Electronic supplementary information

C(sp^2)−H Functionalization of 2*H*−Indazoles at C3-Position *via* Palladium(II)−Catalyzed Isocyanide Insertions Strategy Leading to Diverse Heterocycles

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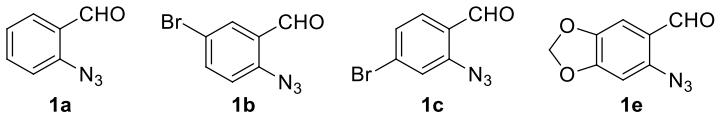
Except **1d** the Following 2-Azidoaldehydes are known in the Literature (Table 1).[24a,b]

Table 1



The Following 2-Azido-4-chlorobenzaldehyde **1d** was Synthesized Using the Below Strategy (Table 2)

Table 2

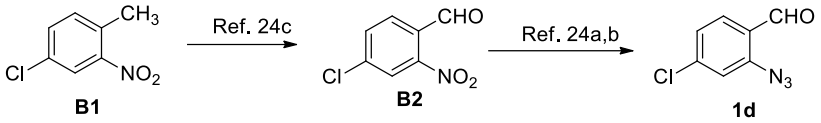


Table 3. 2-(2*H*-Indazol-2-yl)anilines (**3ba-3bg**) Synthesized From Following Method:

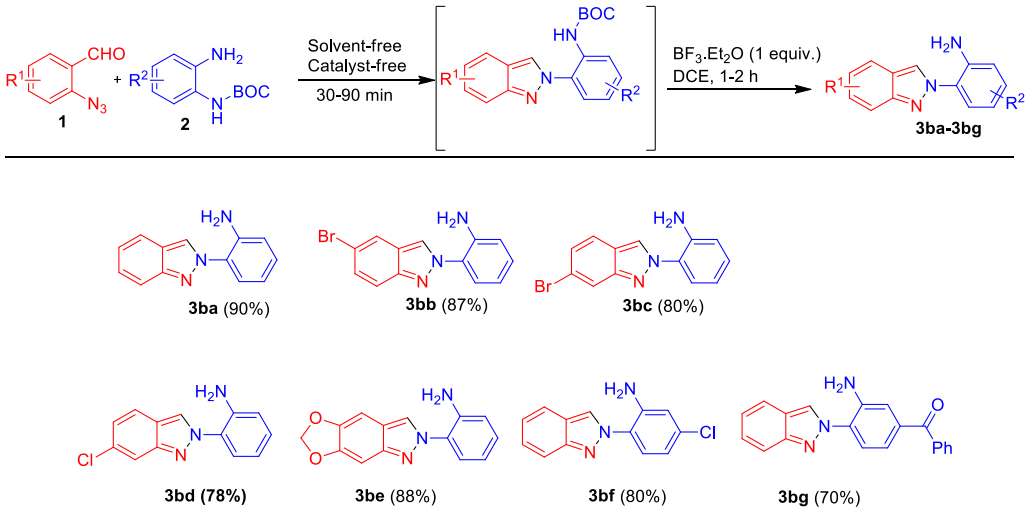
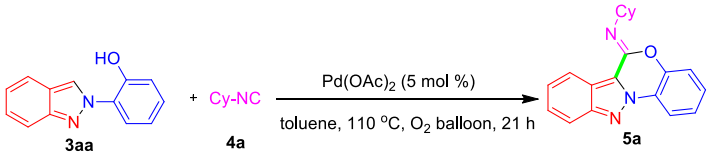
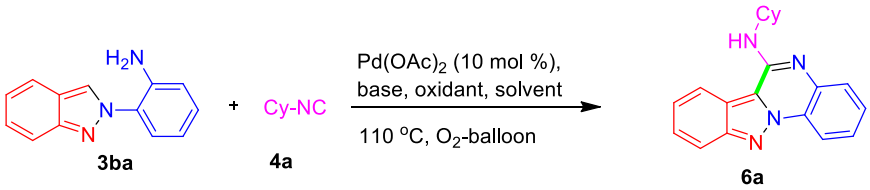


Table 4 Screening of Isocyanide Equivalents for The Synthesis of Benzoxazinoindazole (**5a)**



S.No	Catalyst (5 mol%)	CyNC (equiv.)	Yield (%)
1	$Pd(OAc)_2$	3	89
2	$Pd(OAc)_2$	2.5	92
3	$Pd(OAc)_2$	2	98
4	$Pd(OAc)_2$	1.5	98
5	$Pd(OAc)_2$	1	80

Table 5 Optimization Reaction Conditions for The Synthesis of Benzoxazinoindazole (**6a**)[a,b]

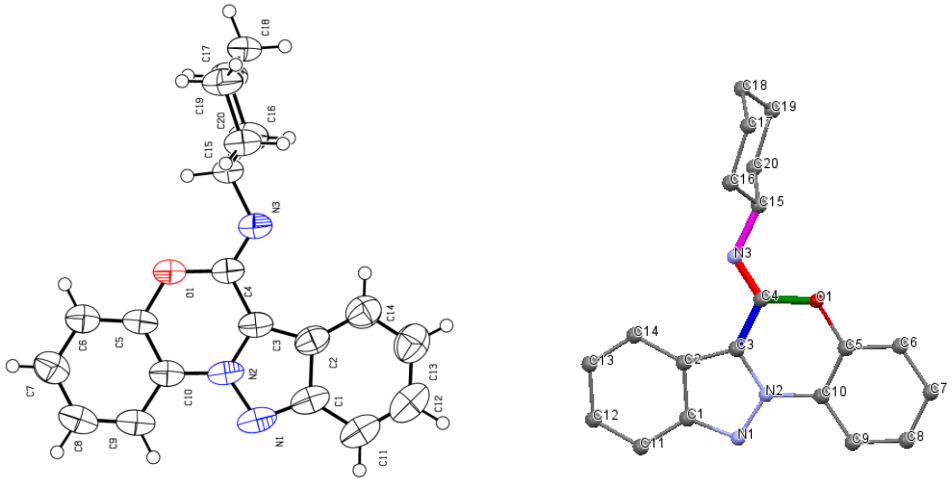


s.no	**catalyst**	**base (equiv.)**	**oxidant (equiv.)**	**solvent (2 mL)**	**time (h)**	**yield (%)**
1[c]	$Pd(OAc)_2$	-	-	toluene	24	45
2	$Pd(OAc)_2$	-	$Cu(OAc)_2$ (1)	toluene	24	38
3	$Pd(OAc)_2$	-	$CuCl_2.2H_2O$ (1)	toluene	24	50
4	$Pd(OAc)_2$	-	$Cu(TFA)_2.XH_2O$ (1)	toluene	24	45
5	$Pd(OAc)_2$	-	$Cu(OAc)_2.2H_2O$ (1)	toluene	24	35
6	$Pd(OAc)_2$	K_2CO_3 (1)	$CuCl_2.2H_2O$ (1)	toluene	24	45
7	$Pd(OAc)_2$	Et_3N (1)	$CuCl_2.2H_2O$ (1)	toluene	24	25
8	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (1)	toluene	24	50
9	$Pd(OAc)_2$	KOAc (1)	$CuCl_2.2H_2O$ (1)	toluene	24	40
10	$Pd(OAc)_2$	NaOAc (1)	$CuCl_2.2H_2O$ (1)	toluene	24	20
11	$Pd(OAc)_2$	NaO^tBu (1)	$CuCl_2.2H_2O$ (1)	toluene	24	20
12	$Pd(OAc)_2$	Ag_2CO_3	$CuCl_2.2H_2O$ (1)	toluene	24	45
13	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (0.2)	toluene	15	40
14	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (0.3)	toluene	15	60
15	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (0.5)	toluene	15	58
16	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (0.8)	toluene	15	48
17	**$Pd(OAc)_2$**	**Cs_2CO_3 (0.5)**	**$CuCl_2.2H_2O$ (0.3)**	**toluene**	**15**	**72**
18	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	$CuCl_2.2H_2O$ (0.3)	THF	15	45
19	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	$CuCl_2.2H_2O$ (0.3)	ACN	15	20

20	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	$CuCl_2.2H_2O$ (0.3)	DMSO	15	20
21	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	$CuCl_2.2H_2O$ (0.3)	1,4-Dioxane	15	50
22	$Pd(OAc)_2$	Cs_2CO_3 (1)	$CuCl_2.2H_2O$ (0.3)	toluene	15	62
23[c]	$Pd(OAc)_2$	Cs_2CO_3 (0.5)	$CuCl_2.2H_2O$ (0.3)	toluene	15	65

[a]All reactions were carried out on 1 mmol scale of **3ba** and 1.5 mmol of **4a**. [b]Isolated yields of chromatographically pure products. [c]4Å MS (100 mg) were used.

Figure 1. X-Ray Crystal Structure Data for (*Z*)-*N*-(6*H*-Benzo[5,6][1,4]oxazino[4,3-*b*]indazol-6-ylidene)cyclohexanamine (5a) CCDC 1442923

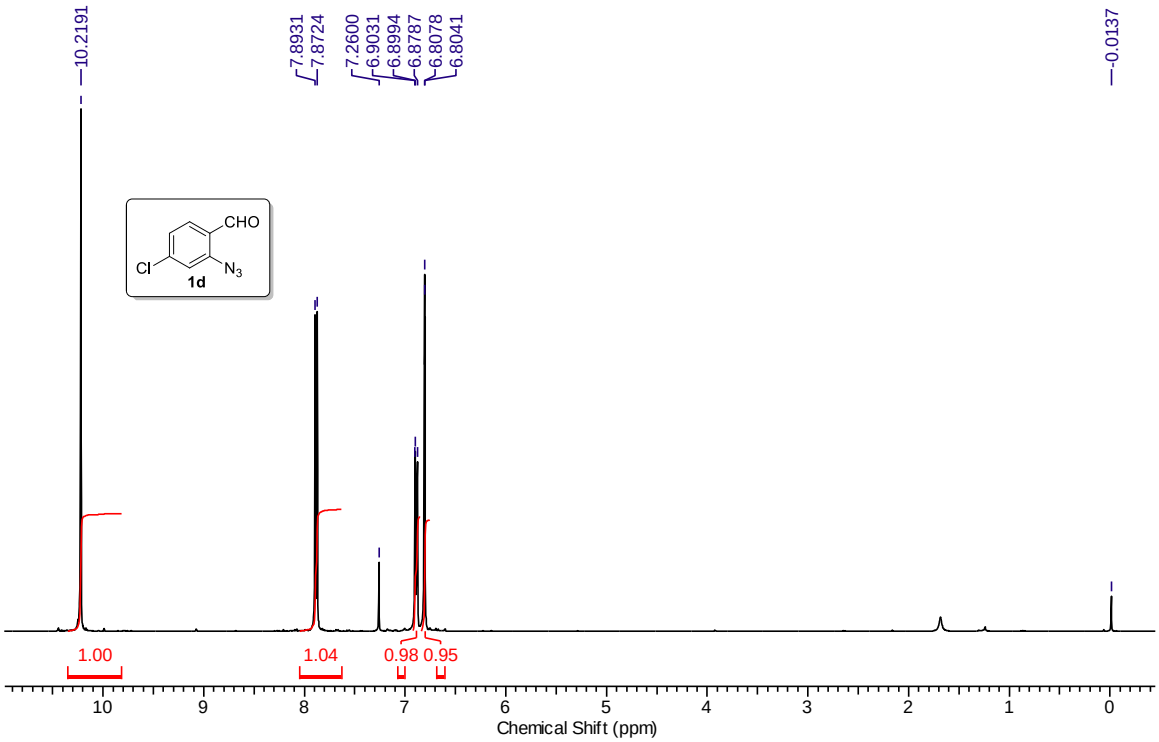


X-ray crystal structure of product **5a**. Thermal ellipsoids are drawn at 25% probability level.

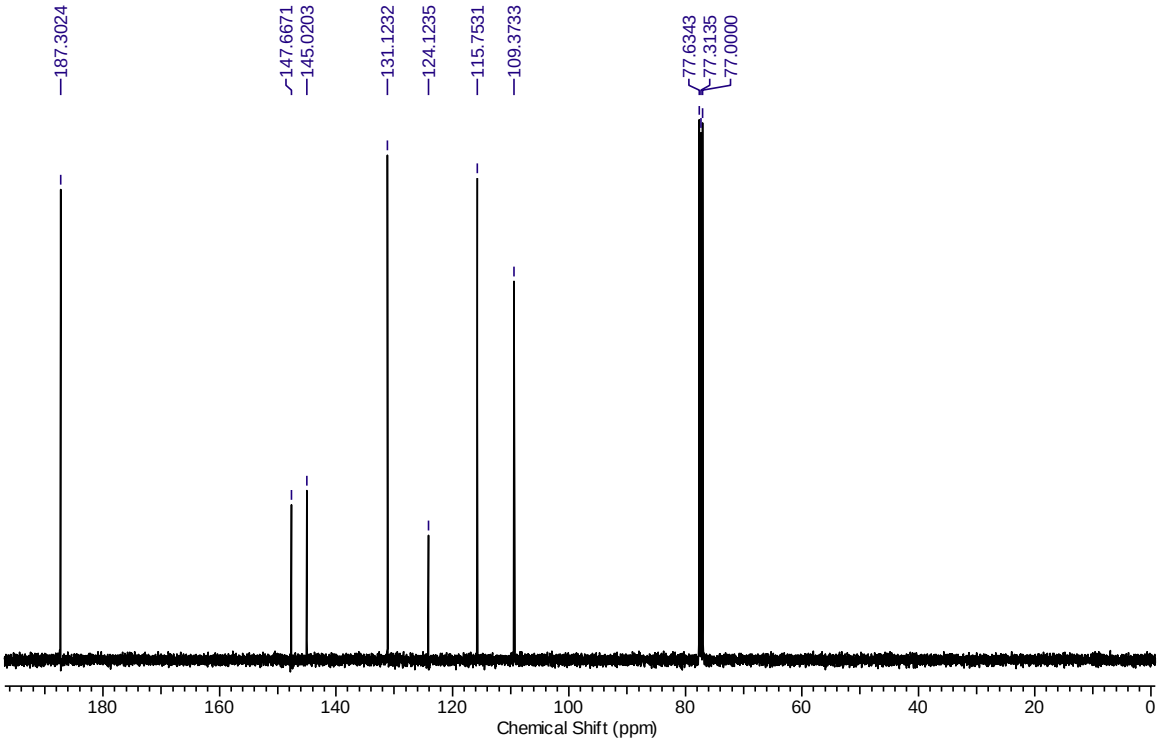
Identification code	exp_5371
Empirical formula	$C_{20}H_{19}N_3O$
Formula weight	317.39
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.3402(17)
b/Å	5.2971(6)
c/Å	17.7876(19)

α/°	90
β/°	108.308(12)
γ/°	90
Volume/Å^3	1640.6(3)
Z	4
ρ_{calc}g/cm^3	1.2849
μ/mm^{-1}	0.642
F(000)	674.0
Crystal size/mm^3	0.24 × 0.2 × 0.14
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.1 to 143.18
Index ranges	$-18 \leq h \leq 22$, $-6 \leq k \leq 5$, $-21 \leq l \leq 15$
Reflections collected	5076
Independent reflections	3129 [R_{int} = 0.0185, R_{sigma} = 0.0307]
Data/restraints/parameters	3129/0/216
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0528, wR_2 = 0.1402
Final R indexes [all data]	R_1 = 0.0781, wR_2 = 0.1597
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27

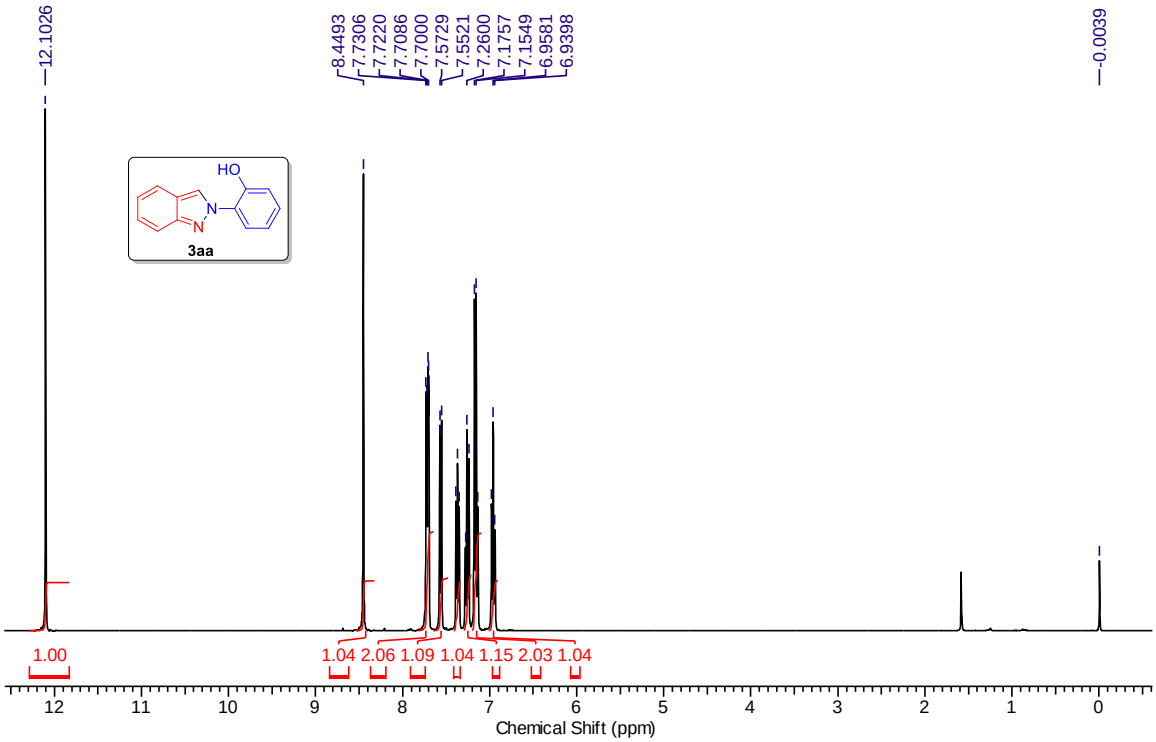
Copies of ^{1}H, ^{13}C NMR Spectra of all Compounds



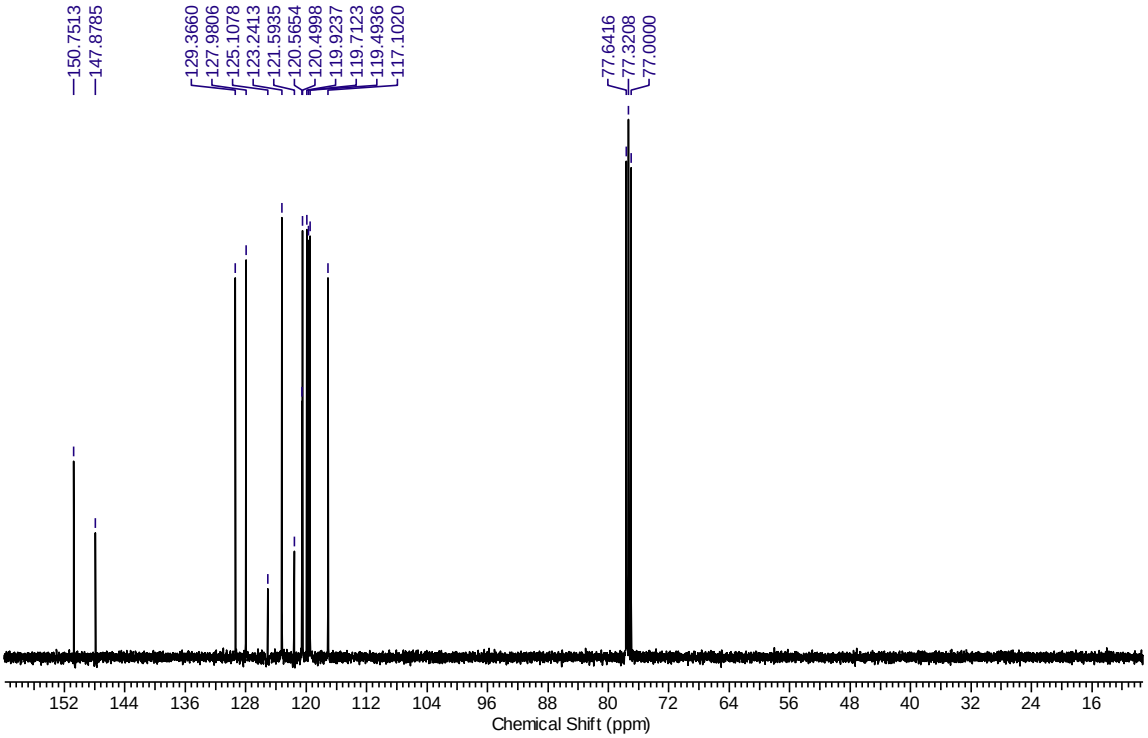
^{1}H NMR (400 MHz) spectrum of compound **1d** in $CDCl_3$



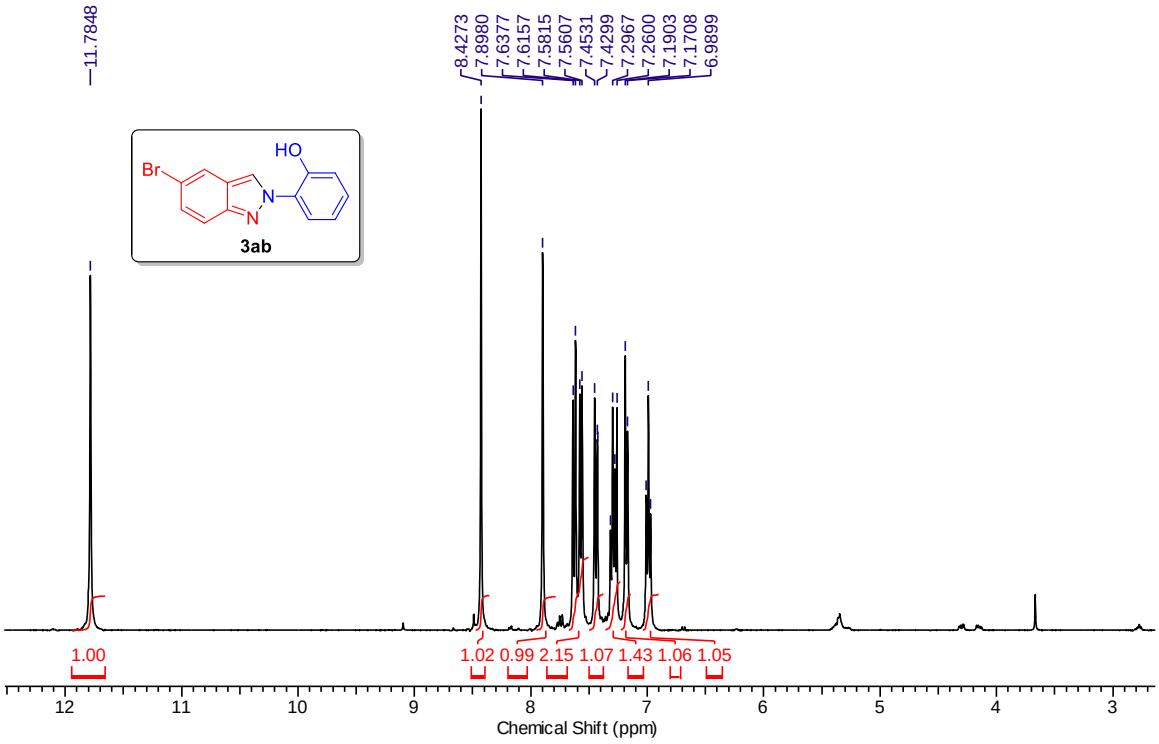
^{13}C NMR (100 MHz) spectrum of compound **1d** in $CDCl_3$



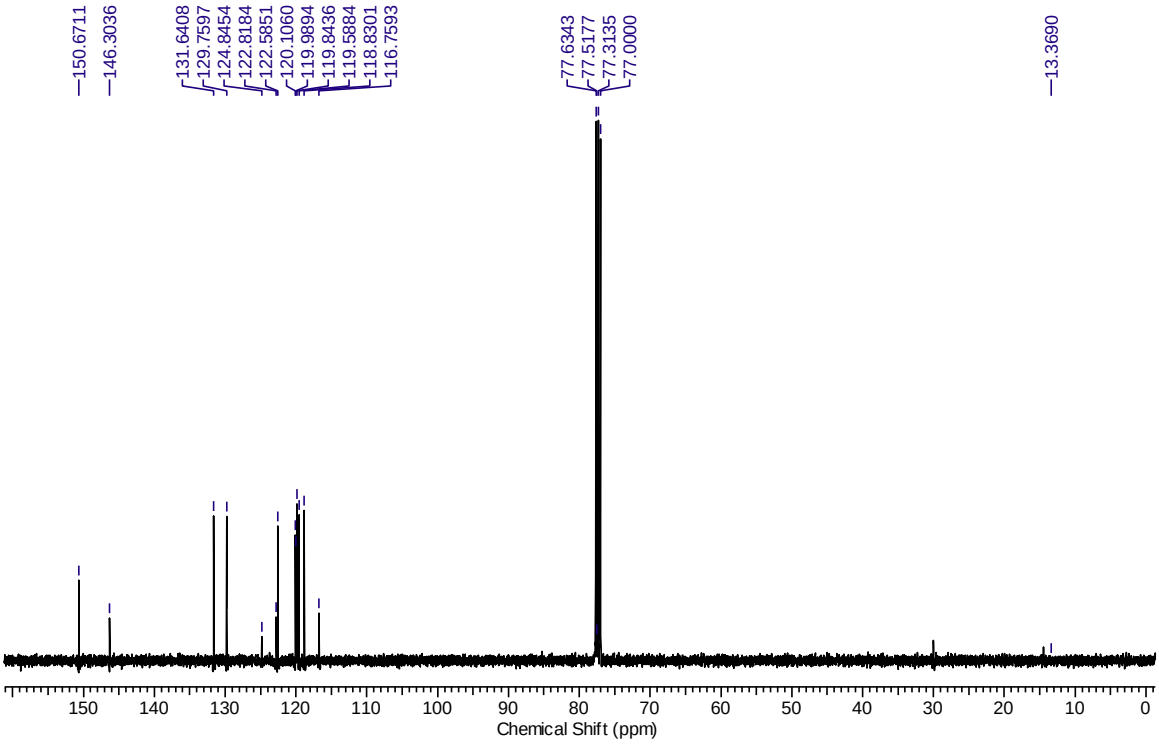
^{1}H NMR (400 MHz) spectrum of compound **3aa** in $CDCl_3$



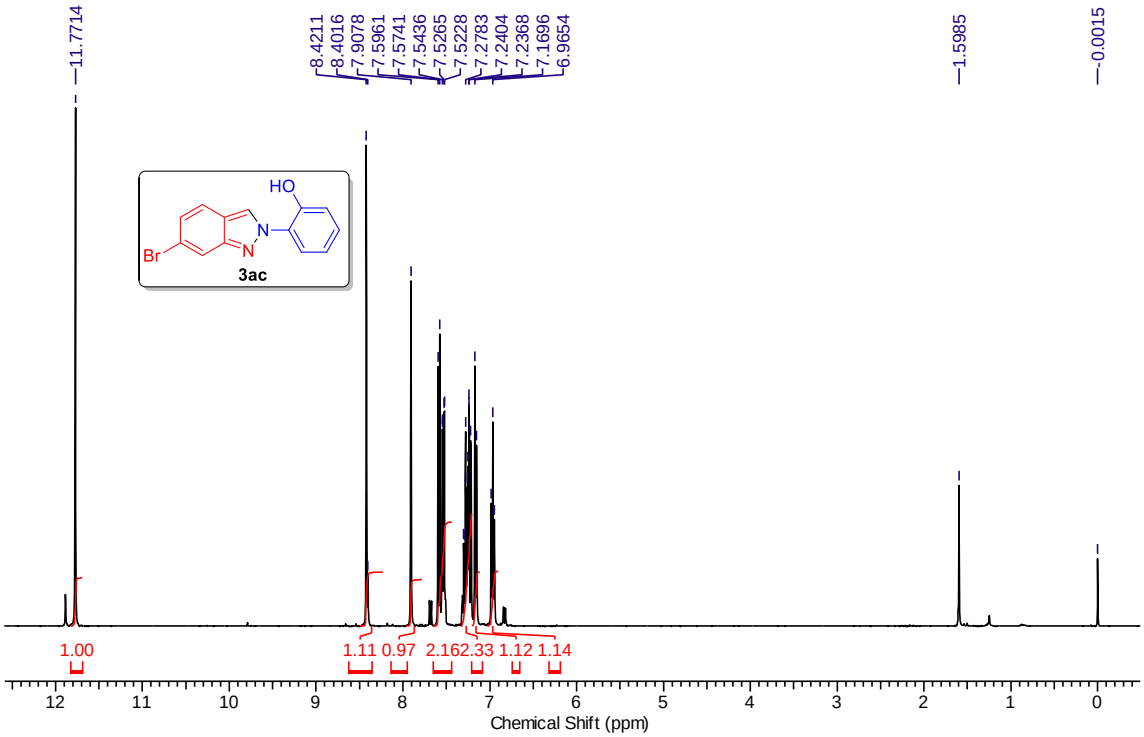
^{13}C NMR (100 MHz) spectrum of compound **3aa** in $CDCl_3$



