Electronic Supplementary Material (ESI) for RSC Advances

Solvent free, Ni-nanoparticles catalyzed synthesis and photophysical studies of novel 2*H*-indazolo[2,1-*b*] phthalazine-trione derivatives

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1. Experimental Section

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (υ_{max} in cm^{-1}) on KBr disks. ^{1}H NMR and ^{13}C NMR (400, 300 MHz and 100, 75 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in $CDCl_3$ (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on Waters ZQ-4000. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). XRD was recorded on Bruker D8 XRD instrument SWAX .CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II). Silica gel G (E-mark, India) was used for TLC. Hexane refers to the fraction boiling between 60 ^{o}C and 80 ^{o}C.

The organic solvents (ethylacetate and DMSO) used for the photophysical characterization were of spectroscopic grade (>99.5%) as received from Alfa Aesar. The solvent water was obtained from Elix10 water purification system (Millipore India Pvt. Ltd.). Sample concentration (0.5~1 μM) was kept sufficiently dilute to avoid any effect from aggregation and/or inner filter effect.

Steady state absorption and fluorescence emission/excitation spectra were recorded in Lambda25 and LS-55 (both from PerkinElmer Inc.) spectrometers, respectively. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively. For fluorescence emission, the sample was excited at

365 nm unless otherwise mentioned. In all the cases, 10 nm band pass was used in the excitation and 20nm for emission side.

Fluorescence quantum yields (Δf) were calculated by comparing the total fluorescence intensity(F) under the whole fluorescence spectral range with that of quinine bisulfate in 0.5 M H_2SO_4 solution (ϕ_f = 0.546).[25]

$$\phi_f^i = \phi_f^s \times \frac{F^i}{F^s} \times \frac{(1-10^{-A^i})}{(1-10^{-A^s})} \times (\frac{n^i}{n^s})^2$$

where, A^i and A^s are the optical density of the sample and standard ,respectively, and n^i is the refractive index of solvent at 293 K. The relative experimental error of the measured quantum yield was estimated within ±10%.

Fluorescence decay measurements were performed by using time correlated single photon counting (TCSPC) technique using LED based nanosecond time-resolved spectrophotometer from Photon Technology International (PTI), USA. The excitation was done at 365 nm. The instrument response function (IRF) was obtained by using a dilute colloidal suspension of dried non-dairy coffee whitener. The details of the data collection, analysis procedure for both the steady state and time-resolved measurements and method of calculation of fluorescence yield can be found elsewhere.[26]

General procedure

A mixture of, dimedone **1** (2 mmol), phthalhydrazide **2** (2 mmol), aryl aldehyde **3a-n** (2 mmol) and Ni NPs (10 mol %) was heated at 80 ^oC for the time mentioned in the **table1**. After completion (TLC), the reaction mixture was cooled to room temperature; 10 mL of ethyl acetate was added to dissolve to it and filtered. The filtrate was recovered and

removed in high vacuum and product was purified by column chromatography using ethyl acetate: hexane (4:6) to afford the pure products **4a-n.**

Table S1: Spectral parameters of the synthesized phthalazine derivatives **(4a-k)** in ethyl acetate (EA) and DMSO[a] .

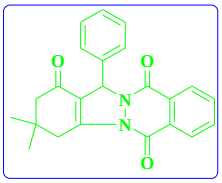
Products	Solvents	λ_{abs} /nm	λ_{em} /nm	φ	Decay parameters[b]		$<\tau>^{c}$ /ns
					τ_1 (a_1)	τ_2 (a_2)	
4a	DMSO	368	466-485	0.030	0.7 (99.8)	13.4 (0.2)	0.73
	EA	364	478	0.006	0.3 (99.8)	4.5 (0.2)	0.31
4b	DMSO	369	461-485	0.031	0.6 (99.6)	3.0 (0.4)	0.60
	EA	365	478	0.007	0.6 (99.7)	3.8 (0.3)	0.61
4c	DMSO	369	464-488	0.032	0.5 (99.8)	5.0 (0.2)	0.51
	EA	365	478	0.008	0.6 (99.2)	5.0 (0.8)	0.64
4d	DMSO	368	460-483	0.049	0.9 (99.8)	11.9(0.2)	0.92
	EA	364	470	0.010	0.5(99.8)	5.2(0.2)	0.51
4e	DMSO	368	460-485	0.008	0.9 (99.0)	6.3(1.0)	0.95
	EA	364	480	0.010	0.6(99.8)	6.2 (0.2)	0.61
4f	DMSO	368	462-485	0.041	0.4(99.7)	2.4(0.3)	0.41

	EA	364	475	0.007	0.5(99.8)	4.0 (0.2)	0.51
4g	DMSO	368	460-480	0.017	0.5(99.9)	3.2 (0.1)	0.50
	EA	364	472	0.007	0.8 (99.7)	4.7(0.3)	0.81
4h	DMSO	368	462-483	0.017	0.6(99.9)	6.8 (0.1)	0.61
	EA	364	470	0.006	1.0(99.7)	14.0 (0.3)	1.04
4i	DMSO	368	461-483	0.054	0.9(99.8)	9.7 (0.2)	0.92
	EA	364	477	0.010	0.4 (99.9)	4.5(0.1)	0.40
4j	DMSO	369	458-485	0.024	0.5 (99.8)	3.7 (0.2)	0.51
	EA	366	506	0.005	0.7(99.7)	5.0(0.3)	0.71
4k	DMSO	368	458-485	0.017	0.5 (99.5)	5.3(0.5)	0.52
	EA	363	472	0.020	0.6(99.8)	6.3(0.2)	0.61

[a] λ_{abs} = absorbance maxima, λ_{abs} = emission maxima, φ = quantum yield, [b]the measured values are within ± 0.1 ns; [c]calculated from equation (1b)

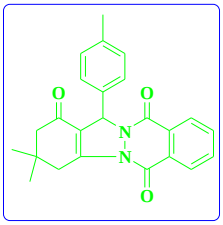
Spectral Data

1. Compound 4a



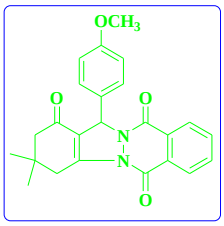
Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28-8.17 (m, 2H), 7.79-7.75 (m, 2H), 7.34-7.19 (m, 5H), 6.37 (s, 1H), 3.36-3.13 (AB system, *J* = 18.4 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). · ESI- MS: *m/z* 373 $[M + H]^+$. Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.07; H, 5.35; N, 7.35.

2. Compound 4b



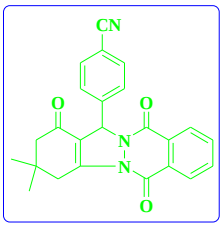
Yellow solid. IR (KBr): cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ =8.28-8.18 (m, 2H), 7.78-7.76 (m, 2H), 7.23 7.07 (d, *J* = 7.6 Hz, 2H), (d, *J* = 7.6 Hz, 2H), 6.34 (s, 1H), 3.36-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 2.22 (s, 3H), 1.13 (s, 6H). ESI- MS: *m/z* 387 $[M + H]^+$. Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.51; H, 5.80; N, 7.08.

3. Compound 4c



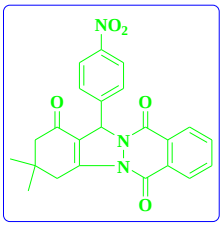
Yellow solid. IR (KBr): 2963, 2376, 1660 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28-8.18 (m, 2H), 7.78-7.75 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.69 (s, 3H), 3.37-3.13 (AB system, *J* = 19.2 Hz, 2H), 2.27 (s, 2H), 1.15 (s, 3H), 1.13 (s, 3H). ESI- MS: *m/z* 403 $[M + H]^+$. Anal. Calcd for $C_{24}H_{22}N_2O_4$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.83; H, 5.65; N, 6.87.

4. **Compound 4d**



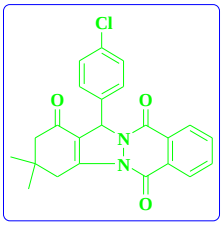
Yellow solid. IR (KBr): 2966, 2375, 1665 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.31-8.17 (m, 2H), 7.82-7.79 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.38 (s, 1H), 3.34-3.15 (AB system, *J* = 19.2 Hz, 2H), 2.26 (s, 2H), 1.14 (s, 3H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 191.0, 154.9, 153.5, 150.5, 140.5, 133.7, 132.9, 131.5, 127.9, 127.6, 127.1, 126.8, 126.7, 117.4, 116.3, 111.5, 63.3, 49.7, 37.0, 33.7, 27.6, 27.3. ESI- MS: *m/z* 398 $[M + H]^+$. Anal. Calcd for $C_{24}H_{19}N_3O_3$: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.71; H, 4.70; N, 10.73.

5. **Compound 4e**



Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29-8.08 (m, 4H), 7.80-7.79 (m, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 3.35-3.15 (AB system, *J* = 19.2 Hz, 2H), 2.25 (s, 2H), 1.13 (s, 3H), 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.1, 155.9, 154.5, 151.7, 147.8, 143.4, 134.8, 133.9, 128.9, 128.5, 128.2, 128.0, 127.7, 124.0, 117.2, 64.1, 50.7, 37.9, 34.7, 28.6, 28.3. ESI- MS: *m/z* 418 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}N_3O_5$: C, 66.18; H, 4.59; N, 10.07. Found: C, 65.90; H, 4.45; N, 10.23.

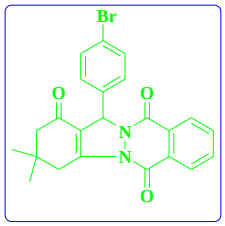
6. **Compound 4f**



Yellow solid. IR (KBr): 2939, 2229, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.1, 156.0, 154.3, 151.1, 134.9, 134.6, 134.5, 133.6, 128.97, 128.93, 128.91, 128.5, 128.0, 127.7, 118.0, 64.3, 50.8, 38.0, 34.6, 28.6, 28.4. ESI- MS:

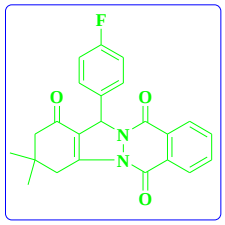
m/z 407, 409 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 68.17; H, 4.87; N, 6.98.

