Electronic Supplementary Material (ESI) for RSC Advances.

NANO-FERRITE SUPPORTED GLUTATHIONE AS A REUSABLE NANO-ORGANOCATALYST FOR THE SYNTHESIS OF PHTHALAZINE-TRIONE AND DIONE DERIVATIVES UNDER SOLVENT FREE CONDITION.

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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 and 300 MHz and 100 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. Thermogravimetric analysis (TGA) was recorded by using Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II), ICP-OES was done by using ULTIMA2 HORIBA JOBIN YVON model. Silica gel G (E-mark, India) was used for TLC.

General procedure

Phthalic anhydride (1 mmol) (**1**), hydrazinium hydroxide (1.2 mmol) (**2**), active methylene compounds (1 mmol) (**3/4/5**), aryl aldehydes (1 mmol) (**6a-q**) and nano-FGT (10 mg) were added to a round bottom flask and since the reaction is under solvent free condition so it was mixed properly by using a glass rod. Following this, a magnetic bit was added and the reaction mixture was set on a pre-heated oil bath at 80 ^{0} C accompanied with magnetic stirrer (model no: IKA C-MAG, HS4 Digital) and stirring was started and continued for the time mentioned in the **Table 2**. During stirring a centrifugal force was generated, which mixed the reactants nicely thereby making a reasonable contact between the surface of the catalyst and the reactants. This fact was clearly explained from the observation that when no catalyst was added to the reaction

mixture, no desired product was formed even after 24 h of stirring. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. 10 mL of ethyl acetate was added to the reaction mixture and nano-FGT attached to magnetic bit was separated by another external magnet. After that, in order to reuse the catalyst, it was washed several times with ethyl acetate, acetone to remove presence of any residual product and dried. The catalyst was then applied in subsequent reactions. The organic extract was then washed with water (3x10 ml), followed by brine and dried with anhydrous Na_2SO_4. The solvent was removed under vacuum and the crude reaction mixture was purified by column chromatography using ethyl acetate: hexane (4:6) to afford the pure products (**15a-p, 16a, 17a, 18a**).

X-ray crystallography

The X-ray diffraction data were collected with Mo Kα radiation (λ = 0.71073 Å) at 293 K by using Agilent Xcalibur (Eos, Gemini) diffractometer which is equipped with a graphite monochromator. The softwares which are used for data collection are CrysAlis PRO (Agilent, 2011), data reduction CrysAlis PRO and cell refinement CrysAlis PRO. Structure was solved by direct methods and was refined by full-matrix least-squares calculation using SHELXS-97[1] and SHELXL-97.[2]

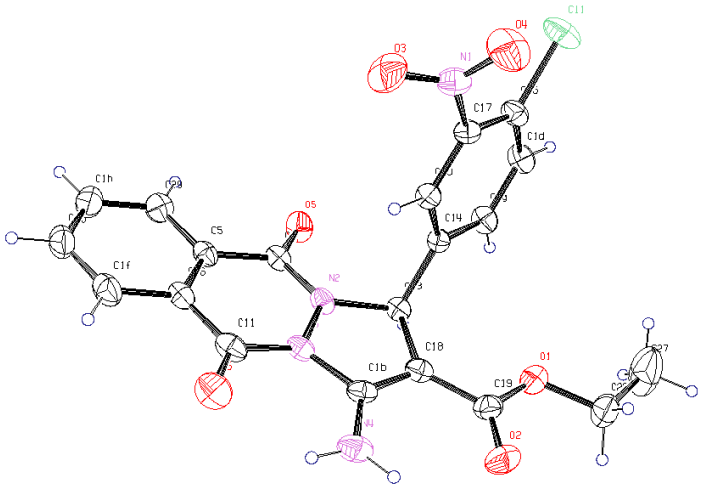
Procedure for the synthesis of Fe_3O_4 NPs.[3]

3.4 g of ferric nitrate and 3 g of ferrous sulphate were taken in a 250 mL round bottom flask. To that mixture 100 mL of deionized water was added and stirred for 15 min and the solution became homogeneous. After that, 25 % ammonium hydroxide was added drop-wise till its pH became 10. Then the solution was stirred at 60 ^{0}C for 1 h and a black

precipitate was appeared. This was then magnetically separated by an external magnet, washed with water until the pH became neutral and dried inside the oven for 5 h.

Procedure for the synthesis of nano-FGT.

0.5 g of Fe_3O_4 NPs was dispersed in 15 mL of deionized water and 5 mL of MeOH was added to it, this was then sonicated for 15 min. Following that, 0.4 g of glutathione was dissolved in 5 mL of water and was added to this colloidal solution. This resulting solution was then sonicated for another 2h leading to the formation of magnetic nano-FGT. Synthesized nano-FGT was then isolated by external magnet, washed with water (3 x 10 mL), MeOH (3 X 10 mL) and dried in oven at 50-60 ^{o}C.



References

[1] Sheldrick, G. M. Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta. Crystallog. Sec A.* **1990**, *46*, 467.

[2] Sheldrick, G. M. A short history of SHELX. *Acta. Crystallog. Sec A.* **2008**, *64*, 112.

[3] C. Hui, C. Shen, T. Yang, L. Bao, J. Tian, H. Ding, C. Li, H. J. Gao, *J. Phys. Chem. C*, **2008**, *112*, 11336.

Table S.I.1. X-ray crystallography data for compound **17a** (**CCDC No. 1438715**).

Empirical formula	$C_{20}H_{15}ClN_4O_6$
Formula weight	442.8
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	11.4898 (8)
b(Å)	8.3928 (8)
c(Å)	20.0409 (17)
α(°)	90.00
β(°)	94.127 (8)
γ(°)	90.00
Volume (Å^3)	1927.6 (3)
ρ (calculated) (mg mm^{-3})	1.5258
T(K)	295.2(8)
Absorption coefficient (μ/mm^{-1})	0.247
Total reflection collected	9774
Independent reflection	4397
θ range (°)	6.28 to 57.66°

Final R Indexes [1>=2σ(I)]	R_1 = 0.0586, wR_2 = 0.1642
Final R indexes [all data]	R_1 = 0.0892, wR_2 = 0.1889
Goodness-of-fit on F^2	1.113

1. A. FT-IR of nano-FGT:

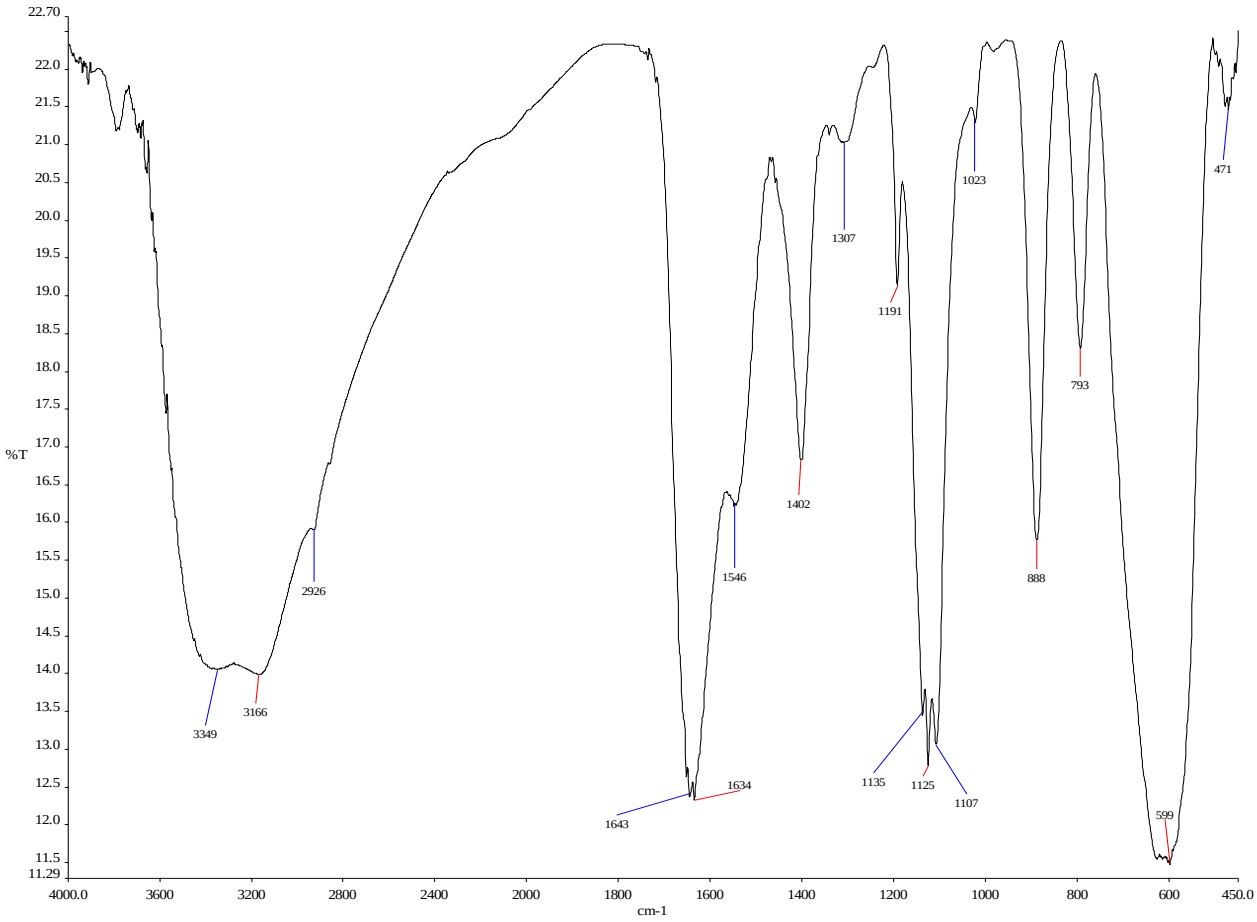


Fig SI 1a: FT-IR of nano-FGT

B. FT_IR of nano-FGT after 5 consequtive runs:

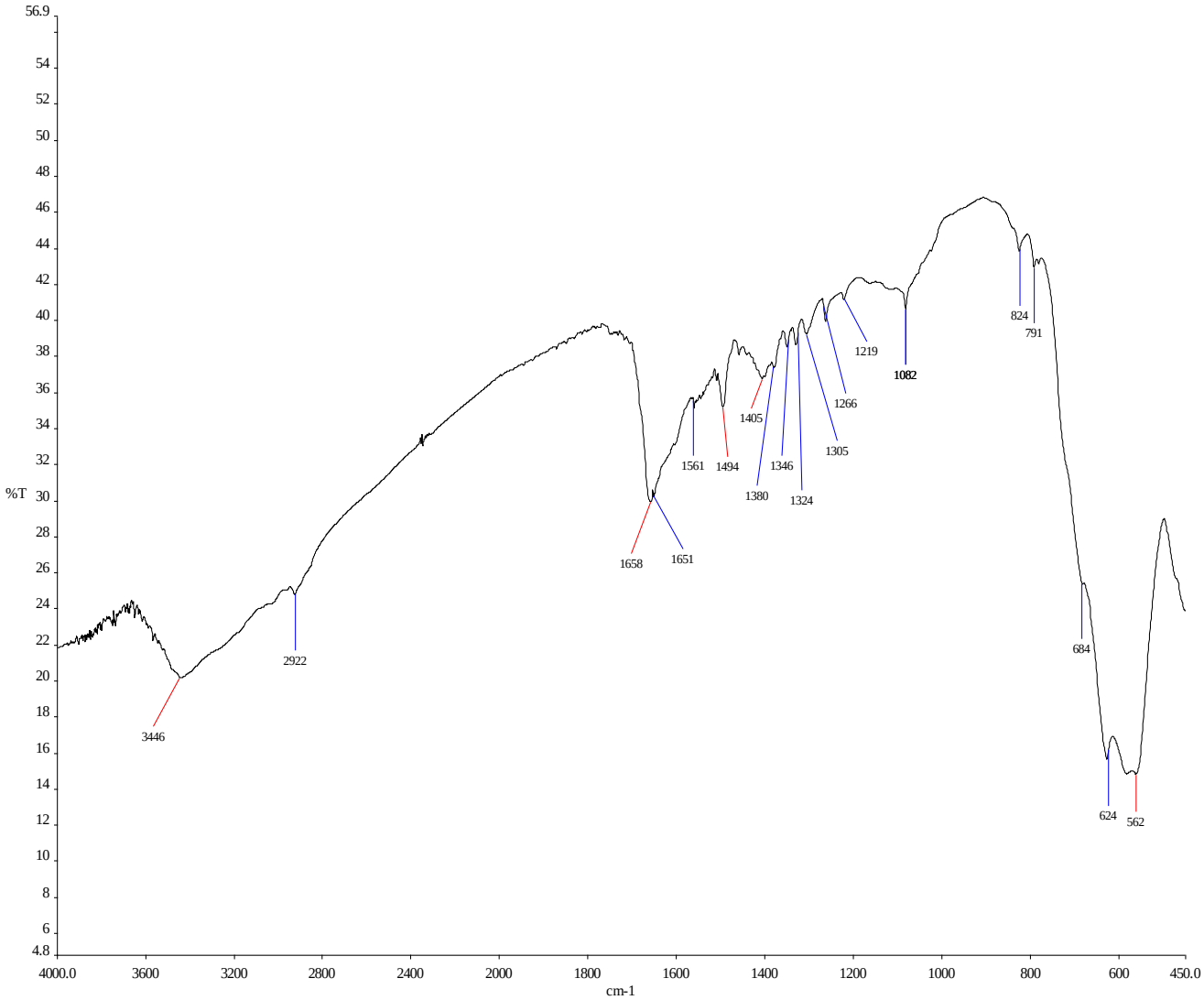


Fig SI 1b: FT-IR of nano-FGT after 5th run

2. FT-IR Spectrum of bis-adduct 2,2′-(4-chlorophenylmethylene)- bis(3 hydroxy-5,5-dimethylcyclohex-2-enone) (15a'):

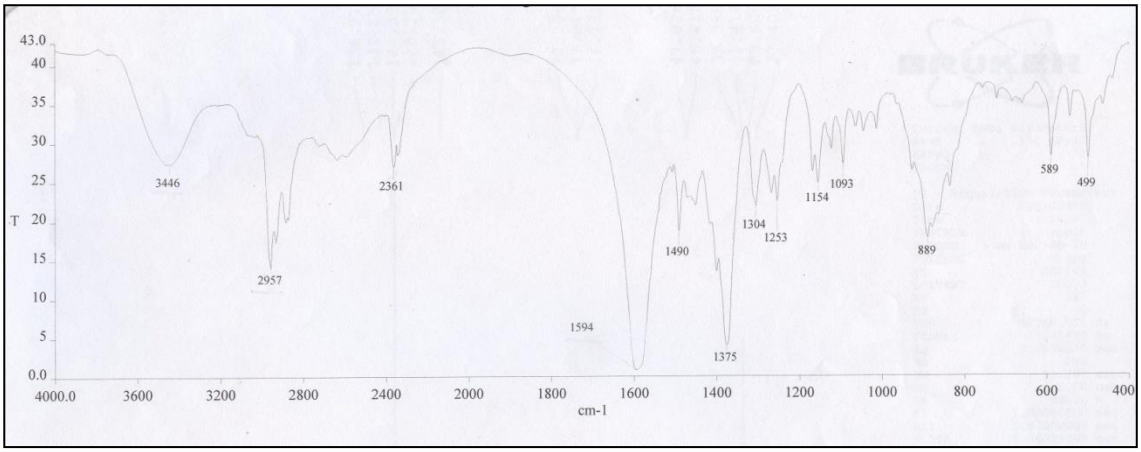


Fig SI 2: FT-IR of 15a'

3. ^{1}H NMR Spectrum of bis-adduct 2,2′-(4-chlorophenylmethylene)- bis(3 hydroxy-5,5-dimethylcyclohex-2-enone) (15a'):

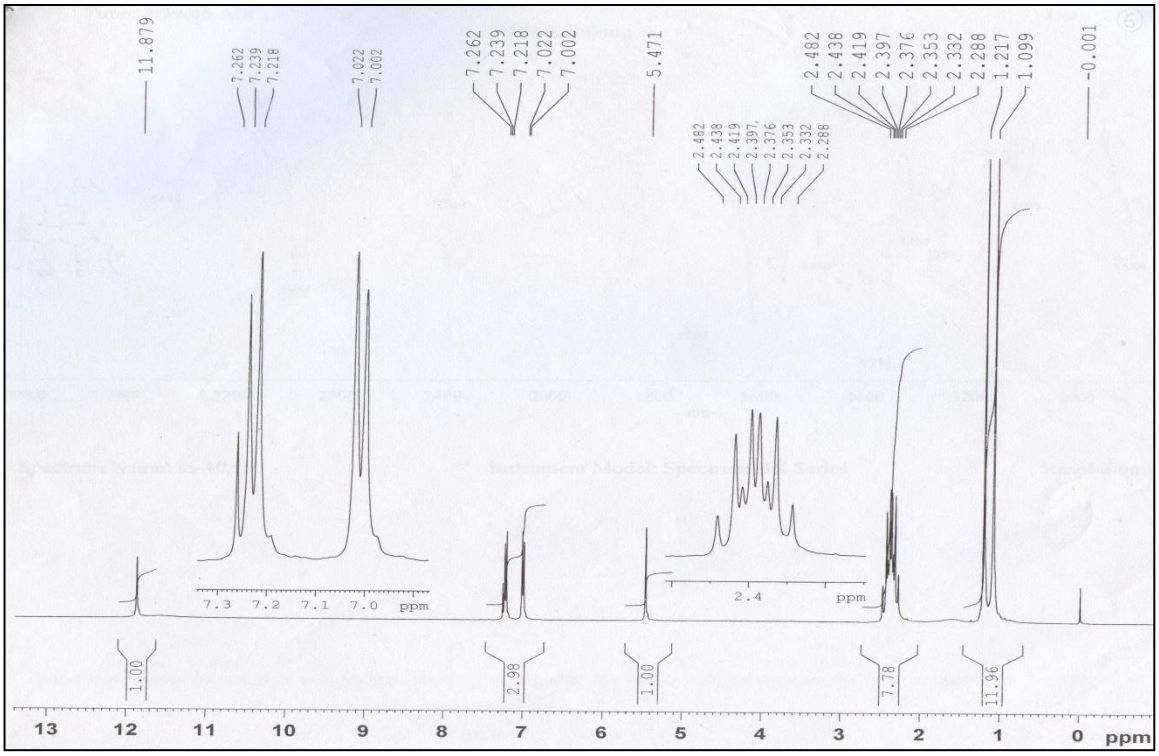


Fig SI 3: ^{1}H NMR Spectrum of 15a'

