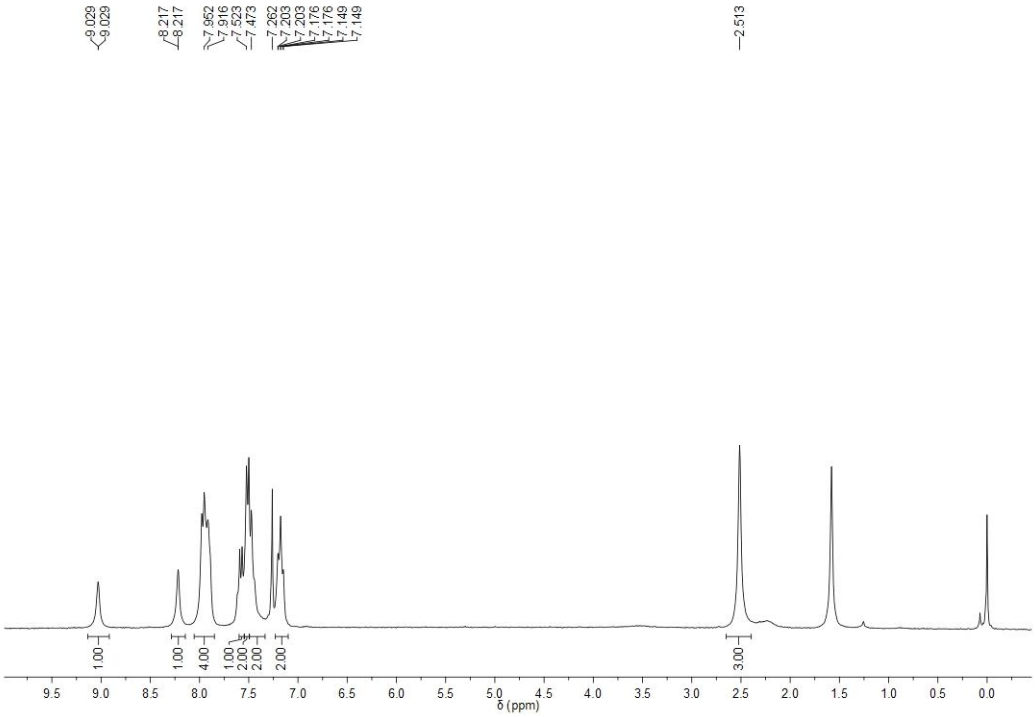


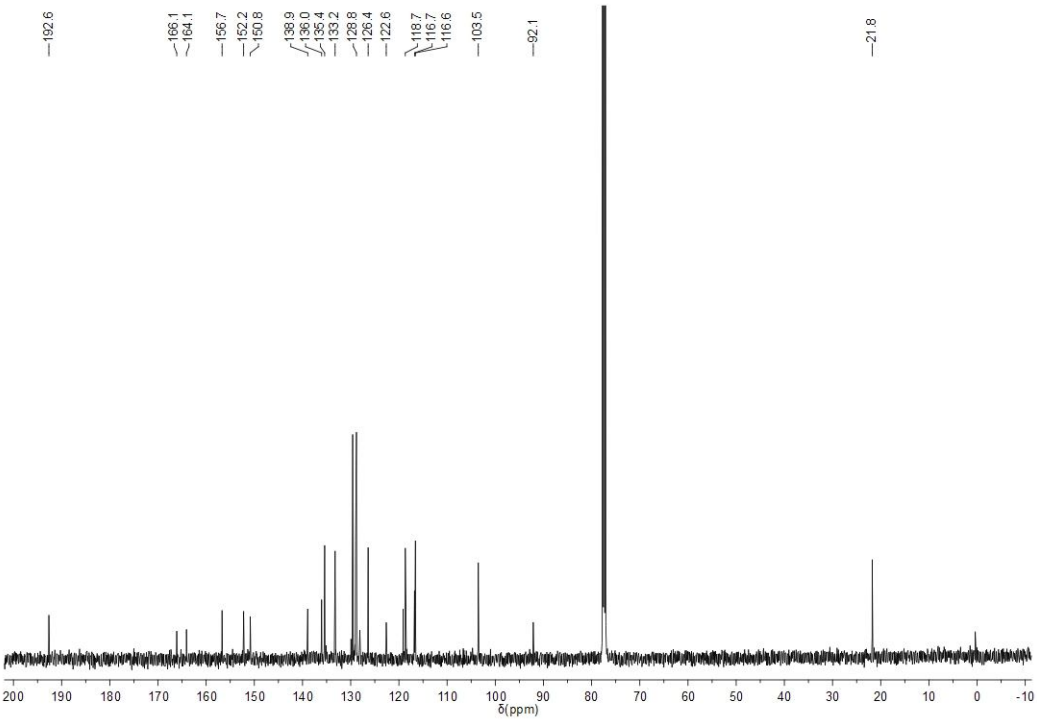




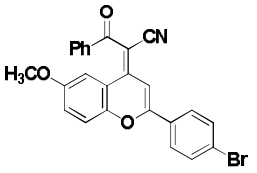
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ga

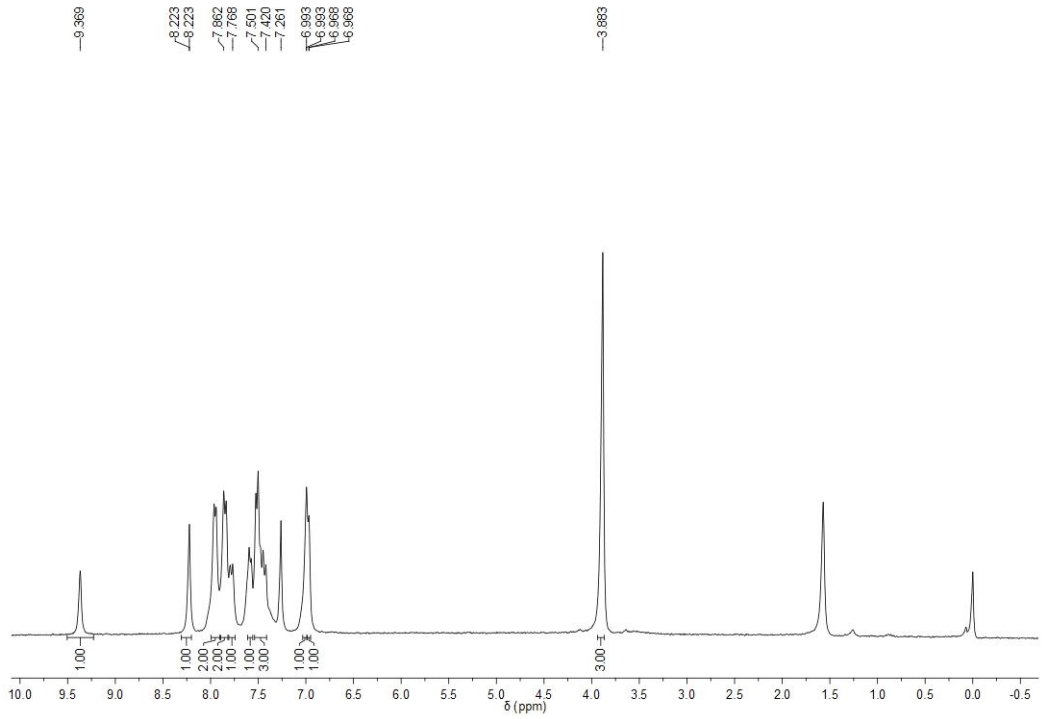


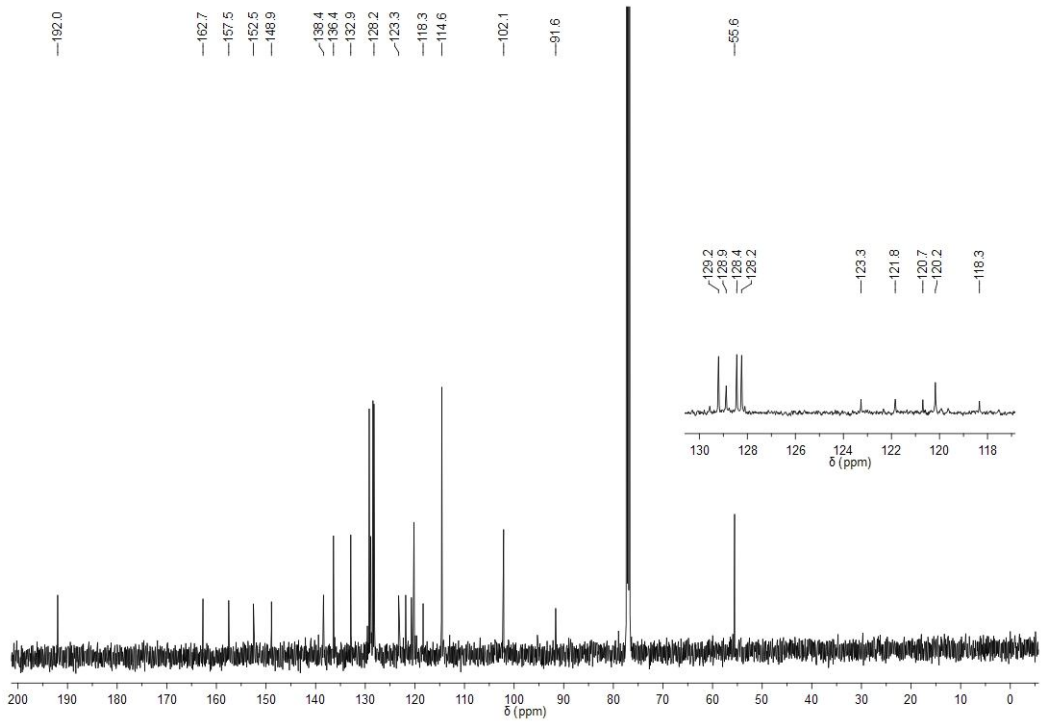




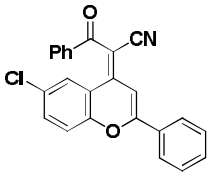
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ha

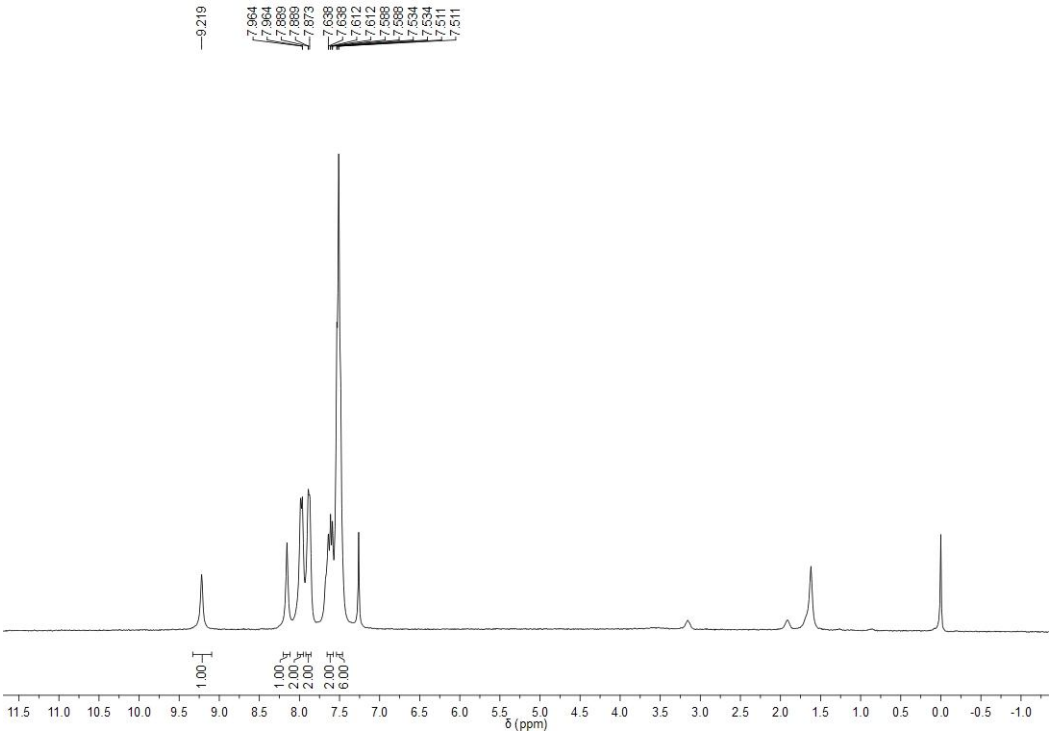


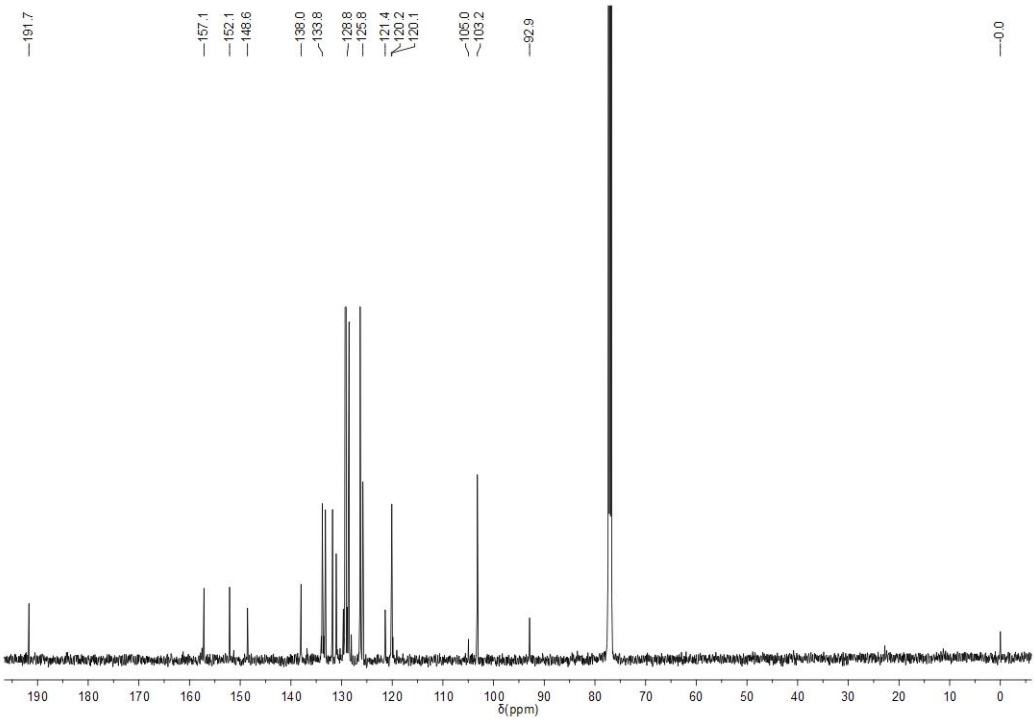




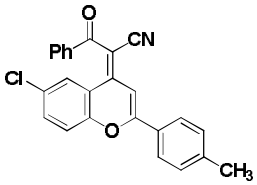
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ia

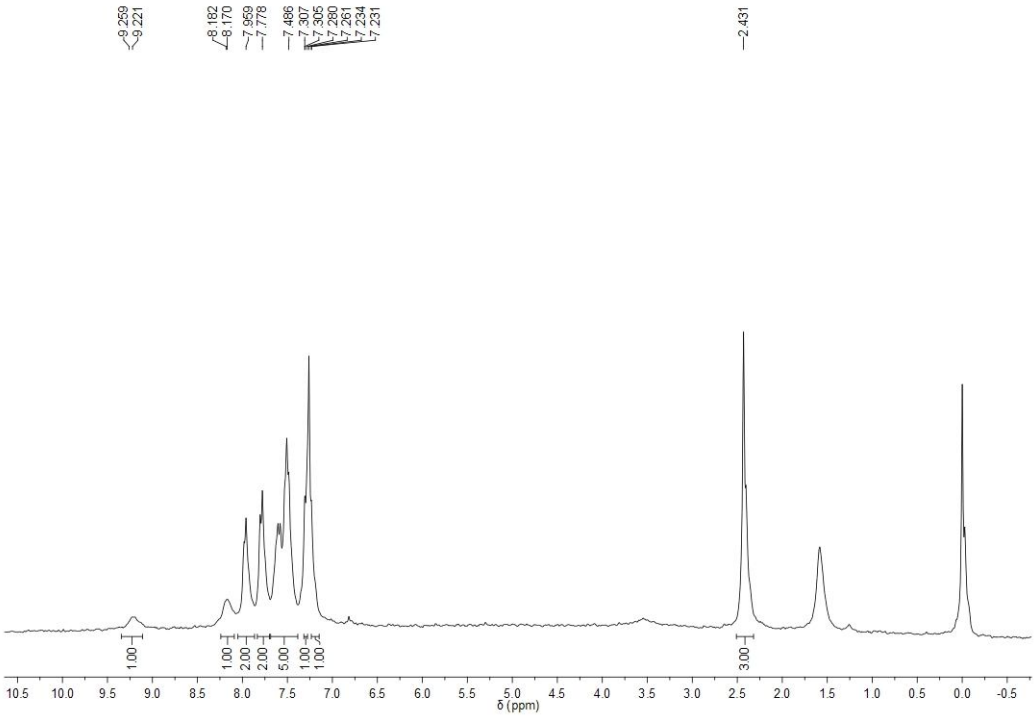


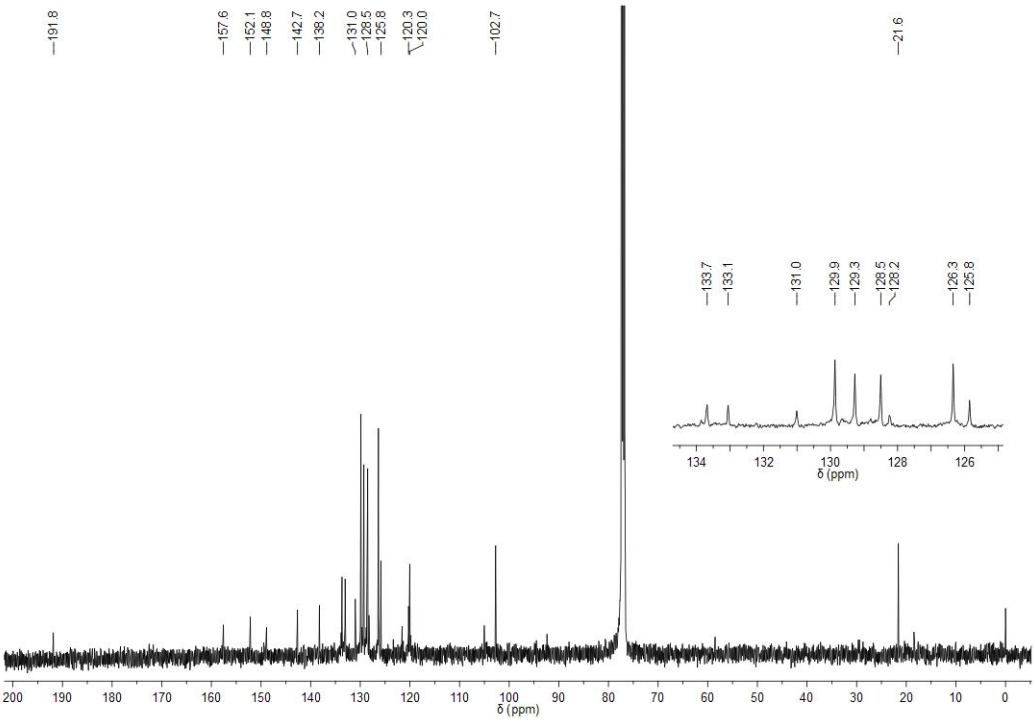




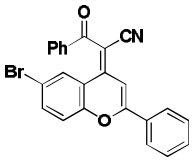
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ja

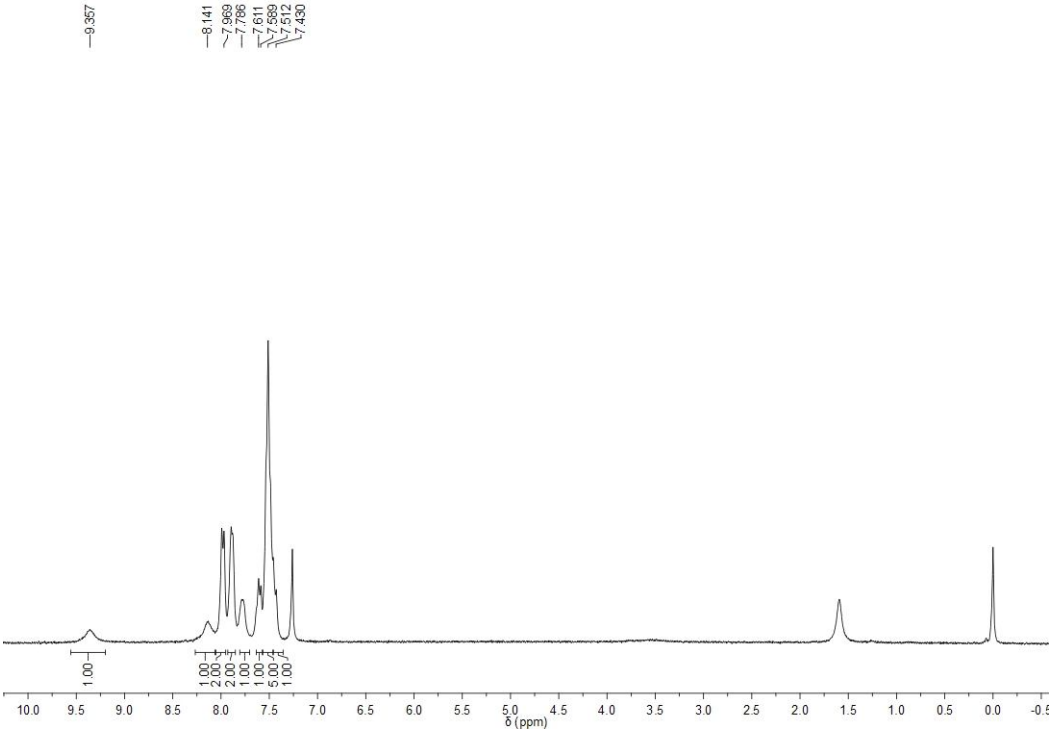


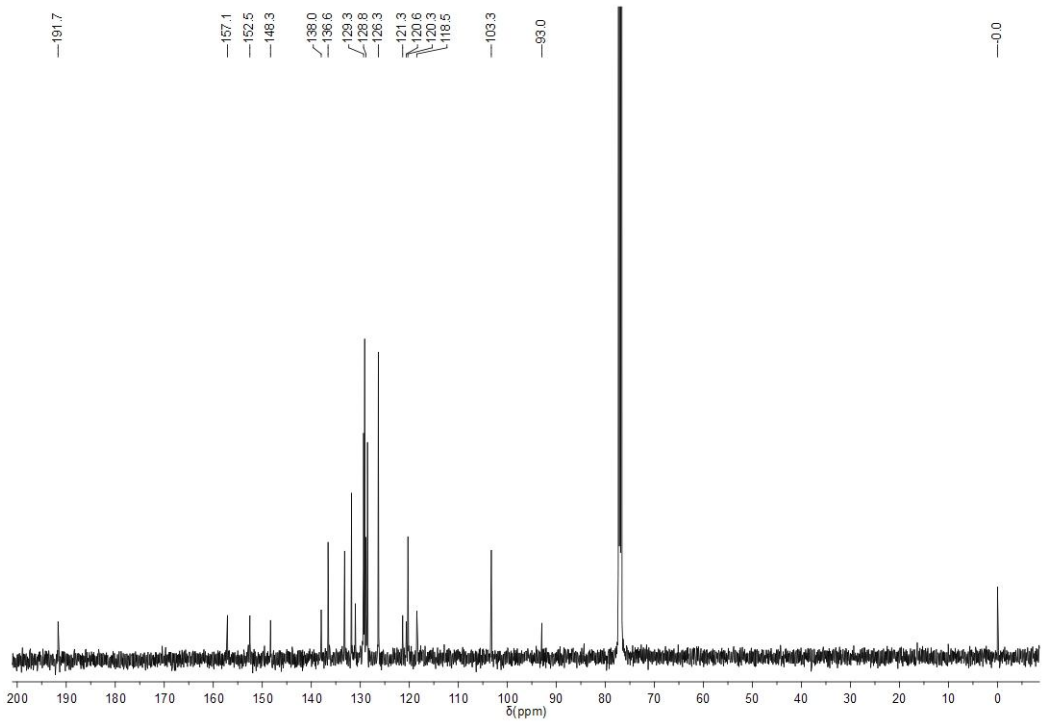




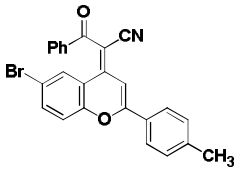
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ka

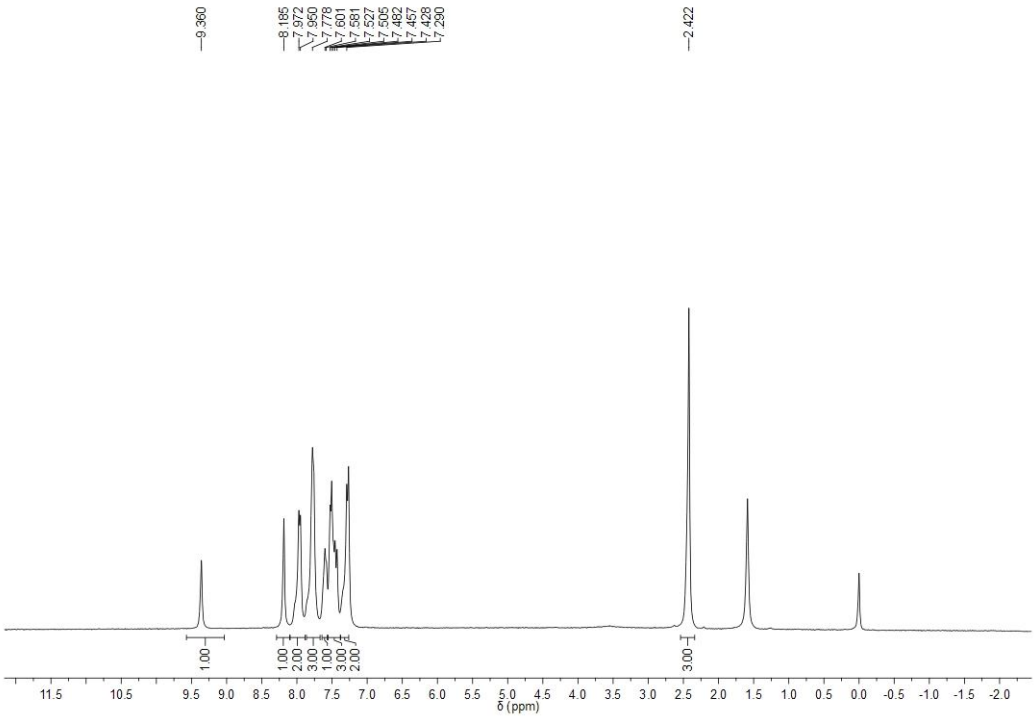


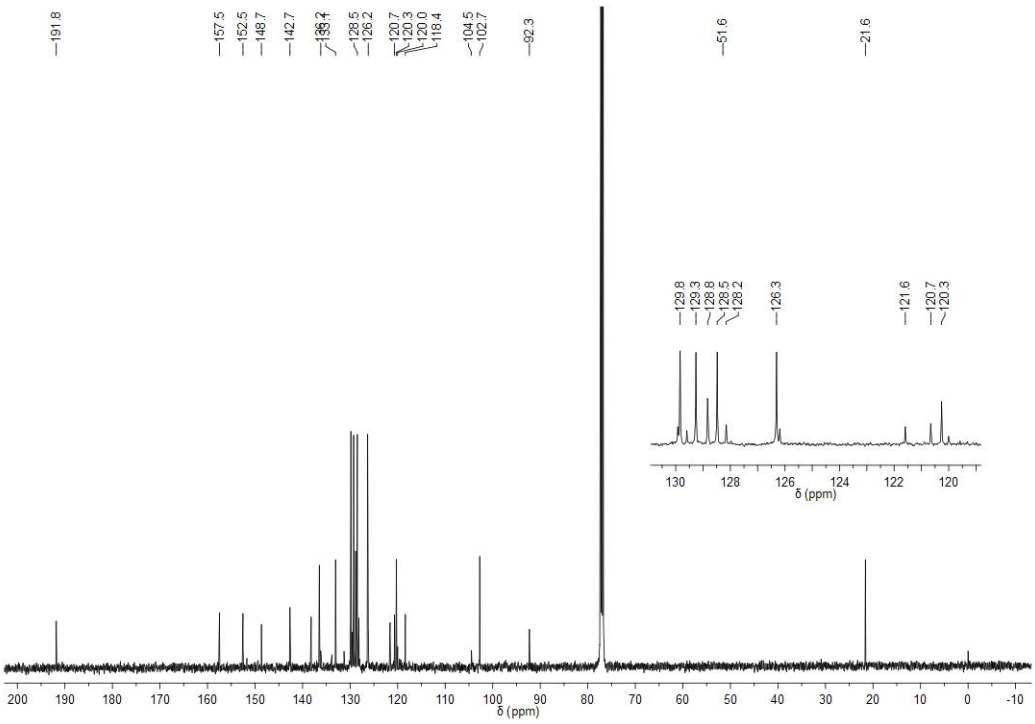




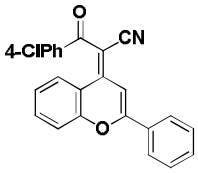
^{1}H NMR and ^{13}C NMR Spectra of Compound 4la