7. **Compound 4g**



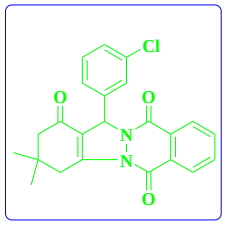
Yellow solid. IR (KBr): cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.1, 156.0, 154.3, 151.1, 135.4, 134.6, 133.7, 131.9, 128.9, 128.89, 128.82, 128.0, 127.7, 122.7, 118.0, 64.4, 50.8, 38.0, 34.6, 28.6, 28.4. ESI- MS: *m/z* 451, 453 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}BrN_2O_3$: C, 61.21; H, 4.24; N, 6.21. Found: C, 61.40; H, 4.12; N, 6.48.

8. **Compound 4h**



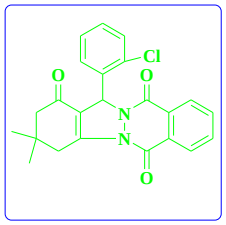
Yellow solid. IR (KBr): 2965, 2369, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.34-7.31 (m, 2H), 6.97 (t, *J* = 8.2 Hz, 2H), 6.36 (s, 1H), 3.36-3.14 (AB system, *J* = 18.8 Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). ESI- MS: *m/z* 391 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}FN_2O_3$: C, 70.76; H, 4.91; N, 7.18. Found: C, 70.65; H, 4.88; N, 7.30.

9. **Compound 4i**



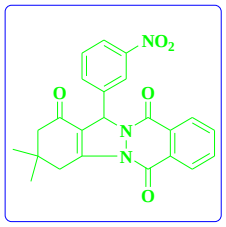
Yellow solid. IR (KBr): 2959, 2362, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.30-8.19 (m, 2H), 7.81-7.78 (m, 2H), 7.30-7.19 (m, 4H), 6.33 (s, 1H), 3.35-3.15 (AB system, *J* = 18.6 Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 67.61; H, 4.56; N, 7.15.

10. Compound 4j



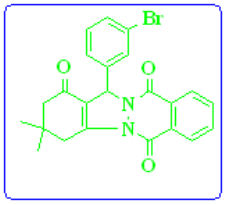
Yellow solid. IR (KBr): cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.30-8.16 (m, 2H), 7.79-7.77 (m, 2H), 7.41-7.14 (m, 4H), 6.60 (s, 1H), 3.35-3.14 (AB system, *J* = 18.0 Hz, 2H), 2.25 (s, 2H), 1.14 (s, 6H). ESI- MS: *m/z* 407, 409 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 67.93; H, 4.77; N, 6.71.

11. Compound 4k



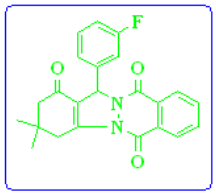
Yellow solid. IR (KBr): 2960, 2382, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.32-8.08 (m, 4H), 7.83-7.82 (brs, 3H), 7.51-7.47 (m, 1H), 6.45 (s, 1H), 3.38-3.18 (AB system, *J* = 18.7 Hz, 2H), 2.28 (s, 2H), 1.15 (s, 6H). ESI- MS: *m/z* 418 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}N_3O_5$: C, 66.18; H, 4.59; N, 10.07. Found: C, 66.37; H, 4.47; N, 10.34.

12. Compound 4l



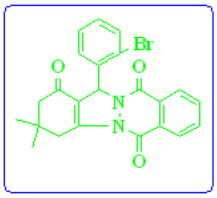
Yellow solid. IR (KBr): 2965, 2372, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.37-8.24 (m, 4H), 7.87-7.13 (m, 4H), 6.71 (s, 1H), 3.43-3.21 (AB system, *J* = 19.2 Hz, 2H), 2.32 (s, 2H), 1.25 (s, 3H), 1.21 (s, 3H). ESI- MS: *m/z* 451, 453 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}BrN_2O_3$: C, 61.21; H, 4.24; N, 6.21. Found: C, 61.10; H, 4.10; N, 6.24.

13. Compound 4m



Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.27-8.24 (m, 4H), 7.88-6.98 (m, 4H), 6.53 (s, 1H), 3.45-3.18 (AB system, *J* = 18.0 Hz, 2H), 2.33 (s, 2H), 1.25 (s, 3H), 1.92 (s, 3H). ESI- MS: *m/z* 391 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}FN_2O_3$: C, 70.76; H, 4.91; N, 7.18. Found: C, 70.71; H, 5.14; N, 7.06.

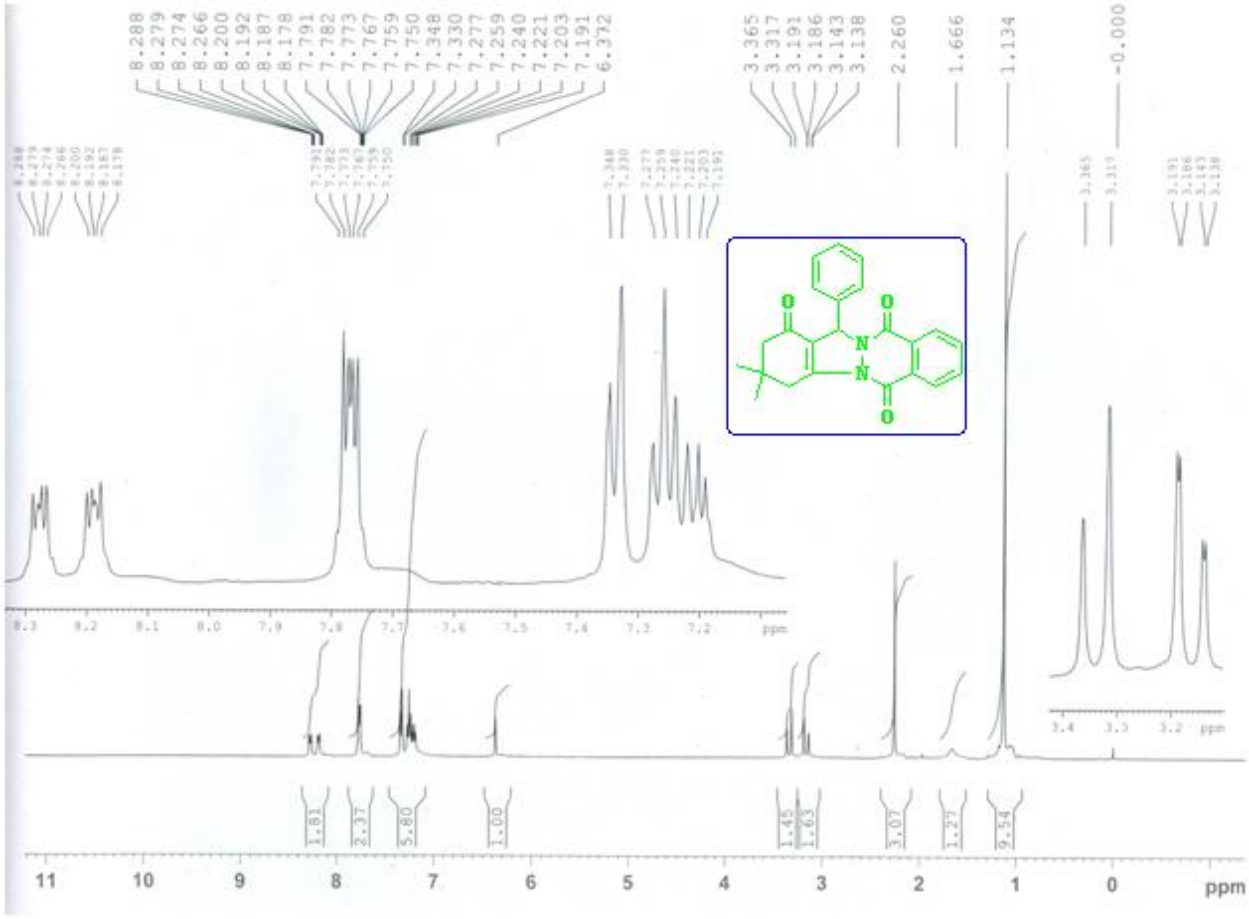
14. Compound 4n



Yellow solid. IR (KBr): 2966, 2375, 1665 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.35-8.25 (m, 4H), 7.90-7.84 (m, 4H), 6.39 (s, 1H), 3.44-3.20 (AB system, *J* = 17.5 Hz, 2H), 2.34 (s, 2H), 1.21 (s, 6H). ESI- MS: *m/z* 398 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}BrN_2O_3$: C, 61.21; H, 4.24; N, 6.21. Found: C, 60.93; H, 4.12; N, 6.30.