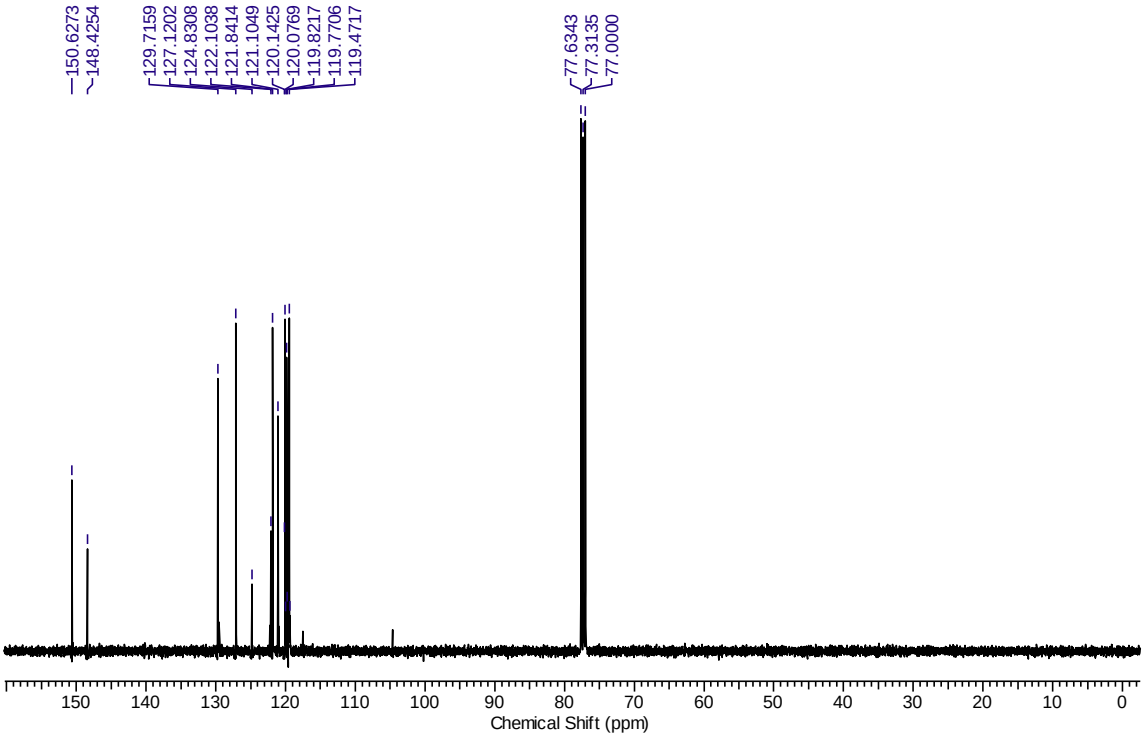
^{1}H NMR (400 MHz) spectrum of compound **3ab** in $CDCl_3$



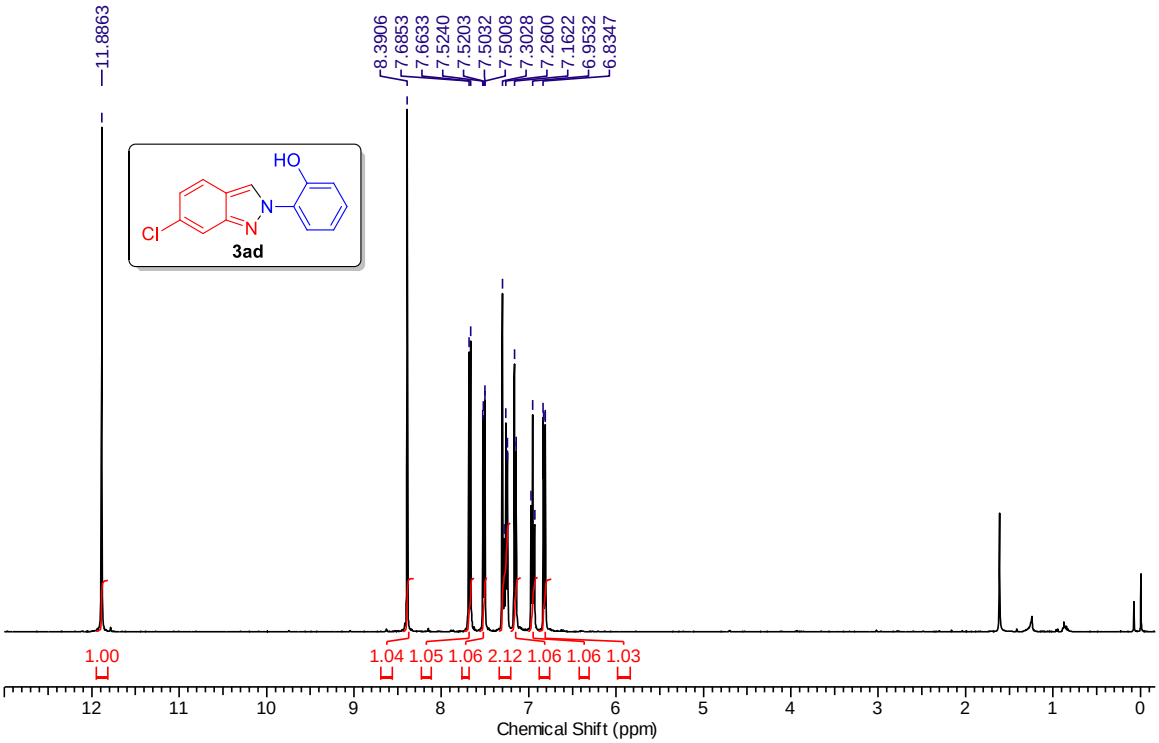
^{13}C NMR (100 MHz) spectrum of compound **3ab** in $CDCl_3$



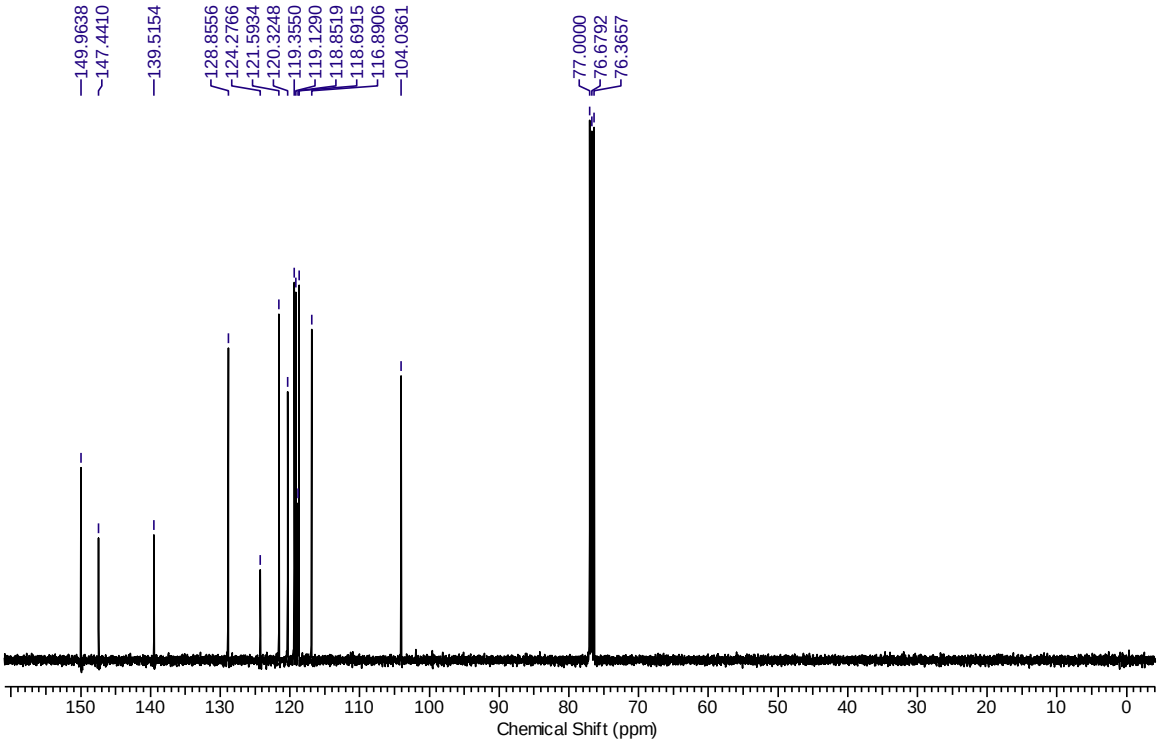
^{1}H NMR (400 MHz) spectrum of compound **3ac** in $CDCl_3$



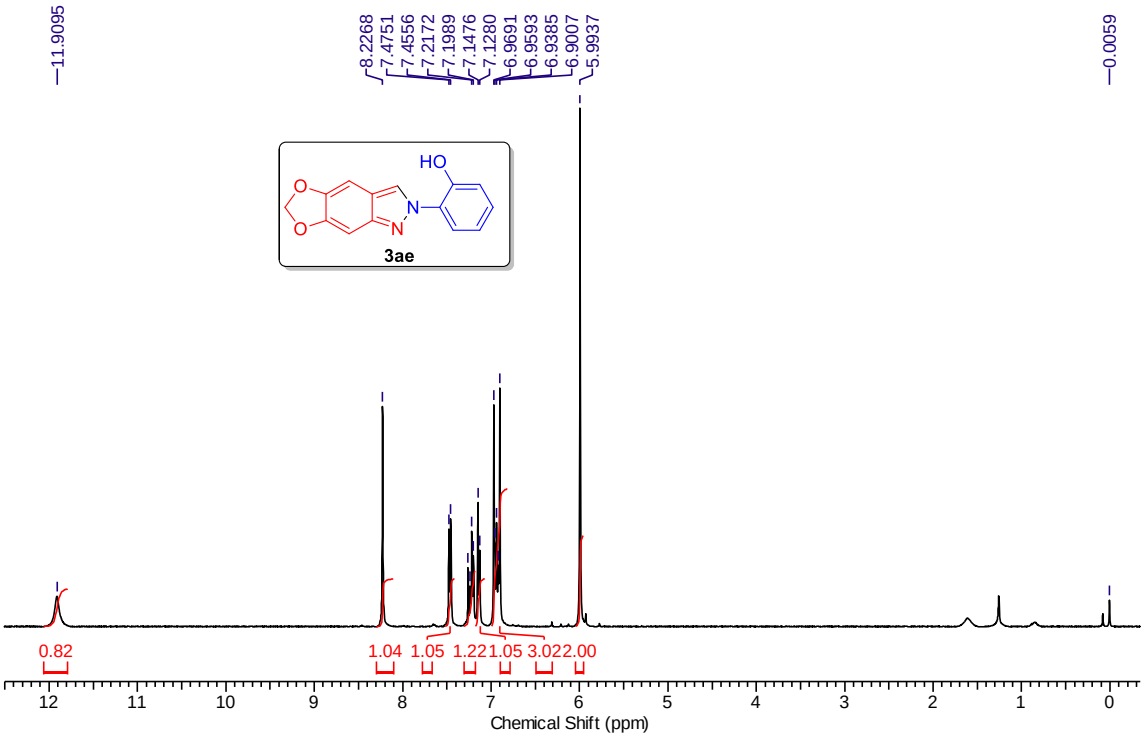
^{13}C NMR (100 MHz) spectrum of compound **3ac** in $CDCl_3$



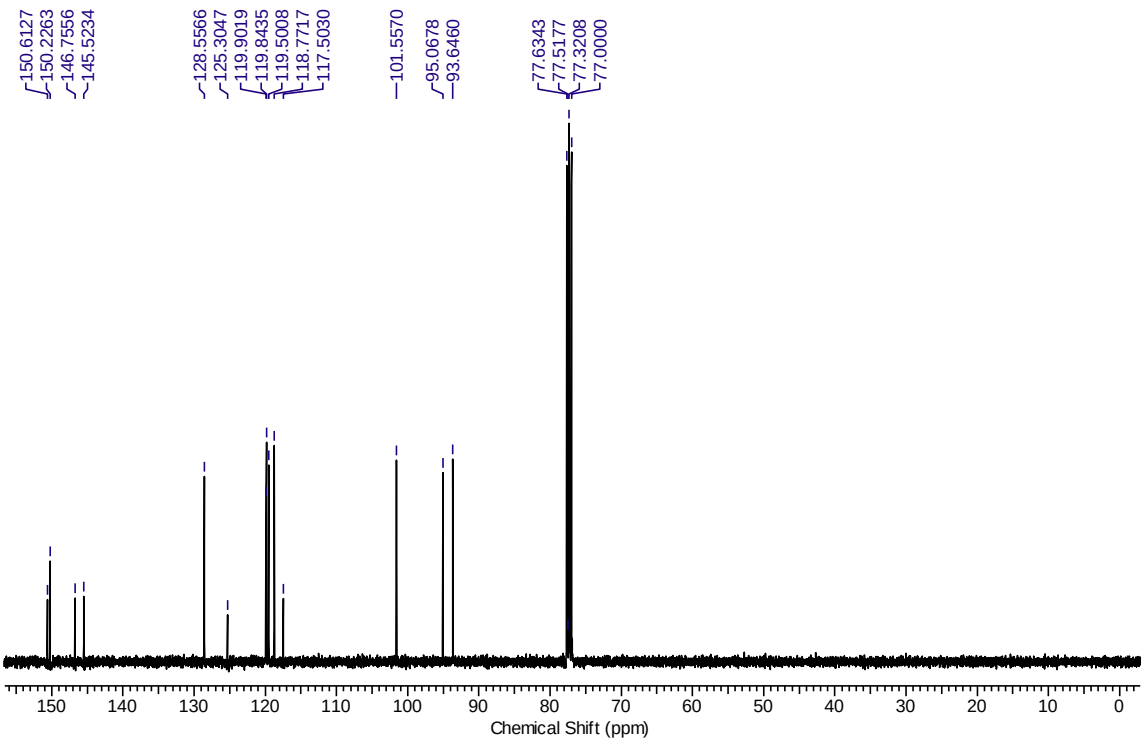
^{1}H NMR (400 MHz) spectrum of compound **3ad** in $CDCl_3$



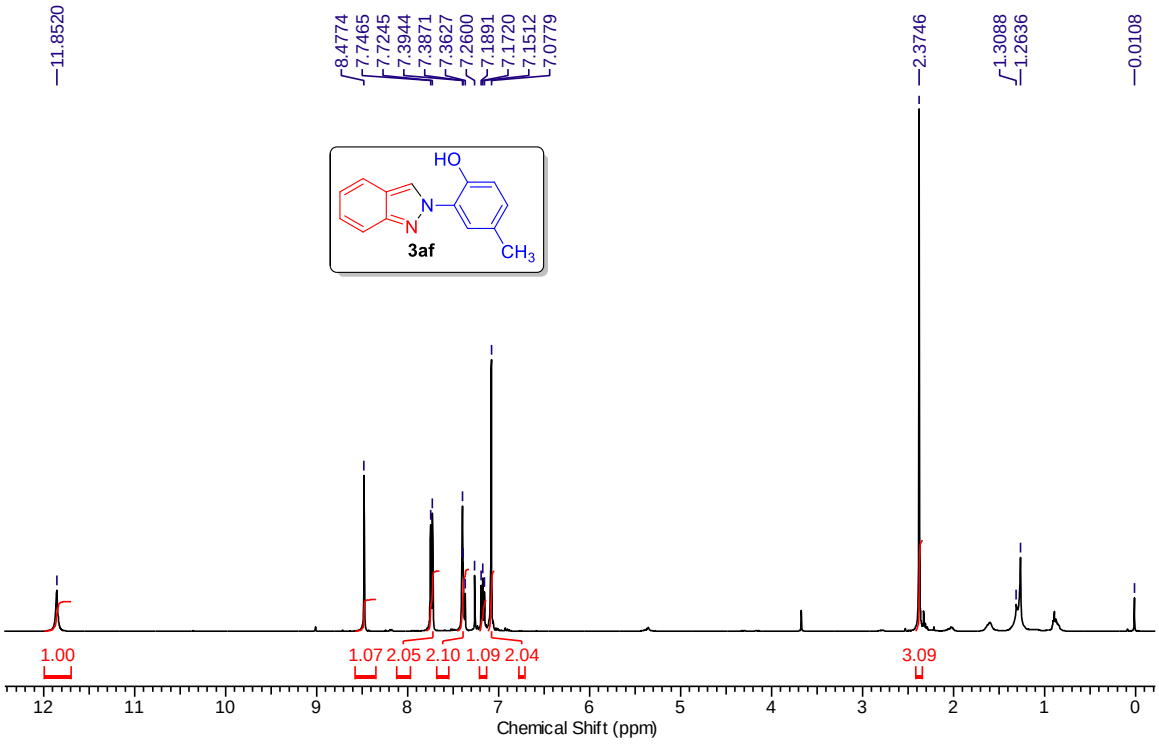
^{13}C NMR (100 MHz) spectrum of compound **3ad** in $CDCl_3$



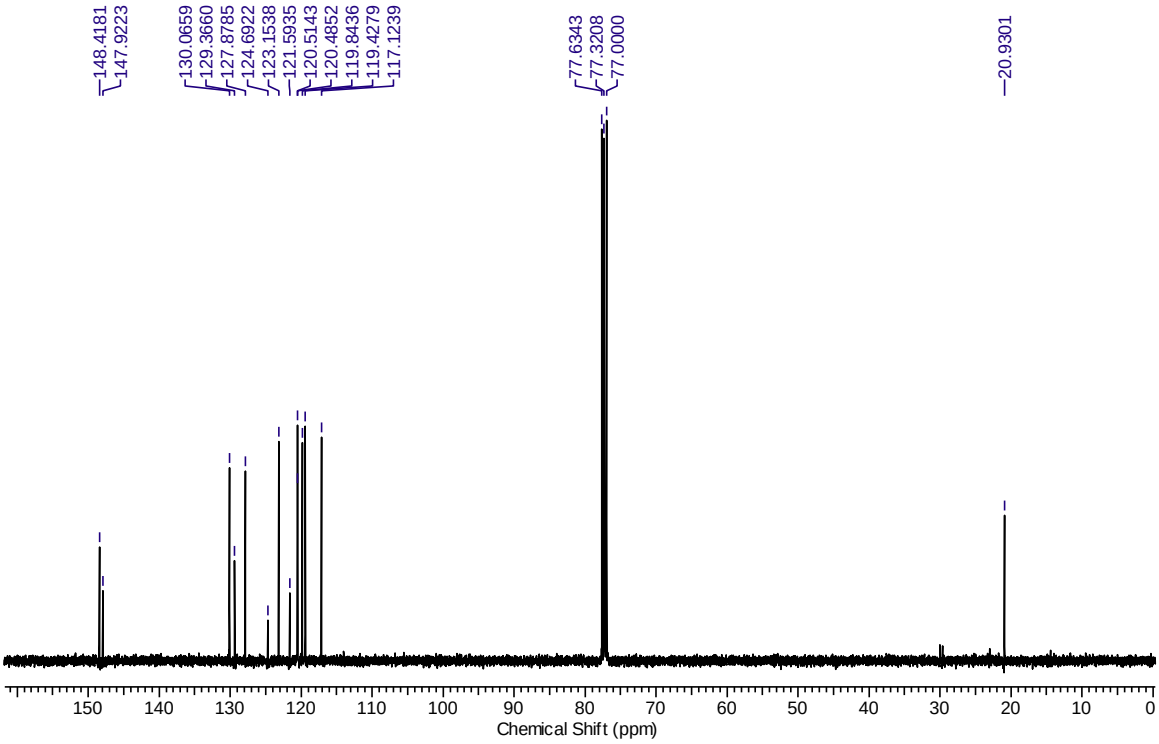
^{13}C NMR (100 MHz) spectrum of compound **3ae** in $CDCl_3$



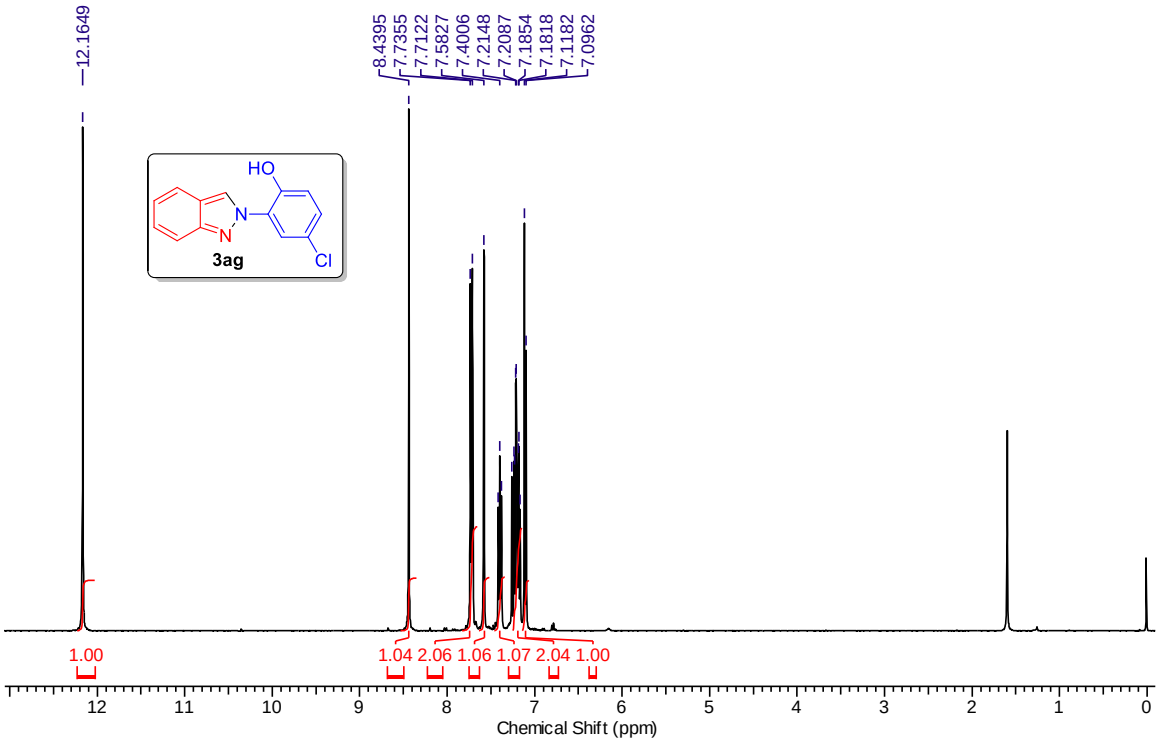
^{13}C NMR (100 MHz) spectrum of compound **3ae** in $CDCl_3$



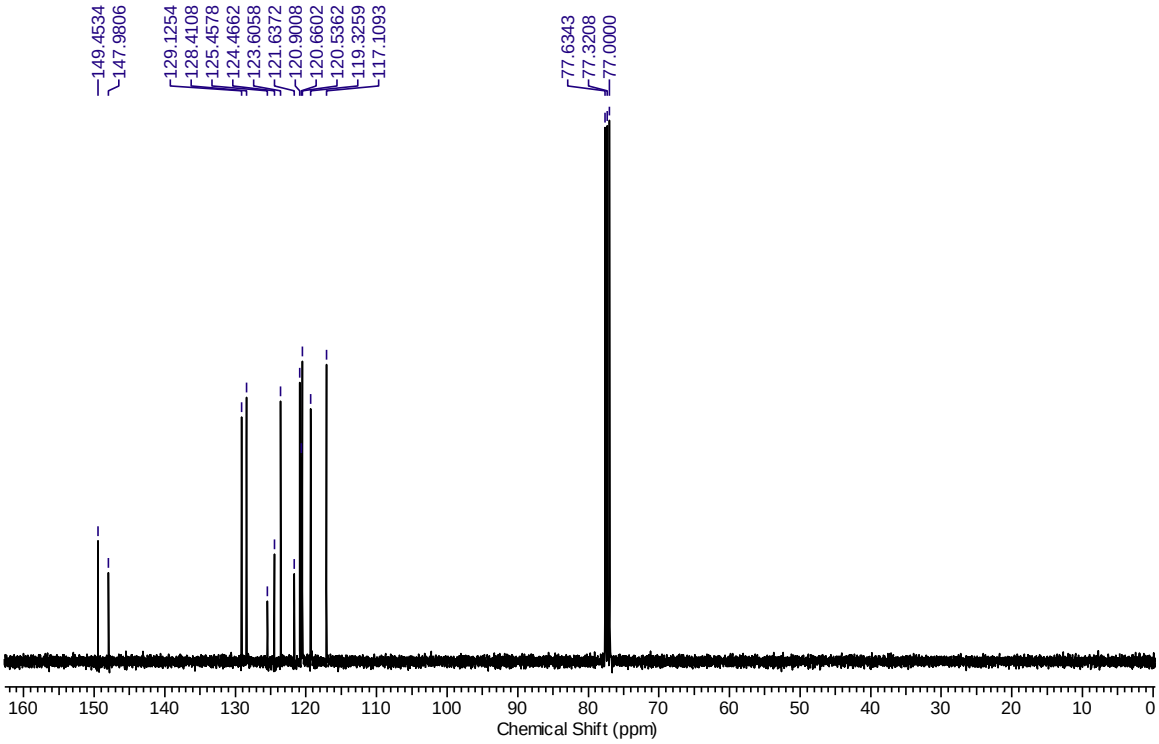
^{1}H NMR (400 MHz) spectrum of compound **3af** in $CDCl_3$



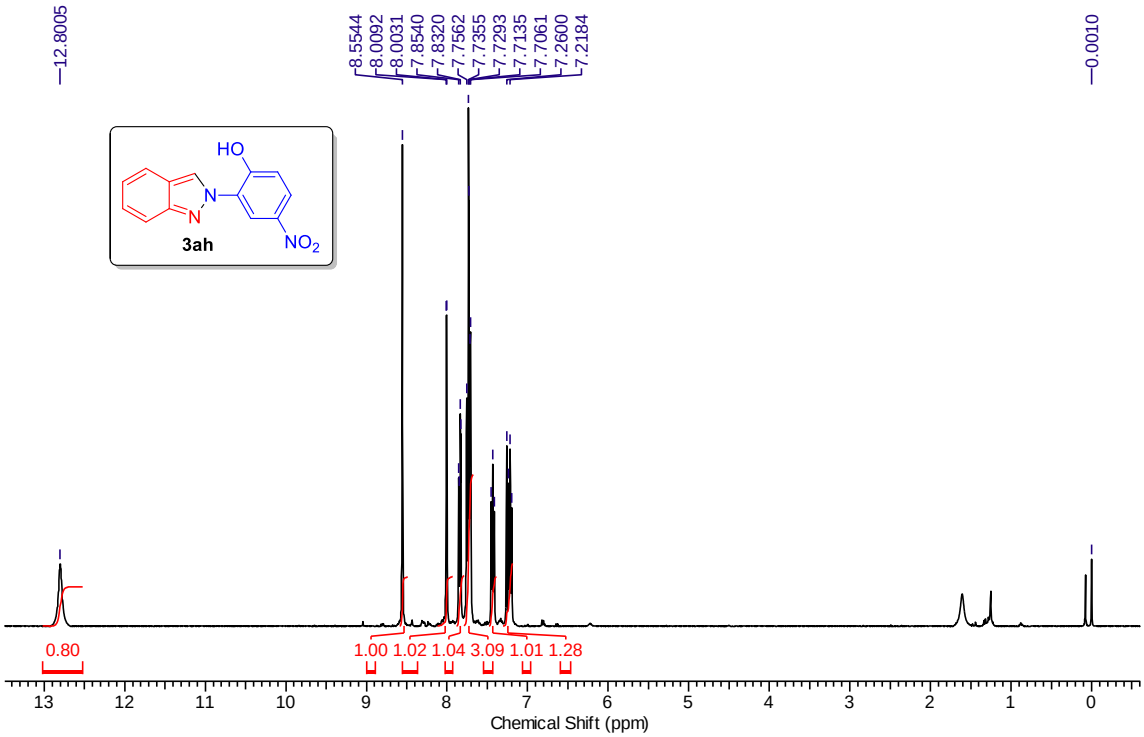
^{13}C NMR (100 MHz) spectrum of compound **3af** in $CDCl_3$



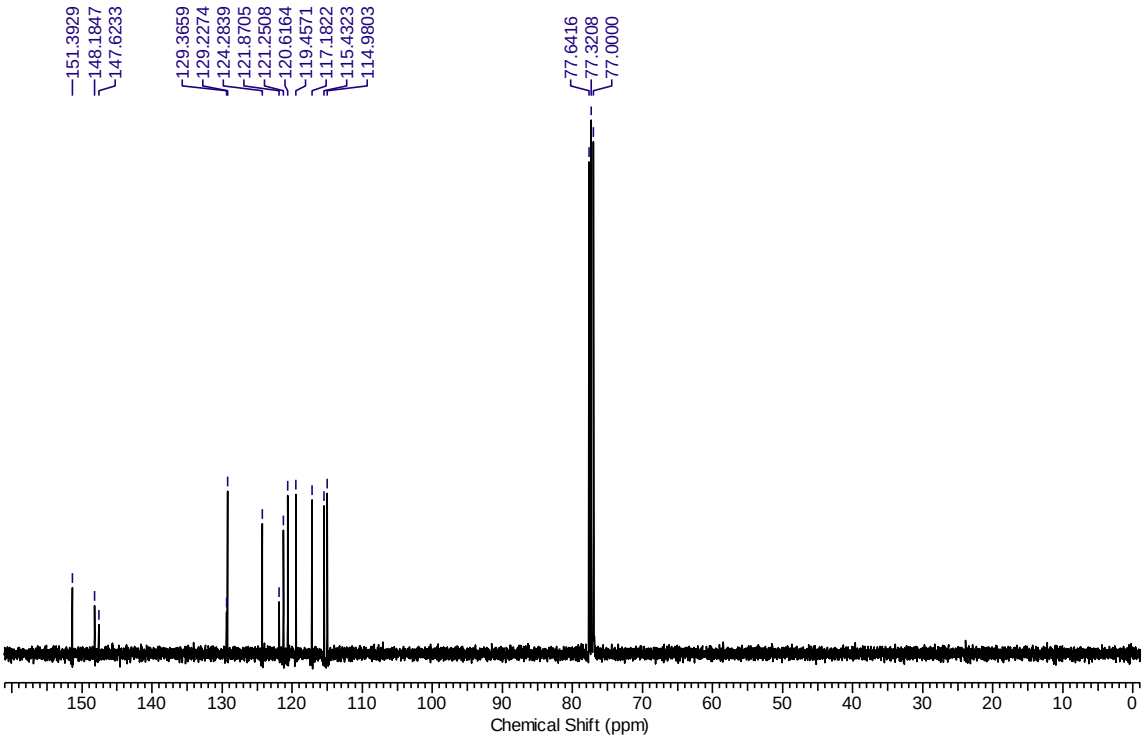
^{1}H NMR (400 MHz) spectrum of compound **3ag** in $CDCl_3$



