Supporting Information for

Rhodium(III)-catalyzed oxidative annulation of *N*-arylbenzamidines with maleimides *via* dual C-H bondactivation

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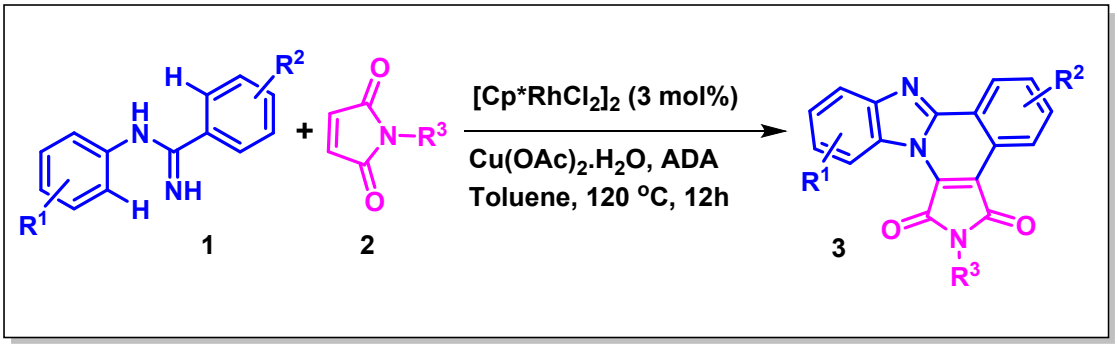


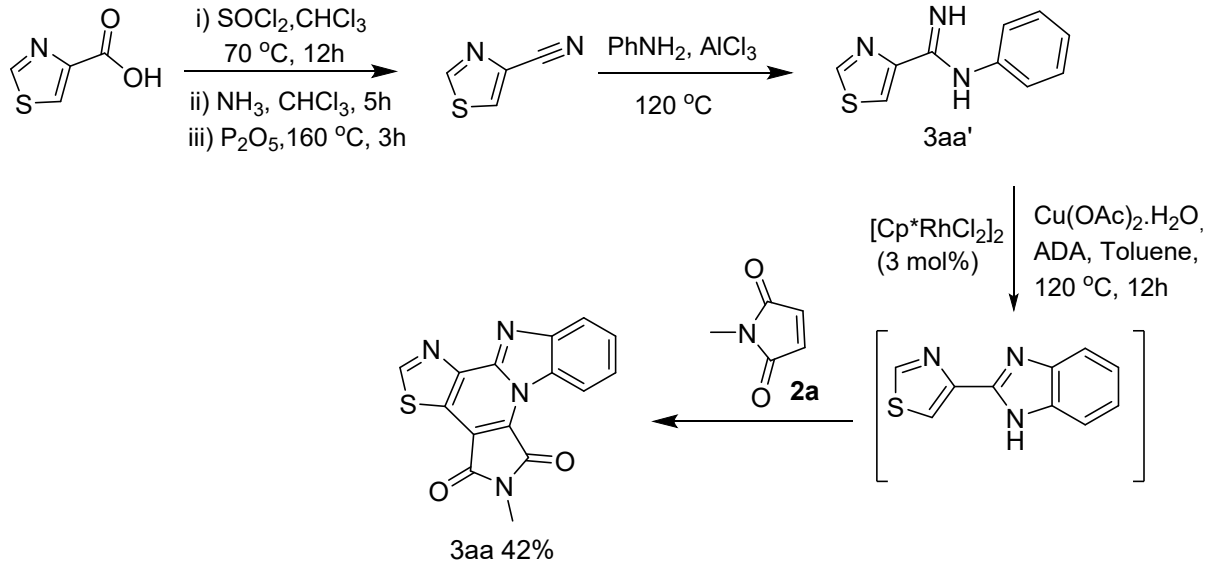
1. Experimental Section

All solvents were dried by a standard literature procedure. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography (**TLC**) plates were visualized by exposure to ultraviolet light at 254 nm, and by exposure to iodine vapors and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250°C). Organic solvents were concentrated on rotary evaporator at 35–40 °C. Melting points (**m.p.**) were measured on Buchi B-540. **^{1}H** and **^{13}C NMR** (proton-decoupled) spectra were recorded in $CDCl_3$ solvent on 300, 400 or 500 MHz, NMR spectrometer. Chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. Coupling constants (*J*) are quoted in hertz (Hz). Mass spectra and **HRMS** were recorded on mass spectrometer by Electrospray ionization (ESI) or Atmospheric pressure chemical ionization (APCI) technique.

General procedure for the synthesis of 3a-jj:

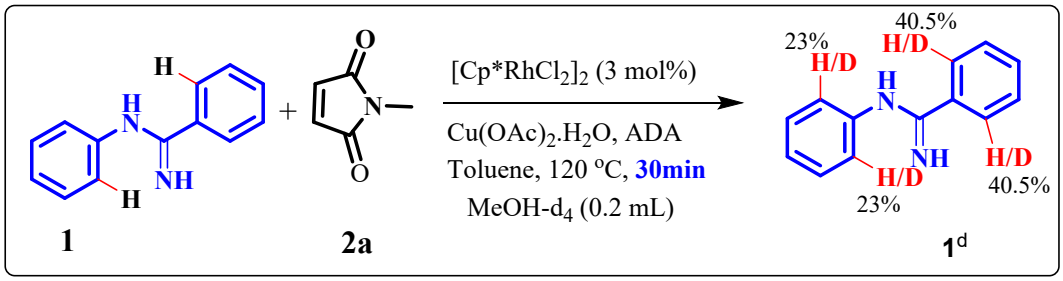
To an oven dried sealed tube was equipped with a stir bar were charged with *N*-phenylbenzimidamide (**1a**, 1.0 equiv), *N*-methylmaleimide (**2a**, 1.3 equiv) in 3mL of toluene, followed by addition of $[RhCp^*Cl_2]_2$ (3 mol%) and $Cu(OAc)_2$ (2.0 equiv) and ADA(Adamantane-1-carboxylic acid) as an additive (1.0 equiv) at room temperature. The resulting mixture was stirred at 120°Cfor 12h and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to afford the pure product **3a**.

Application of present protocol for the synthesis of biologically active tiabendazole and its further annulation:



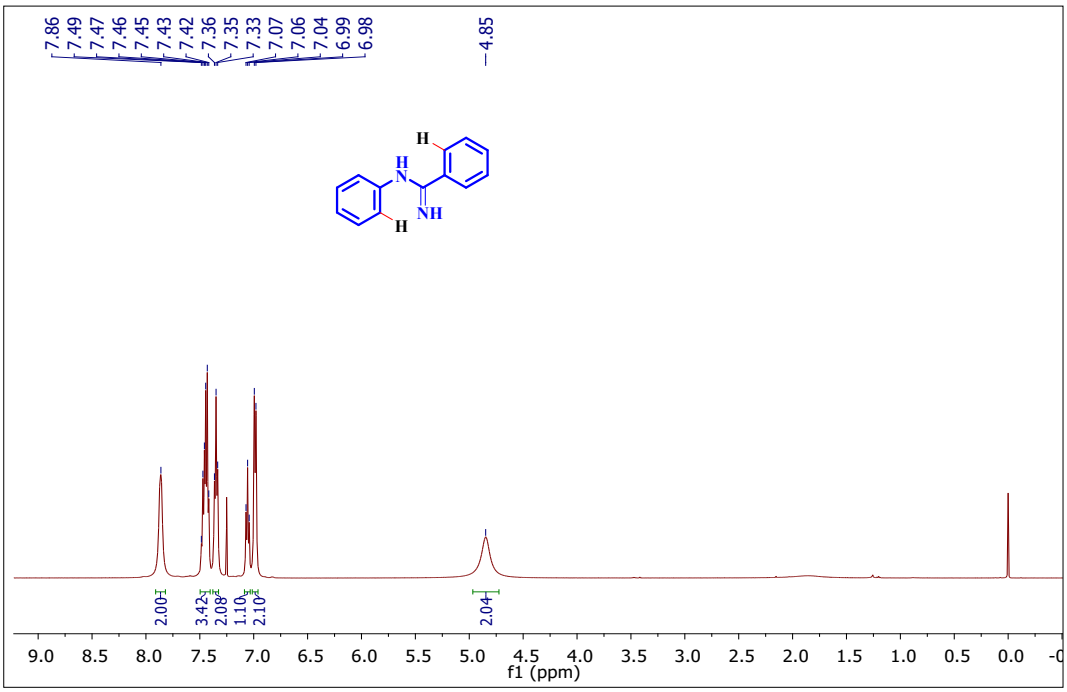
To a round bottom flask containing thiazole-4-carboxylic acid (1.0g, 7.75 mmol) in 15 mL $CHCl_3$ was added $SOCl_2$ (1 mL) drop wise under N_2 atmosphere at room temperature. Then the mixture was heated to reflux for 10h. The mixture was concentrated under reduced pressure and the resulting residue was dissolved in $CHCl_3$ and then NH_3 solution (2 mL) was added drop wise at 0 °C. After addition, the mixture was allowed to stir at room temperature for 5h. The mixture was concentrated under reduced pressure to get the product as a white solid (0.5 g, 1 equiv), which was then treated with P_2O_5 (1.55g, 1.2 equiv) at 160 °C for 3h. The mixture was quenched with water, extracted with ethyl acetate and concentrated under vacuo to get the nitrile. To a stirred mixture of nitrile and aniline (200 mg, 1 equiv) was added $AlCl_3$ (290 mg, 1 equiv) portion wise. The resulting mixture was heated to 120 °C. After completion of the reaction, ice cold water was added and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated under vacuo. The imidine (**3aa'**) was purified by column chromatography (87% yield). Further reaction was performed between imidine **3aa'** and *N*-methylmaleimide **2a** under present reaction conditions. The corresponding polycyclic compound **3aa** was obtained in 42% yield.

DEUTERIUM EXCHANGE EXPERIMENT:

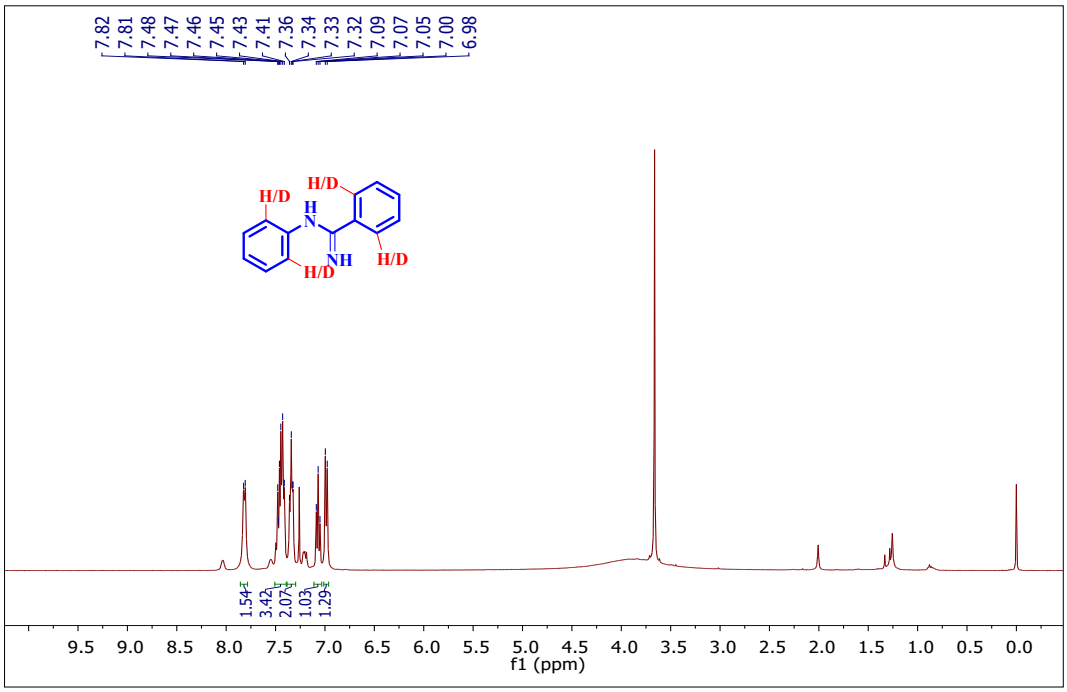


To an oven dried sealed tube was equipped with a stir bar were charged with *N*-phenylbenzimidamide (**1a**, 1.0 equiv), *N*-methylmaleimide (**2a**,1.3 equiv) in 3mL of toluene and 0.2mL MeOH, followed by addition of $[RhCp^*Cl_2]_2$(3 mol%) and $Cu(OAc)_2$ (2.0 equiv) and ADA(Adamantane-1-carboxylic acid) (1.0 equiv)at room temperature. The resulting mixture was stirred at 120°C for 30 min and then concentrated under reduced pressure and the crude sample was submitted for ^1H NMR. The H/D exchanges were found to be 23% and 40.5%.

^{1}H NMR of compound **1** in $CDCl_3$:

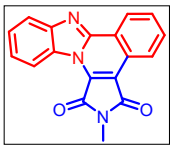


^{1}H NMR of deuterated compound **1d** in $CDCl_3$:



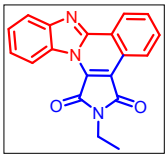
2. Characterization data of the products:

2-Methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3a):



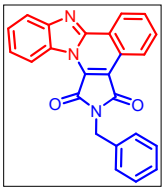
Yellow semi-solid (0.118 g, 77%), m.p. 207-208 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.2 Hz, 1H), 8.79 (s, 1H), 8.68 (d, *J* = 6.1 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 4.0 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H),3.20(s,3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 163.7, 147.8, 143.4, 132.0, 131.5, 130.7, 129.6, 126.6, 126.0, 125.1, 124.7, 124.5, 123.9, 119.6, 116.2, 115.2,24.2. HRMS calcd for $C_{18}H_{12}O_2N_3$:302.0924 $[M+H]^+$, found: 302.0911.

2-Ethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3b):



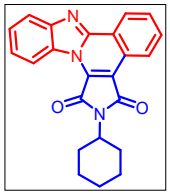
Yellow semi-solid (0.130 g, 81%),mp 215-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 8.3 Hz, 1H), 8.90 – 8.85 (m, 1H), 8.83 – 8.78 (m, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.81 (dd, *J* = 9.1, 5.1 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 3.85 (q, *J* = 7.1 Hz, 2H),1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 163.7, 148.2, 144.1, 132.2, 131.2, 130.5, 129.8, 126.3, 125.8, 125.0, 124.8, 123.7, 119.8, 116.2, 114.8, 33.3, 14.1. HRMS calcd for $C_{19}H_{14}O_2N_3$: 316.1081 [M+H], found: 316.1065.

2-Benzyl-1*H*-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3c):



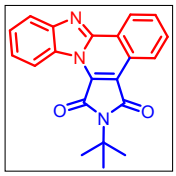
Yellow semi-solid (0.140 g, 73%), mp 220-222 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.4 Hz, 1H), 8.88 (dd, *J* = 5.9, 3.1 Hz, 1H), 8.82 (dd, *J* = 6.0, 3.0 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 4.95 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 163.5, 144.2, 136.0, 132.2, 131.3, 130.6, 129.5, 129.2, 128.9, 128.7, 128.2, 126.8, 126.4, 125.8,125.72,125.5, 125.2, 123.7, 119.9,116.3,41.9. HRMS calcd for $C_{24}H_{16}O_2N_3$: 378.1237 $[M+H]^+$, found: 378.1218.

2-Cyclohexyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3d):



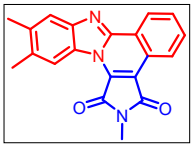
Yellow semi-solid (0.143 g, 76%), mp 215-216 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 7.6 Hz, 1H), 8.95 (d,*J* =6.8 Hz ,1H), 8.77 (t, *J* = 7.2Hz ,1H), 8.00 (s, 1H), 7.78 (s, 2H), 7.56 (s, 1H), 7.47 (d, *J* = 6.7 Hz, 1H), 4.15 – 4.08 (m, 1H), 2.21– 2.15 (m, 2H), 1.89 – 1.79 (m, 4H), 1.69 – 1.60 (m, 1H), 1.34 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 163.9, 148.3, 144.2, 132.1, 131.2, 130.4, 129.8, 126.2, 125.7, 124.9, 124.9, 124.8, 123.6, 119.8, 116.3, 114.4, 51.4, 30.2, 26.1, 25.2. HRMS calcd for $C_{23}H_{20}O_2N_3$:370.1550 $[M+H]^+$, found: 370.1530.

2-(tert-Butyl)-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3e):



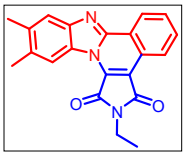
Yellow semi-solid (0.138 g, 79%), mp 218-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.4 Hz, 1H), 8.95 – 8.89 (m, 1H), 8.88 – 8.83 (m, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 1.80 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 164.9, 148.3, 144.2, 131.8, 131.1, 130.2, 129.7, 126.1, 125.7, 125.0, 124.7, 123.5, 120.2, 119.7, 116.5, 114.2, 58.7, 29.3. HRMS calcd for $C_{21}H_{18}O_2N_3$: 344.1394 $[M+H]^+$, found: 344.1375.

2,10,11-Trimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3f):



Yellow semi-solid (0.119 g, 71%), mp 235-236 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 2H), 8.70 (s, 1H), 7.71 – 7.68 (m, 3H), 3.22 (s, 3H), 2.41 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2 , 163.5 , 136.8 , 134.1, 131.6 , 131.0, 128.5, 127.6, 126.2, 124.8 , 123.7, 118.7, 116.0, 115.5, 29.7,24.3, 20.7,20.6. HRMS calcd for $C_{20}H_{16}O_2N_3$: 330.1237 $[M+H]^+$, found: 330.1221.

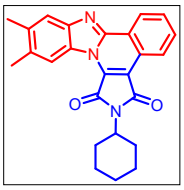
2-Ethyl-10,11-dimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3g):



Yellow semi-solid (0.130g,74%), mp 240-241 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.79 (s, 1H), 8.72 – 8.66 (m, 1H), 7.74 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.67 (s, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 2.37 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0,

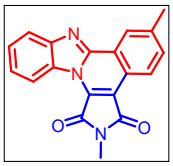
163.4, 137.2, 134.3, 132.0, 131.5, 131.1, 127.5, 126.8, 125.0, 123.4, 118.5, 116.2, 33.5, 29.7, 20.9, 20.6,14.1. HRMS calcd for $C_{21}H_{18}O_2N_3$: 344.1394 $[M+H]^+$, found: 344.1376.

2-Cyclohexyl-10,11-dimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3h):



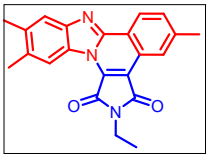
Yellow semi-solid (0.140 g, 69%), mp 243-244 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.8 Hz, 2H), 8.72 (s, 1H), 7.71 (d, *J* = 7.3 Hz, 3H), 4.15 – 4.09 (m,,1H), 2.42 (s, 6H), 2.25 – 2.16 (m, 2H), 1.89 – 1.78 (m, 4H), 1.69 –1.62 (m, 2H), 1.39 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 163.5, 146.3, 139.0 , 137.2 , 134.4 , 132.2 131.4 , 127.6, 126.8, 125.2, 123.6, 118.5, 116.5, 115.7, 51.6, 30.6, 29.7, 26.1, 25.2, 21.0, 20.7. HRMScalcd for $C_{25}H_{24}O_2N_3$: 398.1863 $[M+H]^+$, found: 398.1841.

2,6-Dimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3i):



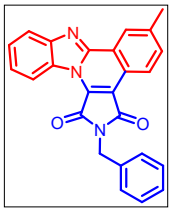
Yellow semi-solid (0.113g, 70%), mp 230-231°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.3 Hz, 1H), 8.68 (s, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 9.1, 5.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 3.20 (s, 3H), 2.54 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.9, 142.2, 133.9, 132.1, 130.9, 130.4, 129.8, 127.9, 125.6, 125.3, 124.9, 124.5, 119.3, 115.7, 115.6, 114.7, 24.1, 22.2. HRMS calcd for $C_{19}H_{14}O_2N_3$: 316.1081$[M+H]^+$, found: 316.1065.

2-Ethyl-5,10,11-trimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3j):



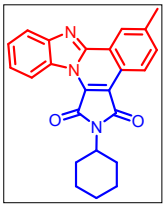
Yellow semi-solid (0.142g, 78%), mp 288-289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.49 (s, 1H), 7.66 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 3.86 – 3.80 (q, *J* = 7.3 Hz,2H), 2.57 (s, 3H), 2.44 (s, 6H), 1.38 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.8, 147.7, 142.8, 141.4, 135.5, 132.7, 131.7, 128.1, 125.4, 124.6, 124.4, 122.5, 119.4, 115.7, 113.9, 33.1, 22.0, 20.7, 20.6, 14.1. HRMS calcd for $C_{22}H_{20}O_2N_3$: 358.2376 $[M+H]^+$, found: 358.2361.

2-Benzyl-6-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3k):



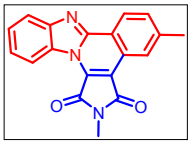
Yellow semi-solid (0.136 g, 68%), mp 245-246 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.3 Hz, 1H), 8.72 – 8.62 (m, 2H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.59 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 3H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 7.1 Hz, 1H), 4.92 (s, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 163.6, 147.8, 141.9, 136.0, 133.2, 131.0, 129.7, 128.8, 128.1, 126.5, 125.8, 124.9, 124.5, 123.8, 122.5, 119.6, 116.3, 115.6, 41.9, 29.7, 22.1. HRMS calcd for $C_{25}H_{18}O_2N_3$: 392.1394$[M+H]^+$, found: 392.1376.