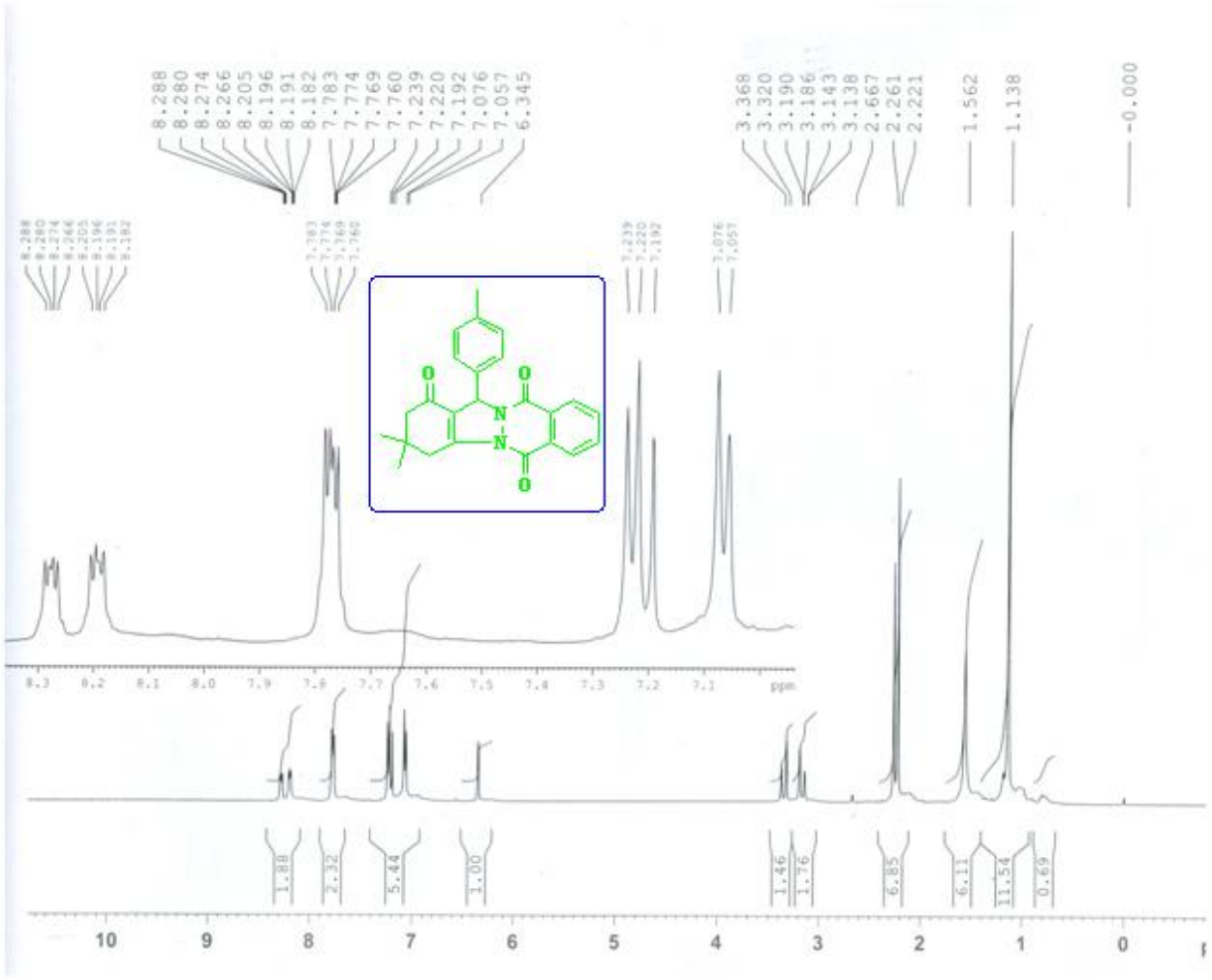
3. ^{1}H and ^{13}C NMR spectra

1. Compound 4a



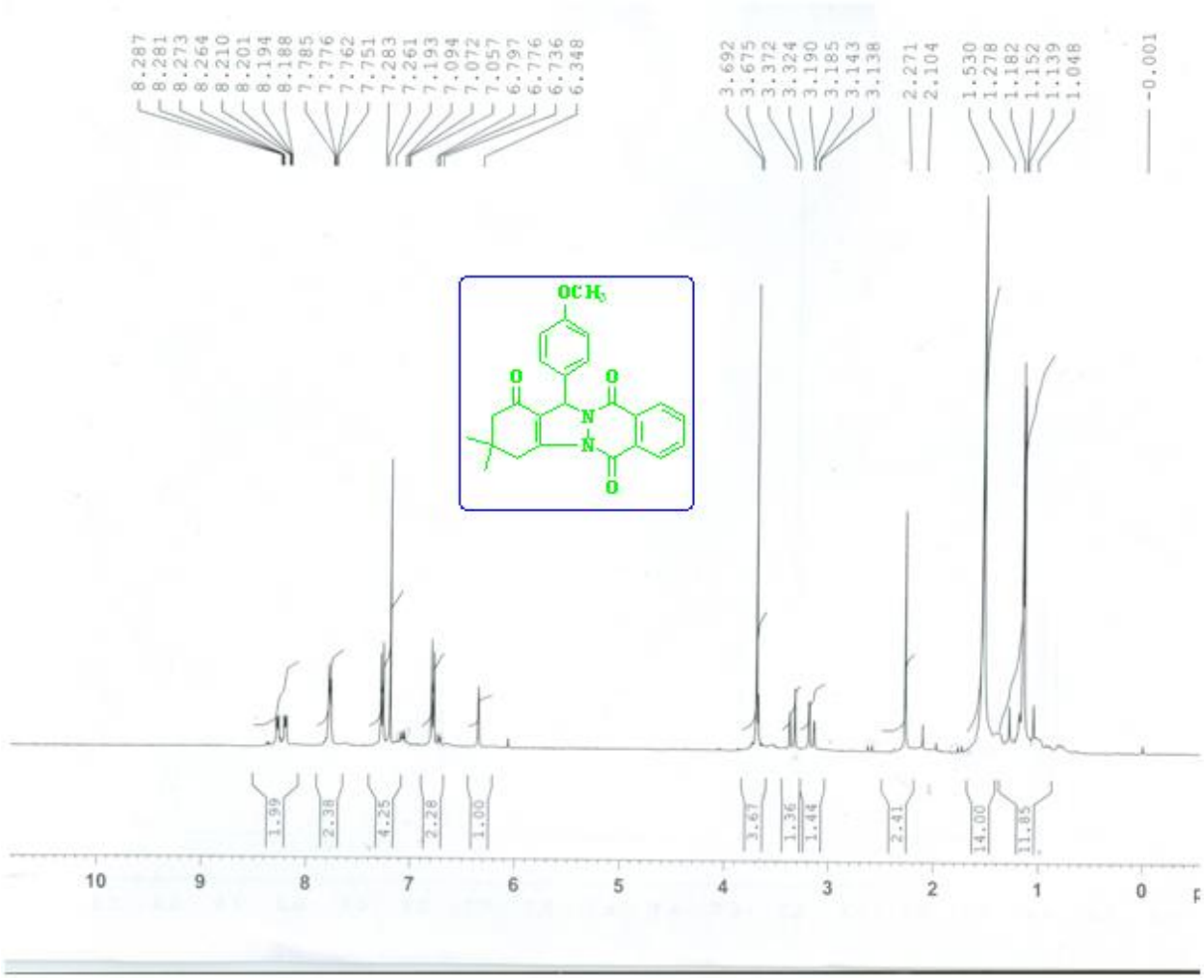
^{1}H NMR Spectra of Compound 4a

2. Compound 4b



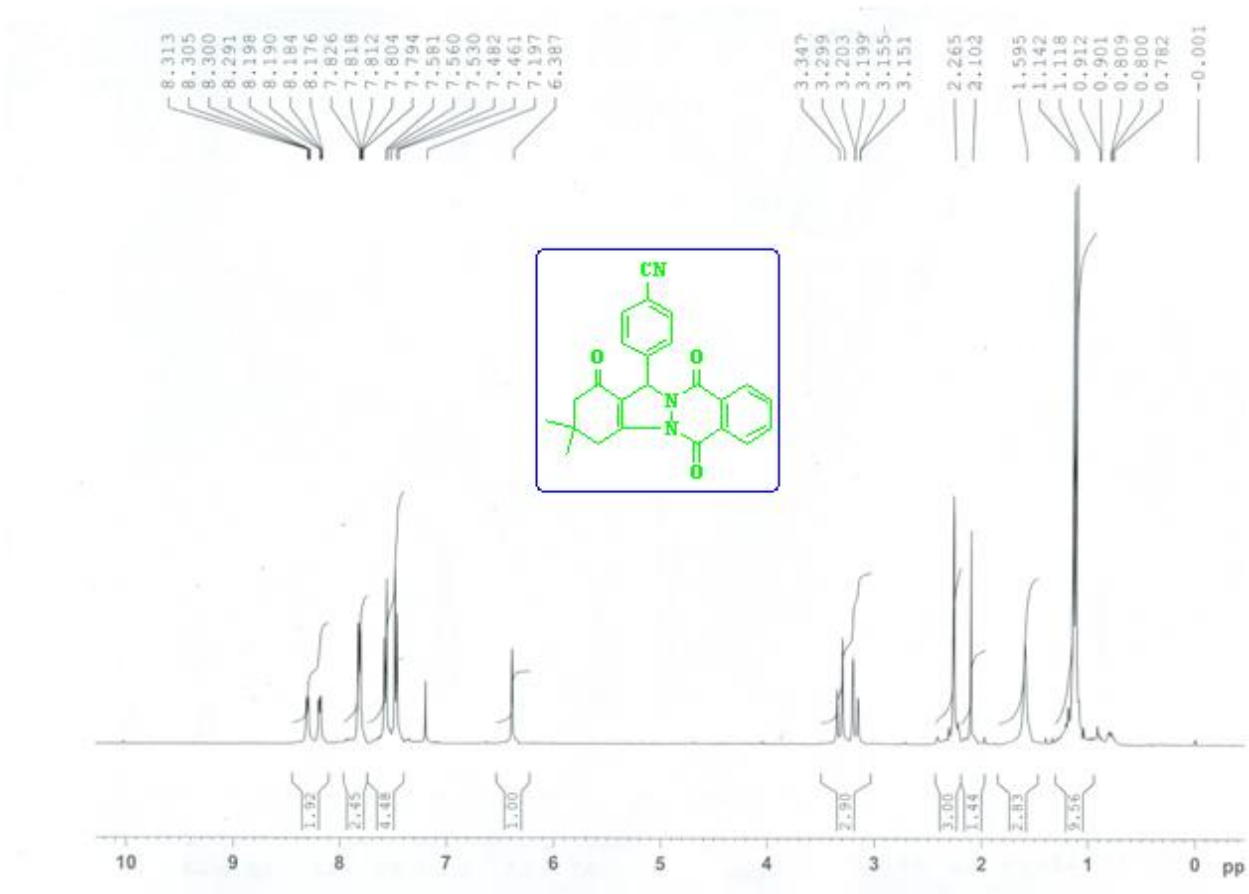
^{1}H NMR Spectra of Compound 4b

3. Compound 4c