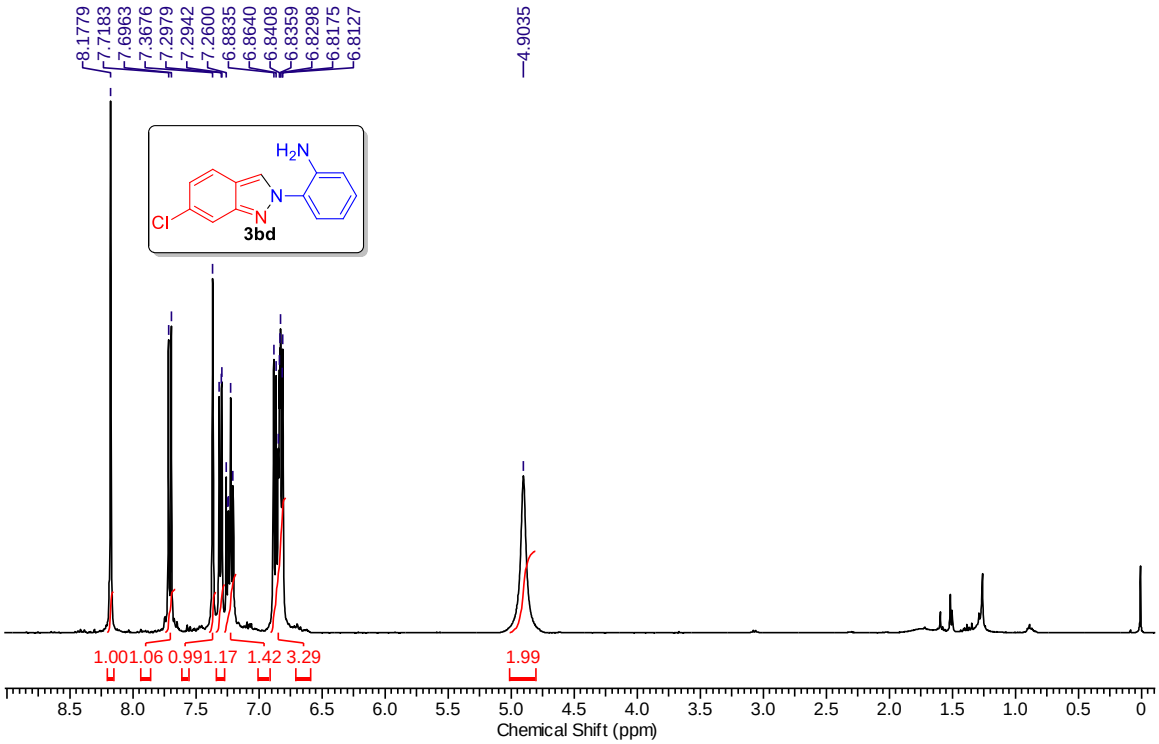
^{13}C NMR (100 MHz) spectrum of compound **3ag** in $CDCl_3$



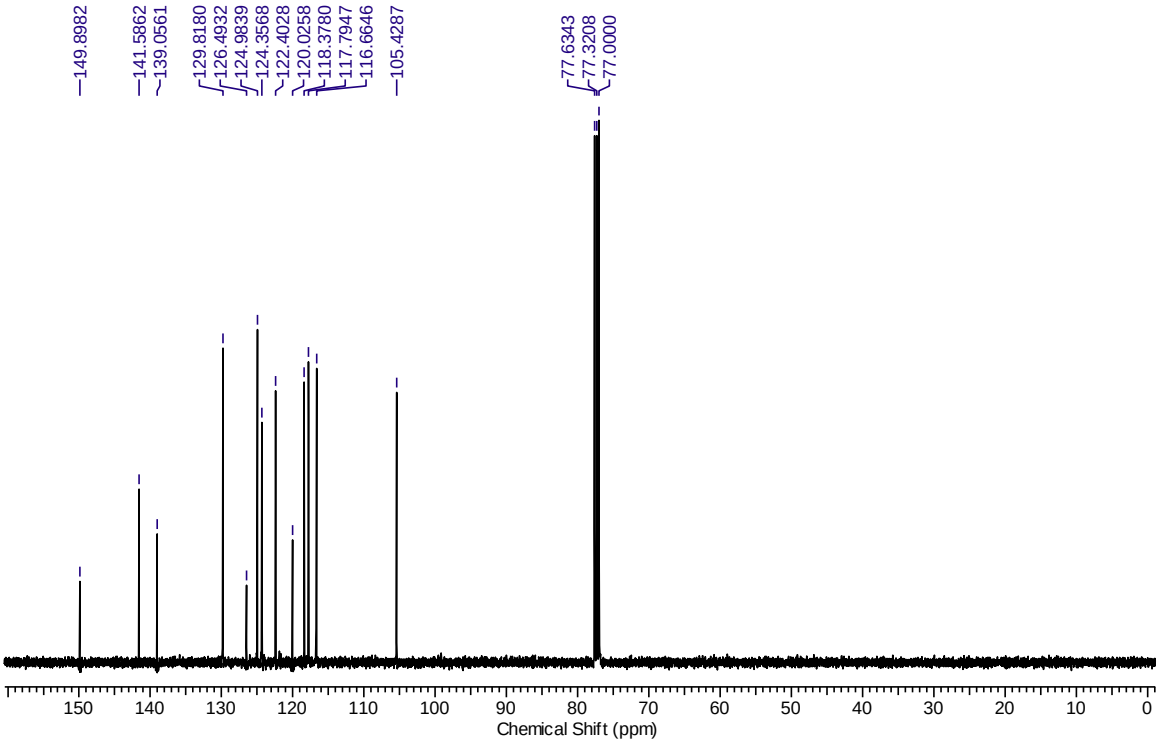
^{1}H NMR (400 MHz) spectrum of compound **3ah** in $CDCl_3$



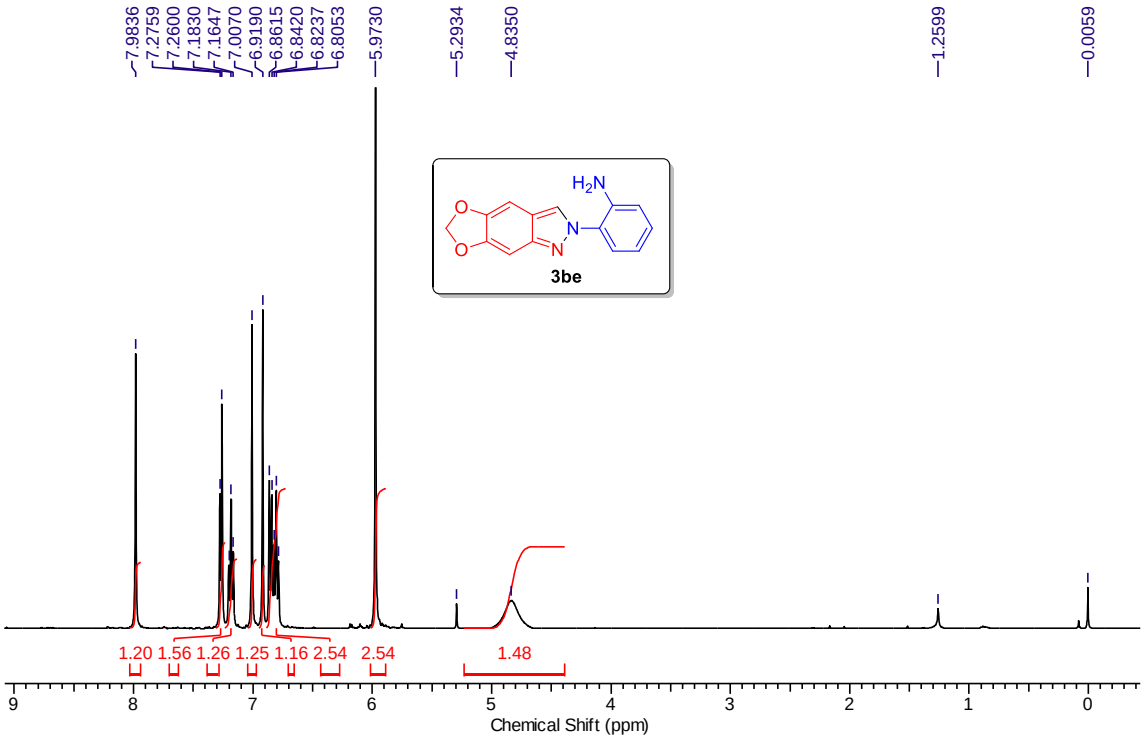
^{13}C NMR (100 MHz) spectrum of compound **3ah** in $CDCl_3$



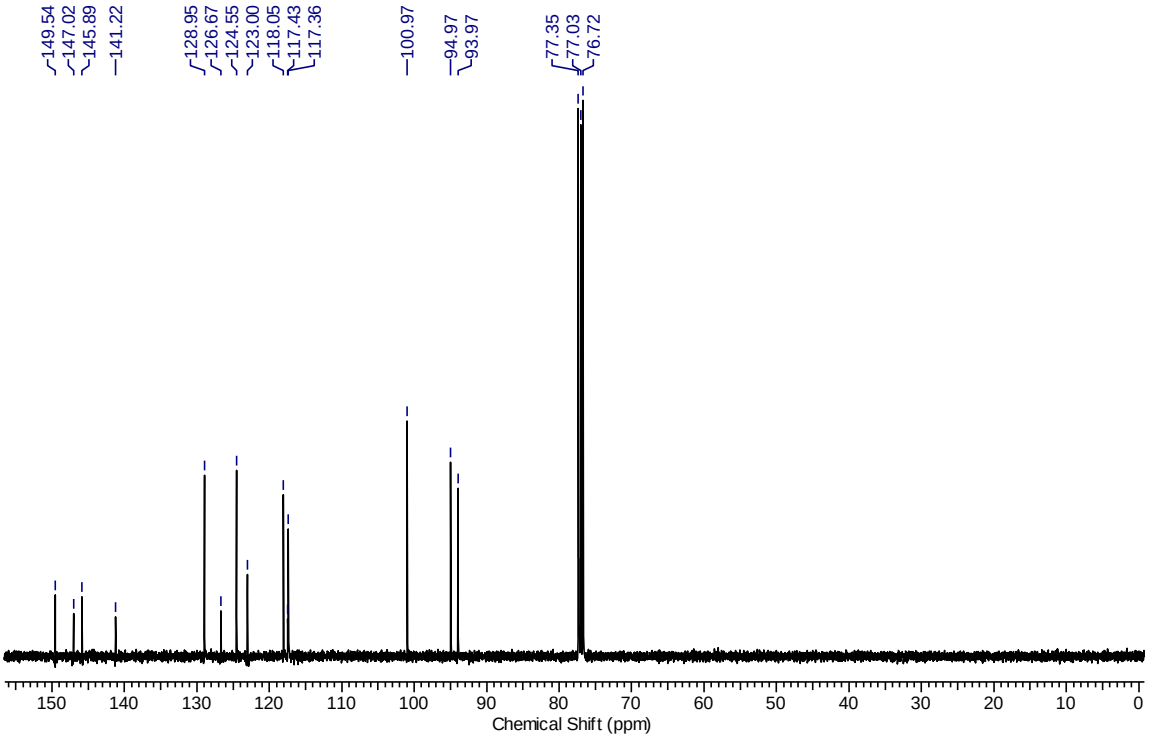
^{1}H NMR (400 MHz) spectrum of compound **3bd** in $CDCl_3$



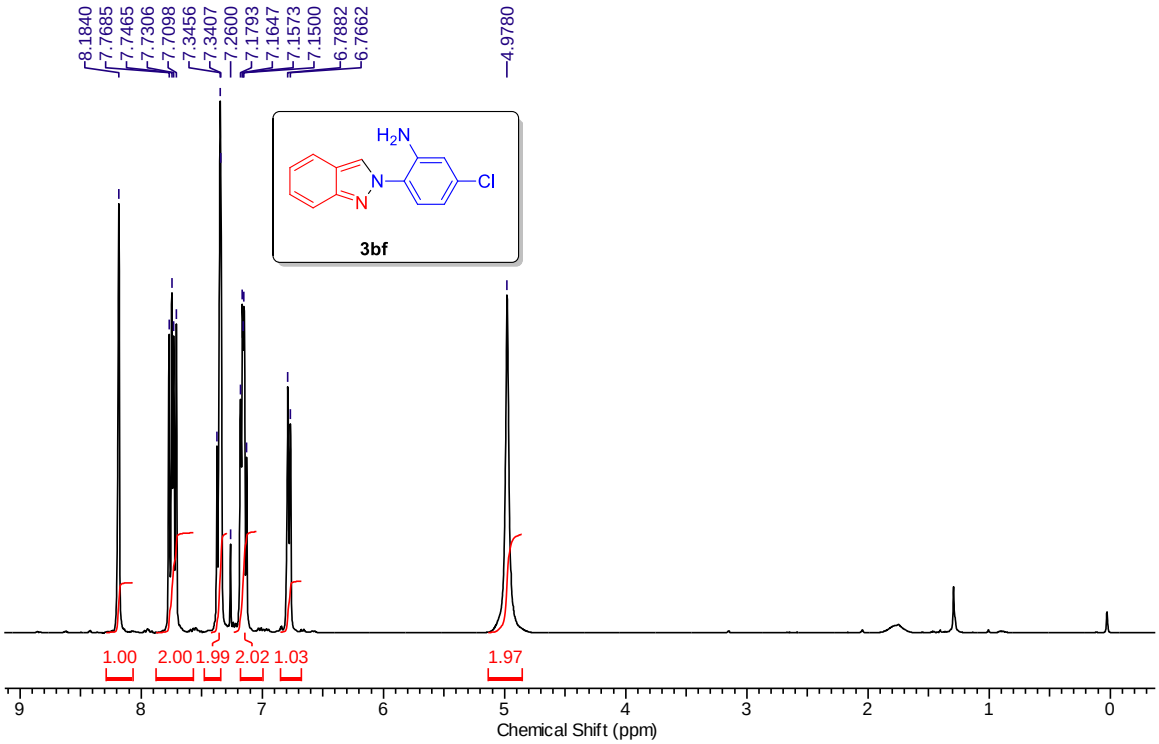
^{13}C NMR (100 MHz) spectrum of compound **3bd** in $CDCl_3$



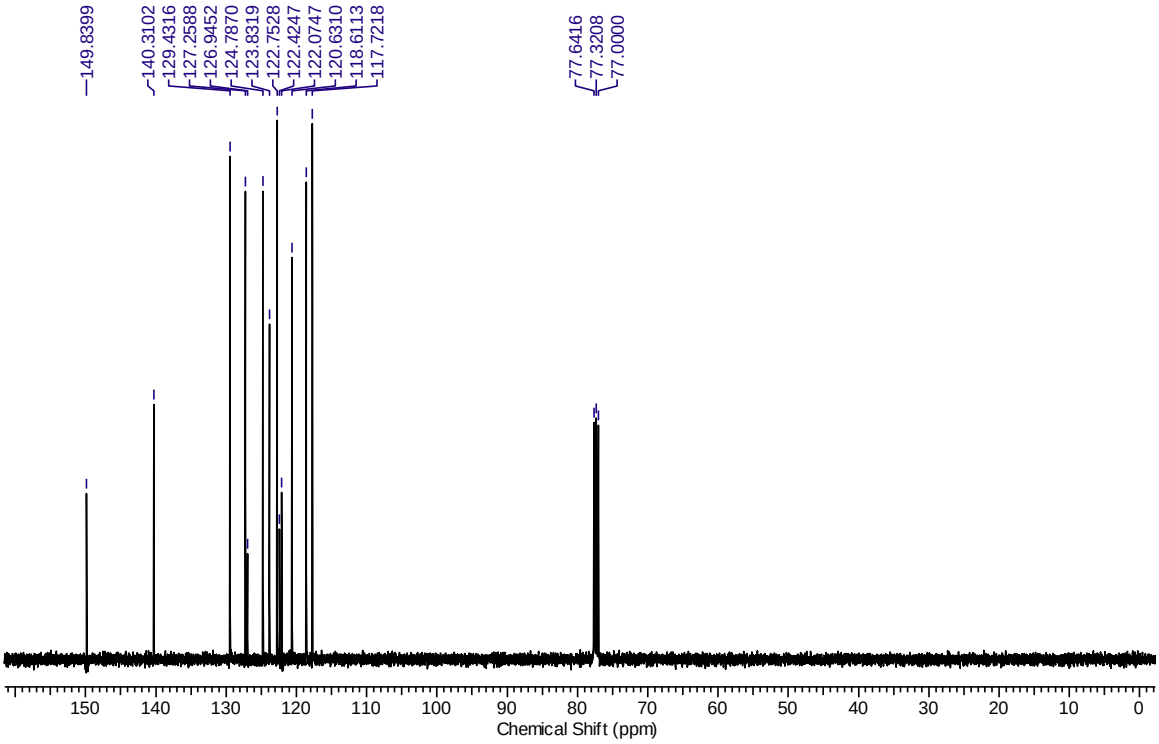
^{1}H NMR (400 MHz) spectrum of compound **3be** in $CDCl_3$



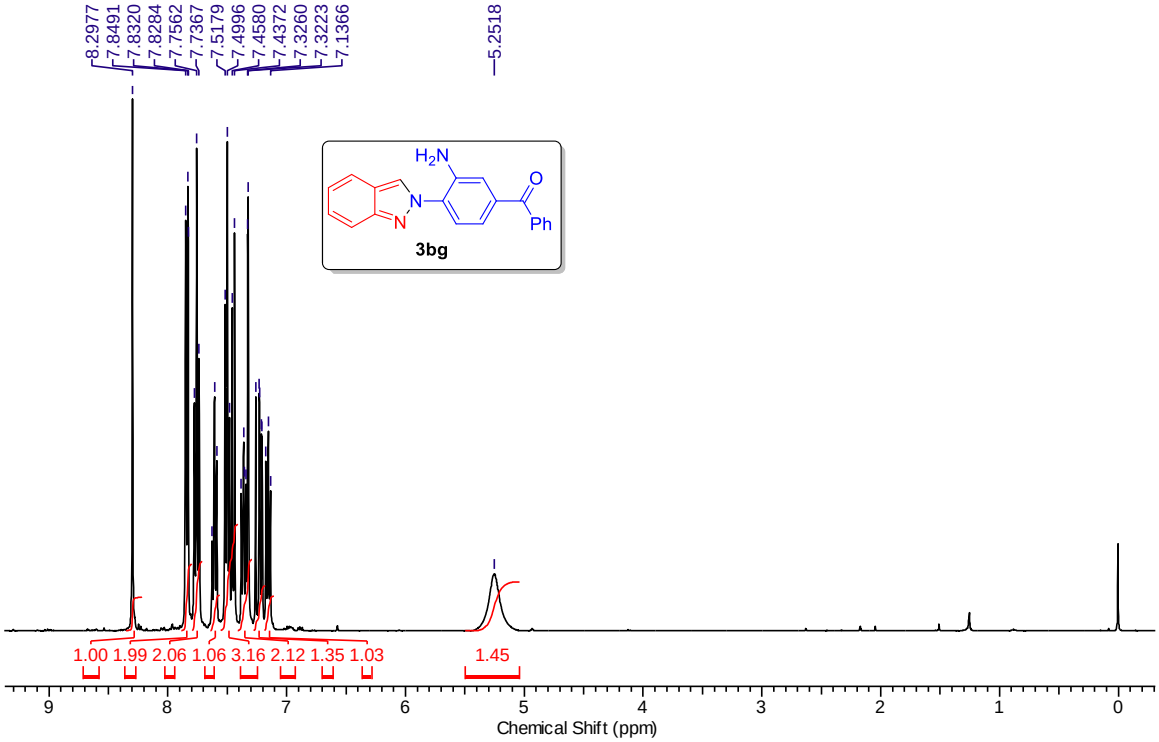
^{13}C NMR (100 MHz) spectrum of compound **3be** in $CDCl_3$



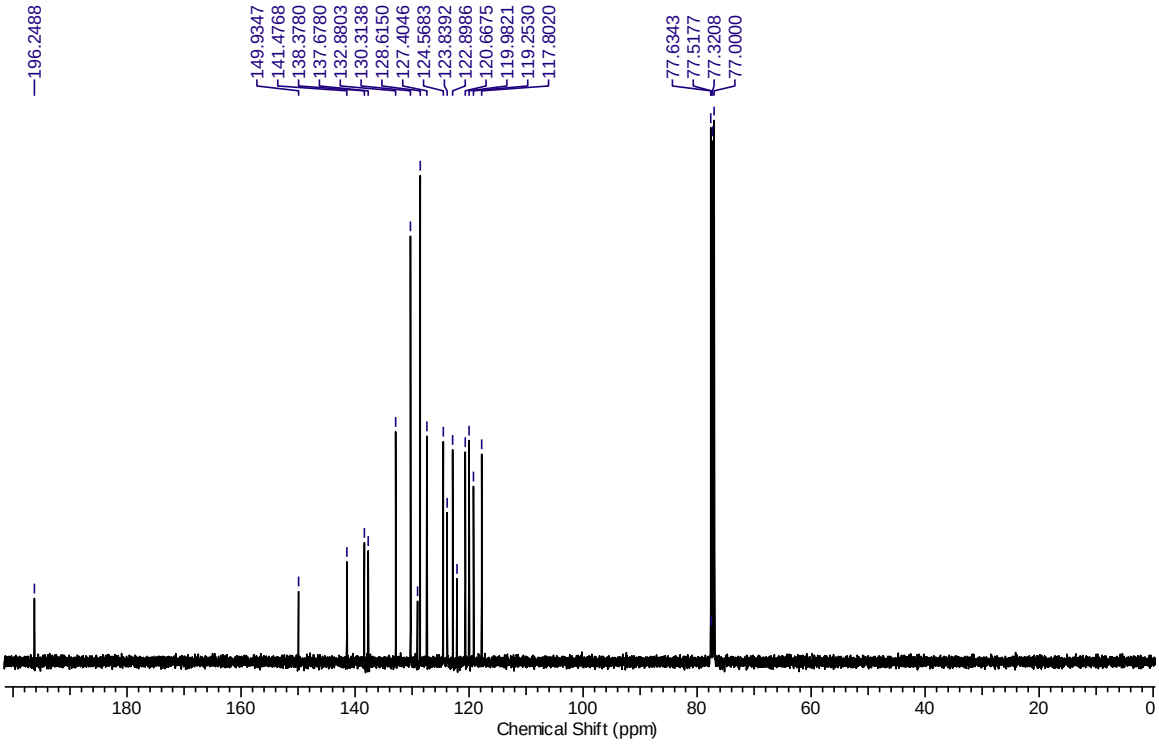
^{1}H NMR (400 MHz) spectrum of compound **3bf** in $CDCl_3$



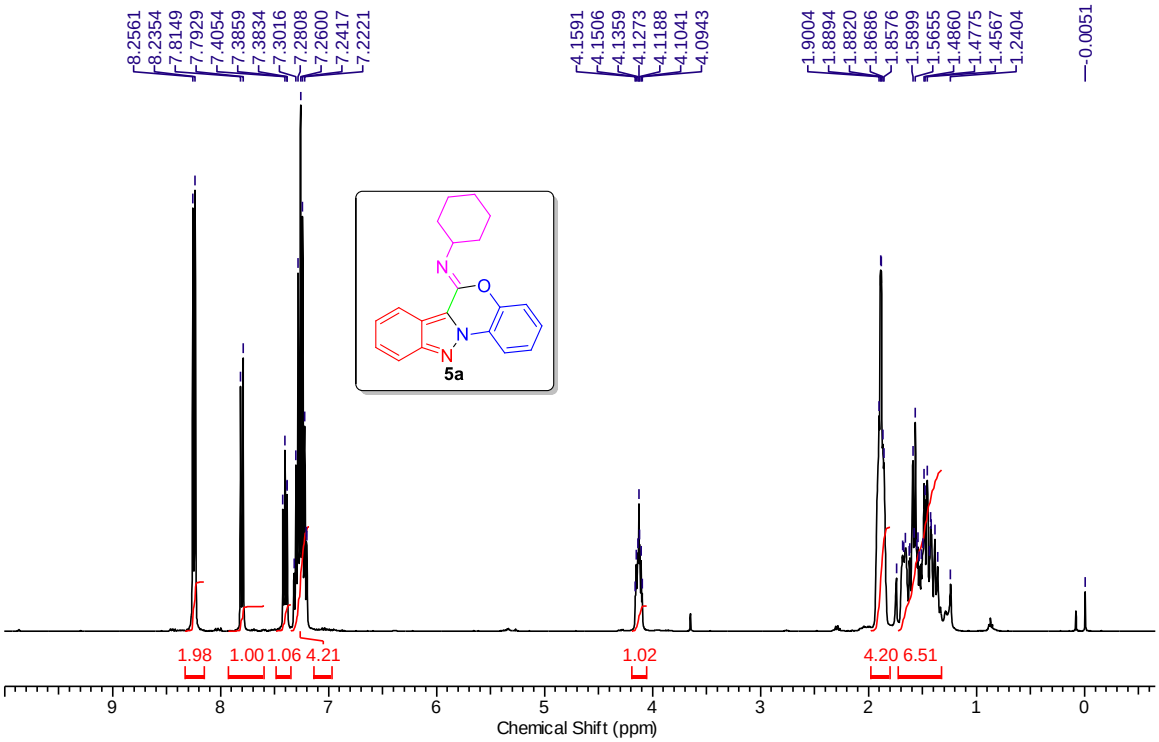
^{13}C NMR (100 MHz) spectrum of compound **3bf** in $CDCl_3$



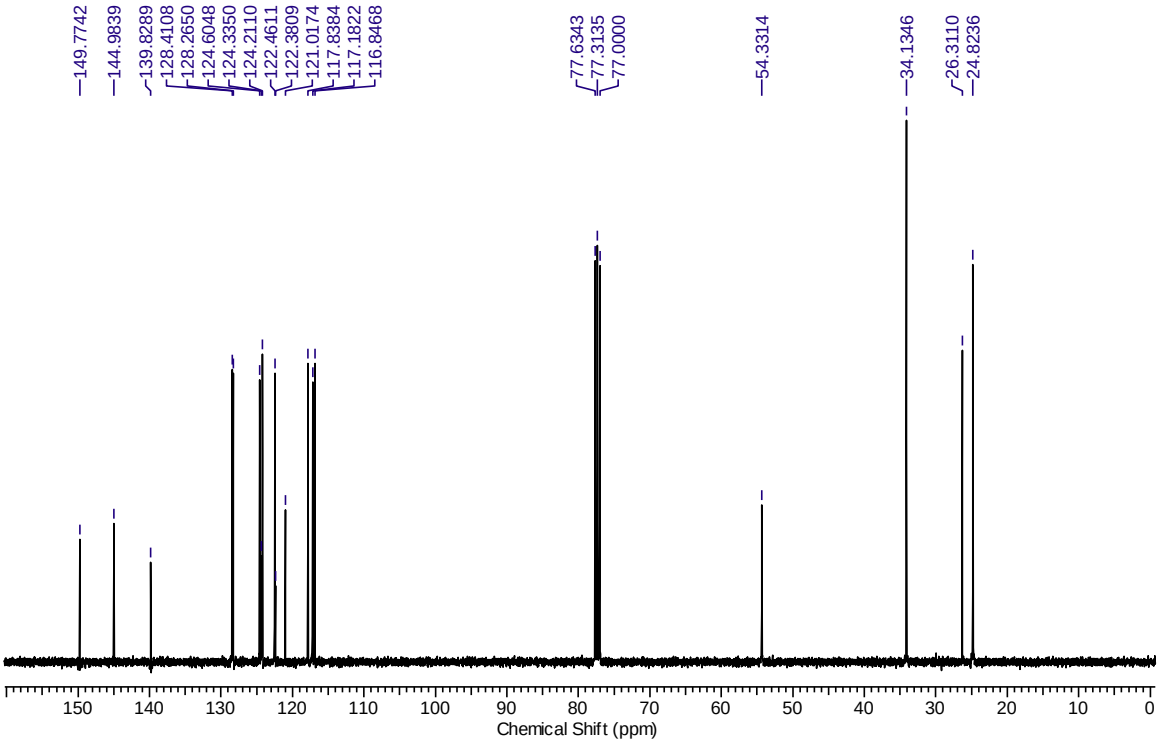
^{1}H NMR (400 MHz) spectrum of compound **3bg** in $CDCl_3$



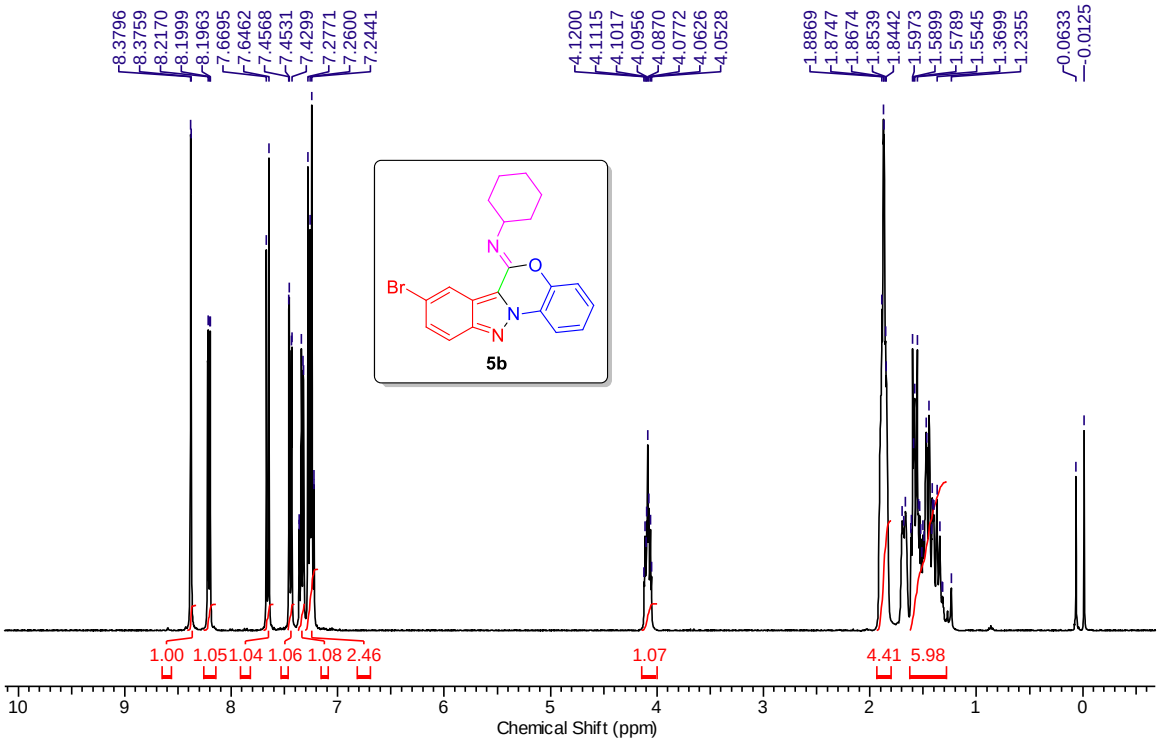
^{13}C NMR (100 MHz) spectrum of compound **3bg** in $CDCl_3$