4. ^{13}C NMR Spectrum of bis-adduct 2,2′-(4-chlorophenylmethylene)- bis(3 hydroxy-5,5-dimethylcyclohex-2-enone) (15a'):

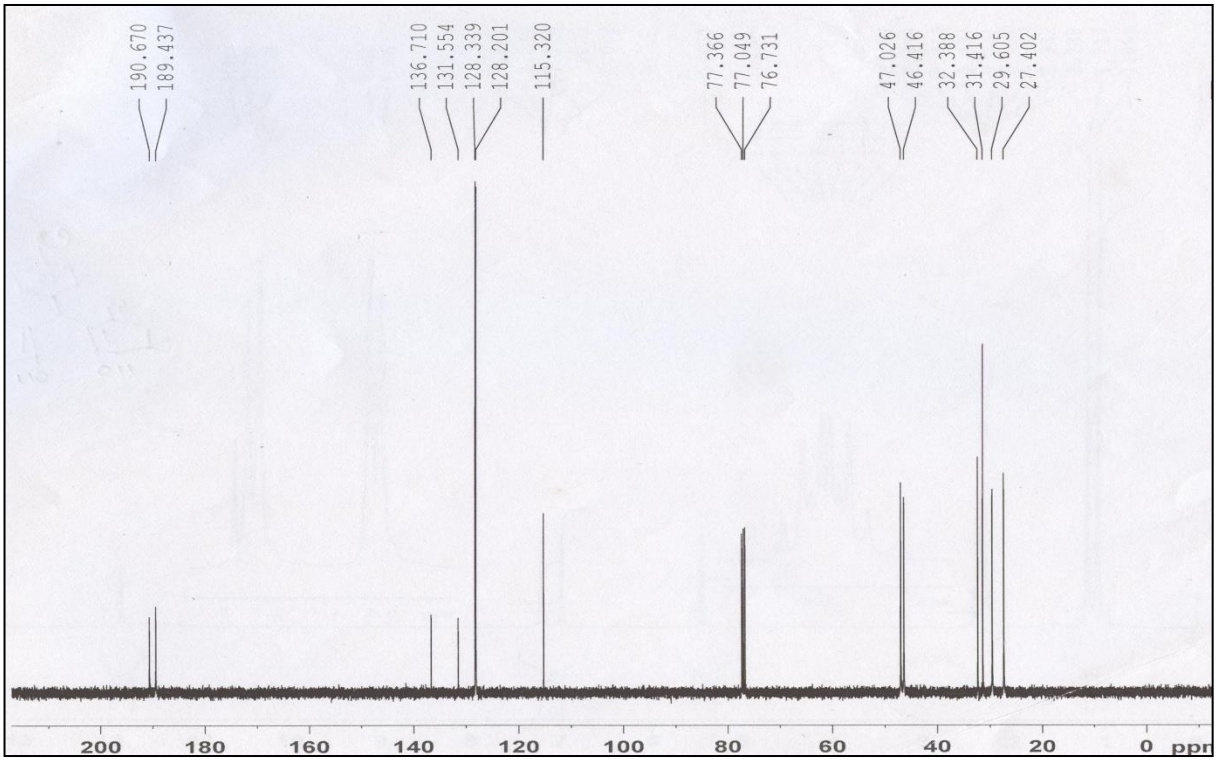
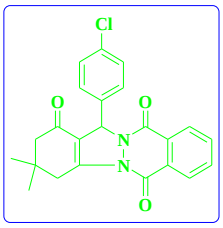


Fig SI 4: ^{13}C NMR Spectrum of 15a'

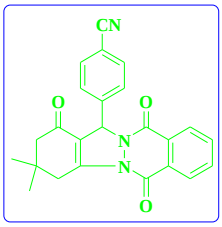
Spectral Data

1. Compound 15a



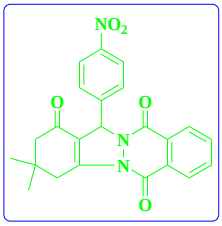
Yellow solid. IR (KBr): 2939, 2229, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.137 (s, 3H), 1.132 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 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.

2. Compound 15b



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.

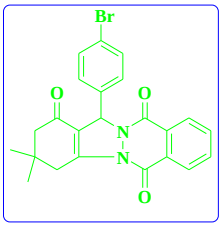
3. Compound 15c



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

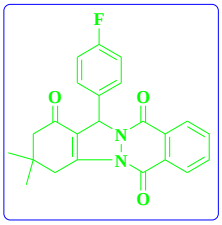
system, *J* = 19.2 Hz, 2H), 2.25 (s, 2H), 1.13 (s, 3H), 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.1, 155.9, 154.5, 151.7, 147.8, 143.4, 134.8, 133.9, 128.9, 128.5, 128.2, 128.0, 127.7, 124.0, 117.2, 64.1, 50.7, 37.9, 34.7, 28.6, 28.3. ESI- MS: *m/z* 418 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}N_3O_5$: C, 66.18; H, 4.59; N, 10.07. Found: C, 65.90; H, 4.45; N, 10.23.

4. Compound 15d



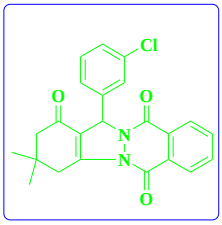
Yellow solid. IR (KBr): cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.29-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 3.35-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.1, 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.

5. Compound 15e



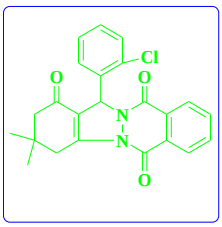
Yellow solid. IR (KBr): 2965, 2369, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28-8.18 (m, 2H), 7.80-7.78 (m, 2H), 7.34-7.31 (m, 2H), 6.97 (t, *J* = 8.2 Hz, 2H), 6.36 (s, 1H), 3.36-3.14 (AB system, *J* = 18.8 Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). ESI- MS: *m/z* 391 $[M + H]^+$. Anal. Calcd for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

6. Compound 15f



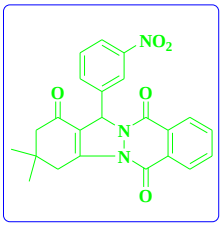
Yellow solid. IR (KBr): 2959, 2362, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.30-8.19 (m, 2H), 7.81-7.78 (m, 2H), 7.30-7.19 (m, 4H), 6.33 (s, 1H), 3.35-3.15 (AB system, *J* = 18.6 Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). ESI- MS: *m/z* 407, 409 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 67.61; H, 4.56; N, 7.15.

7. Compound 15g



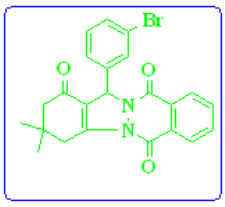
Yellow solid. IR (KBr): 2939, 1664 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.30-8.16 (m, 2H), 7.79-7.77 (m, 2H), 7.41-7.14 (m, 4H), 6.60 (s, 1H), 3.35-3.14 (AB system, *J* = 18.0 Hz, 2H), 2.25 (s, 2H), 1.14 (s, 6H). ESI- MS: *m/z* 407, 409 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}ClN_2O_3$: C, 67.90; H, 4.71; N, 6.89. Found: C, 67.93; H, 4.77; N, 6.71.

8. Compound 15h



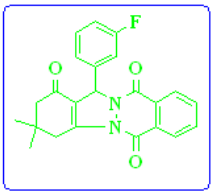
Yellow solid. IR (KBr): 2960, 2382, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.32-8.08 (m, 4H), 7.83-7.82 (brs, 3H), 7.51-7.47 (m, 1H), 6.45 (s, 1H), 3.38-3.18 (AB system, *J* = 18.7 Hz, 2H), 2.28 (s, 2H), 1.15 (s, 6H). ESI- MS: *m/z* 418 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}N_3O_5$: C, 66.18;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

9. Compound 15i



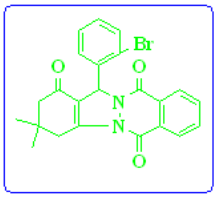
Yellow solid. IR (KBr): 2965, 2372, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.37-8.24 (m, 4H), 7.87-7.13 (m, 4H), 6.71 (s, 1H), 3.43-3.21 (AB system, *J* = 19.2 Hz, 2H), 2.32 (s, 2H), 1.25 (s, 3H), 1.21 (s, 3H). ESI- MS: *m/z* 451, 453 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}BrN_2O_3$: C, 61.21;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

10. Compound 15j



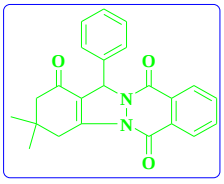
Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.27-8.24 (m, 4H), 7.88-6.98 (m, 4H), 6.53 (s, 1H), 3.45-3.18 (AB system, *J* = 18.0 Hz, 2H), 2.33 (s, 2H), 1.25 (s, 3H), 1.92 (s, 3H). ESI- MS: *m/z* 391 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}FN_2O_3$: C, 70.76;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

11. Compound 15k



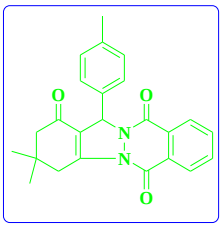
Yellow solid. IR (KBr): 2966, 2375, 1665 cm^{-1} .^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.35-8.25 (m, 4H), 7.90-7.84 (m, 4H), 6.39 (s, 1H), 3.44-3.20 (AB system, *J* = 17.5 Hz, 2H), 2.34 (s, 2H), 1.21 (s, 6H). ESI- MS: *m/z* 451, 453 $[M + H]^+$. Anal. Calcd for $C_{23}H_{19}BrN_2O_3$: C, 61.21; H, 4.24; N, 6.21. Found: C, 60.93; H, 4.12; N, 6.30.

12. Compound 15l



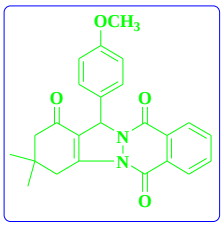
Yellow solid. IR (KBr): 2965, 2375, 1666 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.28-8.17 (m, 2H), 7.79-7.75 (m, 2H), 7.34-7.19 (m, 5H), 6.37 (s, 1H), 3.36-3.13 (AB system, *J* = 18.4 Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). · ESI- MS: *m/z* 373 $[M + H]^+$. Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18;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

13. Compound 15m



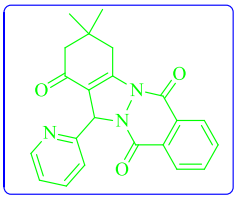
Yellow solid. IR (KBr): 2924, 2324, 1672 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ =8.28-8.18 (m, 2H), 7.78-7.76 (m, 2H), 7.23 7.07 (d, *J* = 7.6 Hz, 2H), (d, *J* = 7.6 Hz, 2H), 6.34 (s, 1H), 3.36-3.13 (AB system, *J* = 18.2 Hz, 2H), 2.26 (s, 2H), 2.22 (s, 3H), 1.13 (s, 6H). ESI- MS: *m/z* 387 $[M + H]^+$. 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.

14. Compound 15n



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.

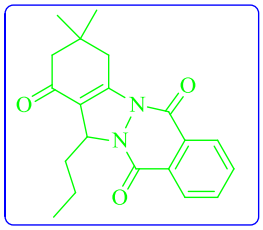
15. Compound 15o



Light Yellow colored solid. IR (KBr): 2927, 2340, 1660 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.43 (d, *J* = 4.0 Hz, 1H), 8.37-8.35 (m, 1H), 8.25-8.23 (m, 1H), 7.85-7.83 (m, 2H), 7.73 (d, *J* = 4.0 Hz, 2H), 7.20-7.17 (m, 1H), 6.45 (s, 1H), 3.46-3.22 (AB system, *J* =

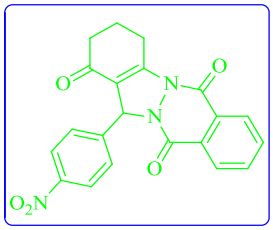
20.0 Hz, 2H), 2.32 (s, 2H), 1.21 (s, 3H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.4, 155.9, 154.5, 153.1, 147.8, 143.3, 134.8, 133.9, 128.8, 128.5, 128.2, 128.1, 127.7, 124.0, 118.3, 64.2, 36.7, 29.7, 24.5, 22.2, 14.1. ESI- MS: *m/z* 374 $[M + H]^+$. Anal. Calcd for $C_{22}H_{19}N_3O_3$: C, 70.76; H, 5.13; N, 11.25. Found: C, 70.81; H, 4.87; N, 11.42.

16. Compound 15p



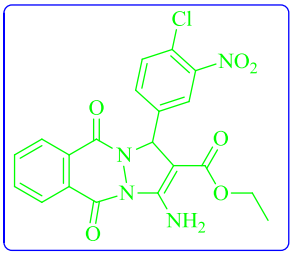
Yellow colored solid. IR (KBr): 2925, 2360, 1667 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.36-8.33 (m, 2H), 7.92-7.84 (m, 2H), 5.70 (s, 1H), 3.35-3.11 (AB system, *J* = 18.0 Hz, 2H), 2.45-2.33 (m, 4H), 2.11-2.04 (m, 2H), 1.22 (s, 3H), 1.19 (s, 3H), 0.88 (t, *J* = 6.0 Hz,3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 193.1, 156.1, 154.7, 151.6, 134.4, 133.4, 129.0, 128.8, 127.8, 127.5, 117.2, 62.8, 50.9, 38.0, 34.5, 31.5, 28.7, 28.4, 16.7, 13.7. ESI-MS: *m/z* 339 $[M + H]^+$. Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.86; H, 6.66; N, 7.99.

17. Compound 16a



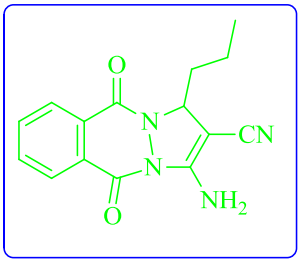
Yellow solid. IR (KBr): 2926, 2854, 1657 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.41-8.38 (m, 1H), 8.27-8.25 (m, 1 H), 8.21 (d, *J* = 6.8 Hz, 2H), 7.91-7.88 (m, 2H) , 7.63 (d, *J*= 7.2 Hz, 2H), 6.51 (s, 1H), 3.60-3.54 (m, 1H), 3.39-3.33 (m, 1H), 2.49 (t, *J* = 5.4 Hz, 2H), 2.30-2.22 (m,2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 192.5, 155.9, 154.5, 153.1, 147.8, 143.3, 134.8, 134.0, 128.8, 128.5, 128.2, 128.1, 127.8, 124.0, 118.3, 64.2, 36.7, 24.5, 22.2. ESI- MS: *m/z* 390 $[M + H]^+$. Anal. Calcd for $C_{21}H_{15}N_3O_5$: C, 64.78; H, 3.88; N, 10.79. Found: C, 64.95; H, 3.65; N, 10.85.

18. Compound 17a



Yellow colored solid. IR (KBr): 2928, 2410, 1670 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.32-8.31 (m, 1H), 8.20-8.19 (m, 1H), 7.88 (s, 1H), 7.84-7.83 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J*= 8.0 Hz, 1H), 7.20 (s, 2H), 6.23 (s, 1H), 4.04-4.02 (m, 2H), 1.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 163.6, 157.2, 154.1, 147.7, 139.2, 134.9, 133.9, 132.5, 131.7, 128.7, 128.5, 127.9, 127.7, 126.8, 124.6, 62.6, 59.9, 14.2, 1.0. ESI- MS: *m/z* 443, 445 $[M + H]^+$. Anal. Calcd for $C_{20}H_{15}ClN_4O_6$: C, 54.25; H, 3.41; N, 12.65. Found: C, 54.36; H, 3.66; N, 12.53.