2-Cyclohexyl-6-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3l):



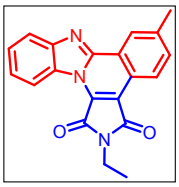
Yellow semi-solid (0.115 g, 71%), mp 240-241 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.4 Hz, 1H), 8.78 (s, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 4.21 – 4.17 (m, 1H), 2.64 (s, 3H), 2.31 – 2.22 (m, 2H), 1.94 –1.88 (m, 2H), 1.86 – 1.80 (m, 2H), 1.78 – 1.71 (m, 2H), 1.42 – 1.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 163.8, 142.1, 134.8, 133.6, 130.9, 129.6, 126.8, 126.1, 125.0, 124.1, 122.8, 119.2, 116.6, 51.5, 30.2, 26.1, 25.2, 22.2. HRMS calcd for $C_{24}H_{22}O_2N_3$: 384.1706 $[M+H]^+$, found: 384.1688.

2,5-Dimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3m):



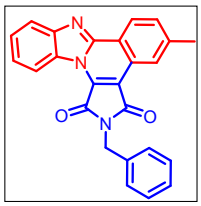
Yellow semi-solid (0.113 g, 70%), mp 240-241 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 8.38 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 3.18 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 163.6, 147.7, 142.7, 132.5, 131.9, 129.5, 126.6, 125.9, 124.9, 124.7, 123.8, 121.8, 119.3, 116.3, 115.2, 29.7, 24.2, 22.1. HRMS calcd for $C_{19}H_{14}O_2N_3$: 316.1080 $[M+H]^+$, found: 316.1065.

2-Ethyl-6-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3n):



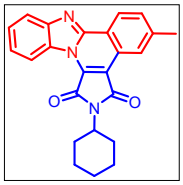
Yellow semi-solid (0.119 g, 71%), mp 235-236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.3 Hz, 1H), 8.74 (s, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 9.2., 6.2 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 3.84 (q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 163.7, 142.9, 142.0, 133.4, 131.1, 129.7, 126.7, 126.0, 125.0, 124.5, 123.9, 122.7, 119.6, 116.4, 115.8, 33.4, 22.3, 14.3. HRMS calcd for $C_{20}H_{16}O_2N_3$: 330.1237 $[M+H]^+$, found: 330.1223.

2-Benzyl-5-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3o):



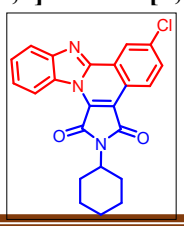
Yellow semi-solid (0.140g, 70%), mp 256-257 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 8.3 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 8.56 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.49 (dd, *J* = 8.2, 4.1 Hz, 3H), 7.39 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 4.93 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 163.4, 147.9, 142.6, 135.9, 132.5, 131.9, 129.5, 128.8 , 128.2, 126.6, 125.9, 125.2 – 125.0, 124.9 , 123.8, 122.1, 119.4, 116.3, 115.1, 41.9, 22.1. HRMS calcd for $C_{25}H_{18}O_2N_2$:392.1393 $[M+H]^+$, found:392.1371.

2-Cyclohexyl-5-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3p):



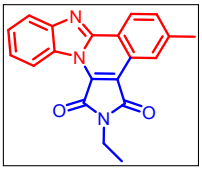
Yellow semi-solid (0.141 g, 72%), mp 248-250 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 8.4 Hz, 1H), 8.89 (d, *J* = 8.2 Hz, 1H), 8.64 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.51 (t, *J* = 7.8 Hz, 1H), 4.25 – 4.17 (m, 1H), 2.62 (s, 3H), 2.32 – 2.22 (m, 2H), 1.96-1.85 (m, 6H), 1.42-1.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 163.7, 143.5, 132.9, 131.8, 129.4, 127.0, 126.6, 125.4, 124.9, 124.2, 121.6, 118.9, 116.7, 115.6, 51.6, 30.3, 29.7, 26.1, 25.2, 22.3 HRMS calcd for $C_{24}H_{22}N_3O_2$: 384.1706 $[M+H]^+$, found:384.1686.

6-Chloro-2-cyclohexyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)dione (3q):



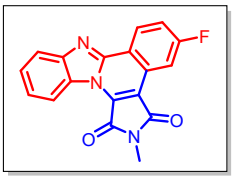
Yellow semi-solid (0.125 g, 61%), mp 266-267 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 7.7 Hz, 1H), 8.87 (s, 1H), 8.82-8.80 (m, 1H), 7.97 (s, 1H), 7.87 – 7.83 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 1H), 4.25 – 4.17 (m, 1H), 2.31-2.21(m, 2H), 1.96-1.93 (m, 2H), 1.90 – 1.83 (m, 2H), 1.78-1.75 (m, 1H), 1.48-1.36 (m,3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 163.9, 132.2, 131.9– 130.6, 130.63 – 130.6, 128.3, 126.1, 125.2, 125.19 – 124.52, 124.2, 123.5, 119.3, 117.4, 115.1, 51.5 30.3, 26.1, 25.2. HRMS calcd for $C_{23}H_{19}O_2N_3Cl$: 404.1160 $[M+H]^+$, found: 404.1138.

2-Ethyl-5-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3r):



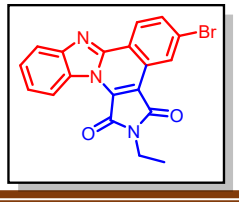
Yellow semi-solid (0.126 g, 75%), mp 243-244 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.4 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 8.51 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 3.83 (q, *J* = 6.8 Hz, 2H), 2.57 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 163.7, 148.2, 143.7, 142.4 , 132.2, 129.7, 126.4, 125.8, 124.9, 124.6, 123.6, 122.3, 119.5, 116.2, 114.8, 33.3, 22.0, 14.1. HRMS calcd for $C_{20}H_{16}O_2N_3$:330.1237 $[M+H]^+$, found: 330.1221.

5-Fluoro-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3s):



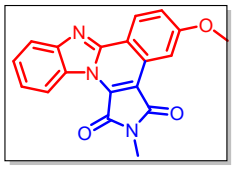
Yellow semi-solid (0.106 g, 65%), mp 269-270 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 8.4 Hz, 1H), 8.83 (dd, *J* = 9.0, 5.4 Hz, 1H), 8.41 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.55 – 7.47 (m, 2H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2 , 164.1 (d, $^{1}J_{C\text{-}F}$= 251.7 Hz, A-F), 163.4, 147.7, 144.1, 133.1, 129.5, 128.4 (d, *J* = 9.3 Hz), 126.5, 126.3 (d, *J* = 10.7 Hz), 123.8, 121.2, 119.8, 119.2 (d, *J* = 23.9 Hz), 116.13 , 113.8, 110.6 (d, $^{2}J_{C\text{-}F}$ = 24.2 Hz, A-F), 24.2(s). HRMS calcd for $C_{18}H_{11}O_2N_3F$: 320.0829 $[M+H]^+$, found: 322.0823.

5-Bromo-2-ethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3t):



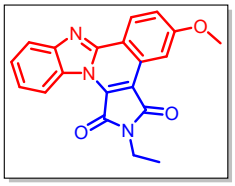
Yellow semi-solid (0.134 g, 67%), mp 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.1 Hz, 1H), 8.95 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 163.2, 133.9, 133.1, 129.6, 127.5, 127.3, 126.8, 126.5, 125.9, 124.2, 123.1, 119.7, 116.3, 113.7, 33.4, 14.1. HRMS calcd for $C_{19}H_{13}O_2N_3Br$: 394.0185 $[M+H]^+$, found: 394.0173.

5-Methoxy-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3u):



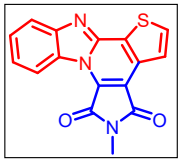
Yellow semi-solid (0.115 g, 68%), mp 242-244 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 9.1 Hz, 1H), 8.82-8.76 (m, 2H), 7.82 – 7.76 (m, 2H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.95 (s, 3H), 3.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 164.0, 158.8, 148.7, 145.7, 131.7, 131.1, 130.4, 125.6, 124.9, 124.5, 124.5, 124.2, 116.8, 114.3, 113.8, 101.0, 55.7, 24.1. HRMS calcd for $C_{19}H_{14}O_3N_3$: 332.1081 $[M+H]^+$, found: 332.1074.

5-Diethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3v):



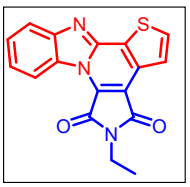
Yellow semi-solid (0.123 g, 70%), mp 251-253 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 9.2 Hz, 1H), 8.79 – 8.68 (m, 2H), 7.78 – 7.71 (m, 2H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.03 (dd, *J*= 9.1, 2.0 Hz, 1H), 3.92 (s, 3H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz ,3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 163.5, 159.1, 147.9, 144.1, 131.4, 131.3, 130.6, 125.8, 124.9, 124.7, 123.7, 116.9, 114.8, 114.3, 100.3, 55.7, 33.3, 14.1. HRMS calcd for $C_{20}H_{16}O_3N_3$: 346.1186 $[M+H]^+$, found: 346.1175.

5-Methyl-4H-benzo[4,5]imidazo[1,2-a]pyrrolo[3,4-e]thieno[2,3-c]pyridine-4,6(5H)-dione (3w):



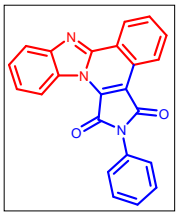
Yellow semi-solid (0.111 g, 71%), mp 269-270 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.4 Hz, 1H), 8.0 (dd, *J*= 8.2, 5.7 Hz, 2H), 7.87 (d, *J* = 5.2 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 3.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 164.0, 145.6, 144.8, 132.4, 131.7, 131.3, 131.1, 129.2, 126.9, 123.3, 122.9, 119.8, 116.4, 24.2. HRMS calcd for $C_{16}H_{10}O_2N_3S$: 308.1160 $[M+H]^+$, found: 308.1138

5-Ethyl-4H-benzo[4,5]imidazo[1,2-a]pyrrolo[3,4-*e*]thieno[2,3-c]pyridine-4,6(5H)-dione (3x):



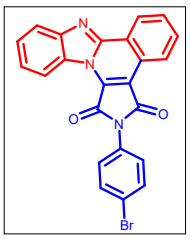
Yellow semi-solid (0.122g, 75%), mp 273-274 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.80 (d, *J* = 5.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 163.8, 145.6, 144.8, 132.4, 131.7, 131.3, 131.2, 129.2, 126.8, 123.3,122.9, 119.8, 116.4, 114.5, 33.4, 14.1. HRMS calcd for $C_{17}H_{12}O_2N_3S$: 322.0644 $[M+H]^+$, found: 322.0631.

2-Phenyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3y):



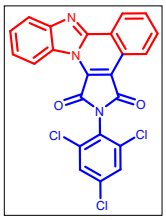
Yellow semi-solid (0.135g, 70%), mp259-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.4 Hz, 1H), 8.98 – 8.92 (m, 1H), 8.88 (dd, *J* = 6.2, 3.0 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 6.1, 3.3 Hz, 2H), 7.64 – 7.48 (m, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 162.9, 144.3, 143.5, 132.1, 131.4, 130.9, 129.9, 129.3, 128.5, 127.9, 126.8, 126.5, 125.9, 125.3, 125.2, 124.7, 123.9, 120.0, 116.3, 114.7. HRMS calcd for $C_{24}H_{18}O_2N_3$: 364.1080 $[M+H]^+$, found: 364.1068.

2-(4-Bromophenyl)-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3z):



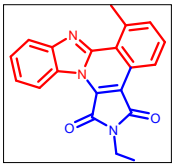
Yellow semi-solid (0.133g, 59%), mp270-272 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.4 Hz, 1H), 8.98 (s, 1H), 8.88 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 3.2 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 162.6, 148.2, 133.1, 132.6, 132.1, 131.8, 131.3, 129.9, 129.8, 129.4, 128.2, 126.8, 126.2, 125.4, 124.8, 124.2, 122.3, 119.9, 117.6, 116.4, 114.0, 29.8. HRMS calcd for $C_{23}H_{13}O_2N_3Br$: 443.1028 $[M+H]^+$, found: 443.1022.

2-(2,4,6-trichlorophenyl)-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3bb):



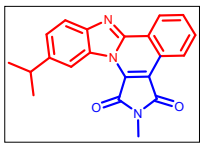
Yellow semi-solid (0.185g, 78%), mp216-218°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.4 Hz, 1H), 8.99 – 8.95 (m, 1H), 8.89 – 8.85 (m, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.65 – 7.60 (m, 1H), 7.58 (s, 2H), 7.52 (dd, *J* = 8.4, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 161.3, 148.3, 144.3, 137.1, 136.6, 132.1, 131.5, 131.2, 129.9, 128.9, 126.6, 126.1, 126.0, 125.5, 125.3, 124.6, 124.0, 120.1, 116.3, 115.4. HRMS calcd for $C_{23}H_{11}O_2N_3Cl_3$: 467.1141 $[M+H]^+$, found: 467.1137.

2,7-Dimethyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3cc):



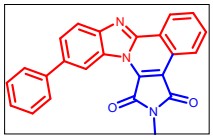
Yellow semi-solid (0.120g, 72%), mp220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.3 Hz, 1H), 8.77 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 9.2, 6.8 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 3.84 (d, *J* = 7.2 Hz, 2H), 3.26 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 162.8, 147.6, 143.2, 138.5, 132.3, 129.2, 127.8, 125.0, 124.8, 122.6, 121.7, 119.1, 114.9, 114.0, 110.6, 32.2, 23.9, 13.1. HRMS calcd for $C_{20}H_{16}O_2N_3$: 330.1221 $[M+H]^+$, found: 330.1216.

11-Isopropyl-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3dd):



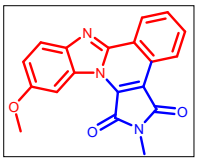
Yellow semi-solid (0.122g, 70%), mp261-263 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.4 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.59 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 3.25 (s, 3H), 3.16 (m, 1H), 1.40 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 163.8, 152.8, 148.3, 144.2, 132.0, 129.7, 126.2, 125.8, 124.9, 123.4, 122.8, 122.2, 119.6, 116.0, 114.9, 34.5, 24.0, 23.7. HRMS calcd for $C_{21}H_{18}O_2N_3$: 344.1041 $[M+H]^+$, found: 344.1039.

2-Methyl-11-phenyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3ee):



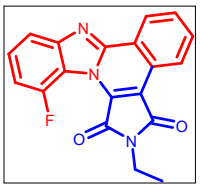
Yellow semi-solid (0.153g, 80%), mp180-183 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 7.3 Hz, 1H), 9.03 (s, 1H), 8.92 (d, *J* = 7.7 Hz, 1H), 8.04 (dd, *J* = 6.1, 8.2 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.61 (s, 1H), 7.53 (d, *J* = 7.3 Hz, 3H), 7.47 (d, *J* = 6.8 Hz, 1H), 3.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.8, 148.1, 145.9, 144.3, 144.0, 139.3, 129.8, 129.5, 129.1, 128.5, 127.52, 126.3, 126.2, 125.2, 123.7, 123.6, 122.8, 119.8, 116.1, 114.8, 24.1. HRMS calcd for $C_{24}H_{16}O_2N_3$: 378.1137 $[M+H]^+$, found: 378.1134.

11-Methoxy-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3ff):



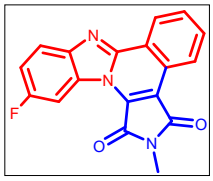
Yellow semi-solid (0.106g, 63%), mp245-246 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.36 (m, 1H), 7.19 (d, *J* = 2.7 Hz, 1H), 3.90 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 163.9, 161.4, 147.5, 143.9, 129.8, 129.1, 127.8, 126.7, 126.6, 126.1, 125.4, 123.5, 121.8, 119.6, 118.4, 116.2, 115.4, 114.3, 113.9, 106.1, 55.9, 23.9.HRMS calcd for $C_{19}H_{14}O_3N_3$: 332.1029 $[M+H]^+$, found: 332.1018.

2-Ethyl-12-fluoro-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3gg):



Yellow semi-solid (0.100g, 59%), mp 240-242 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.4 Hz, 1H), 8.84 (dd, *J* = 9.0, 5.4 Hz, 1H), 8.42 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.59 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.53 – 7.46 (m, 2H), 3.86 (t, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.4 (d, $J_{C\text{-}F}$=230.2 Hz, A-F) 163.3, 147.8, 144.2, 133.2, 129.6, 128.4 (d,$^{2}J_{C\text{-}F}$ = 9.6 Hz, A-F), 126.5, 123.7, 121.3, 119.8, 119.3, 119.1, 116.2, 113.7, 110.6 (d,$^{1}J_{C\text{-}F}$ = 23.5 Hz, A-F), 33.4, 14.1. HRMS calcd for $C_{19}H_{13}O_2N_3F$: 334.1057 $[M+H]^+$, found: 334.1049.

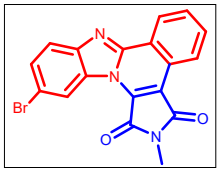
11-Fluoro-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3hh):



Yellow semi-solid (0.101g, 62%), mp 252-254 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.4 Hz, 1H), 8.81 (dd, *J* = 8.9, 5.4 Hz, 1H), 8.40 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.58 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.50 – 7.46 (m, 2H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 164.2 (d, $J_{C\text{-}F}$ = 253.7 Hz, A-F), 163.5, 147.7, 144.1, 133.1, 129.5,

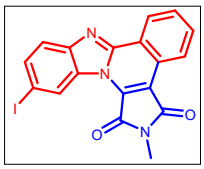
128.5 (d, $^{2}J_{C\text{-}F}$ = 9.4 Hz, A-F), 126.5, 126.4, 126.3, 123.8, 121.2, 119.8, (d, $^{1}J_{C\text{-}F}$ = 23.9 Hz, A-F), 116.1, 113.8, 110.6(d, $J_{C\text{-}F}$ = 24.1 Hz, A-F), 108.3, 24.2. HRMS calcd for $C_{18}H_{11}O_2N_3F$: 320.0830 $[M+H]^+$, found: 320.0829.

11-Bromo-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3ii):



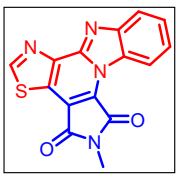
Yellow semi-solid (0.105g, 54%), mp 196-198 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, *J* = 1.7 Hz, 1H), 8.86 (dd, *J* = 6.4, 3.0 Hz, 1H), 8.81 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.82 (m, 2H), 3.30 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 161.2, 143.2, 131.6, 131.3, 130.9, 130.6, 129.7, 129.3, 129.2, 126.4, 125.9, 125.2, 124.8, 123.8, 121.1,119.1, 116.7, 116.2, 24.22. HRMS calcd for $C_{18}H_{11}O_2N_3Br$: 381.0662 $[M+H]^+$, found: 381.0658.

11-Iodo-2-methyl-1H-benzo[4,5]imidazo[2,1-a]pyrrolo[3,4-c]isoquinoline-1,3(2H)-dione (3jj):



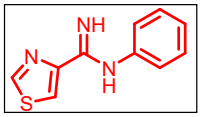
Yellow semi-solid (0.156g, 72%), mp201-203°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 8.4 Hz, 1H), 8.69 (ddd, *J* = 6.8, 3.0, 1.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.74 (m, 1H), 7.73 (s, 1H), 7.56 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.45 (dd, *J* = 8.3, 7.2 Hz, 1H), 3.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 163.7, 147.9, 144.1, 135.2, 131.2, 130.4, 129.6, 126.3, 125.7, 124.9, 124.5, 123.7, 121.3, 119.8, 116.0, 114.7, 86.9, 24.1. HRMS calcd for $C_{18}H_{11}O_2N_3I$: 427.9890 $[M+H]^+$, found: 427.9873.