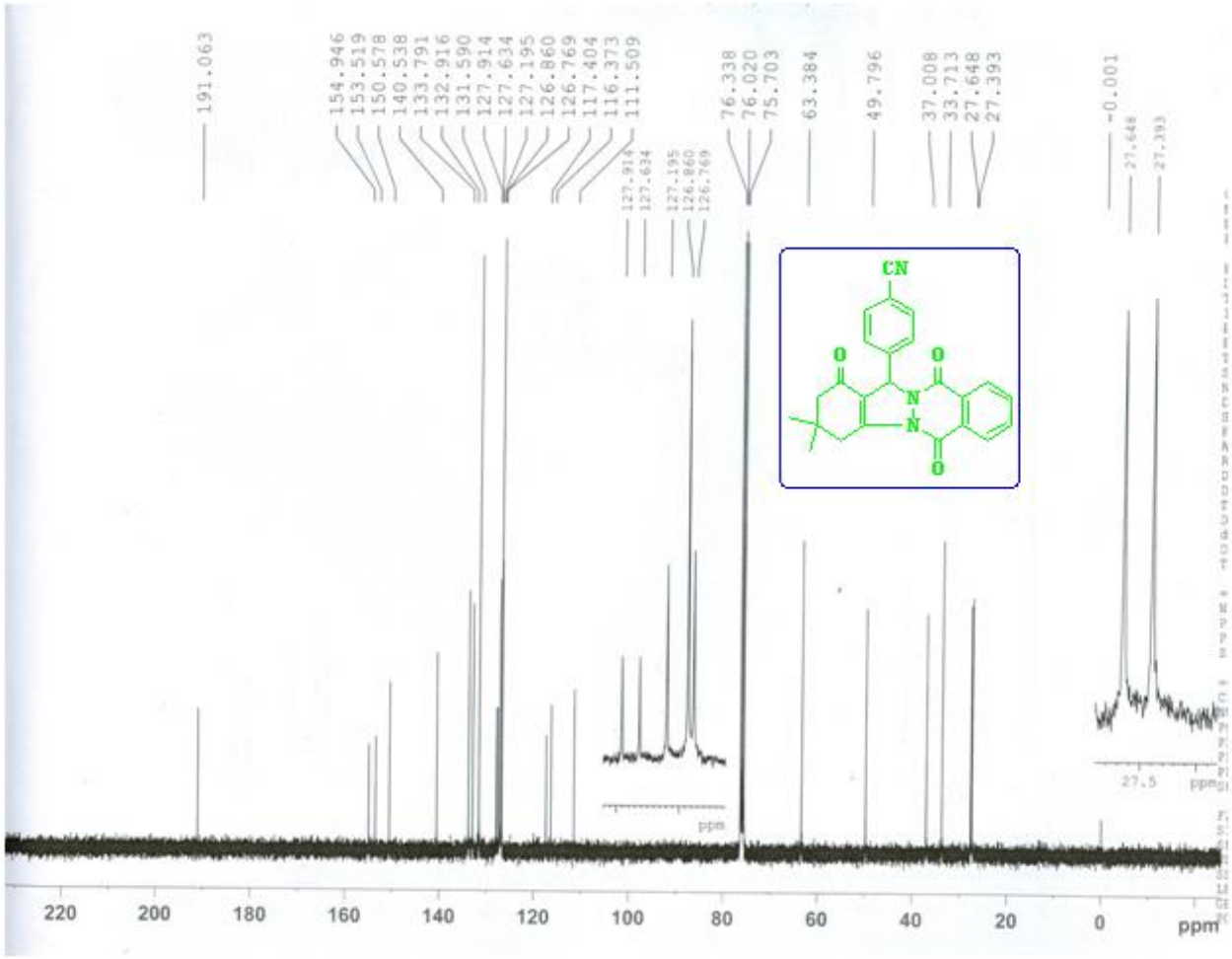
^{1}H NMR Spectra of Compound 4c

4. Compound 4d



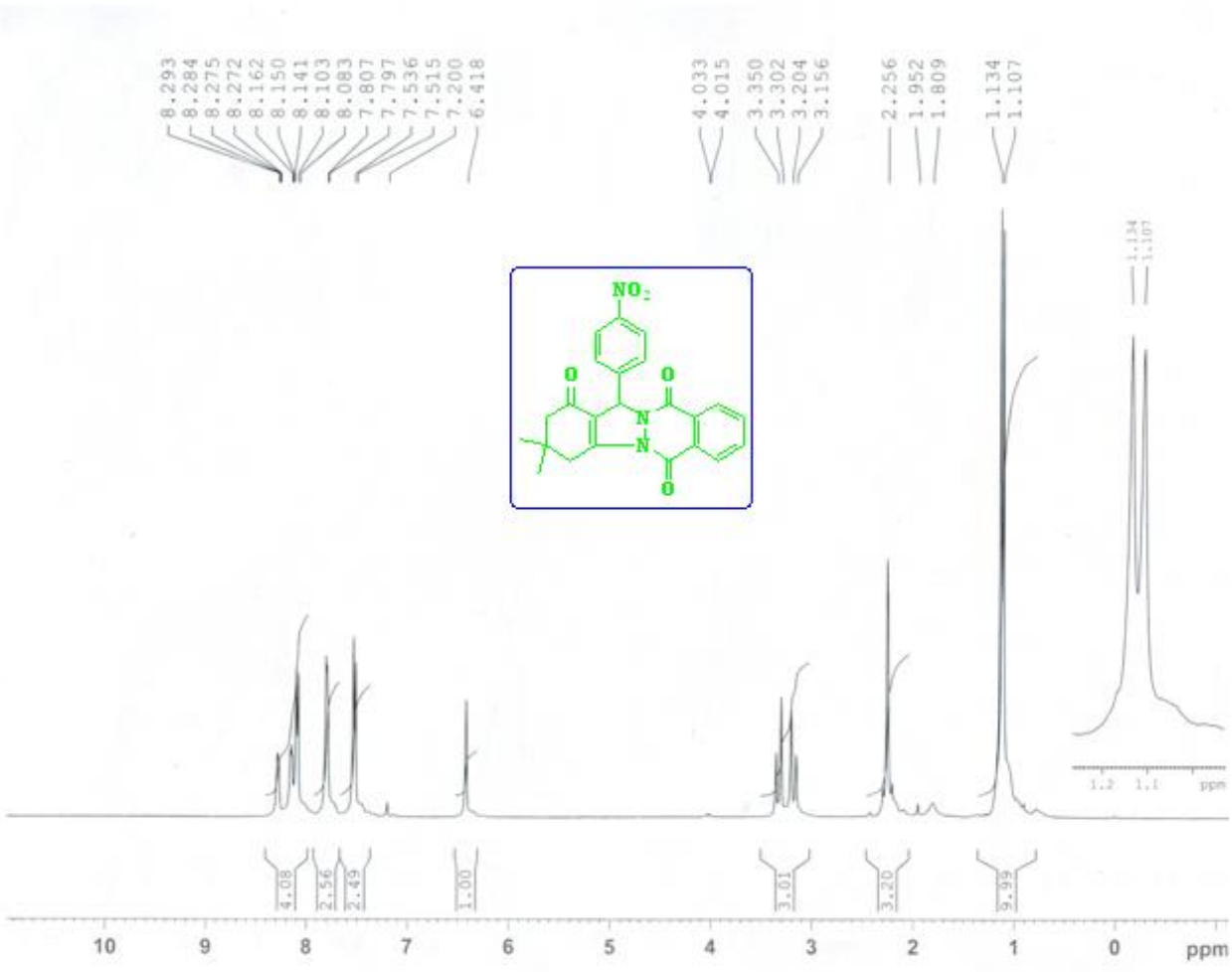
^{1}H NMR Spectra of Compound 4d

5. Compound 4d



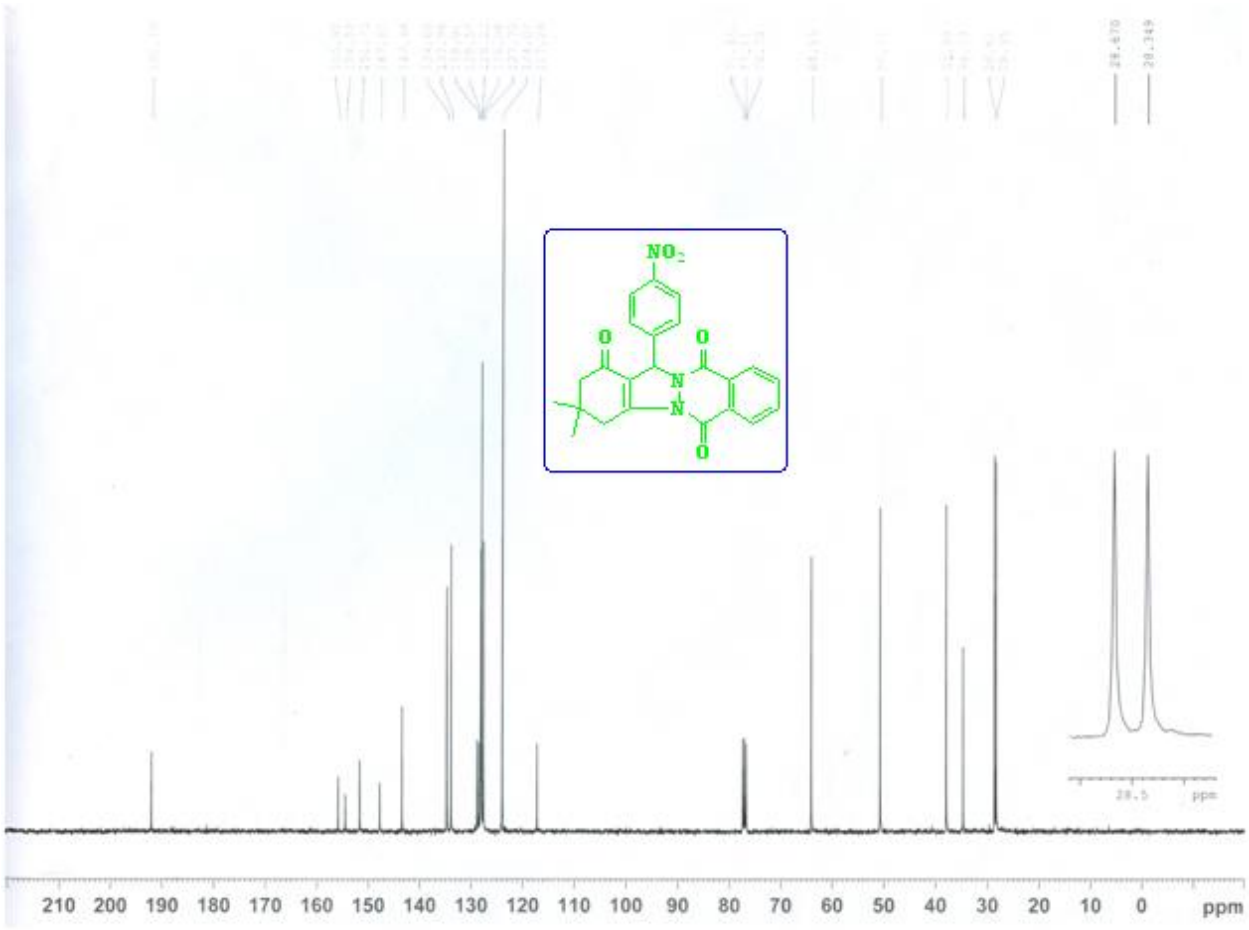
^{13}C NMR Spectra of Compound 4d

6. Compound 4e