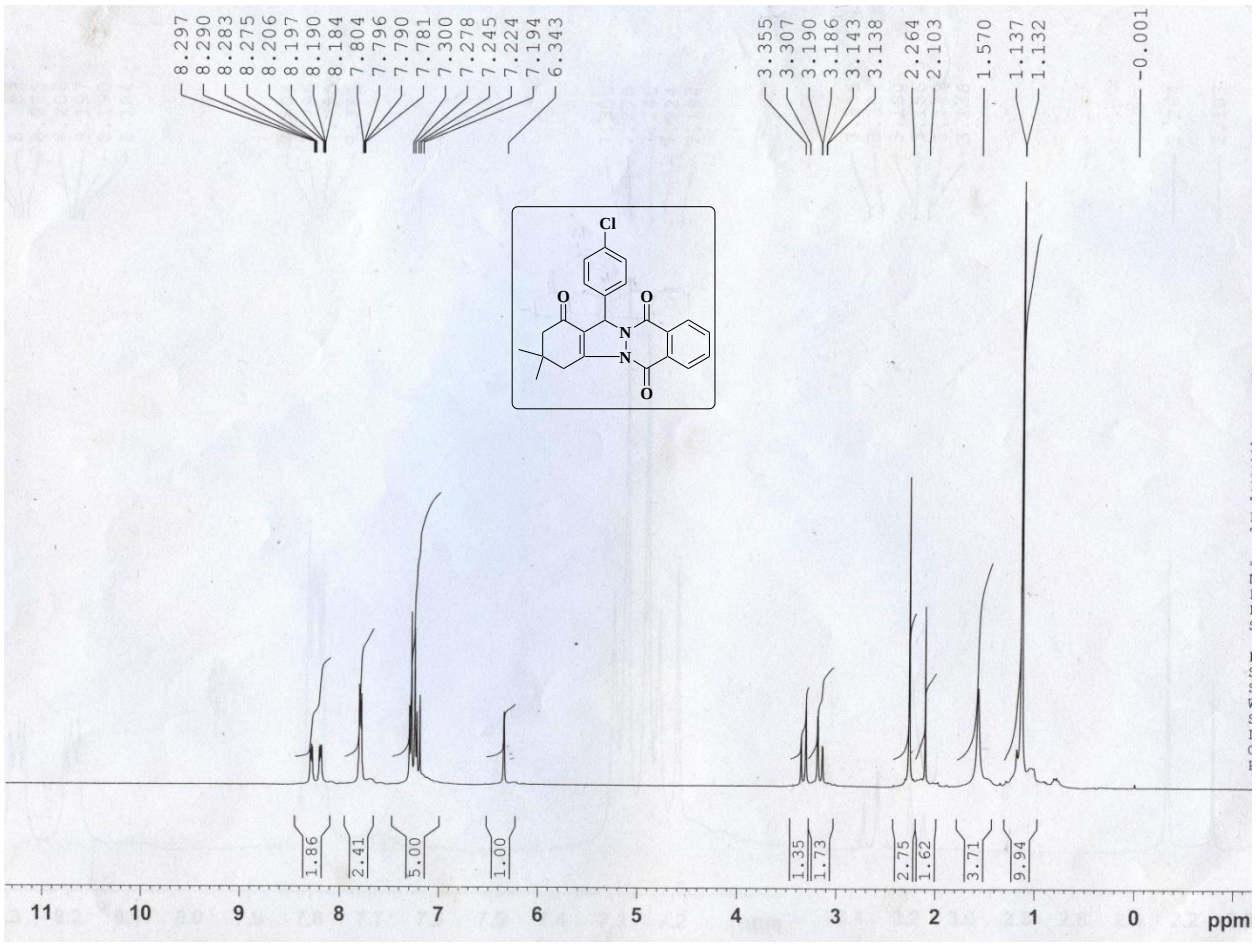
19. Compound 18a



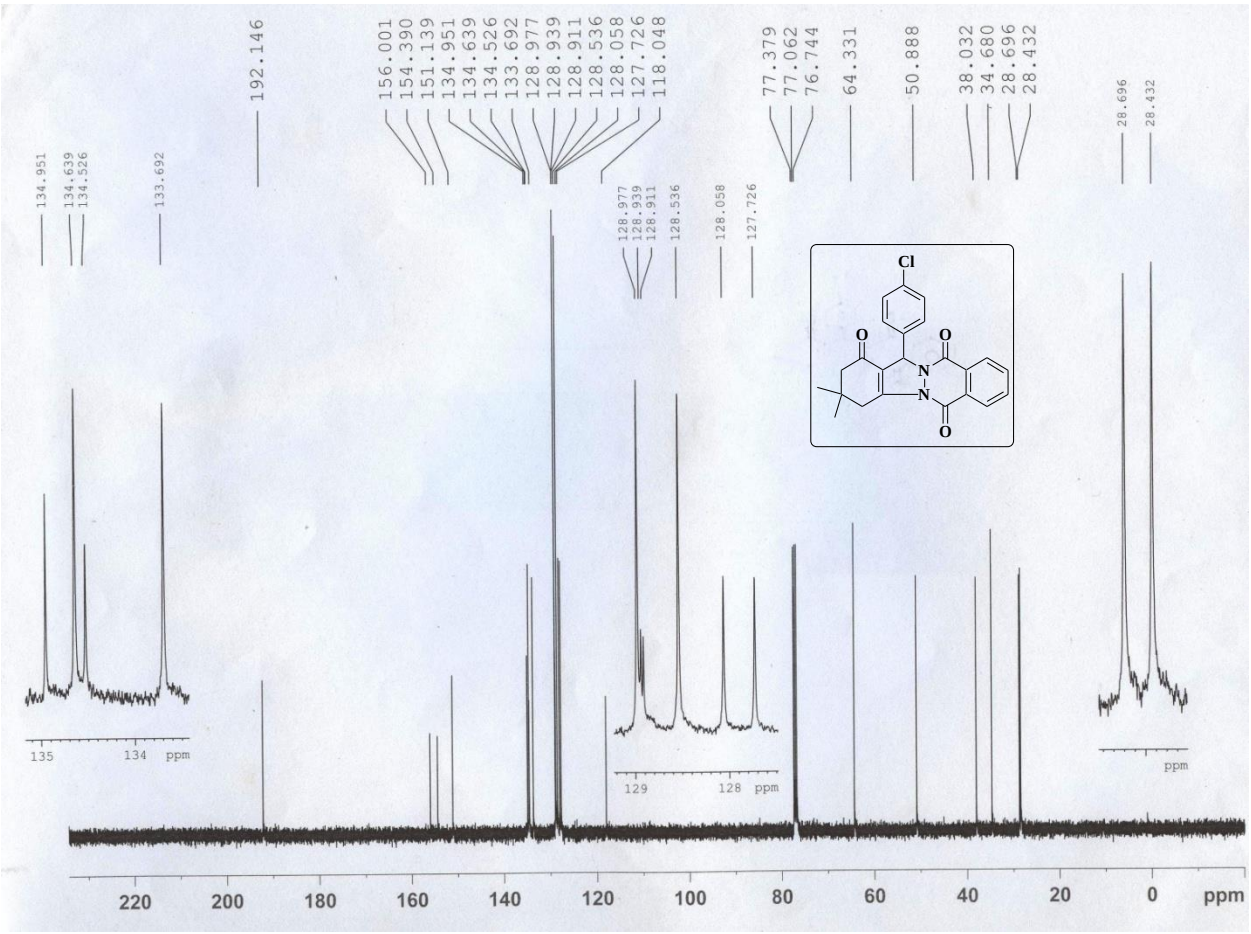
Yellow colored solid. IR (KBr): 2945, 2350, 1657 cm^{-1} .^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.37-8.32 (m, 2H), 7.95-7.86 (m, 2H), 6.66 (s, 2H), 5.43-5.42 (m, 1H), 2.26-2.17 (m, 2 H), 2.01-1.95 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 156.9, 154.3, 151.0, 134.9, 133.7, 128.9, 128.2, 127.8, 127.6, 115.4, 61.1, 34.0, 16.5, 13.7. ESI-MS: *m/z* 283 $[M + H]^+$. Anal. Calcd for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.00; N, 19.85. Found: C, 64.03; H, 4.87; N, 19.63.