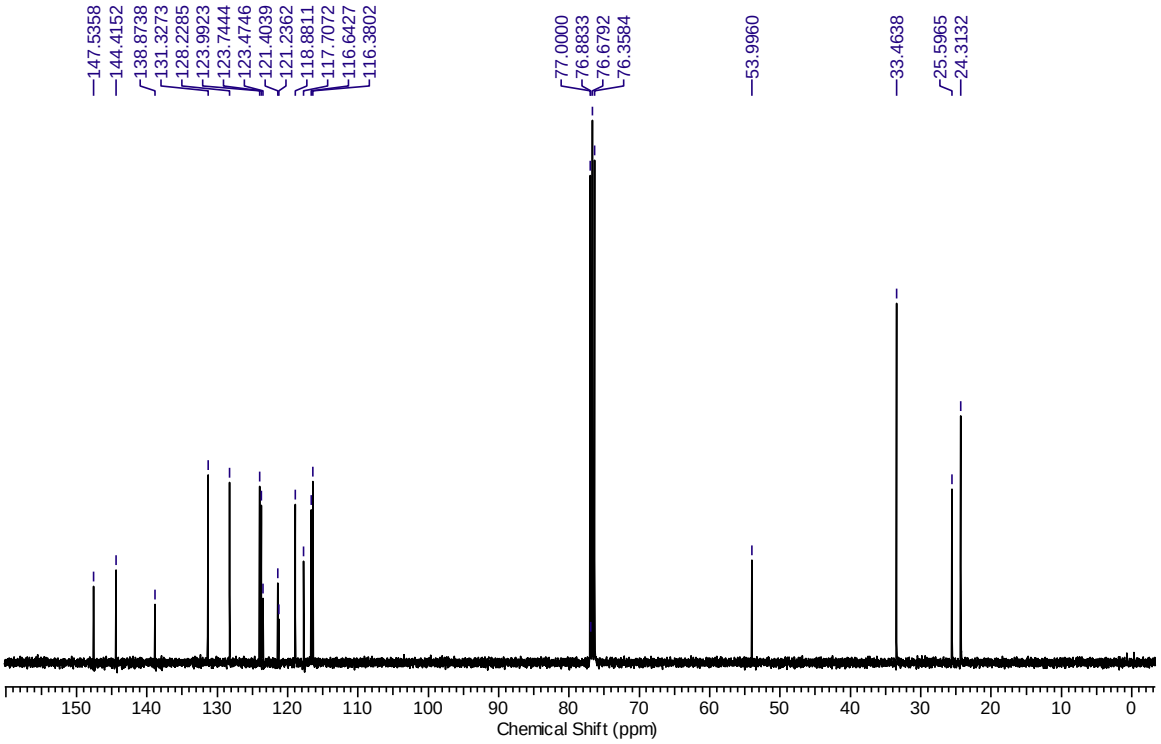
^{1}H NMR (400 MHz) spectrum of compound **5a** in $CDCl_3$



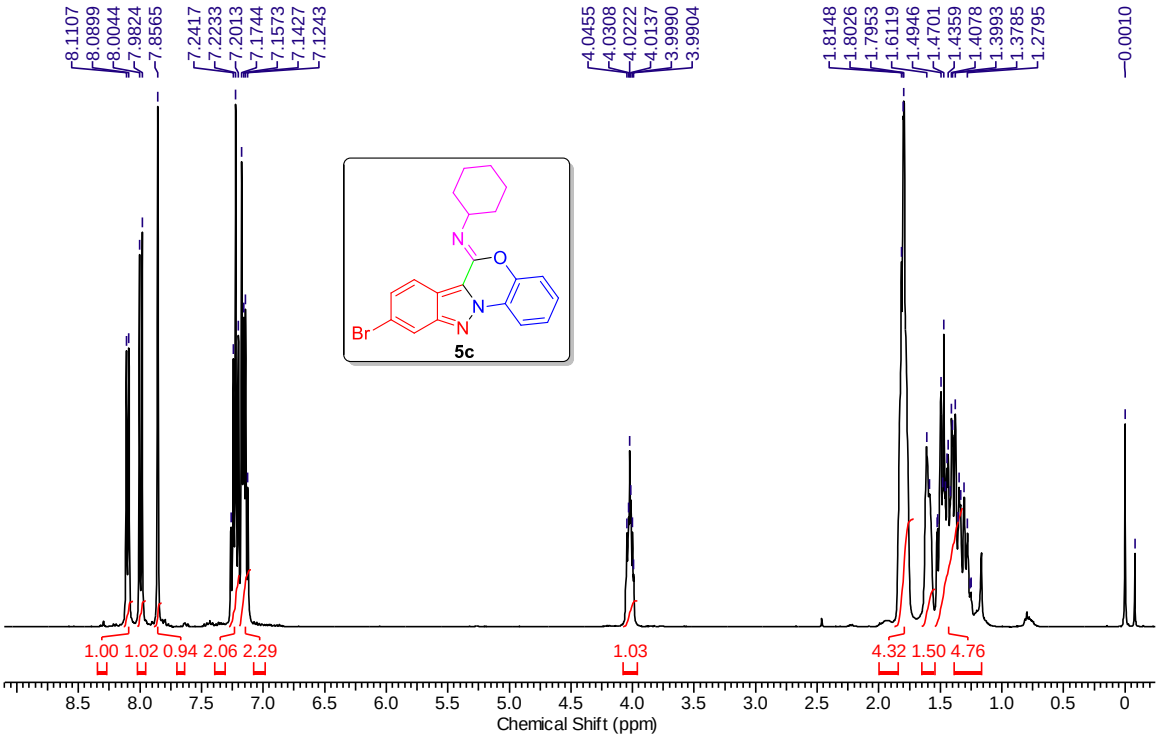
^{13}C NMR (100 MHz) spectrum of compound **5a** in $CDCl_3$



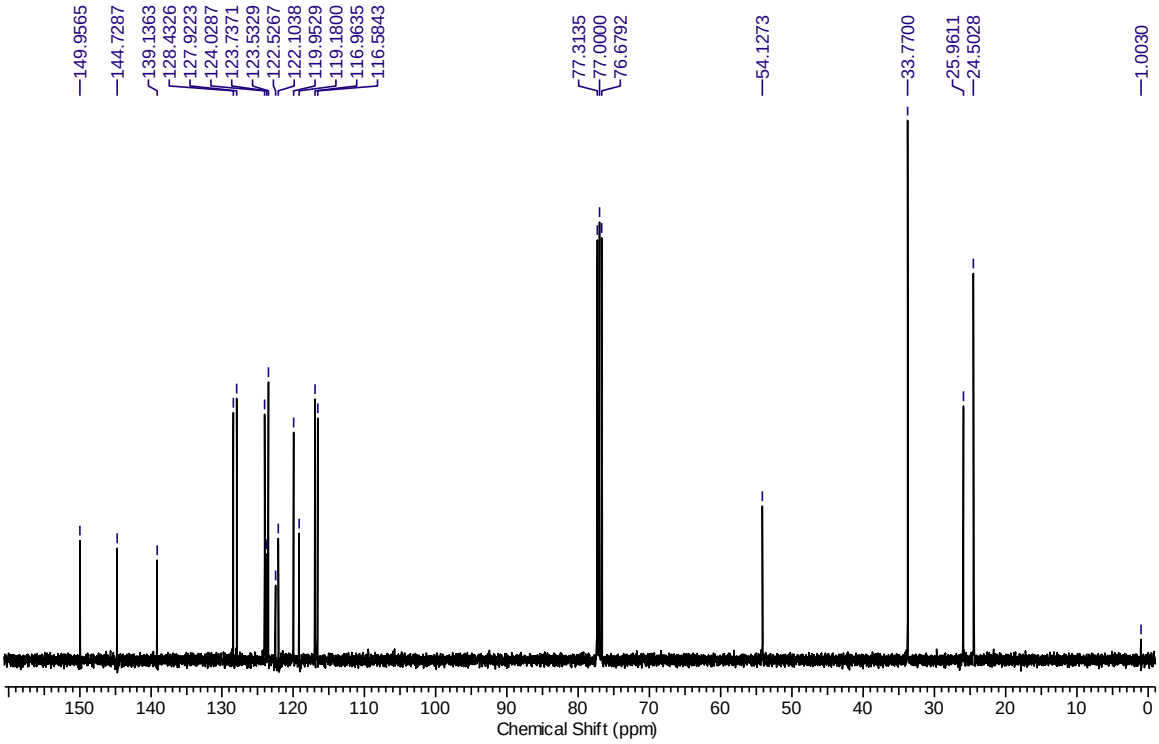
^{1}H NMR (400 MHz) spectrum of compound **5b** in $CDCl_3$



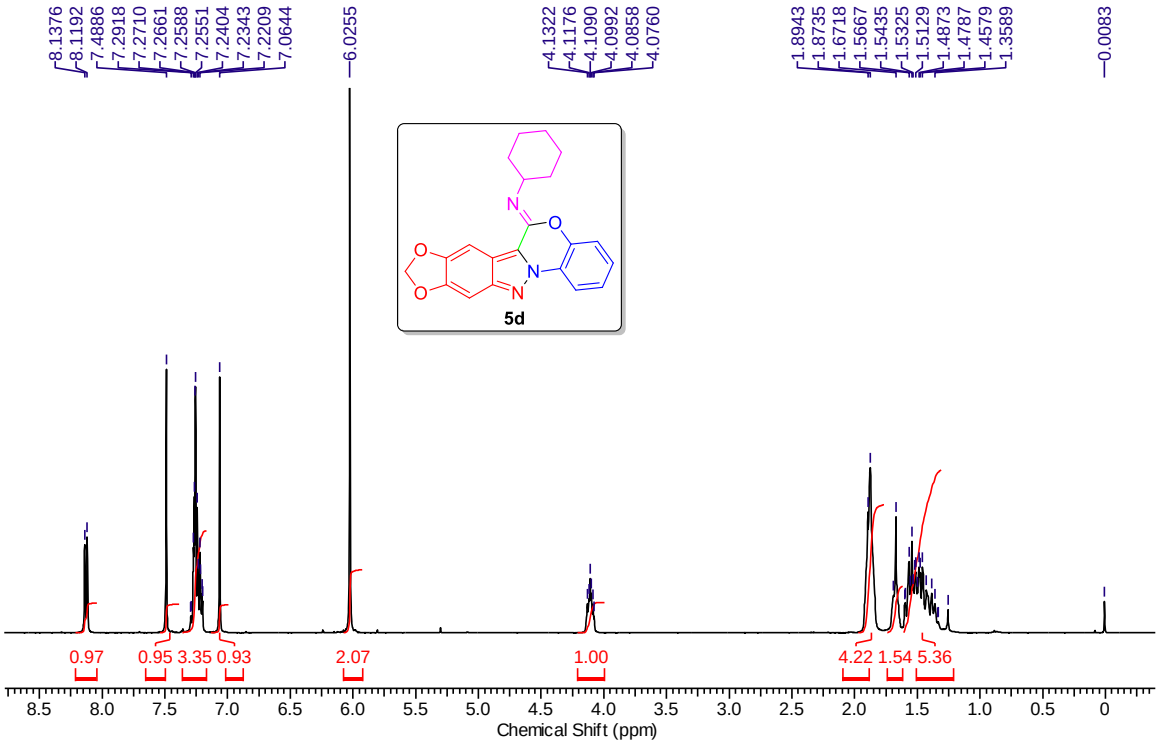
^{13}C NMR (100 MHz) spectrum of compound **5b** in $CDCl_3$



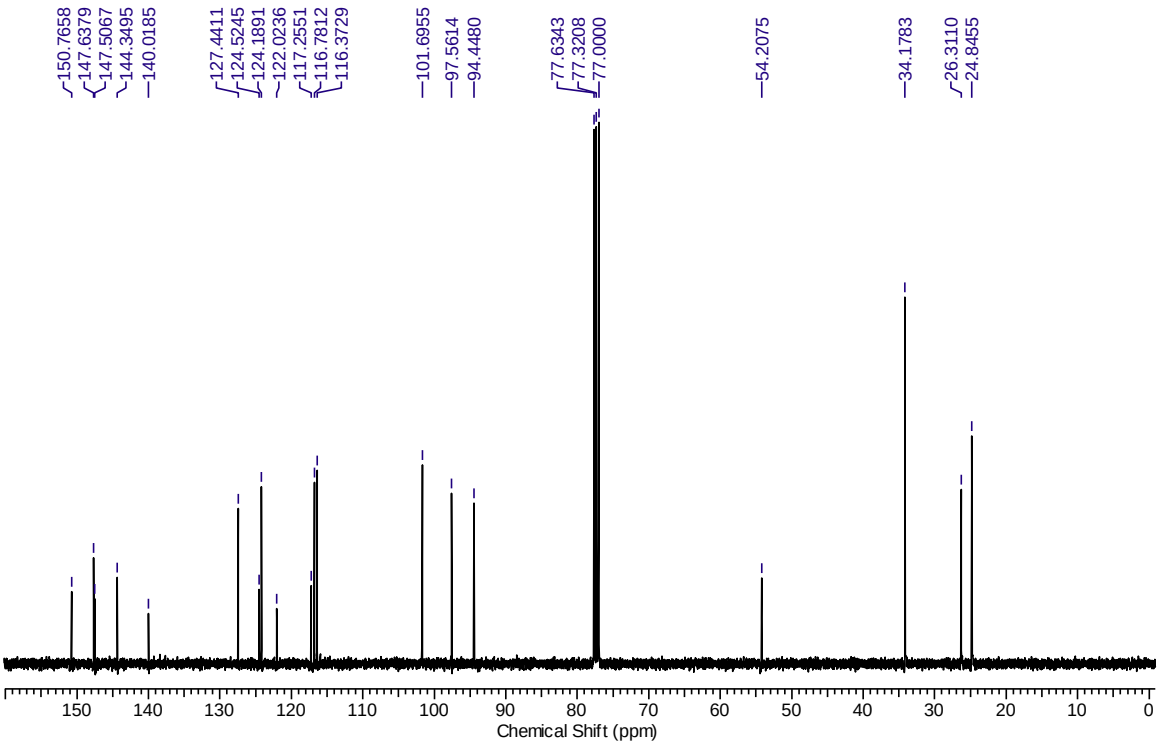
^{1}H NMR (400 MHz) spectrum of compound **5c** in $CDCl_3$



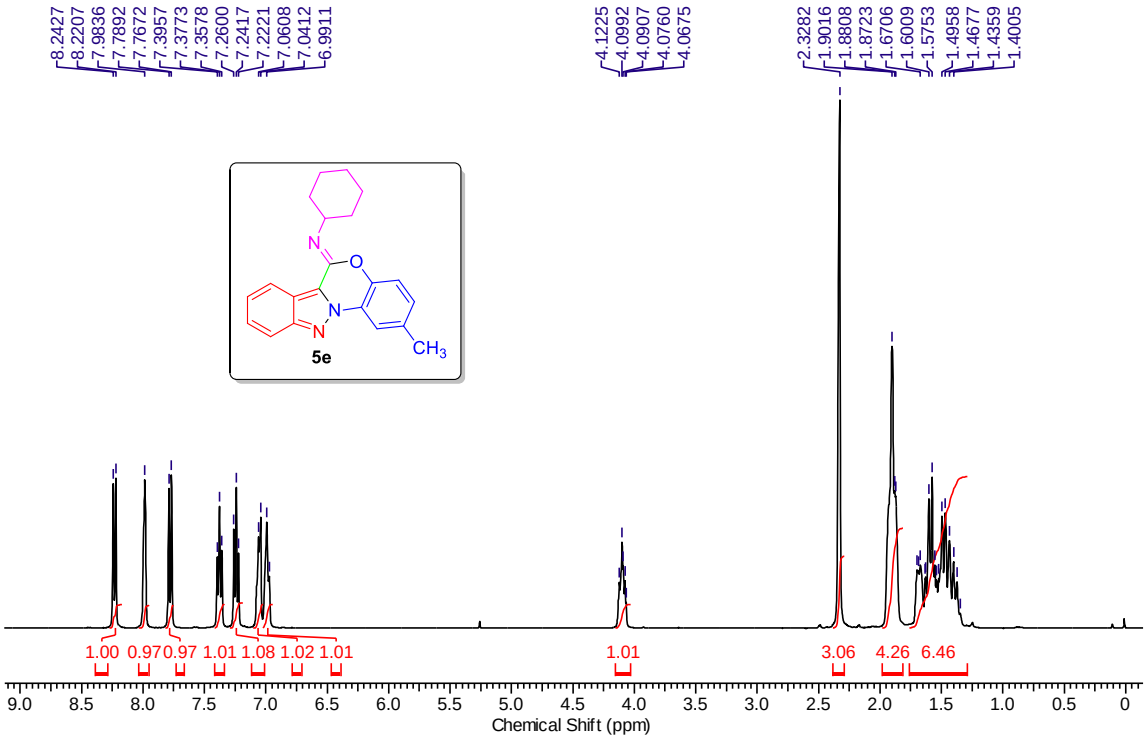
^{13}C NMR (100 MHz) spectrum of compound **5c** in $CDCl_3$



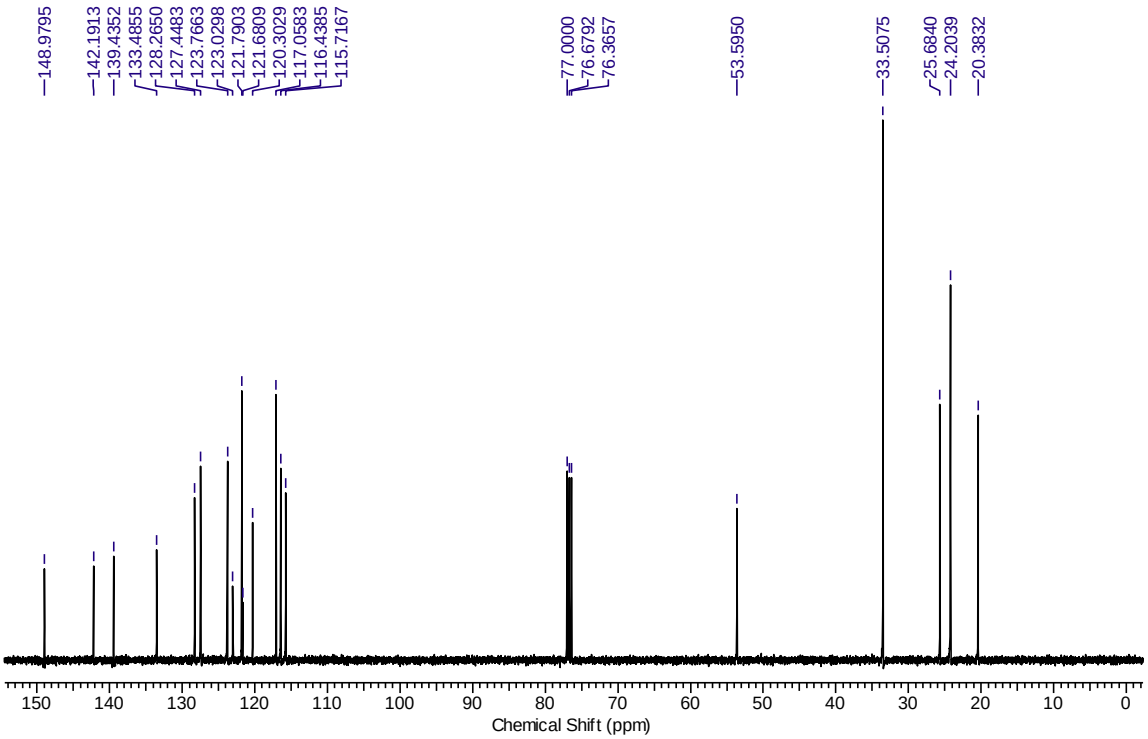
^{1}H NMR (400 MHz) spectrum of compound **5d** in $CDCl_3$



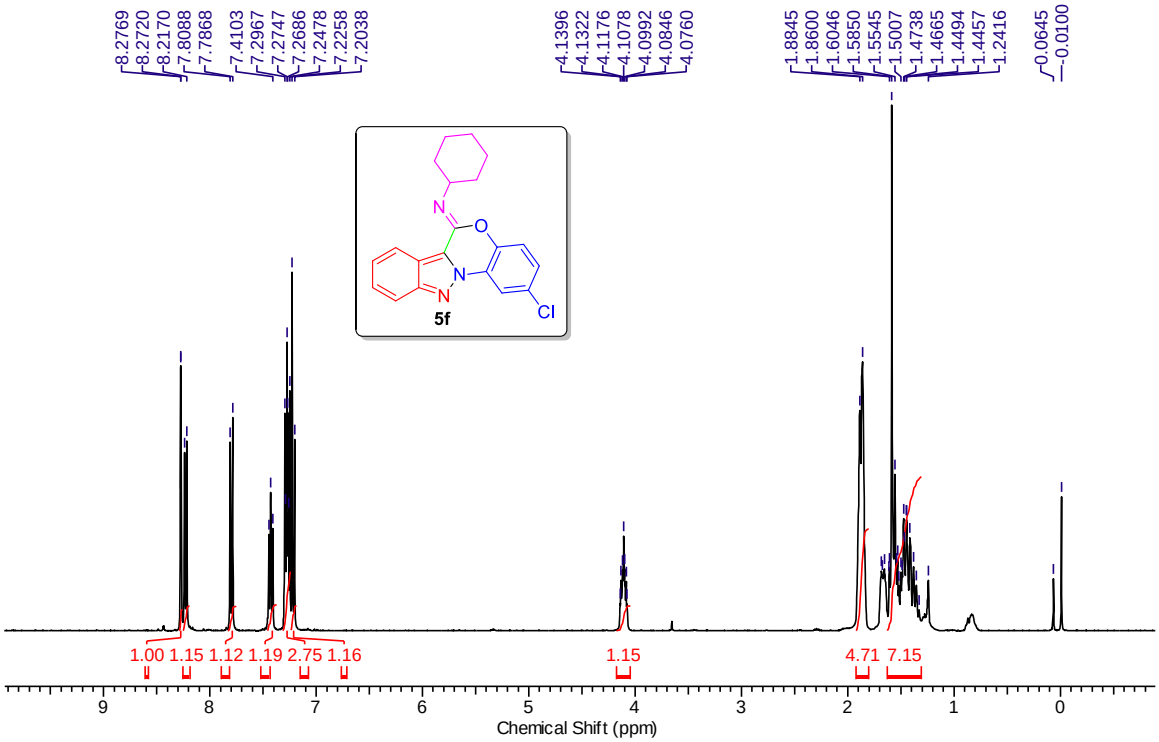
^{13}C NMR (100 MHz) spectrum of compound **5d** in $CDCl_3$



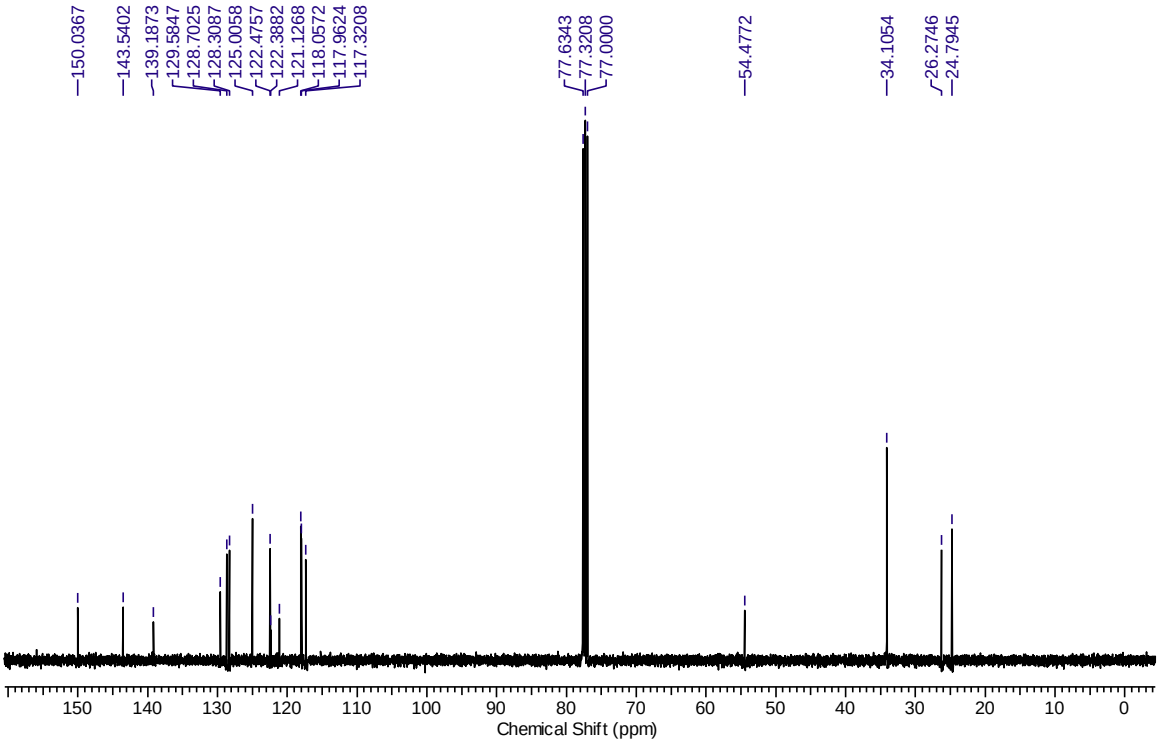
^{1}H NMR (400 MHz) spectrum of compound **5e** in $CDCl_3$



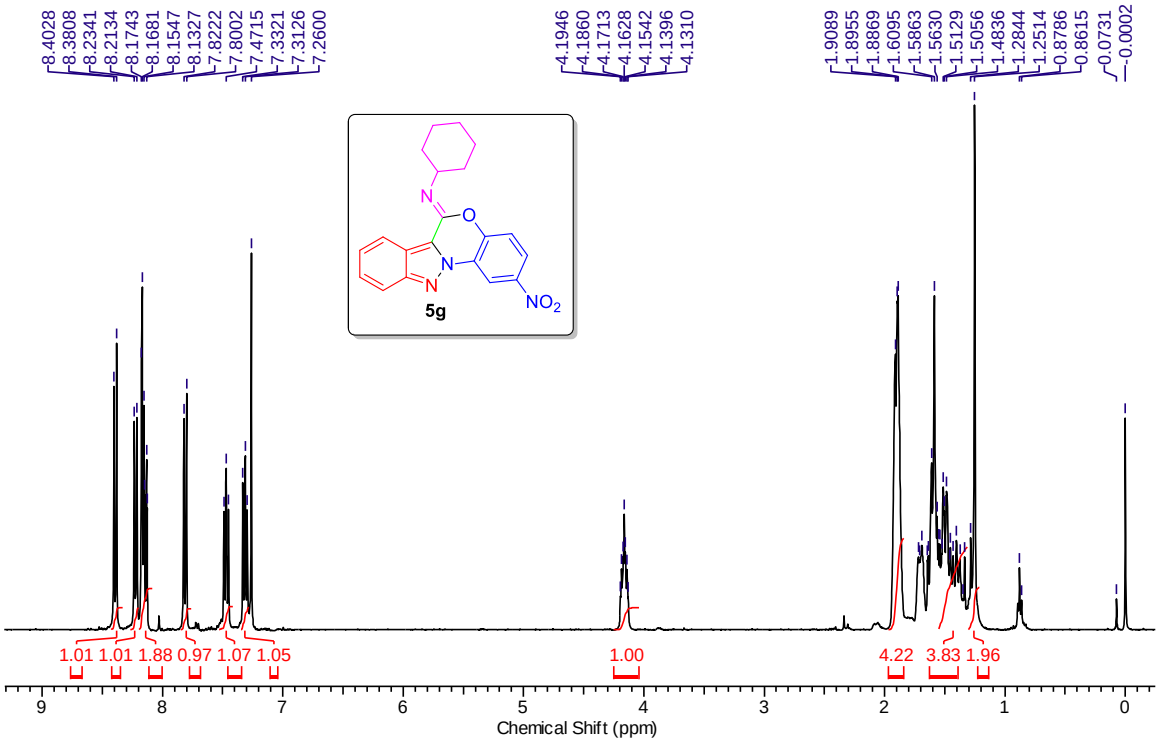
^{13}C NMR (100 MHz) spectrum of compound **5e** in $CDCl_3$