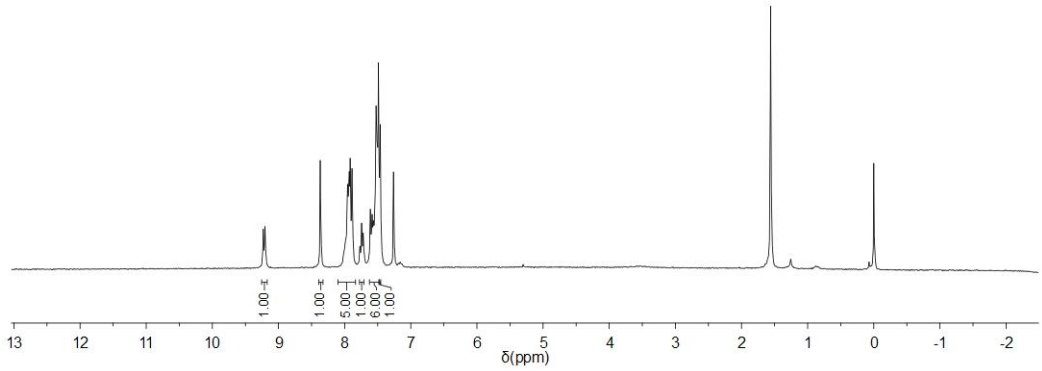


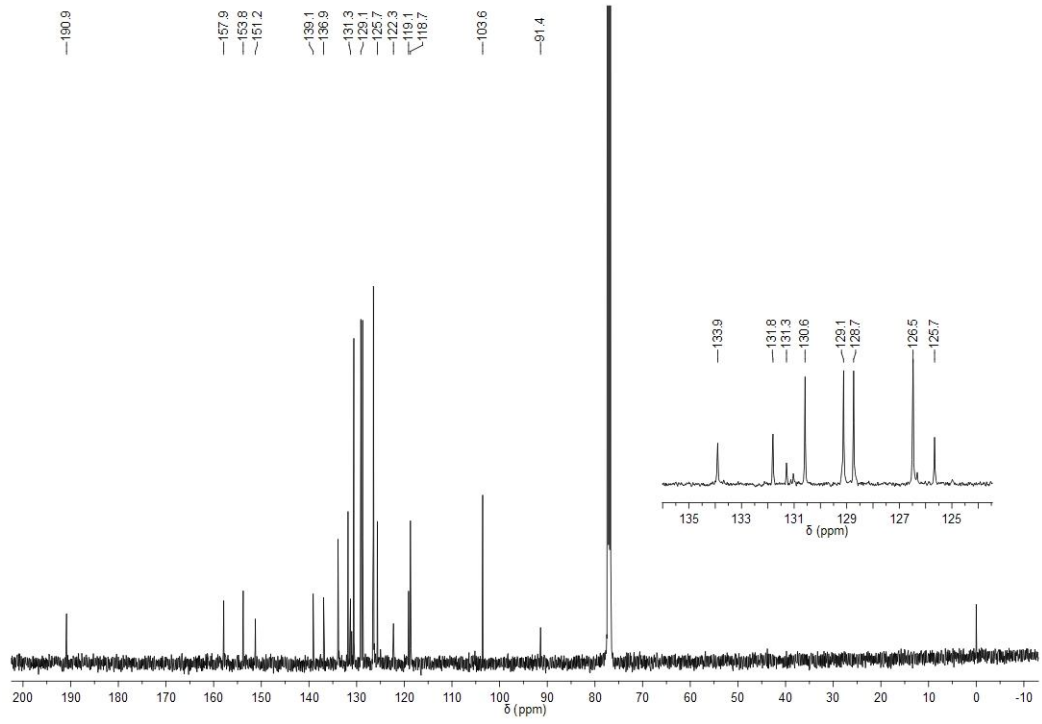




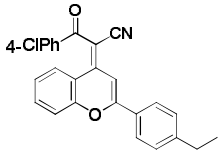
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ab

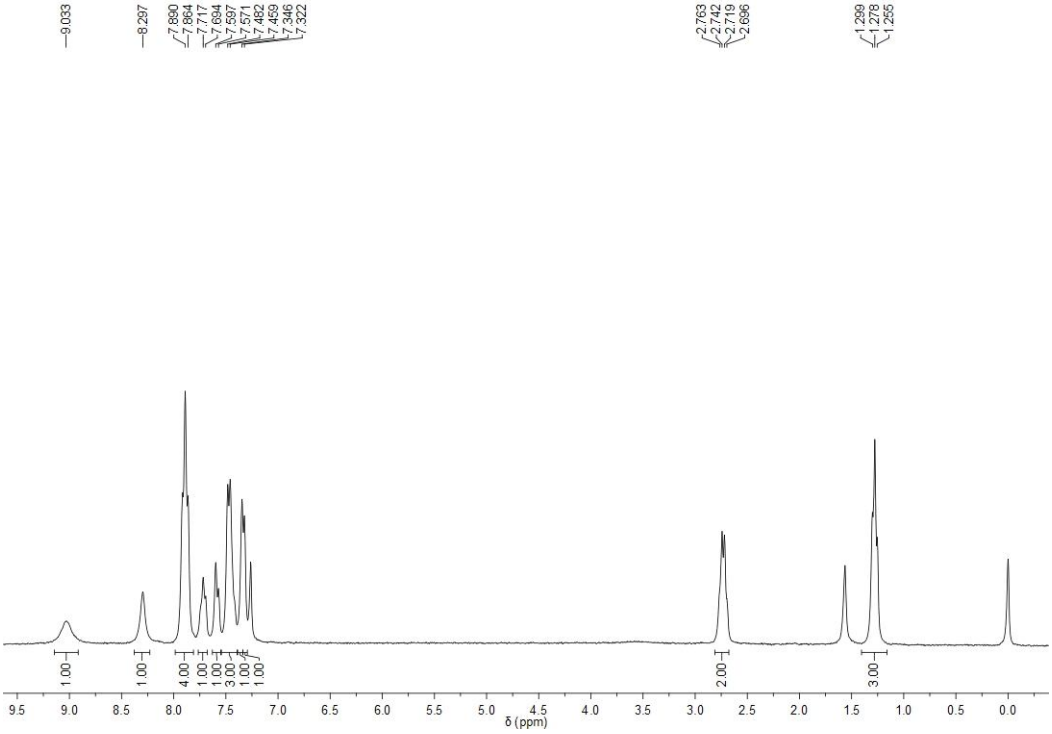


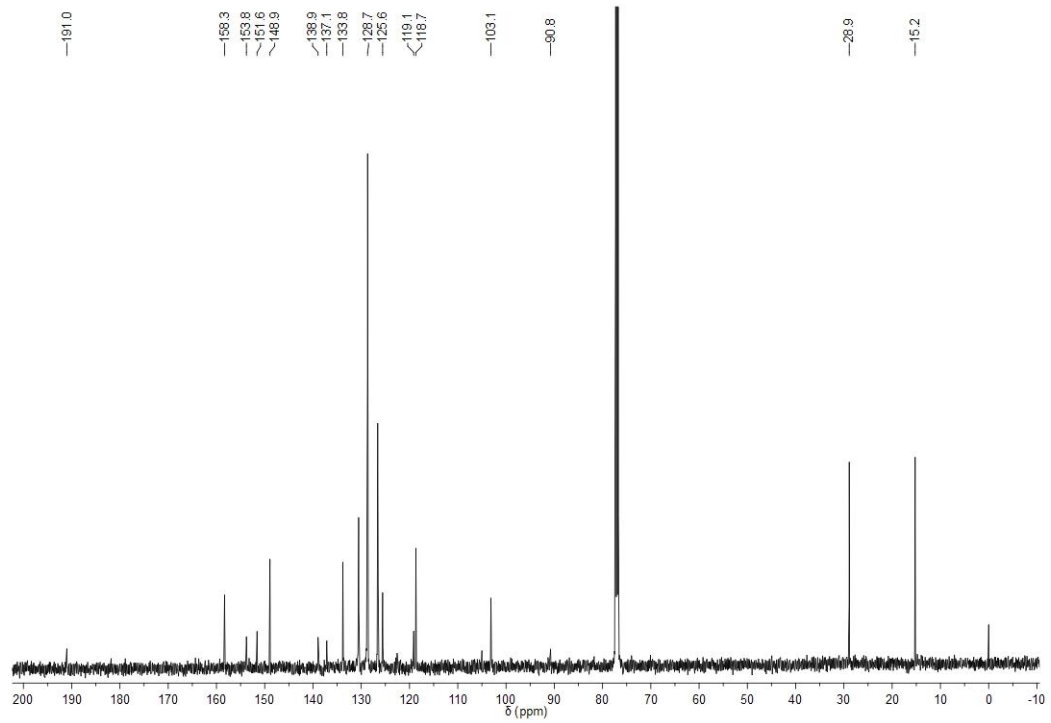




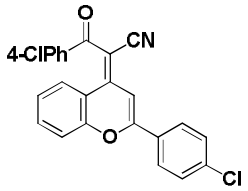
^{1}H NMR and ^{13}C NMR Spectra of Compound 4bb

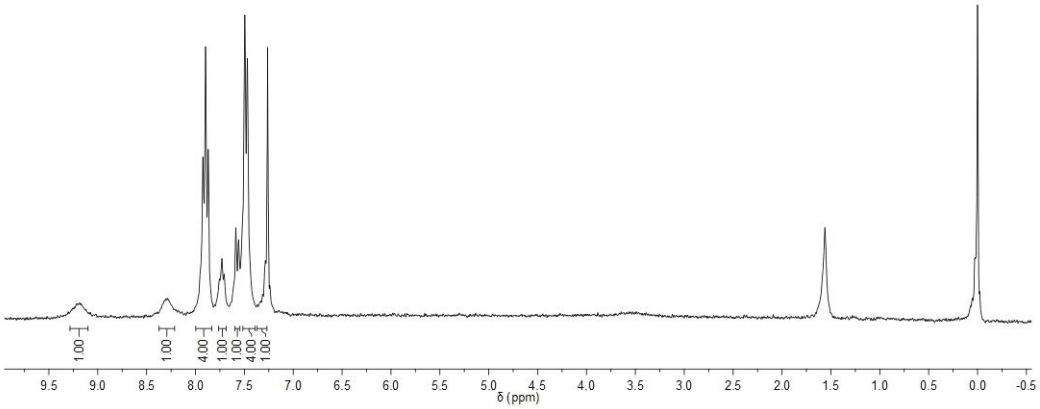


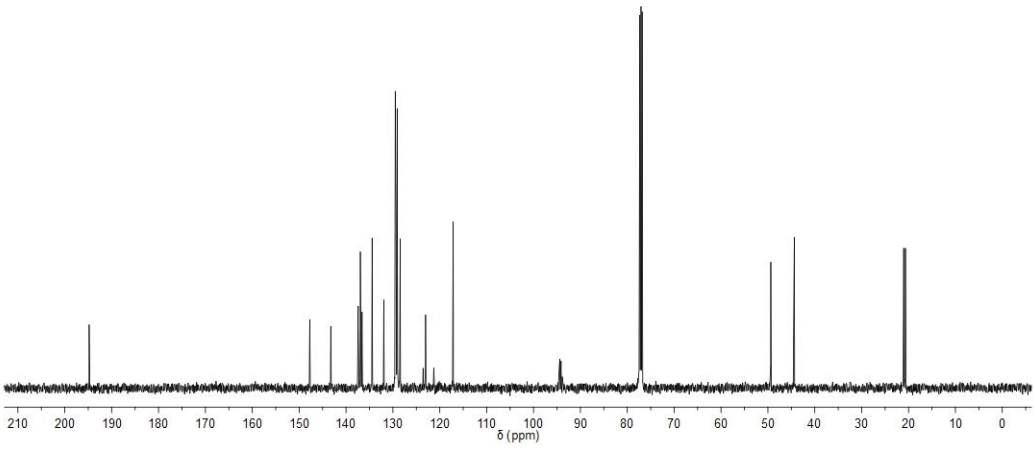




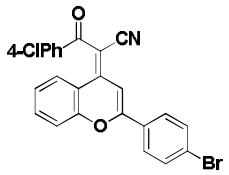
^{1}H NMR and ^{13}C NMR Spectra of Compound 4cb

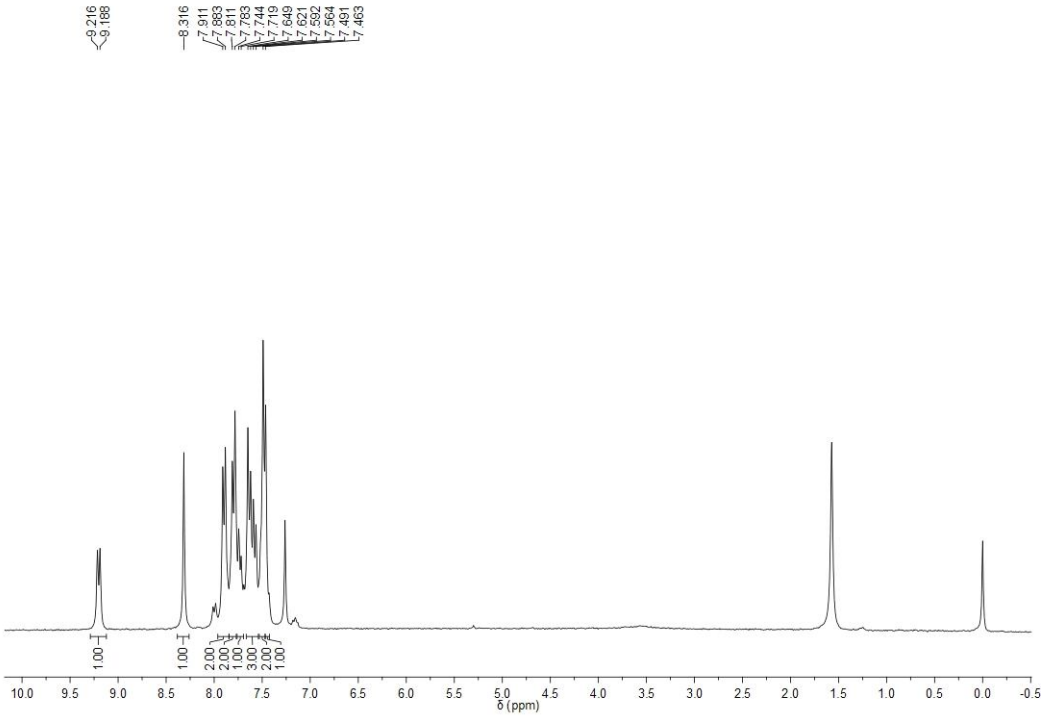


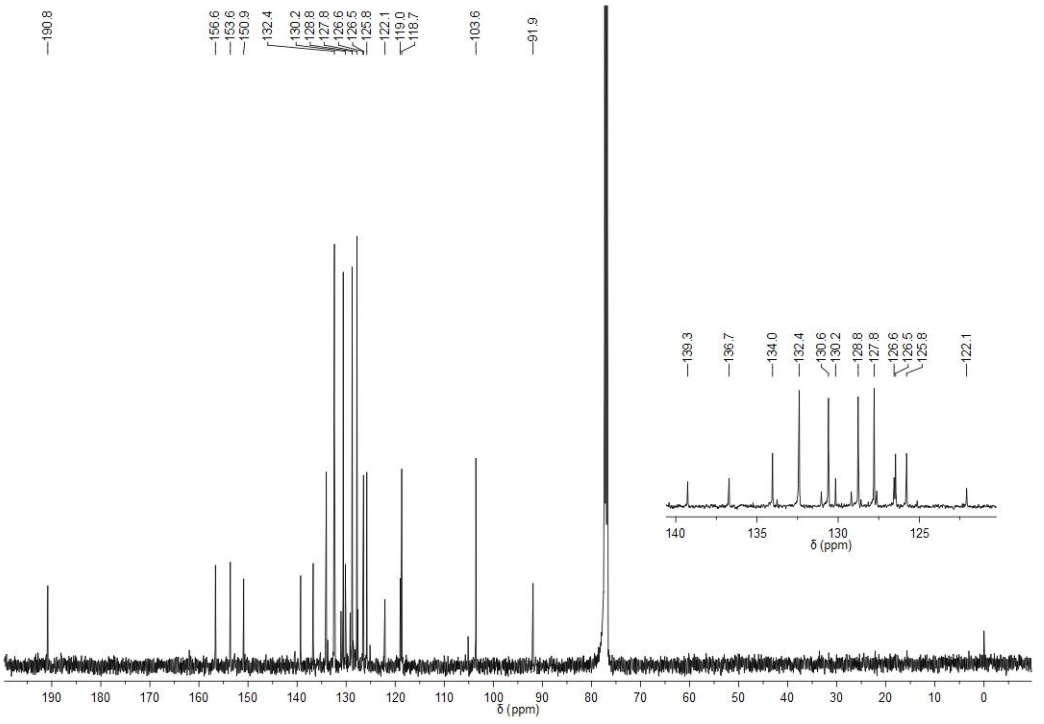




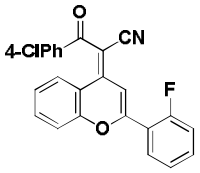
^{1}H NMR and ^{13}C NMR Spectra of Compound 4db

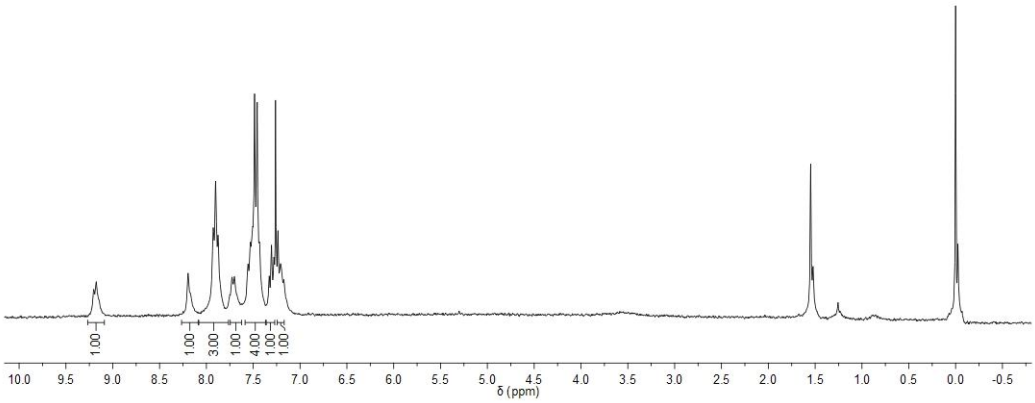


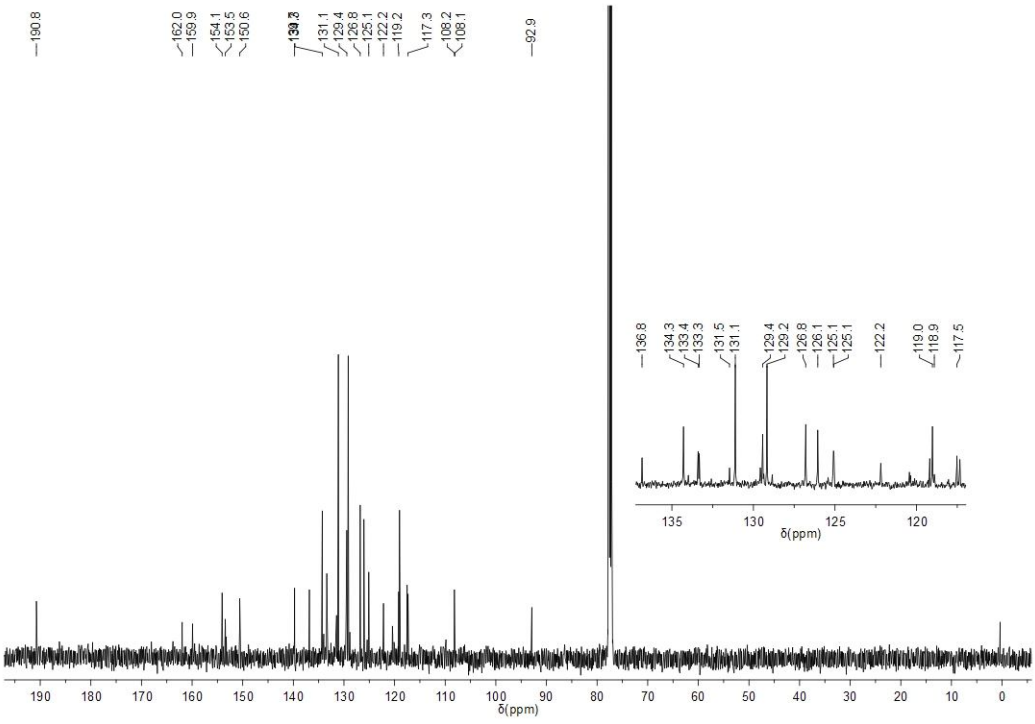




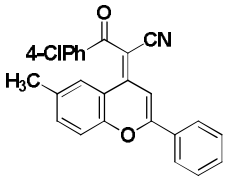
^{1}H NMR and ^{13}C NMR Spectra of Compound 4eb

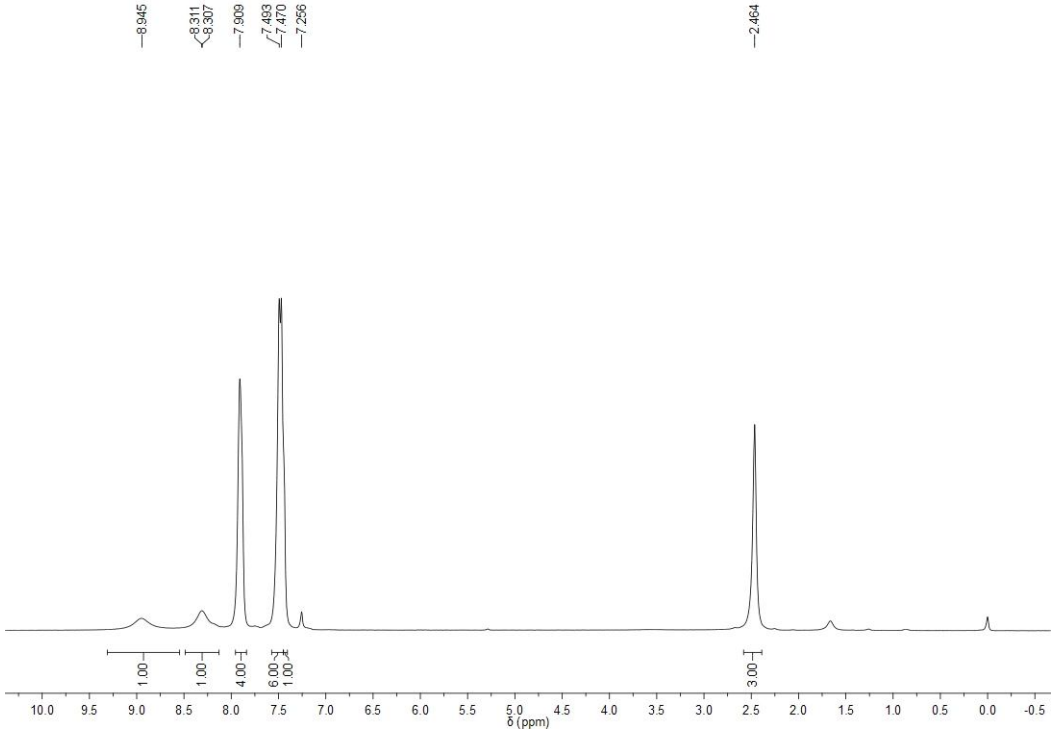


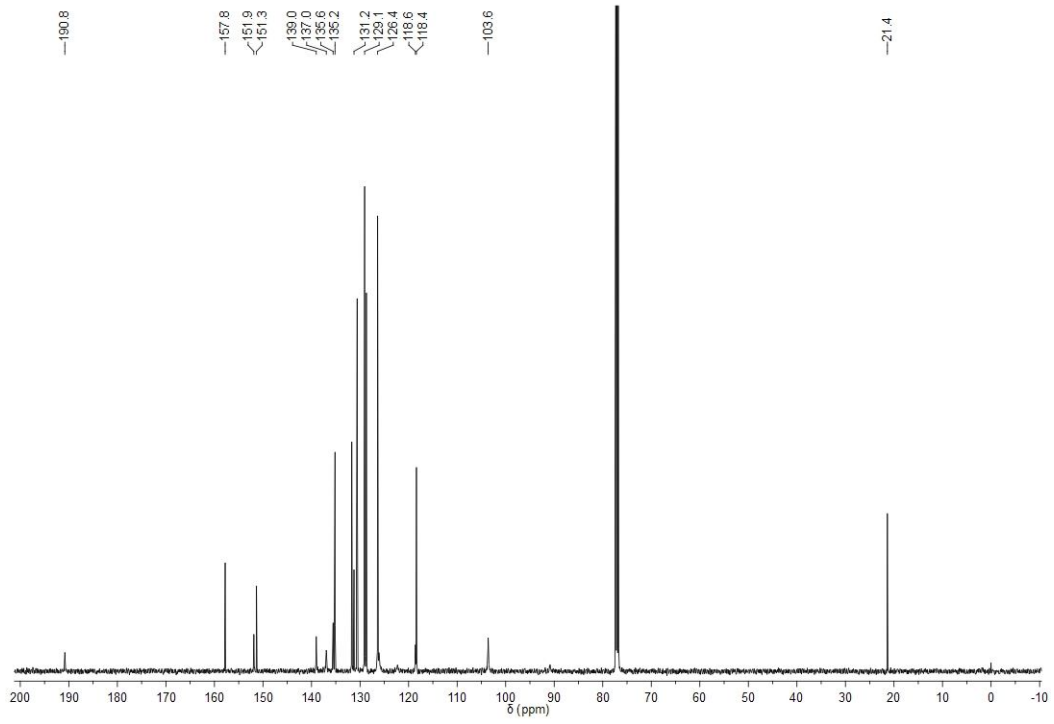




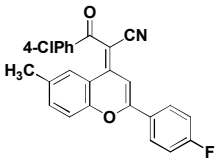
^{1}H NMR and ^{13}C NMR Spectra of Compound 4fb

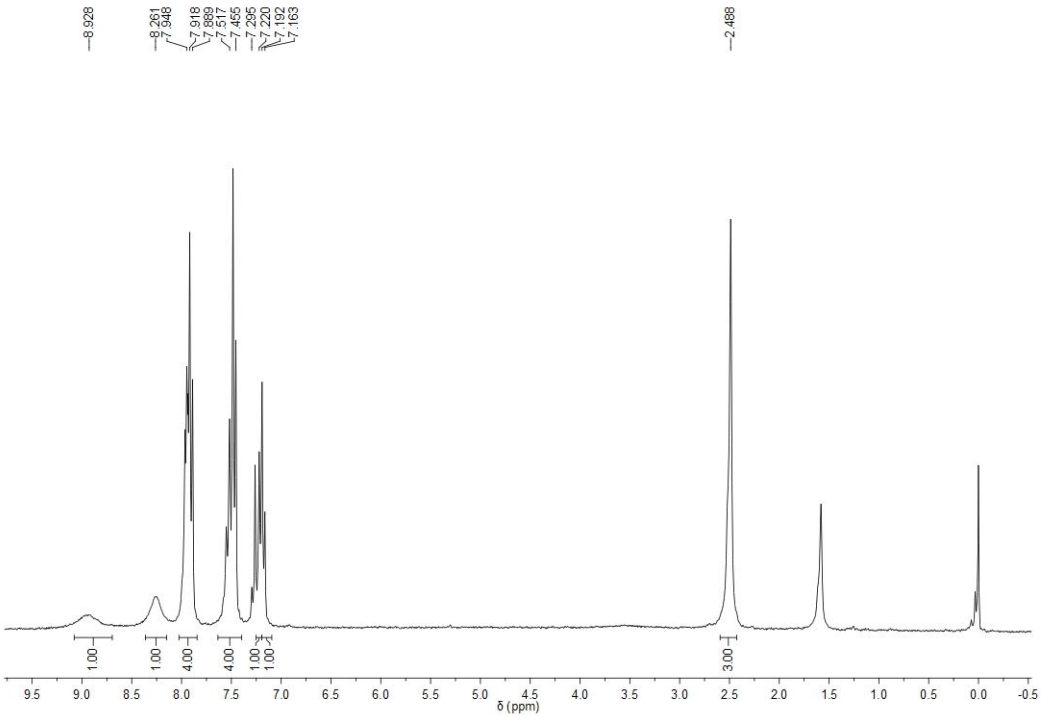


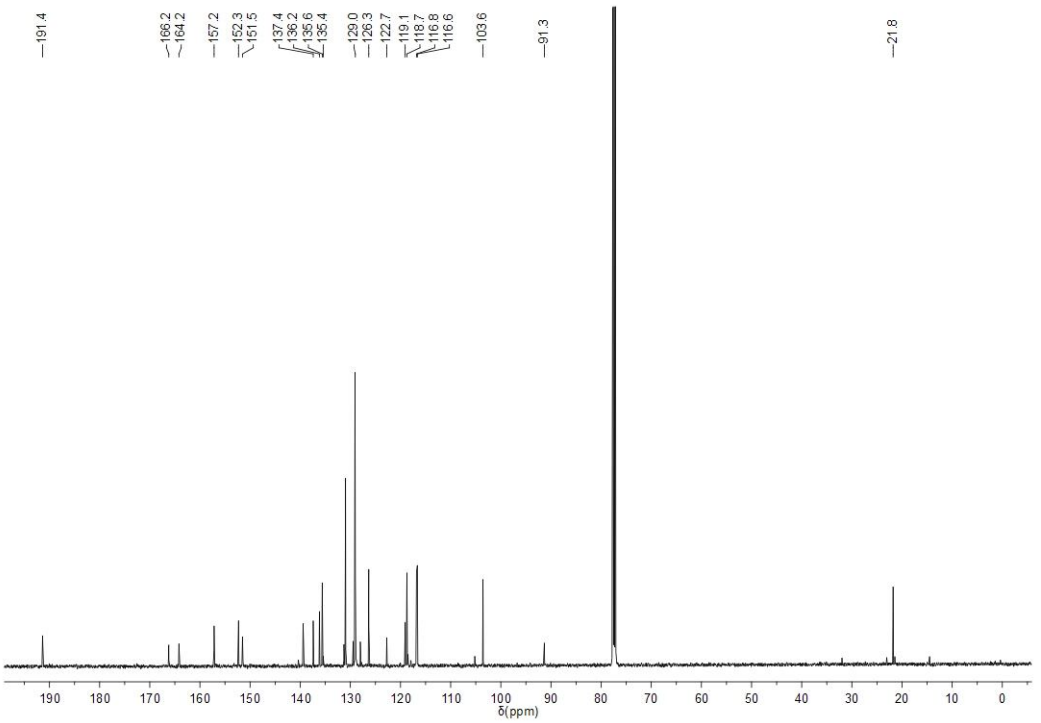




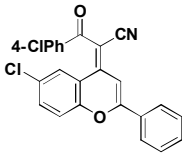
^{1}H NMR and ^{13}C NMR Spectra of Compound 4gb