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

1. Compound 15a

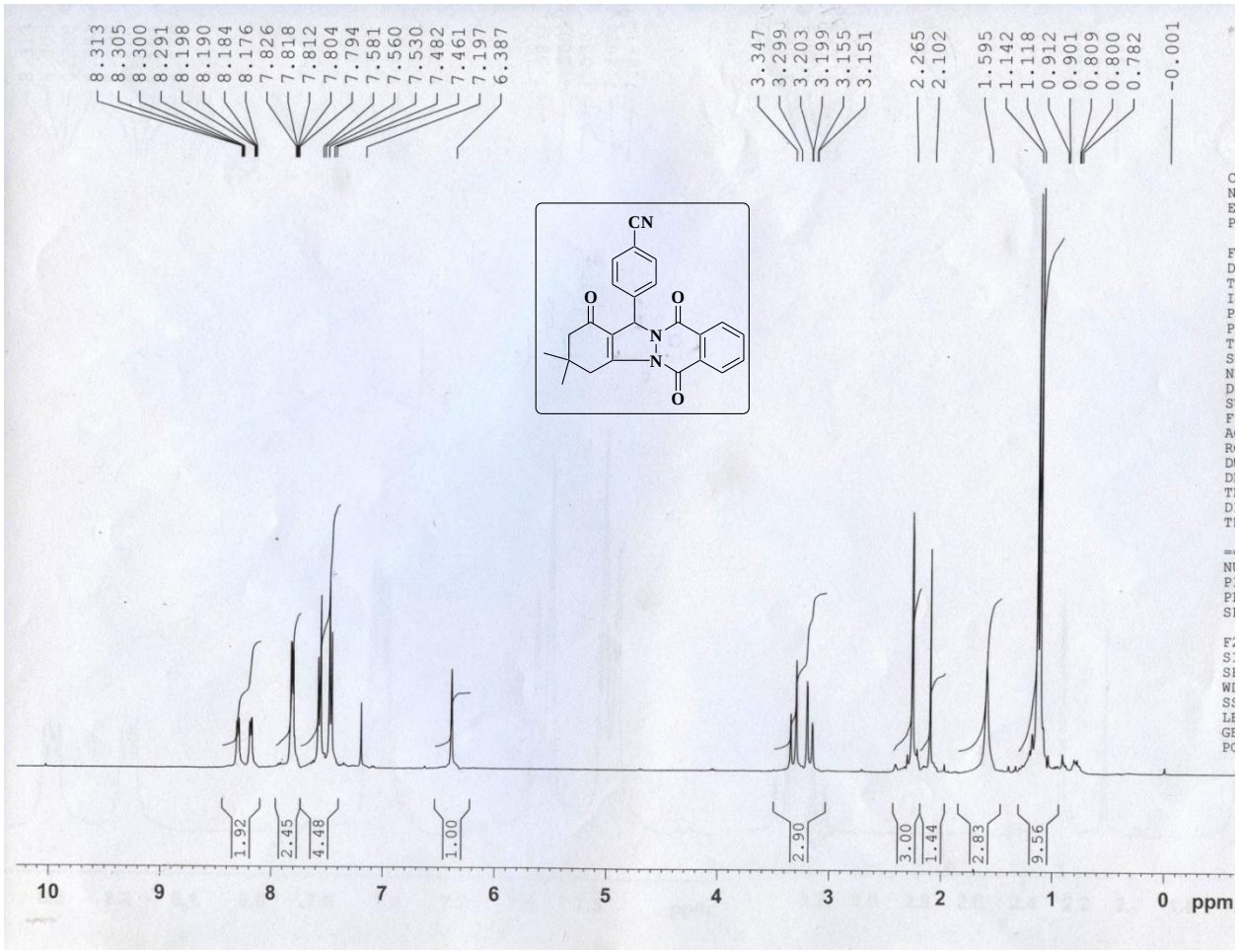


^{1}H NMR Spectra of Compound 15a

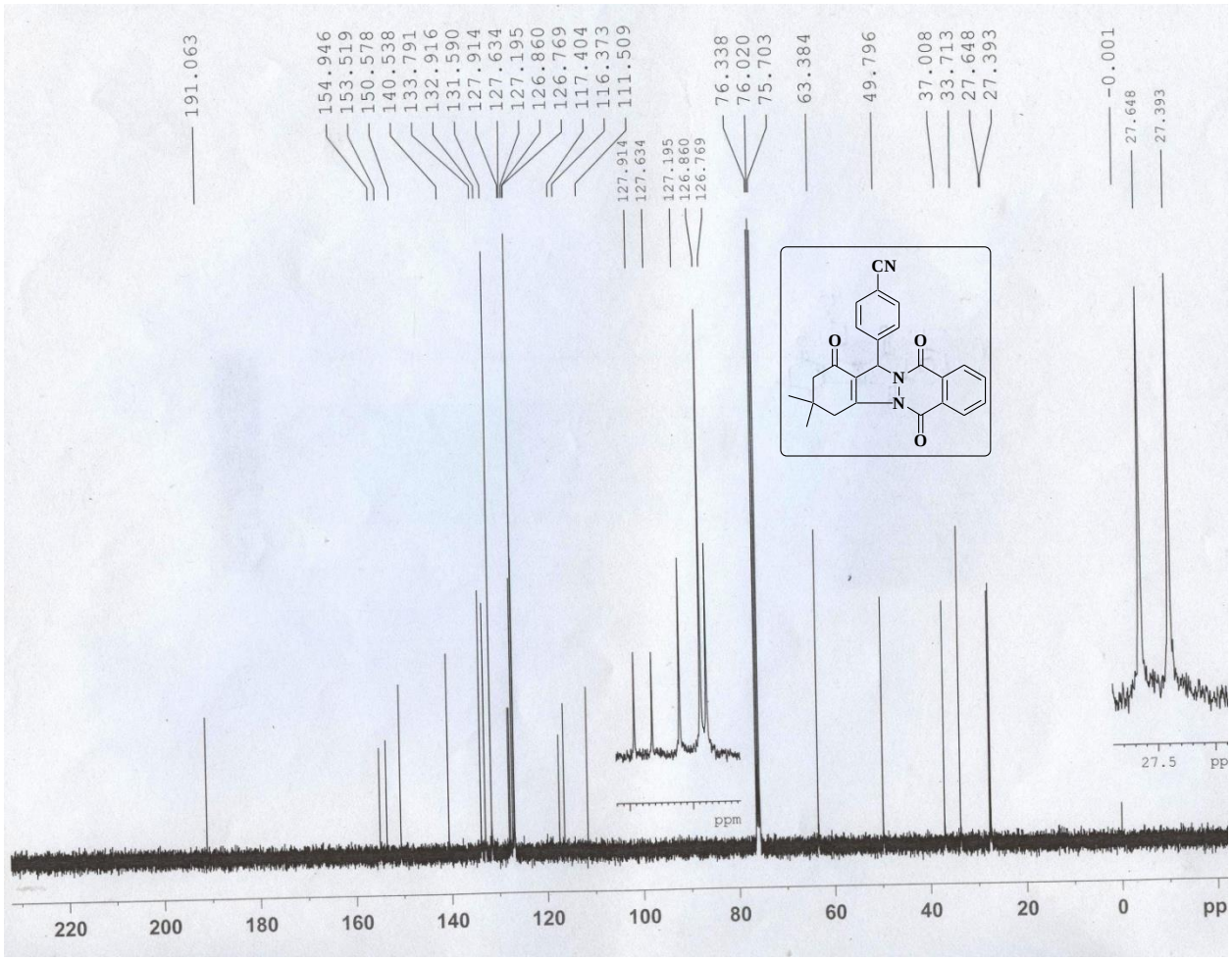


^{13}C NMR Spectra of Compound 15a

2. Compound 15b

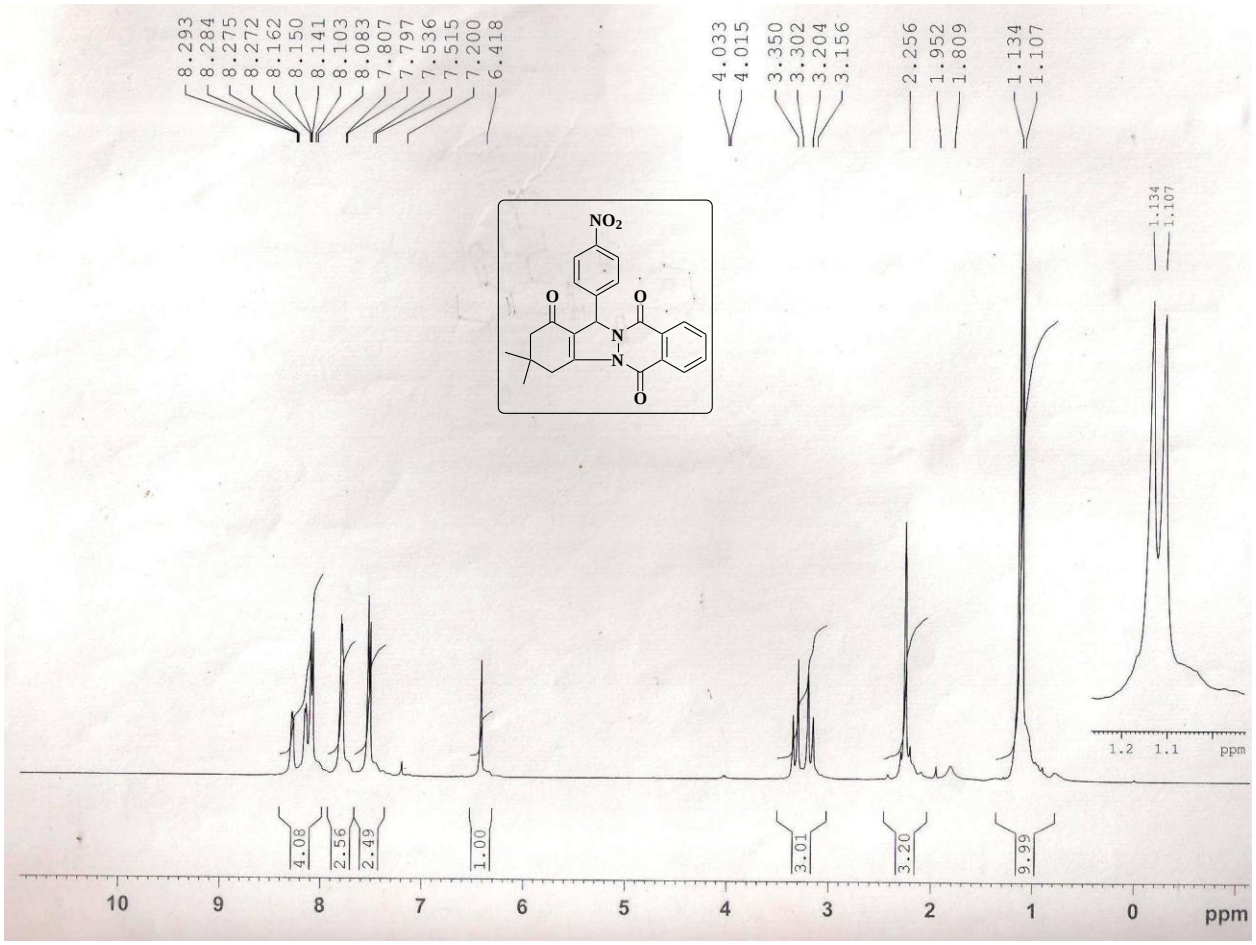


^{1}H NMR Spectra of Compound 15b

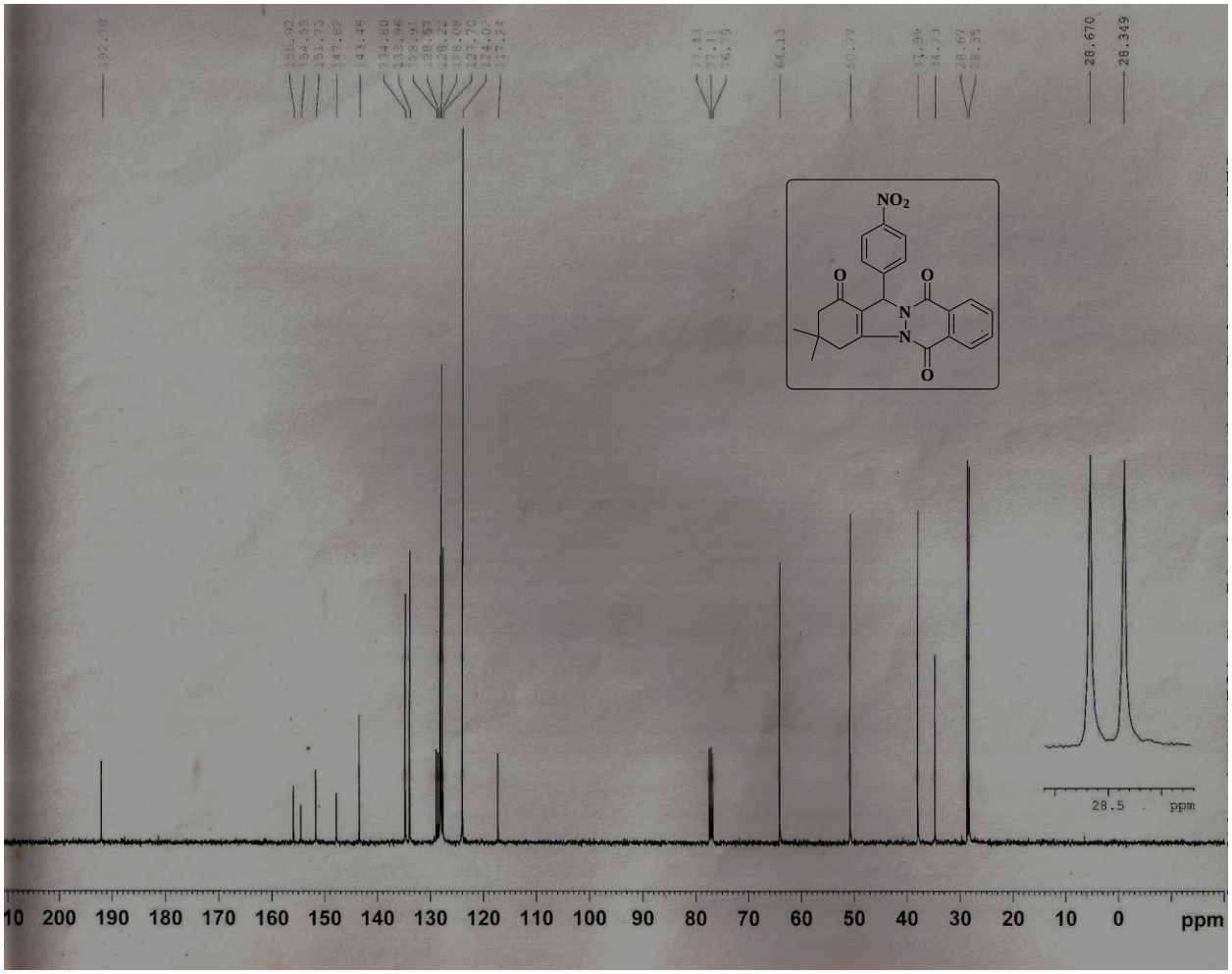


^{13}C NMR Spectra of Compound 15b

3. Compound 15c

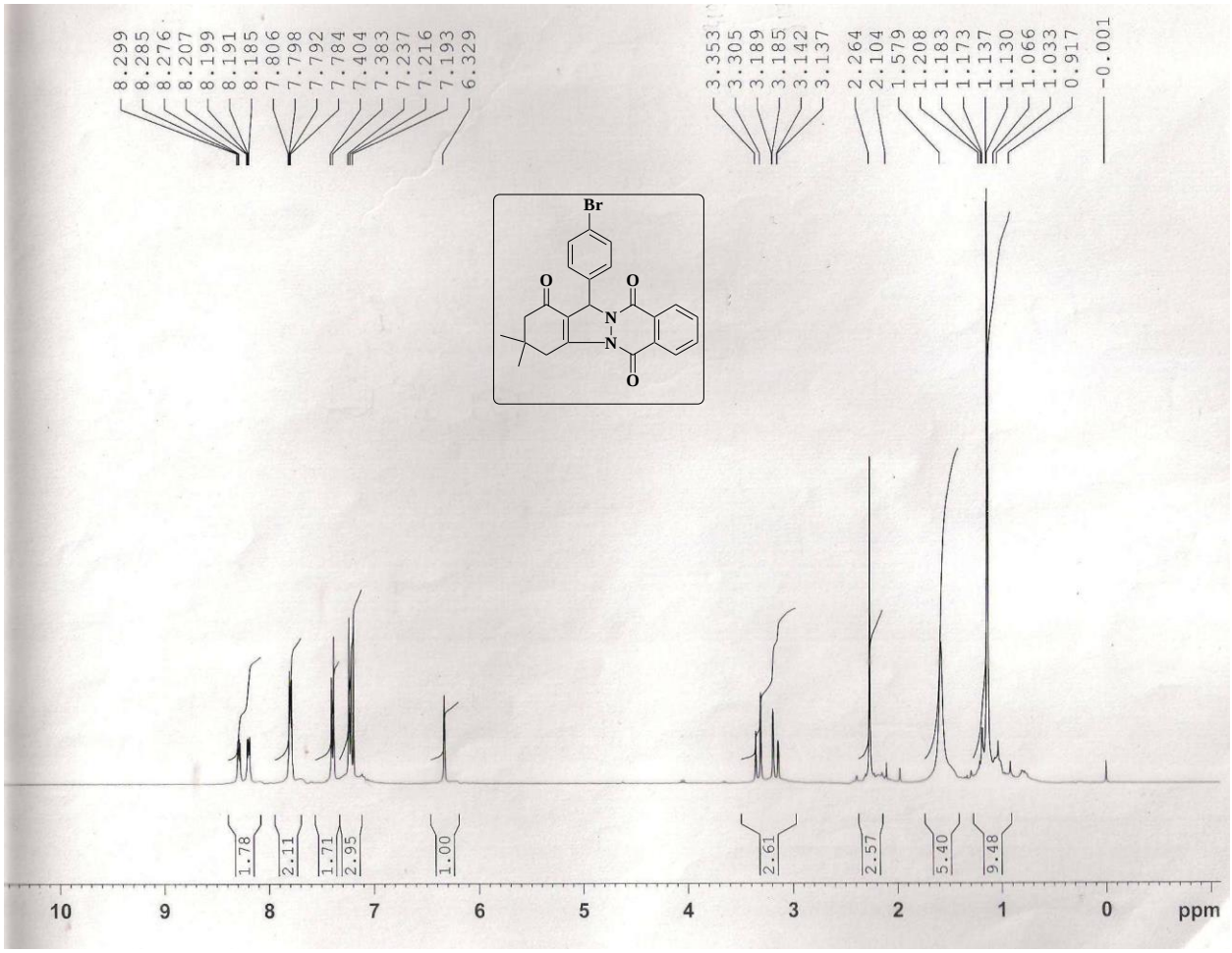


^{1}H NMR Spectra of Compound 15c

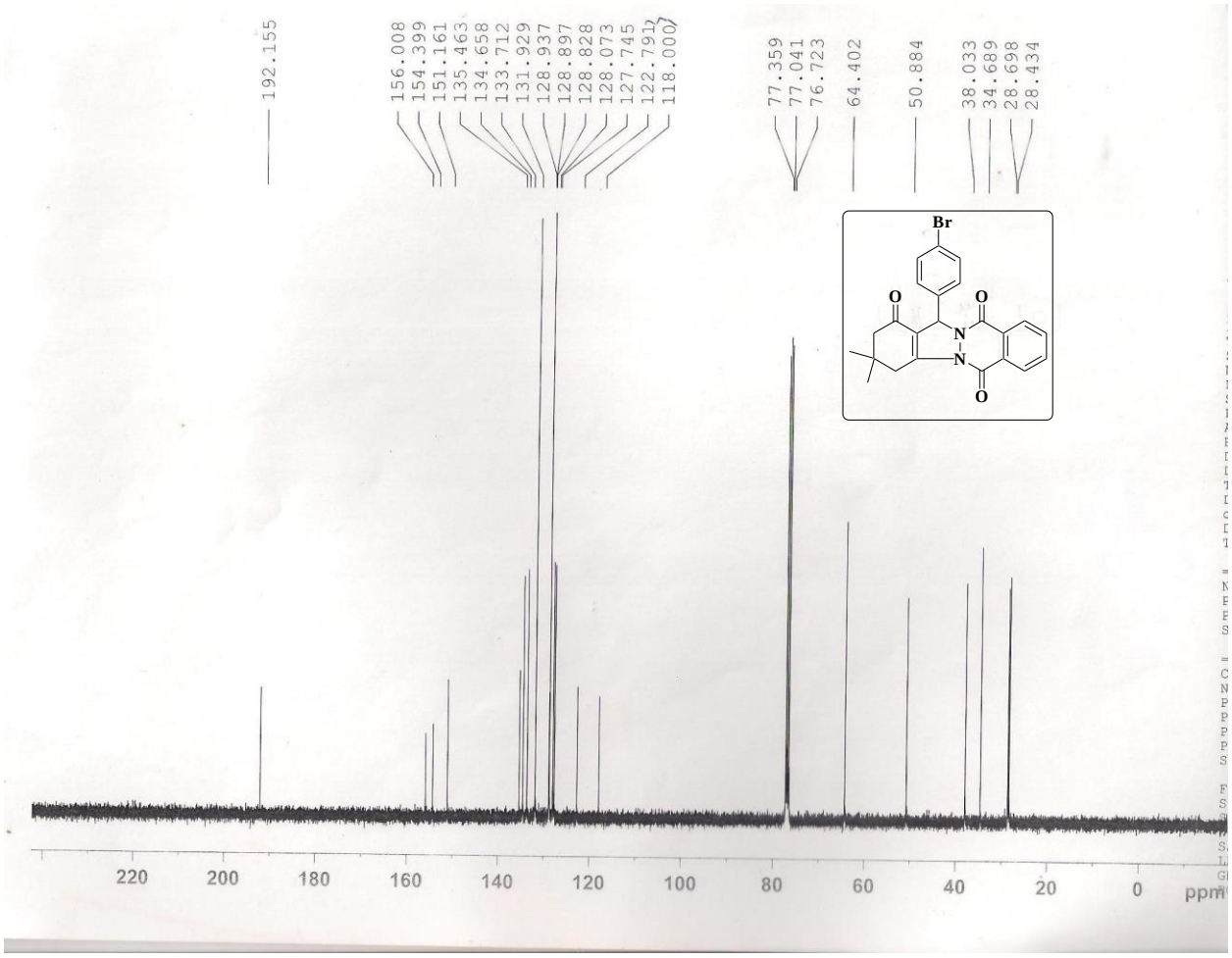