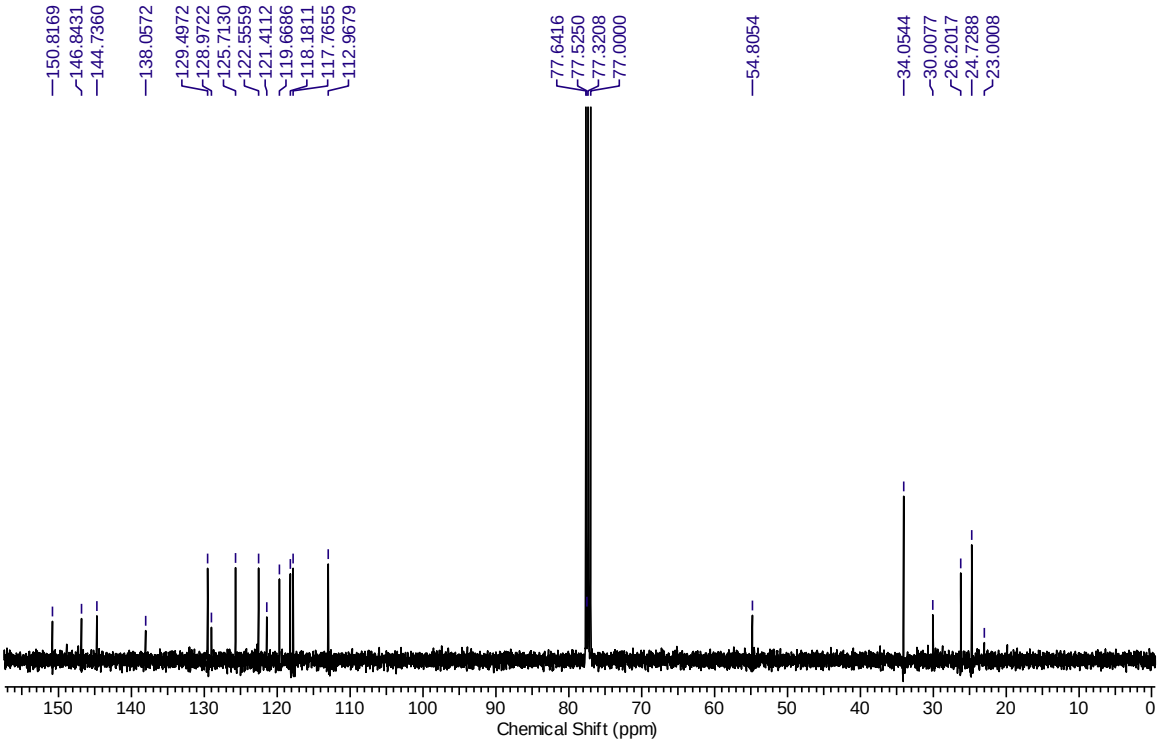
^{1}H NMR (400 MHz) spectrum of compound **5f** in $CDCl_3$



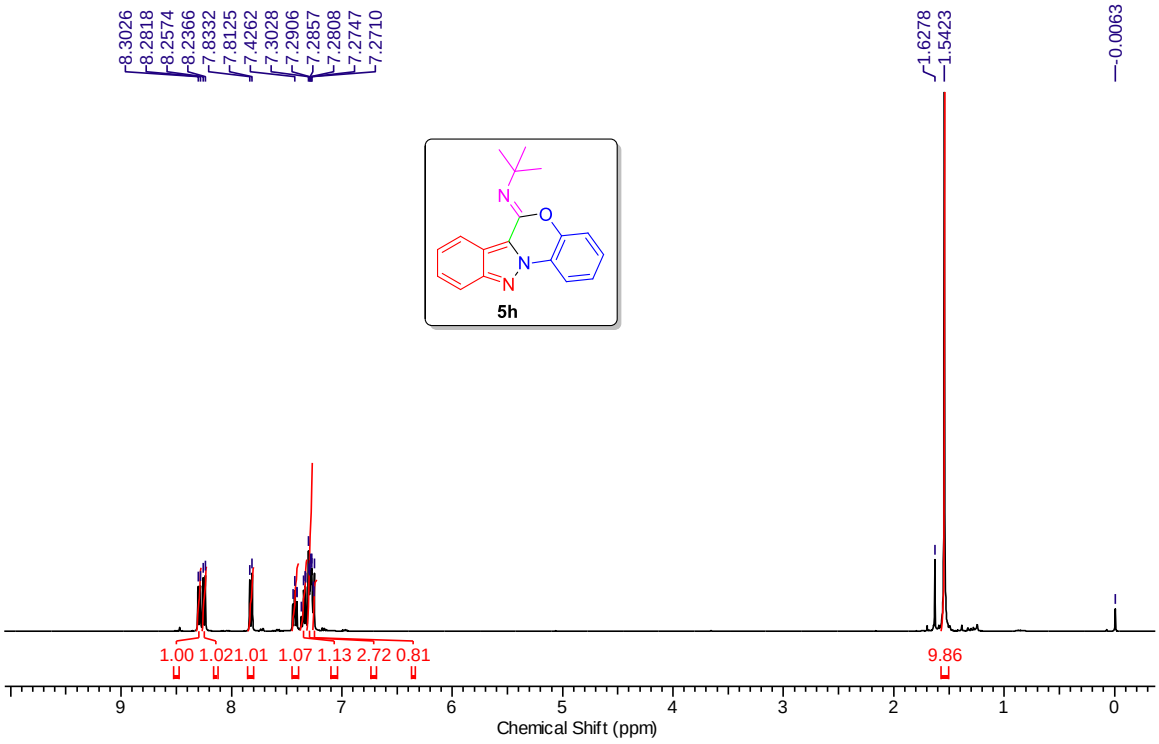
^{13}C NMR (100 MHz) spectrum of compound **5f** in $CDCl_3$



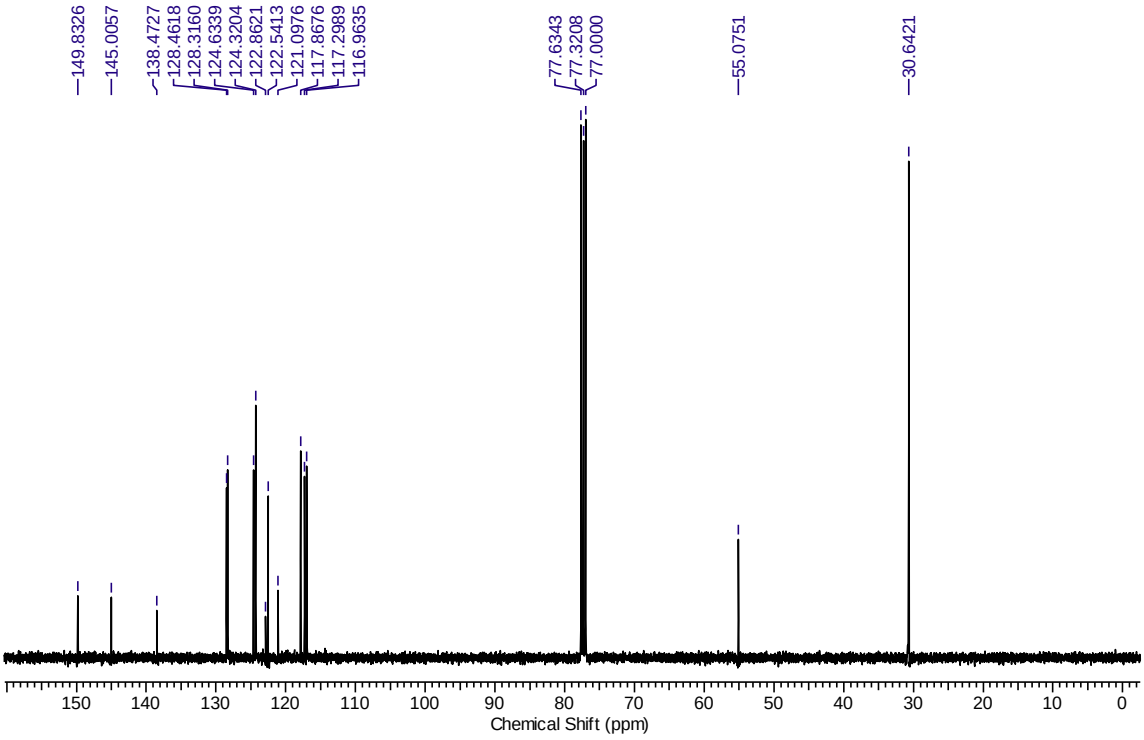
^{1}H NMR (400 MHz) spectrum of compound **5g** in $CDCl_3$



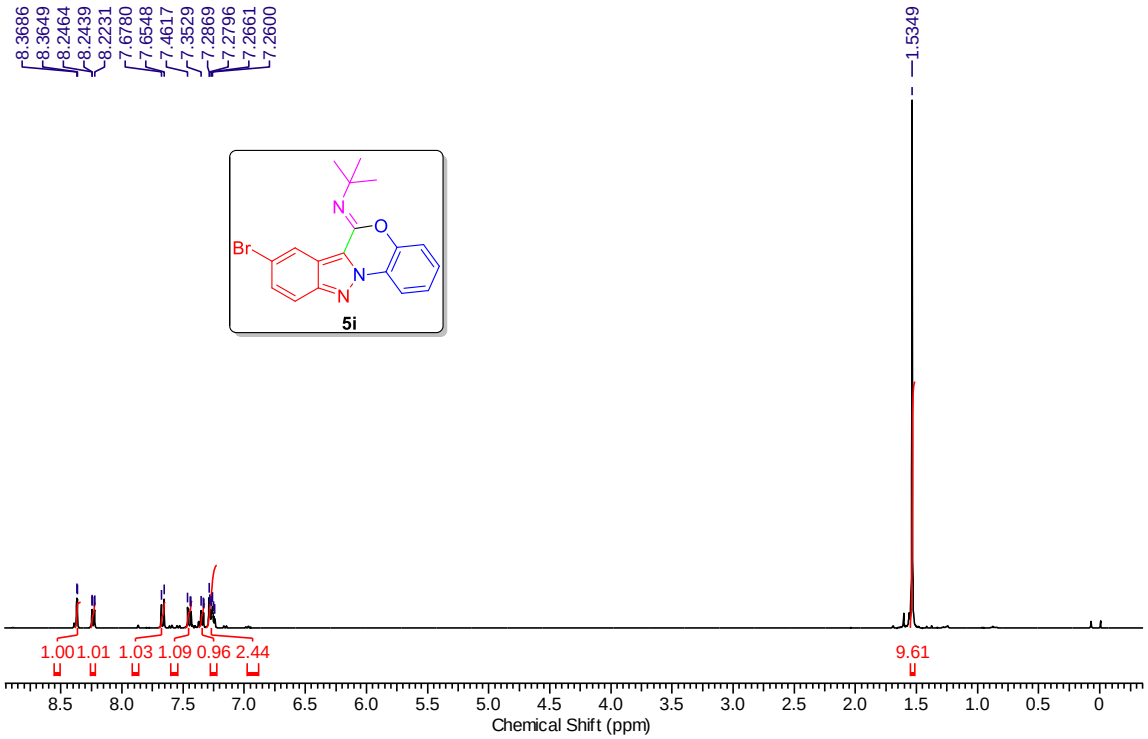
^{13}C NMR (100 MHz) spectrum of compound **5g** in $CDCl_3$



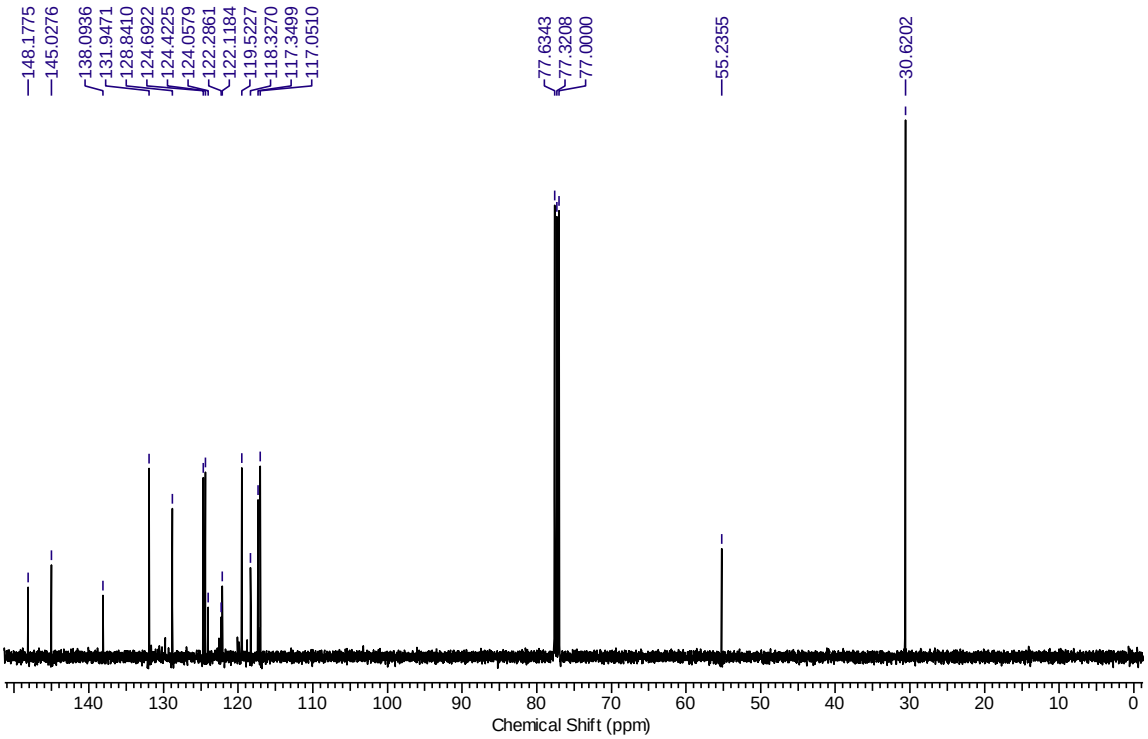
^{1}H NMR (400 MHz) spectrum of compound **5h** in $CDCl_3$



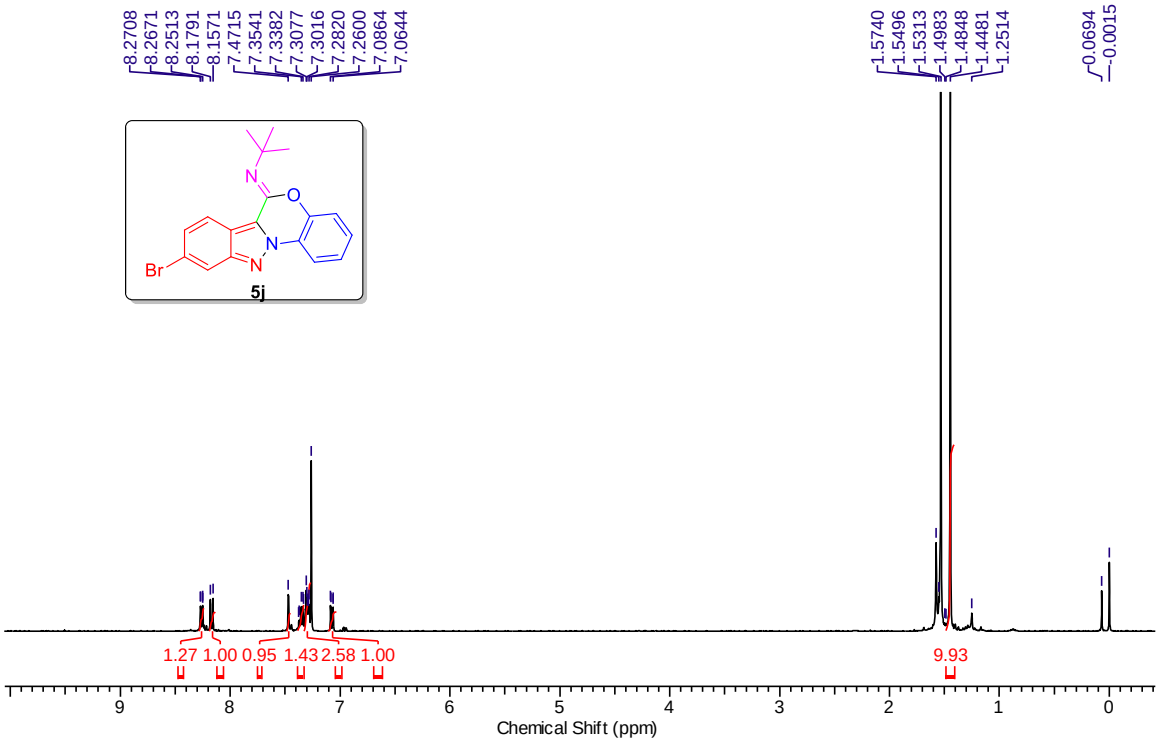
^{13}C NMR (100 MHz) spectrum of compound **5h** in $CDCl_3$



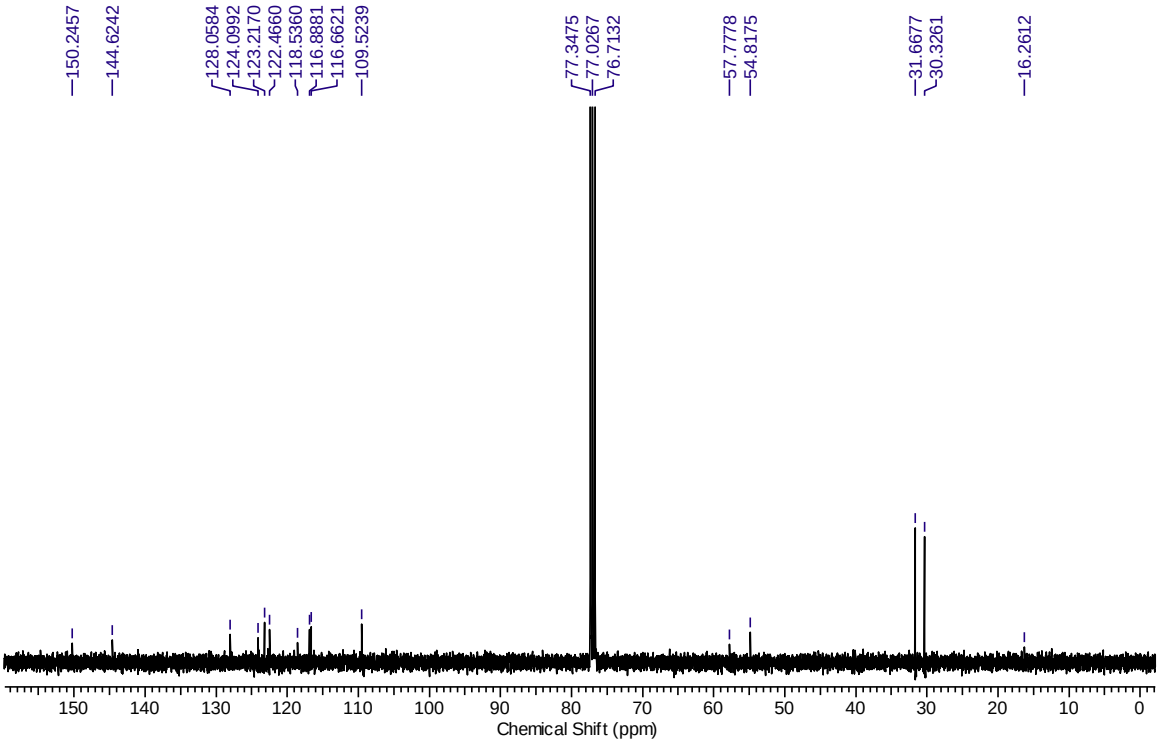
^{1}H NMR (400 MHz) spectrum of compound **5i** in $CDCl_3$



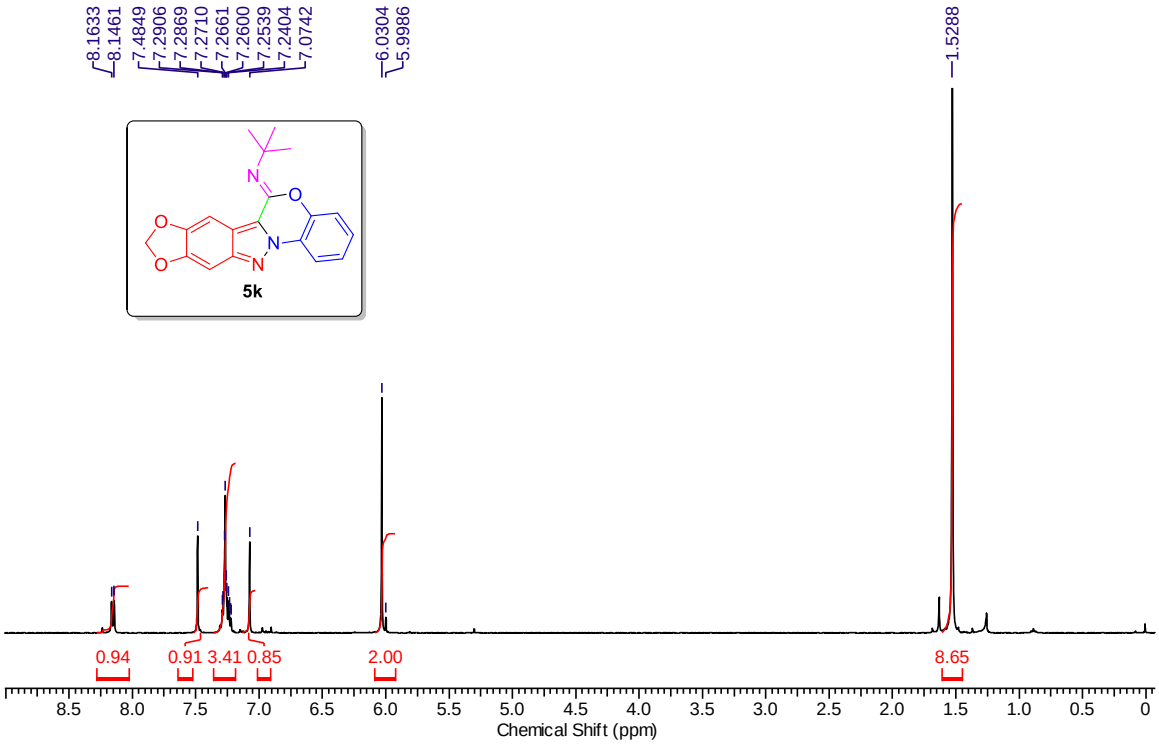
^{13}C NMR (100 MHz) spectrum of compound **5i** in $CDCl_3$



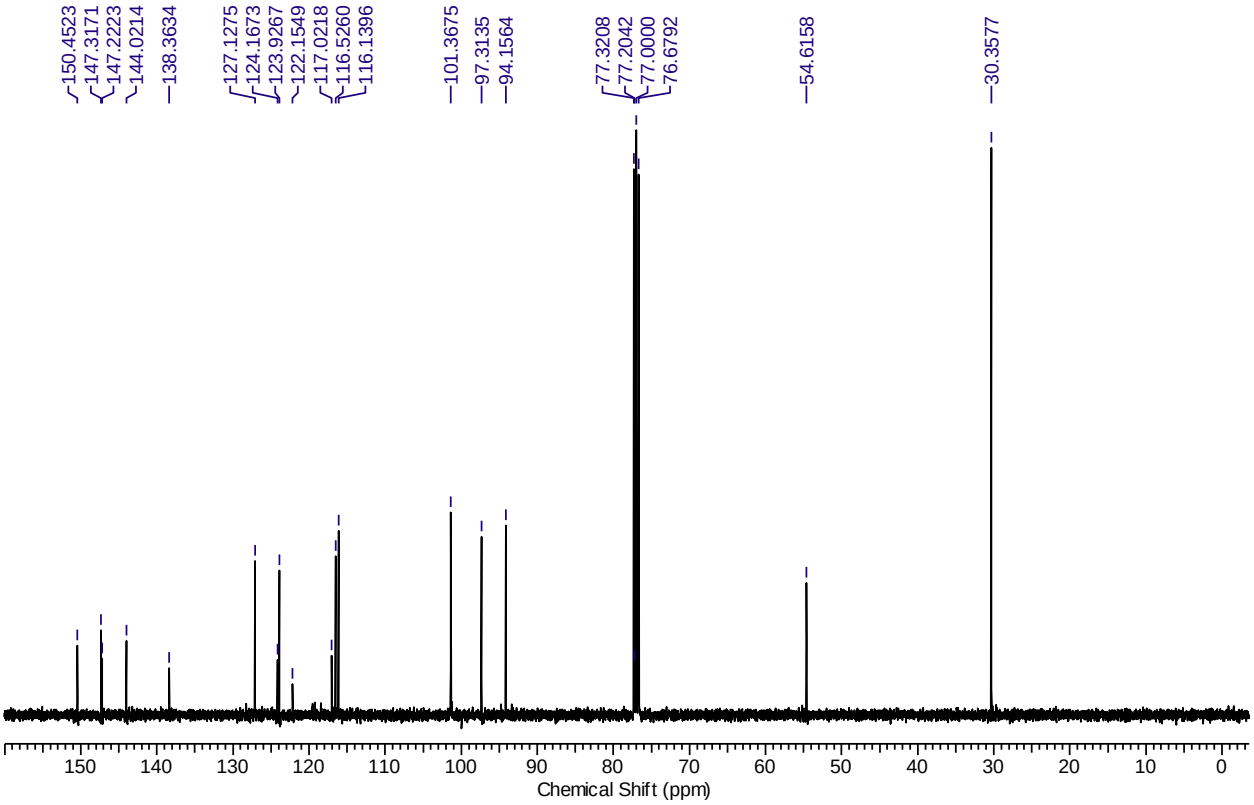
^{1}H NMR (400 MHz) spectrum of compound **5j** in $CDCl_3$



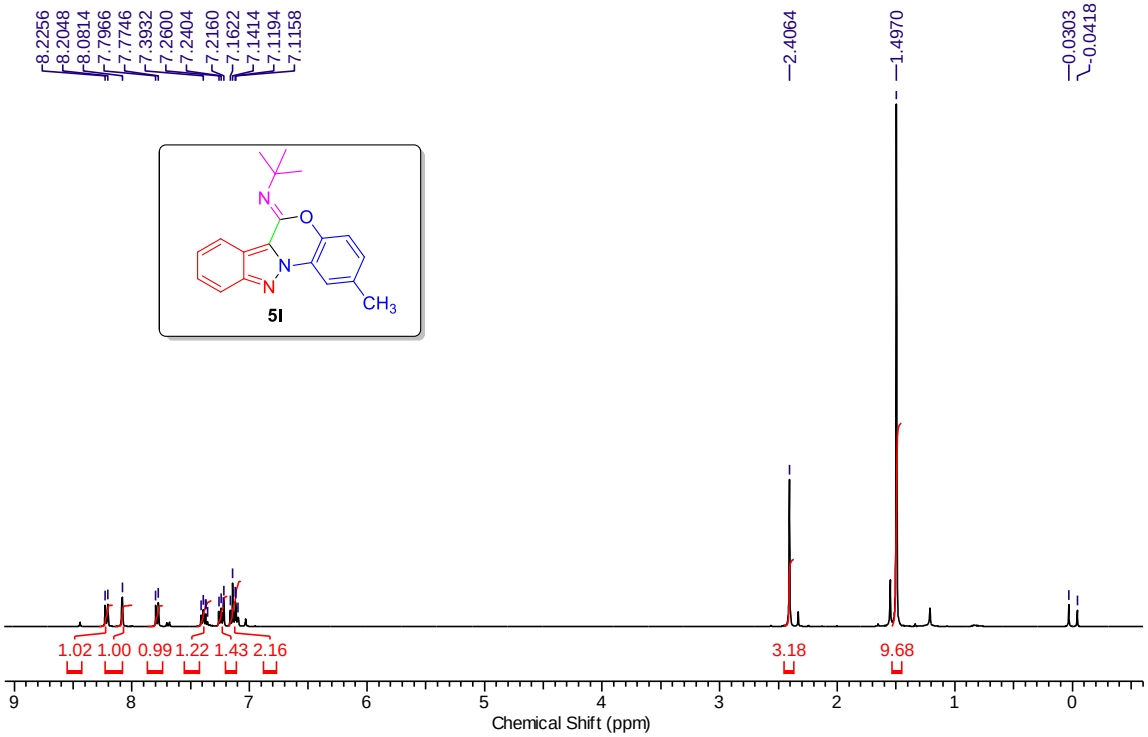
^{13}C NMR (100 MHz) spectrum of compound **5j** in $CDCl_3$



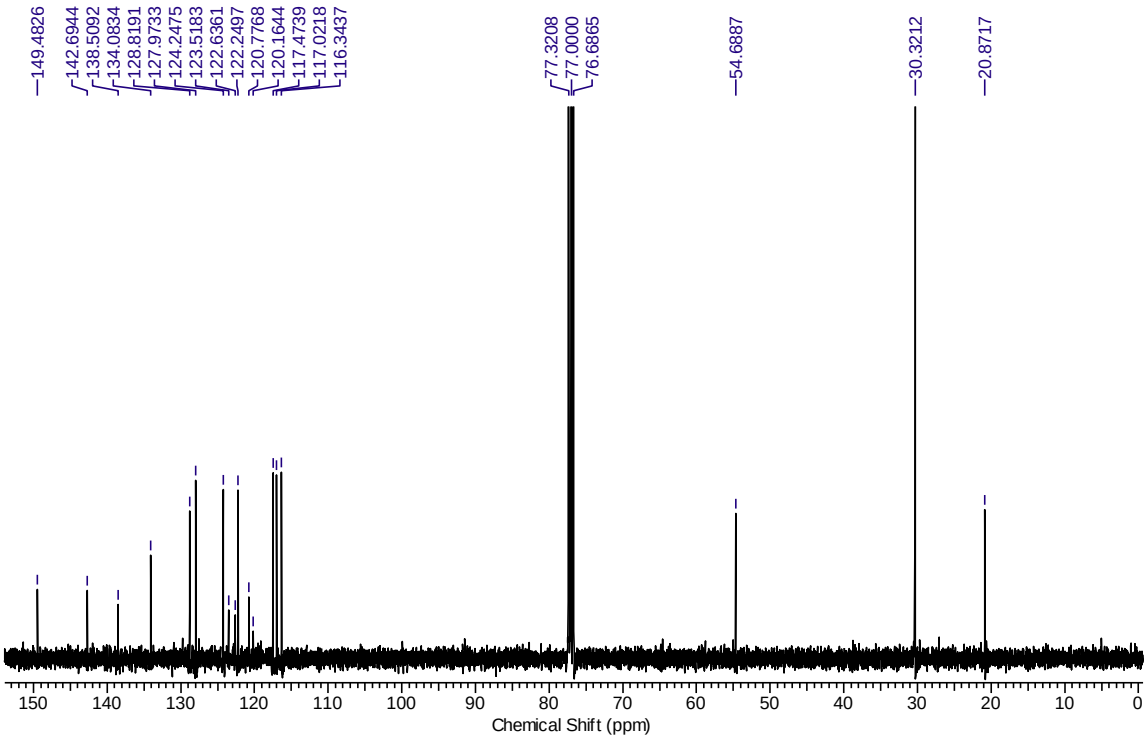
^{1}H NMR (400 MHz) spectrum of compound **5k** in $CDCl_3$