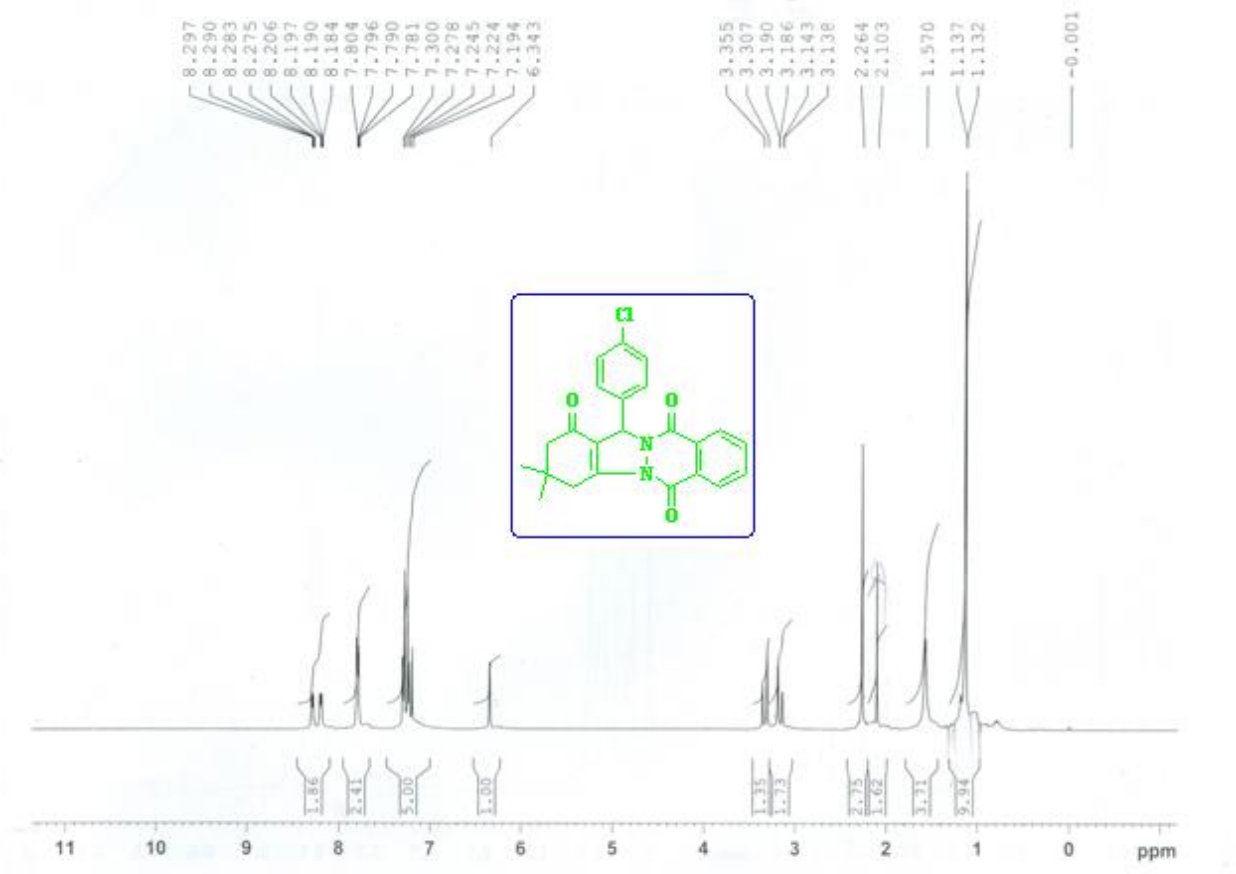
^{1}H NMR Spectra of Compound 4e

7. Compound 4e



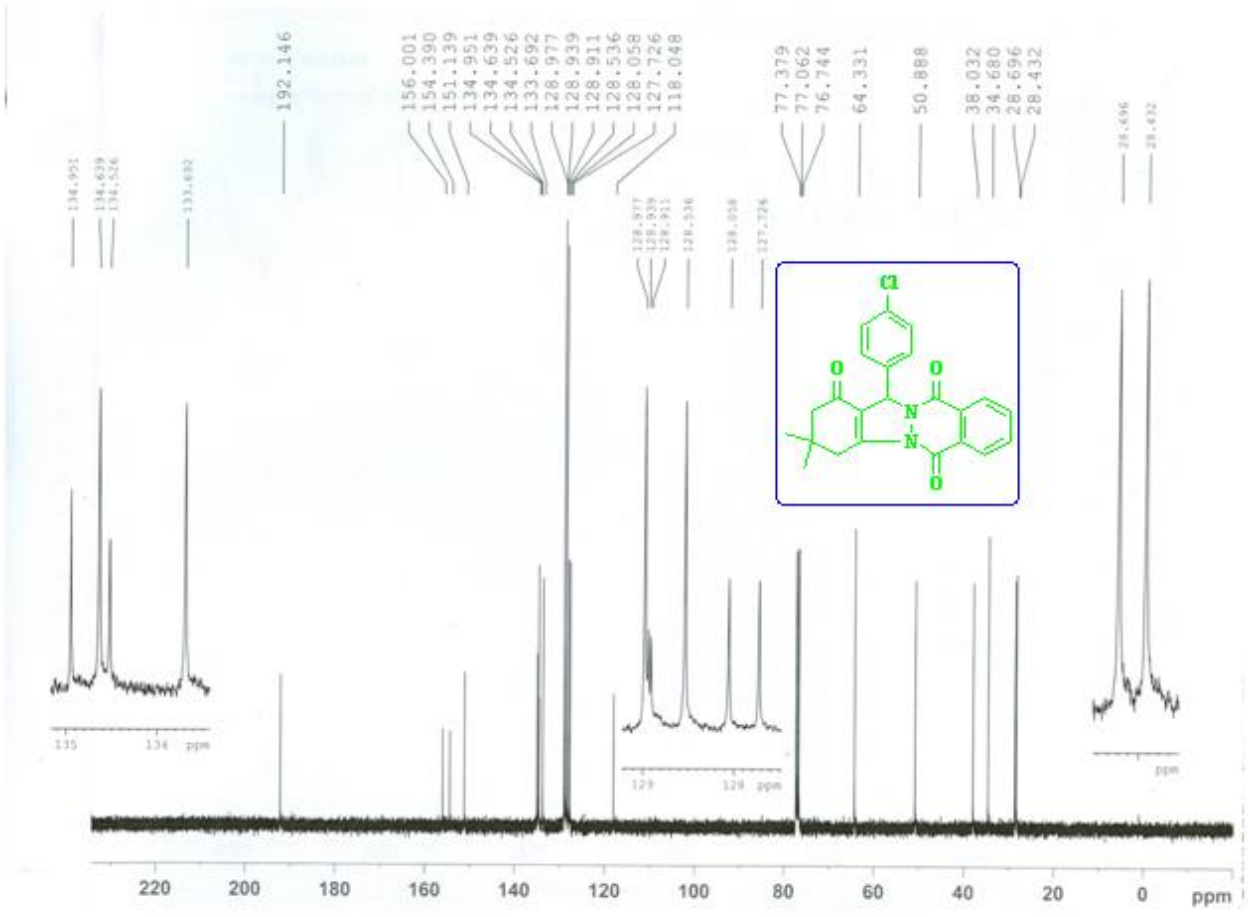
^{13}C NMR Spectra of Compound 4e

8. Compound 4f



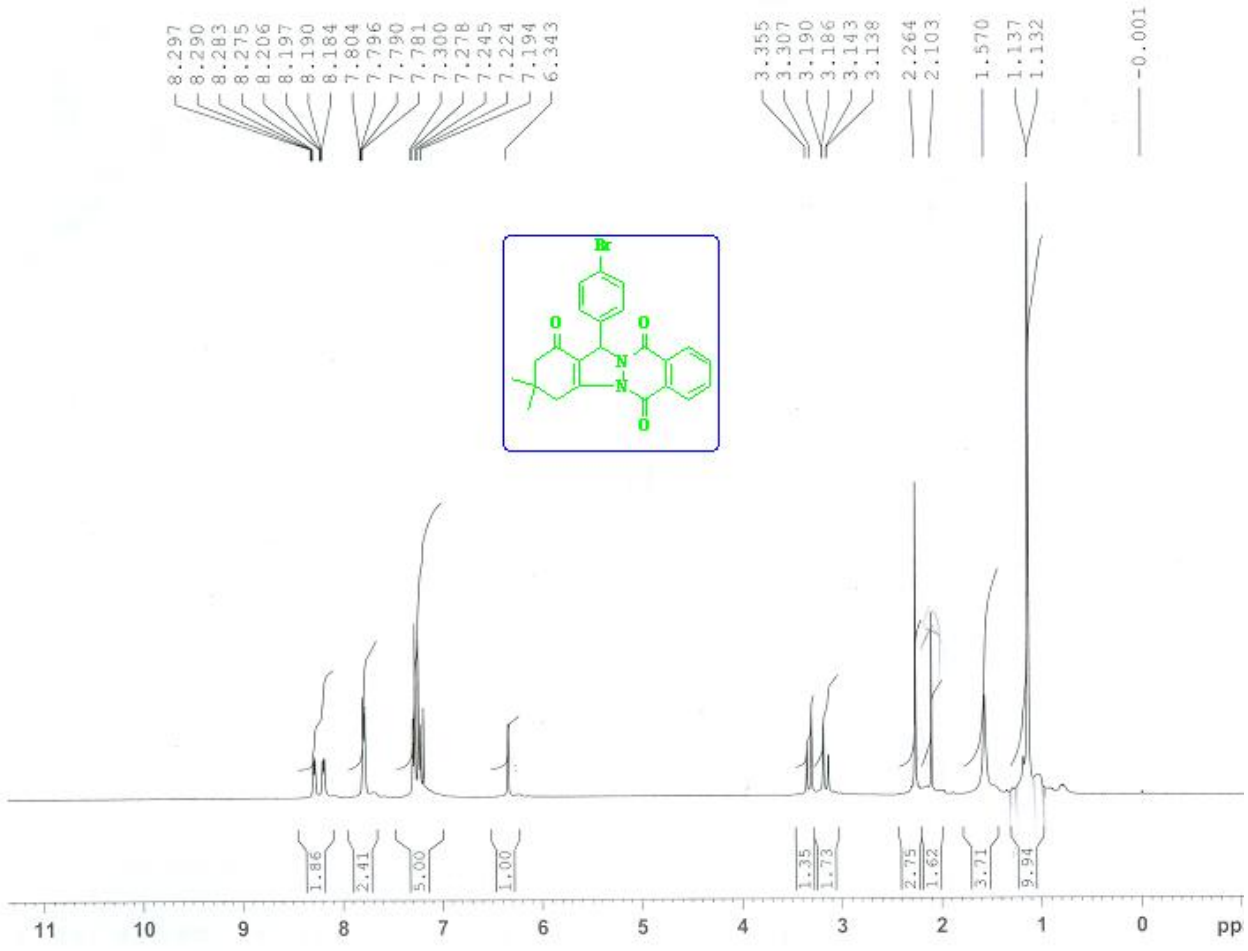
^{1}H NMR Spectra of Compound 4f

9. Compound 4f