^{13}C NMR Spectra of Compound 15c

4. Compound 15d

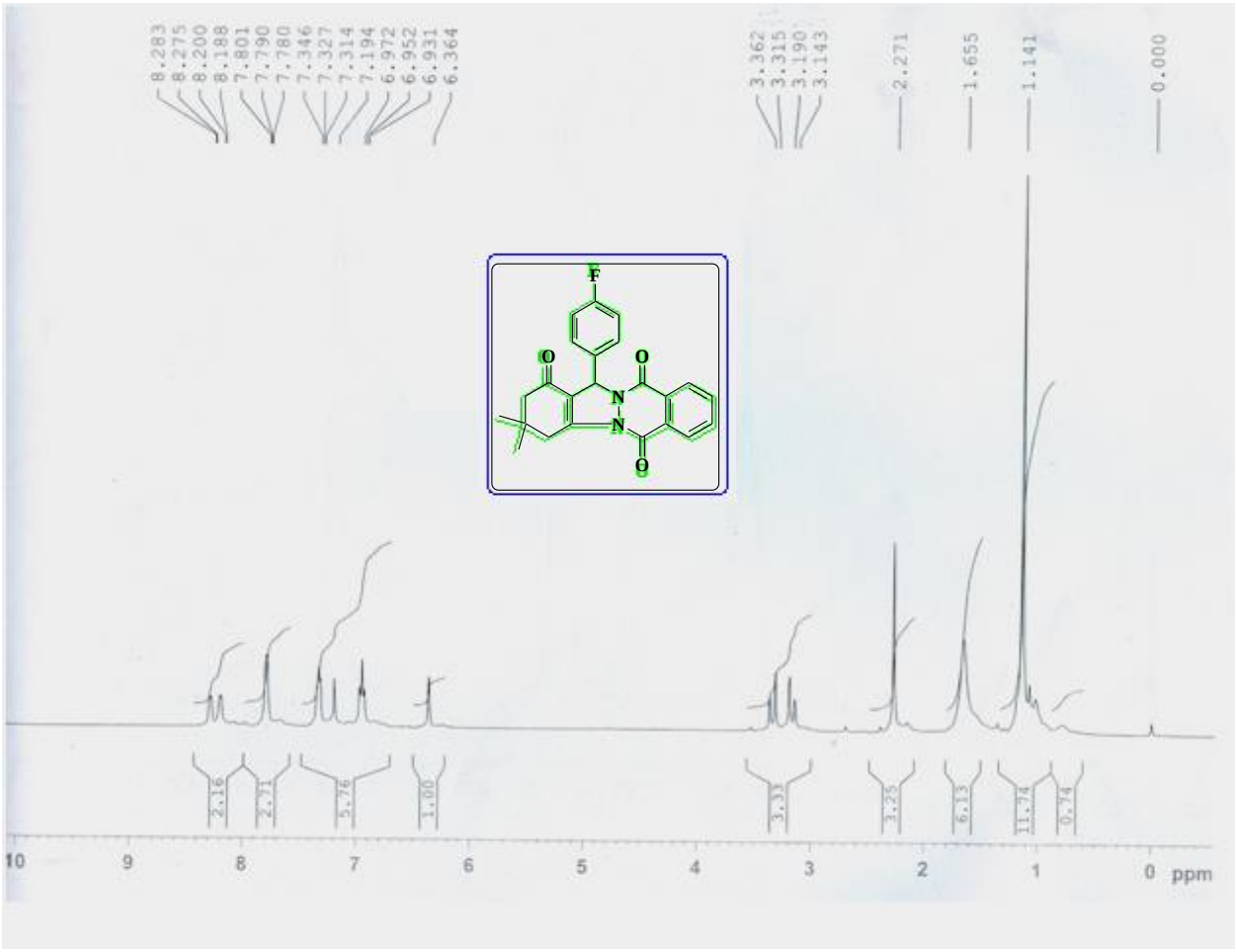


^{1}H NMR Spectra of Compound 15d



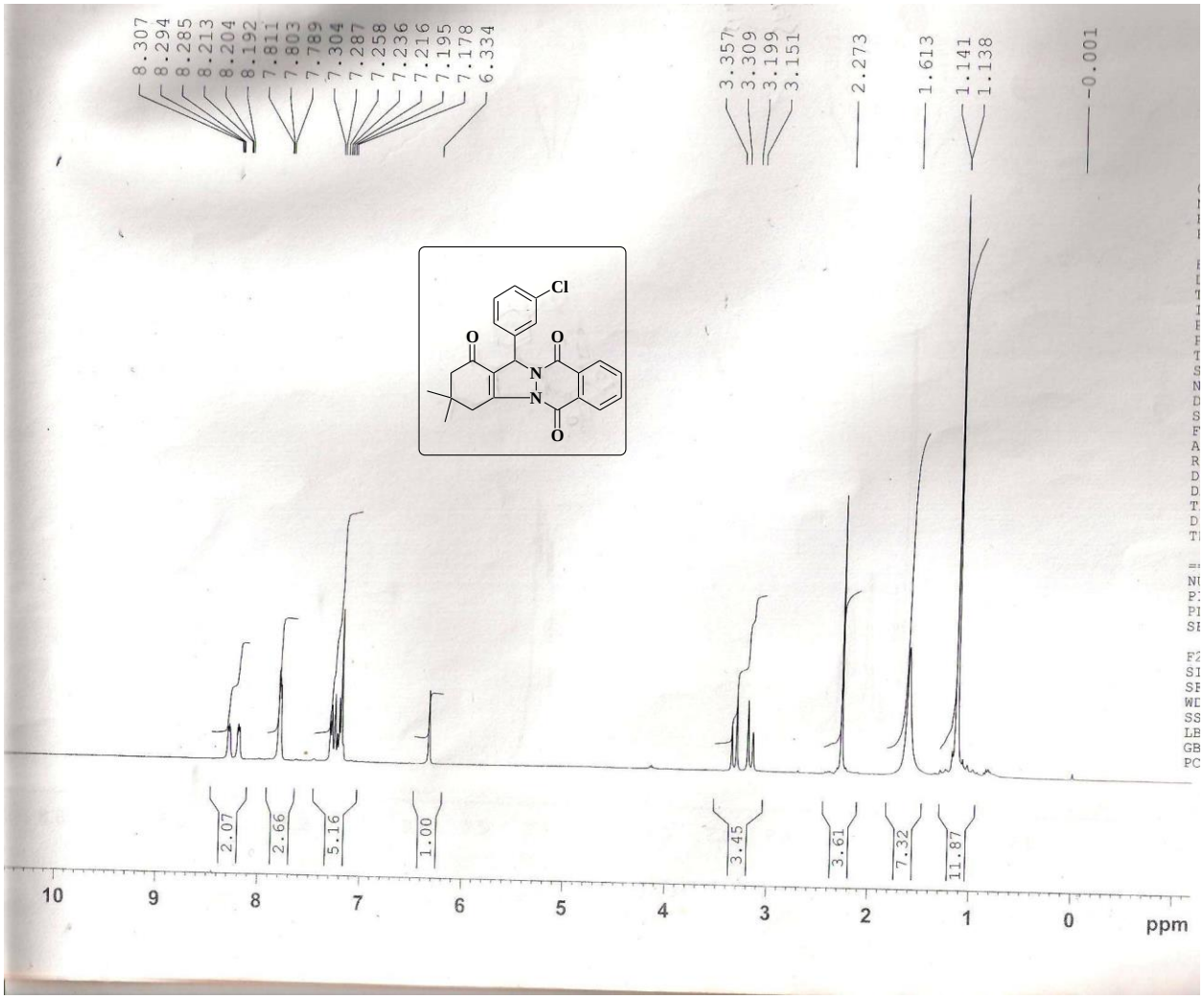
^{13}C NMR Spectra of Compound 15d

5. Compound 15e



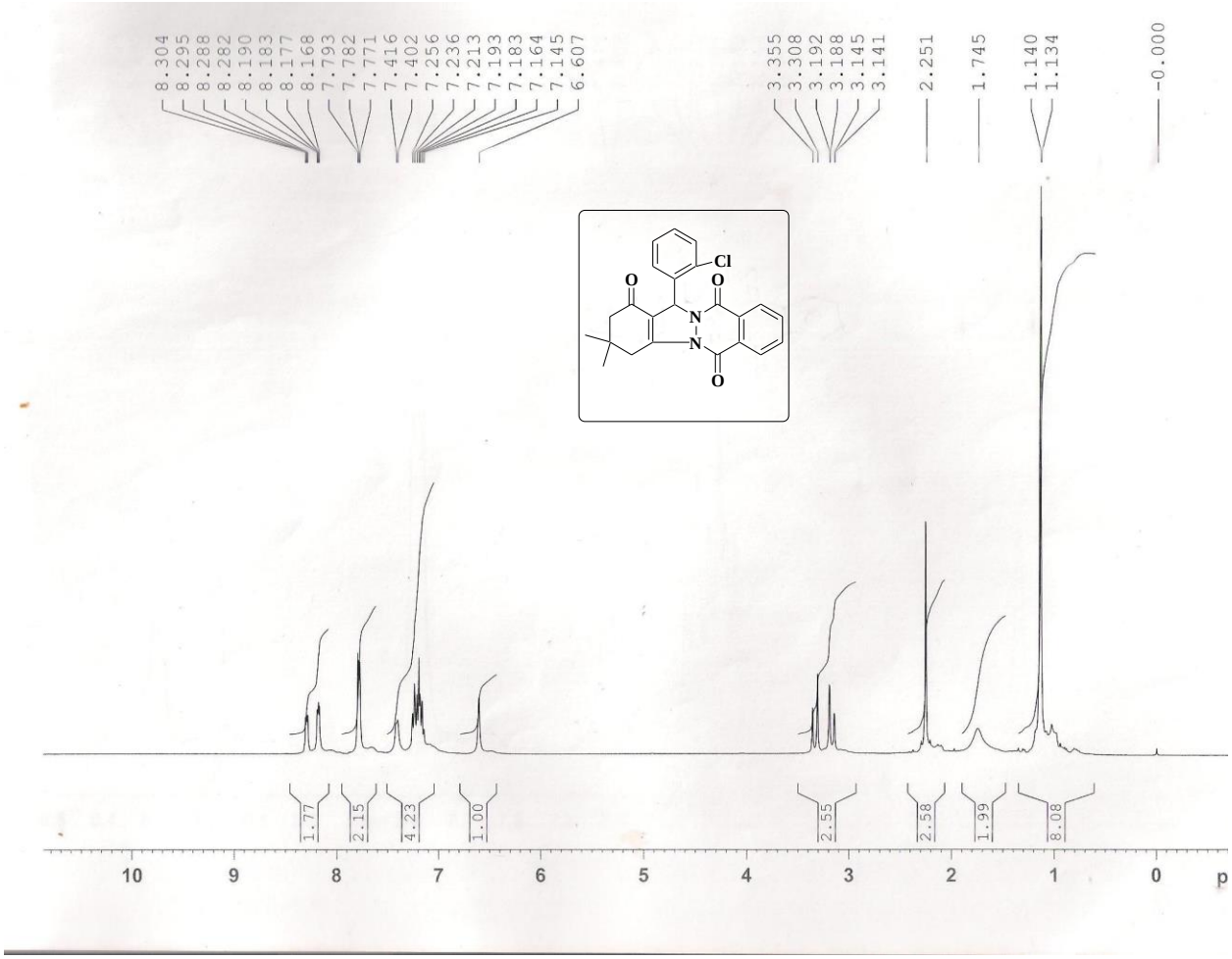
^{1}H NMR Spectra of Compound 15e

6. Compound 15f



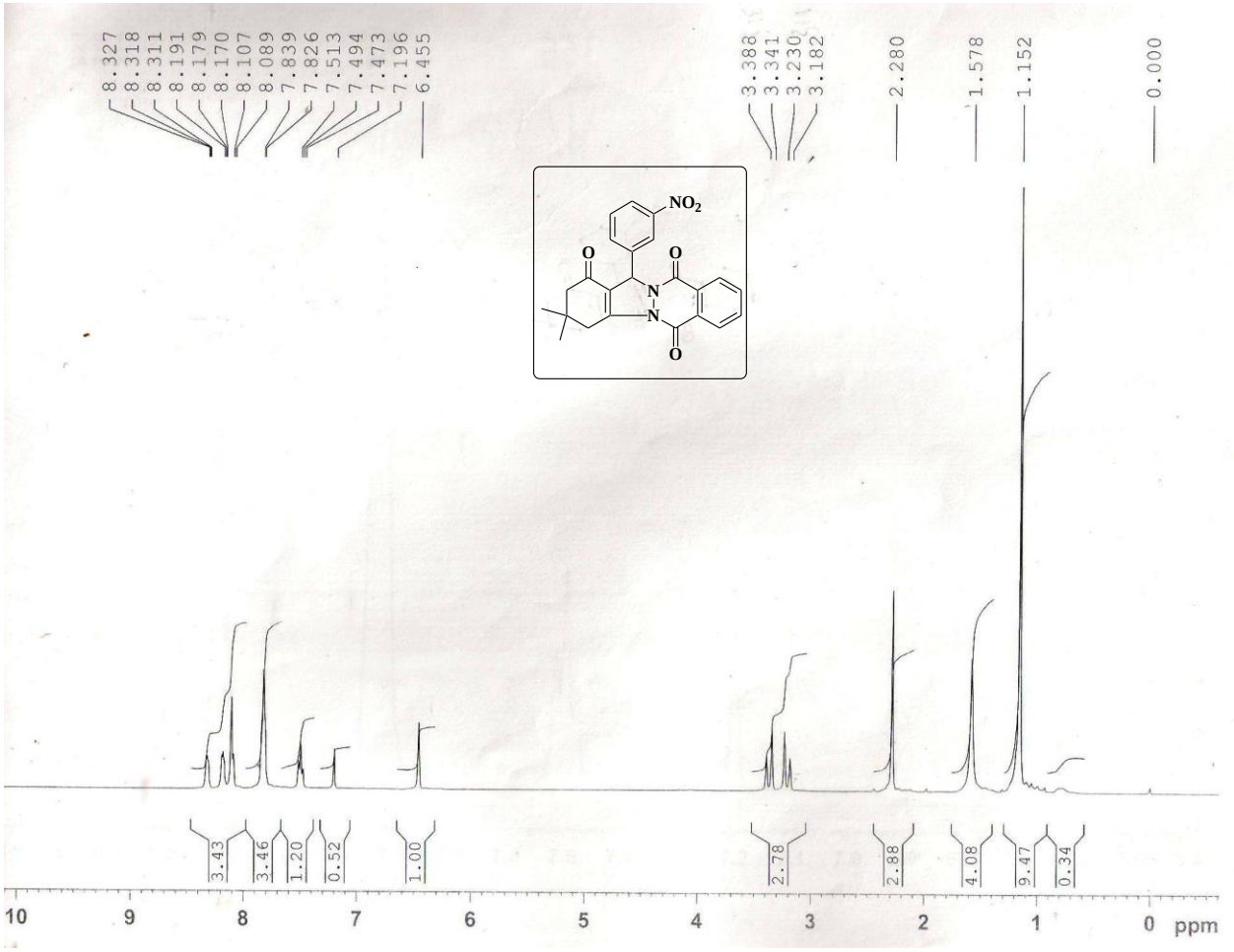
^{1}H NMR Spectra of Compound 15f

7. Compound 15g



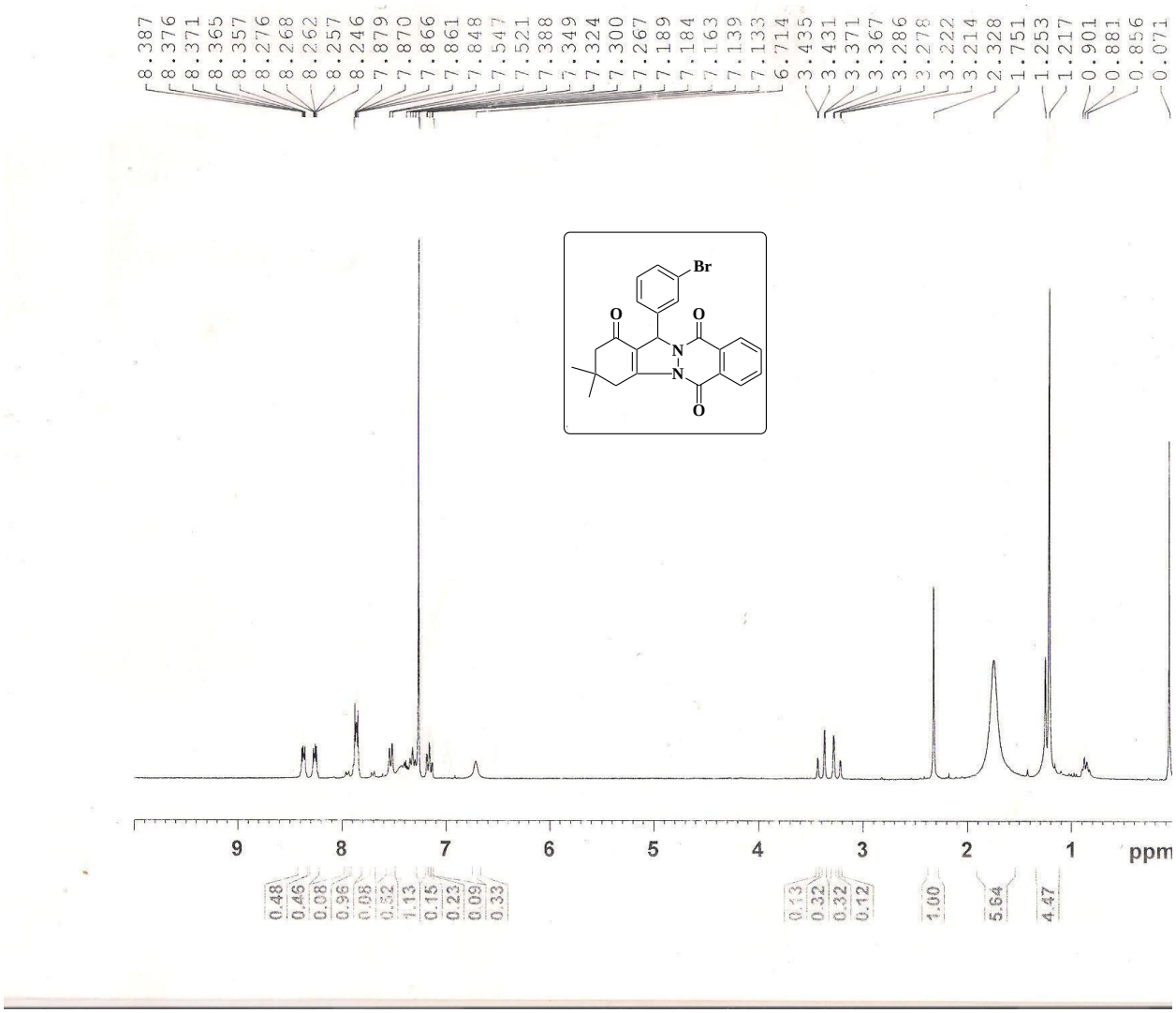
^{1}H NMR Spectra of Compound 15g

8. Compound 15h



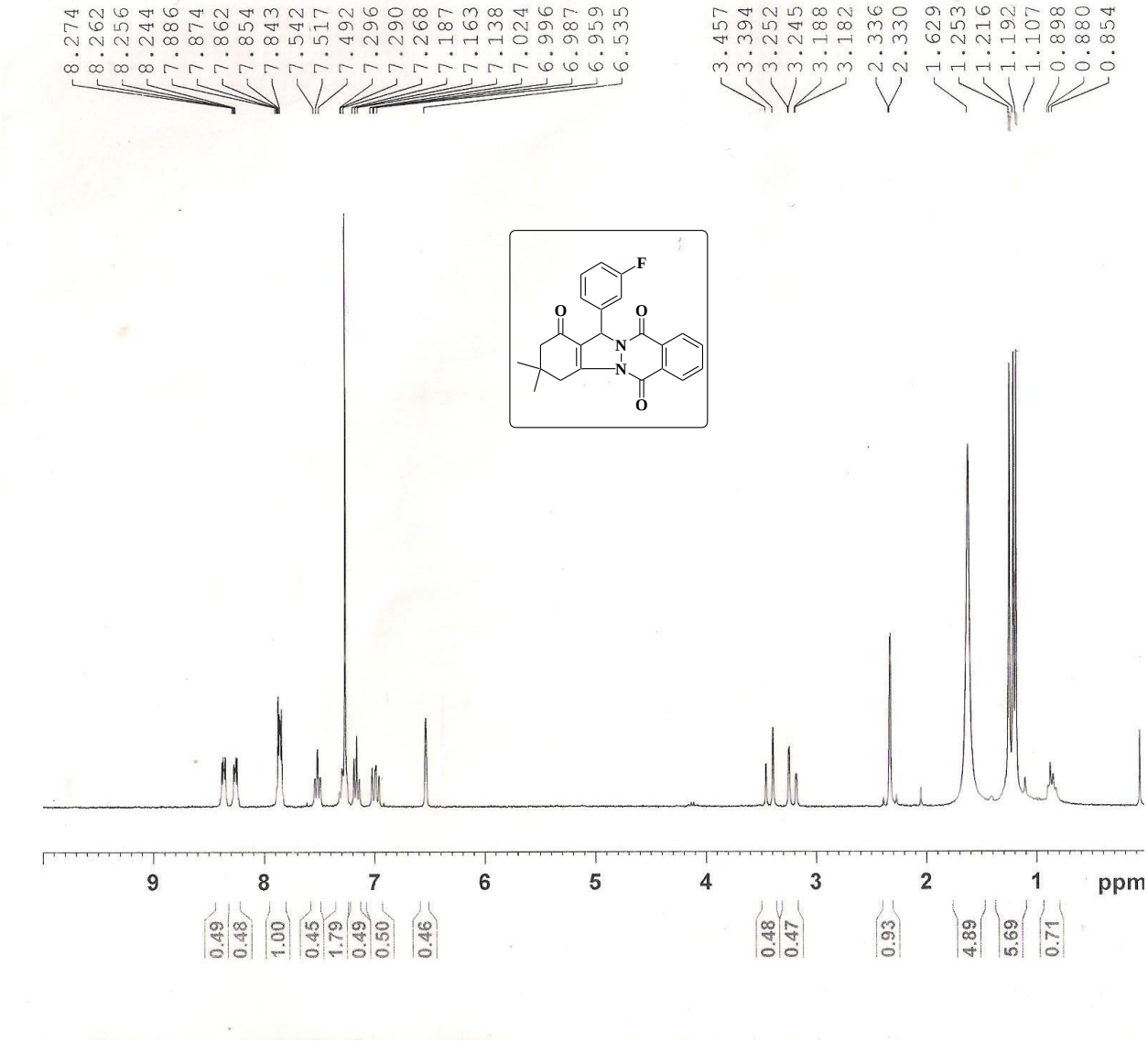