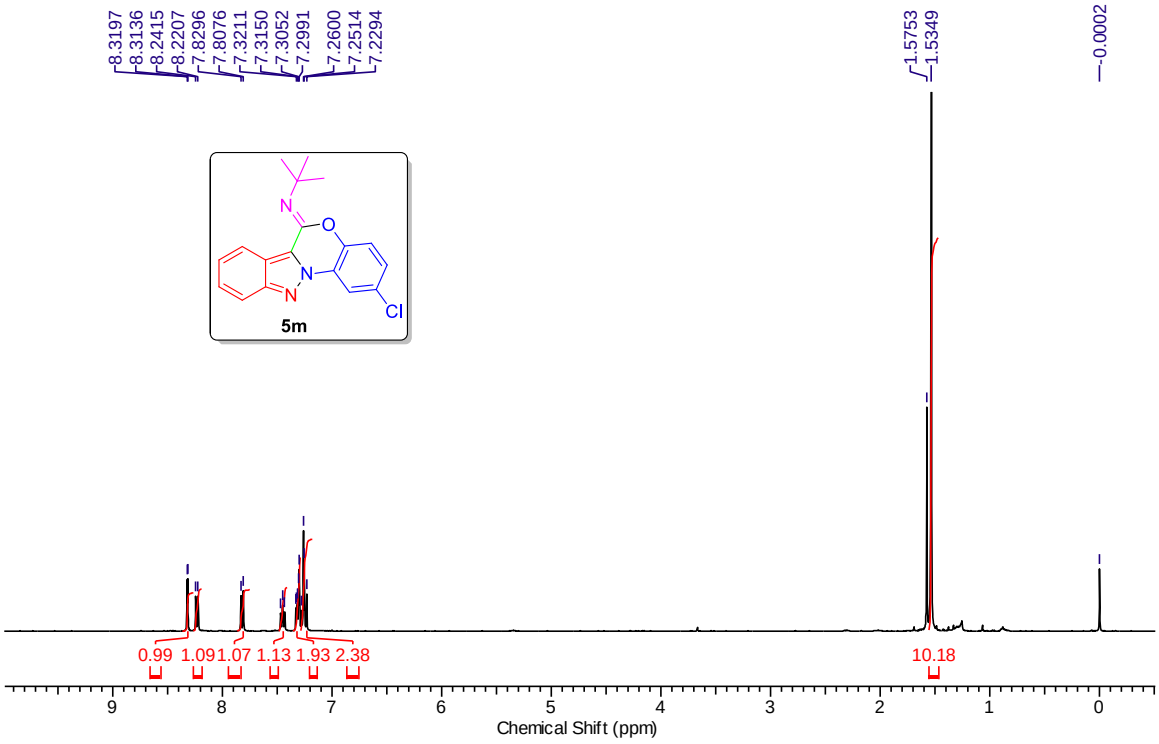
^{13}C NMR (100 MHz) spectrum of compound **5k** in $CDCl_3$



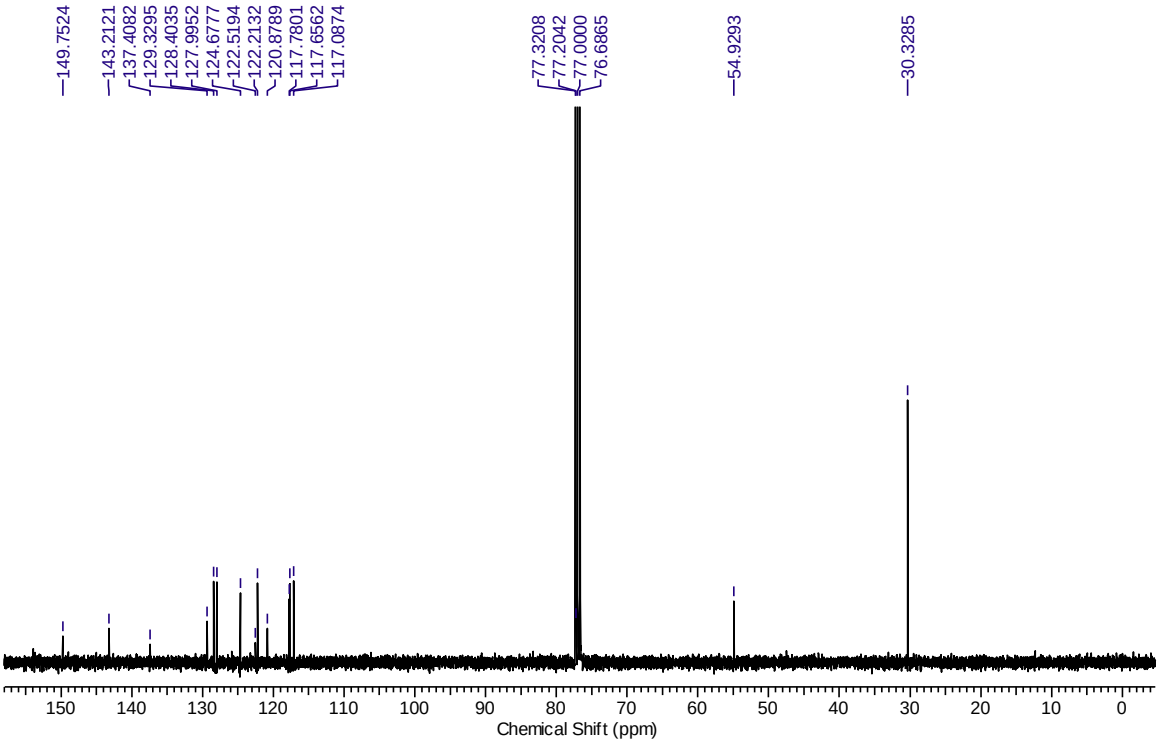
^{1}H NMR (400 MHz) spectrum of compound **5l** in $CDCl_3$



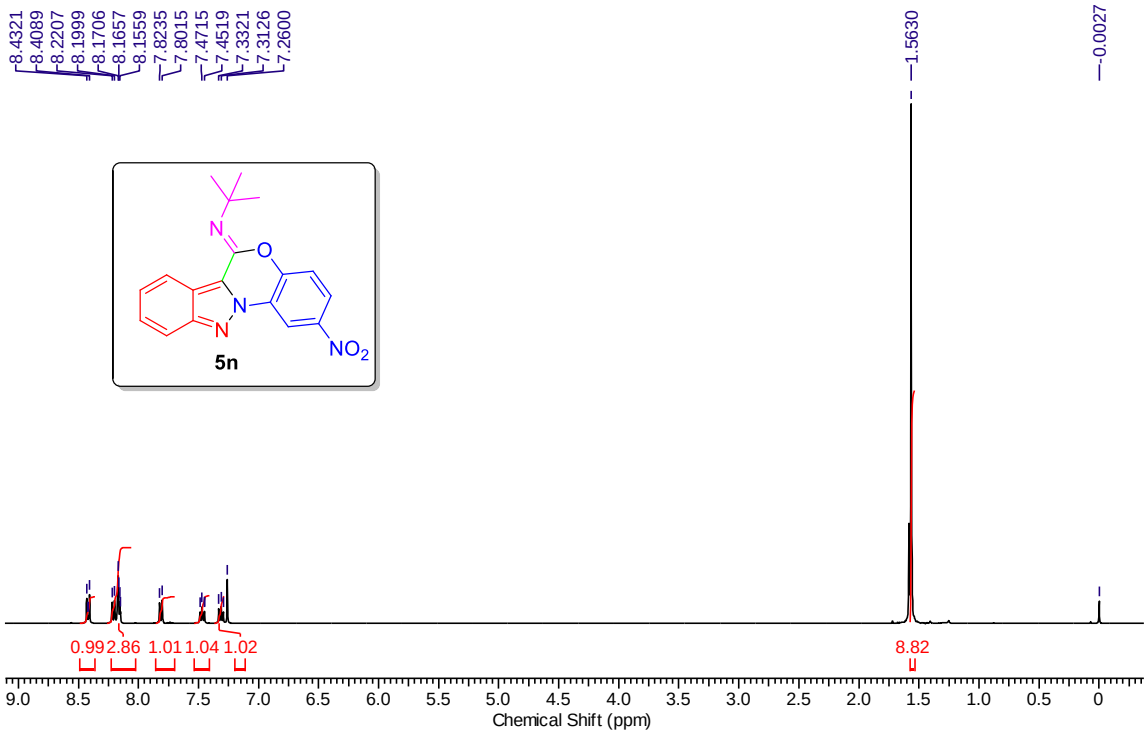
^{13}C NMR (100 MHz) spectrum of compound **5l** in $CDCl_3$



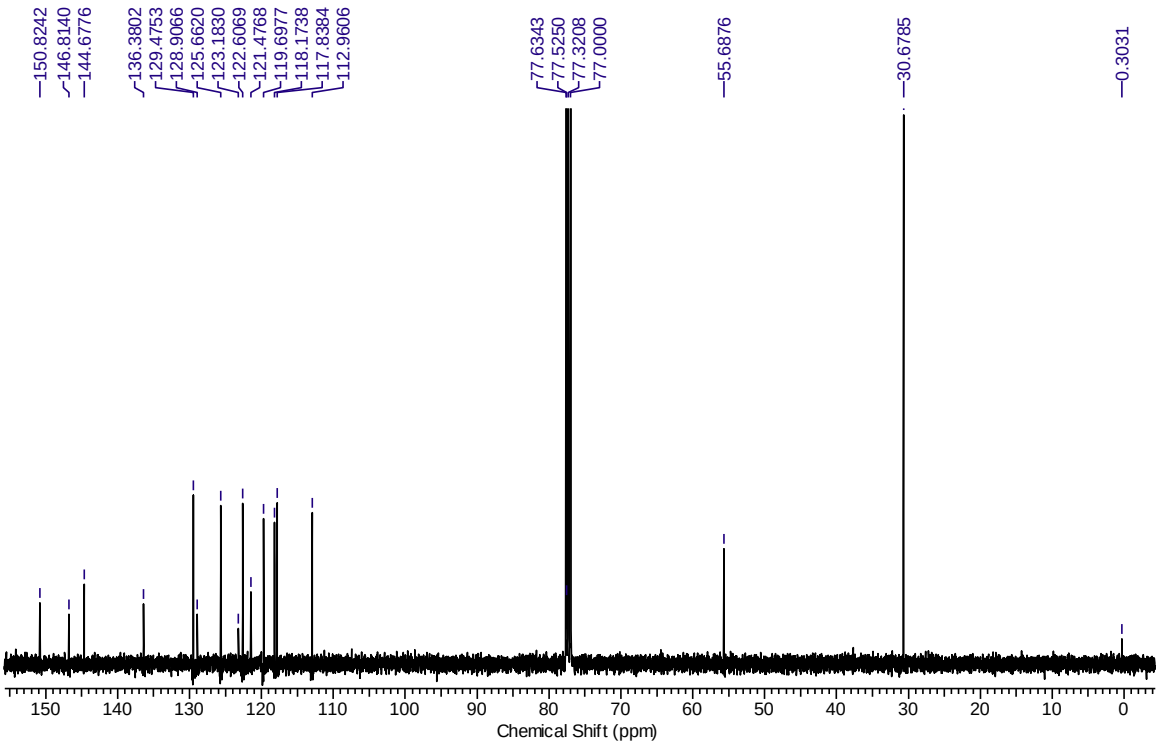
^{1}H NMR (400 MHz) spectrum of compound **5m** in $CDCl_3$



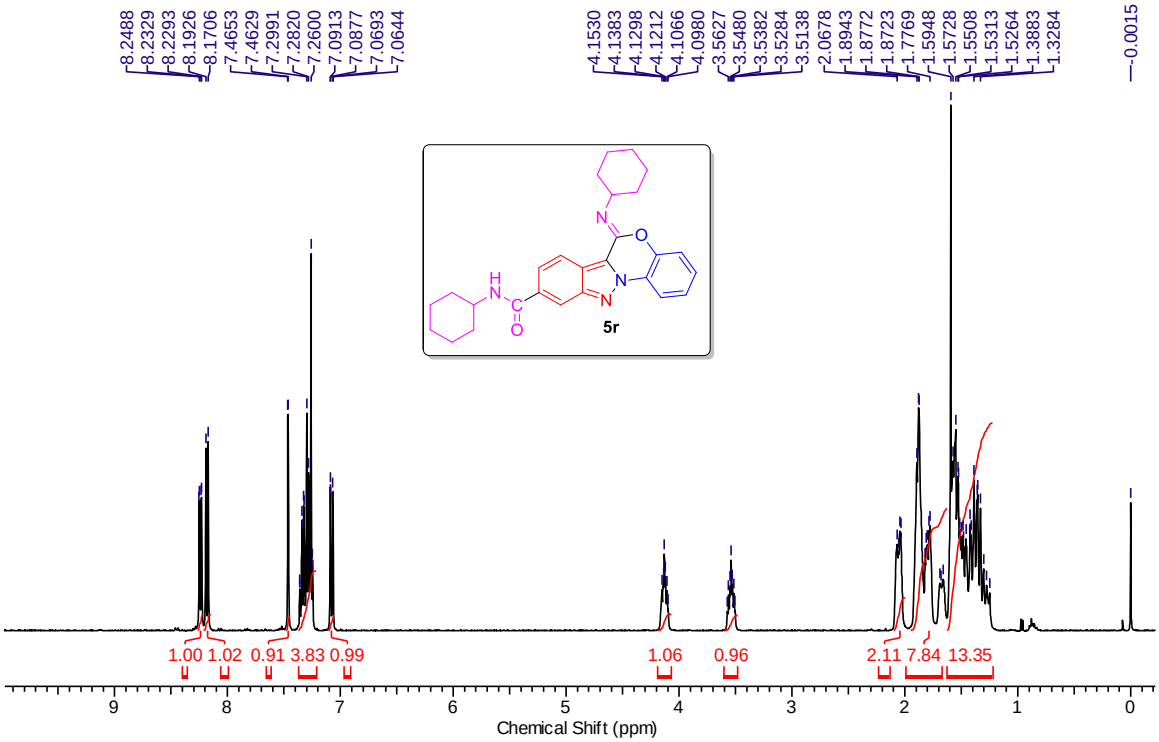
^{13}C NMR (100 MHz) spectrum of compound **5m** in $CDCl_3$



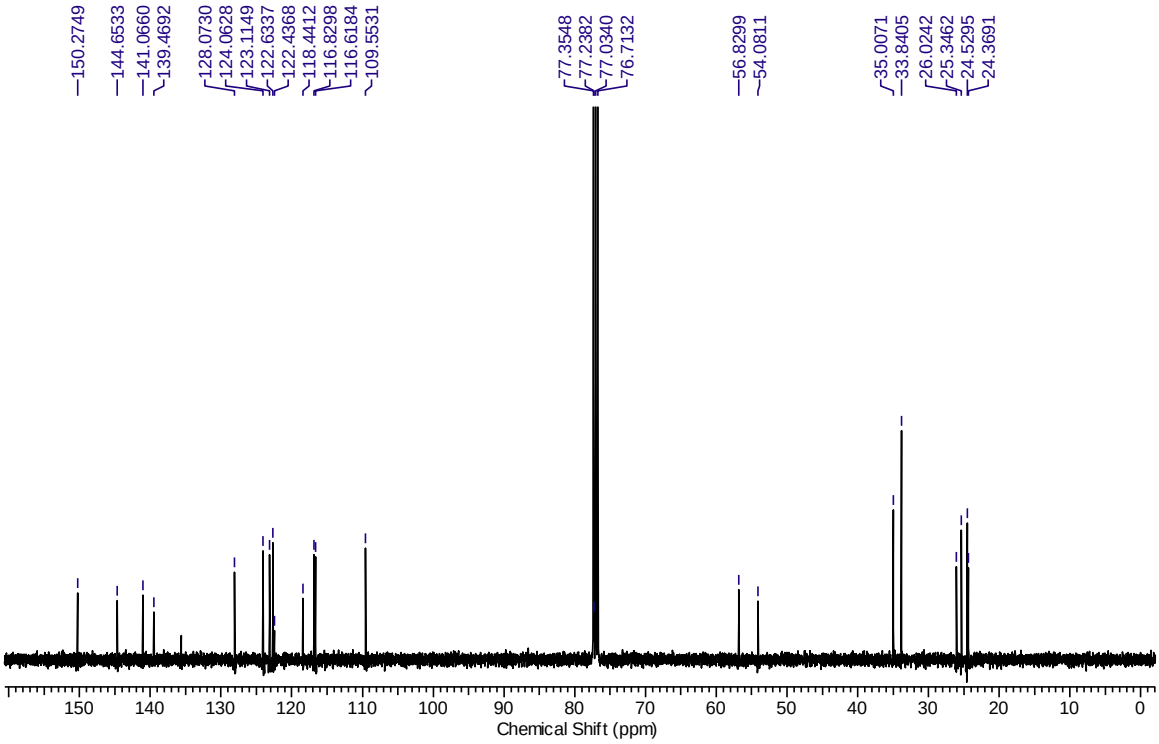
^{1}H NMR (400 MHz) spectrum of compound **5n** in $CDCl_3$



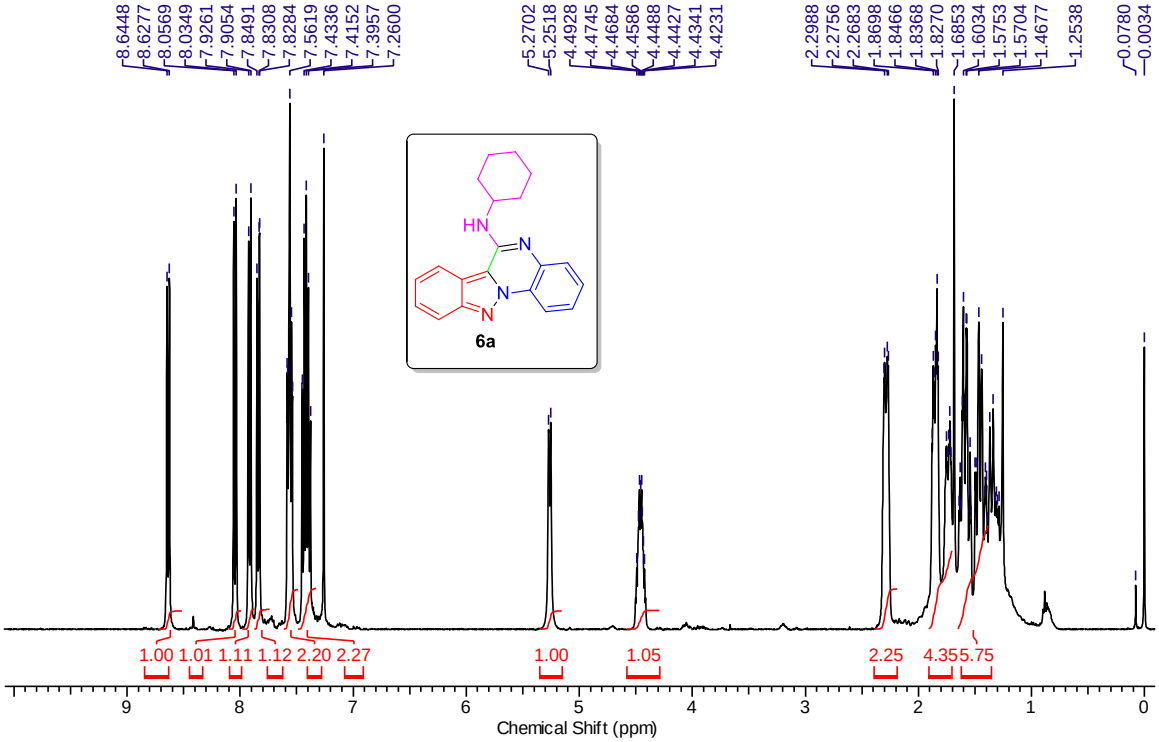
^{13}C NMR (100 MHz) spectrum of compound **5n** in $CDCl_3$



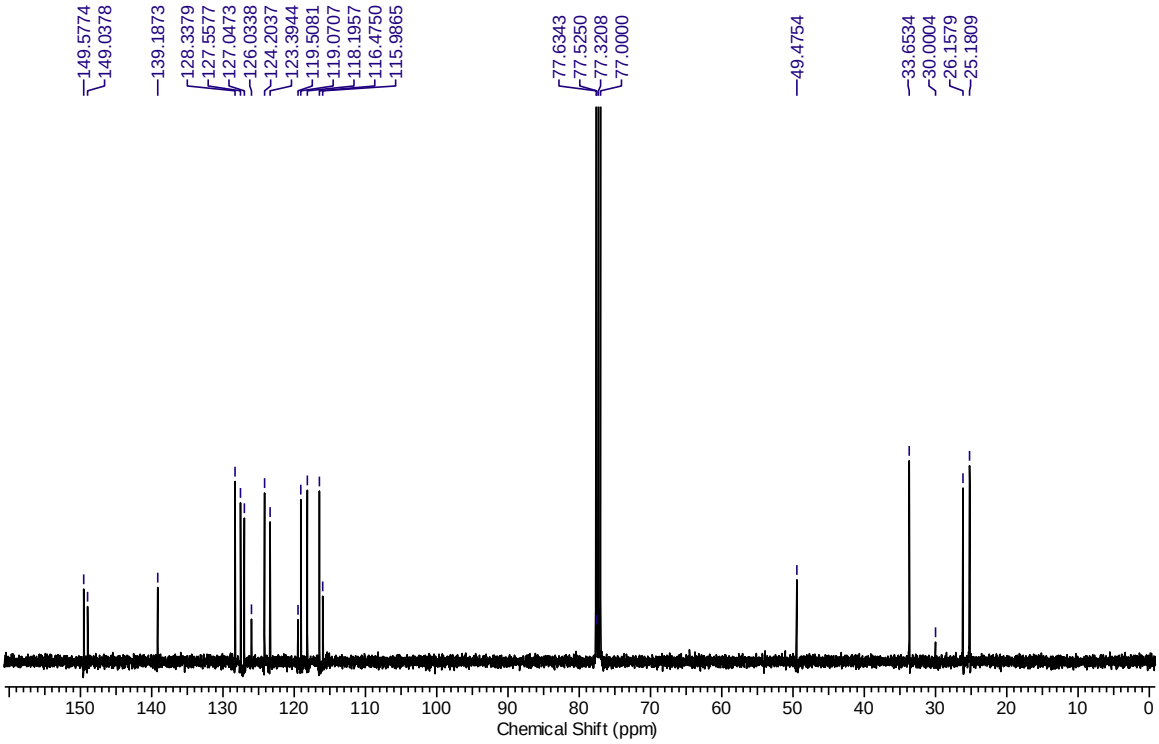
^{1}H NMR (400 MHz) spectrum of compound **5r** in $CDCl_3$



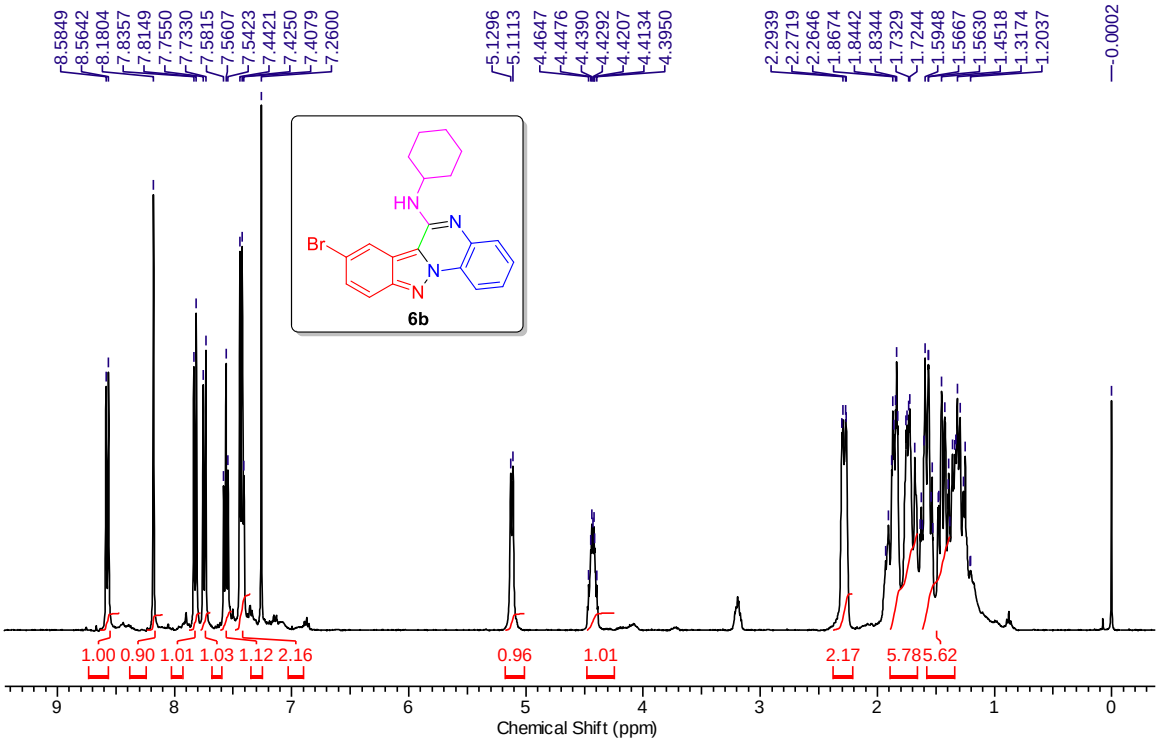
^{13}C NMR (100 MHz) spectrum of compound **5r** in $CDCl_3$



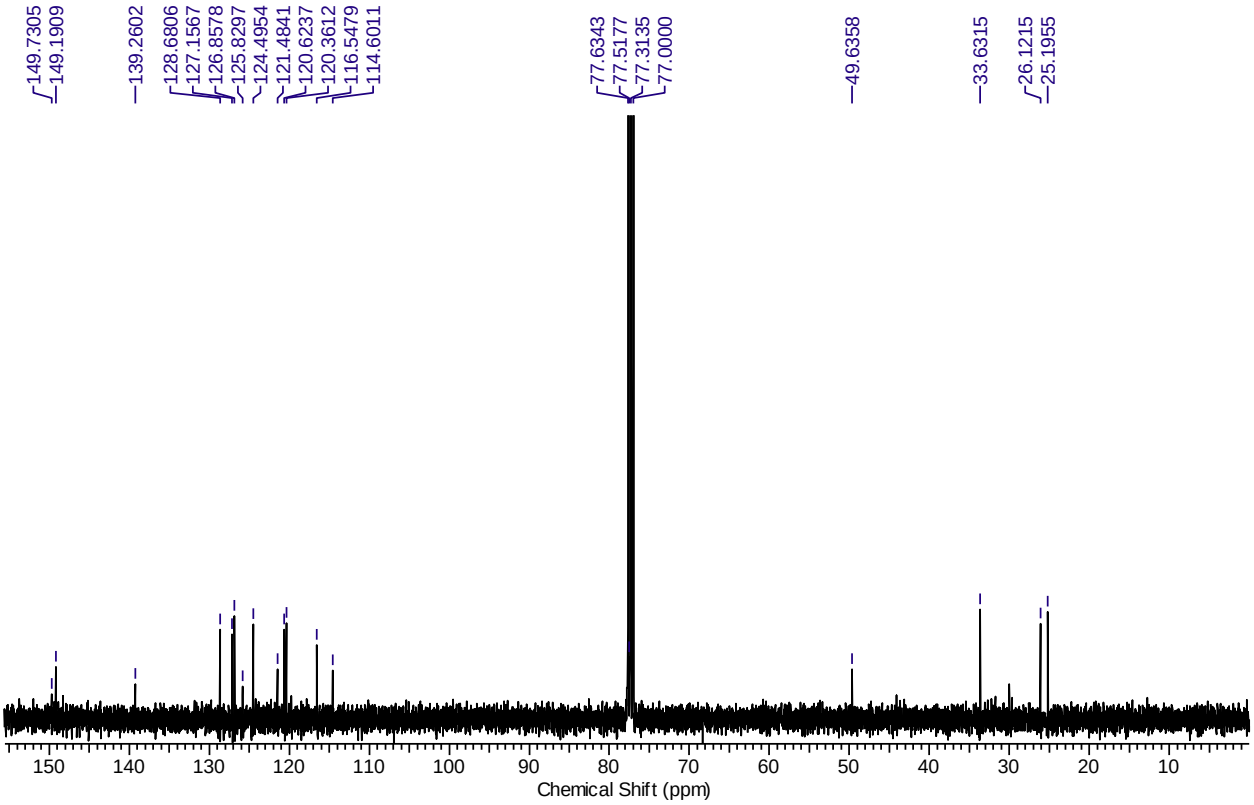
^{1}H NMR (400 MHz) spectrum of compound **6a** in $CDCl_3$