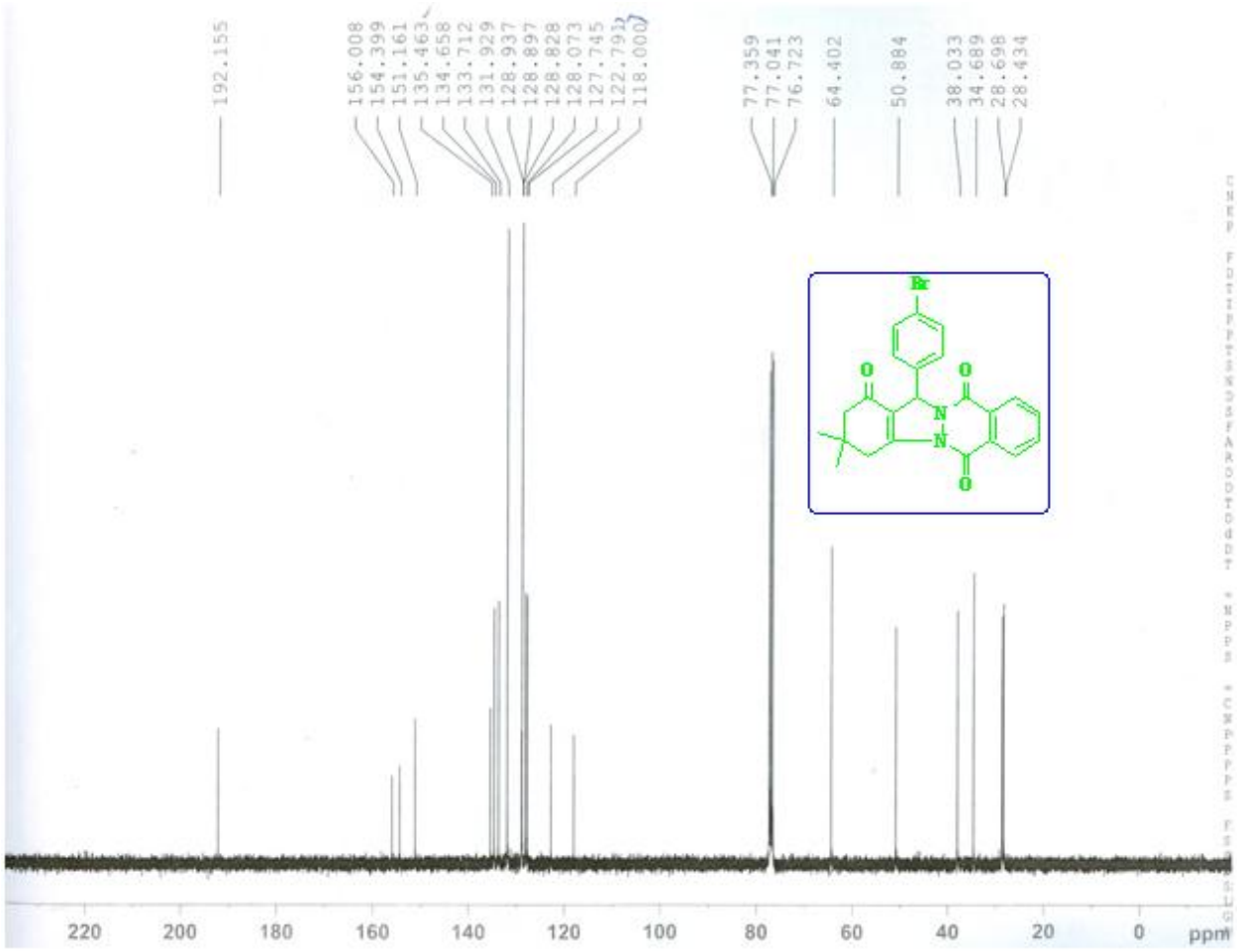
^{13}C NMR Spectra of Compound 4f

10. Compound 4g



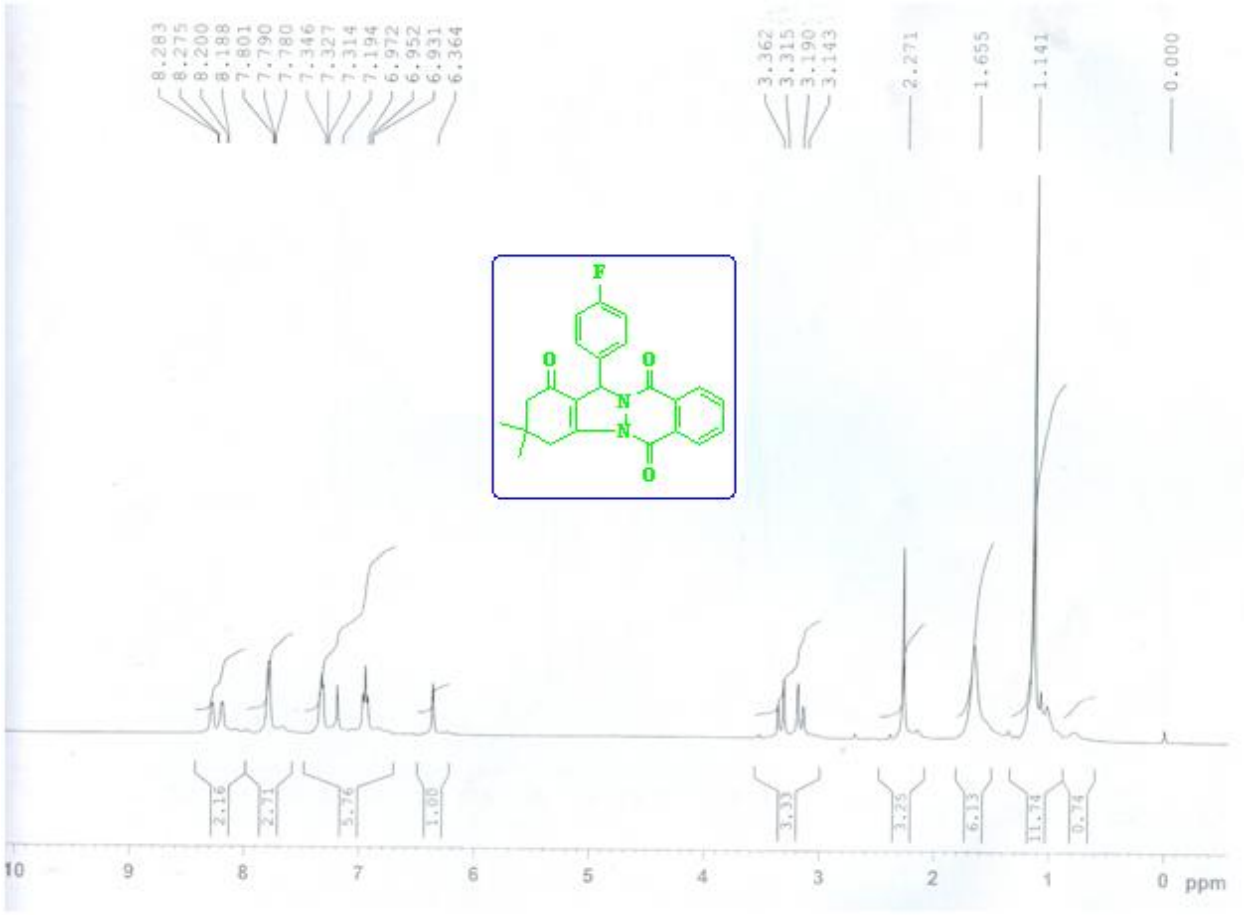
^{1}H NMR Spectra of Compound 4g

11.Compound 4g



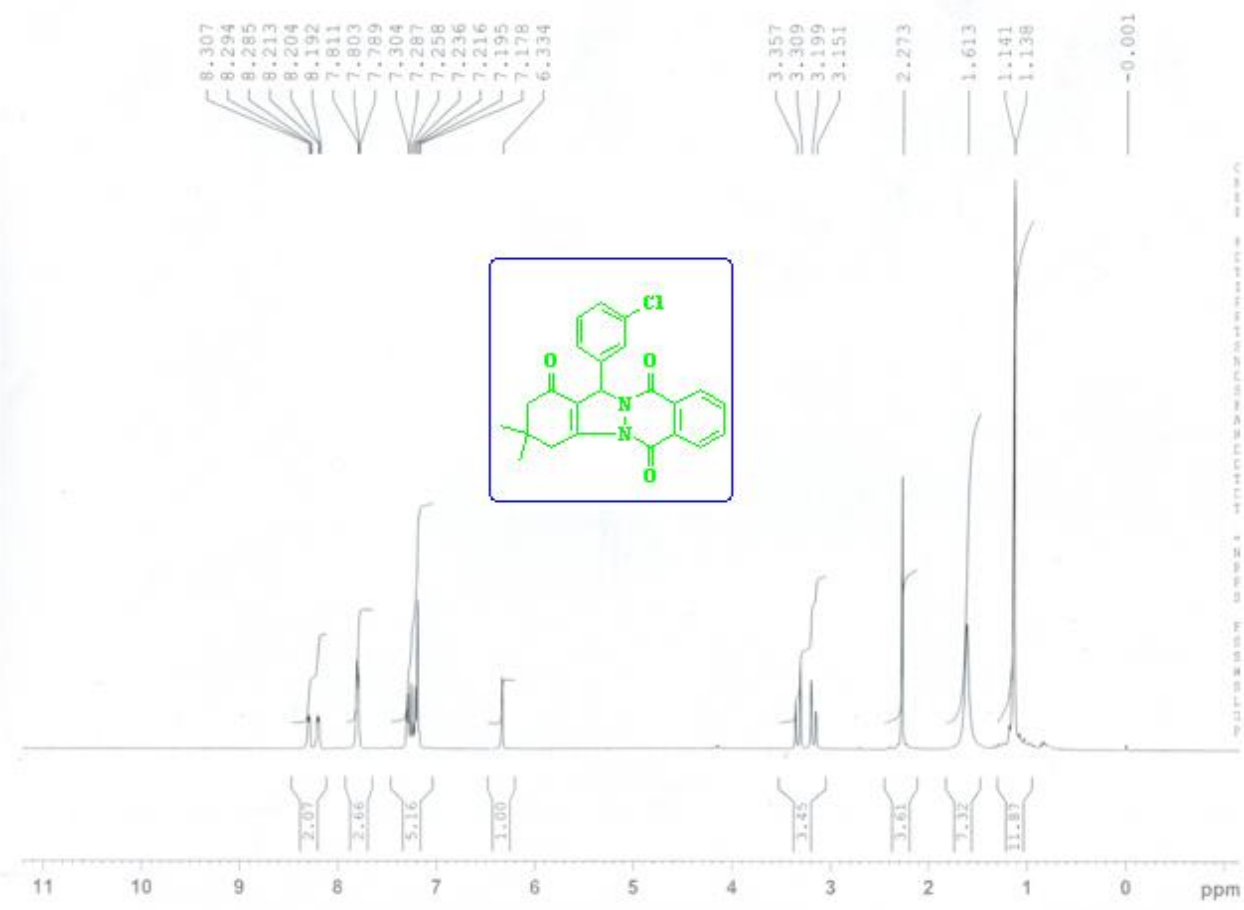
^{13}C NMR Spectra of Compound 4g

12.Compound 4h