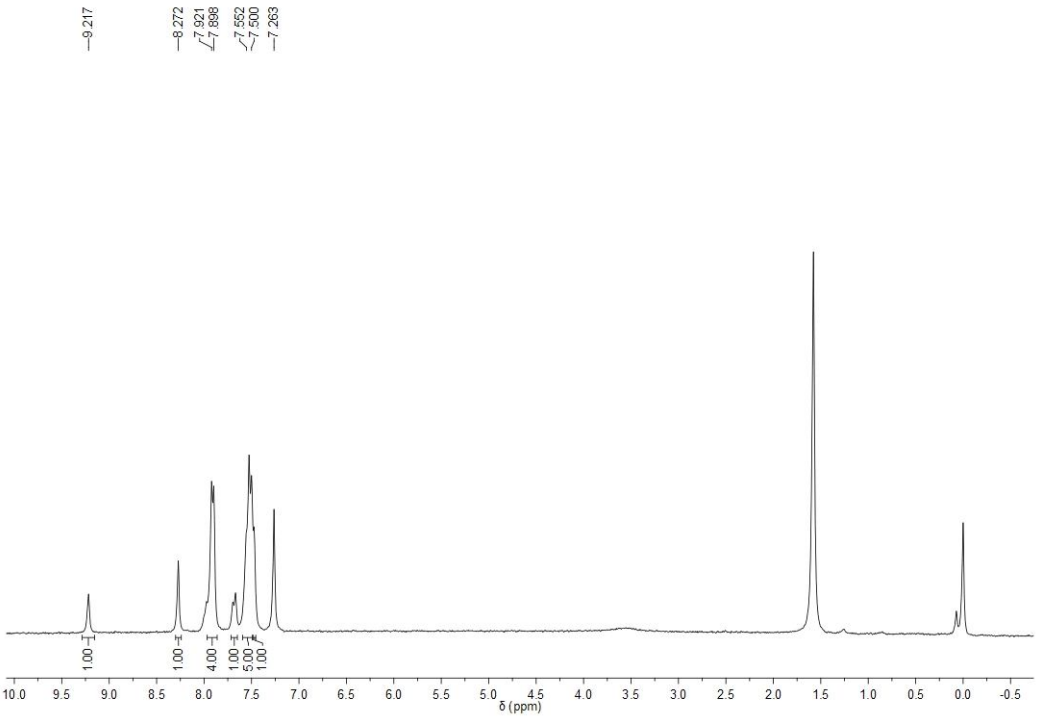


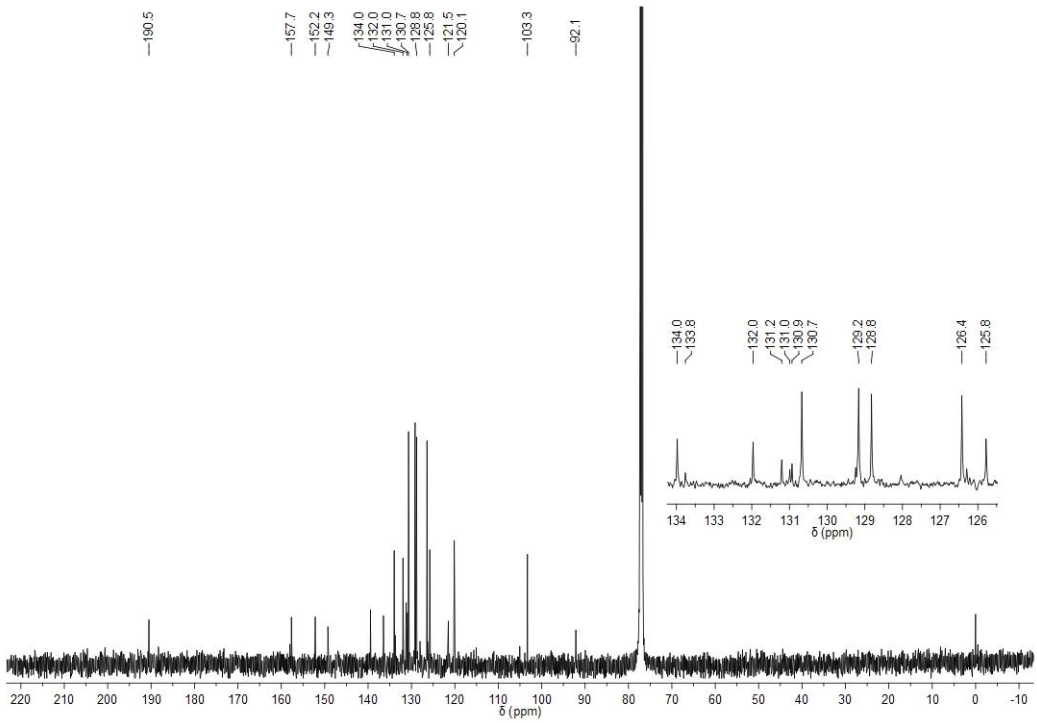




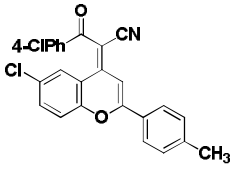
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ib

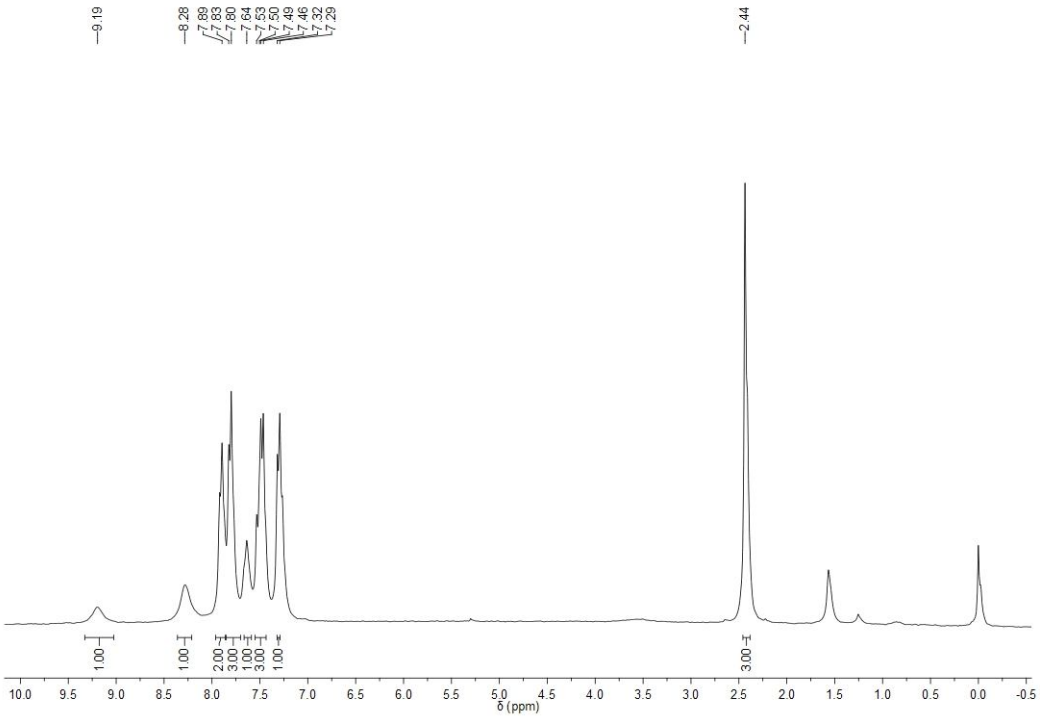


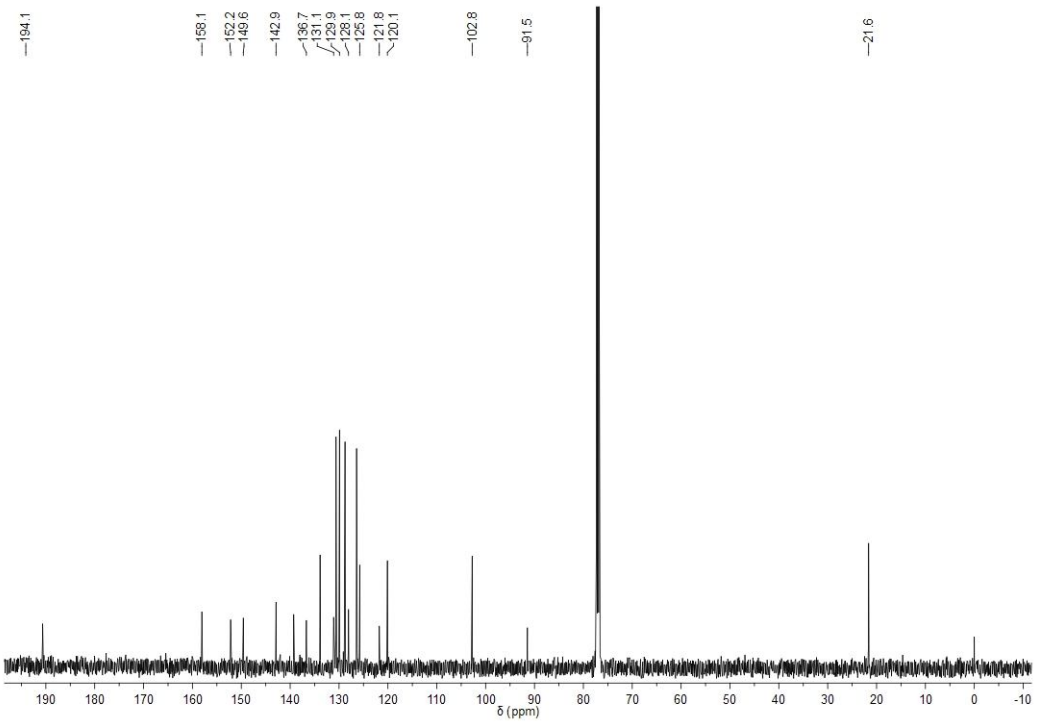




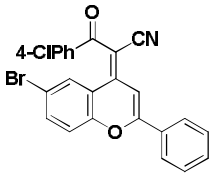
^{1}H NMR and ^{13}C NMR Spectra of Compound 4jb

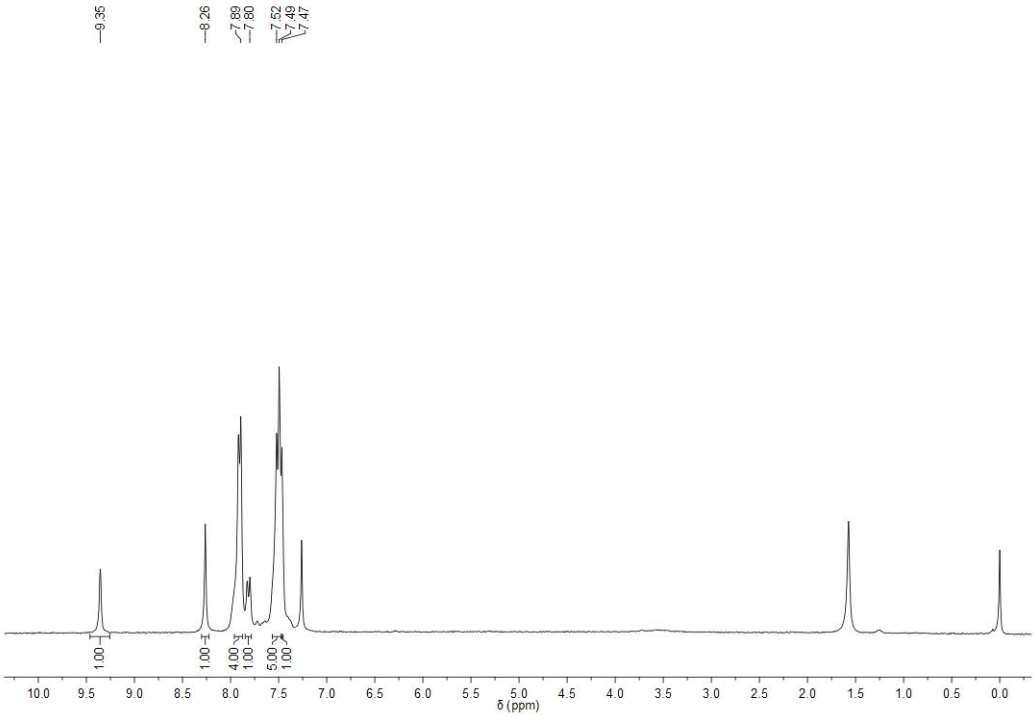


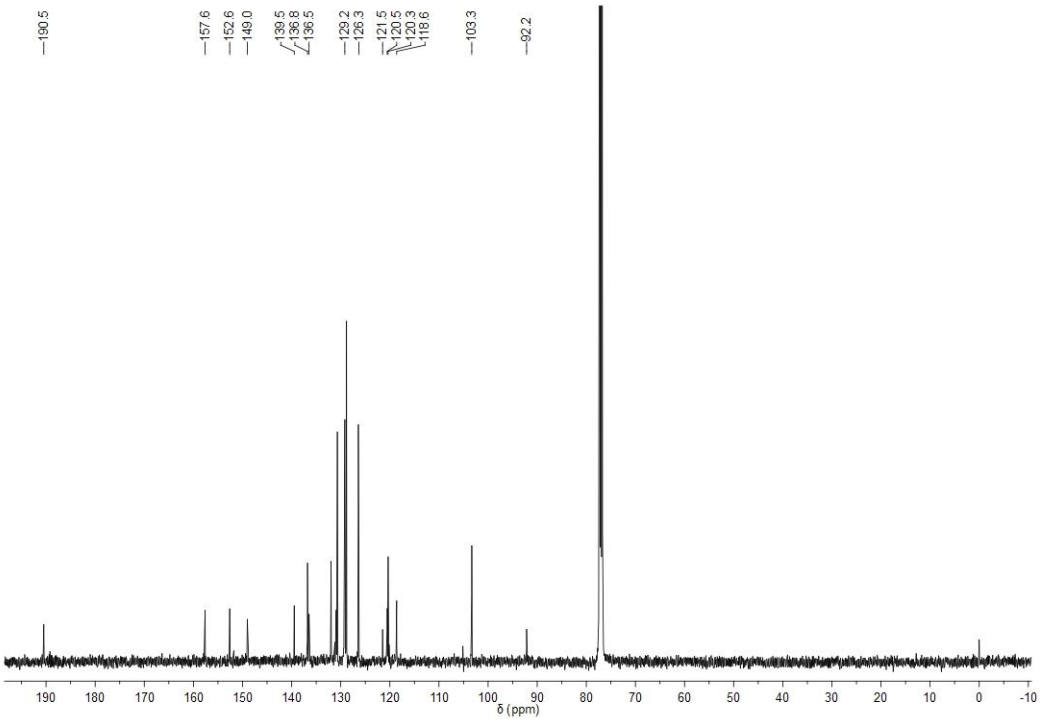




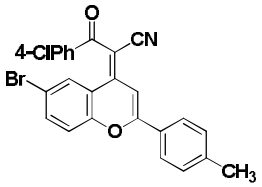
^{1}H NMR and ^{13}C NMR Spectra of Compound 4kb

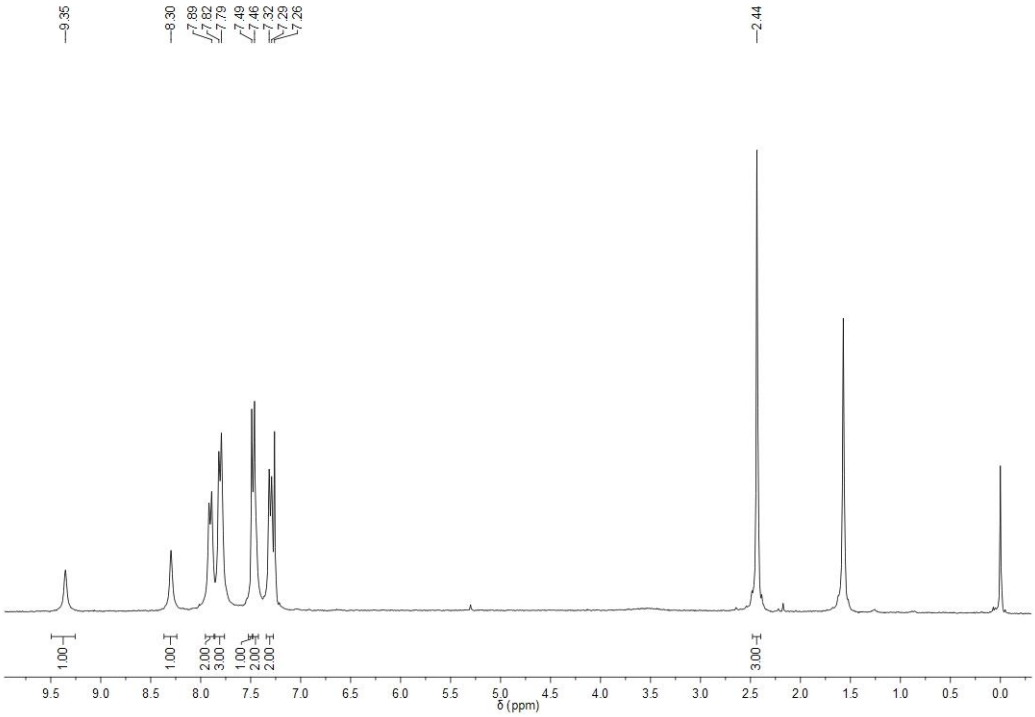


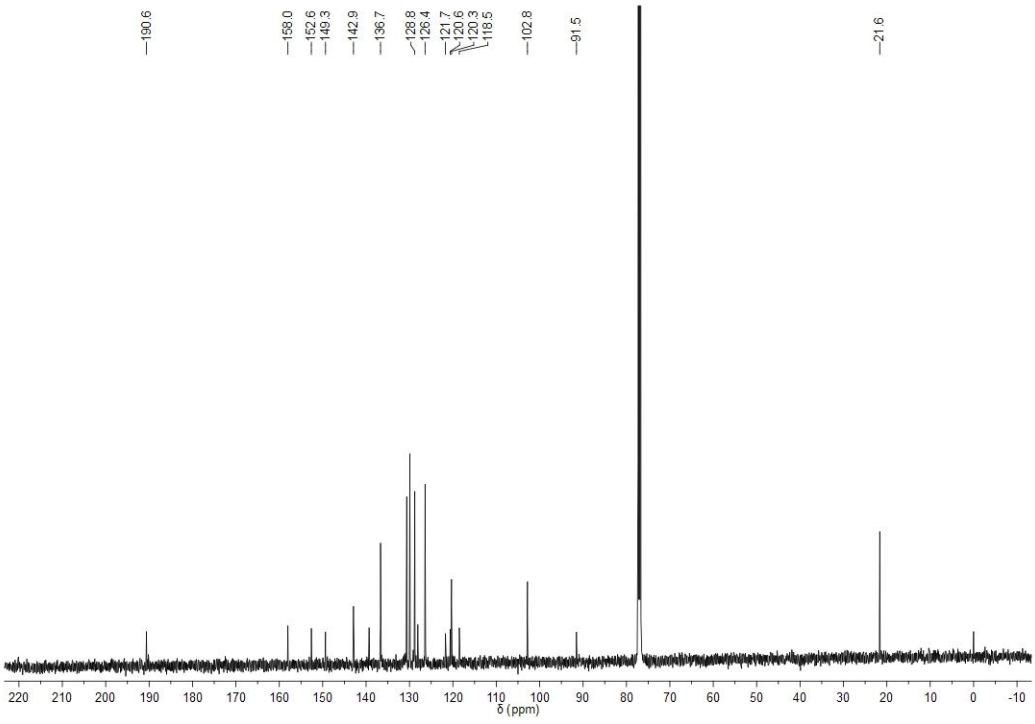




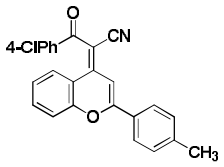
^{1}H NMR and ^{13}C NMR Spectra of Compound 4lb

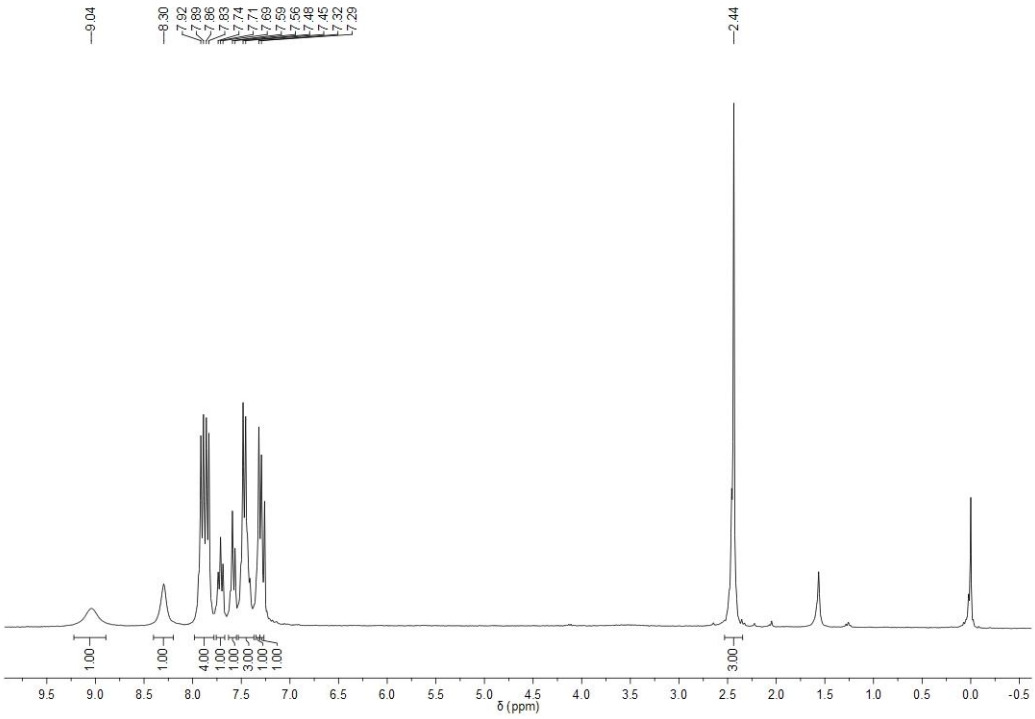


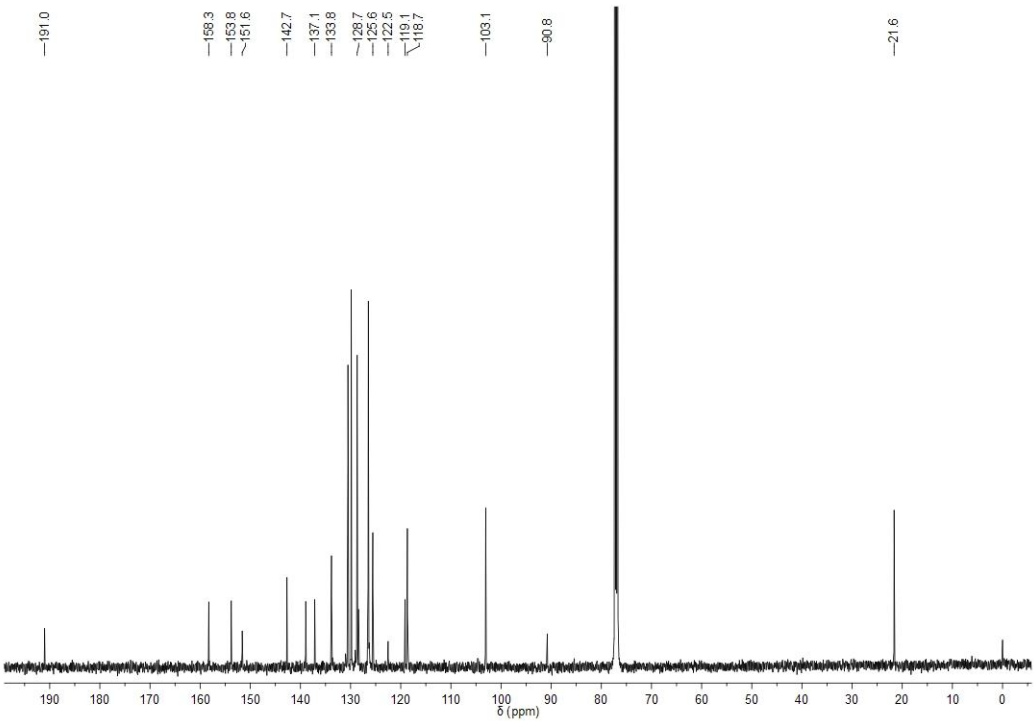




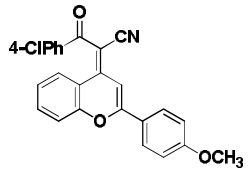
^{1}H NMR and ^{13}C NMR Spectra of Compound 4mb

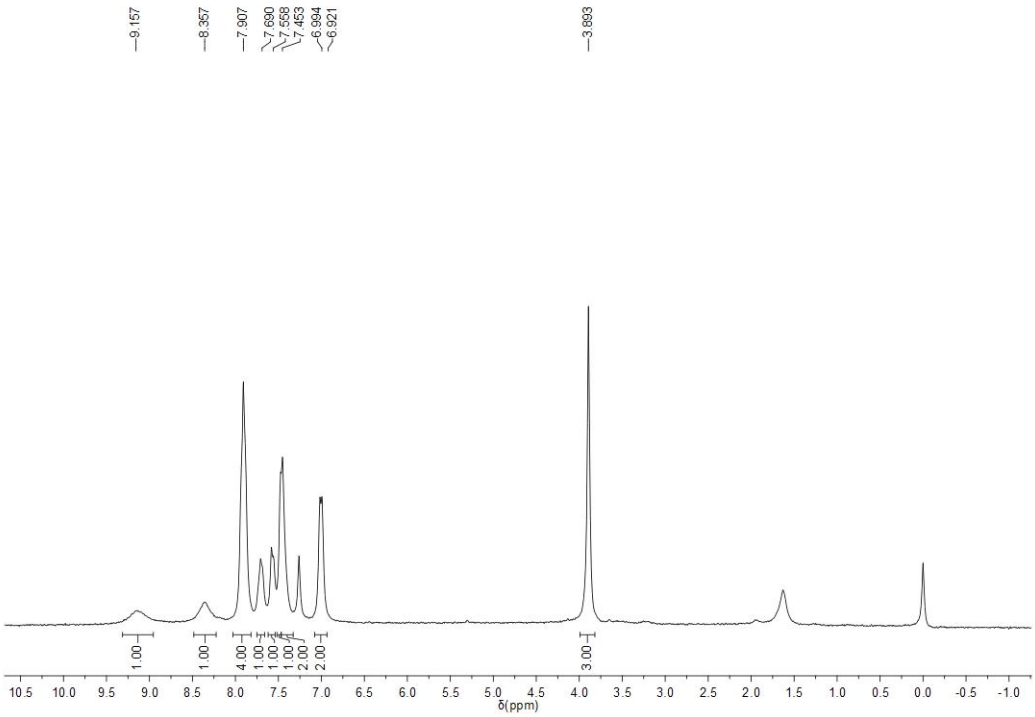


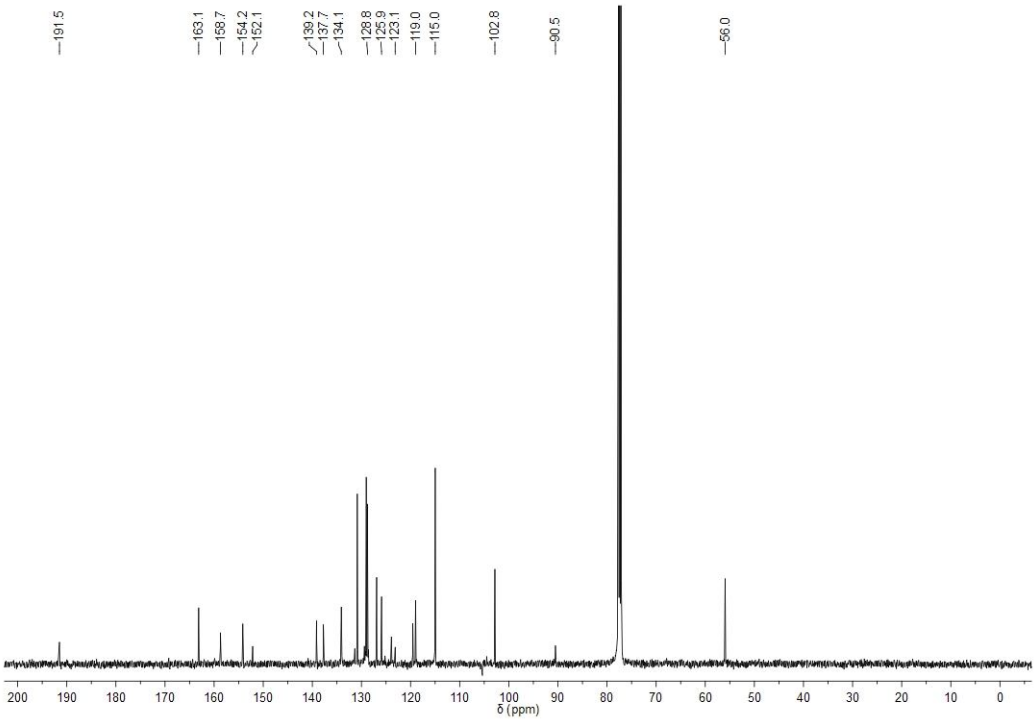




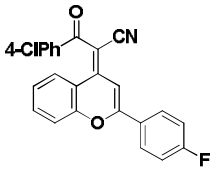
^{1}H NMR and ^{13}C NMR Spectra of Compound 4nb