^{1}H NMR Spectra of Compound 15h

9. Compound 15i



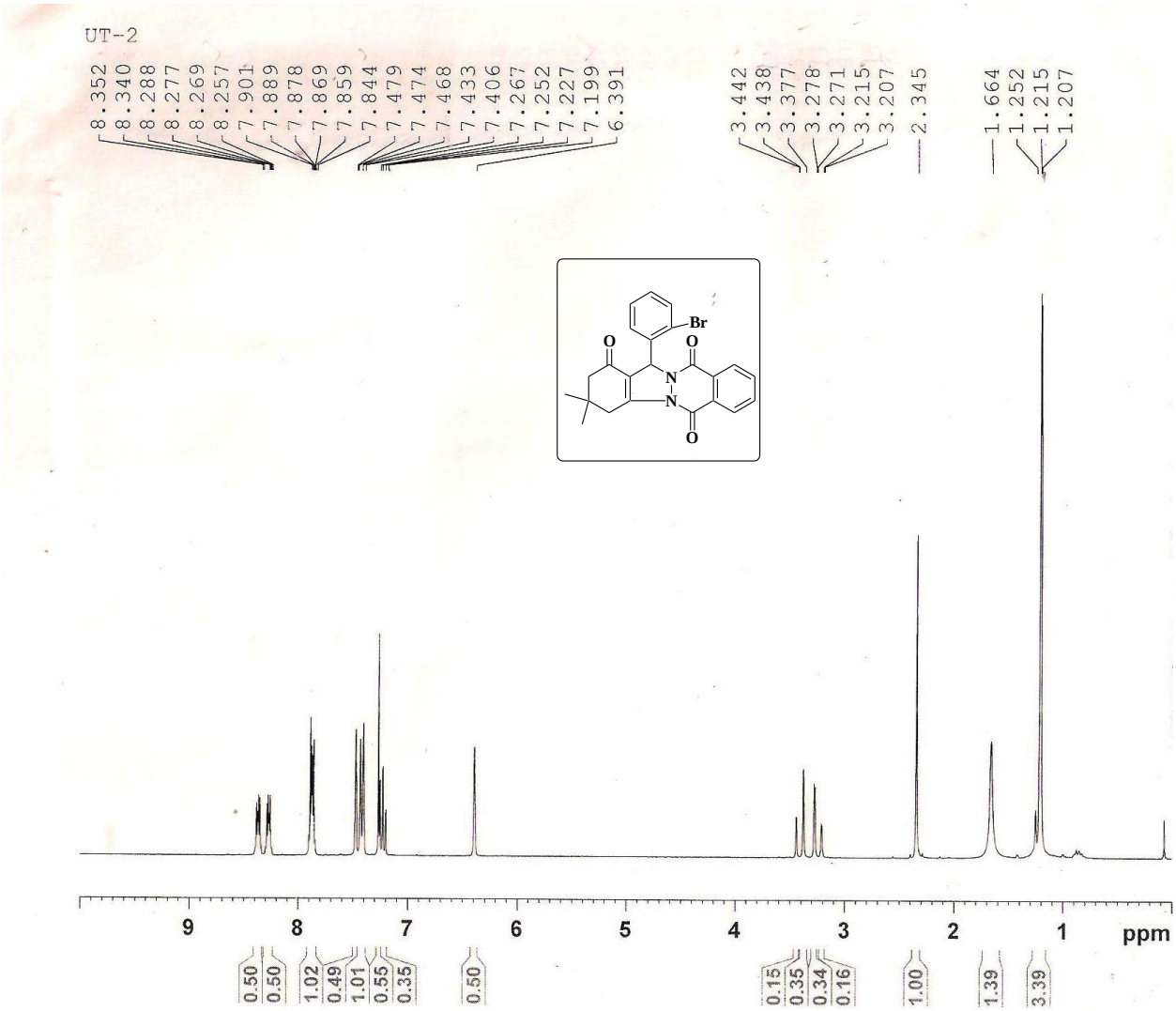
^{1}H NMR Spectra of Compound 15i

10. Compound 15j



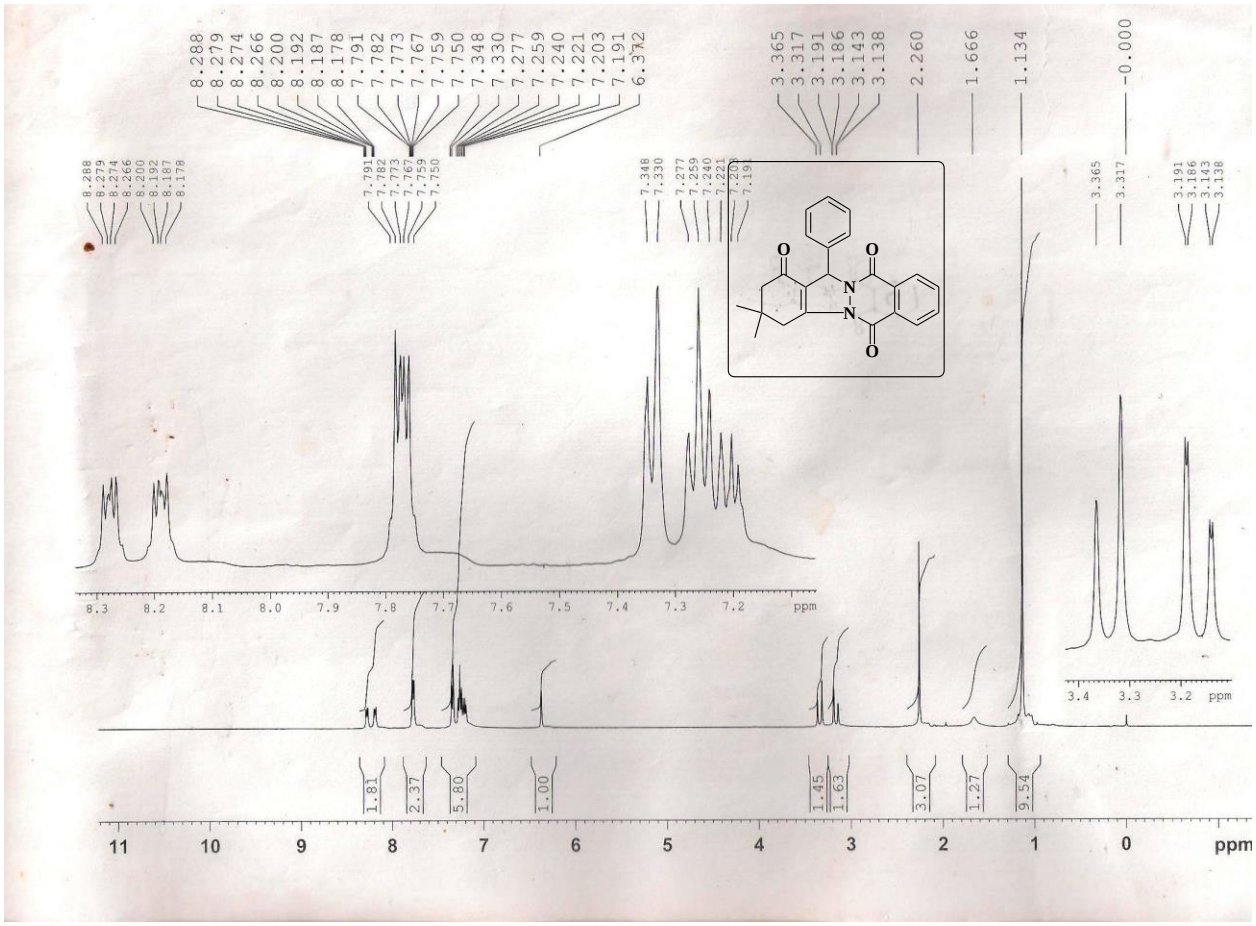
^{1}H NMR Spectra of Compound 15j

11. Compound 15k



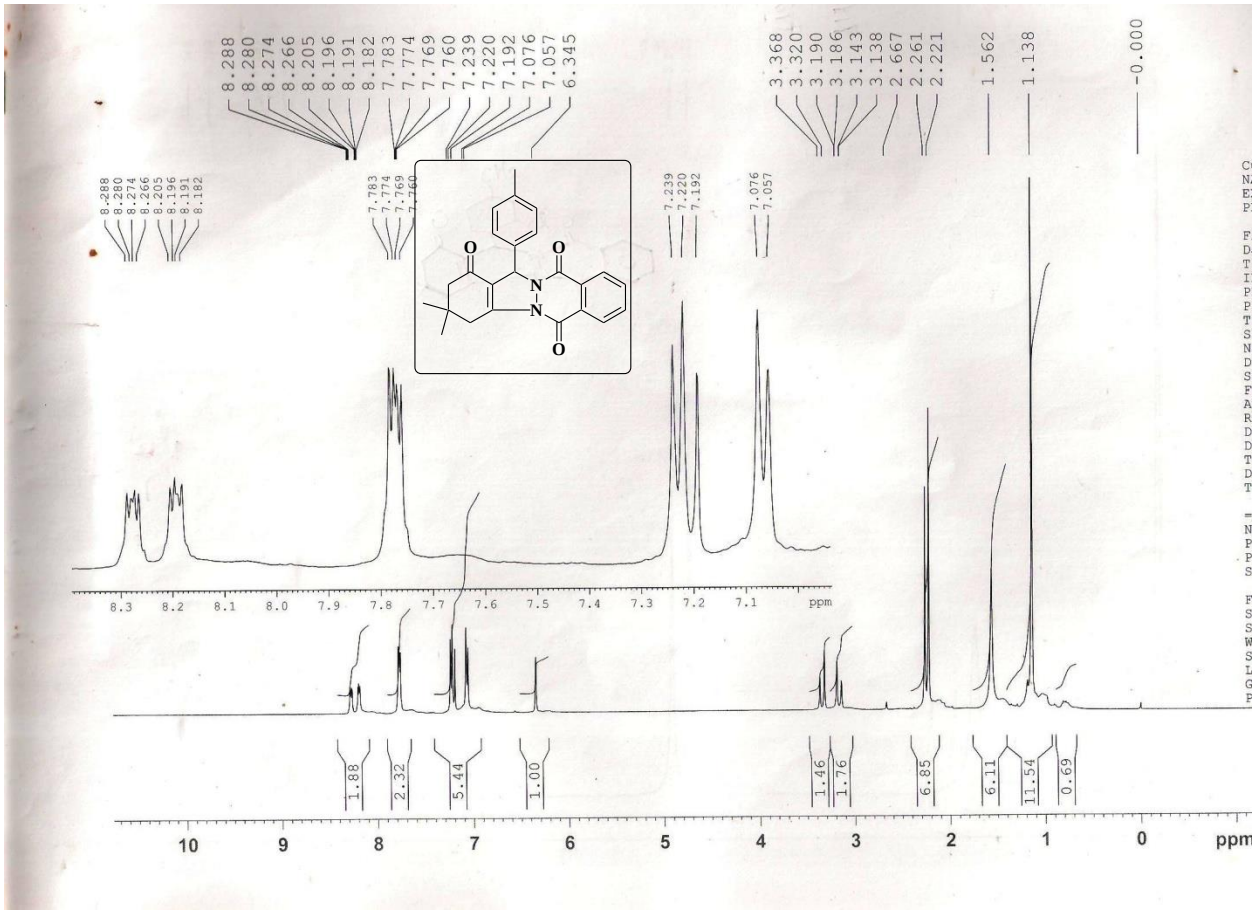
^{1}H NMR Spectra of Compound 15k

12. Compound 15l



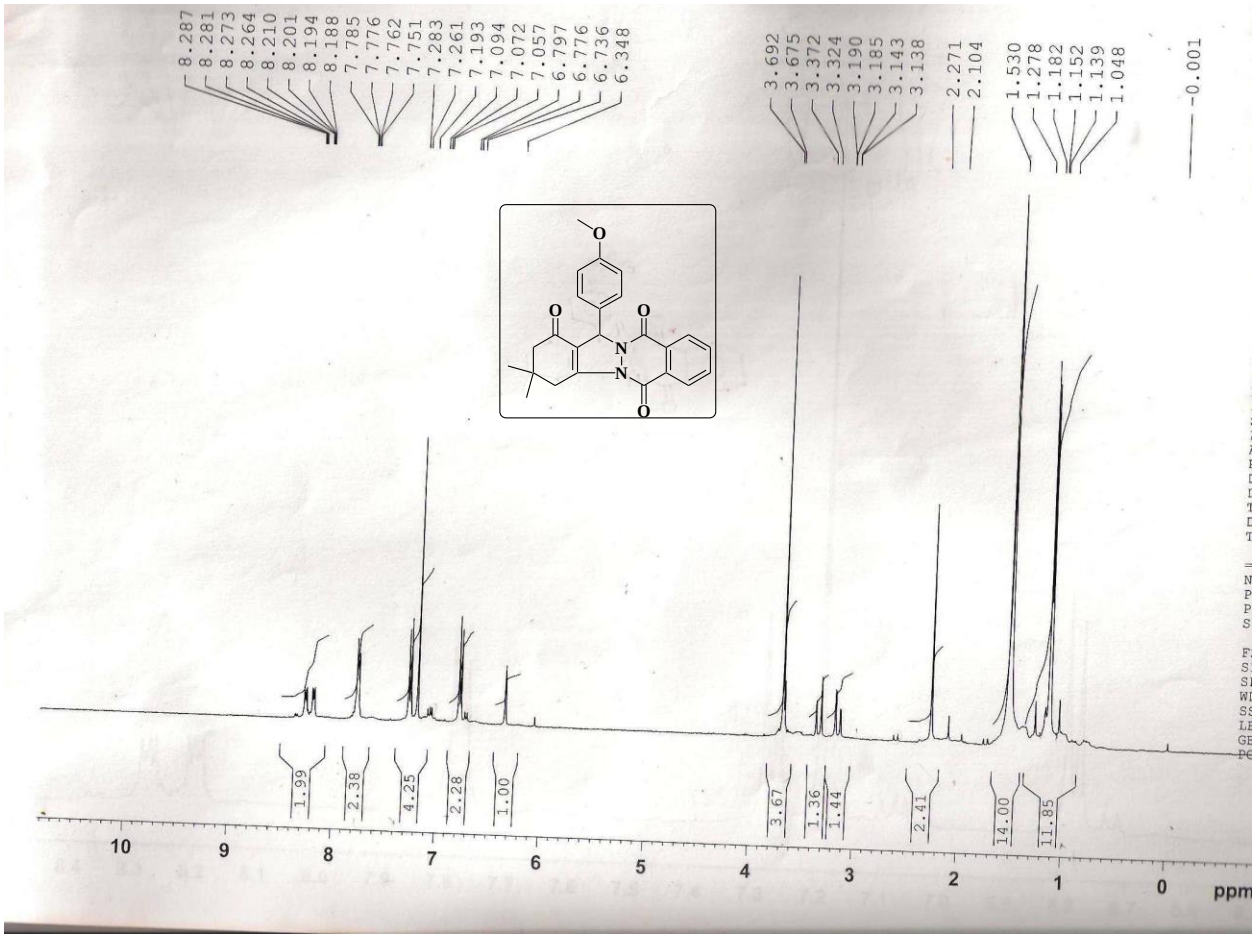
^{1}H NMR Spectra of Compound 15 l

13.Compound 15m



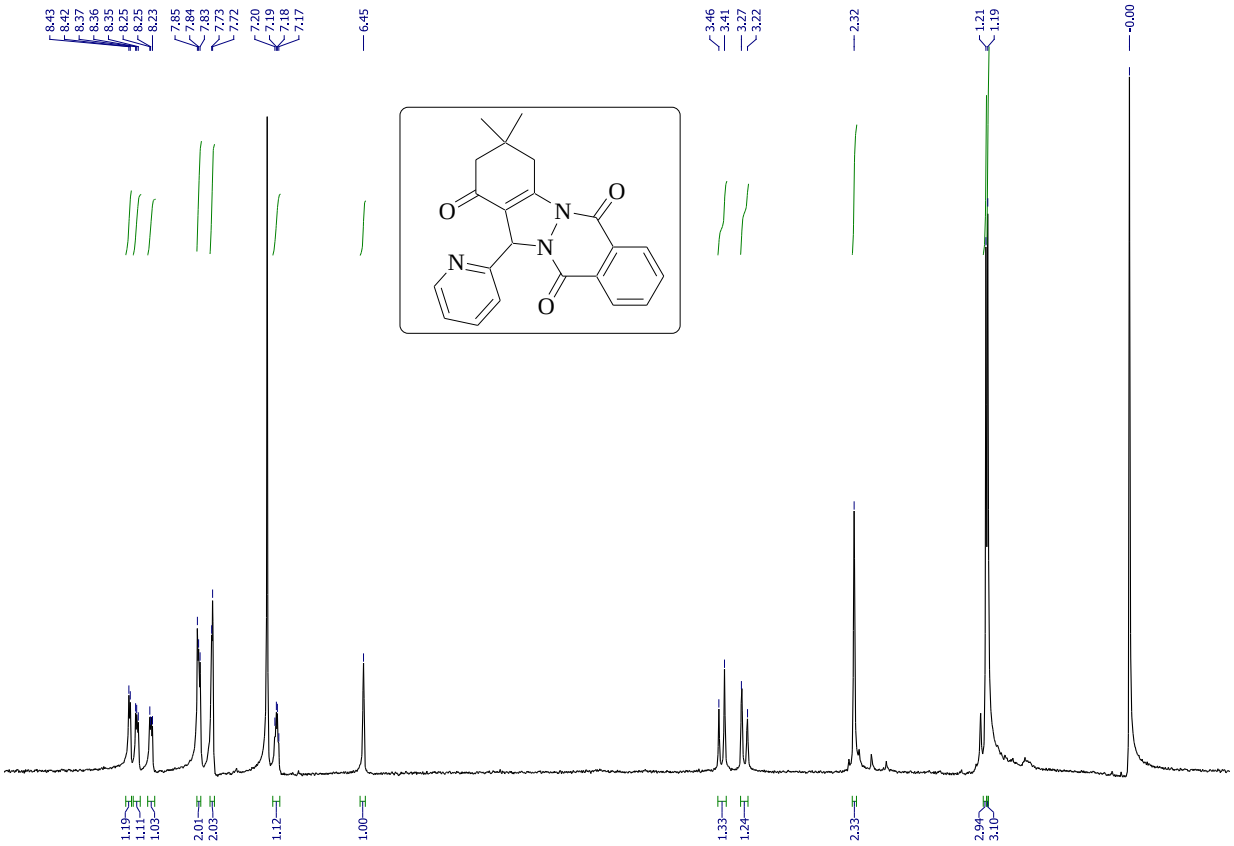
^{1}H NMR Spectra of Compound 15m

14.Compound 15n

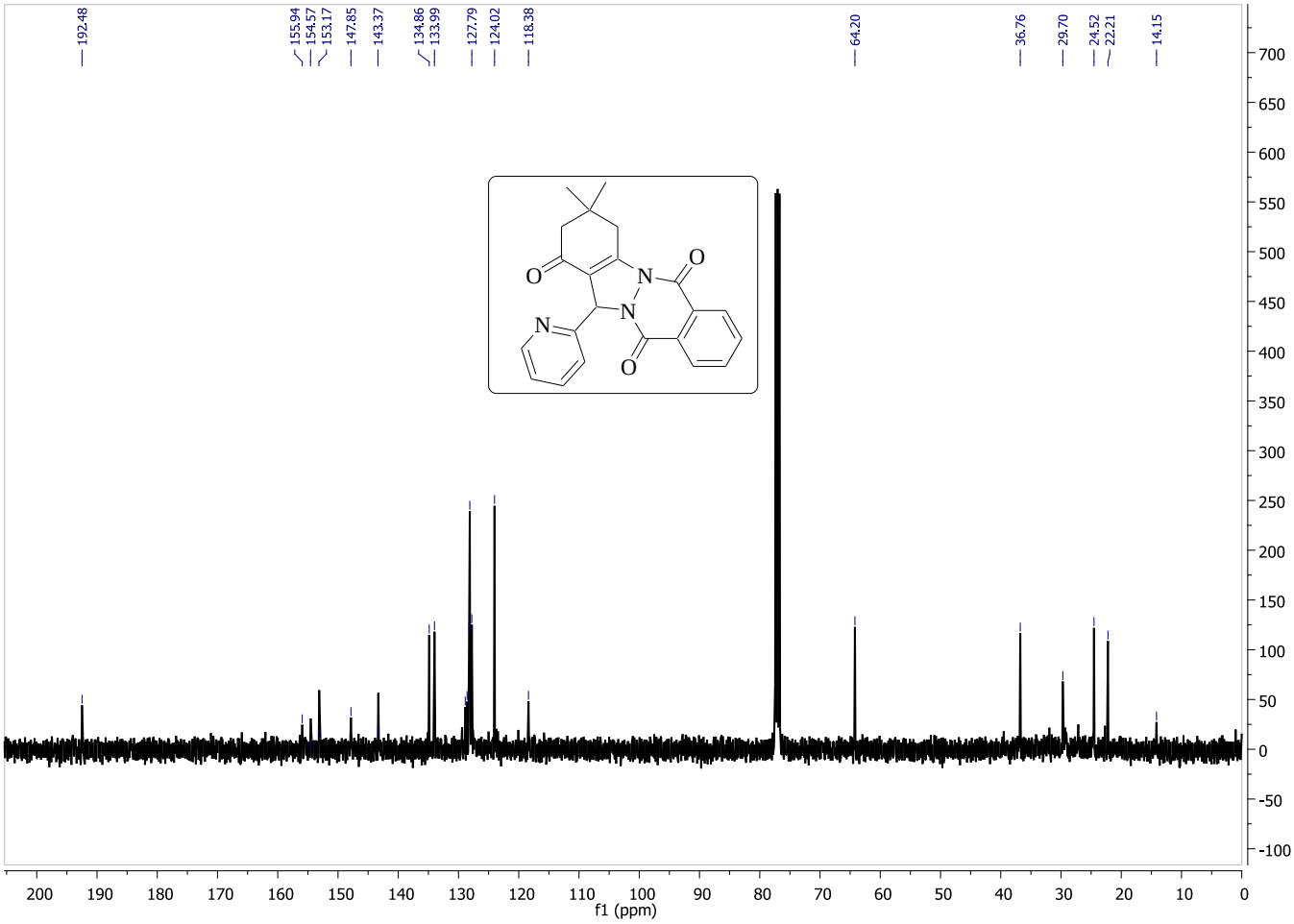