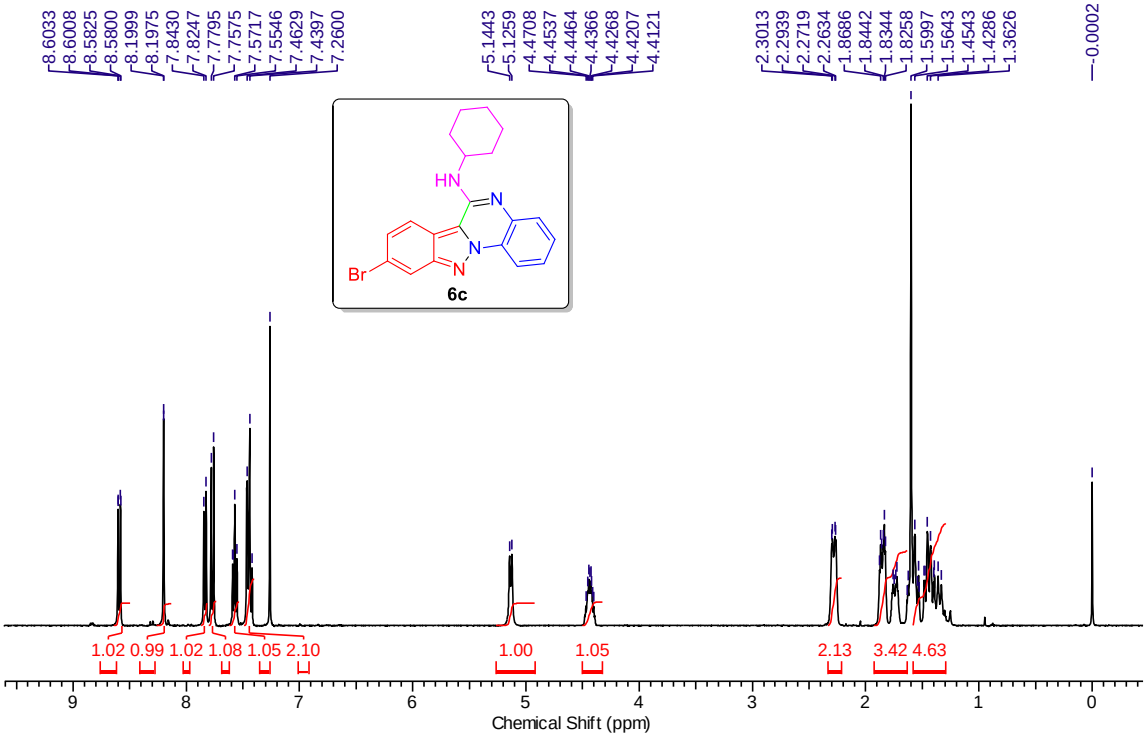
^{13}C NMR (100 MHz) spectrum of compound **6a** in $CDCl_3$



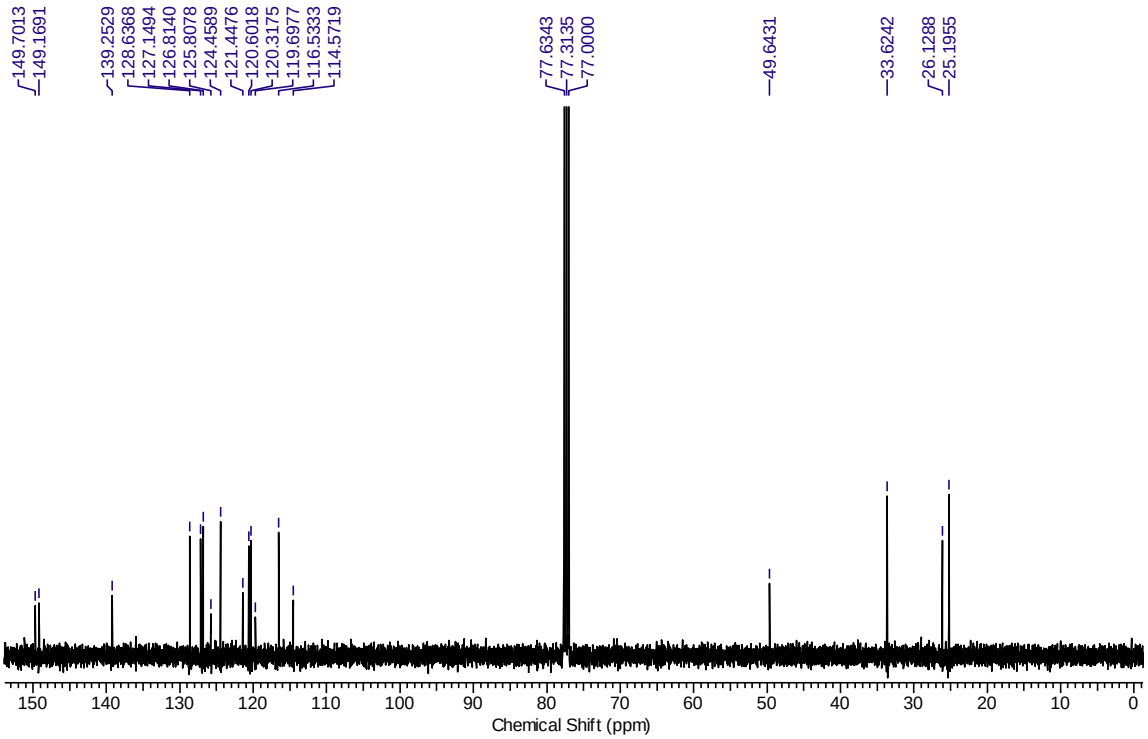
^{1}H NMR (400 MHz) spectrum of compound **6b** in $CDCl_3$



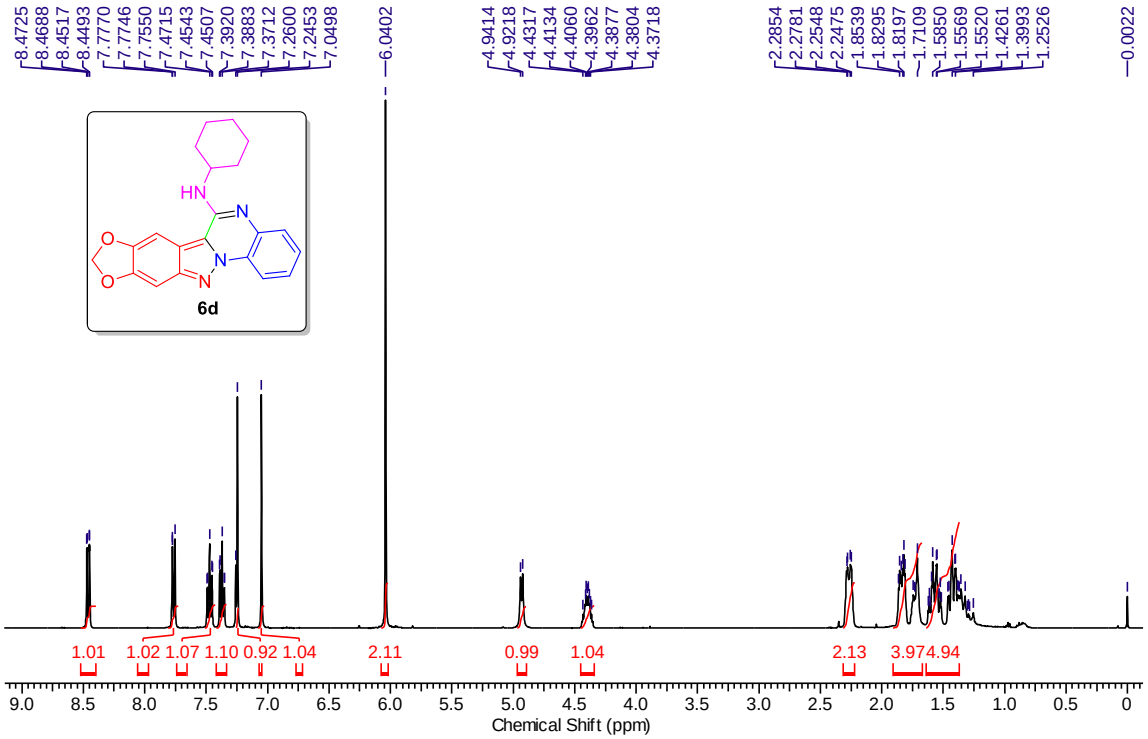
^{13}C NMR (100 MHz) spectrum of compound **6b** in $CDCl_3$



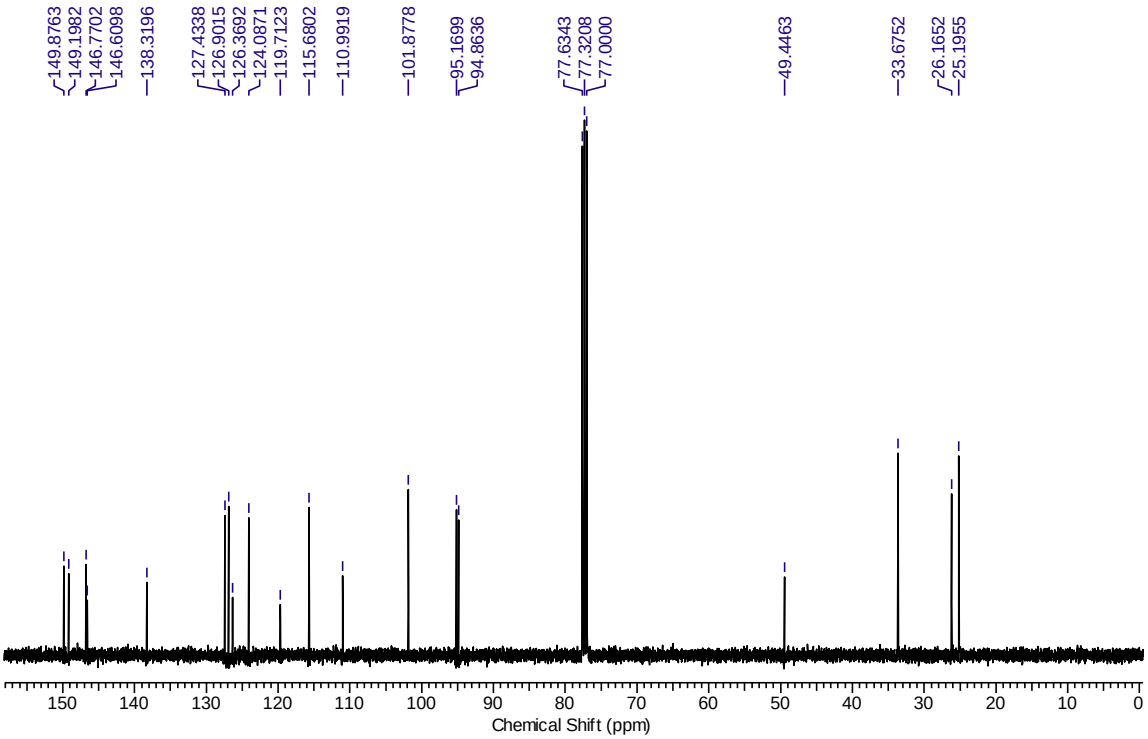
^{1}H NMR (400 MHz) spectrum of compound **6c** in $CDCl_3$



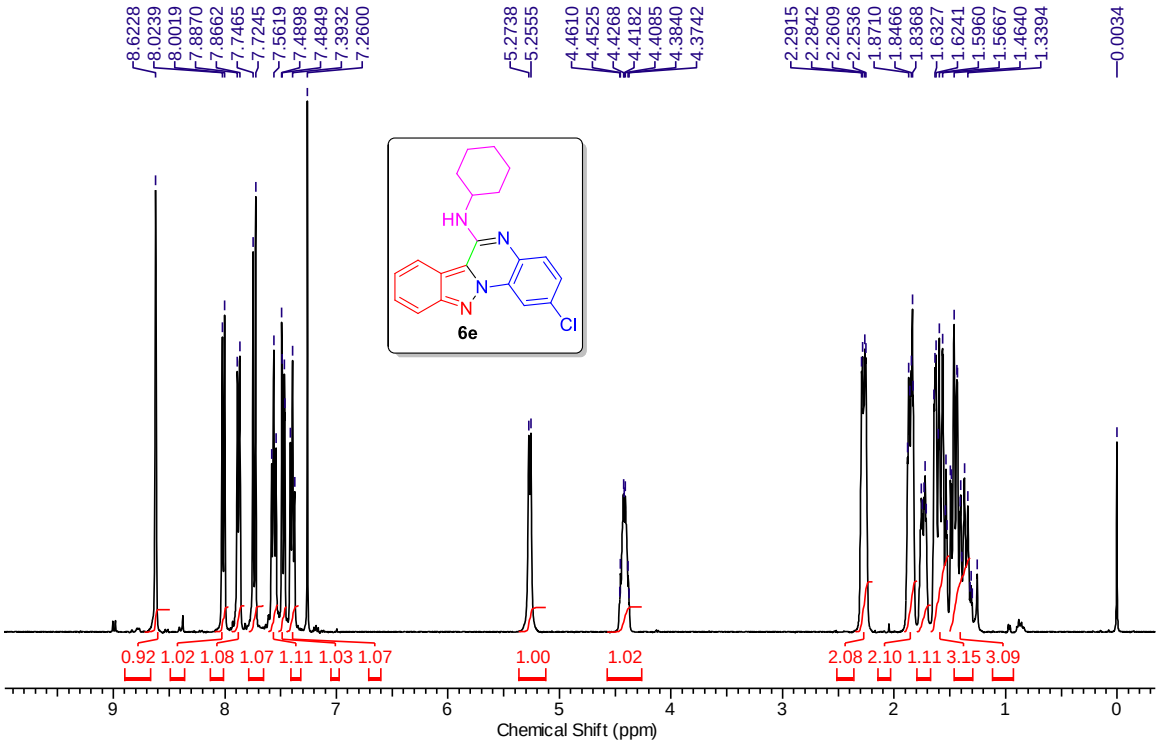
^{13}C NMR (100 MHz) spectrum of compound **6c** in $CDCl_3$



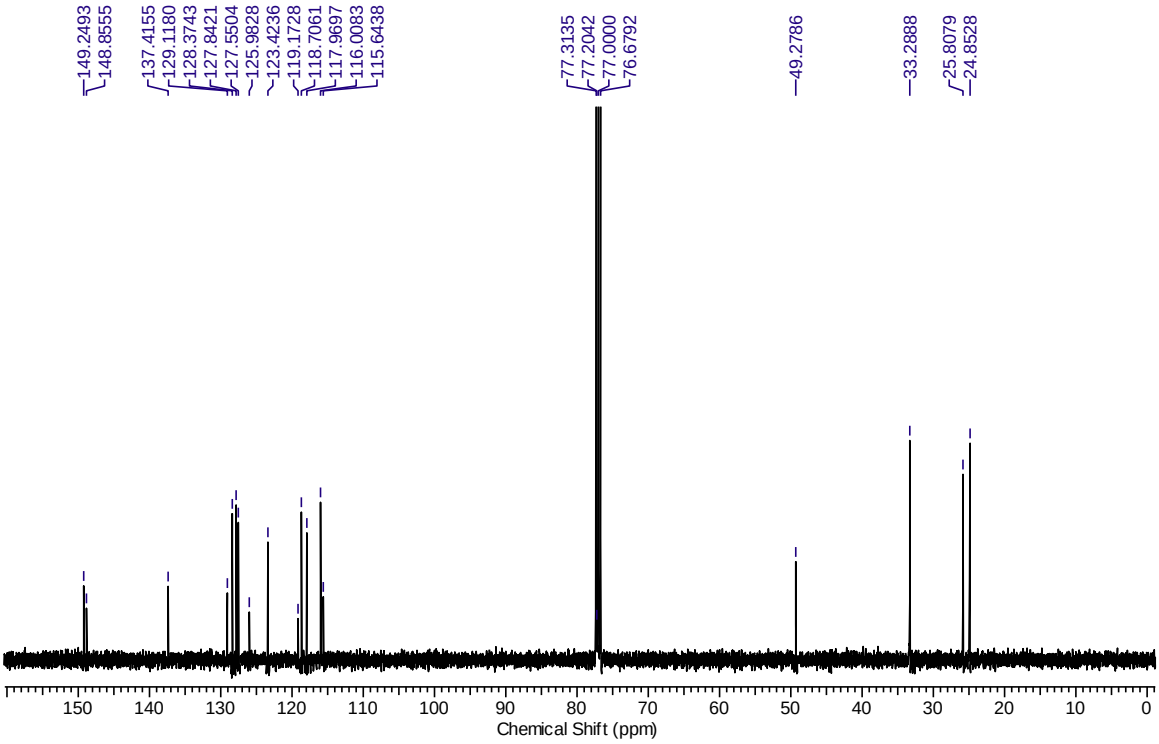
^{1}H NMR (400 MHz) spectrum of compound **6d** in $CDCl_3$



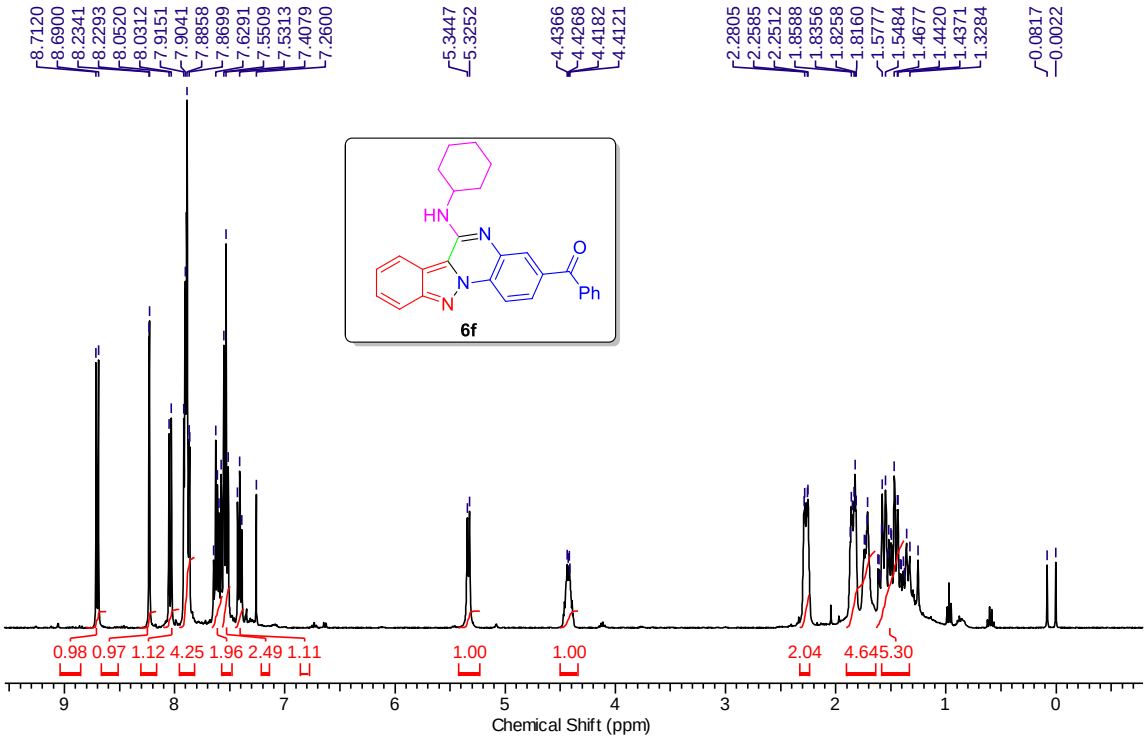
^{13}C NMR (100 MHz) spectrum of compound **6d** in $CDCl_3$



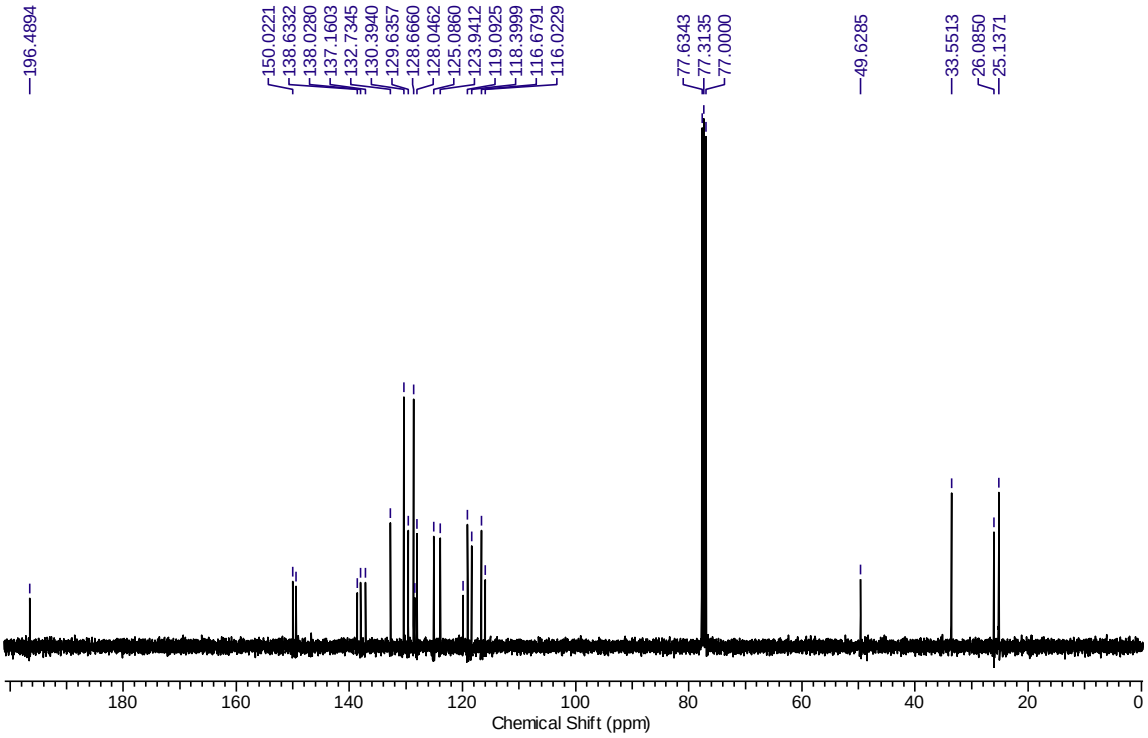
^{1}H NMR (400 MHz) spectrum of compound **6e** in $CDCl_3$



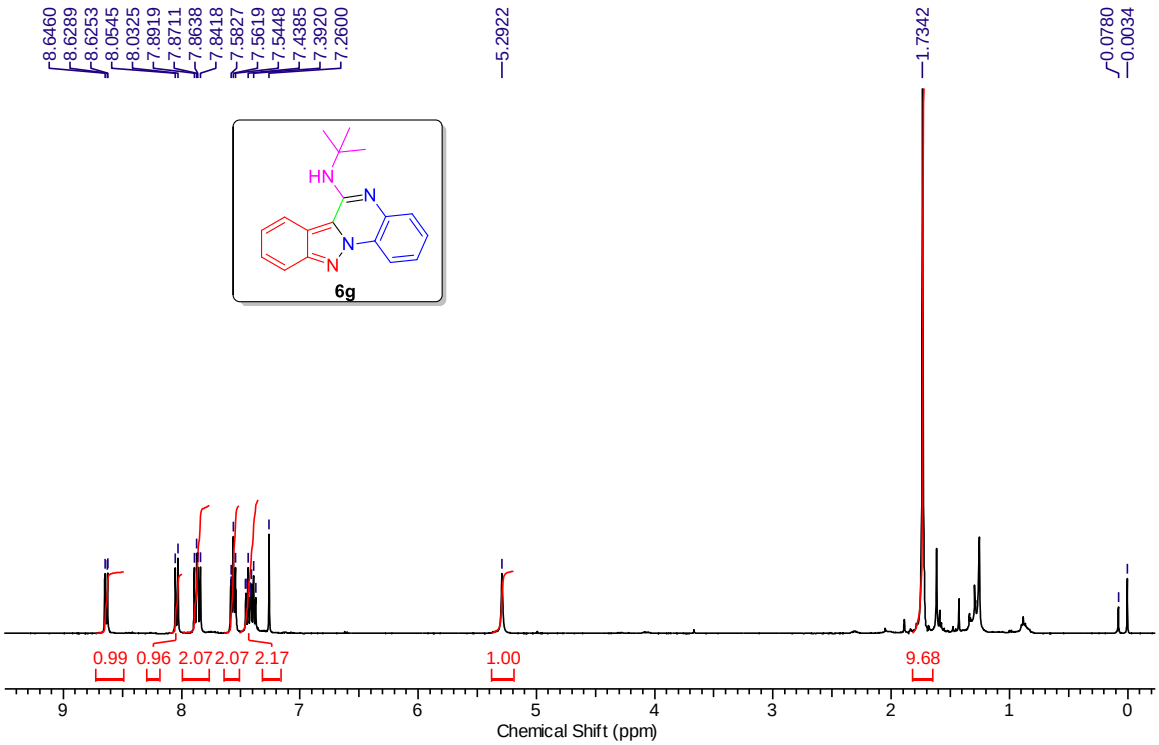
^{13}C NMR (100 MHz) spectrum of compound **6e** in $CDCl_3$



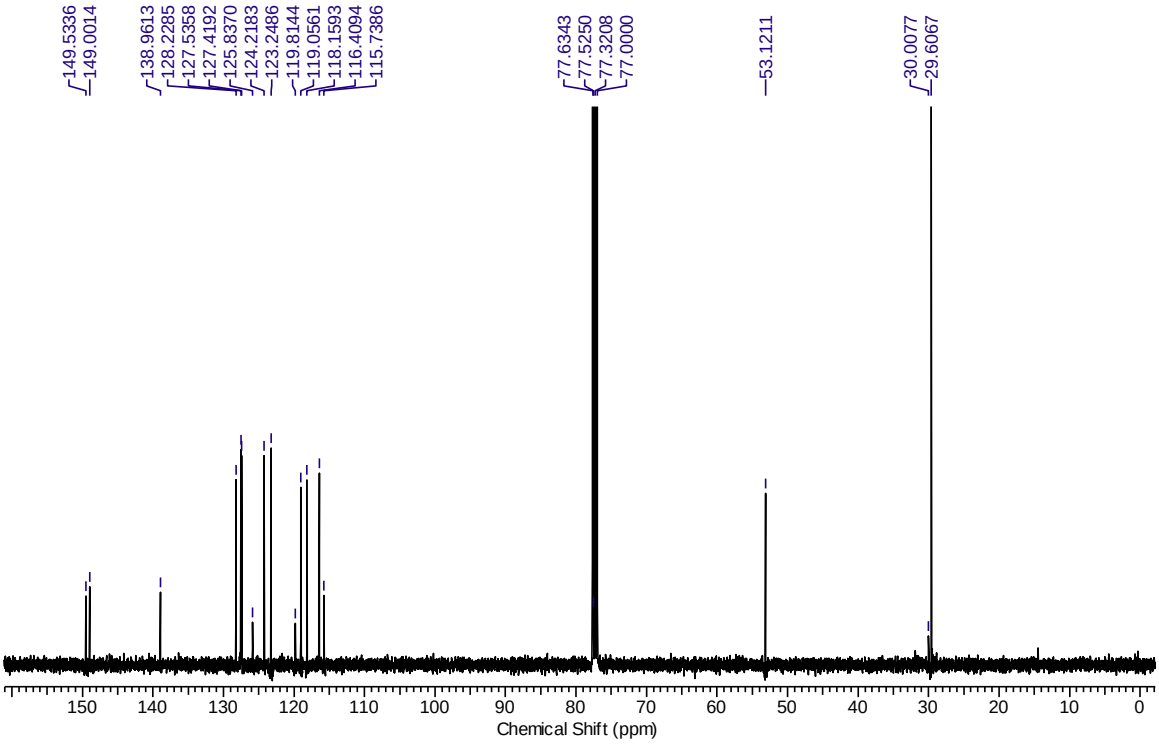
^{1}H NMR (400 MHz) spectrum of compound **6f** in $CDCl_3$



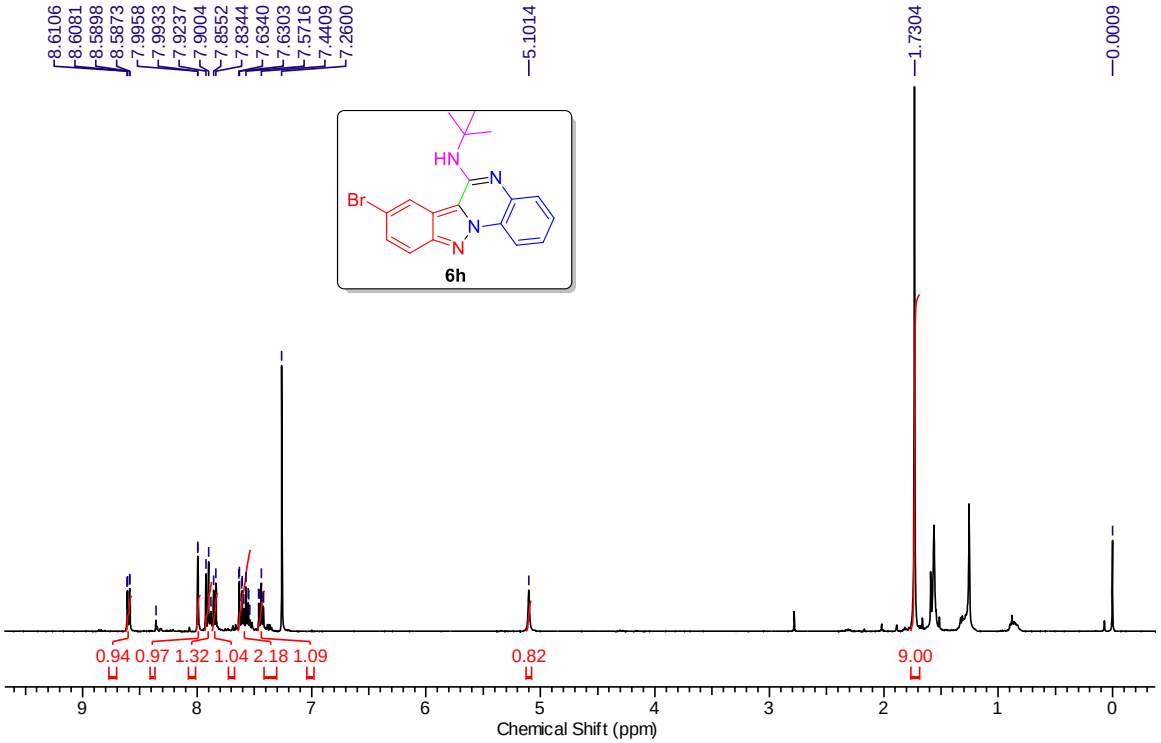
^{13}C NMR (100 MHz) spectrum of compound **6f** in $CDCl_3$