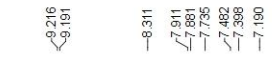


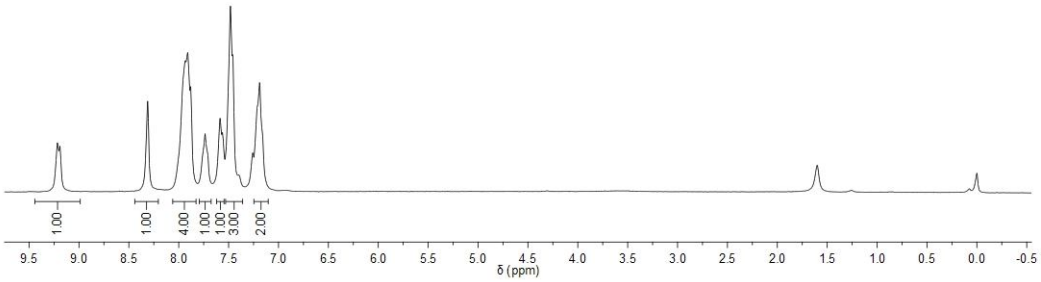


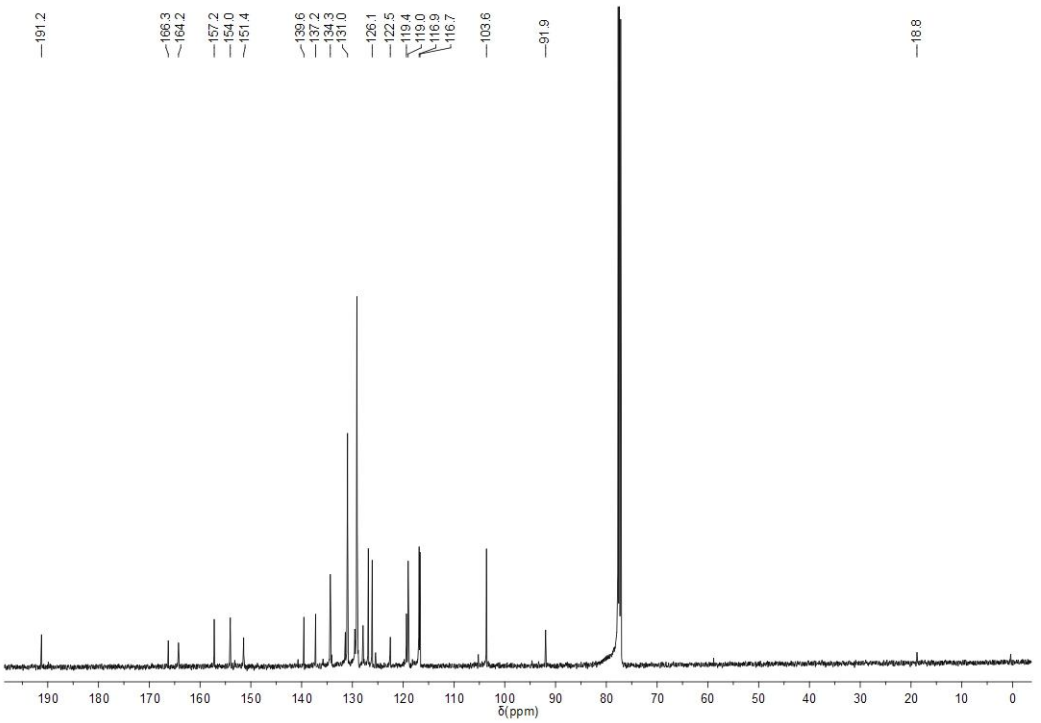


^{1}H NMR and ^{13}C NMR Spectra of Compound 4ob

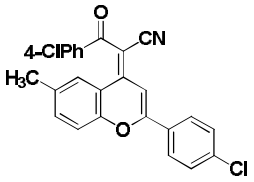


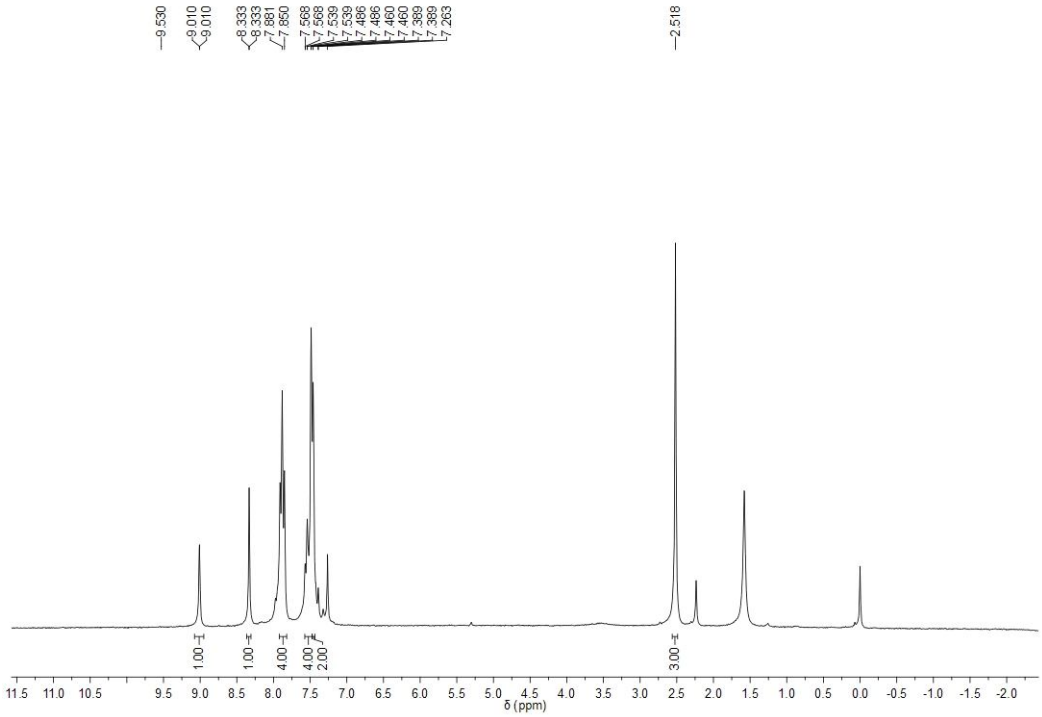


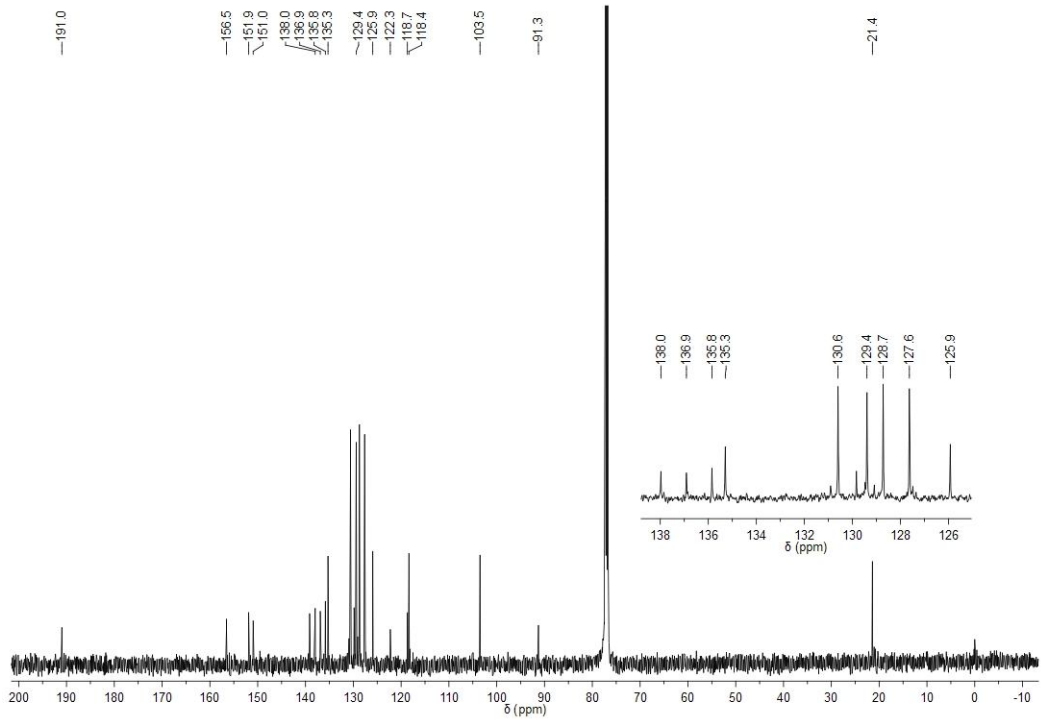




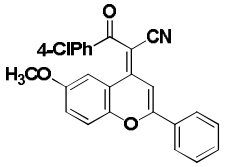
^{1}H NMR and ^{13}C NMR Spectra of Compound 4pb

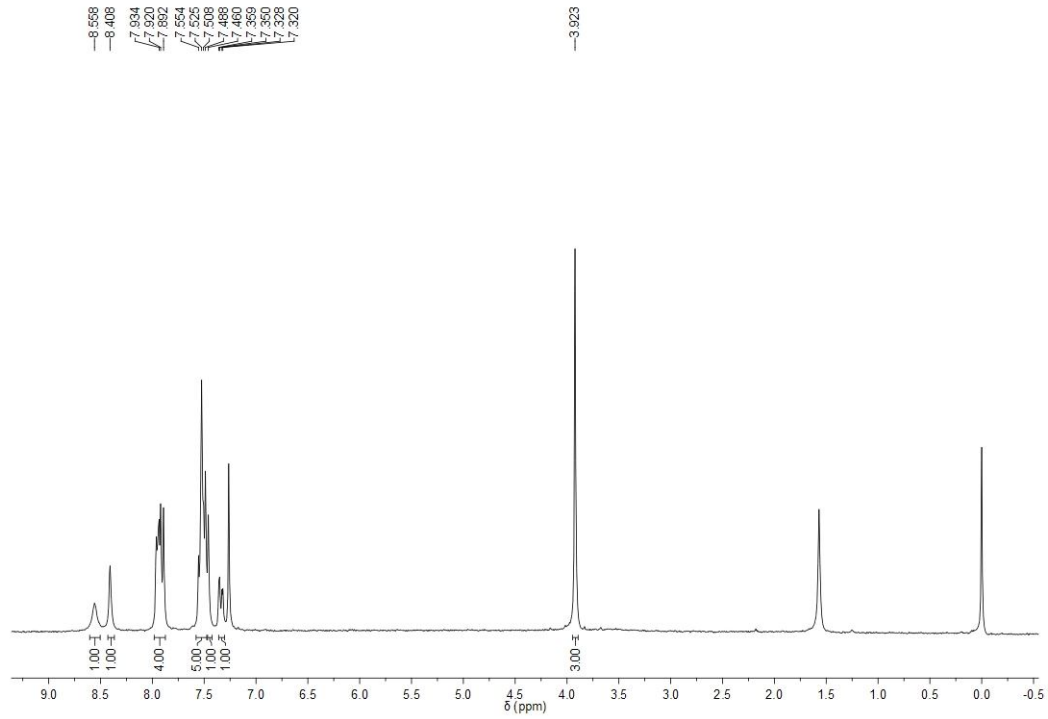


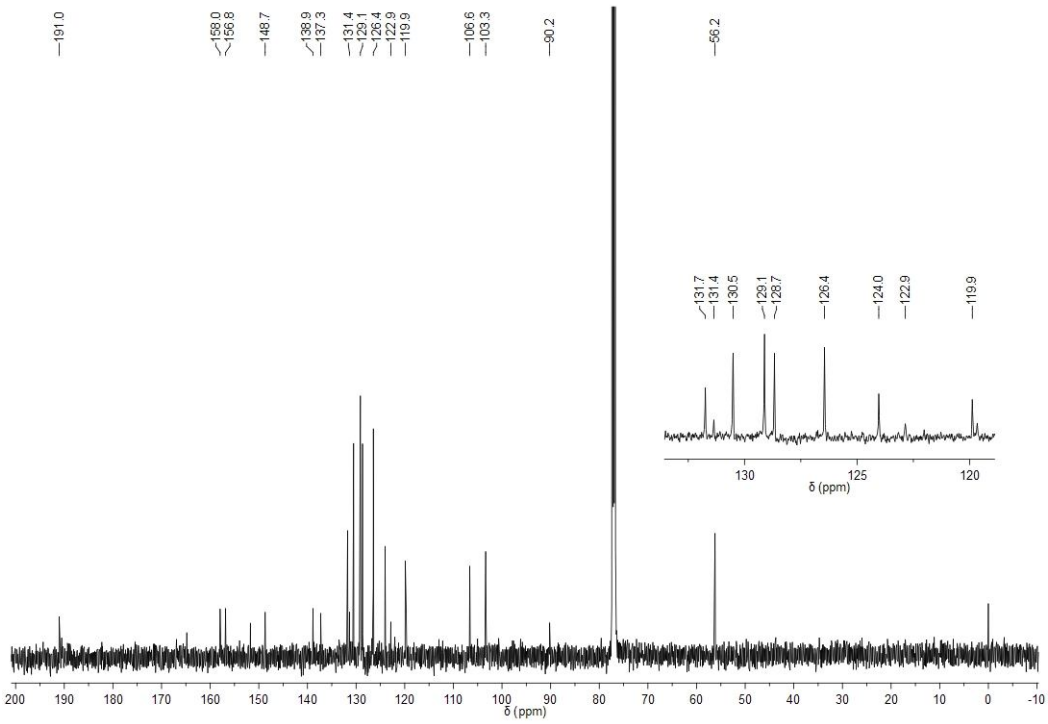




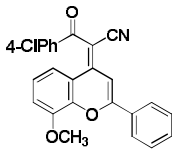
^{1}H NMR and ^{13}C NMR Spectra of Compound 4qb

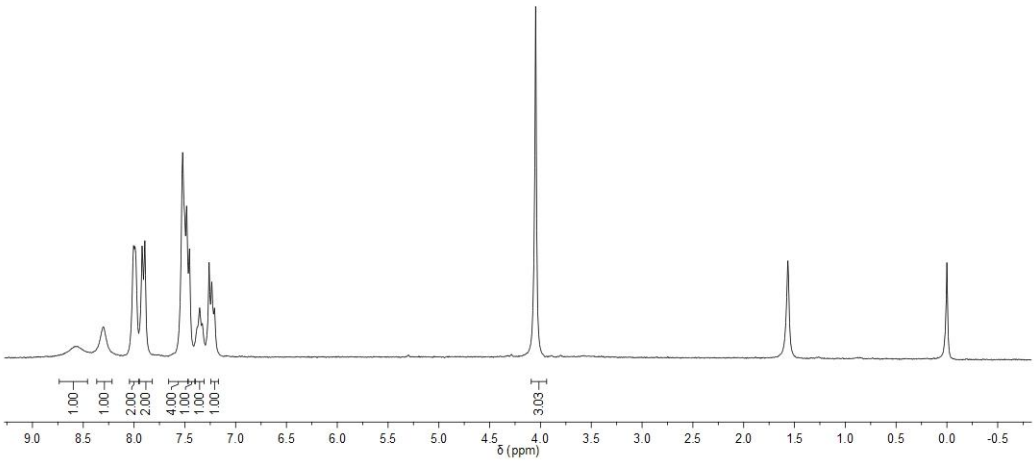


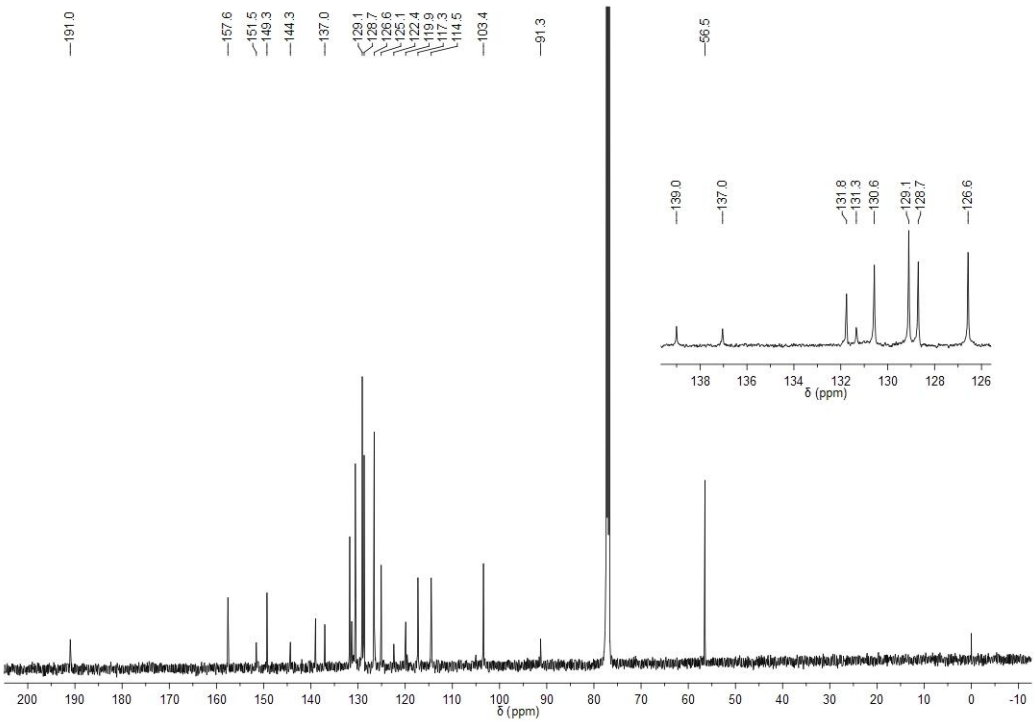




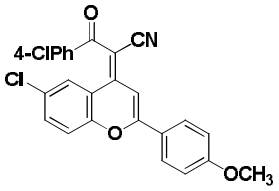
^{1}H NMR and ^{13}C NMR Spectra of Compound 4rb

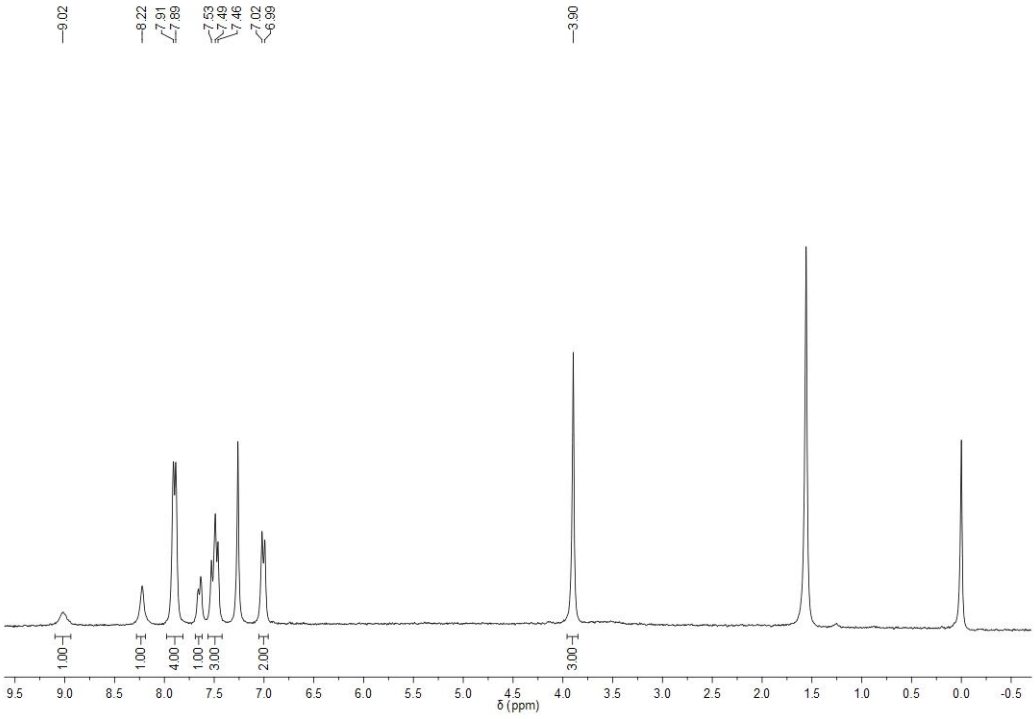


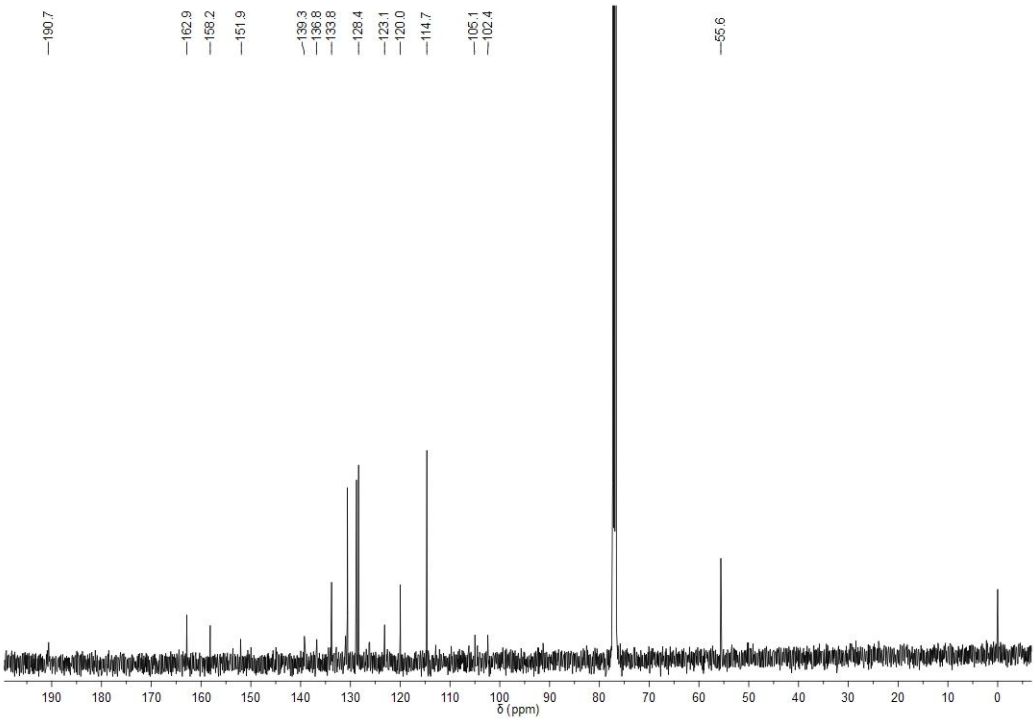




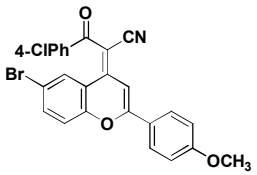
^{1}H NMR and ^{13}C NMR Spectra of Compound 4sb

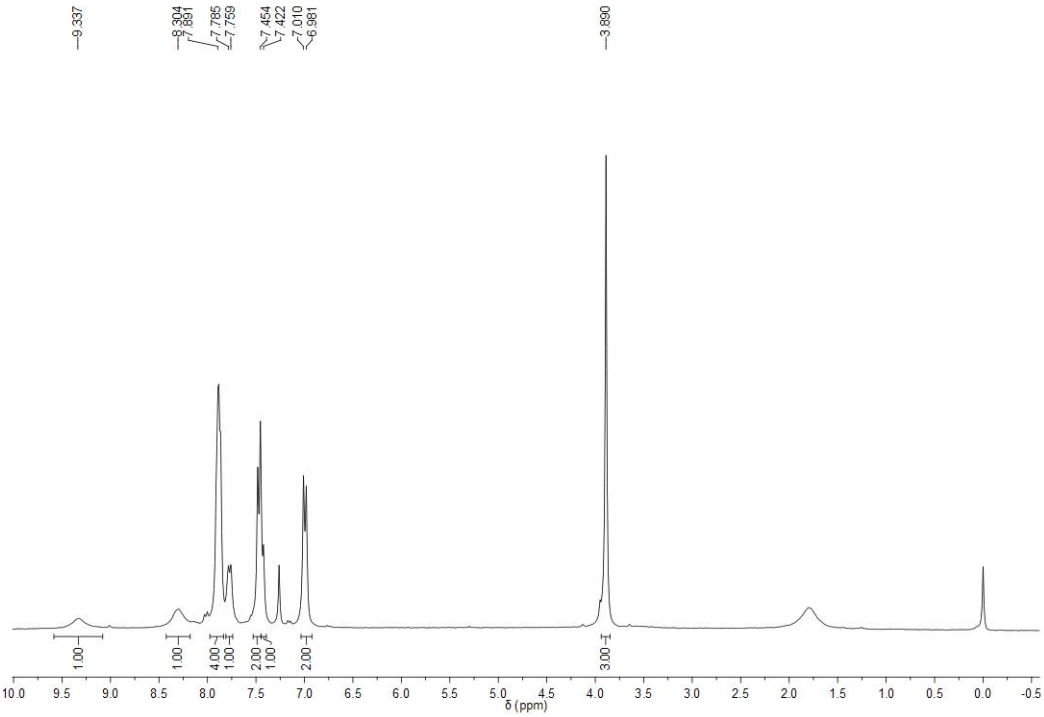


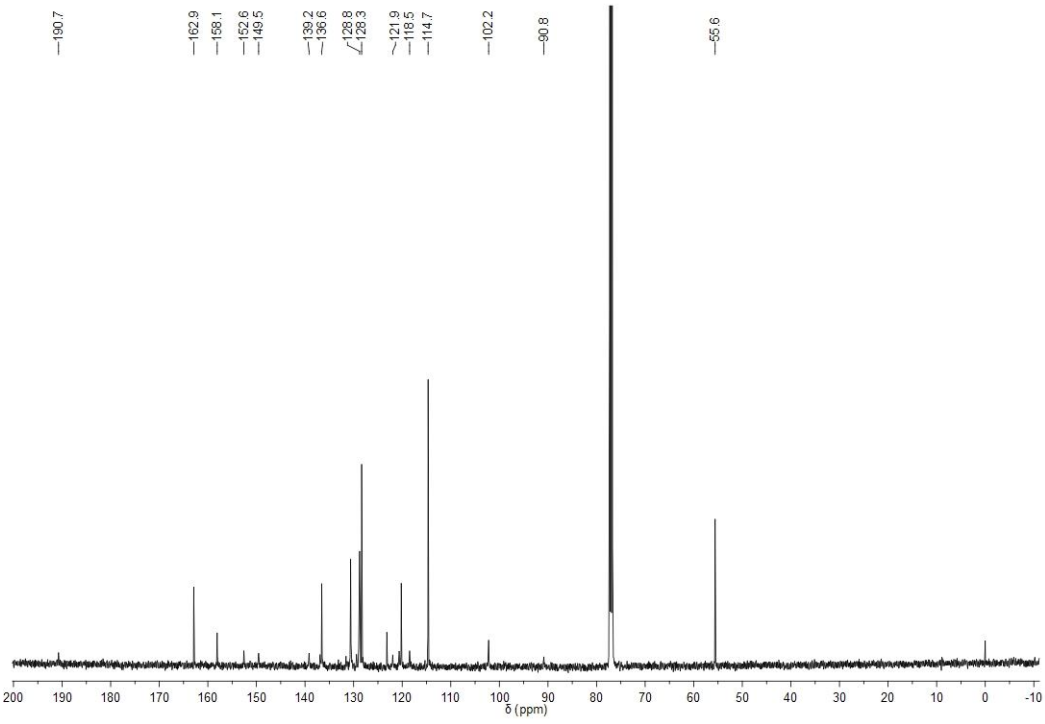




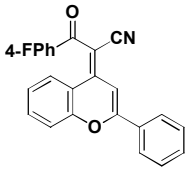
^{1}H NMR and ^{13}C NMR Spectra of Compound 4tb

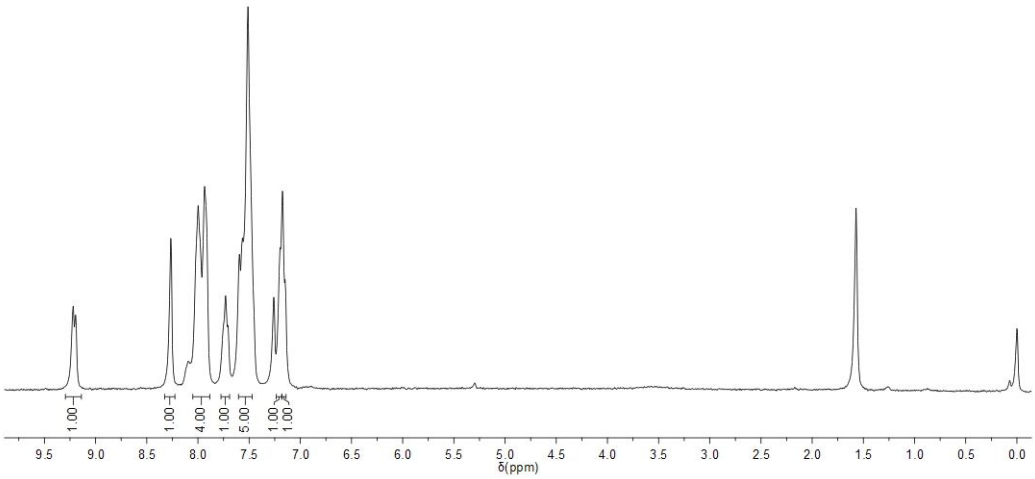


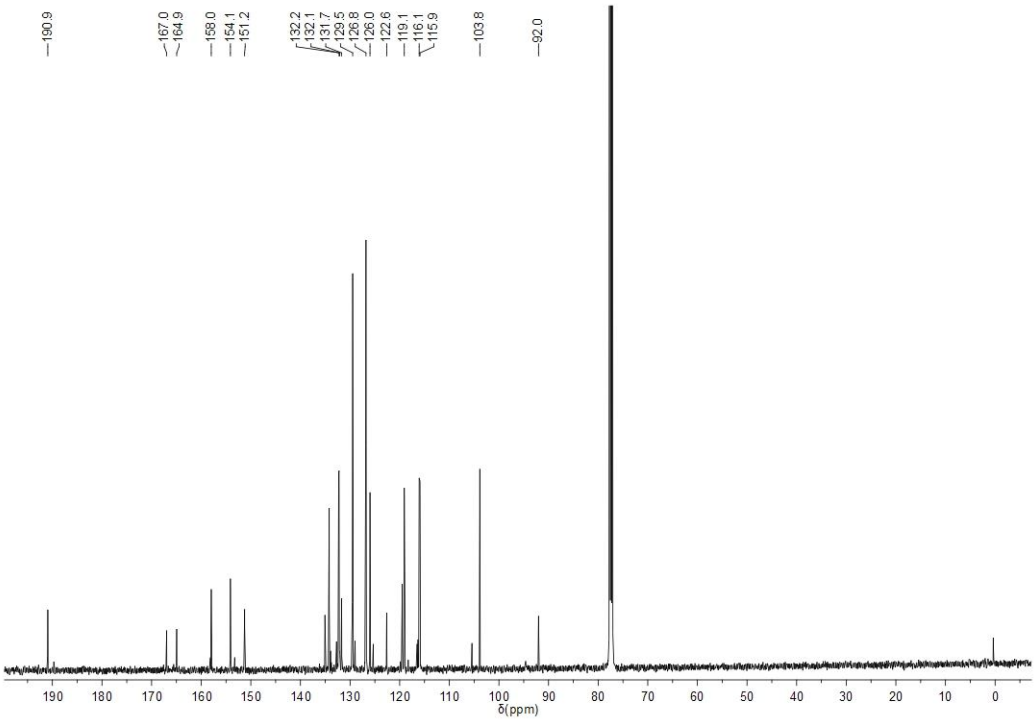




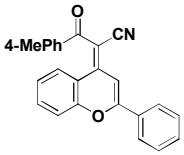
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ac

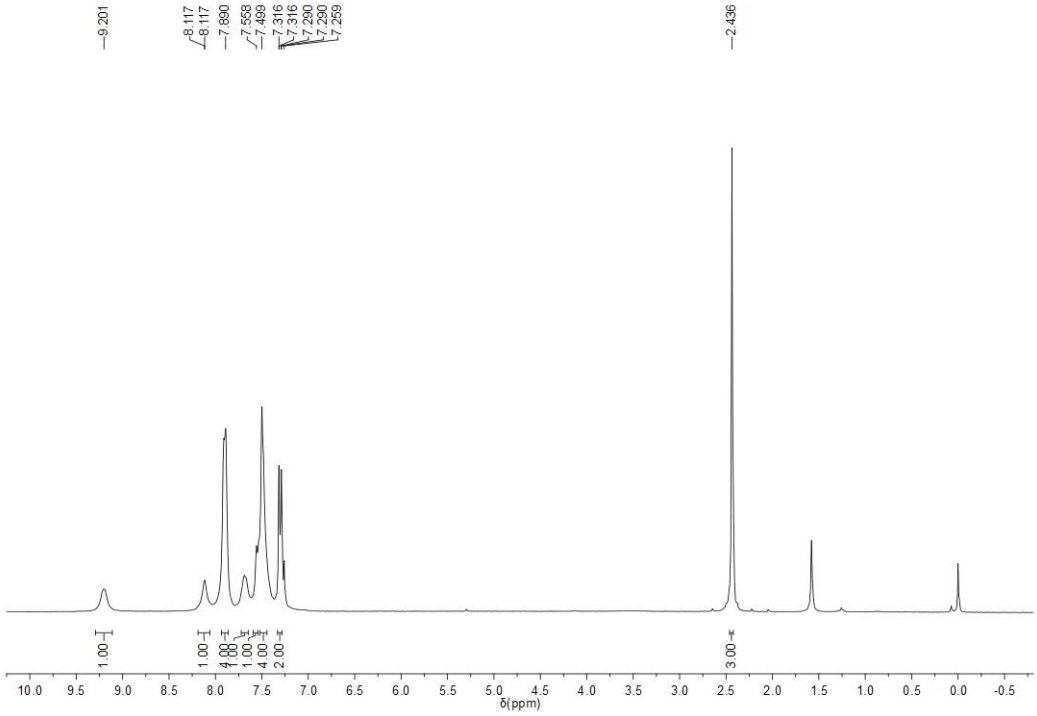


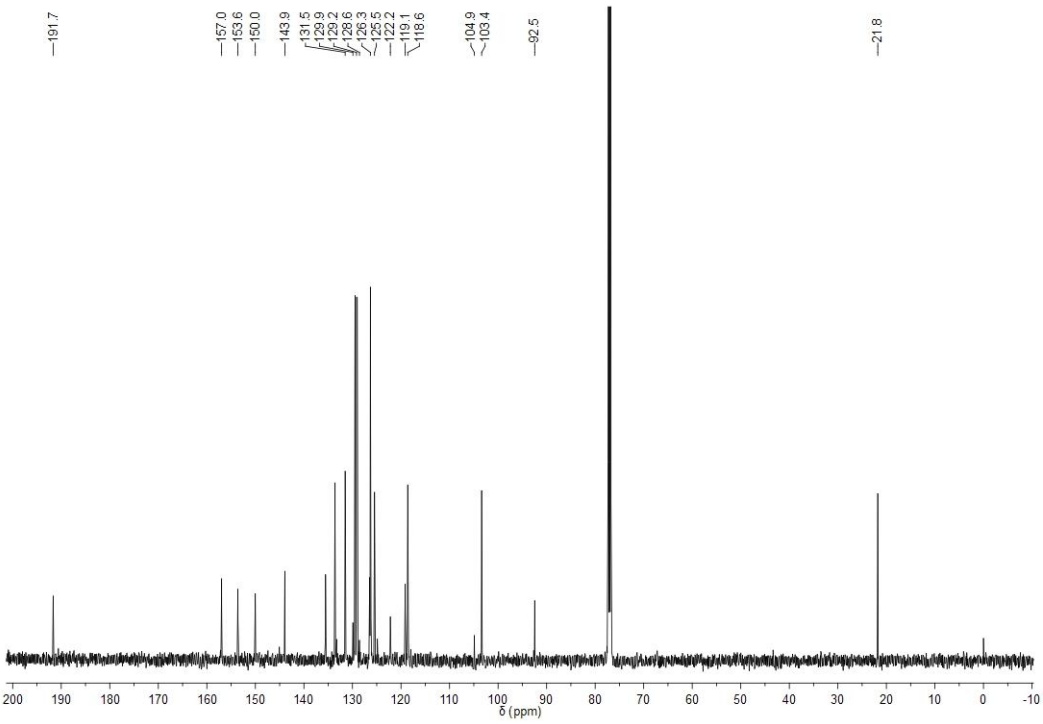




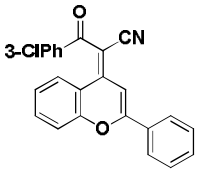
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ad