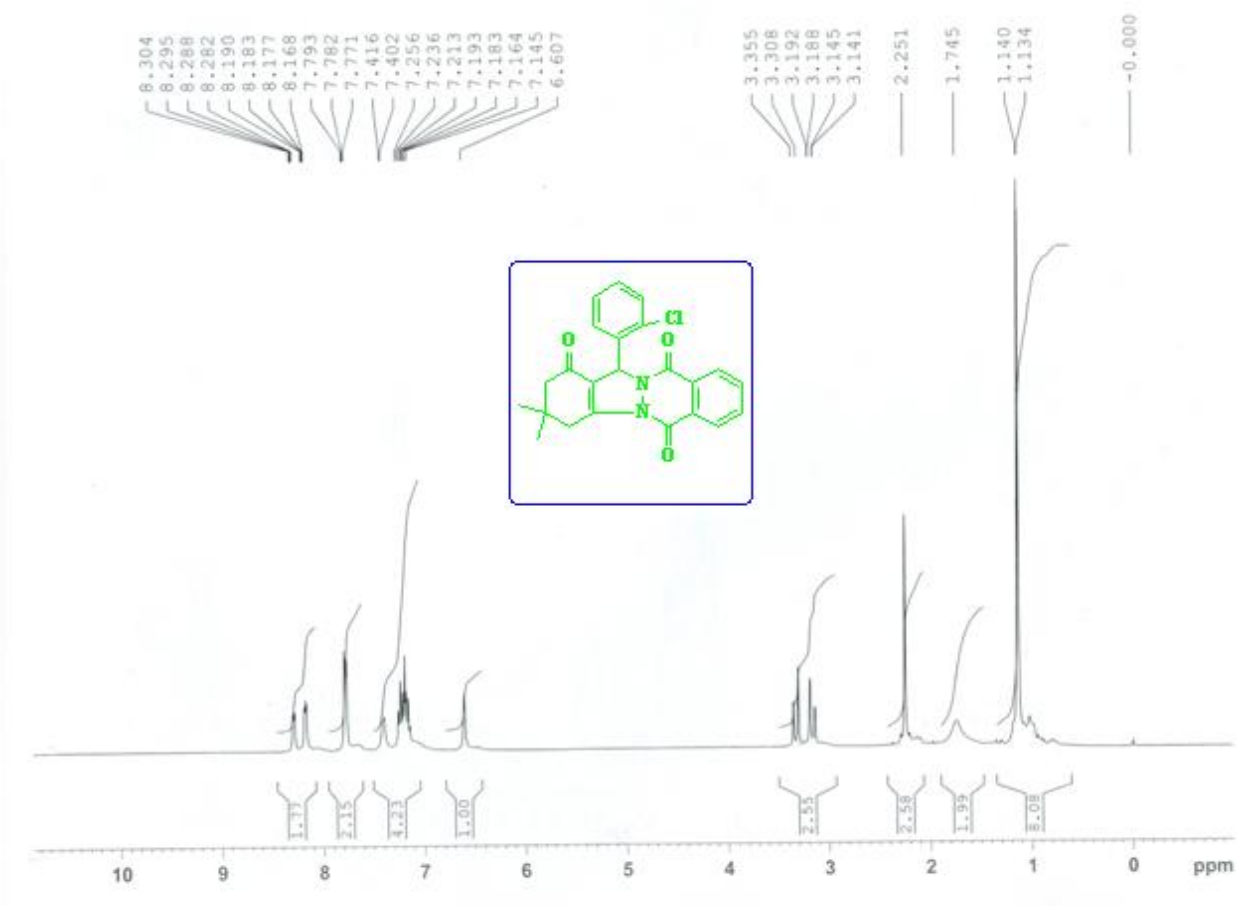
^{1}H NMR Spectra of Compound 4h

13.Compound 4i



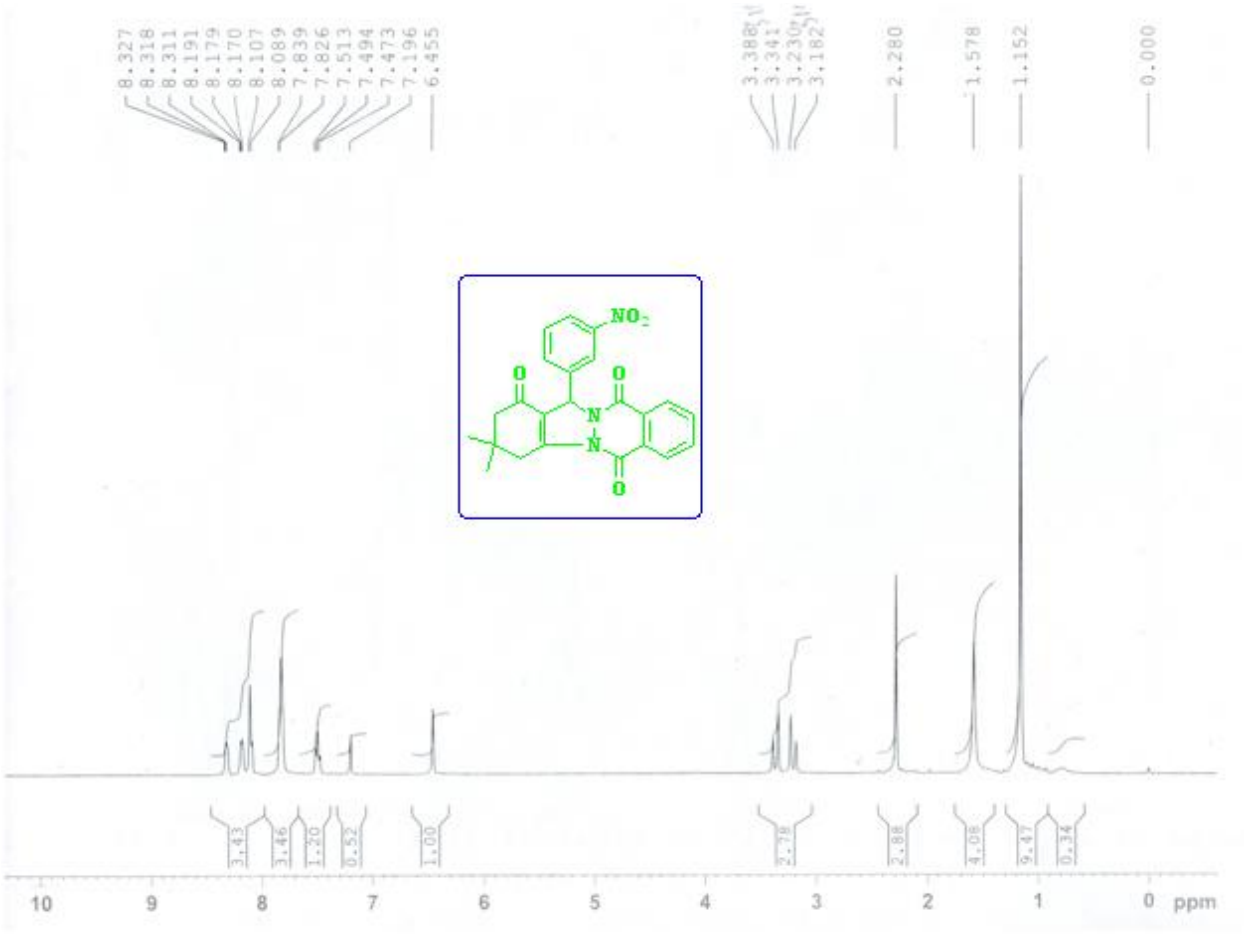
^{1}H NMR Spectra of Compound 4i

14.Compound 4j



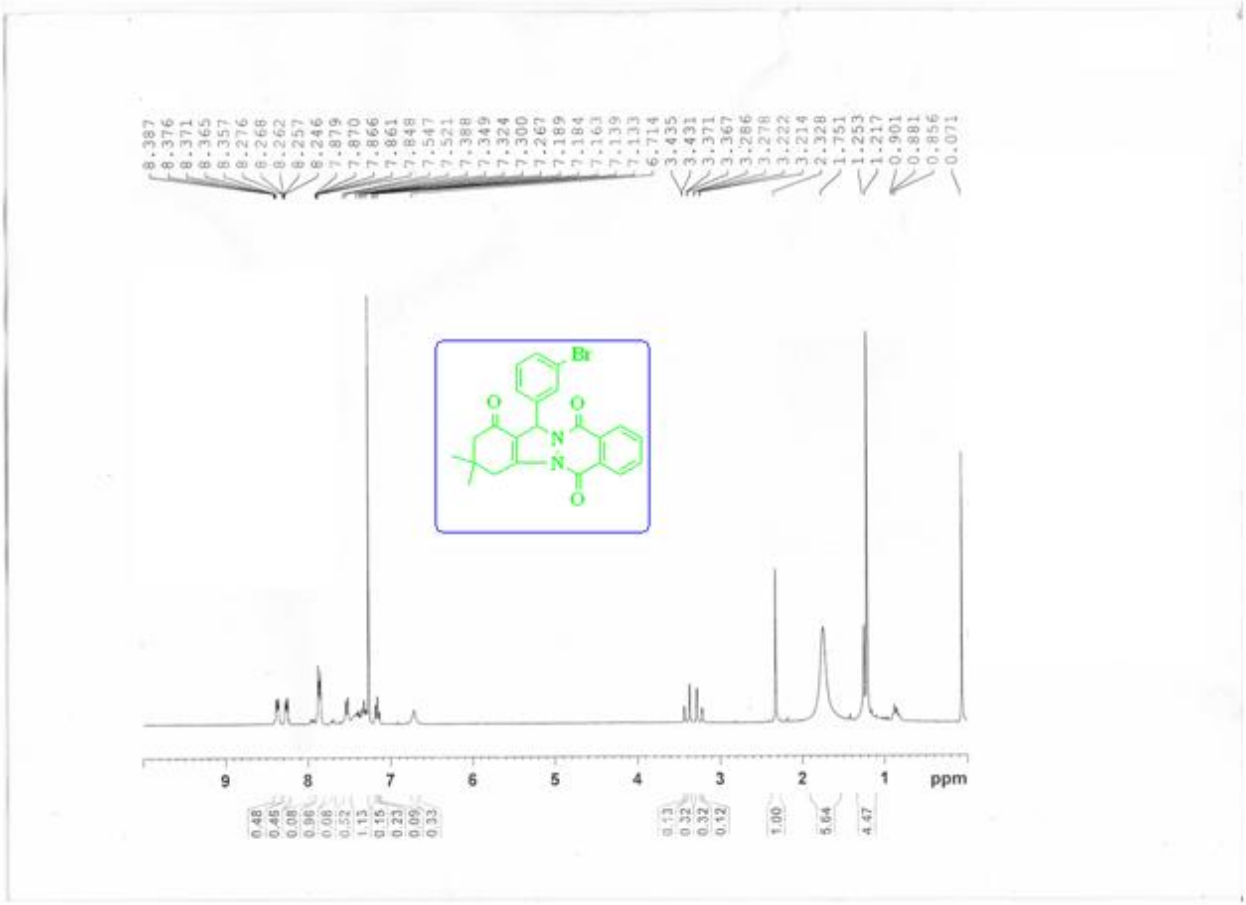
^{1}H NMR Spectra of Compound 4j

15. Compound 4k