5-Methyl-4H-benzo[4,5]imidazo[1,2-a]pyrrolo[3,4-e]thiazolo[4,5-c]pyridine-4,6(5H)-dione (3aa):



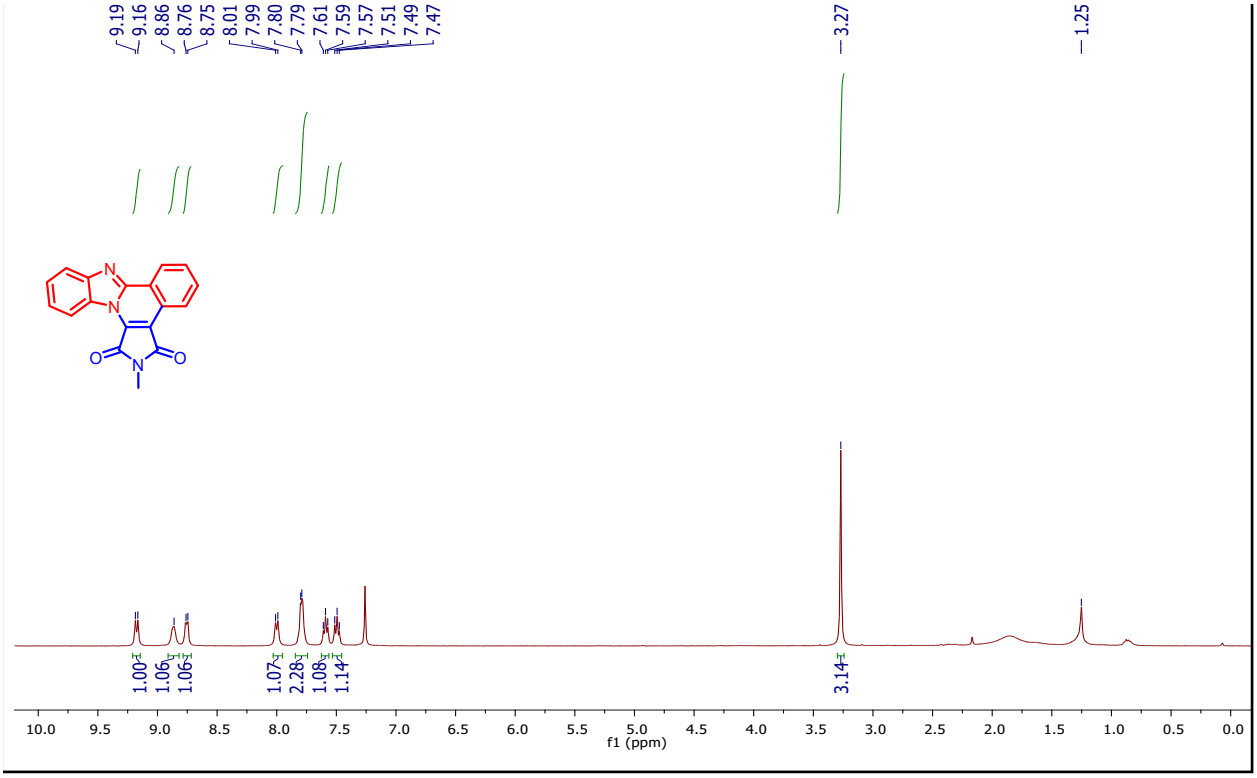
Yellow semi-solid (0.066g, 42%), mp 274-276 °C^{1}H NMR (400 MHz, DMSO) δ 9.79 (s, 1H), 9.21 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 4.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 3.17 – 3.15 (m, 3H).^{13}C NMR (101 MHz, DMSO) δ 166.4, 163.9, 161.5, 145.2, 144.6, 144.5, 132.4, 129.3, 127.3, 123.5, 122.3, 120.4, 116.6, 24.7.HRMS calcd for $C_{15}H_9O_2N_4S$: 309.0441$[M+H]^+$, found: 309.0433.

***N*-Phenylthiazole-4-carboximidamide (3aa'):**

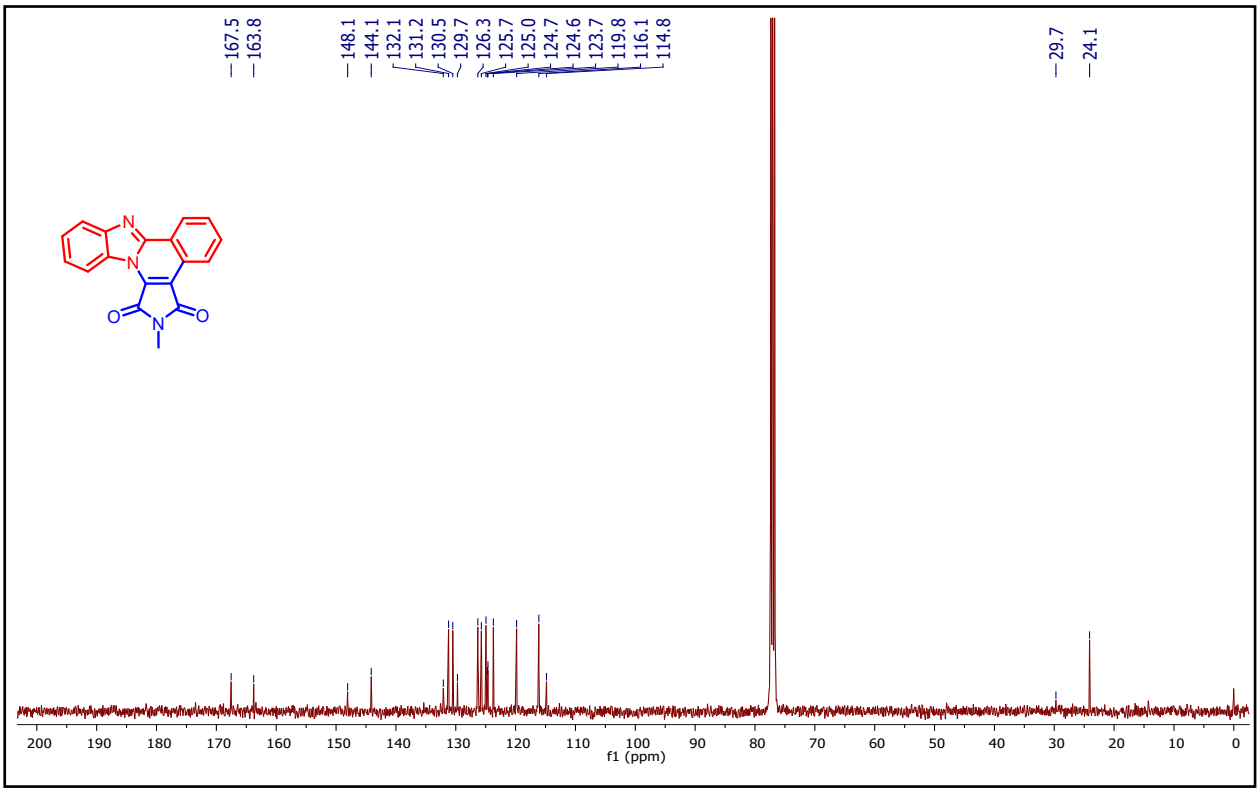


Browne semi-solid (0.130g, 87%),^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.27 (s, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 151.7, 149.6, 148.4, 129.6, 127.8, 123.5, 122.0, 120.4, HRMS calcd for C10 H8 N3 S = 202.0433 $[M+H]^+$, found: 202.0429.

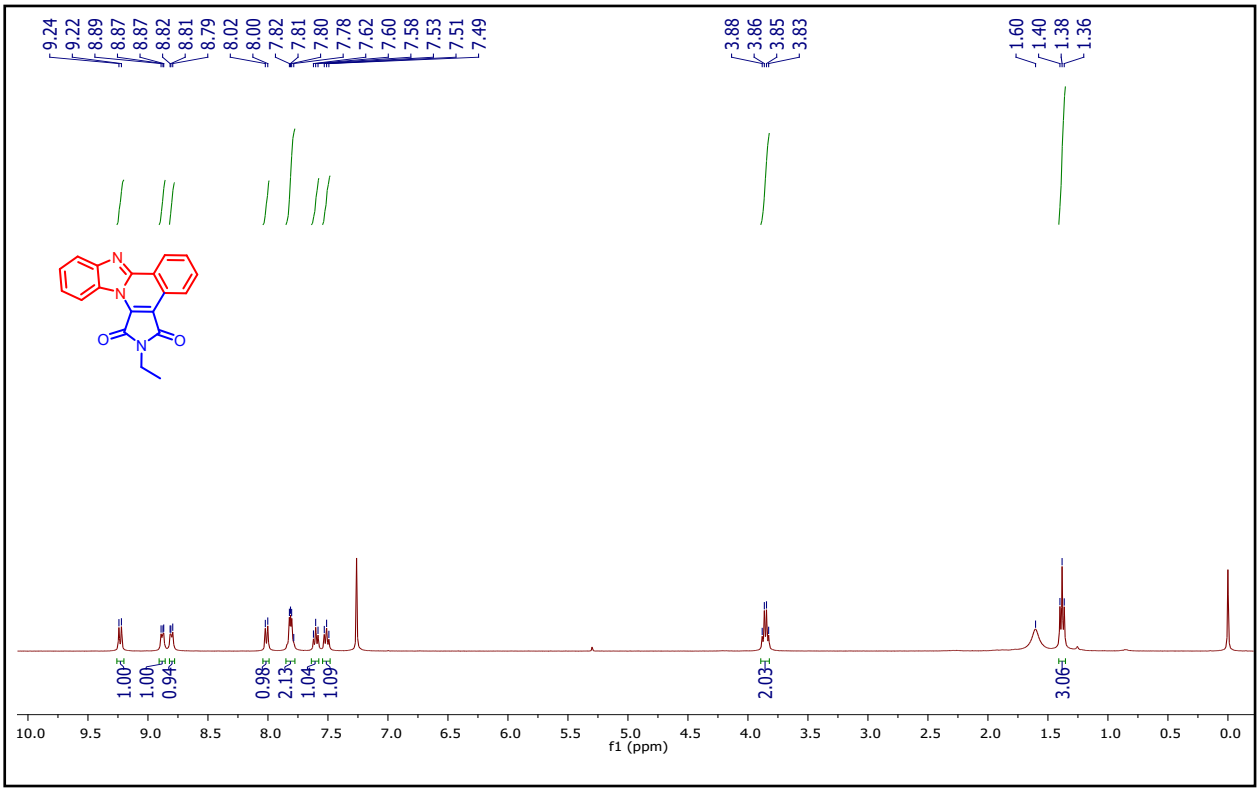
3. NMR spectra of the products: ^{1}H NMR (400MHz, $CDCl_3$) spectrum of **3a**:



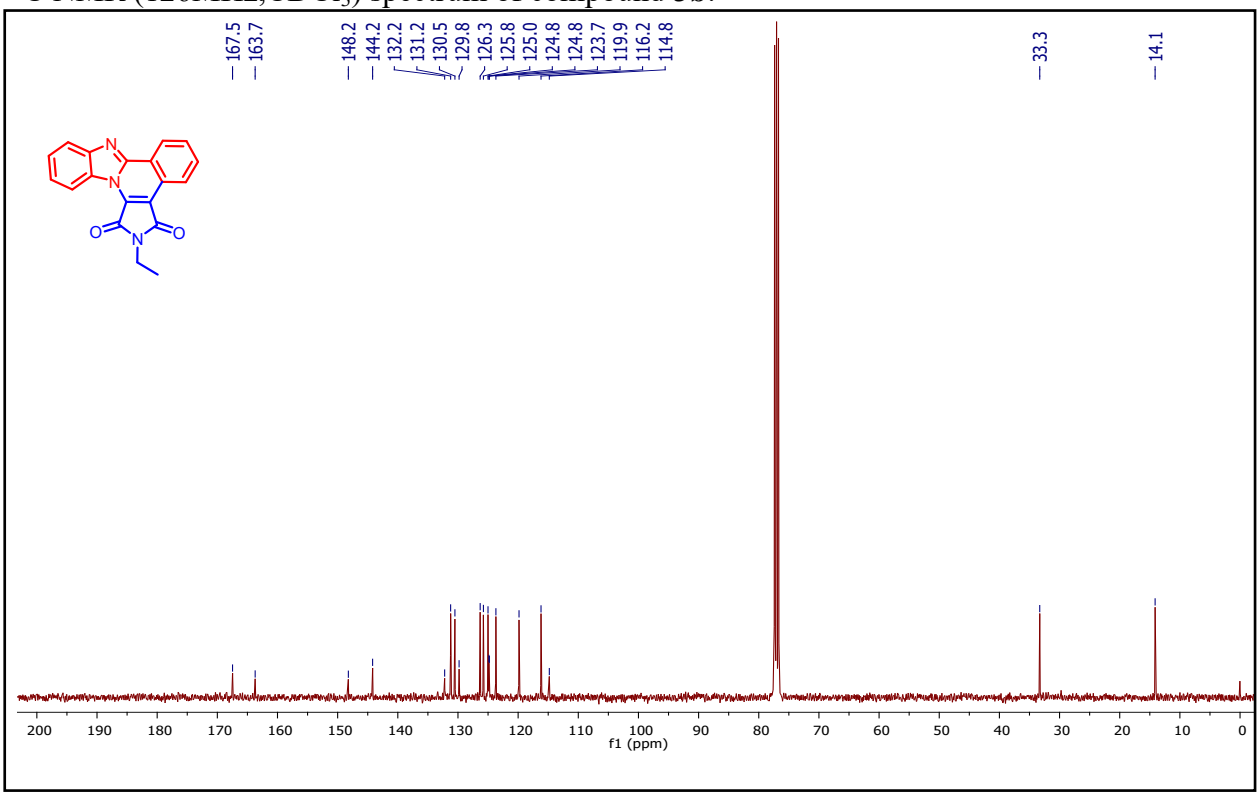
^{13}C NMR(101 MHz,$CDCl_3$) spectrum of compound **3a**:



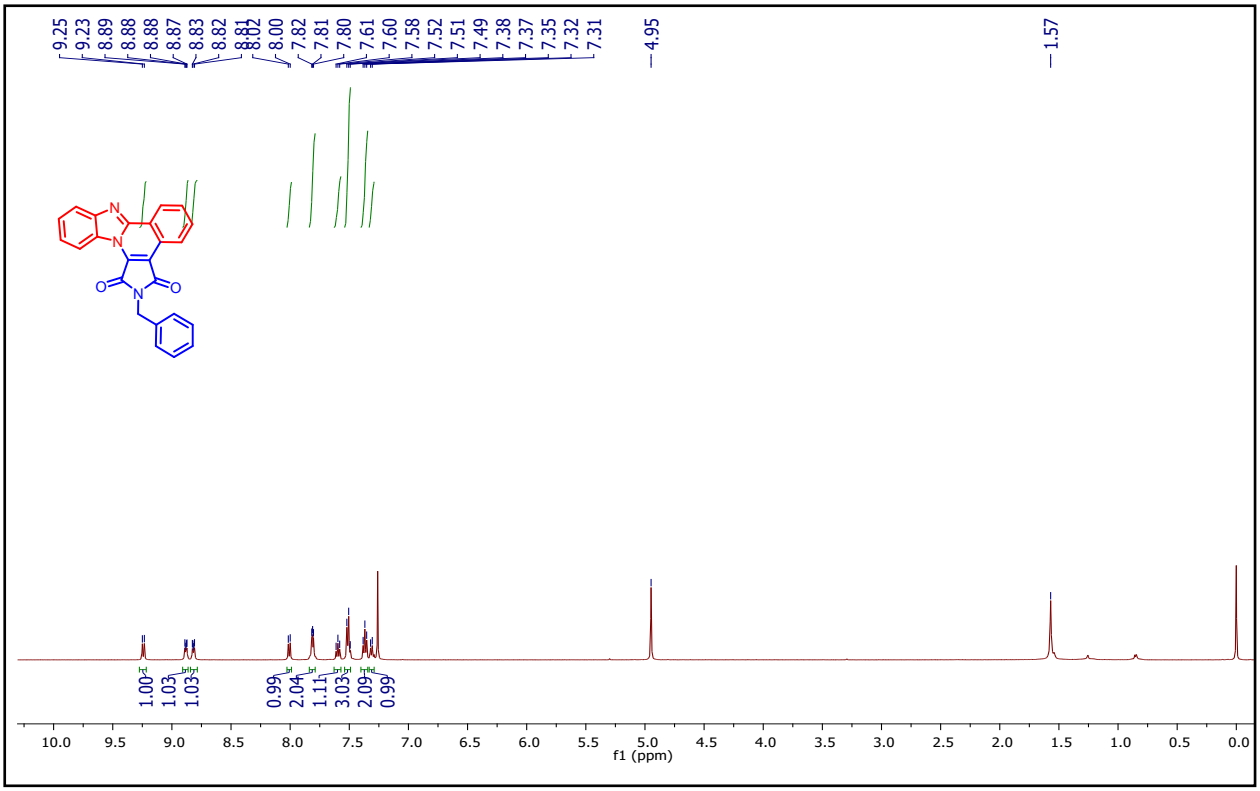
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3b**:



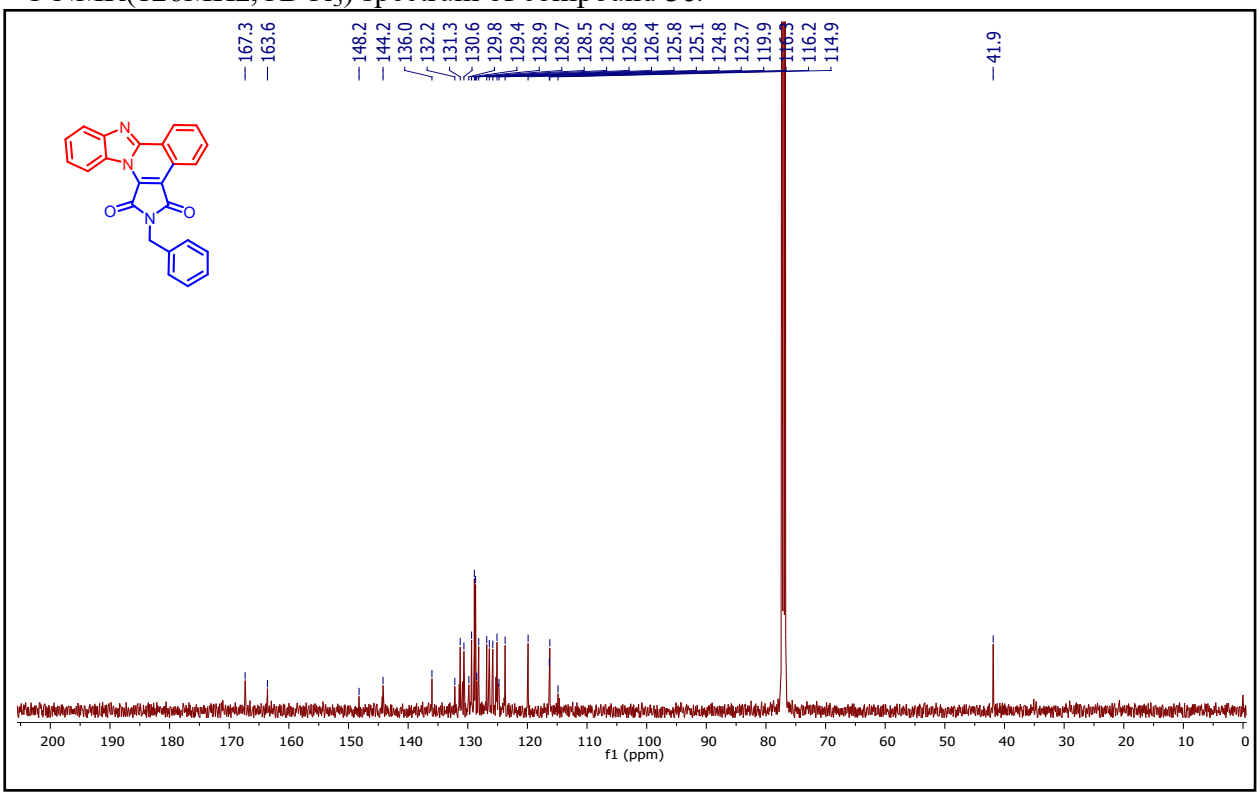
^{13}C NMR (126MHz,$CDCl_3$) spectrum of compound **3b**:



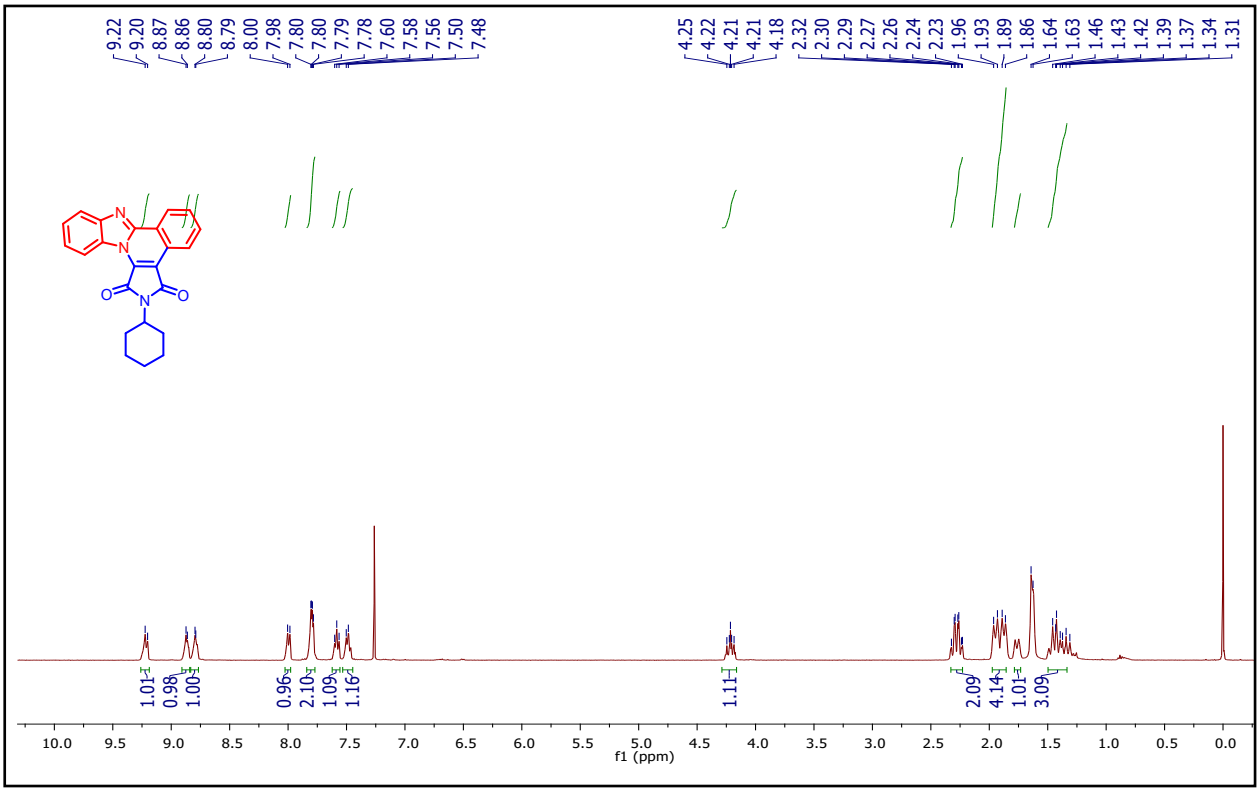
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3c**:



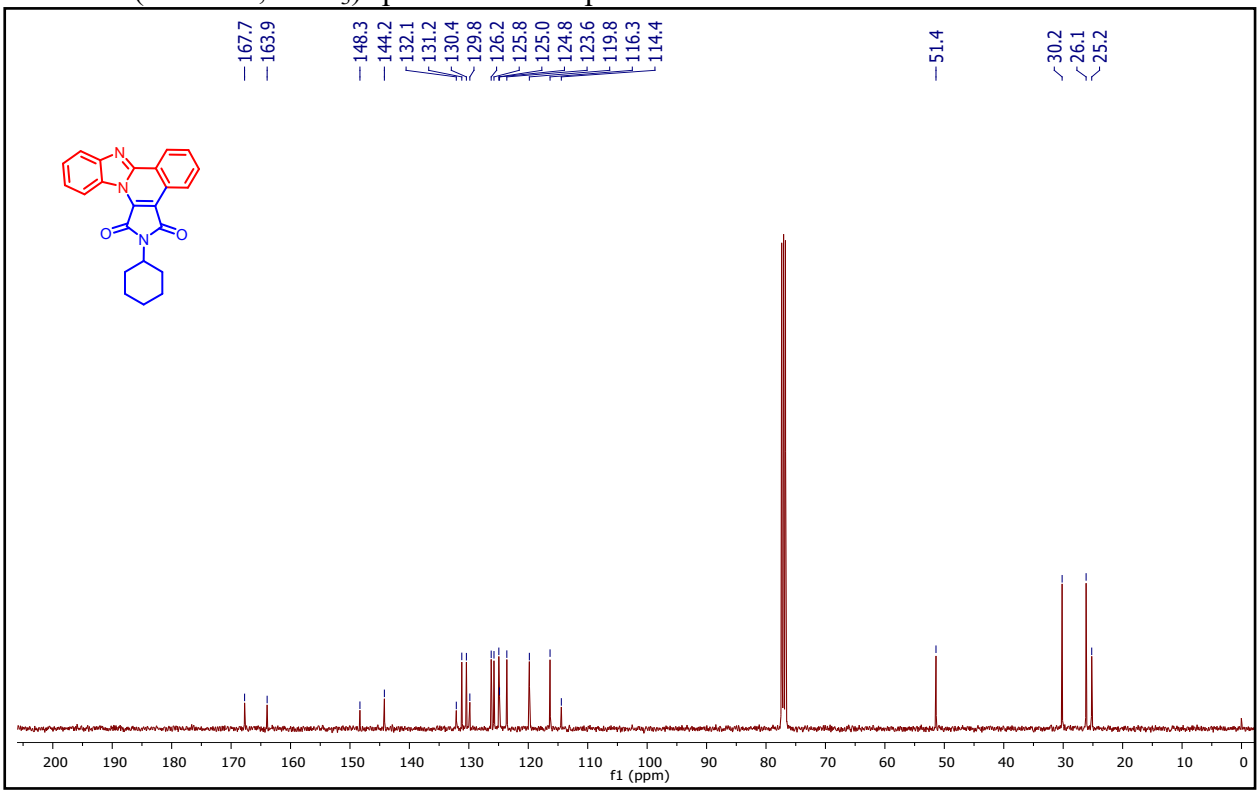
^{13}C NMR(126MHz,$CDCl_3$) spectrum of compound **3c**:



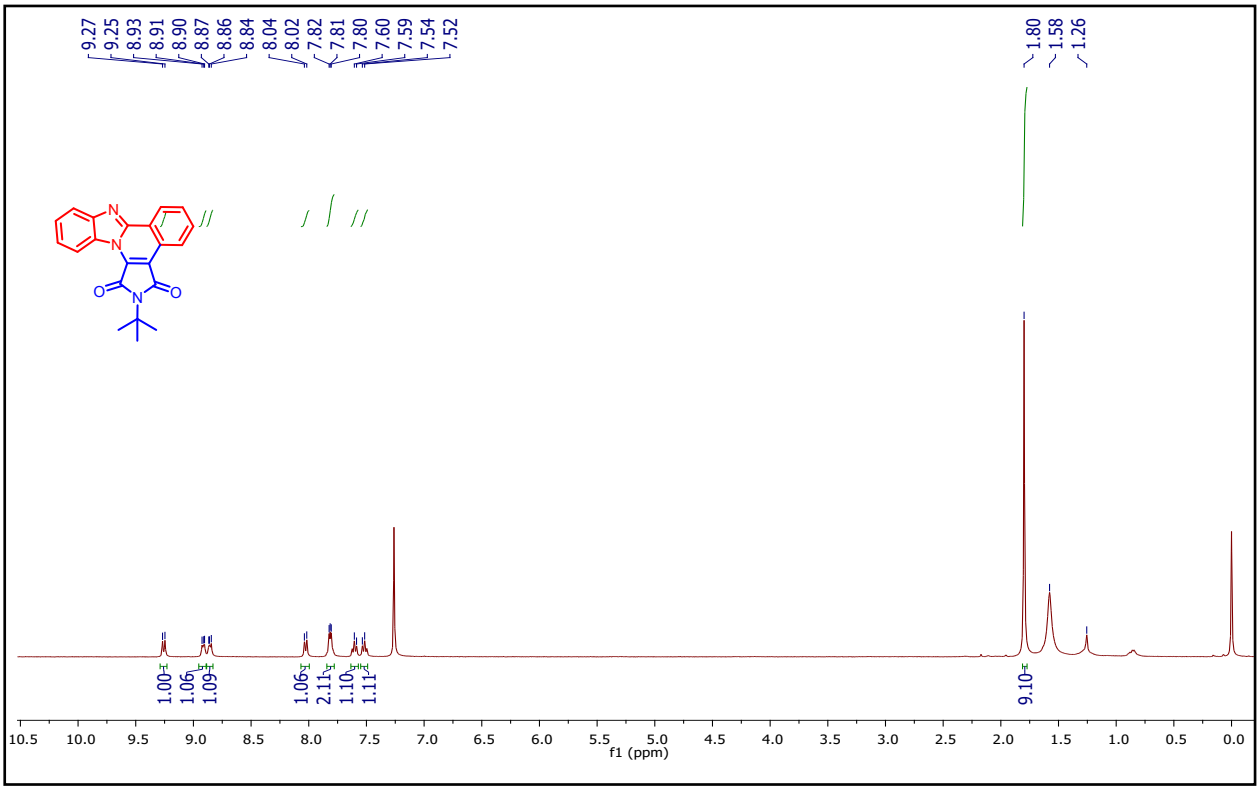
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3d**:



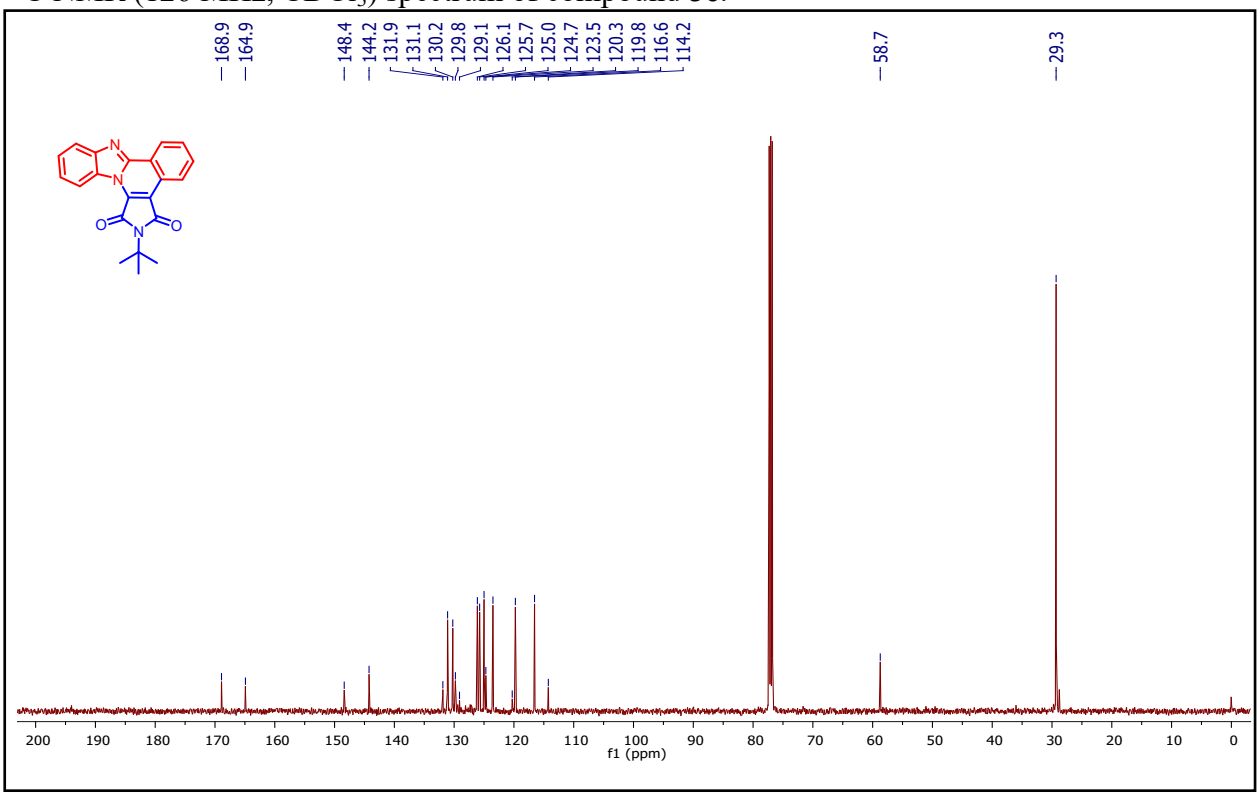
^{13}C NMR (126MHz,$CDCl_3$) spectrum of compound **3d**:



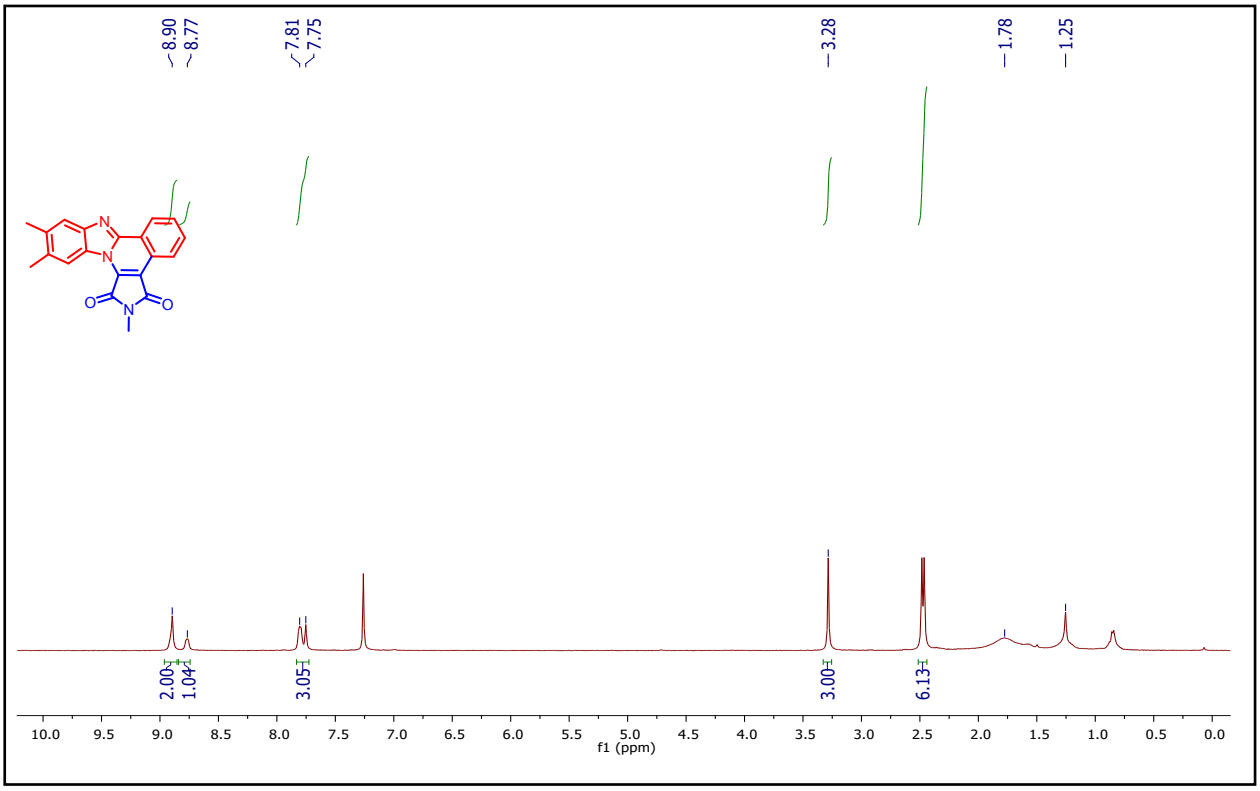
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3e**:



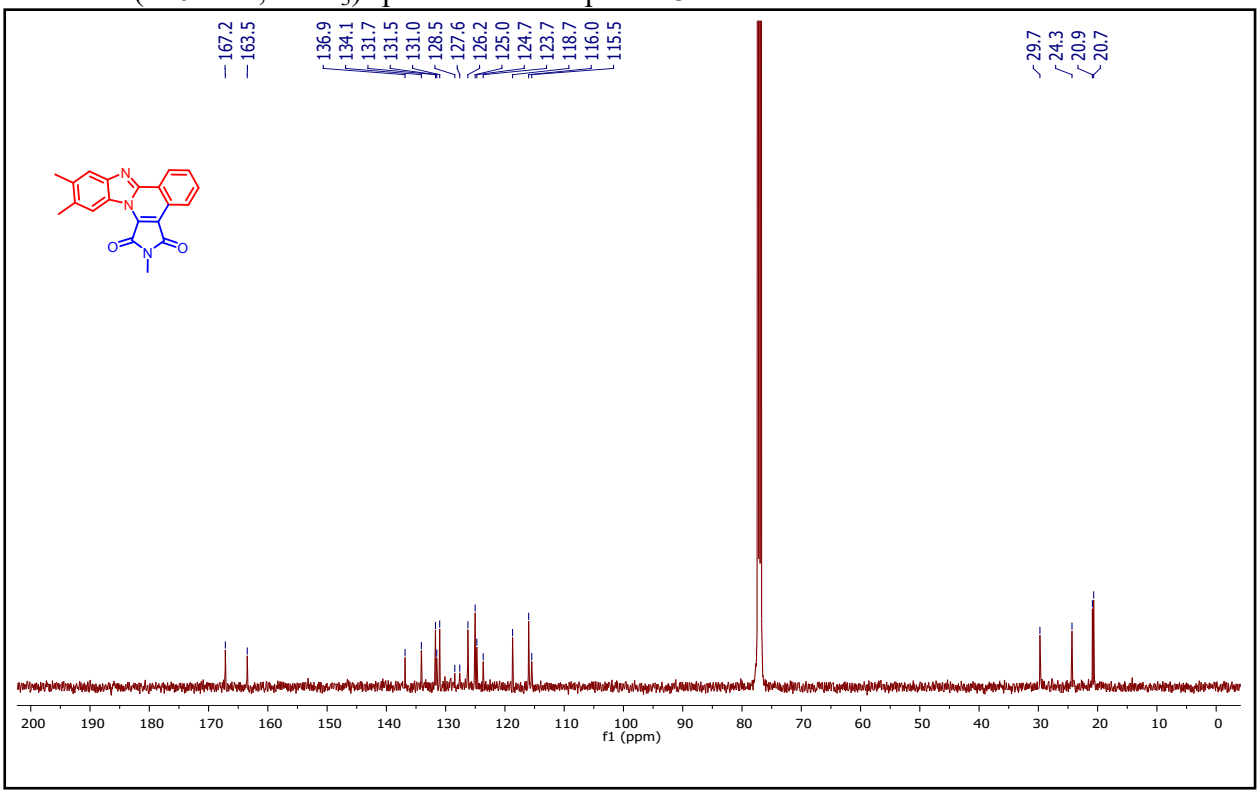
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3e**:



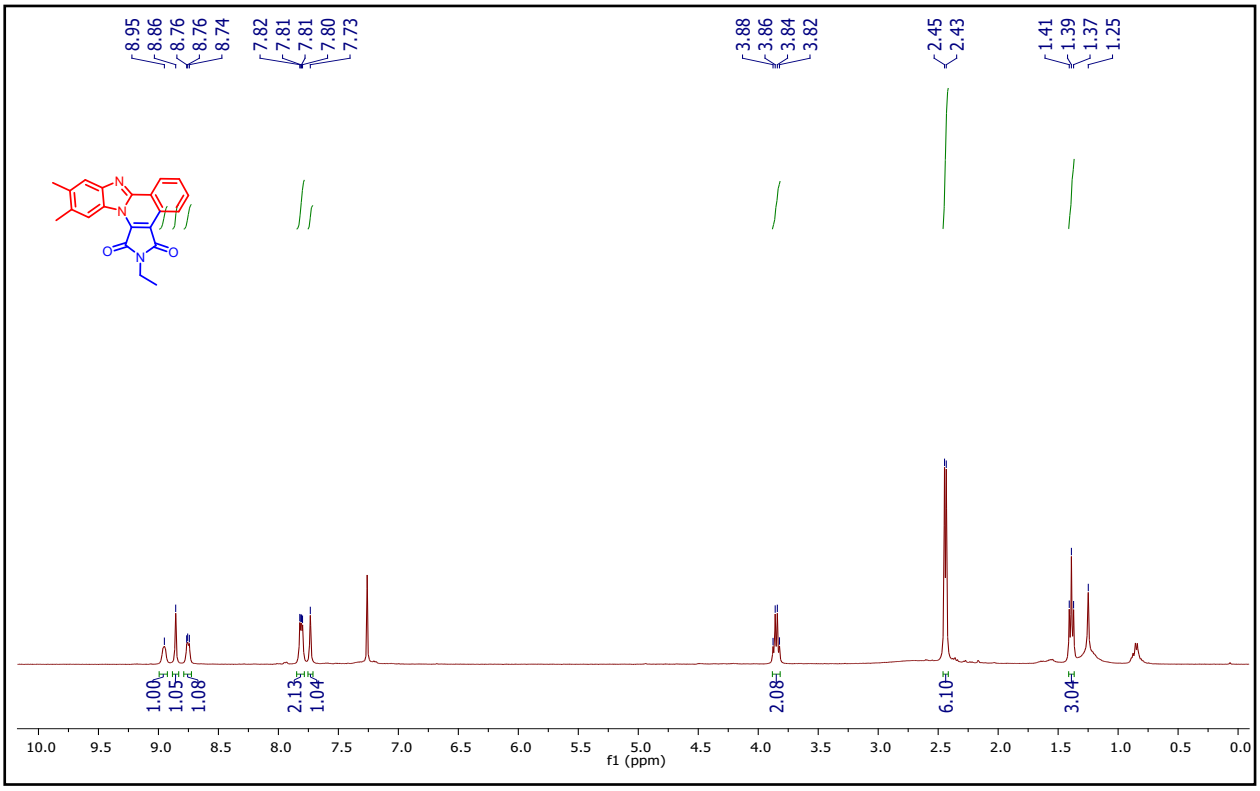
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3f**:



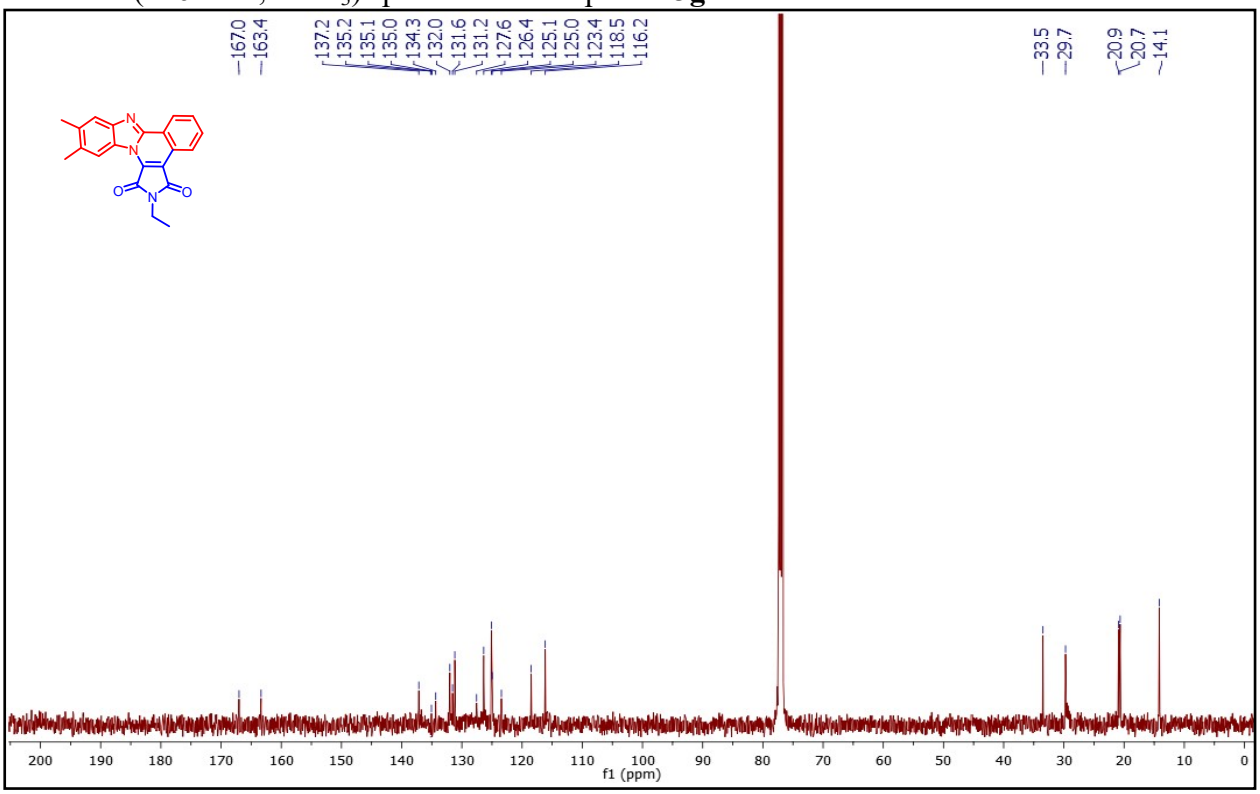
^{13}C NMR (126MHz,$CDCl_3$) spectrum of compound **3f**:



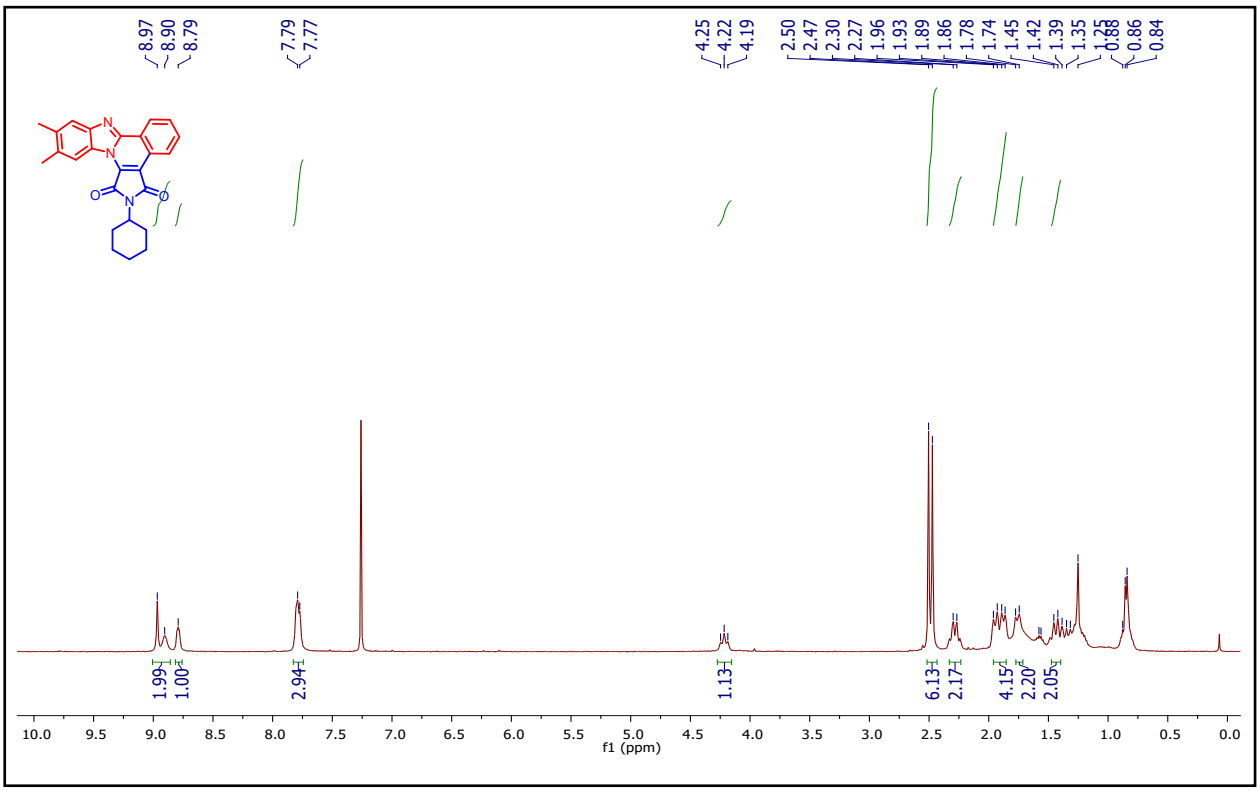
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3g**:



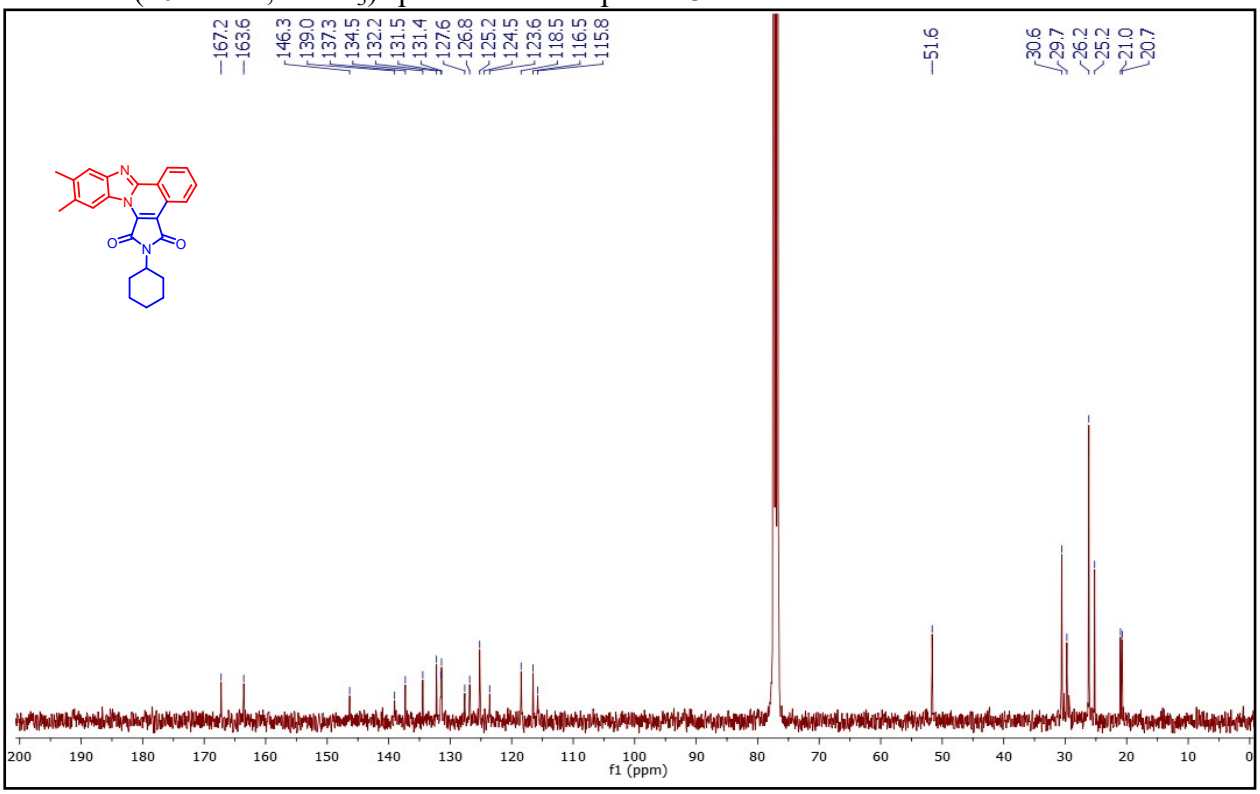
^{13}C NMR (126MHz,$CDCl_3$) spectrum of compound **3g**:



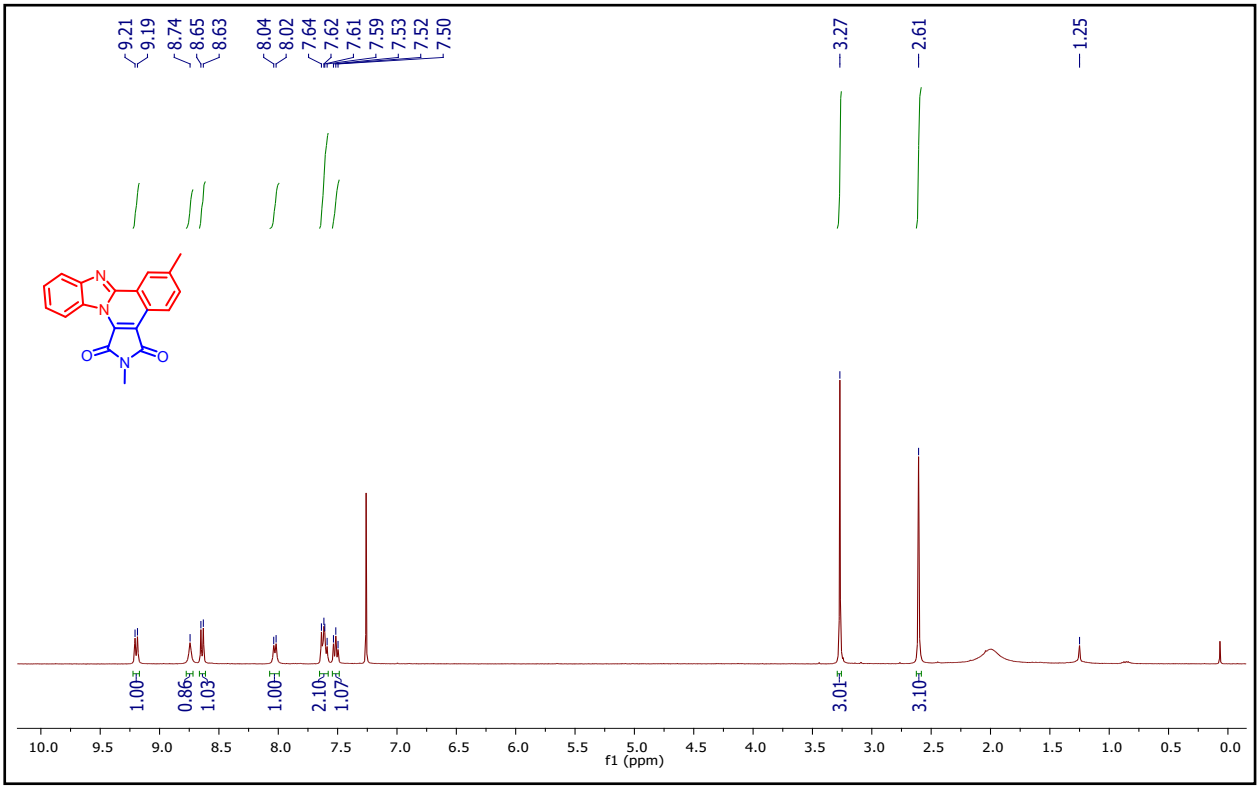
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3h**:



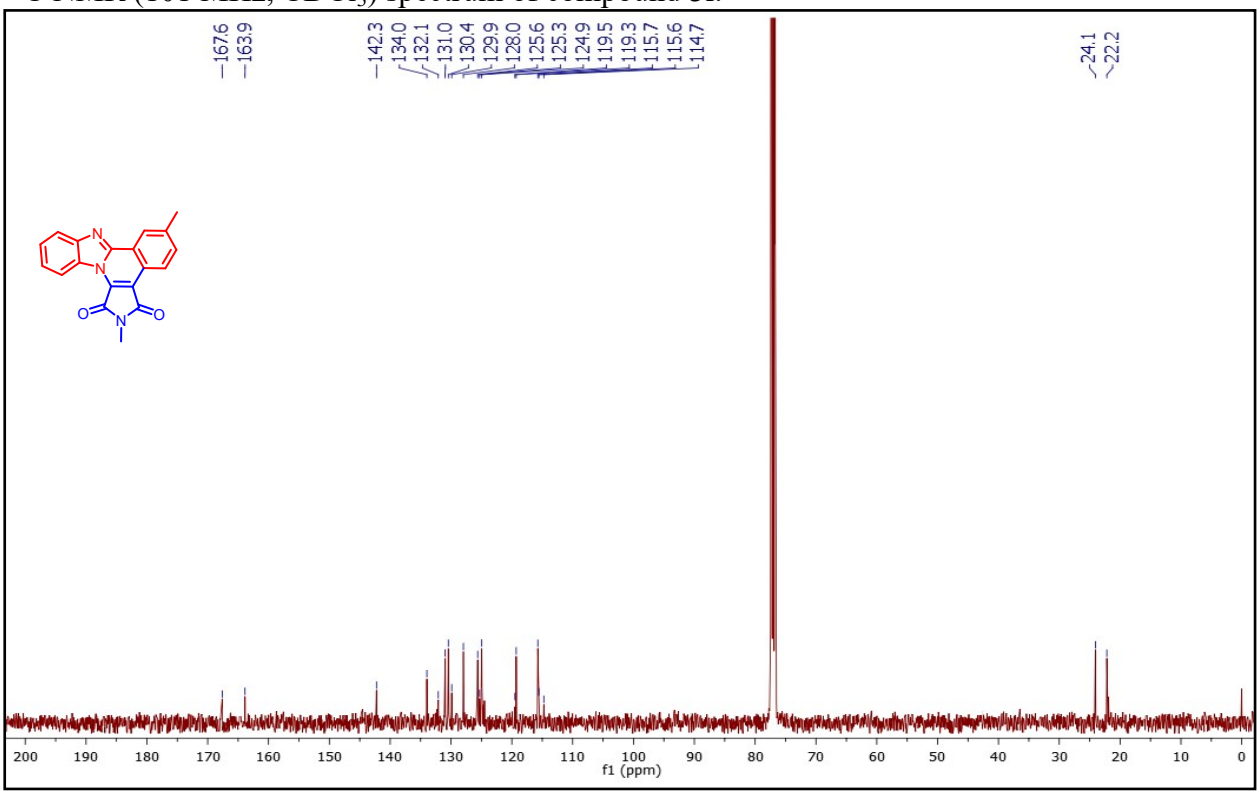
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3h**:



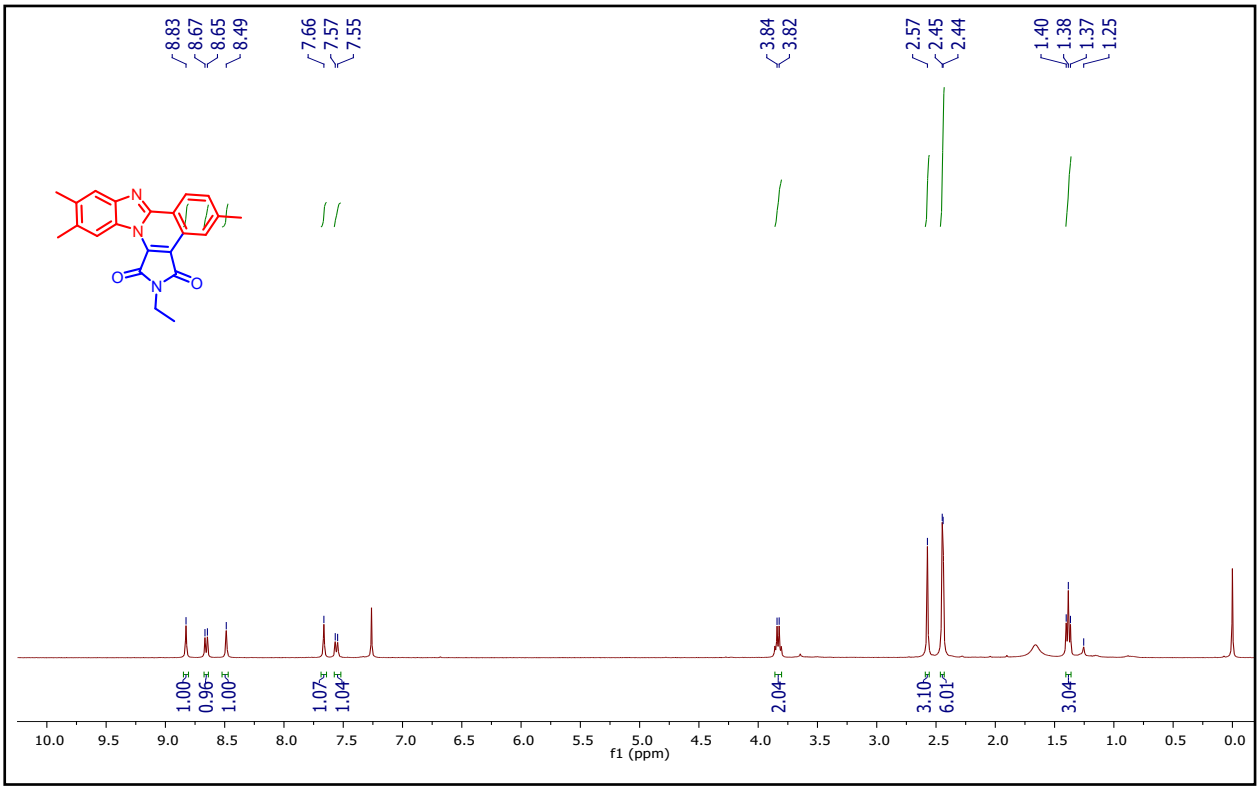
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3i**:



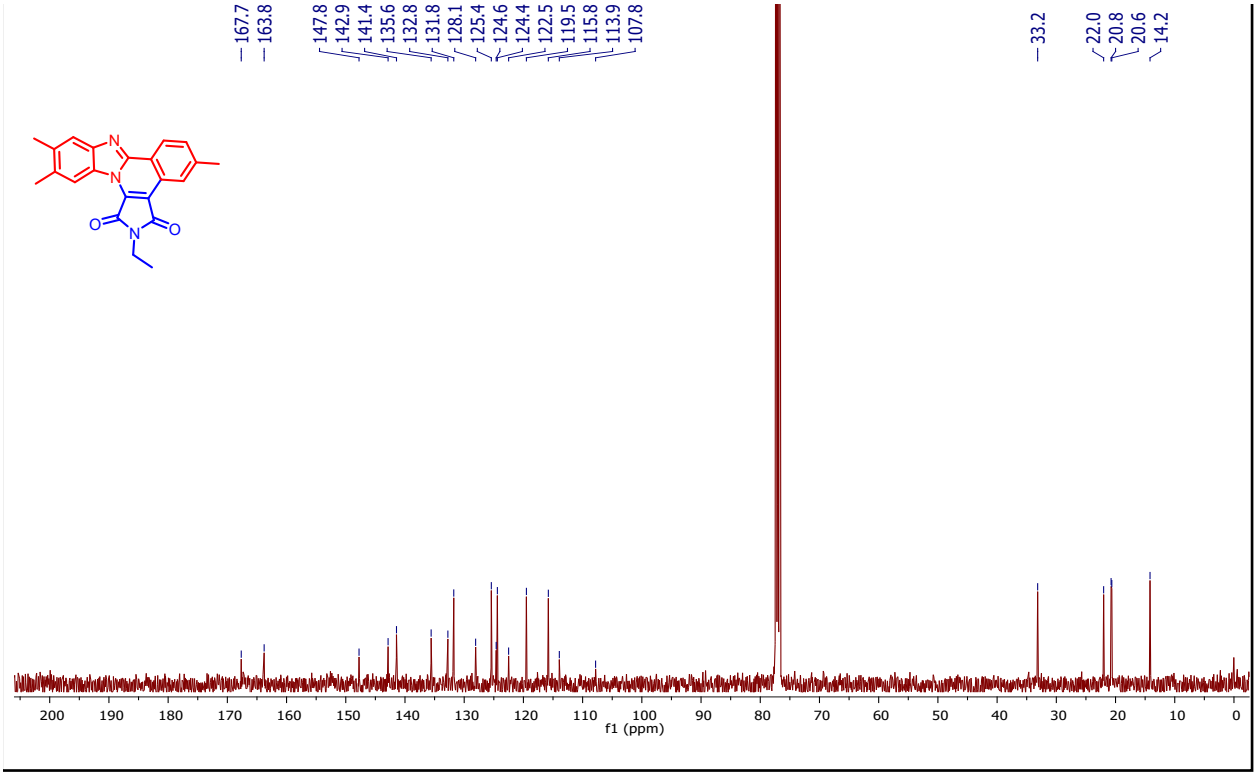
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3i**:



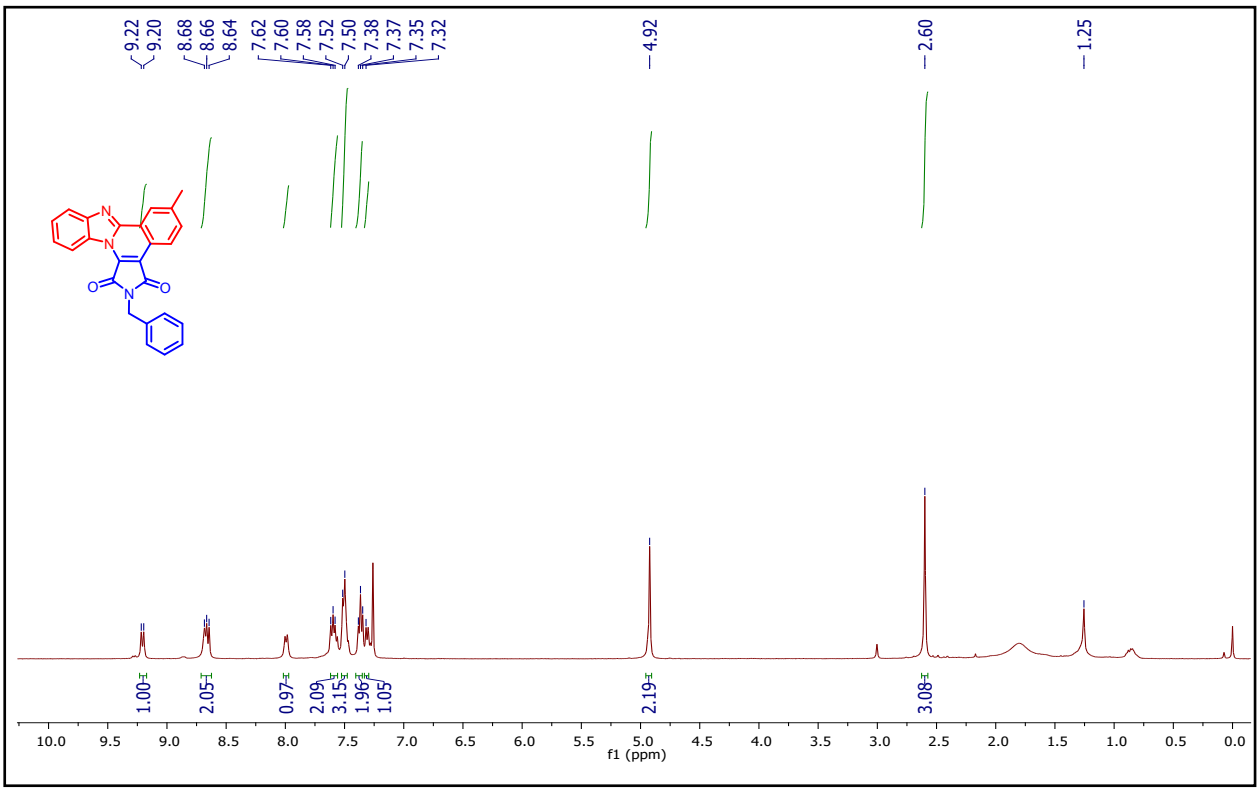
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3j**:



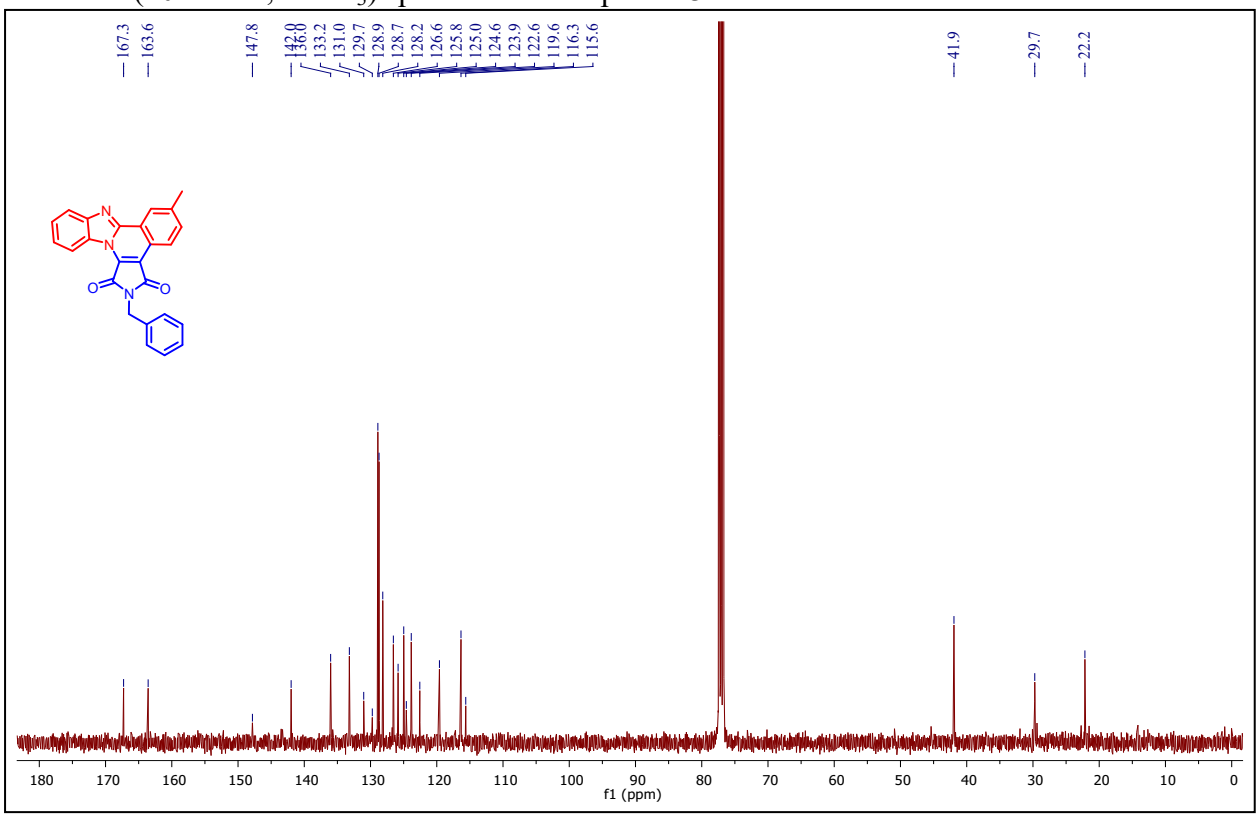
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3j**:



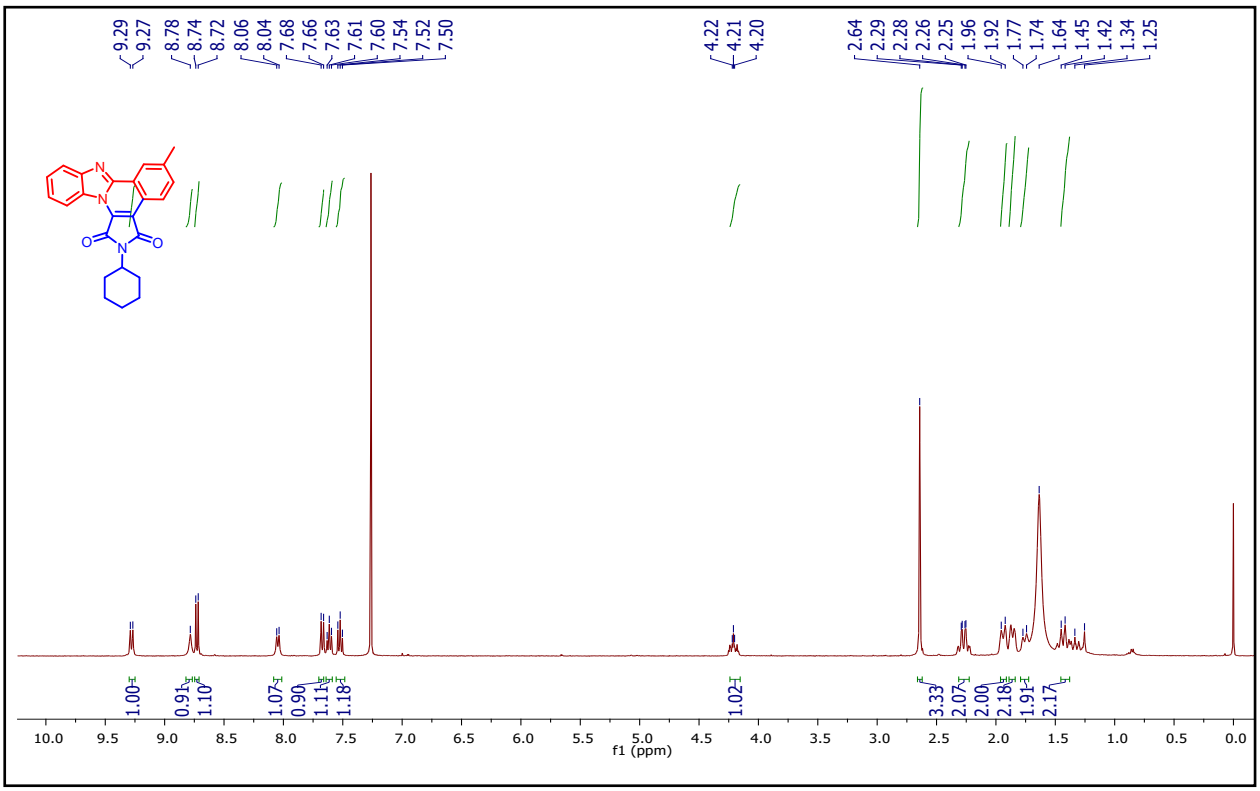
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3k**



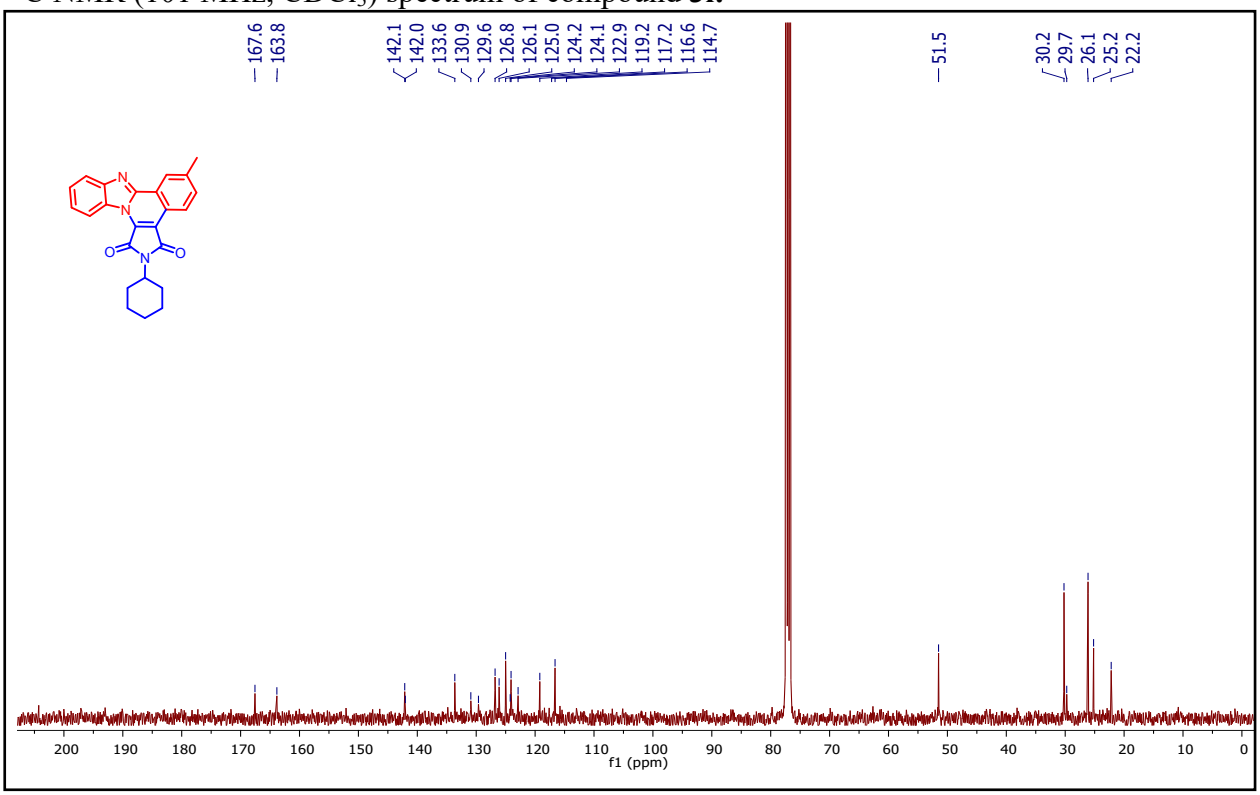
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3k**:



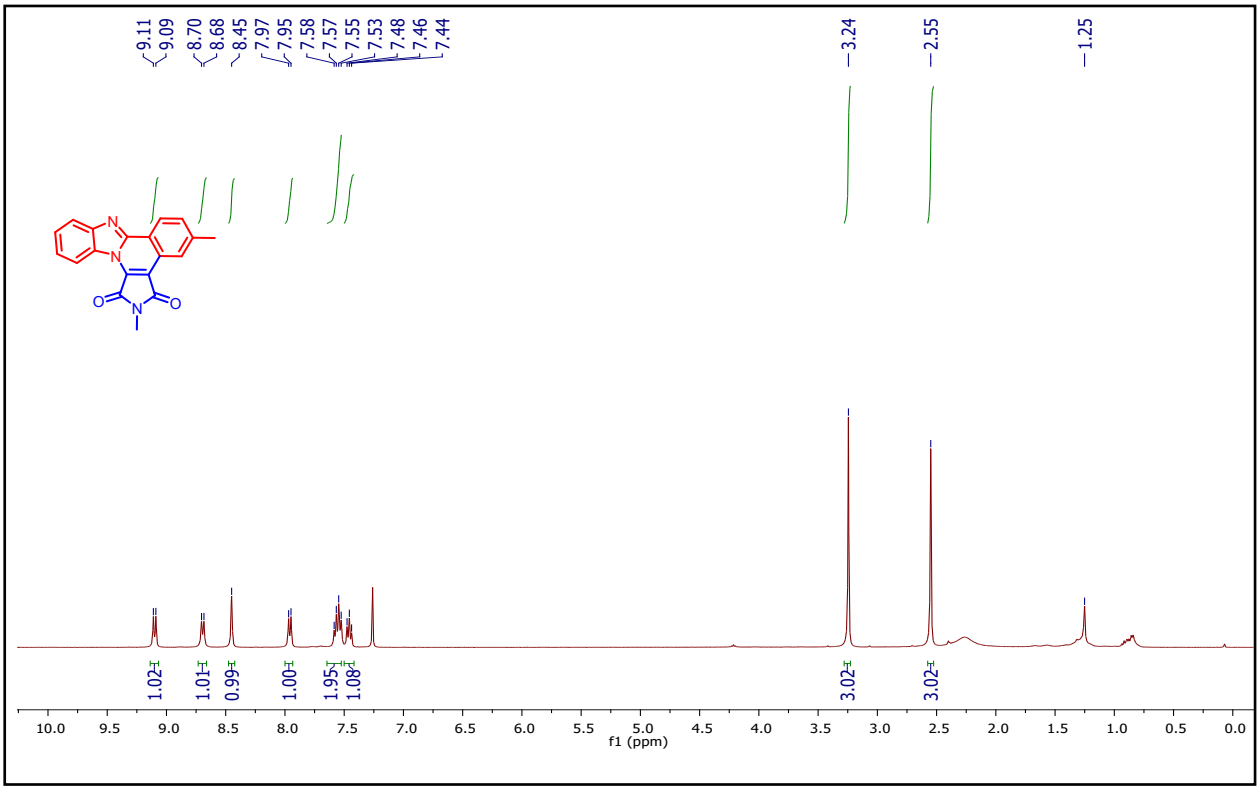
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3l:**



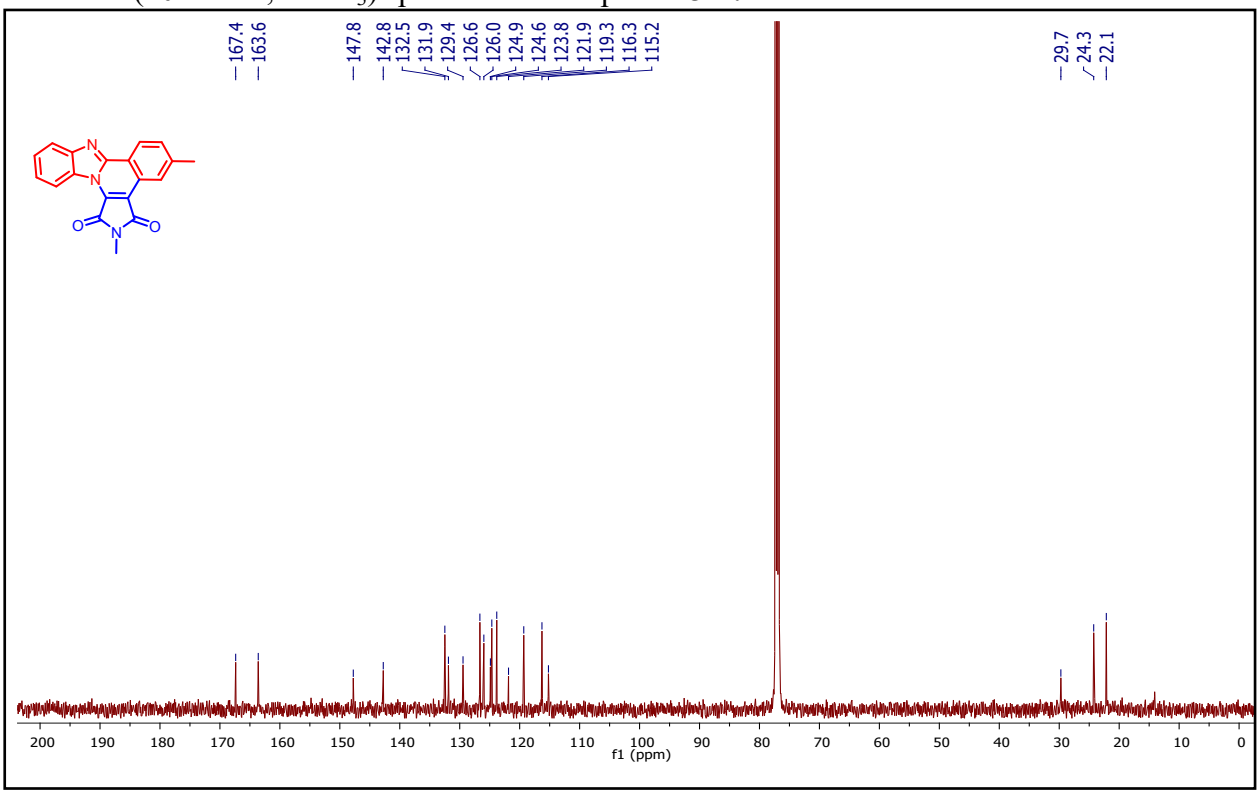
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3l:**



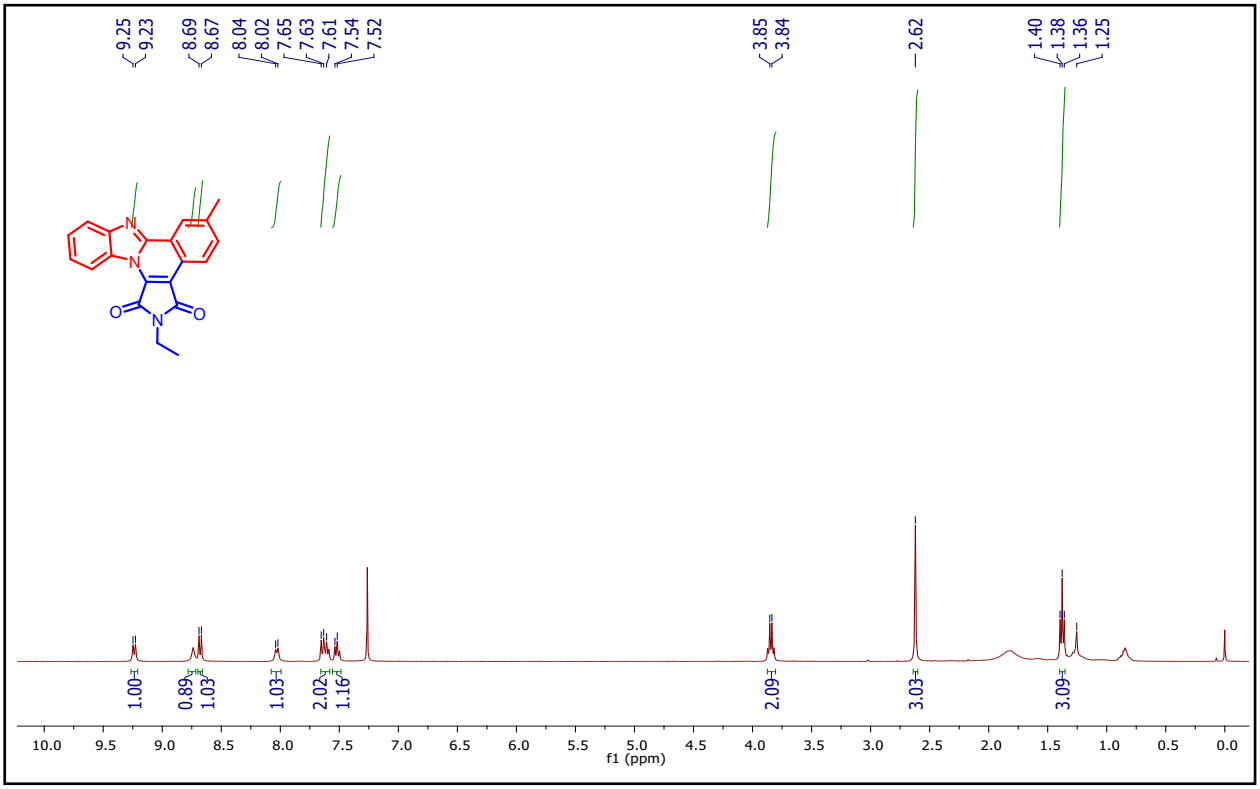
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3m:**