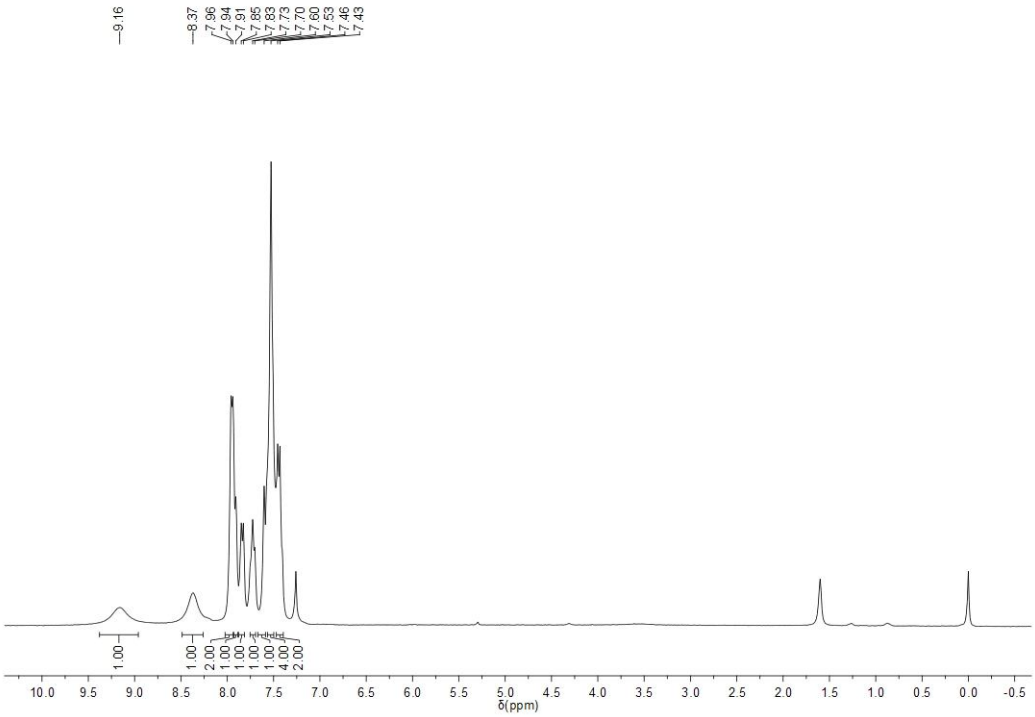


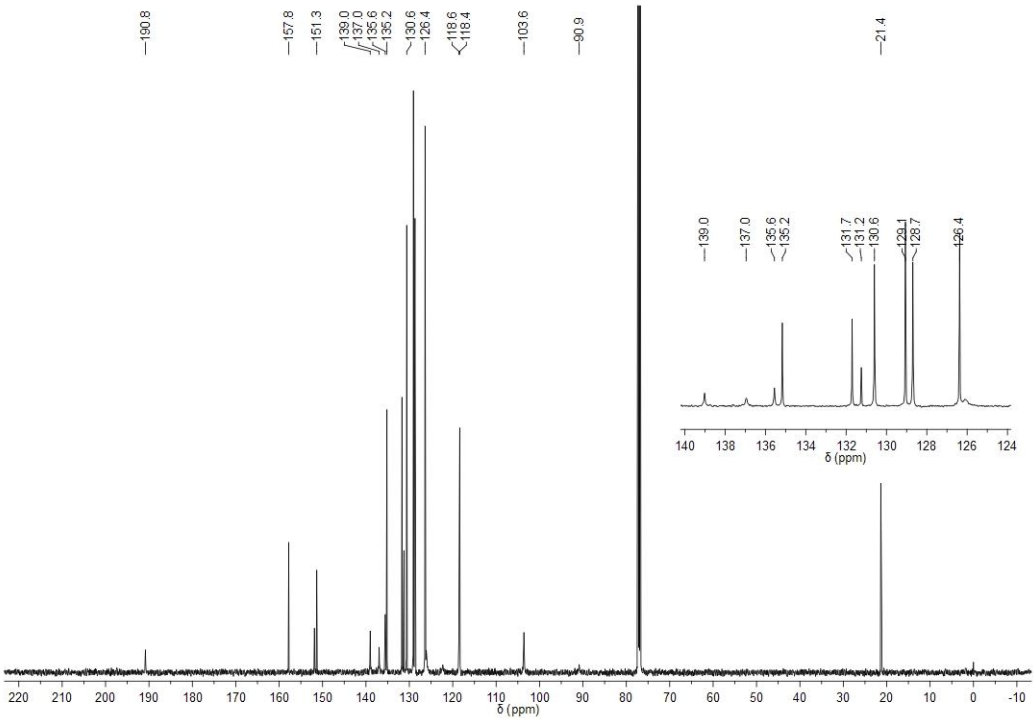




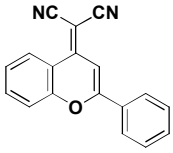
^{1}H NMR and ^{13}C NMR Spectra of Compound 4ae

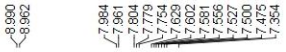


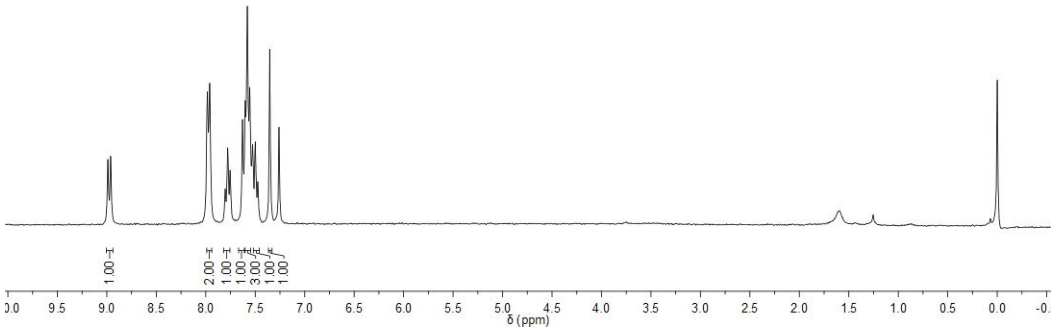


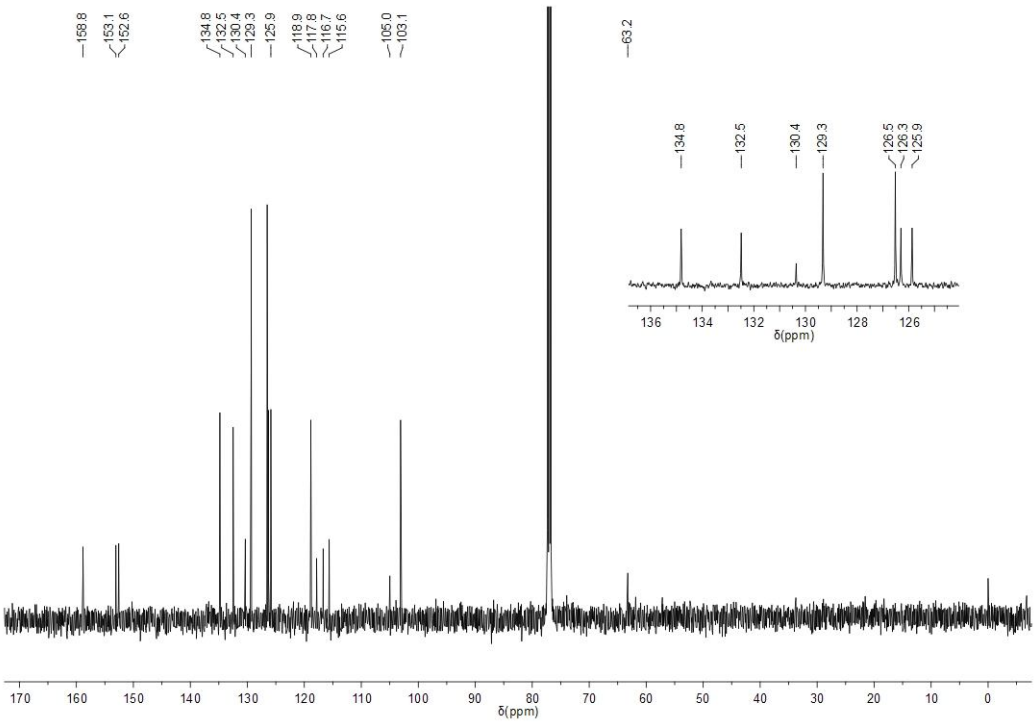


^{1}H NMR and ^{13}C NMR Spectra of Compound 5a

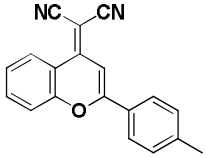


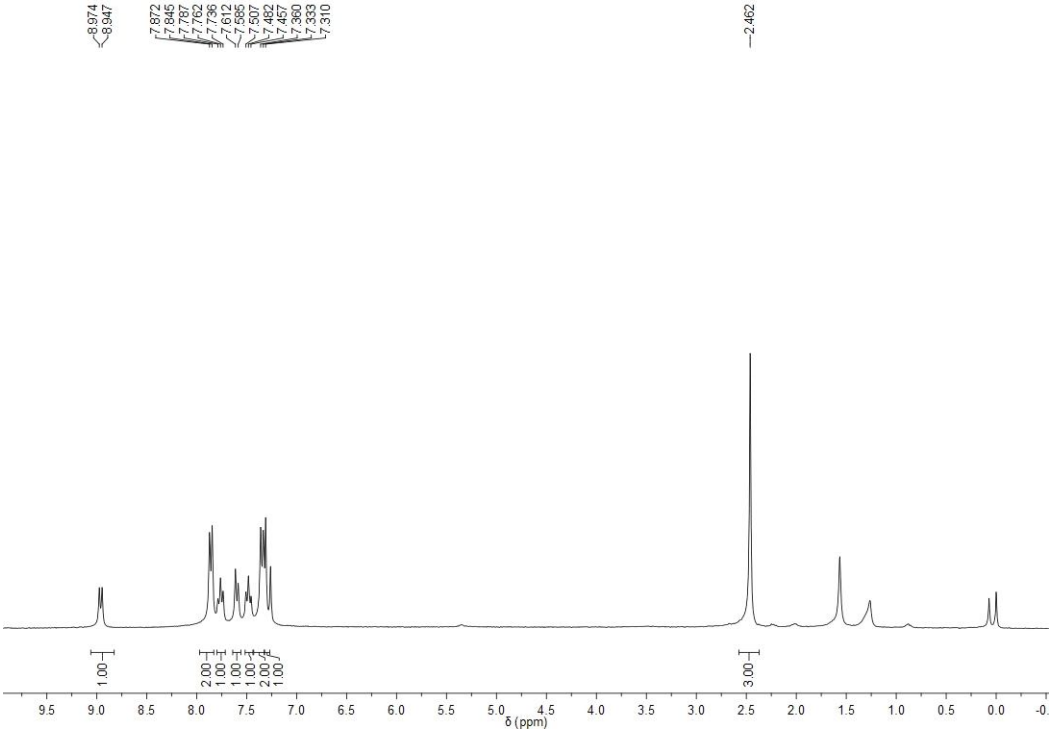


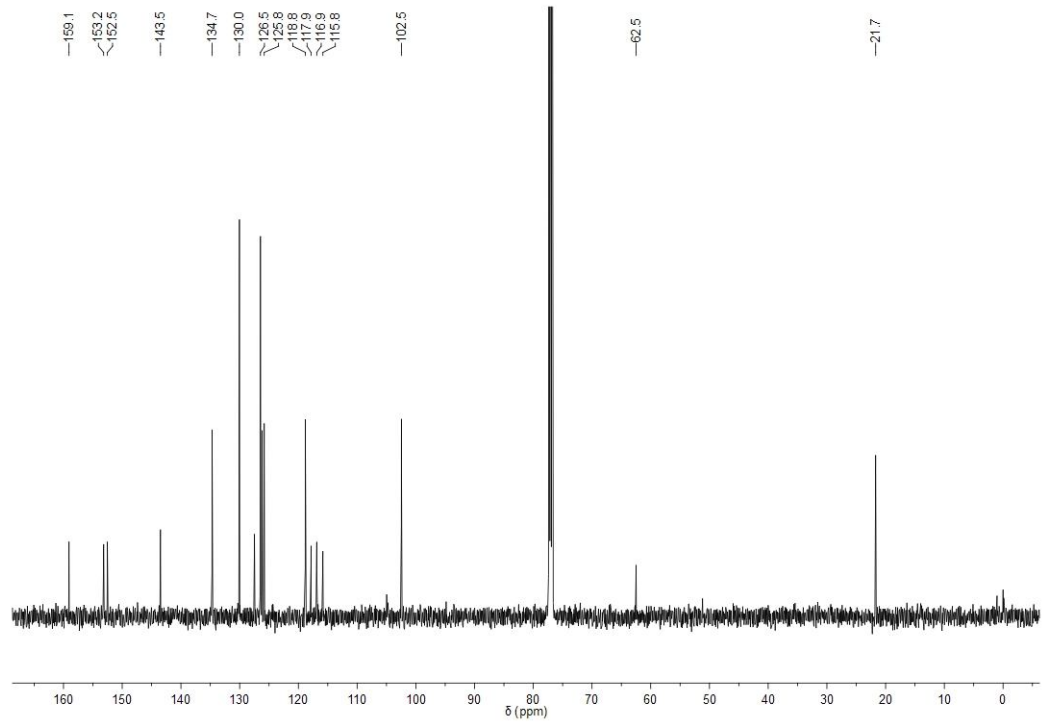




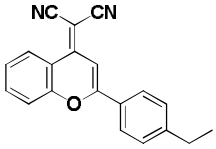
^{1}H NMR and ^{13}C NMR Spectra of Compound 5b

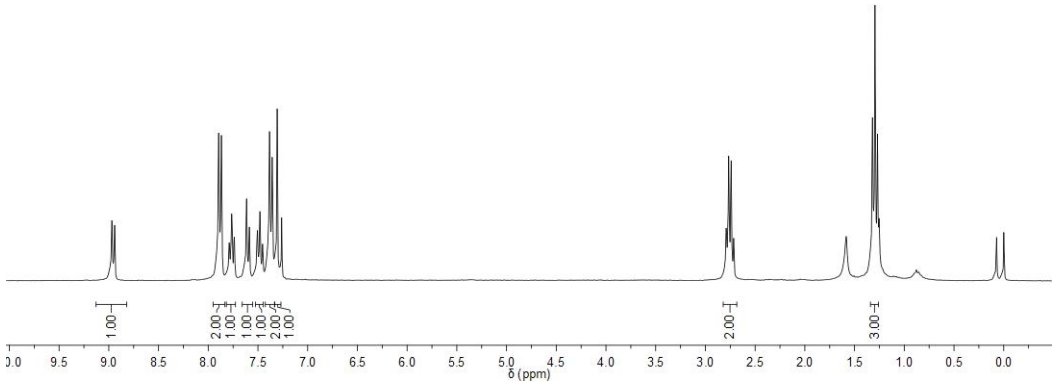


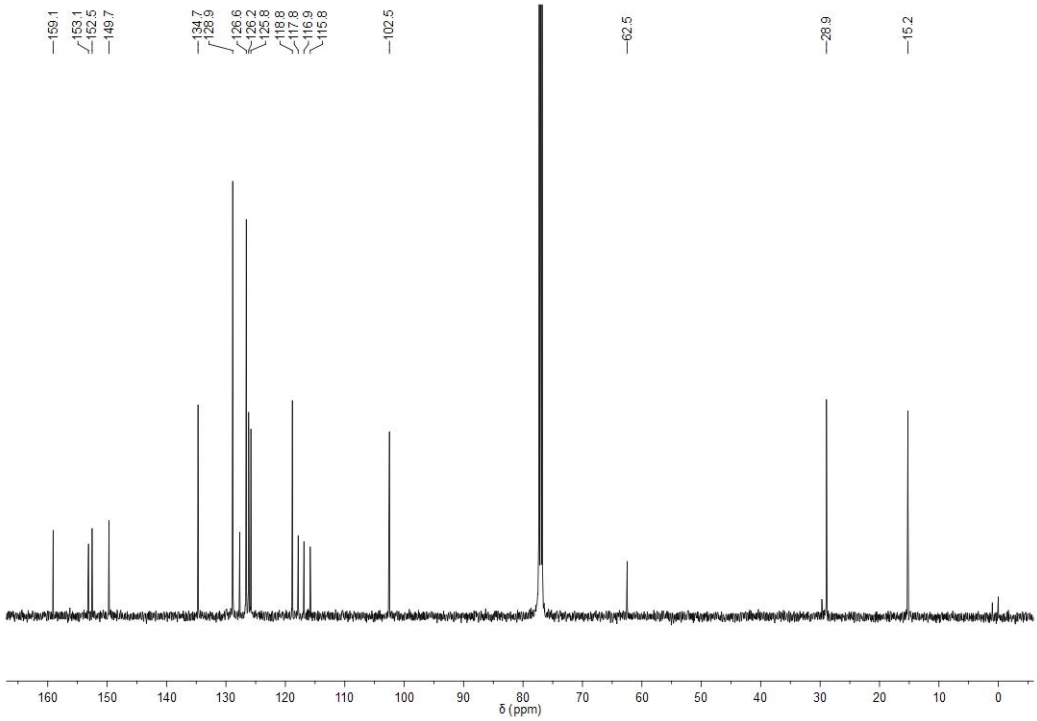




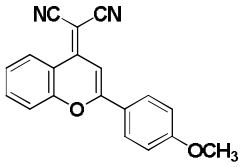
^{1}H NMR and ^{13}C NMR Spectra of Compound 5c

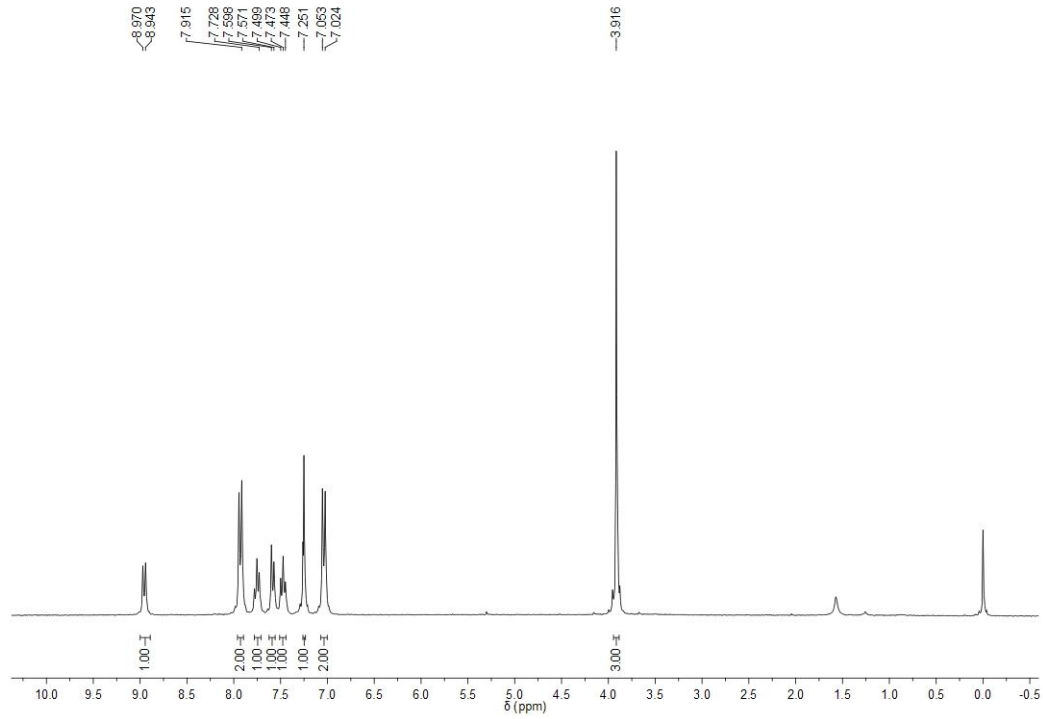


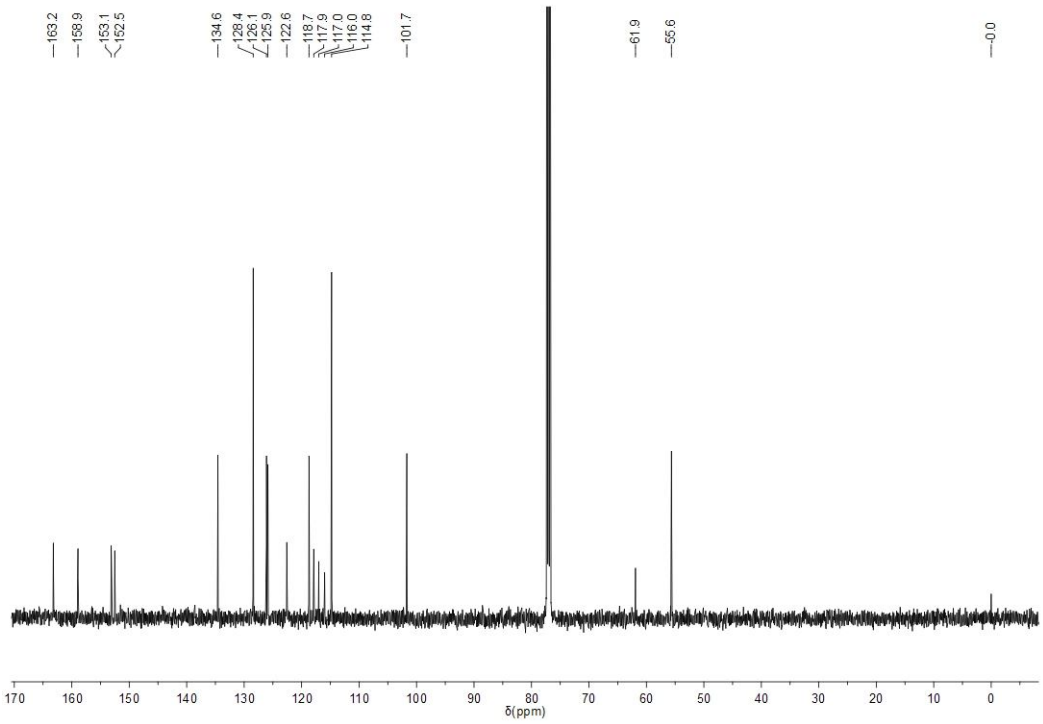




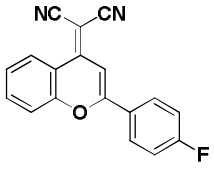
^{1}H NMR and ^{13}C NMR Spectra of Compound 5d

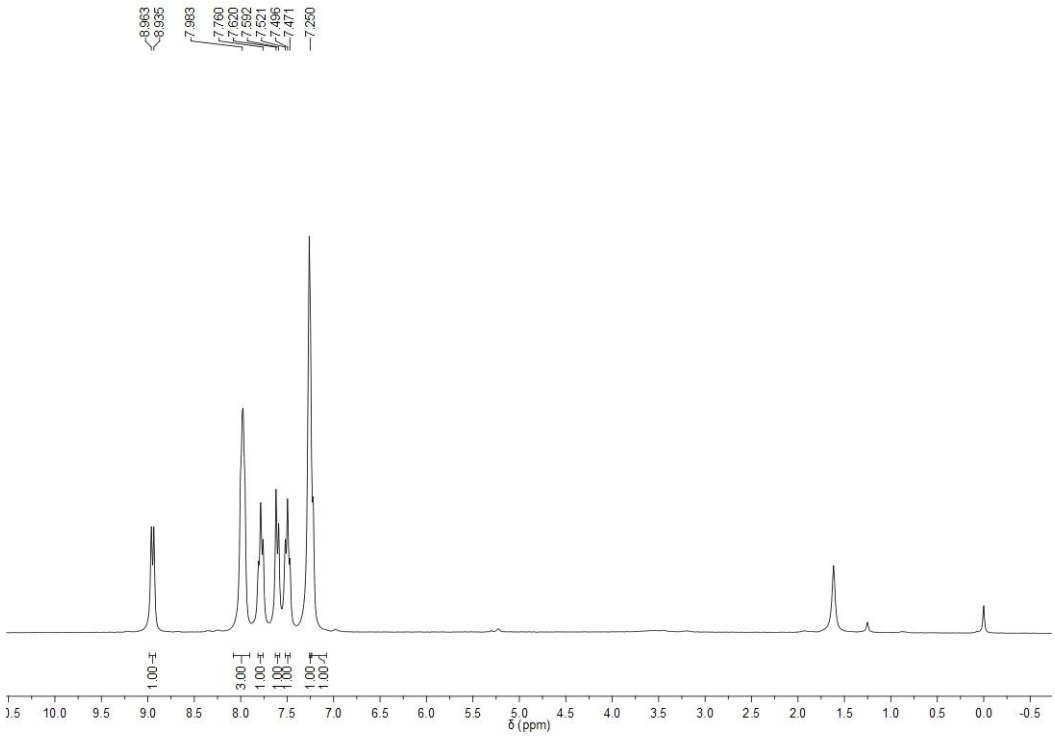


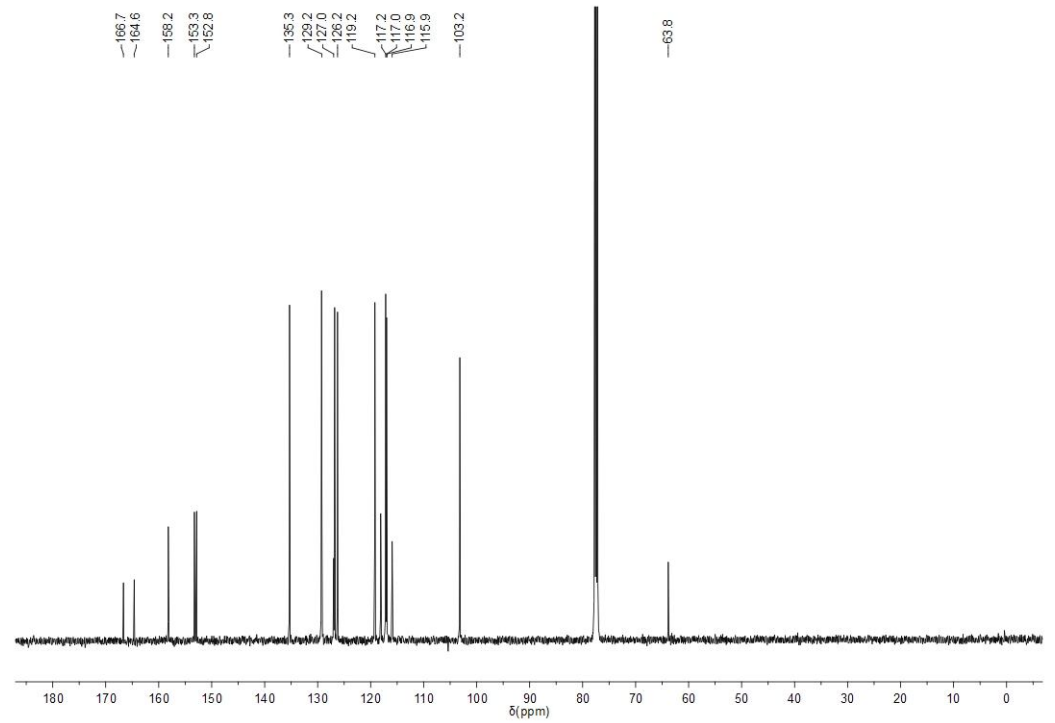




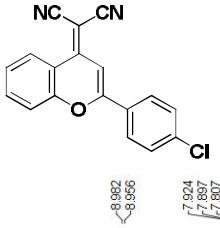
^{1}H NMR and ^{13}C NMR Spectra of Compound 5e