^{1}H NMR Spectra of Compound 15n

15. Compound 15o



^{1}H NMR Spectra of Compound 15o


192.48
155.94
154.57
153.17
147.85
143.37
134.86
133.99
127.79
124.02
118.38
64.20
36.76
29.70
24.52
22.21
14.15
O
N
O
N
N
O
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
200
190
180
170
160
150
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130
120
110
100
90
80
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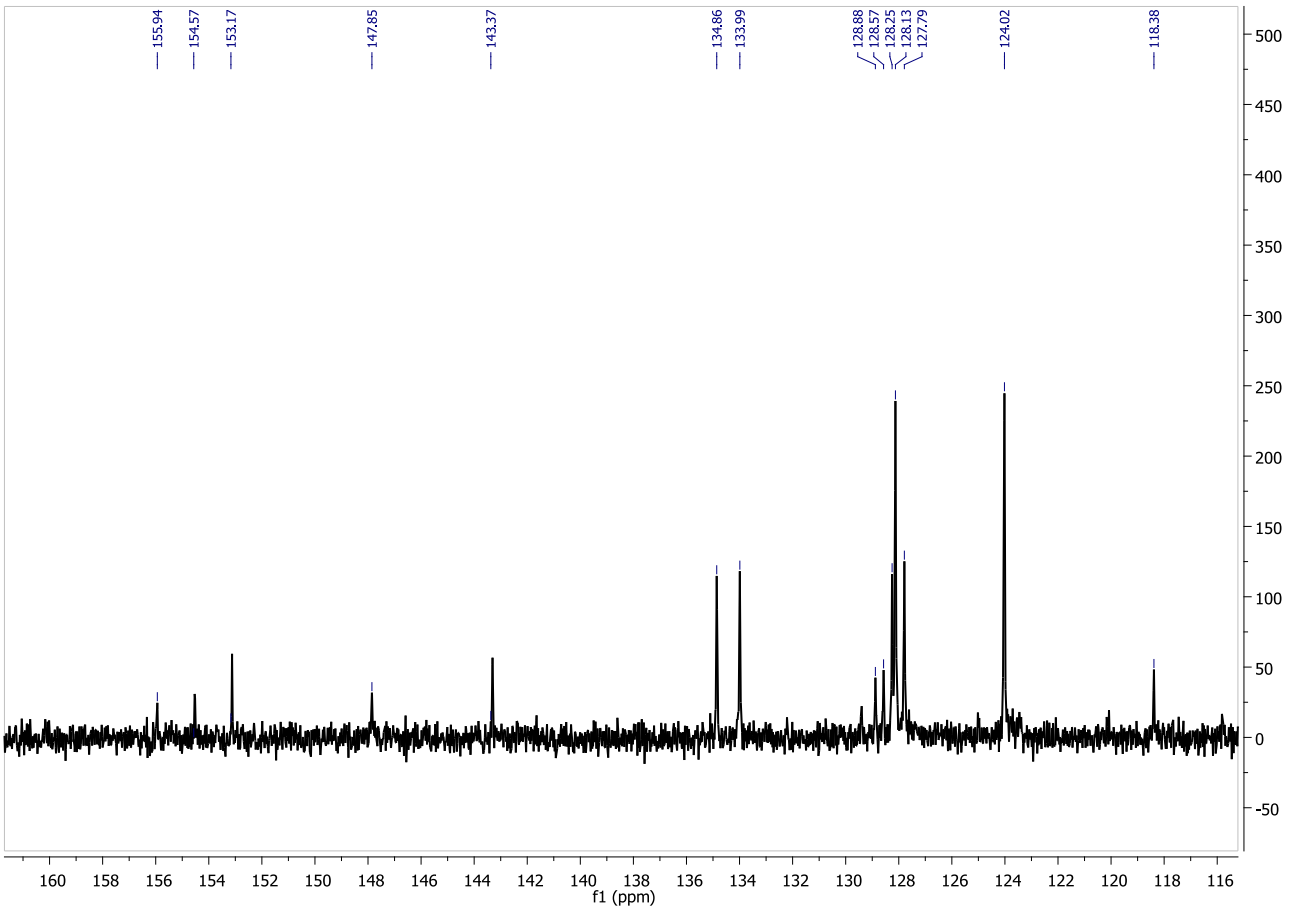
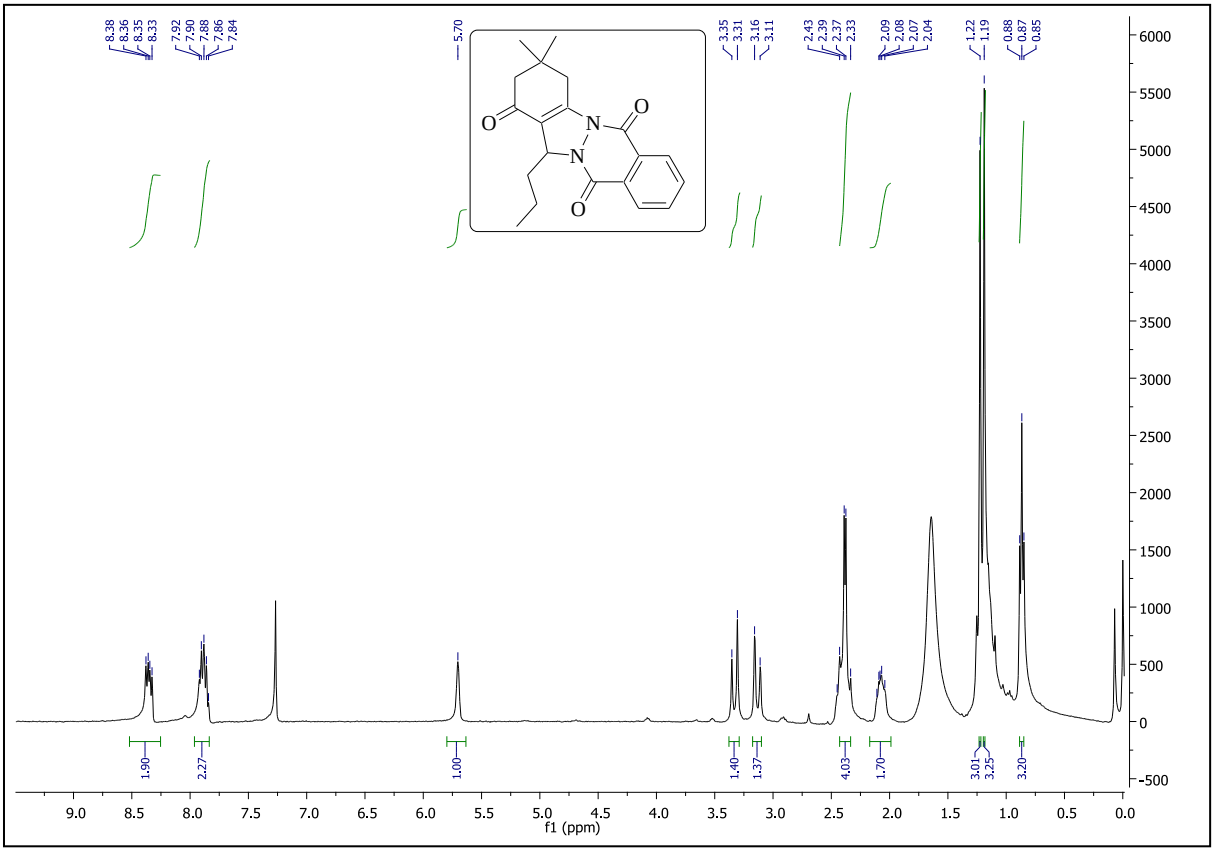
50
40
30
20
10
0
f1 (ppm)