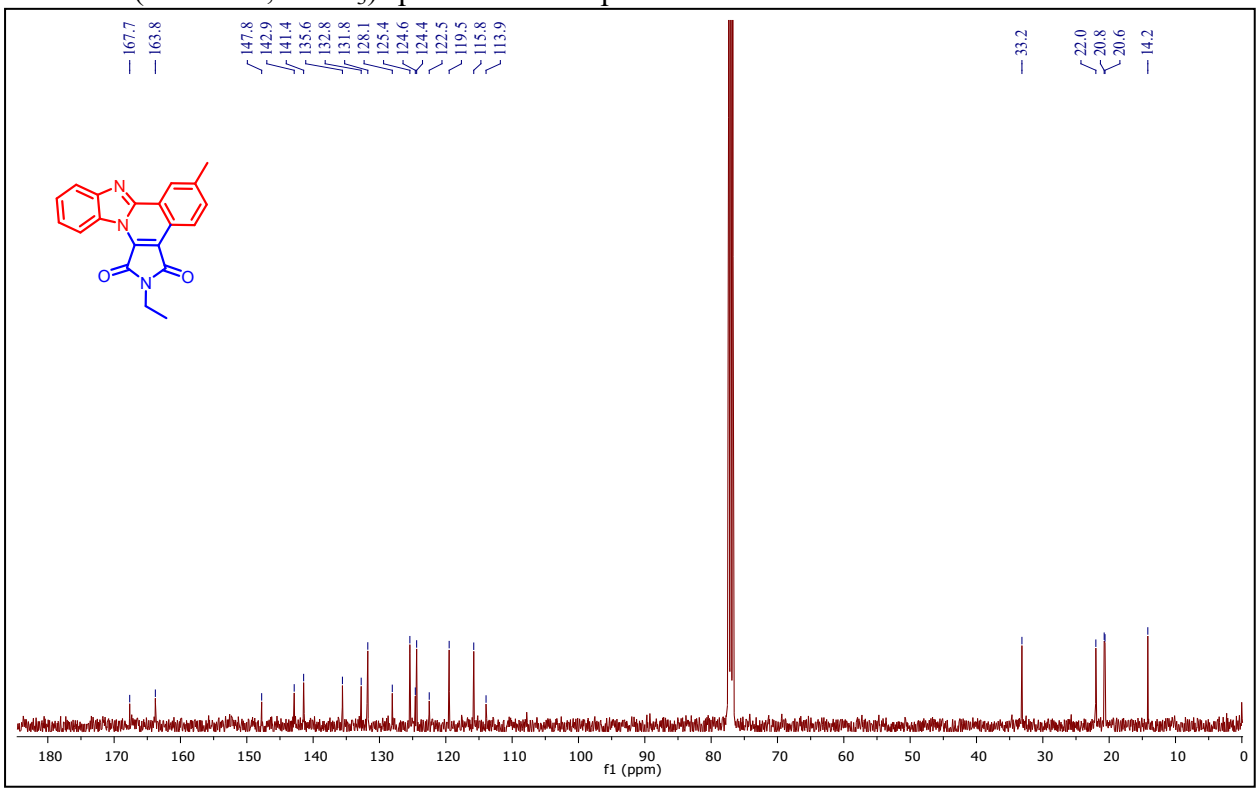
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3m:**



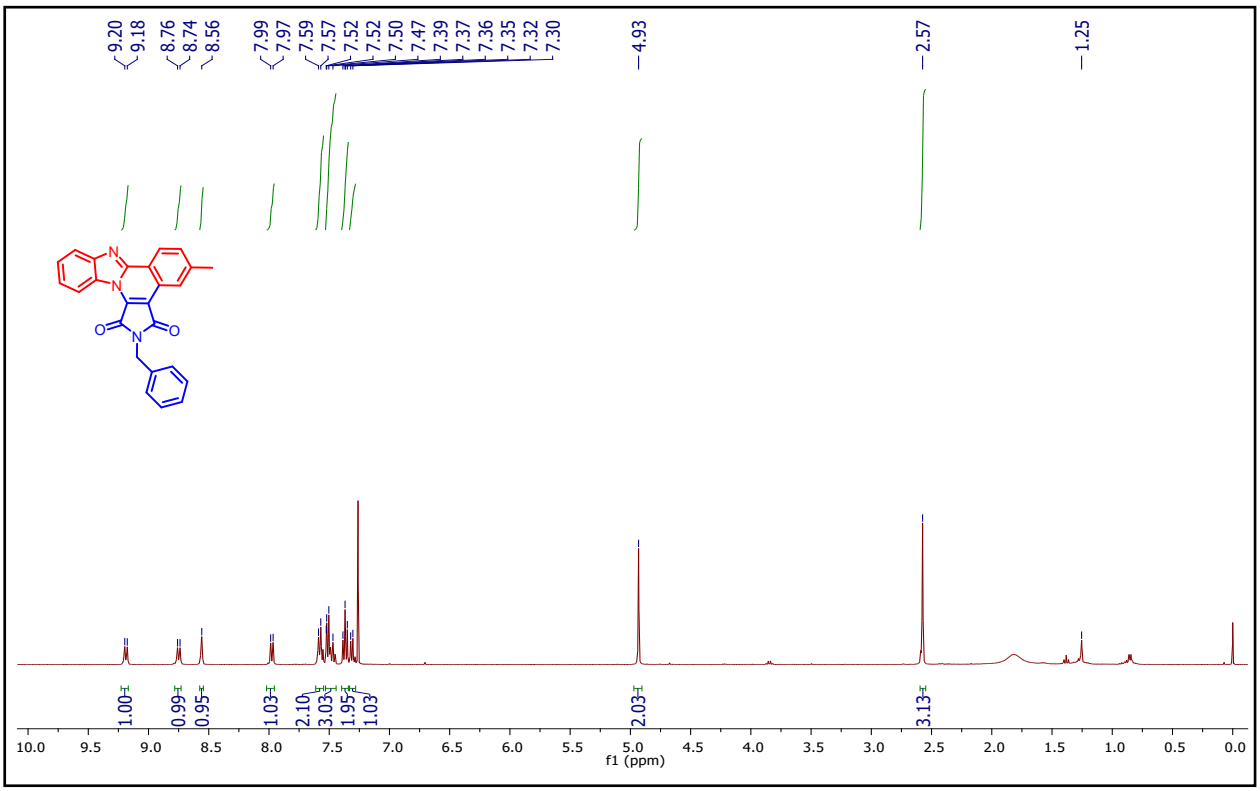
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3n**:



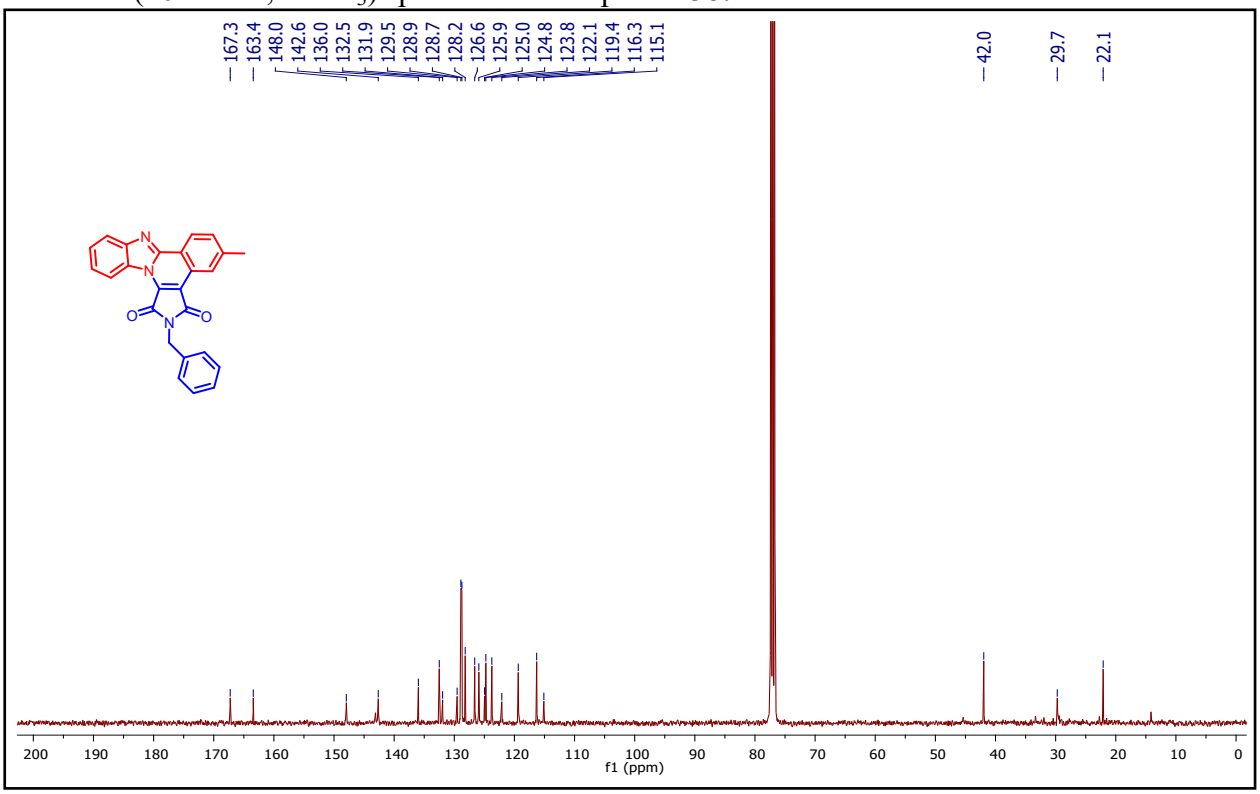
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3n:**



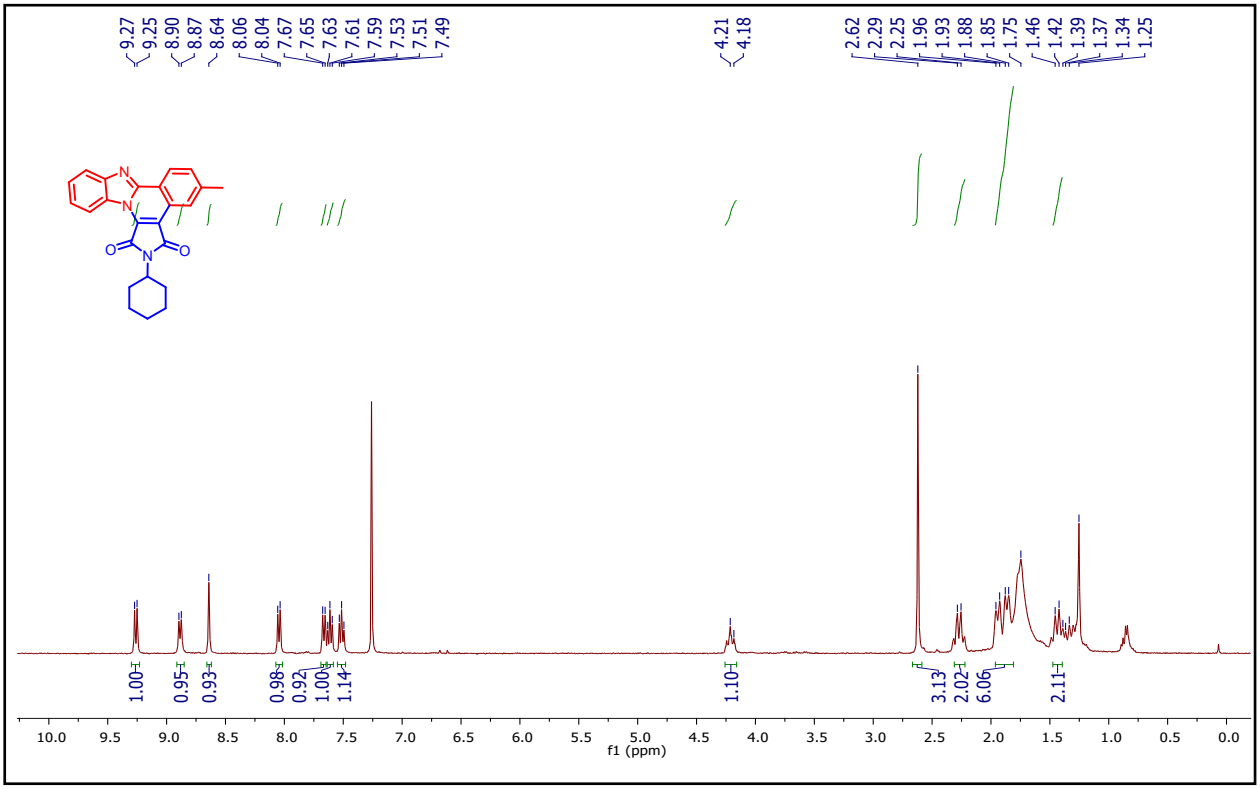
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3o:**



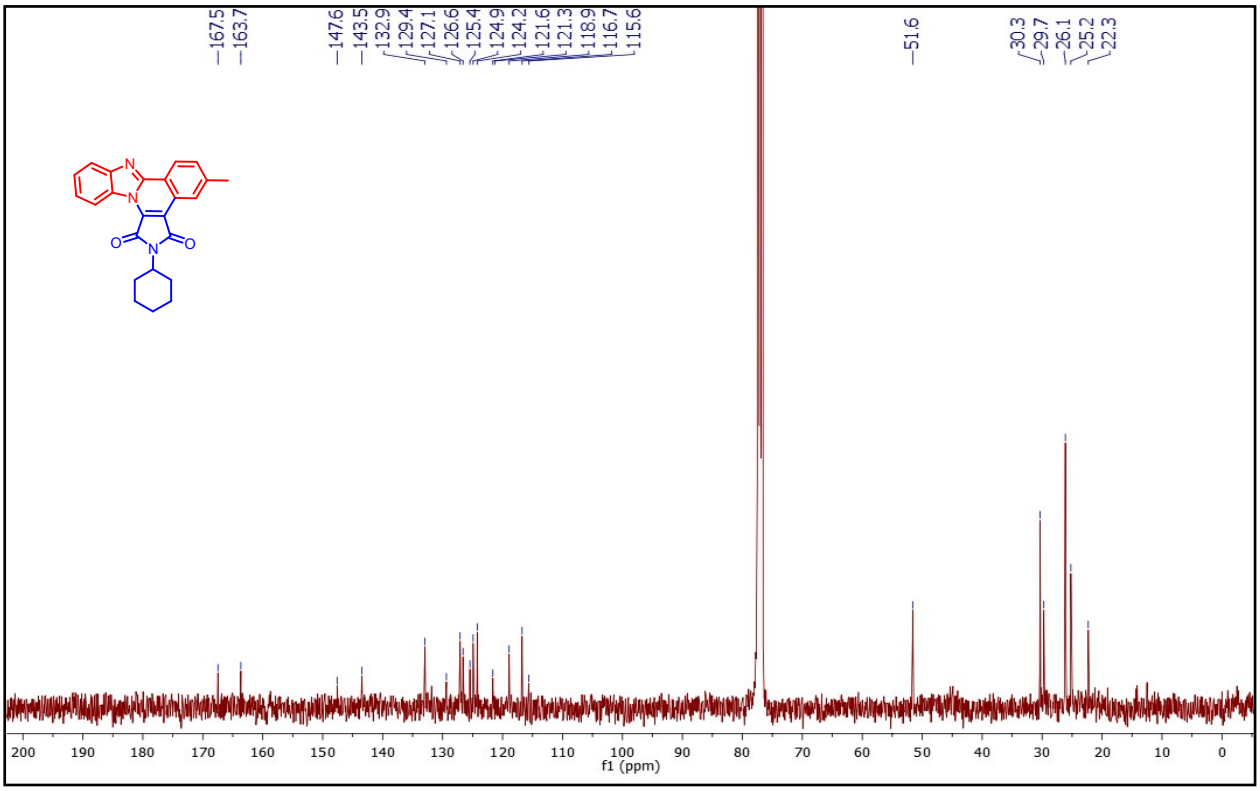
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3o:**



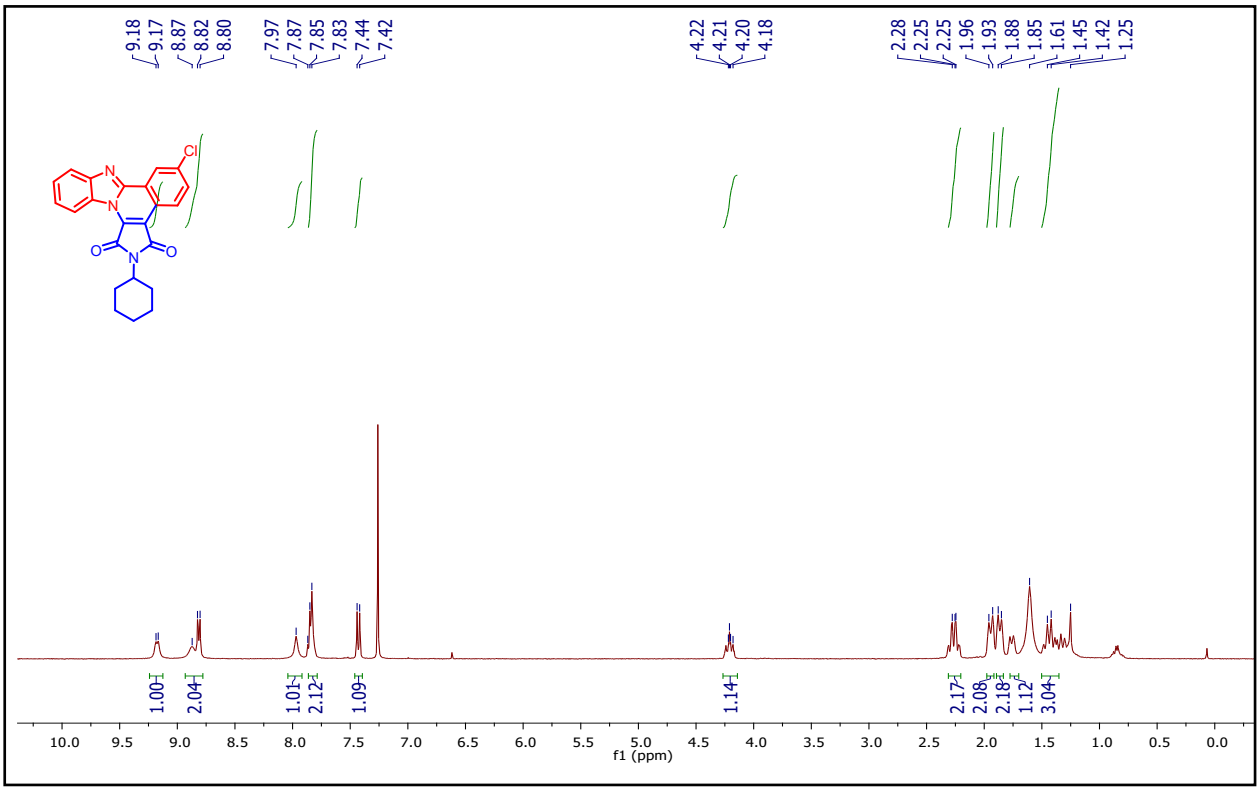
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3p:**