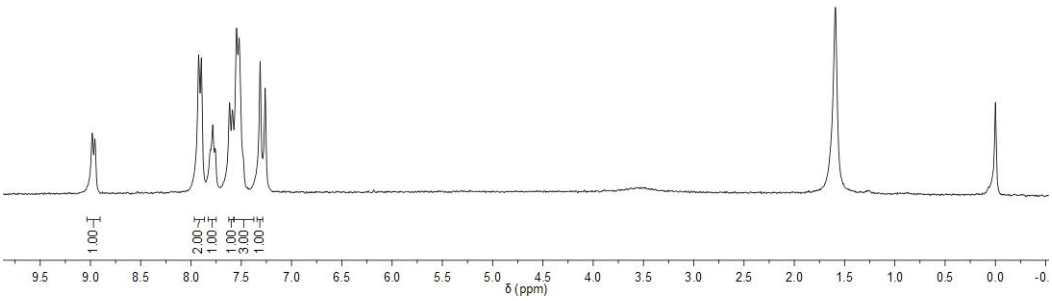


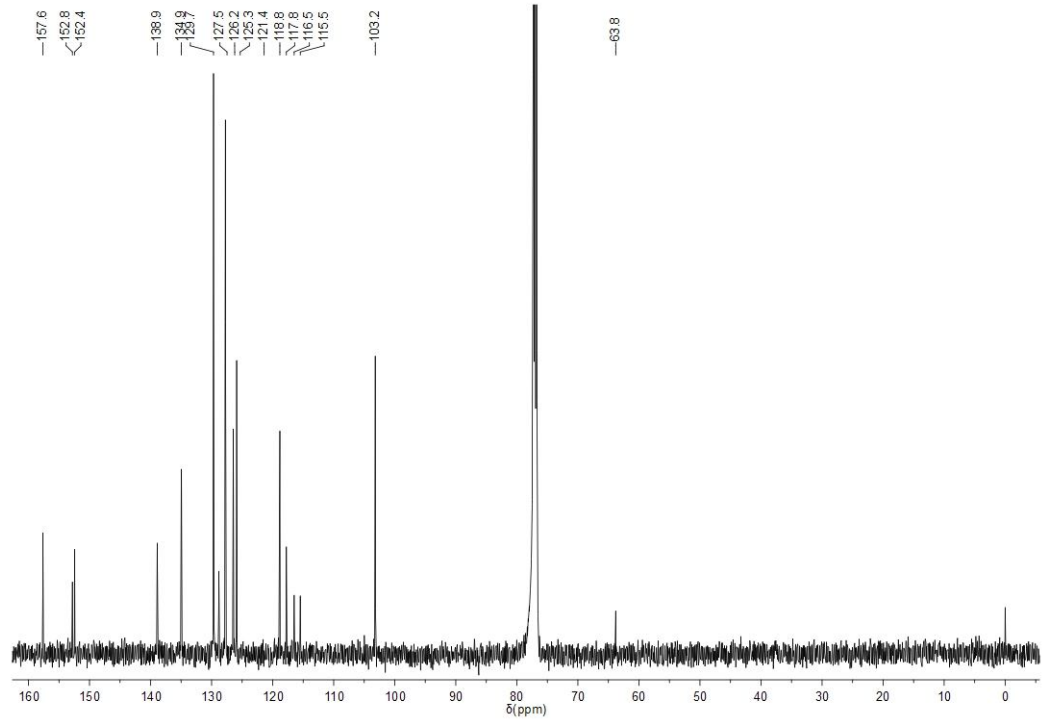




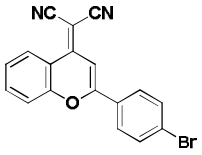
^{1}H NMR and ^{13}C NMR Spectra of Compound 5f

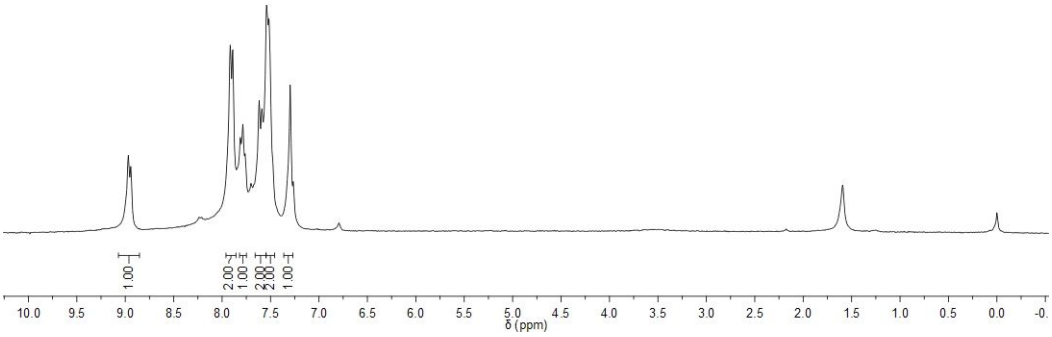


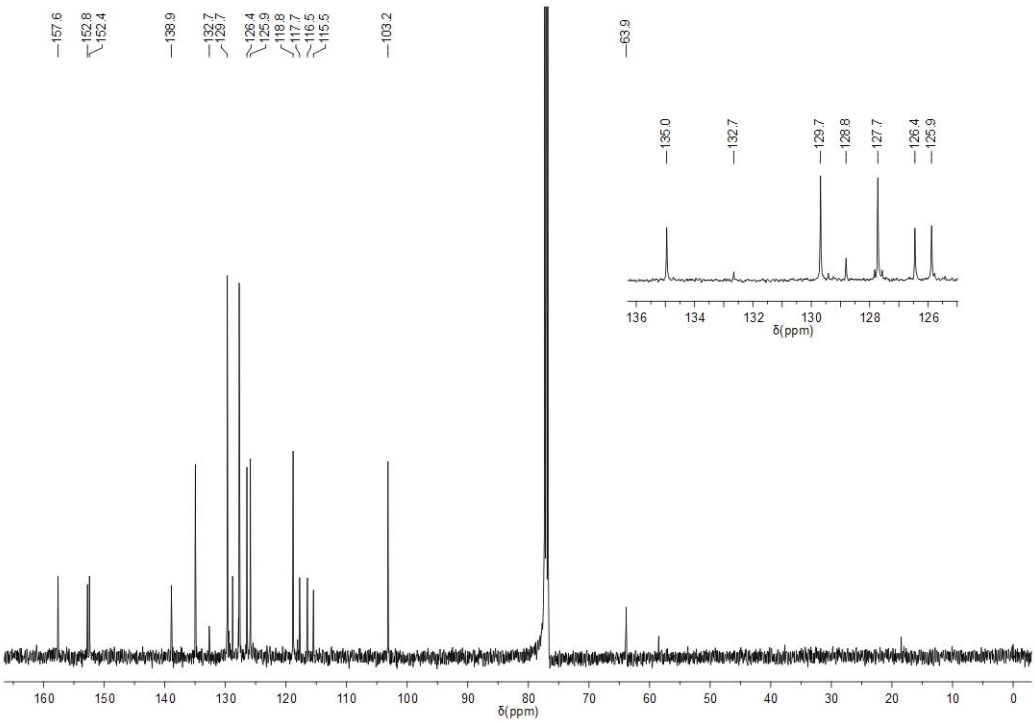




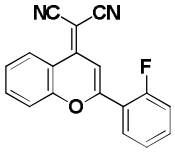
^{1}H NMR and ^{13}C NMR Spectra of Compound 5g

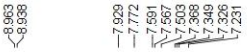


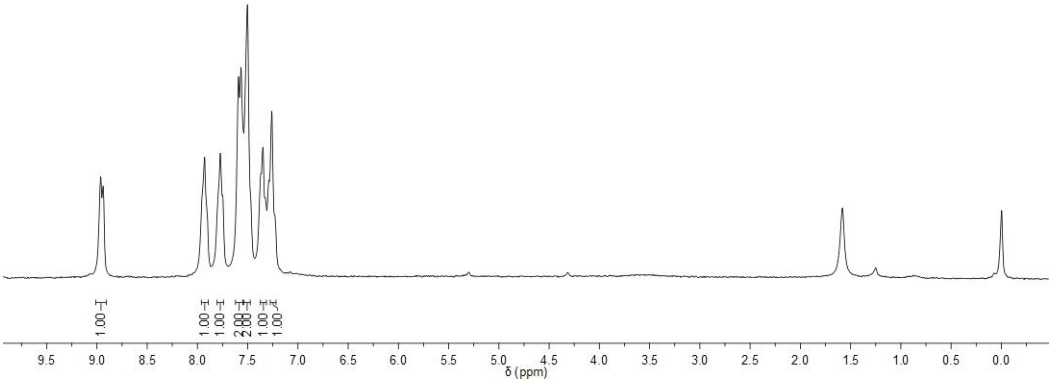


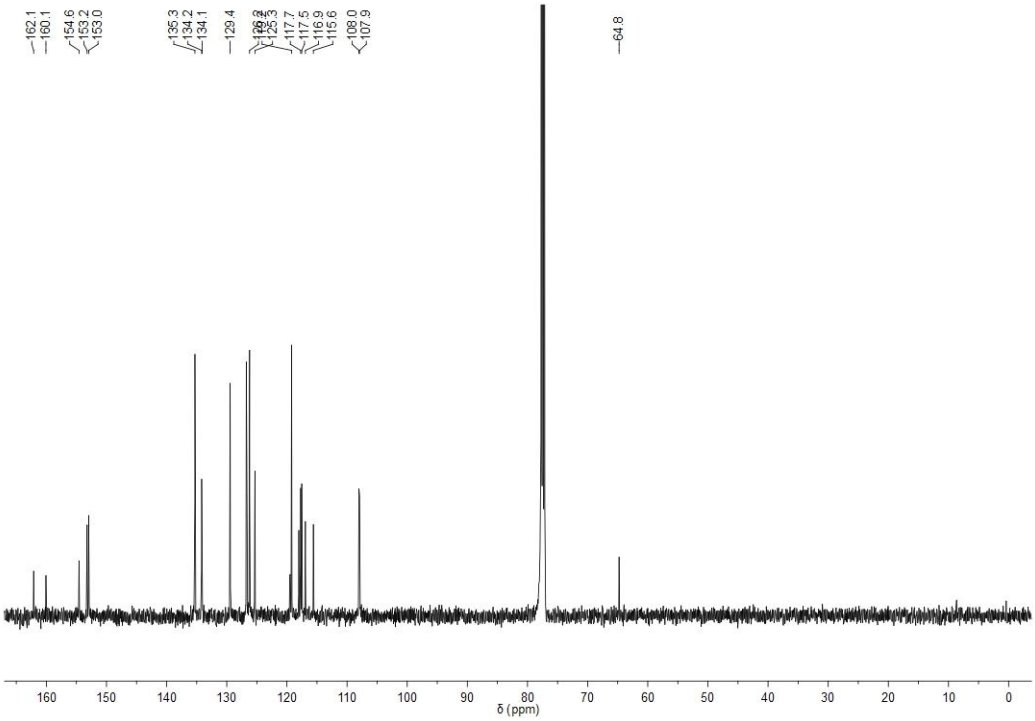


^{1}H NMR and ^{13}C NMR Spectra of Compound 5h

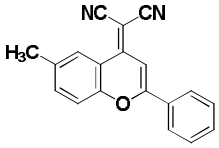


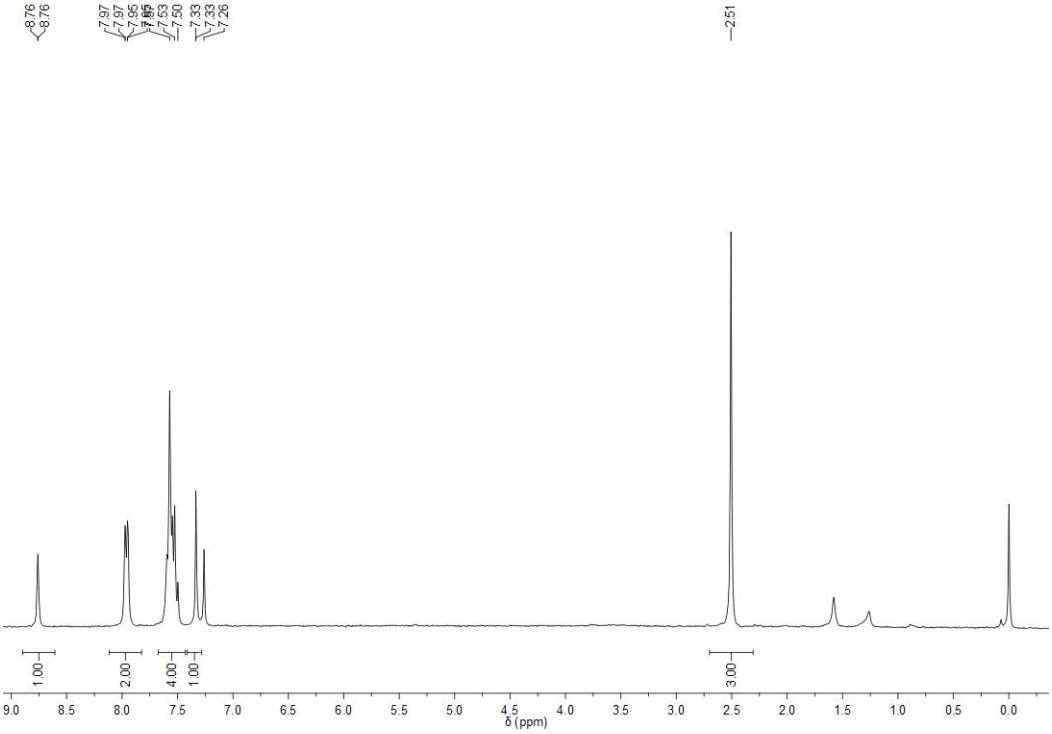


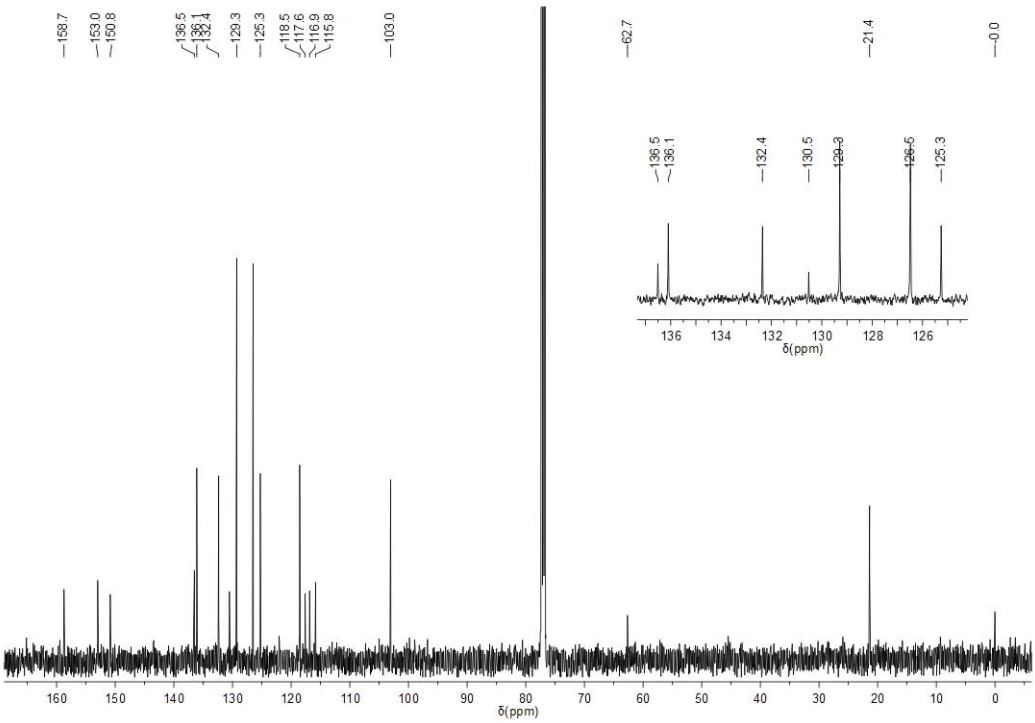




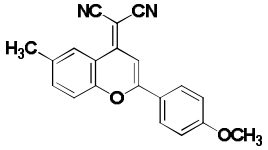
^{1}H NMR and ^{13}C NMR Spectra of Compound 5i

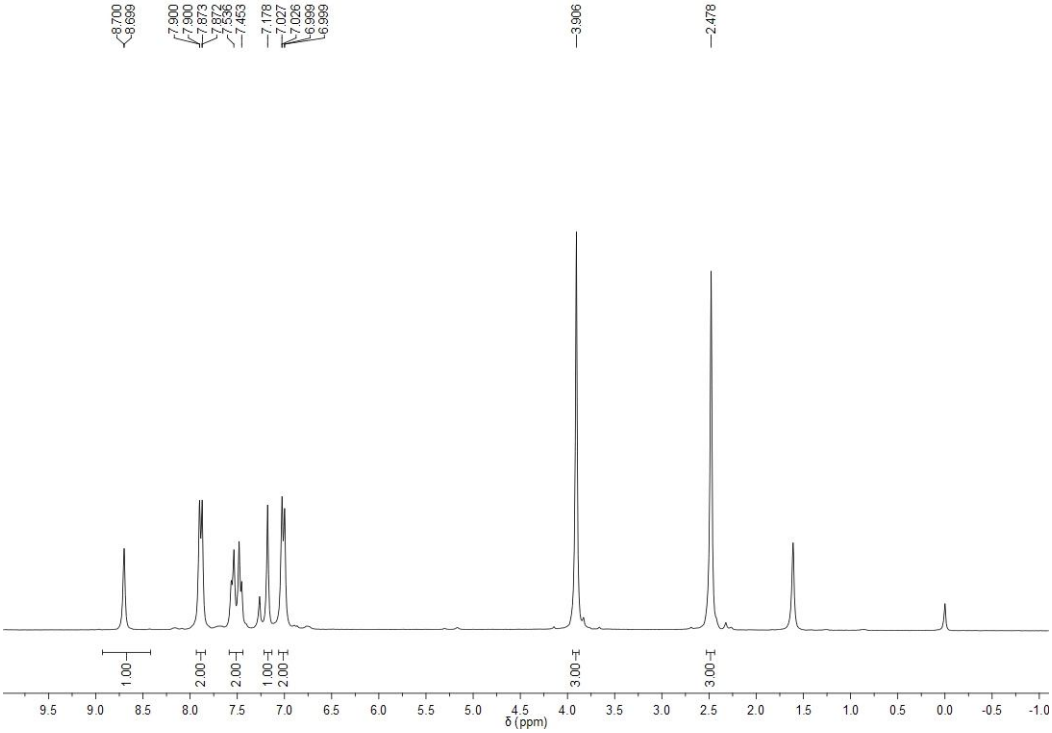


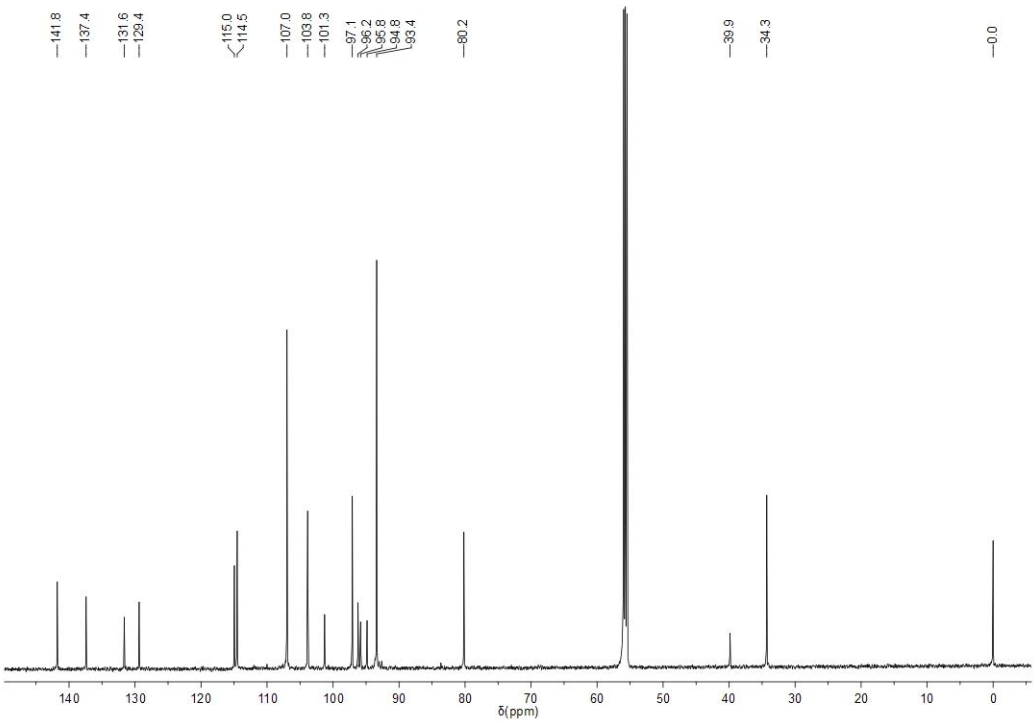




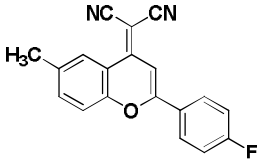
^{1}H NMR and ^{13}C NMR Spectra of Compound 5j

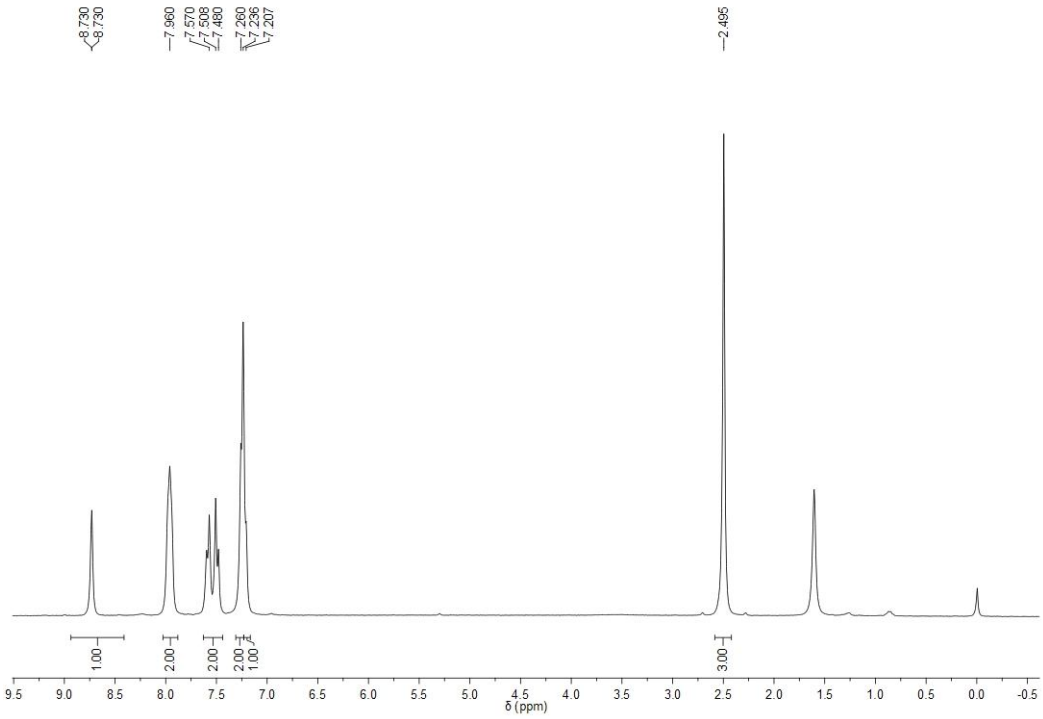


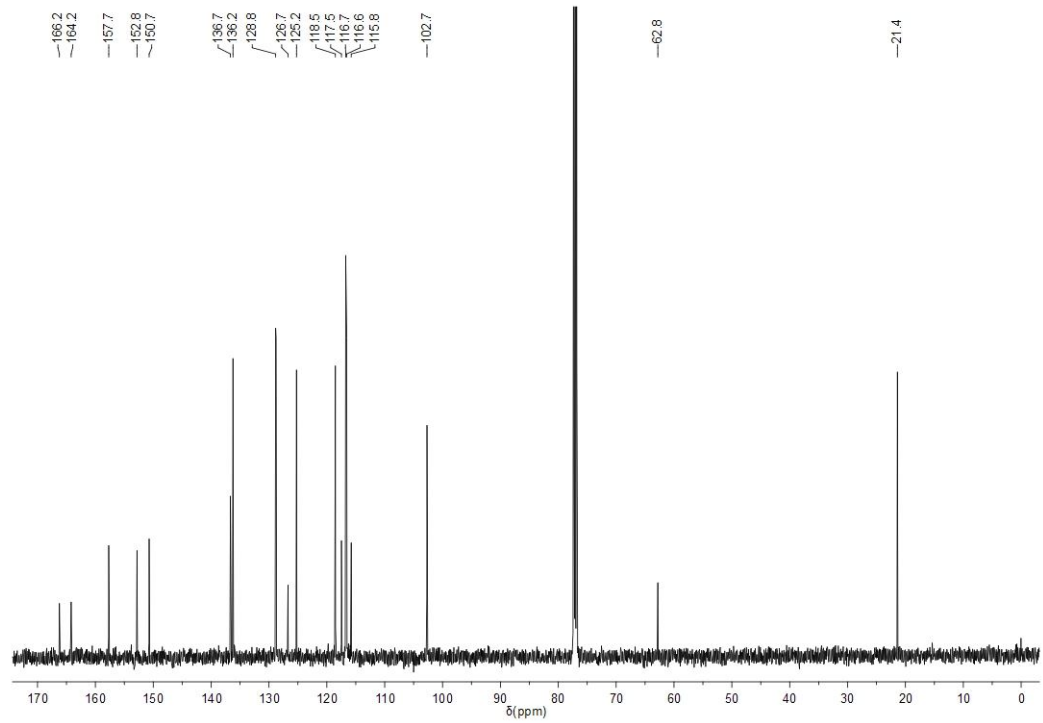




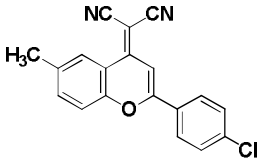
^{1}H NMR and ^{13}C NMR Spectra of Compound 5k

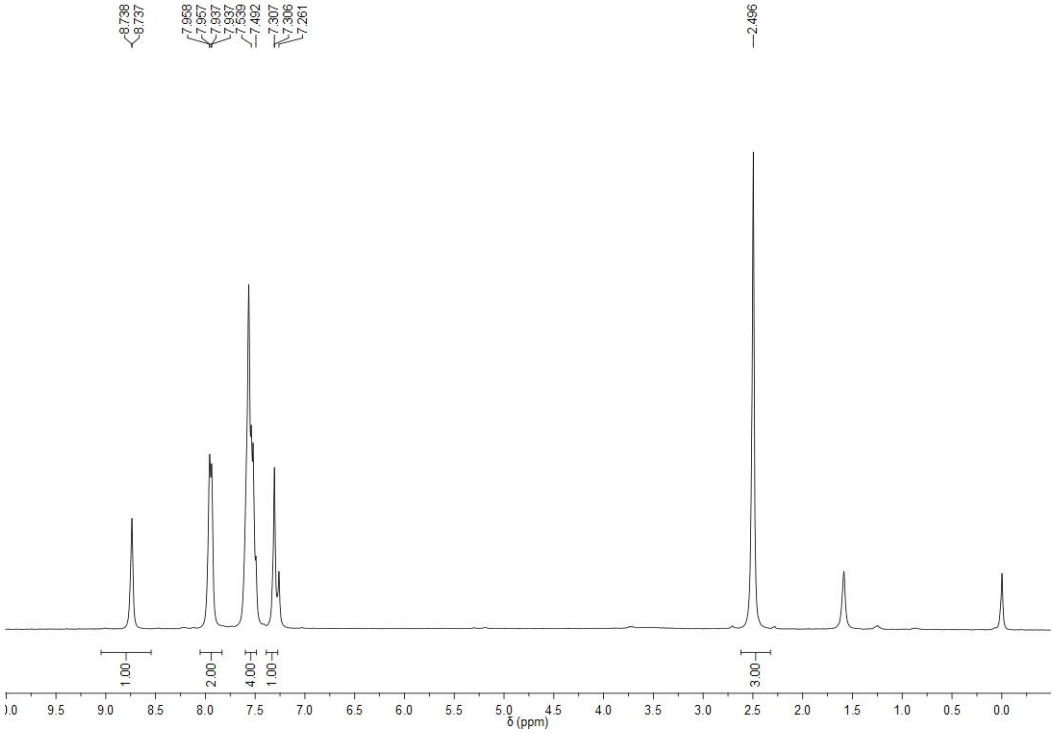


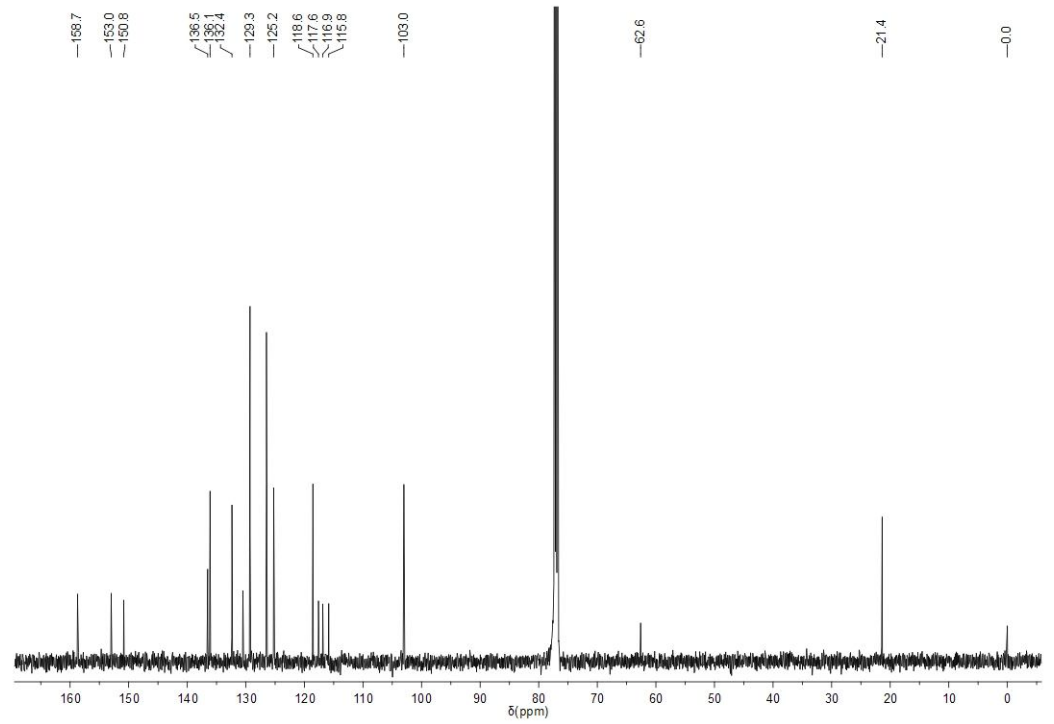




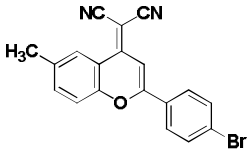
^{1}H NMR and ^{13}C NMR Spectra of Compound 5l