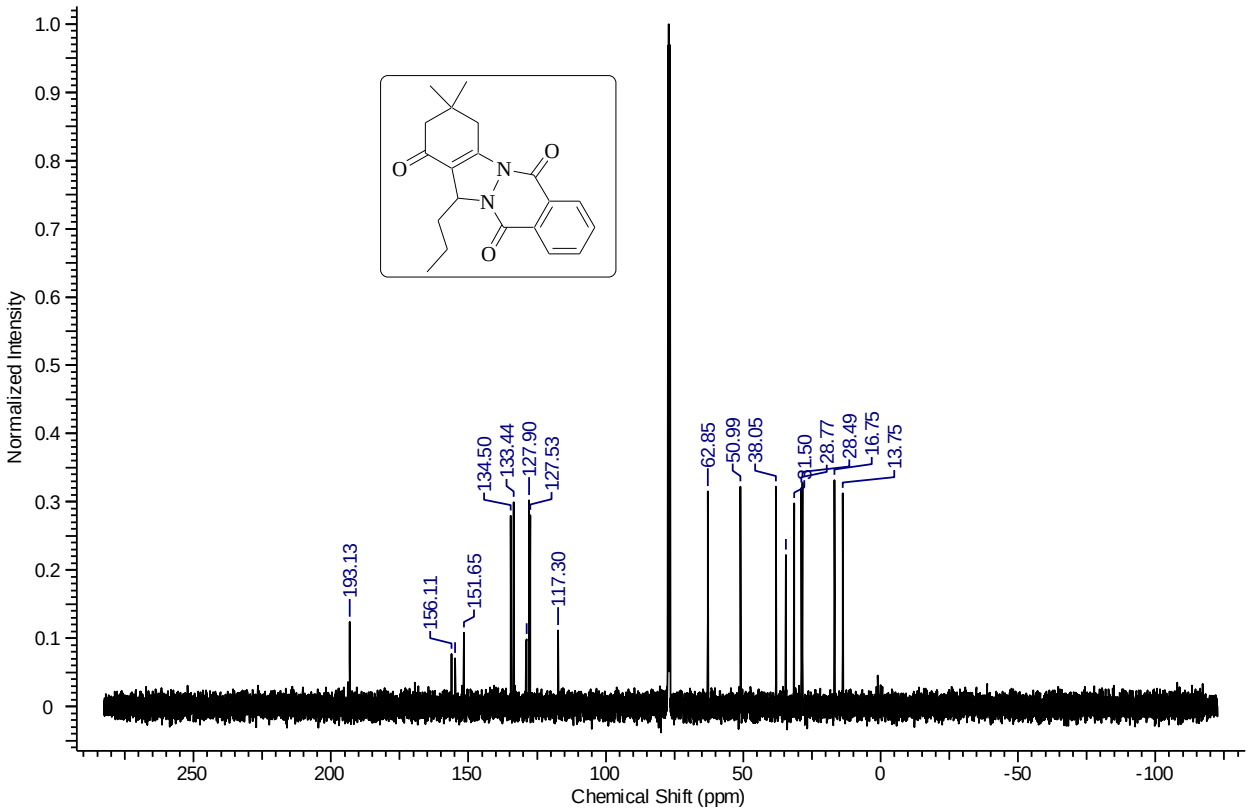


^{13}C NMR Spectra of Compound 15o

16. Compound 15p

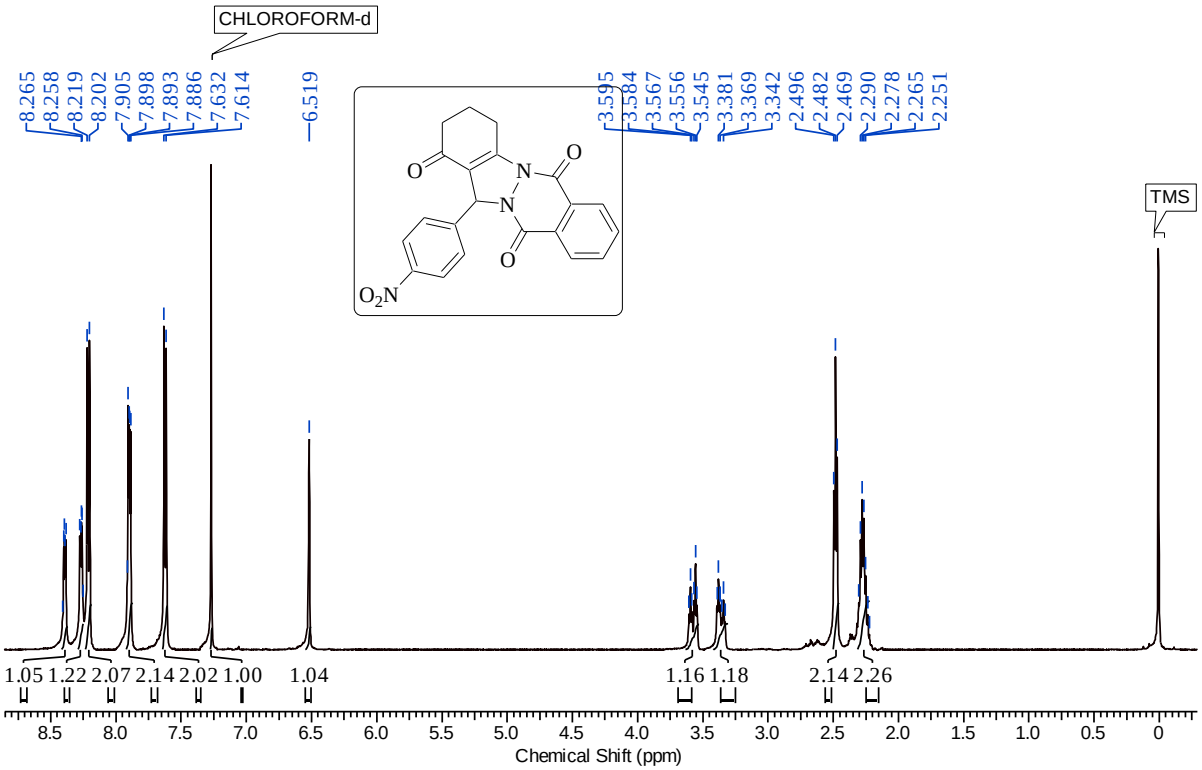


^{1}H NMR Spectra of Compound 15p

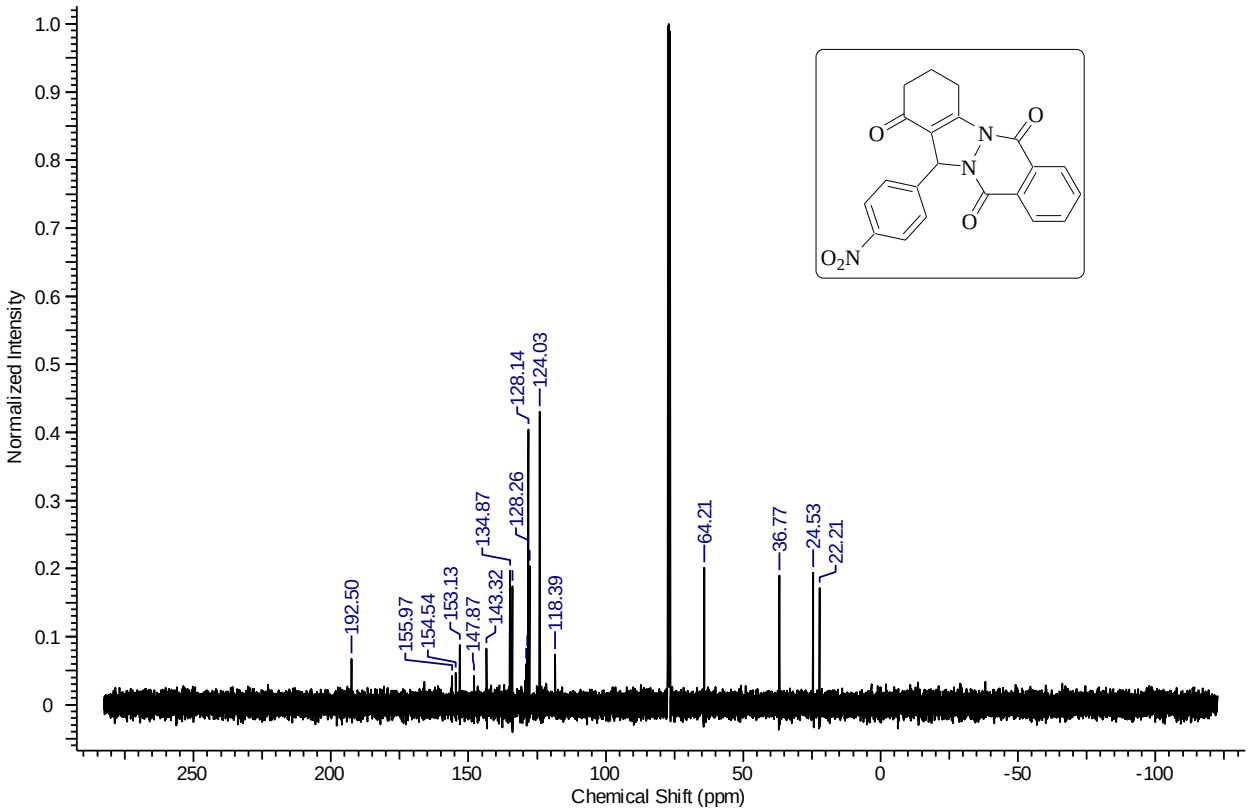


^{13}C NMR Spectra of Compound 15p

17. Compound 16a

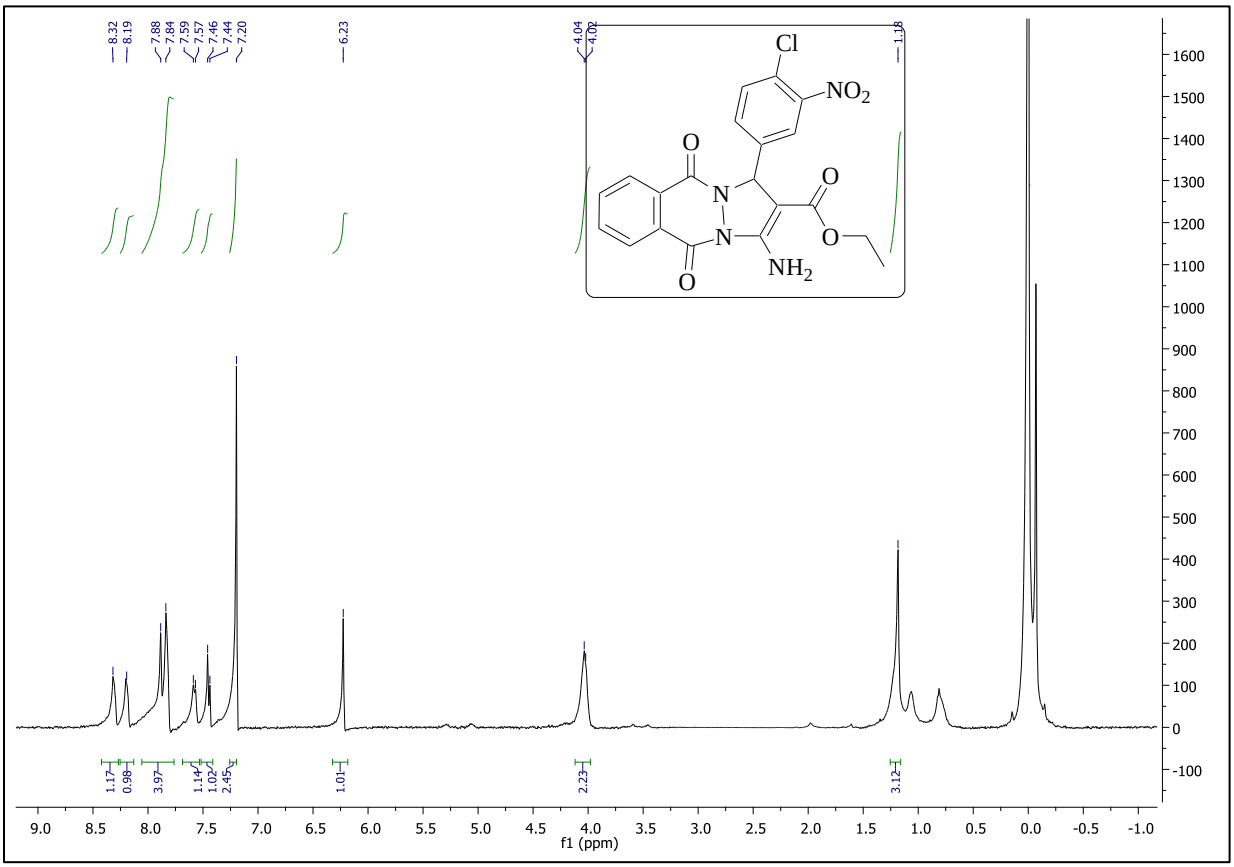


^{1}H NMR Spectra of Compound 16a

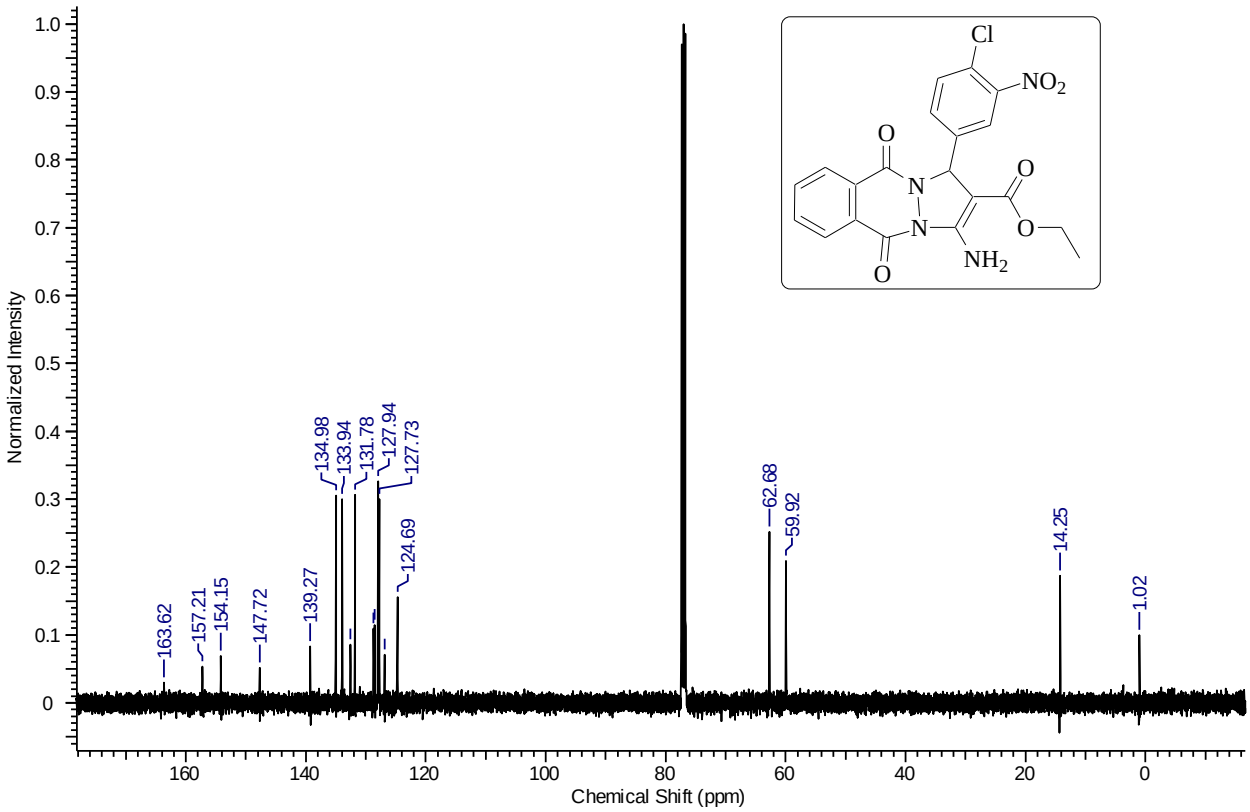


^{13}C NMR Spectra of Compound 16a

18. Compound 17a

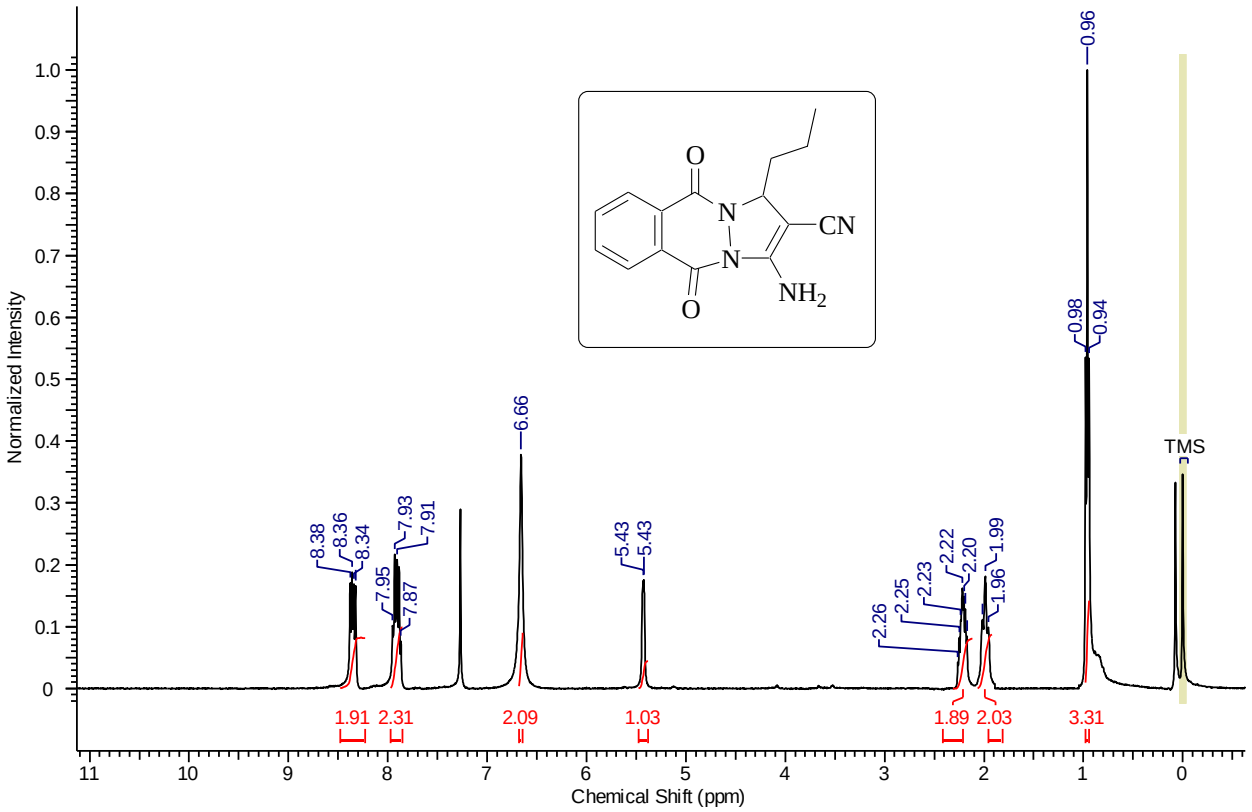


^{1}H NMR Spectra of Compound 17a

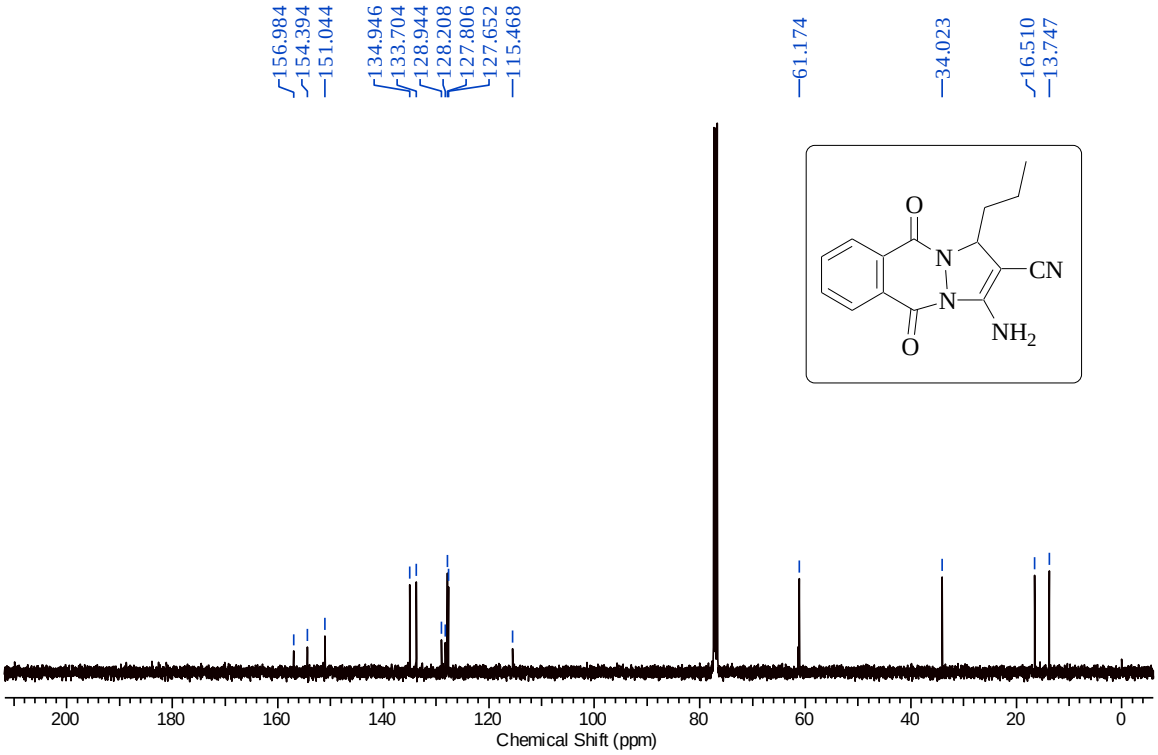


^{13}C NMR Spectra of Compound 17a

19.Compound 18a



^{1}H NMR Spectra of Compound 18a



^{13}C NMR Spectra of Compound 18a