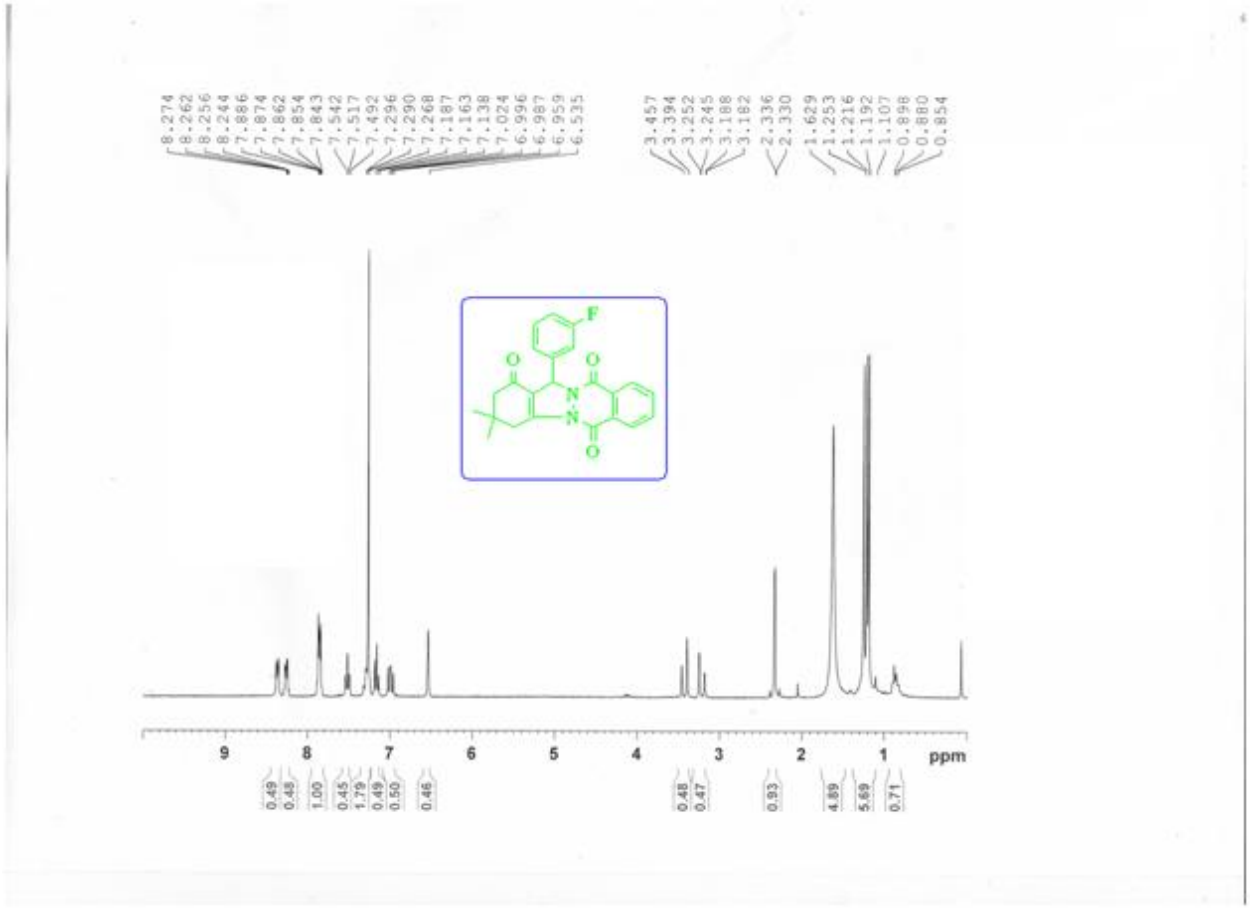
^{1}H NMR Spectra of Compound 4k

16. Compound 4l



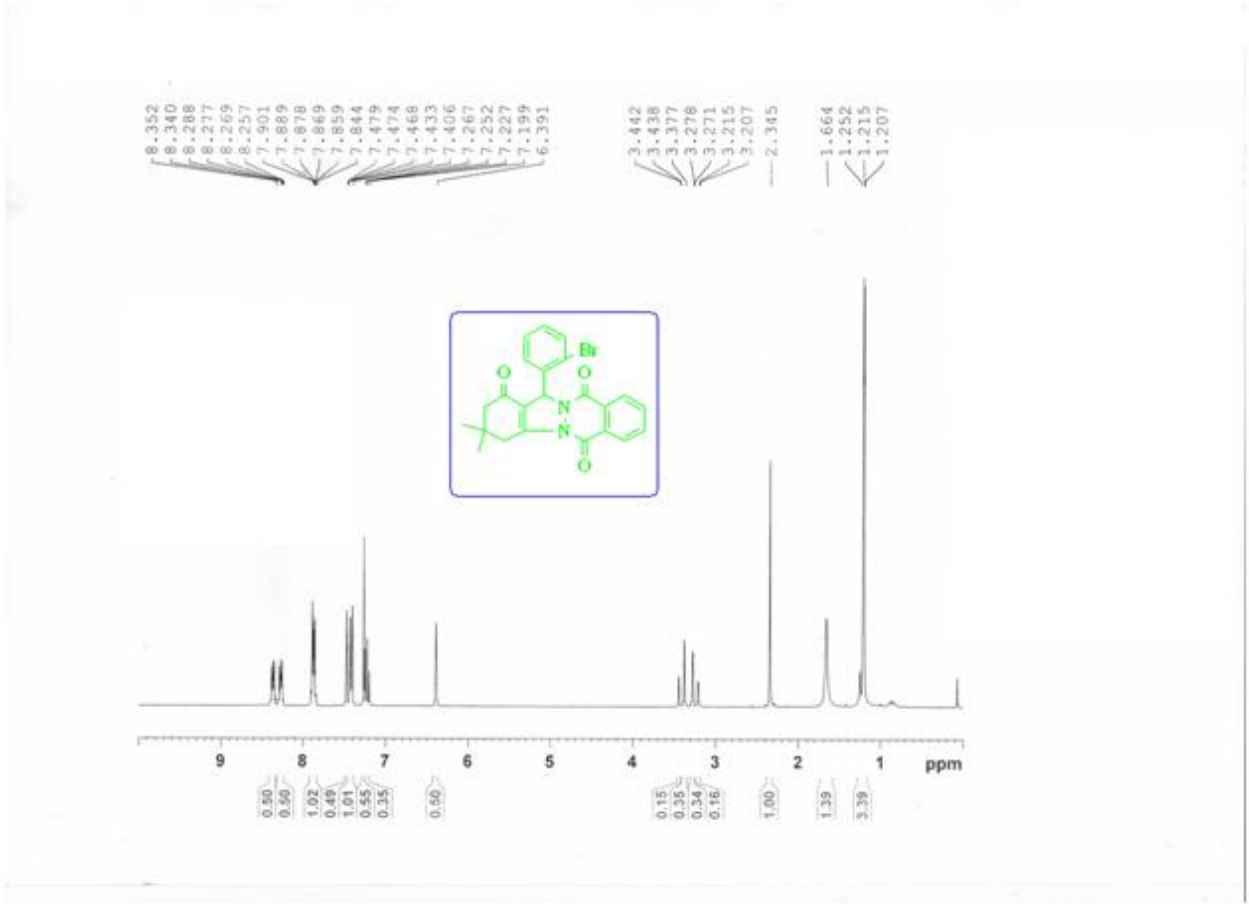
^{1}H NMR Spectra of Compound 4l

17. Compound 4m



^{1}H NMR Spectra of Compound 4m

18. Compound 4n



^{1}H NMR Spectra of Compound 4n