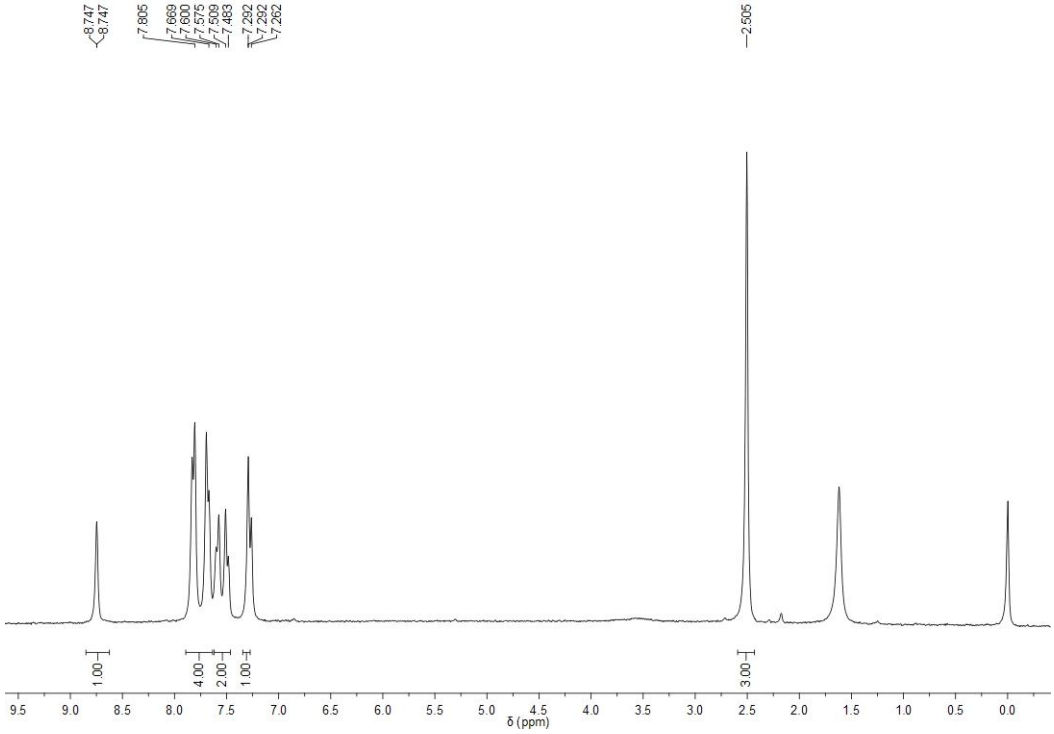


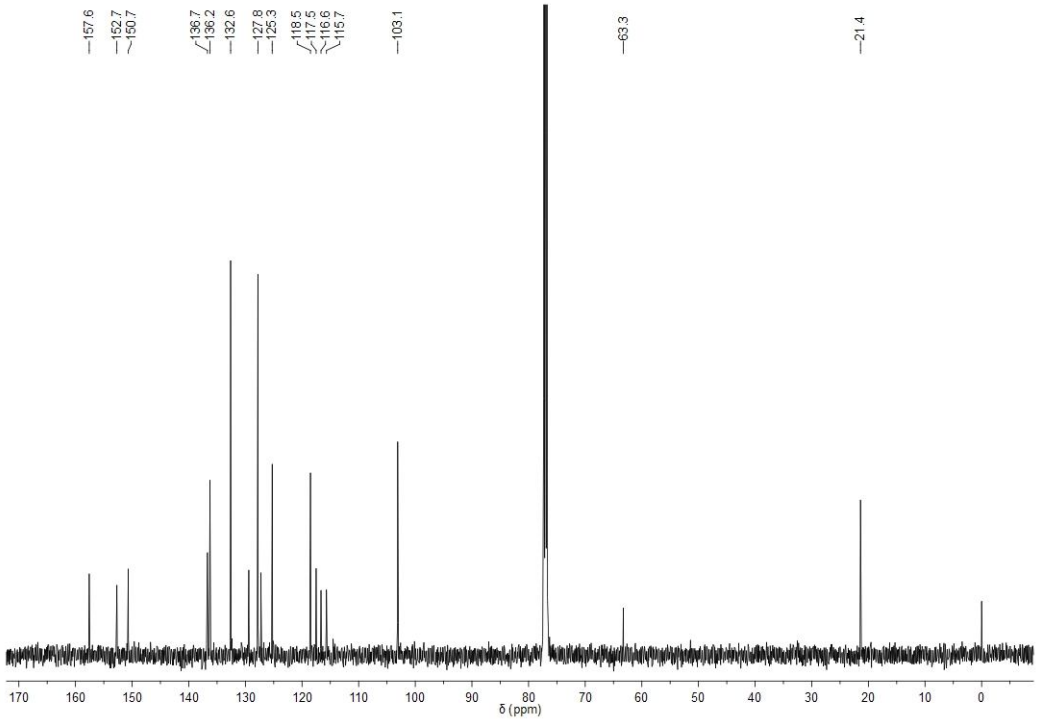




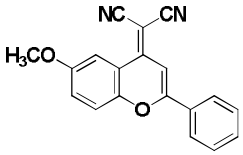
^{1}H NMR and ^{13}C NMR Spectra of Compound 5m

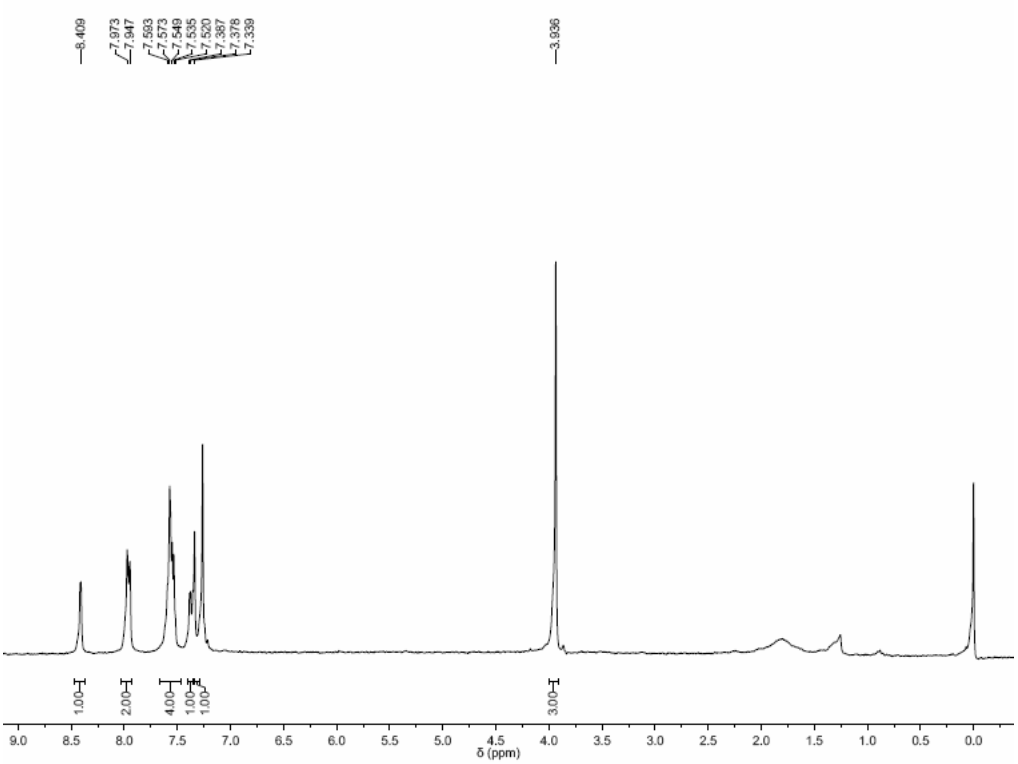


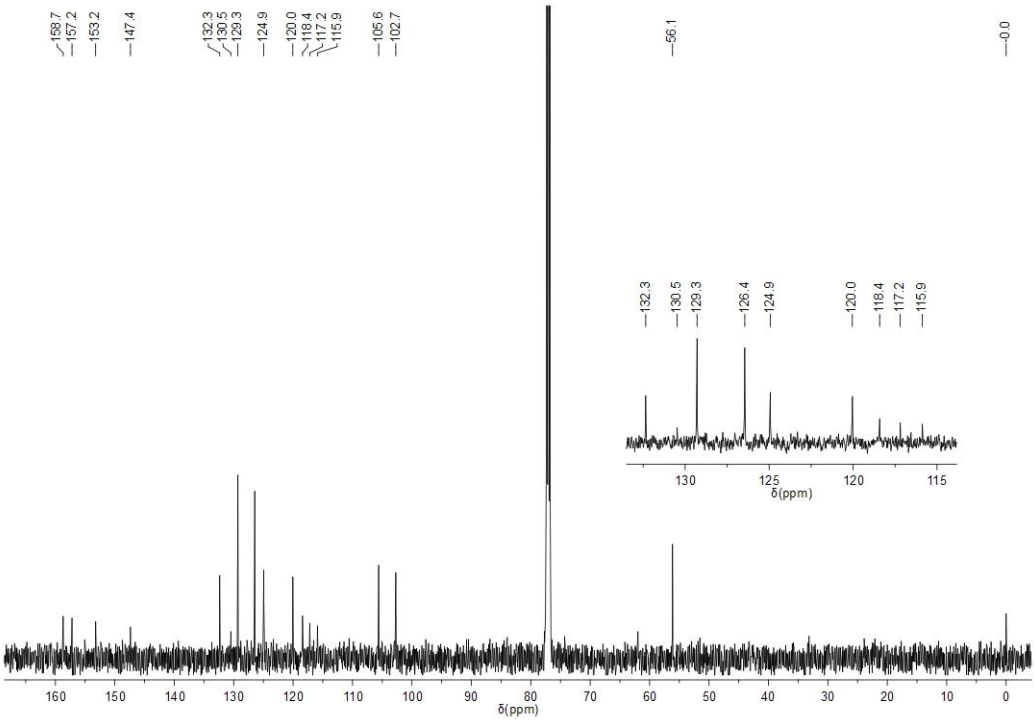




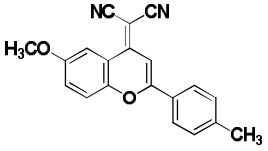
^{1}H NMR and ^{13}C NMR Spectra of Compound 5n

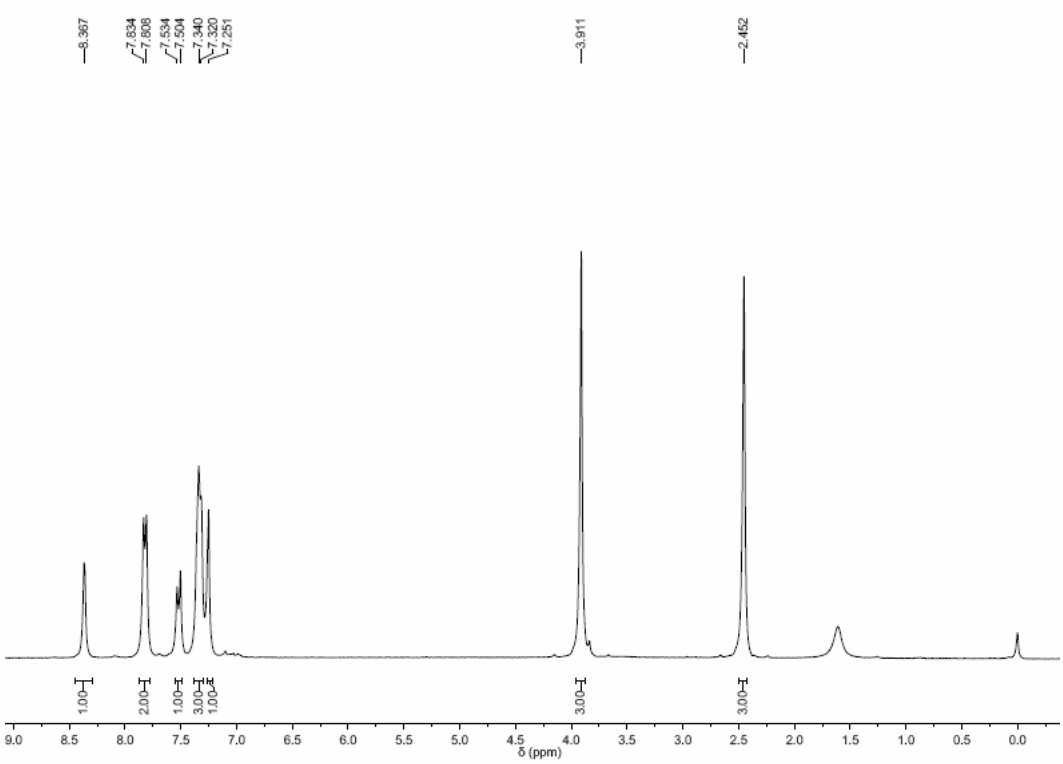


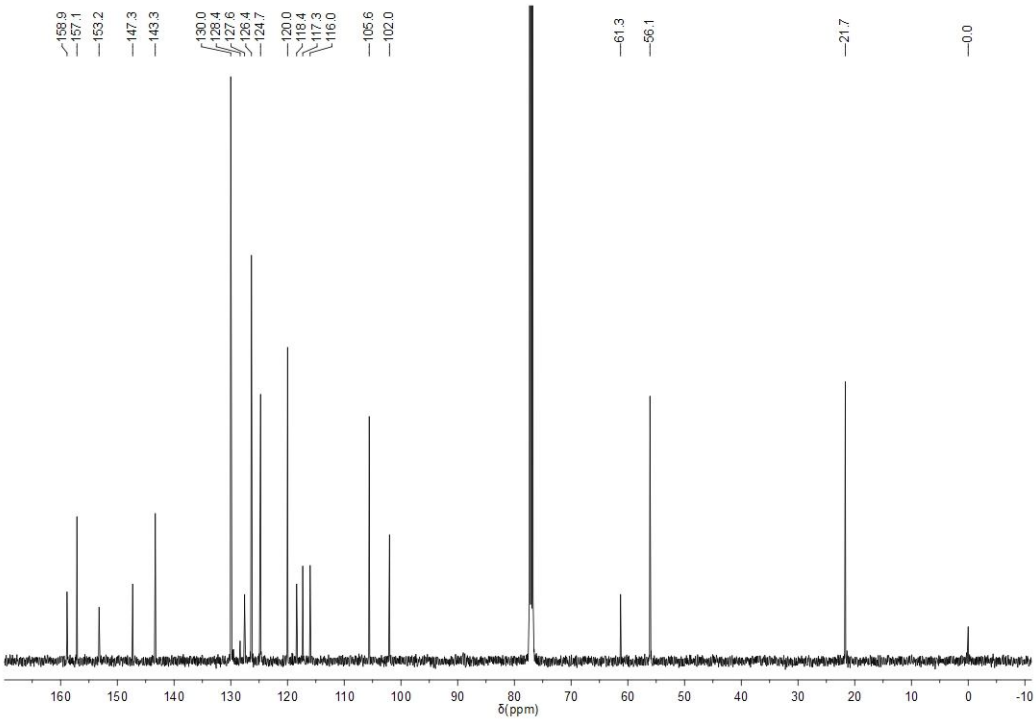




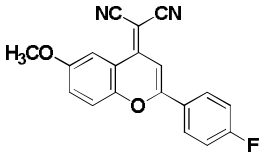
^{1}H NMR and ^{13}C NMR Spectra of Compound 5o

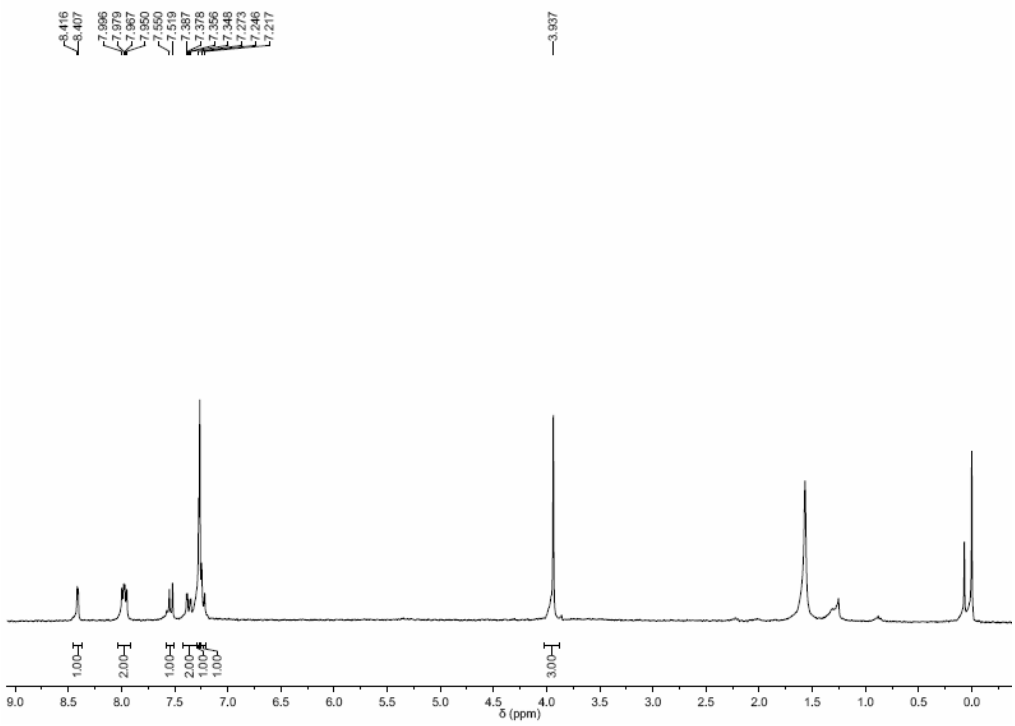


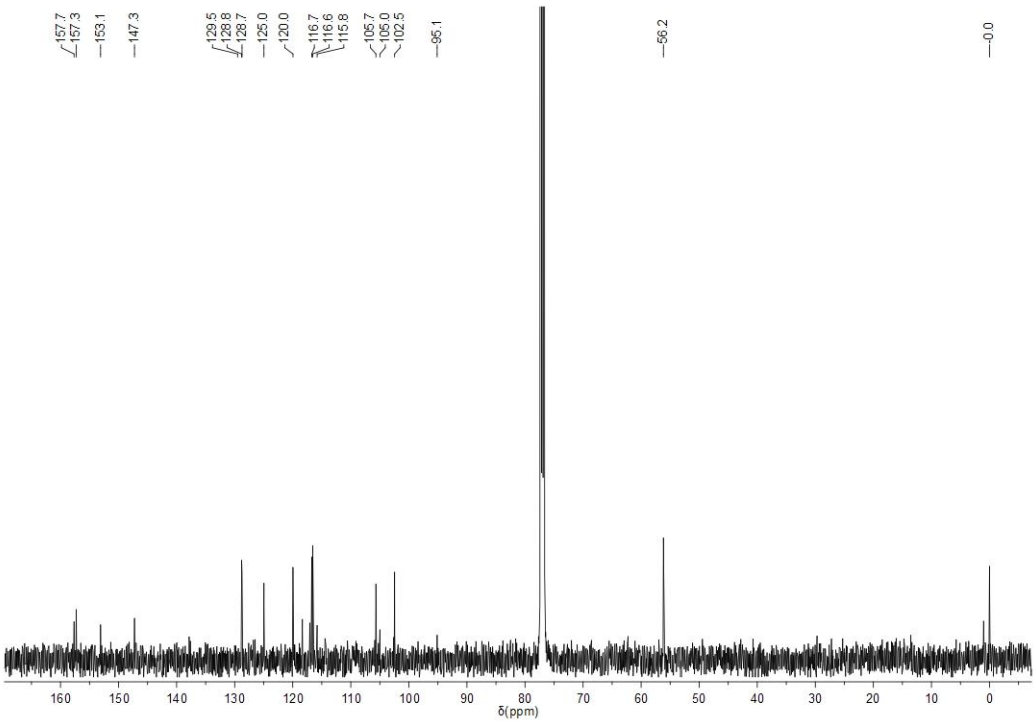




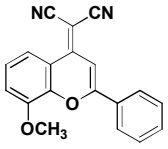
^{1}H NMR and ^{13}C NMR Spectra of Compound 5p

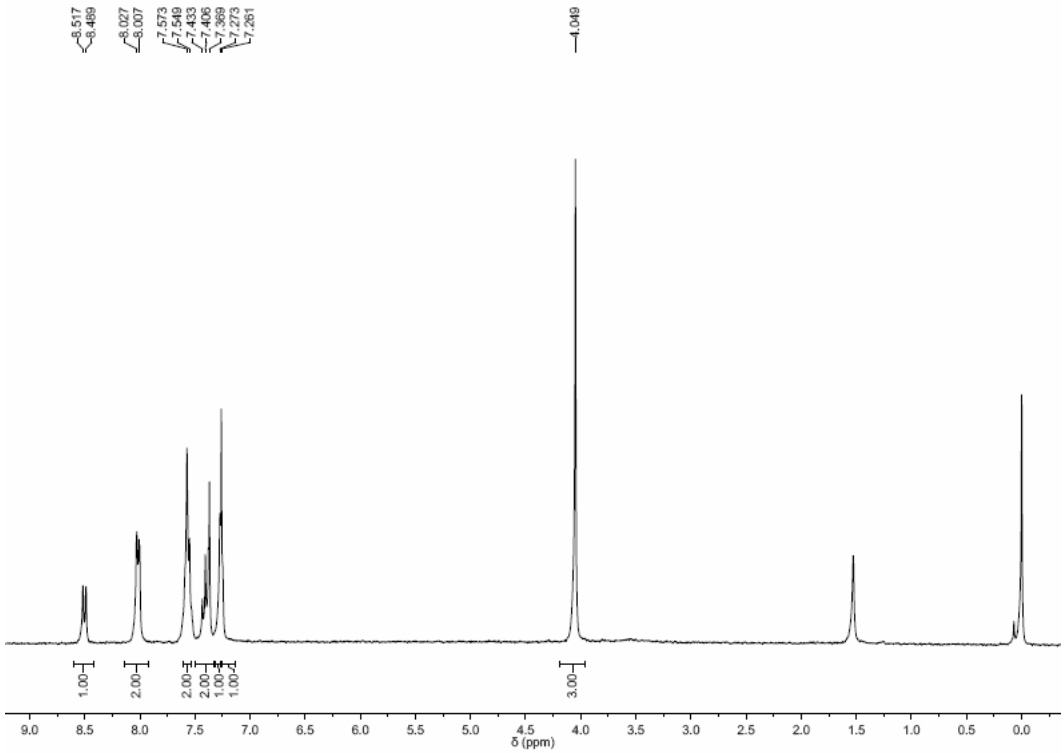


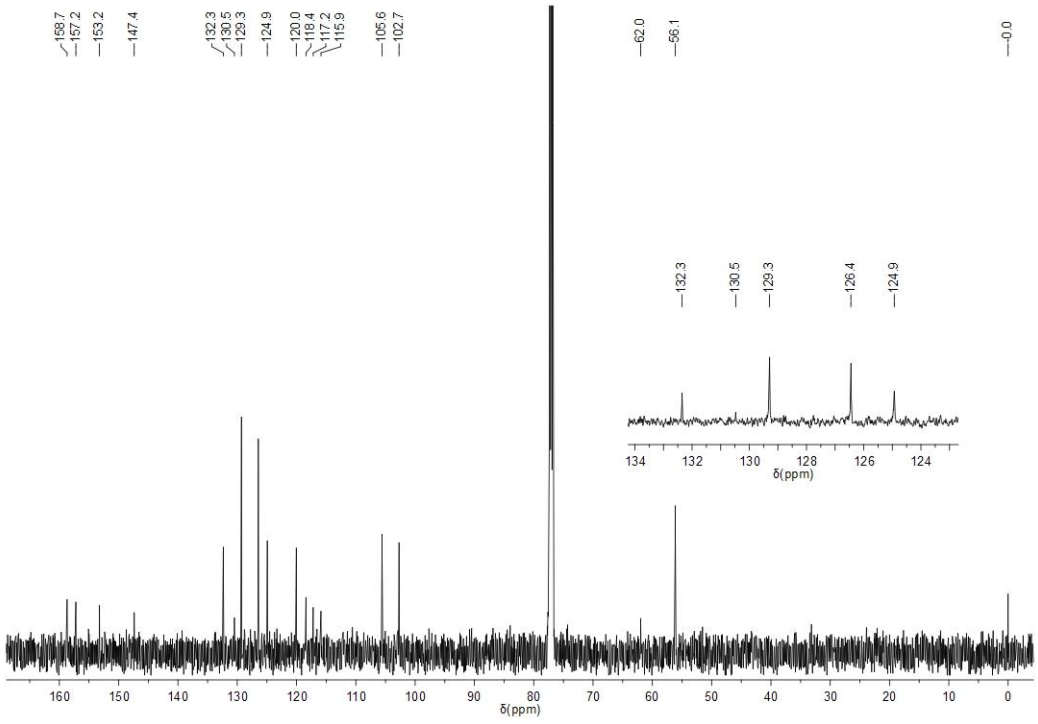




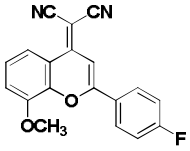
^{1}H NMR and ^{13}C NMR Spectra of Compound 5q

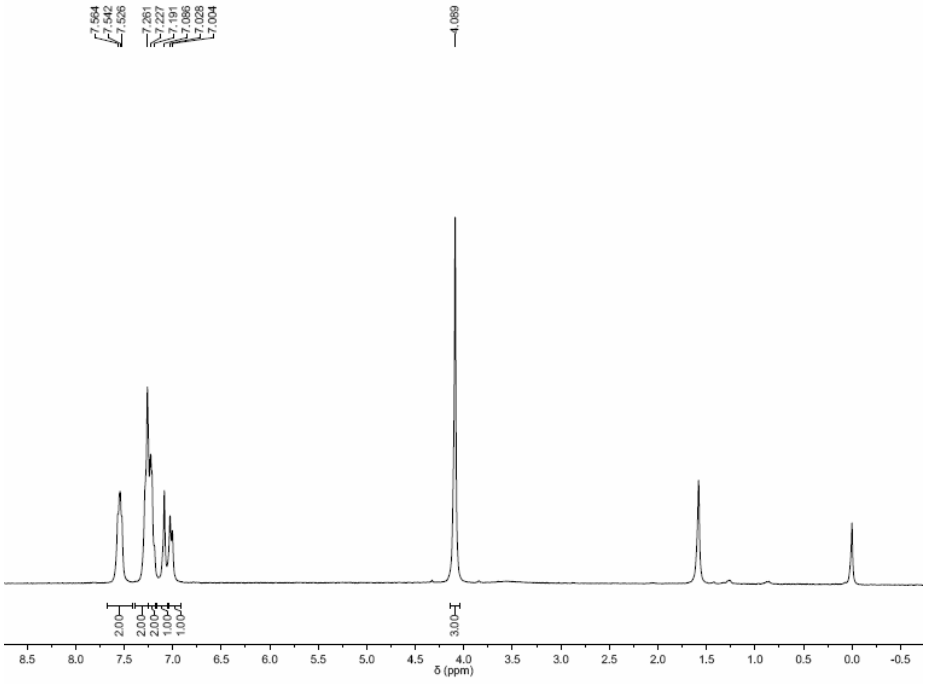


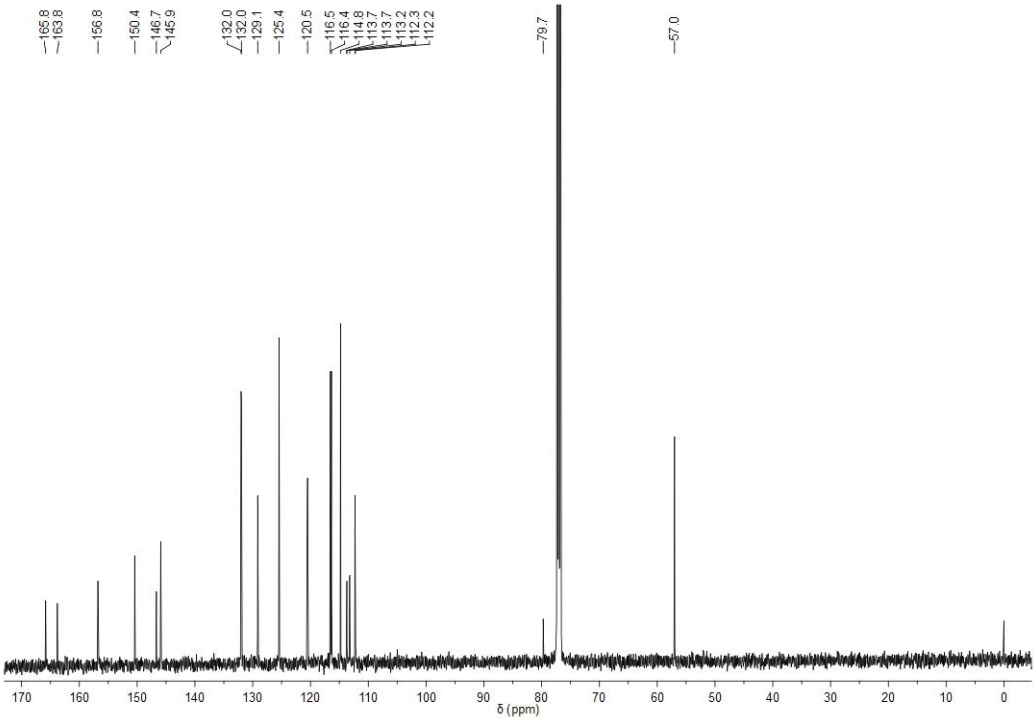




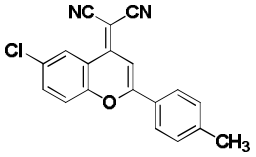
^{1}H NMR and ^{13}C NMR Spectra of Compound 5r

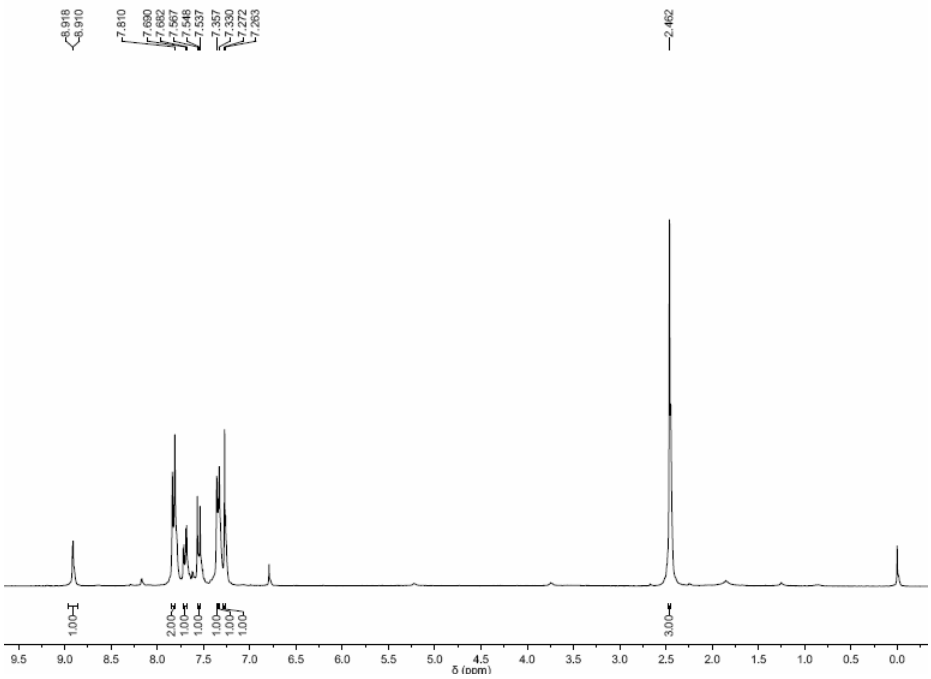


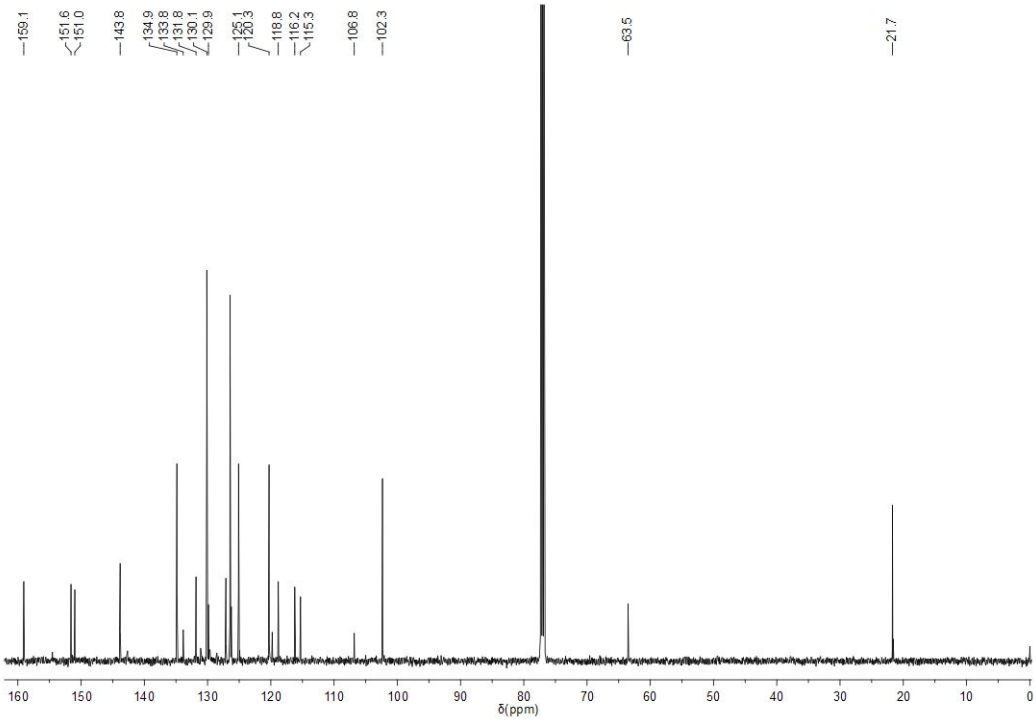




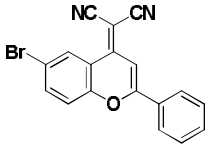
^{1}H NMR and ^{13}C NMR Spectra of Compound 5s