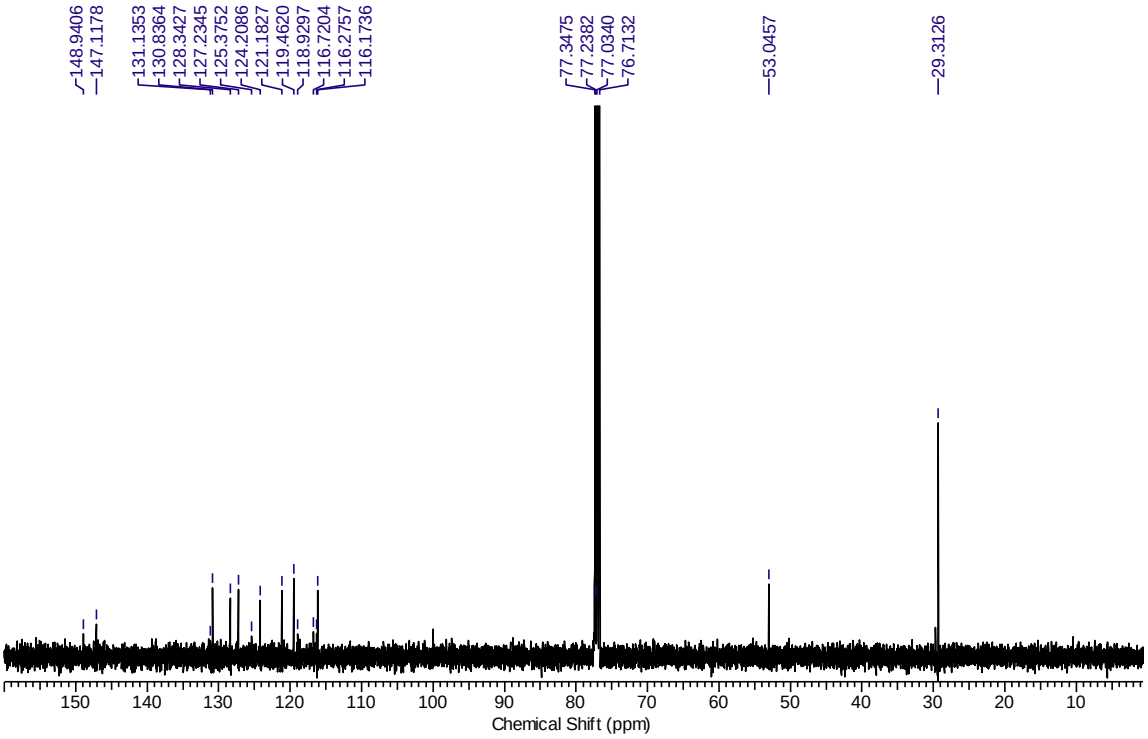
^{1}H NMR (400 MHz) spectrum of compound **6g** in $CDCl_3$



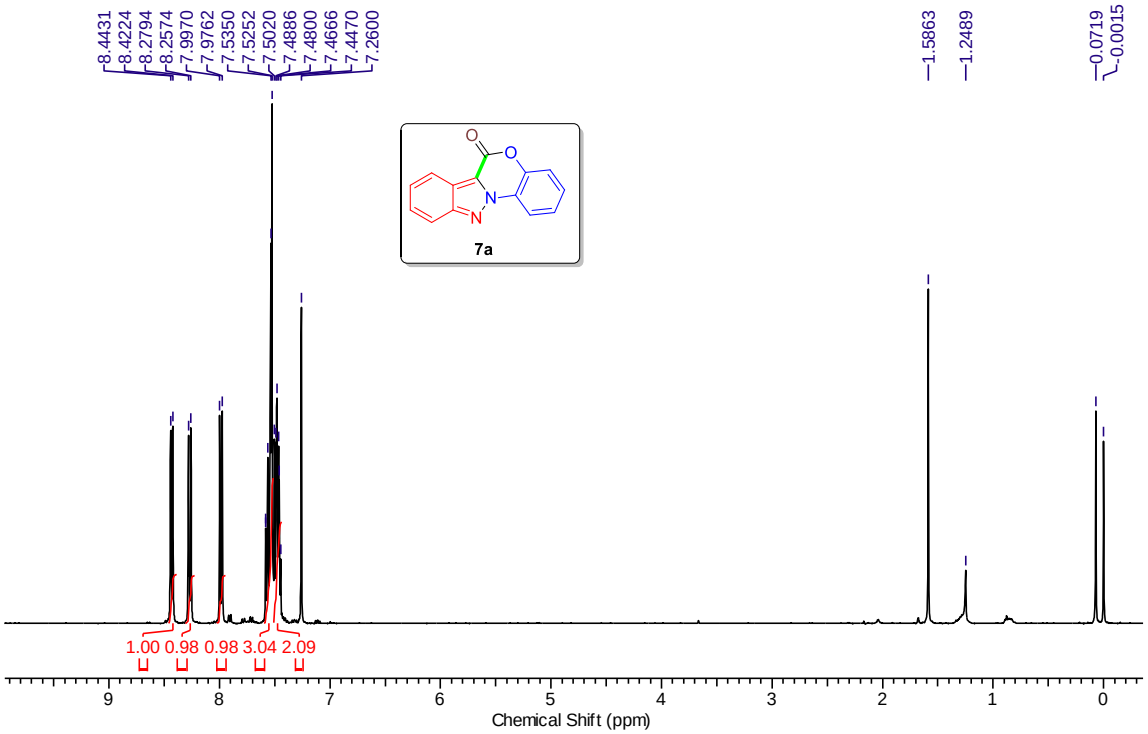
^{13}C NMR (100 MHz) spectrum of compound 6**g** in $CDCl_3$



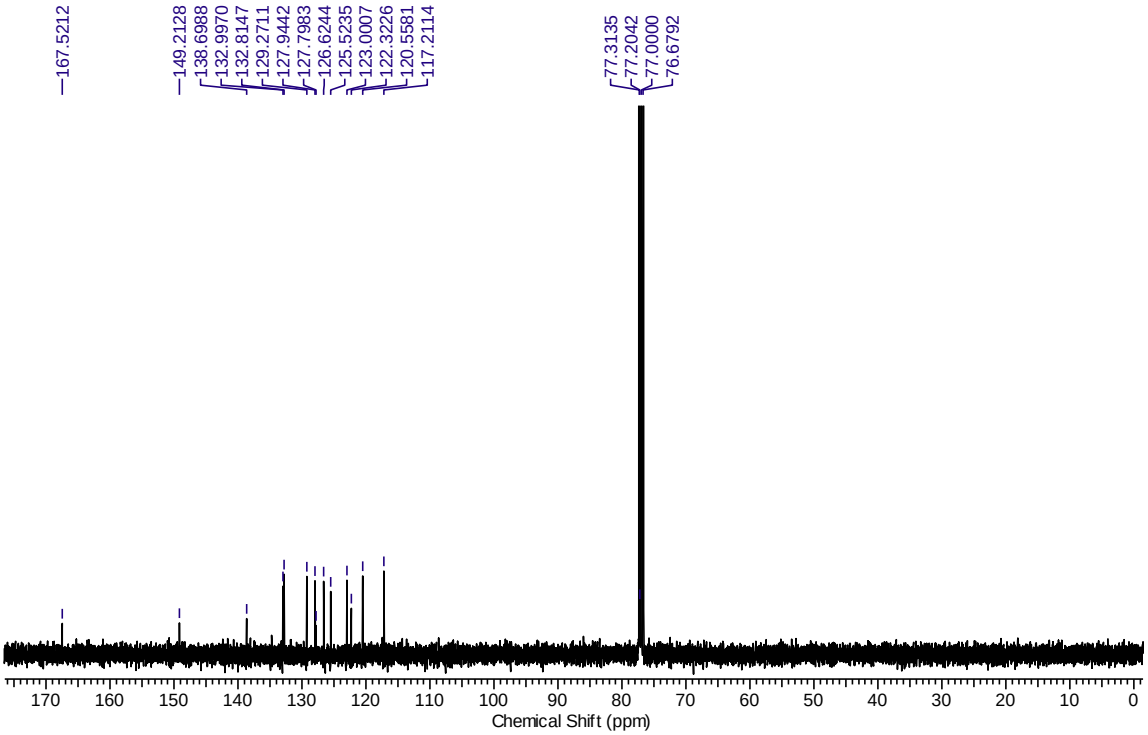
^{1}H NMR (400 MHz) spectrum of compound **6h** in $CDCl_3$



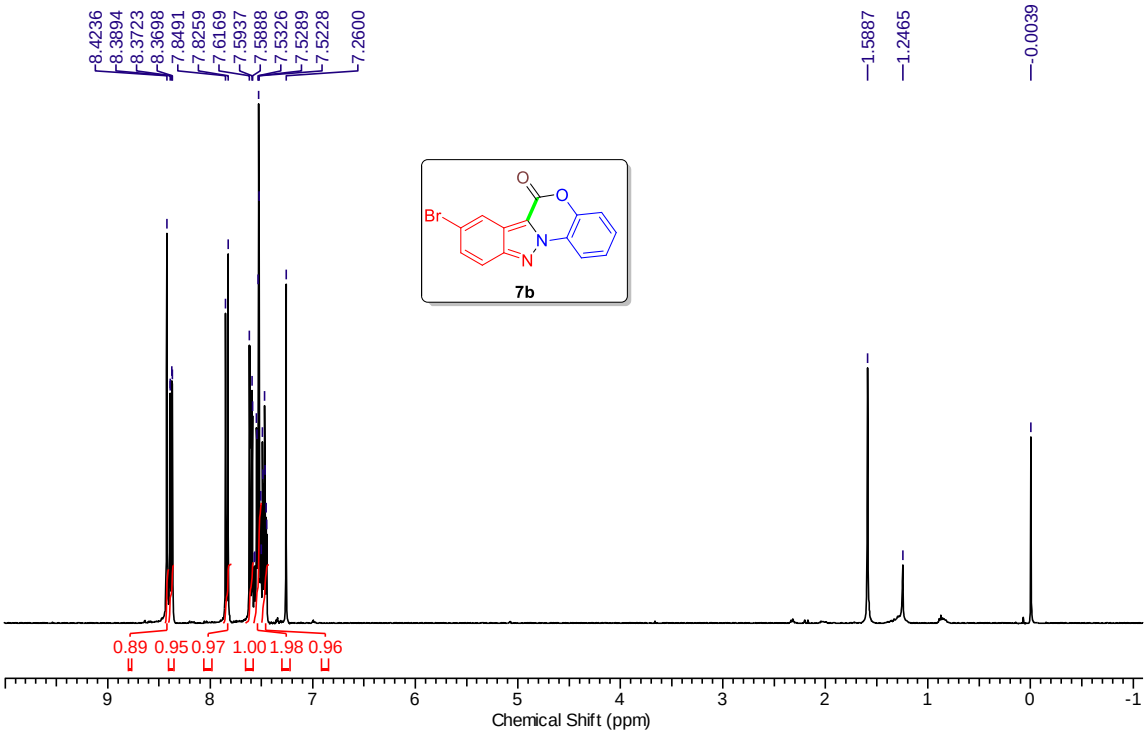
^{13}C NMR (100 MHz) spectrum of compound **6h** in $CDCl_3$



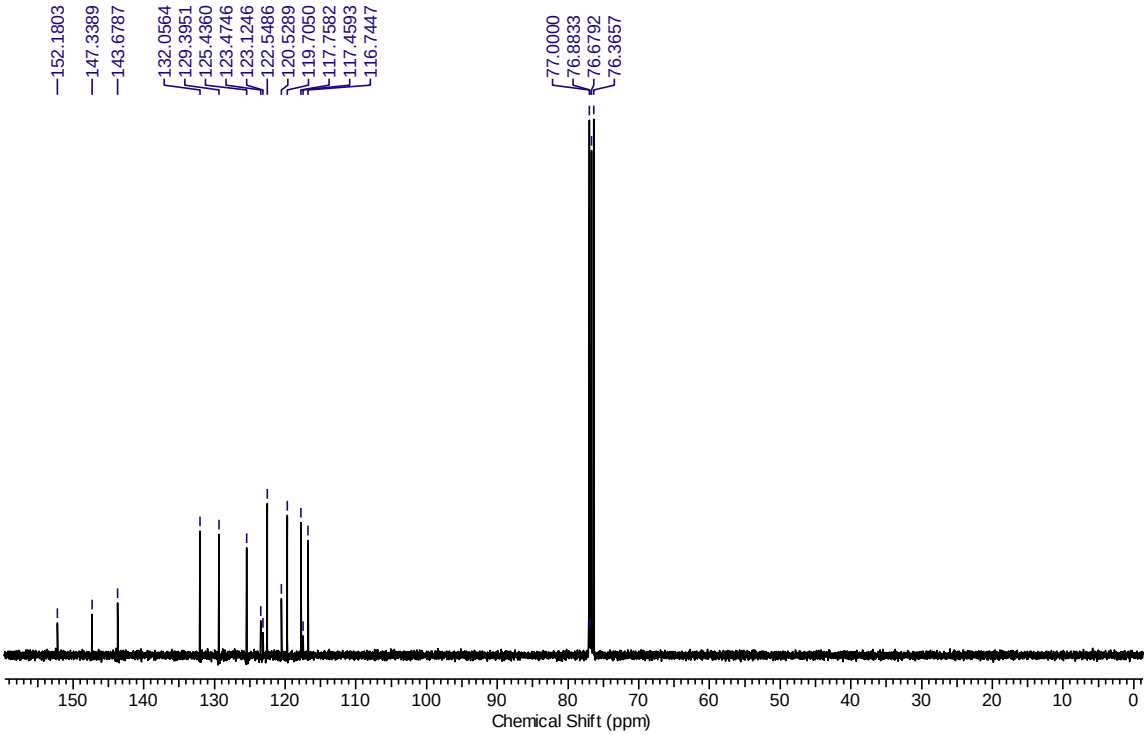
^{1}H NMR (400 MHz) spectrum of compound **7a** in $CDCl_3$



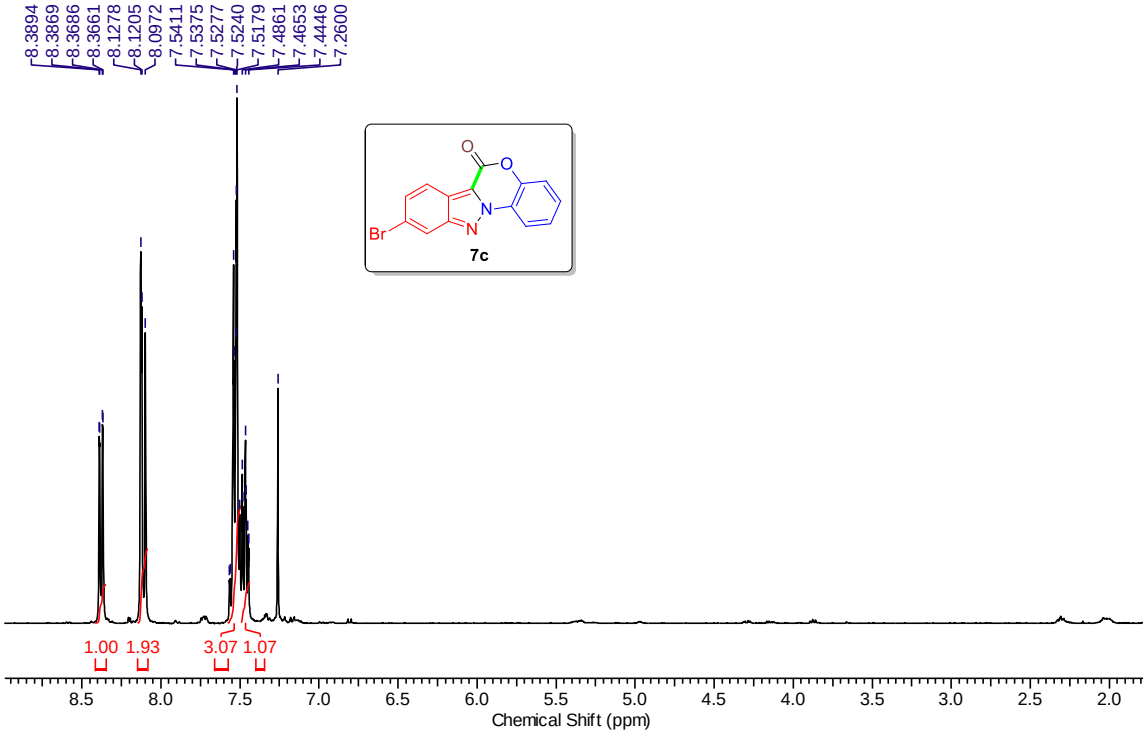
^{13}C NMR (100 MHz) spectrum of compound **7a** in $CDCl_3$



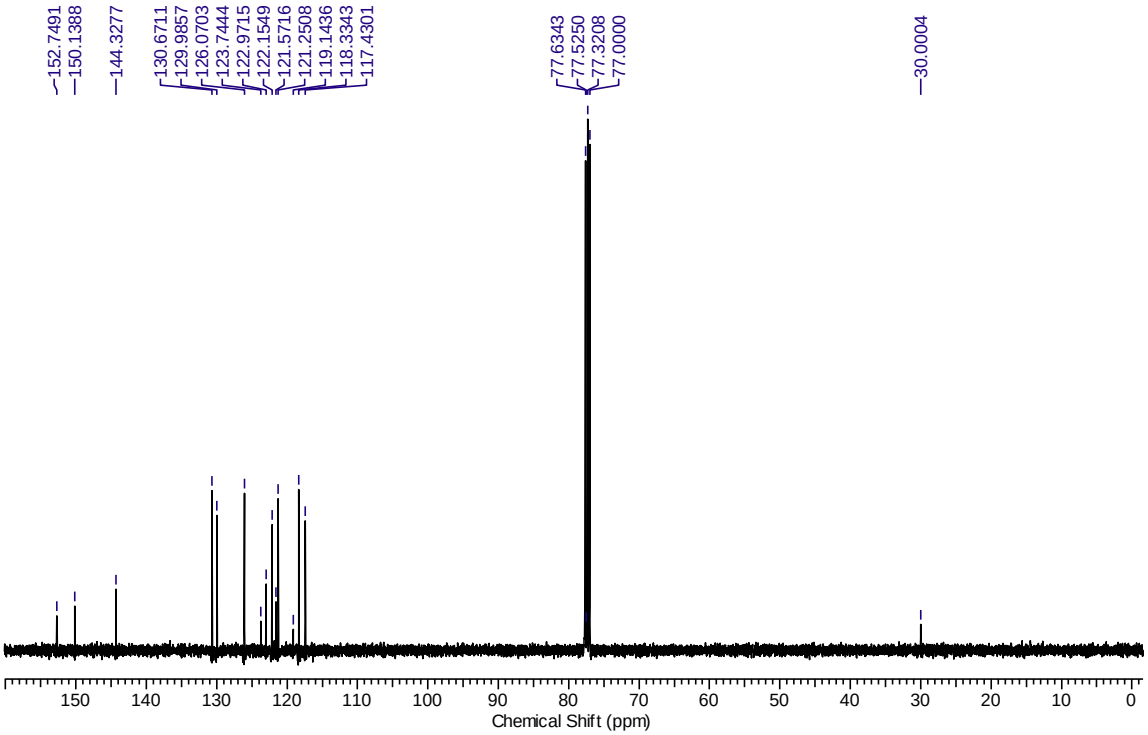
^{1}H NMR (400 MHz) spectrum of compound **7b** in $CDCl_3$



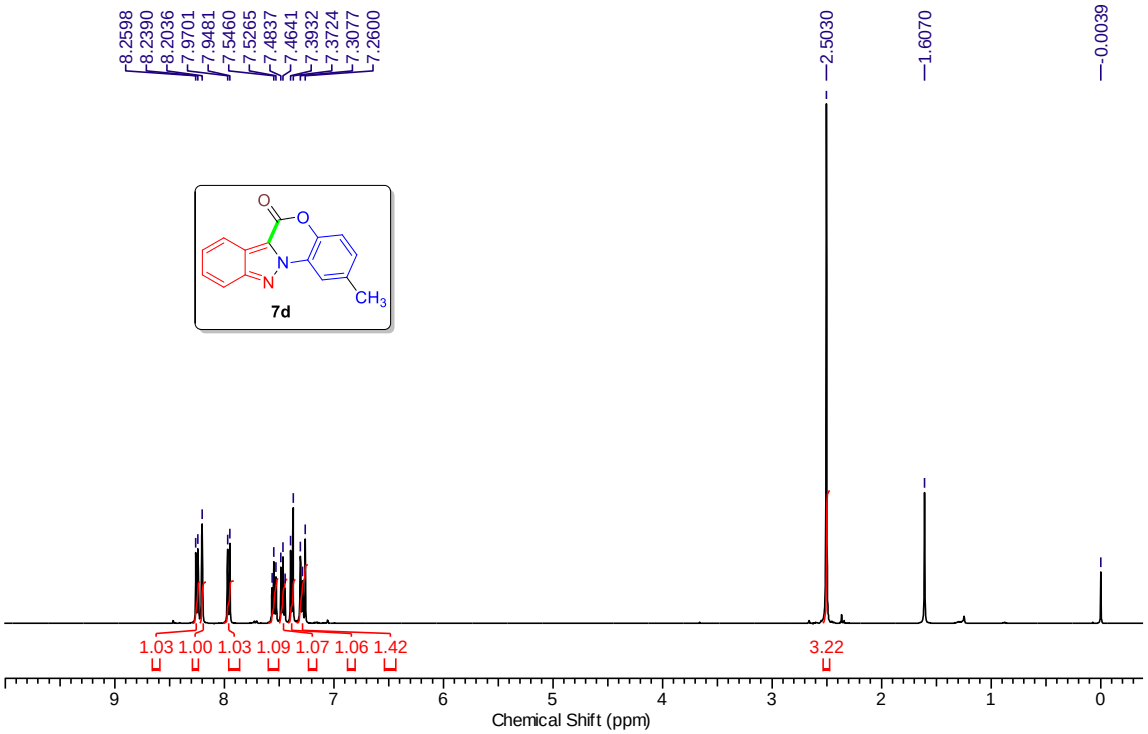
^{13}C NMR (100 MHz) spectrum of compound **7b** in $CDCl_3$



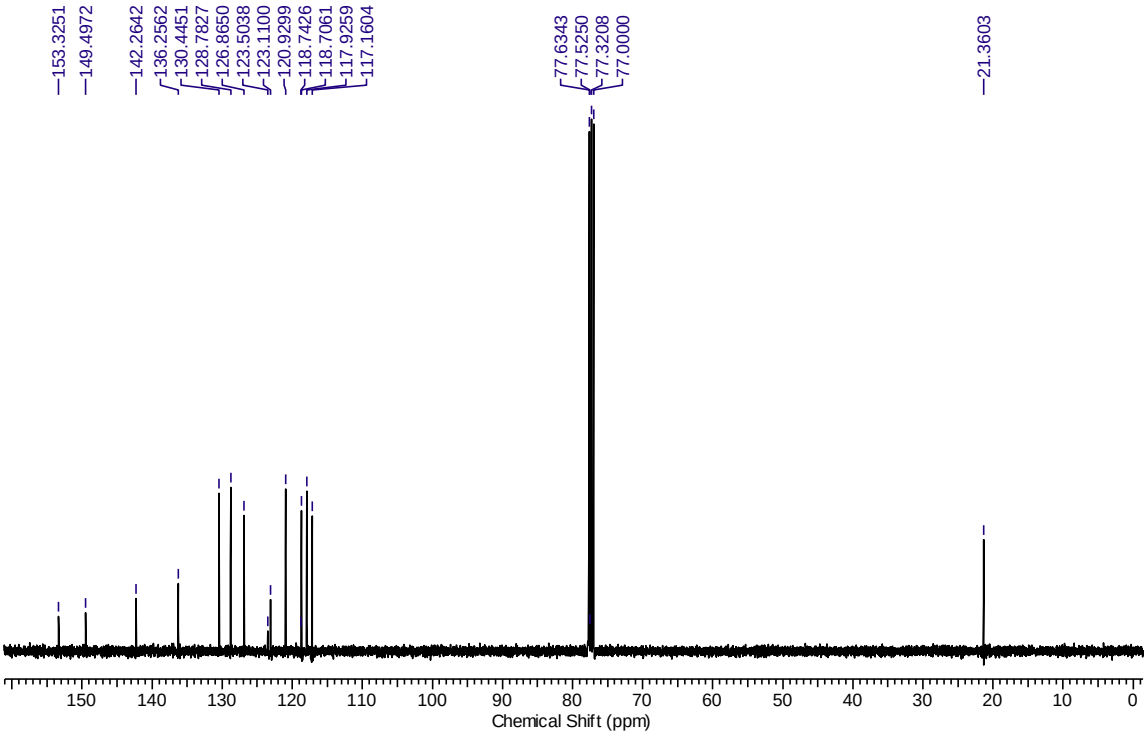
^{1}H NMR (400 MHz) spectrum of compound **7c** in $CDCl_3$



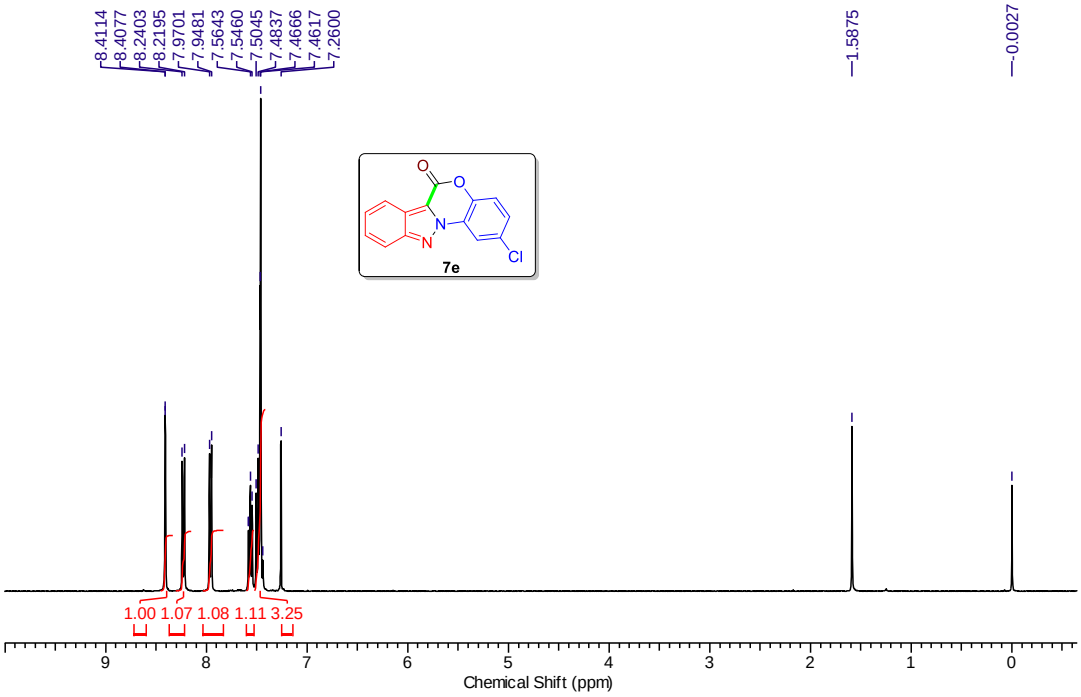
^{13}C NMR (100 MHz) spectrum of compound **7c** in $CDCl_3$



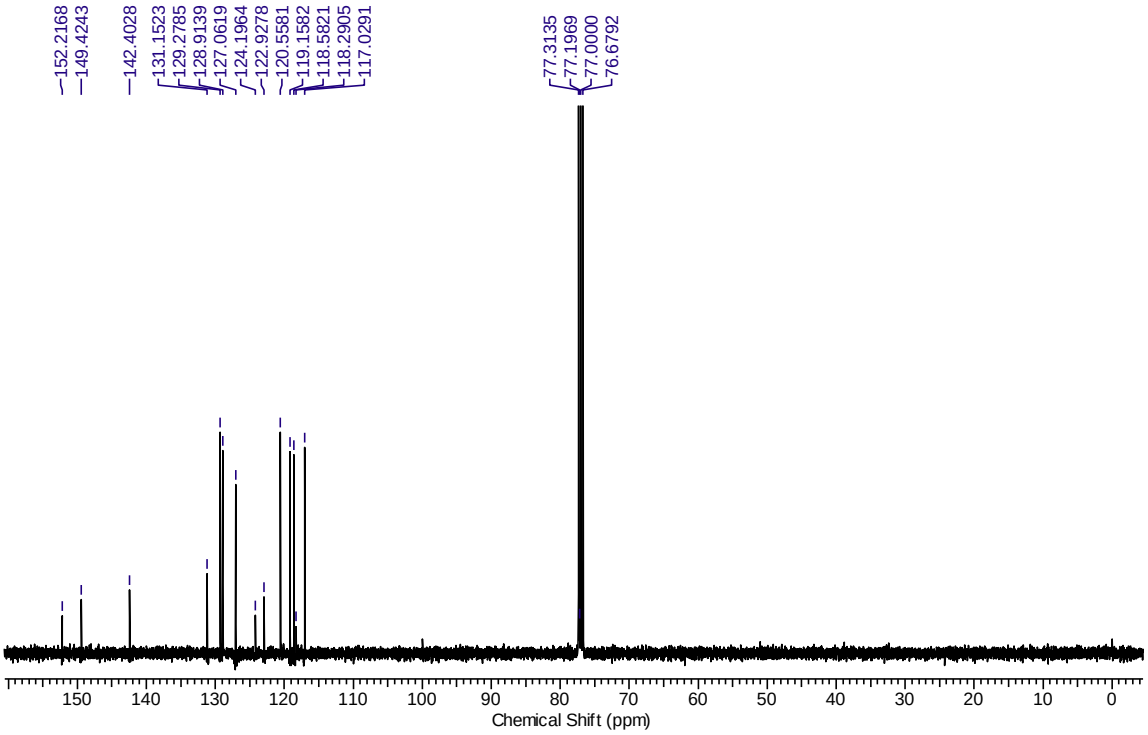
^{1}H NMR (400 MHz) spectrum of compound **7d** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound 7**d** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of compound **7e** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of compound **7e** in $CDCl_3$