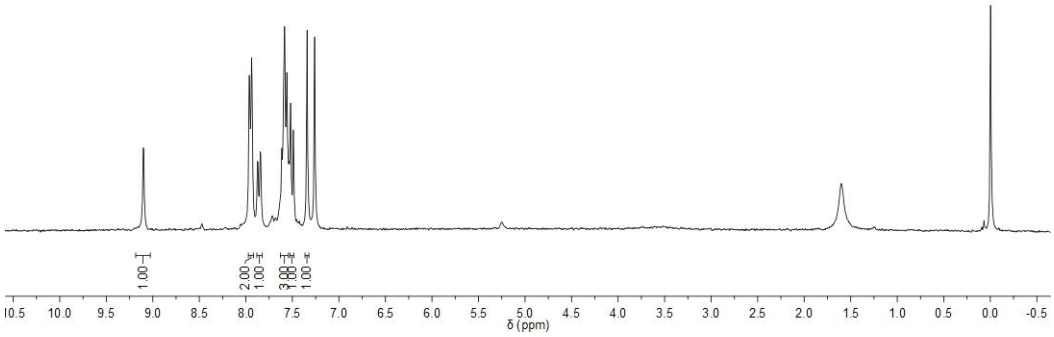


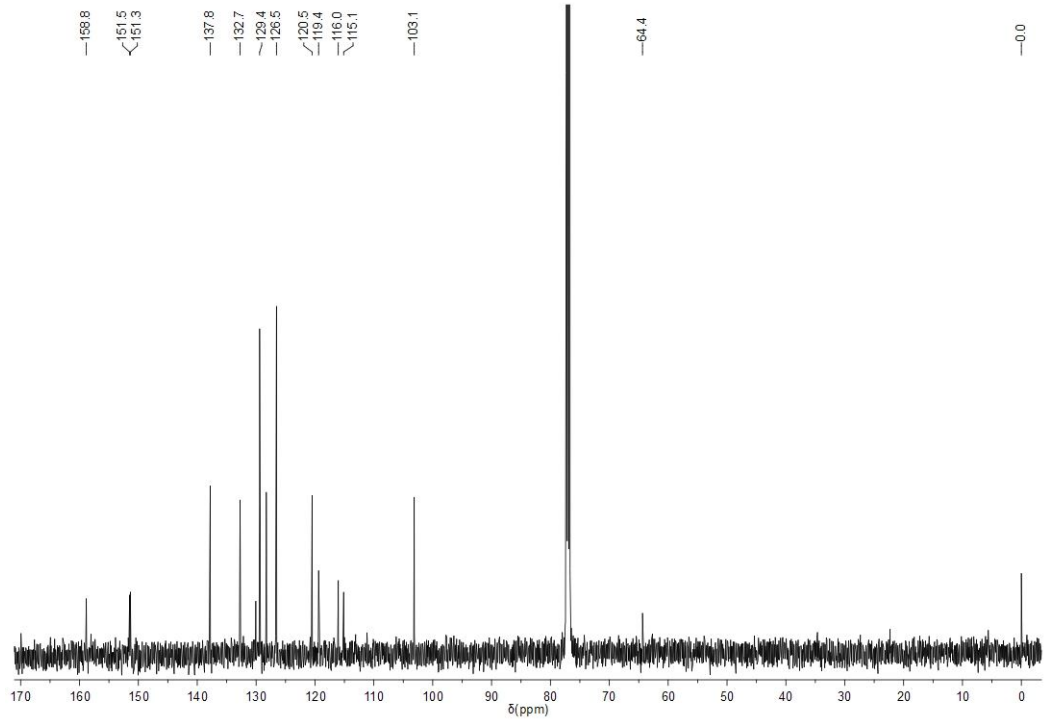




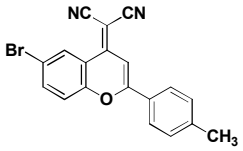
^{1}H NMR and ^{13}C NMR Spectra of Compound 5t

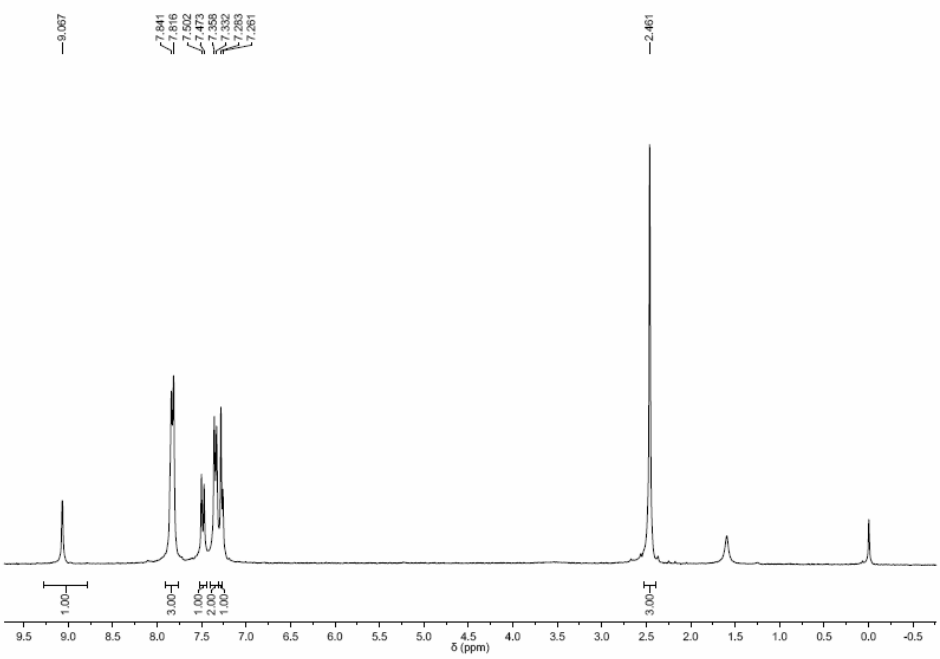


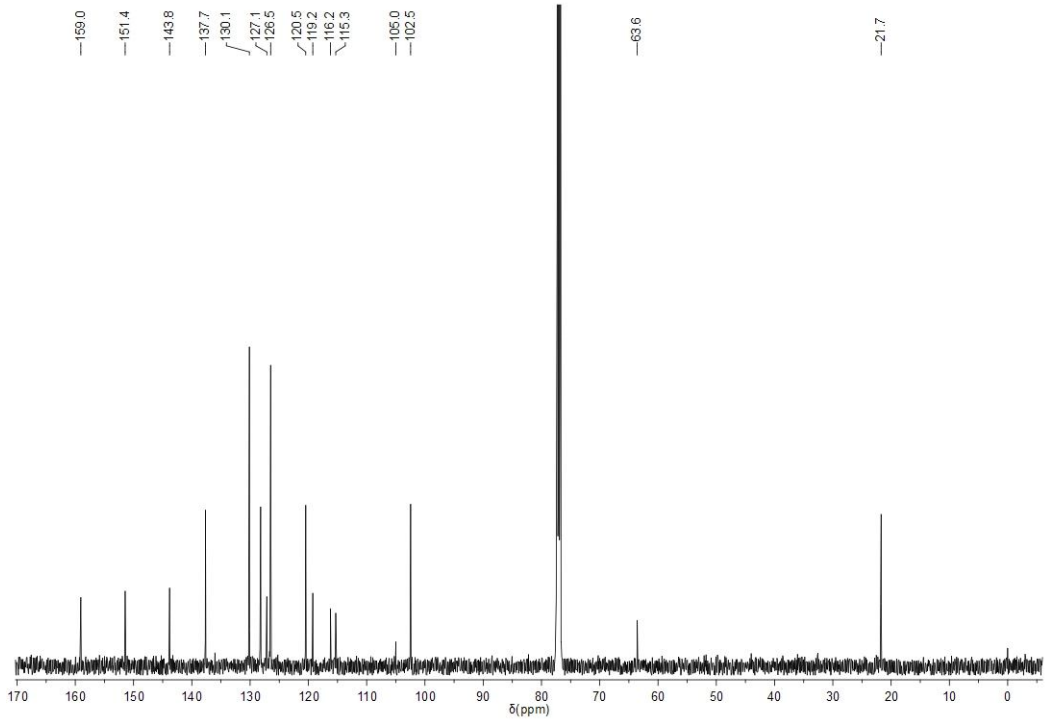




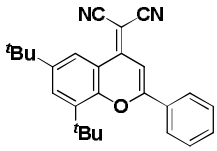
^{1}H NMR and ^{13}C NMR Spectra of Compound 5u

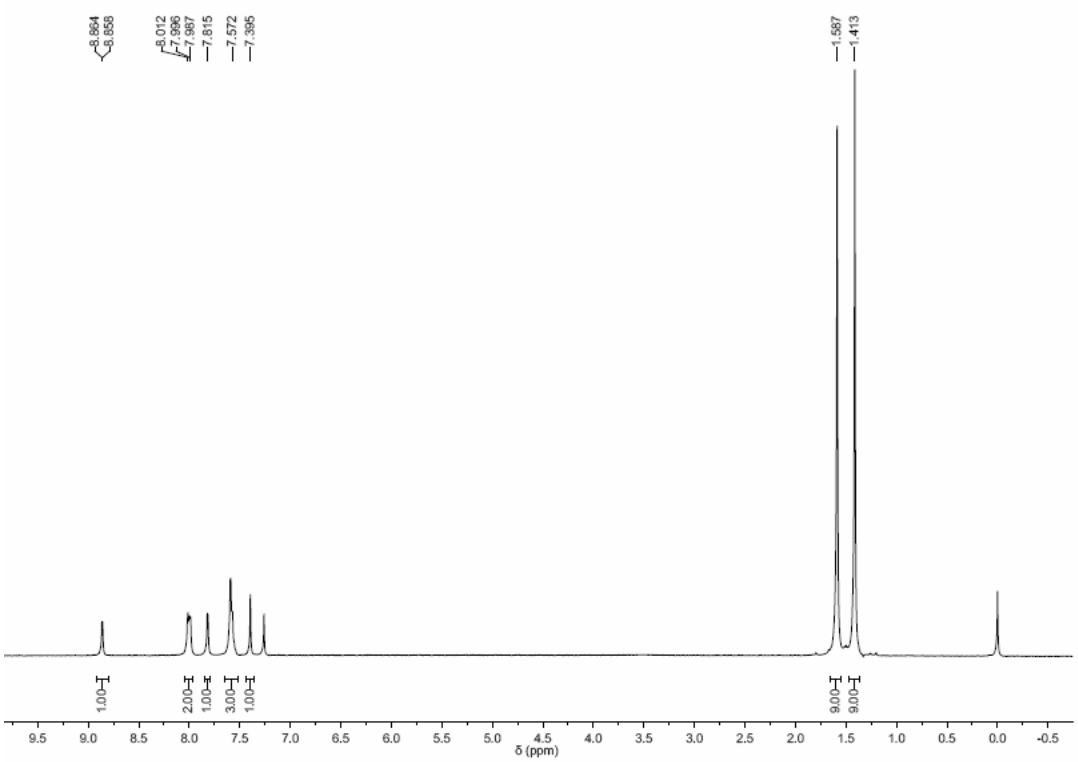


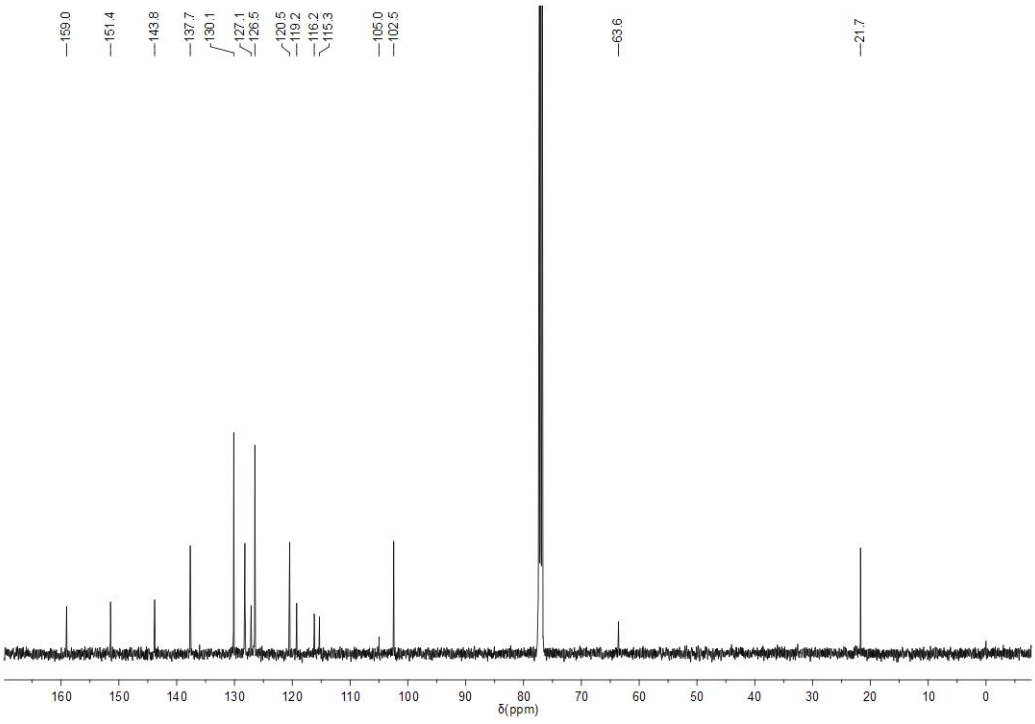




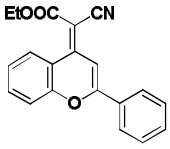
^{1}H NMR and ^{13}C NMR Spectra of Compound 5v

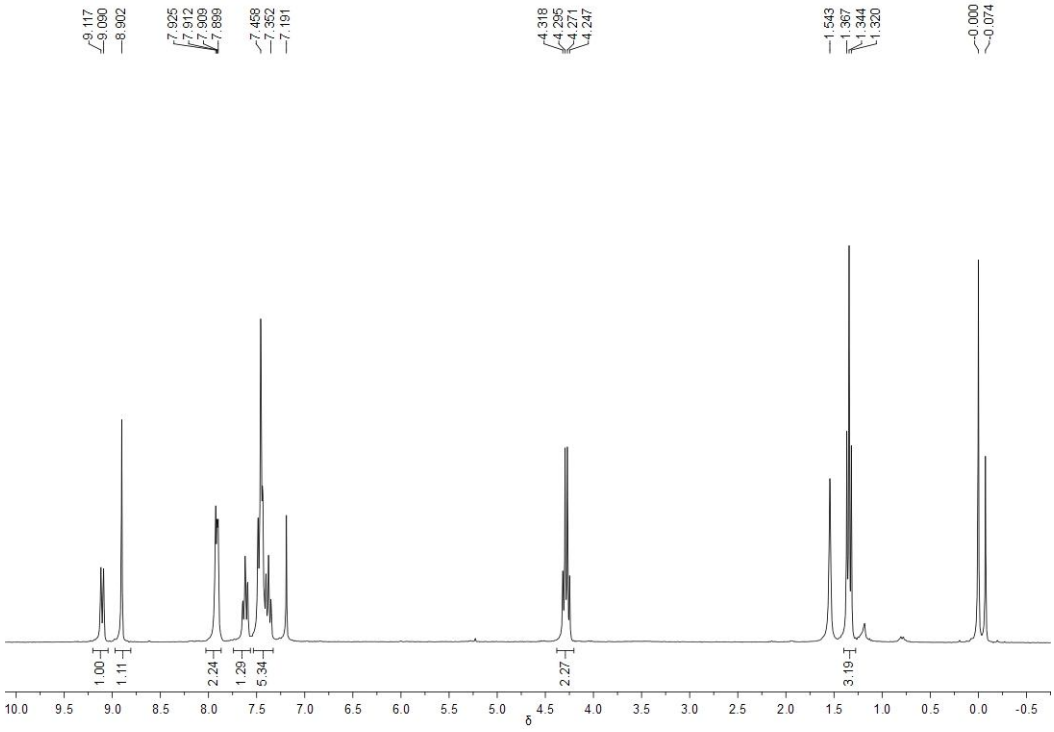


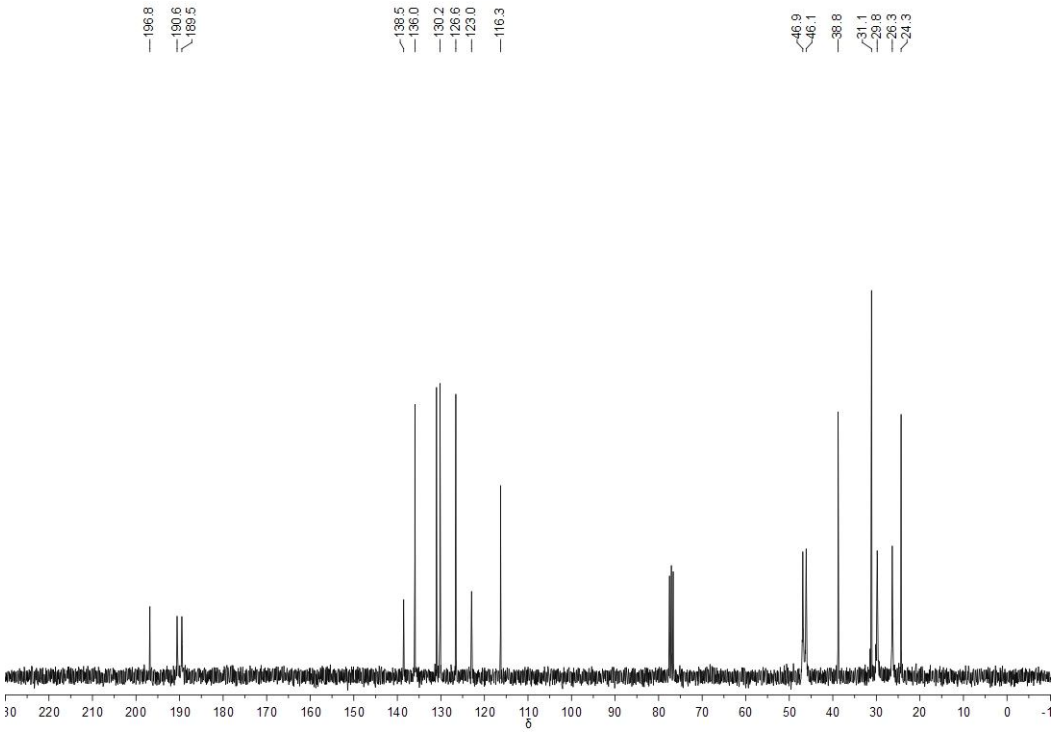




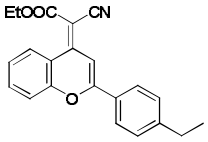
^{1}H NMR and ^{13}C NMR Spectra of Compound 5w

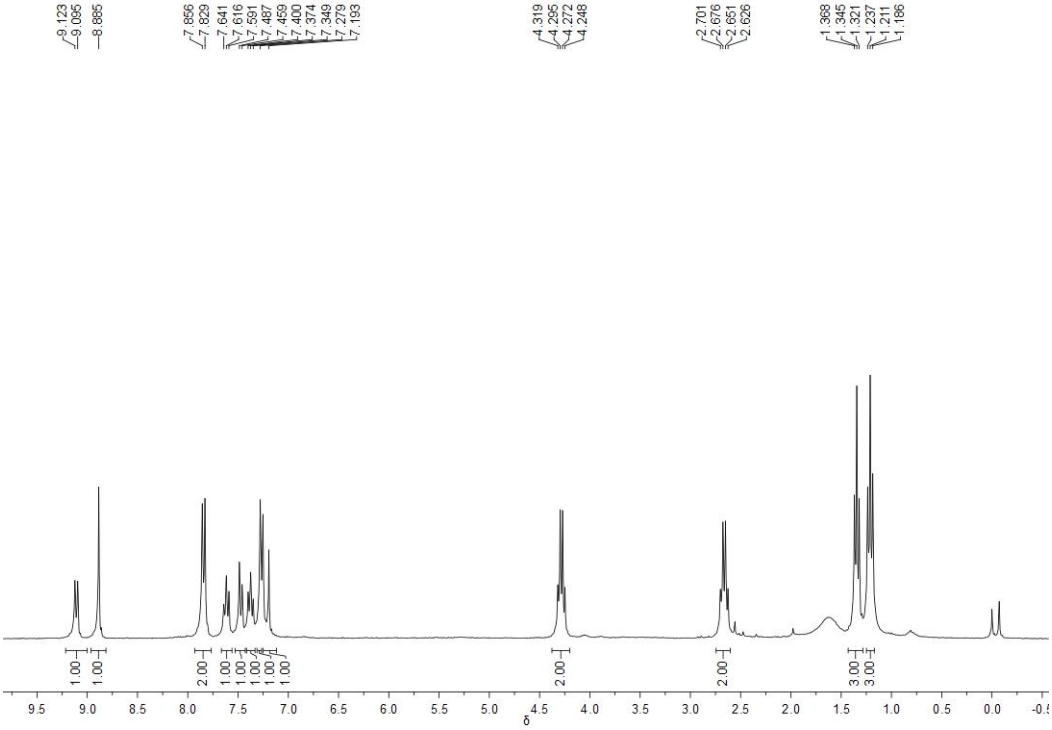


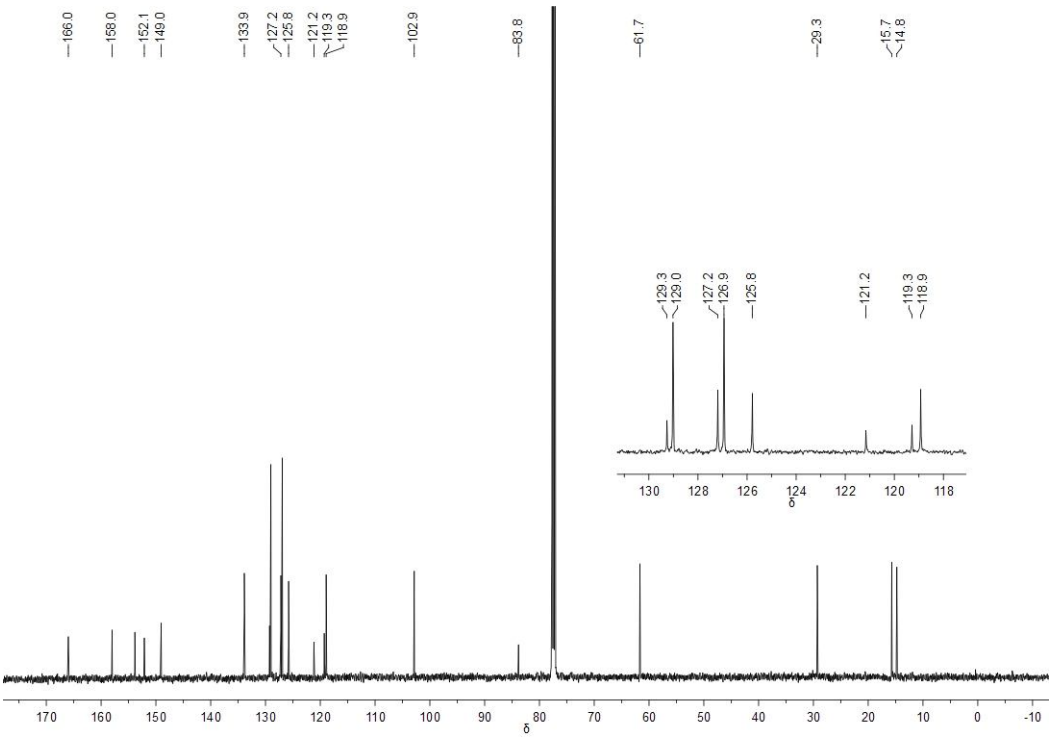




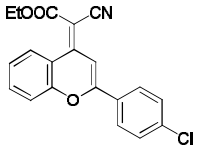
^{1}H NMR and ^{13}C NMR Spectra of Compound 5x

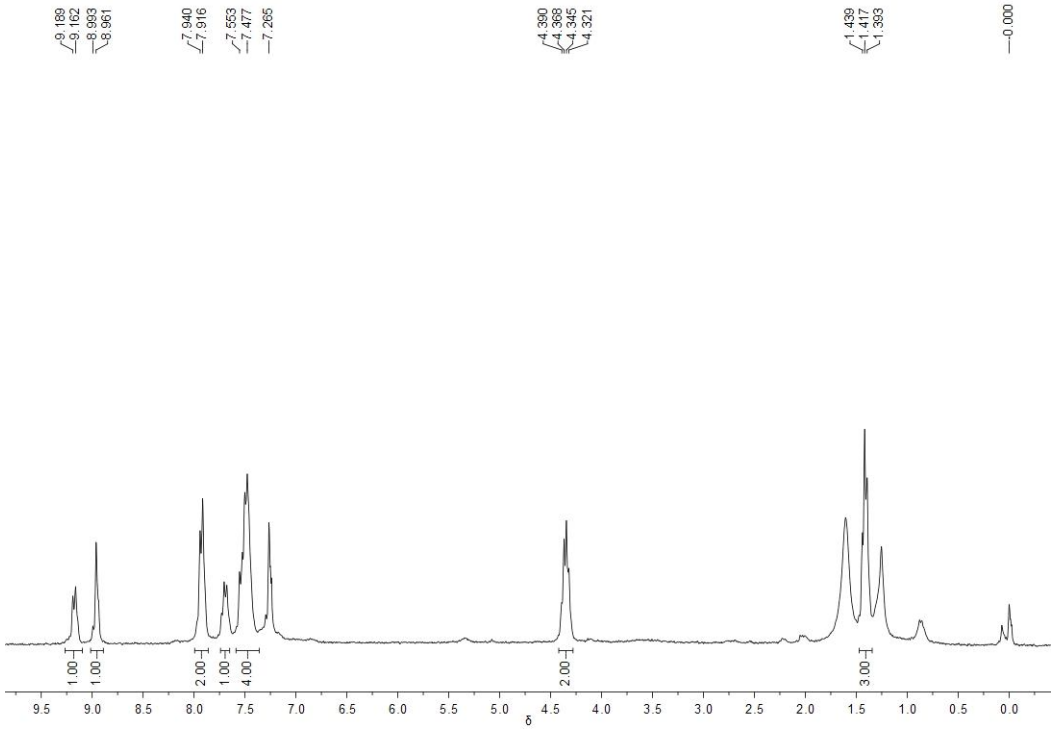


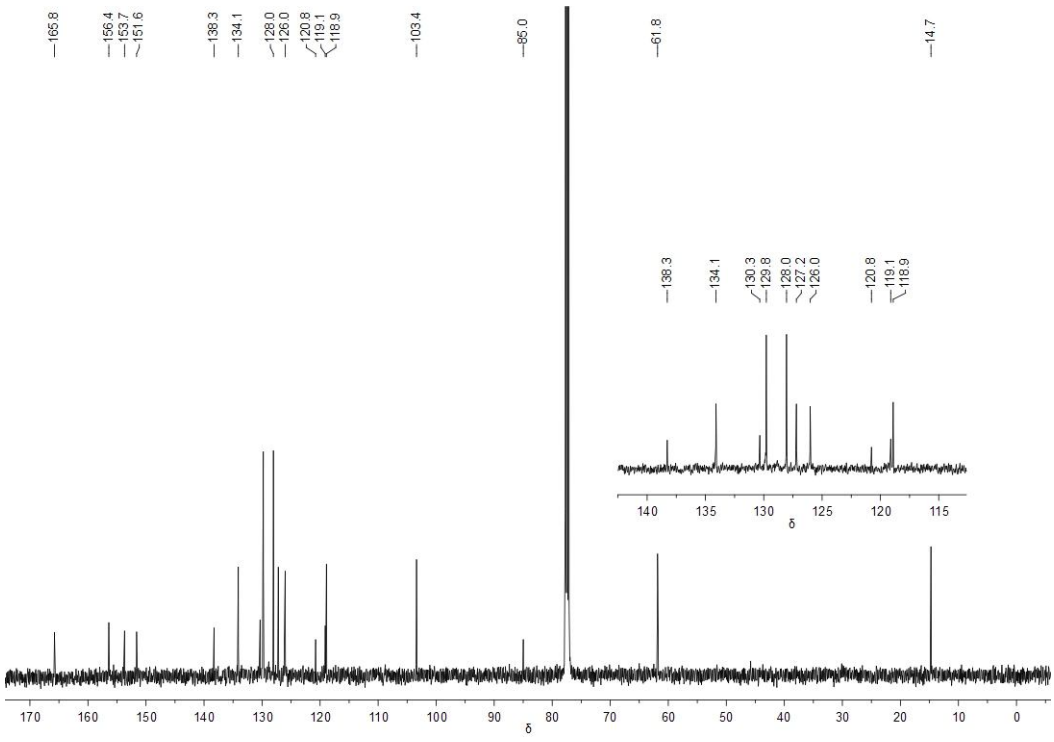




^{1}H NMR and ^{13}C NMR Spectra of Compound 5y







^{1}H NMR and ^{13}C NMR Spectra of Compound 5z