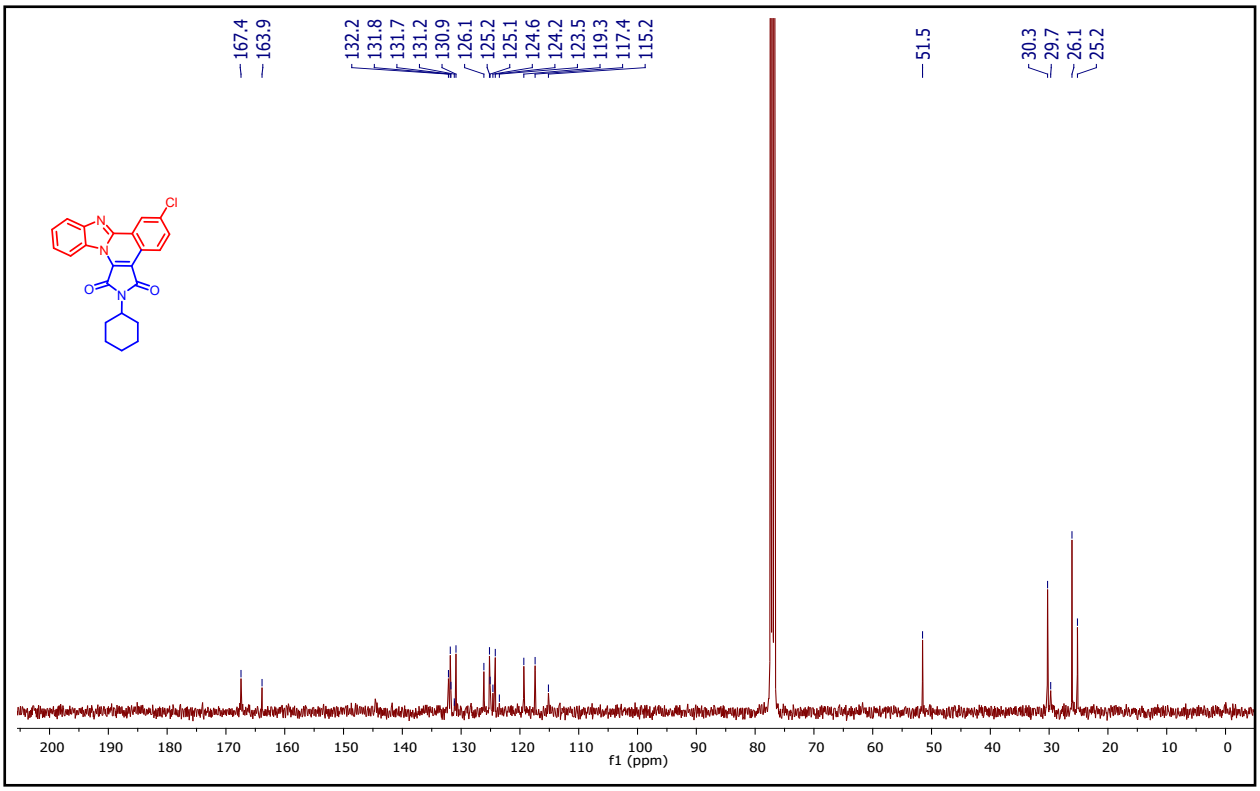
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3p:**



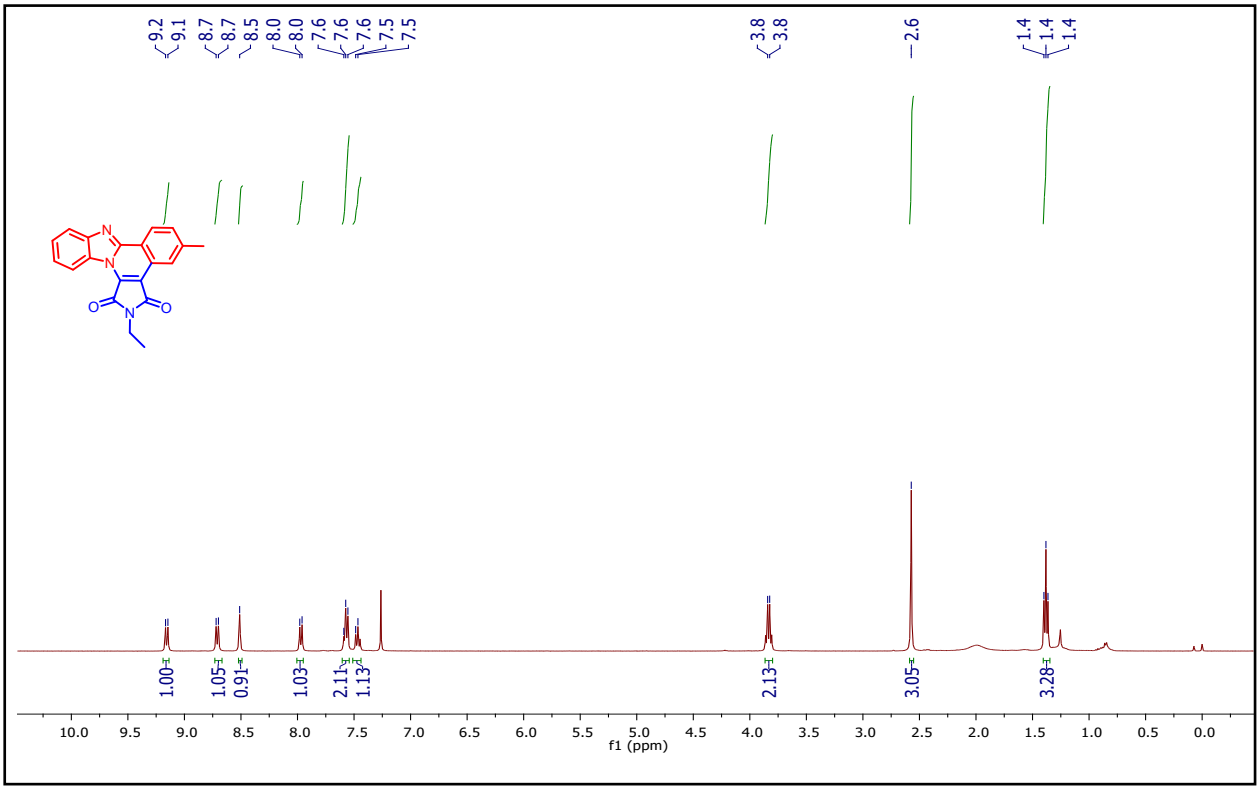
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3q:**



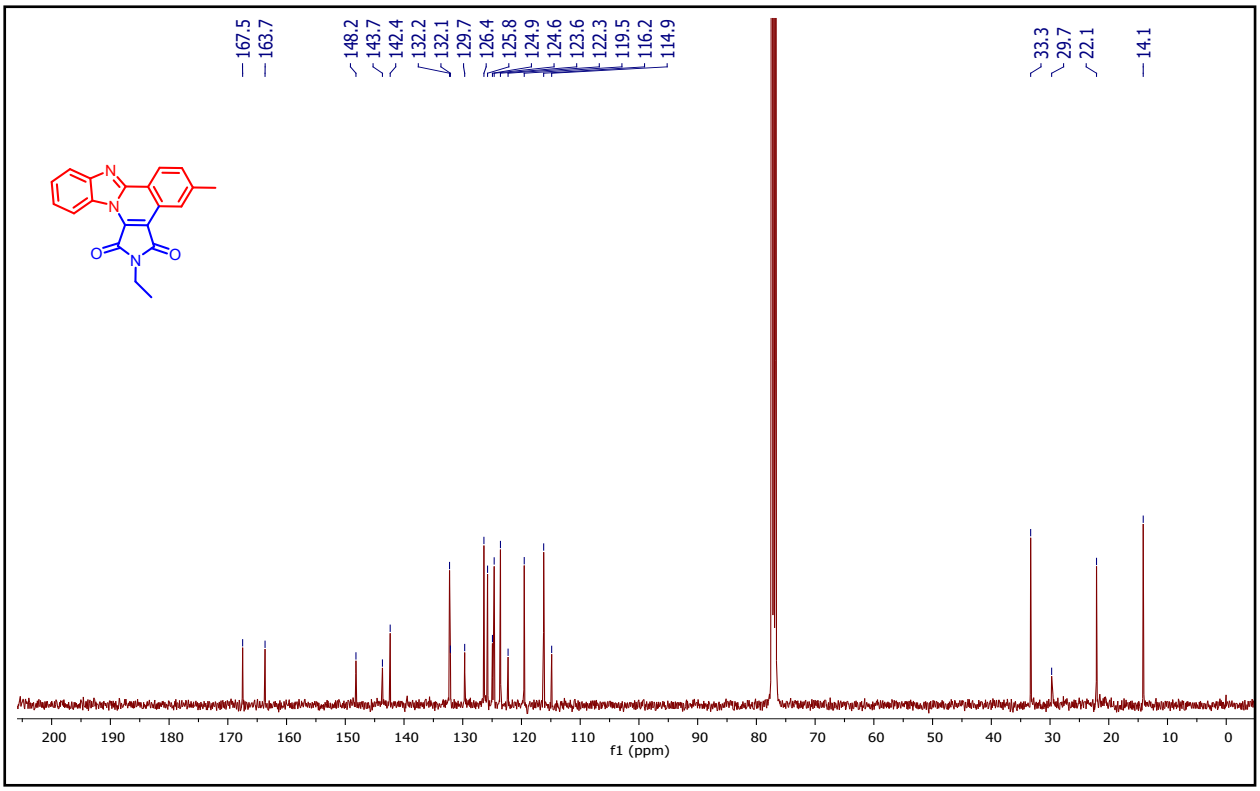
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3q:**



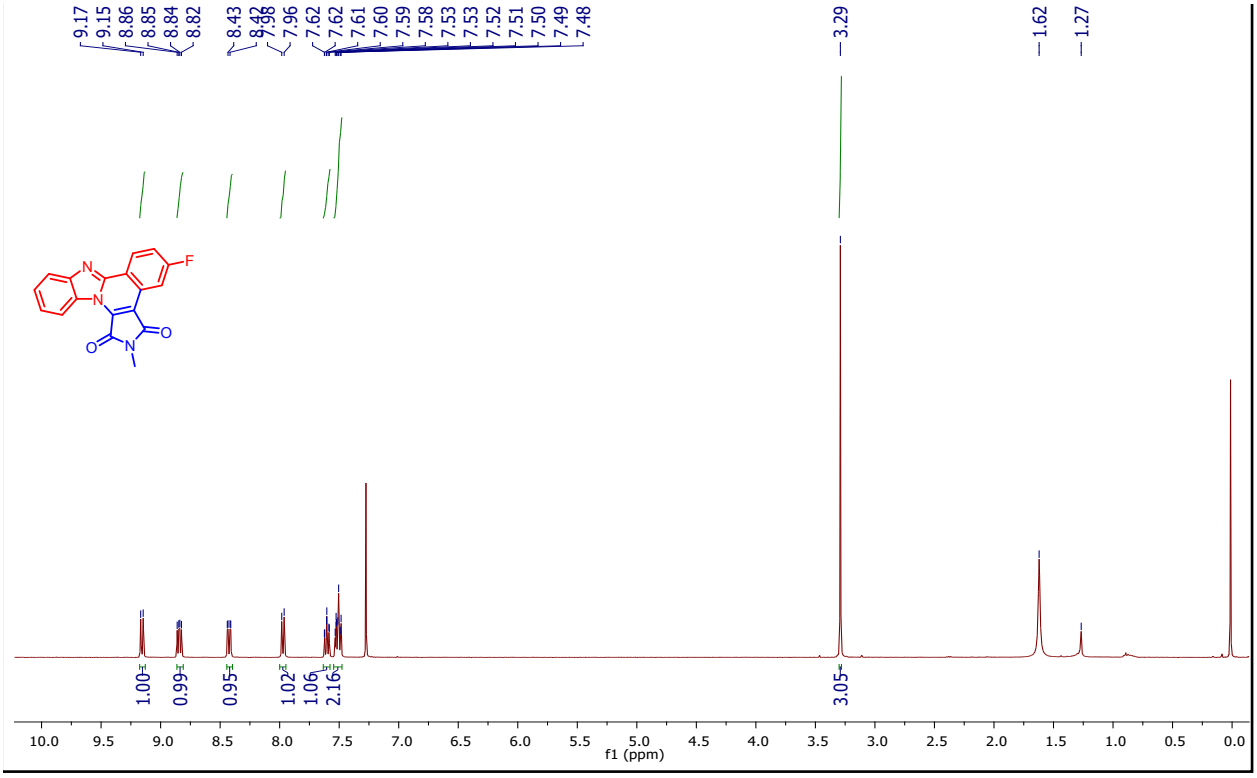
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3r:**



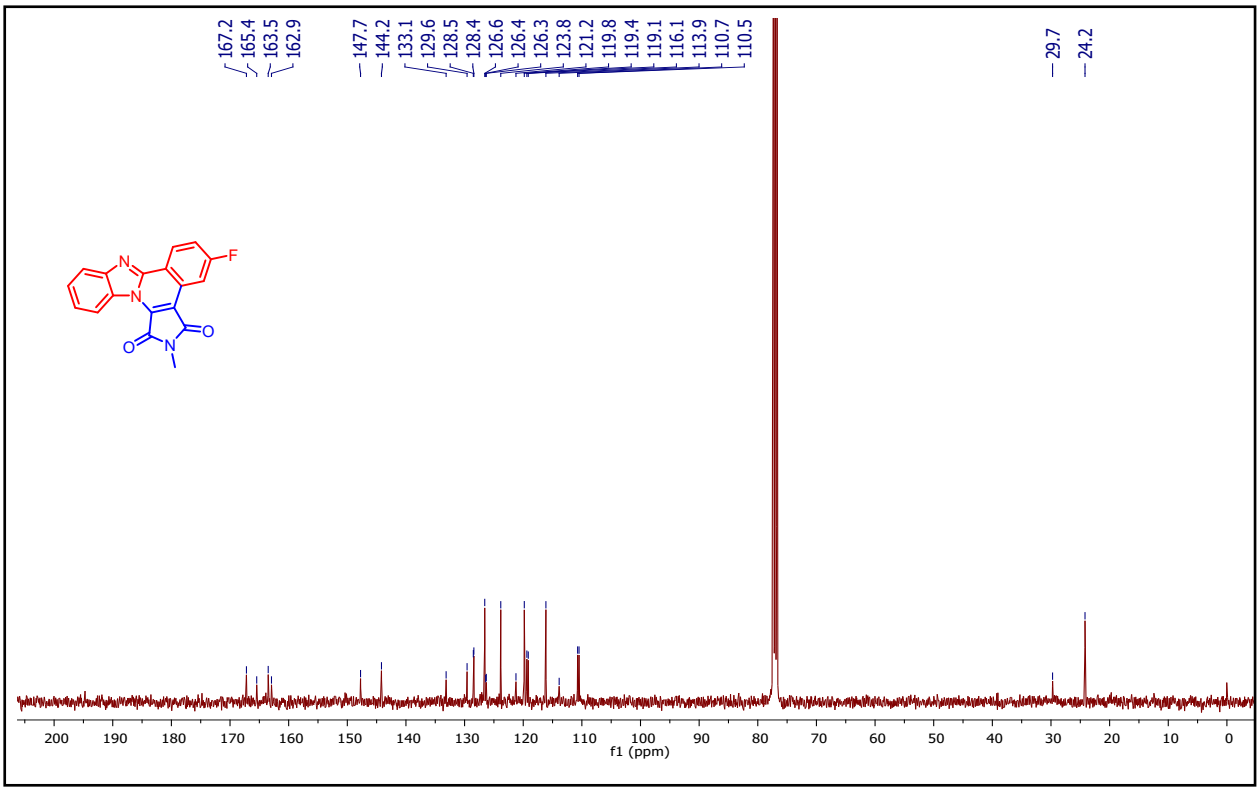
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3r:**



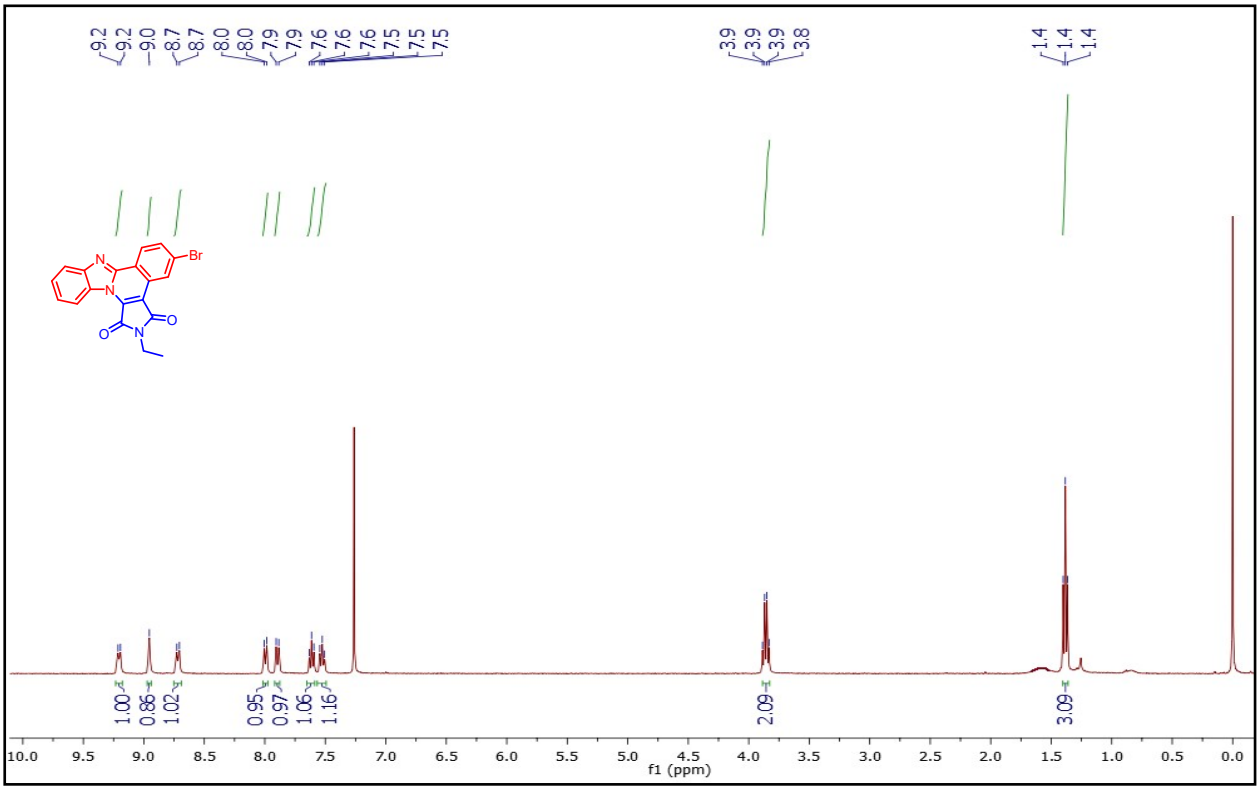
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3s:**



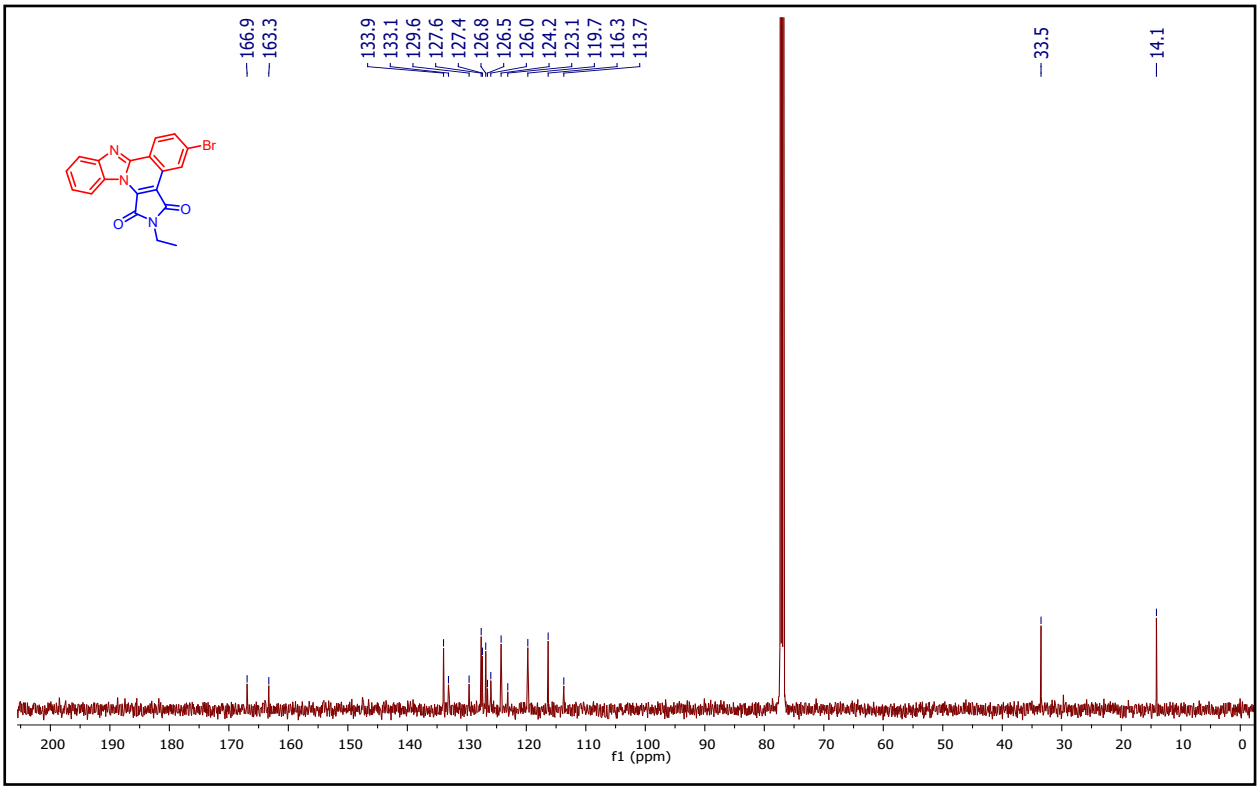
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3s:**



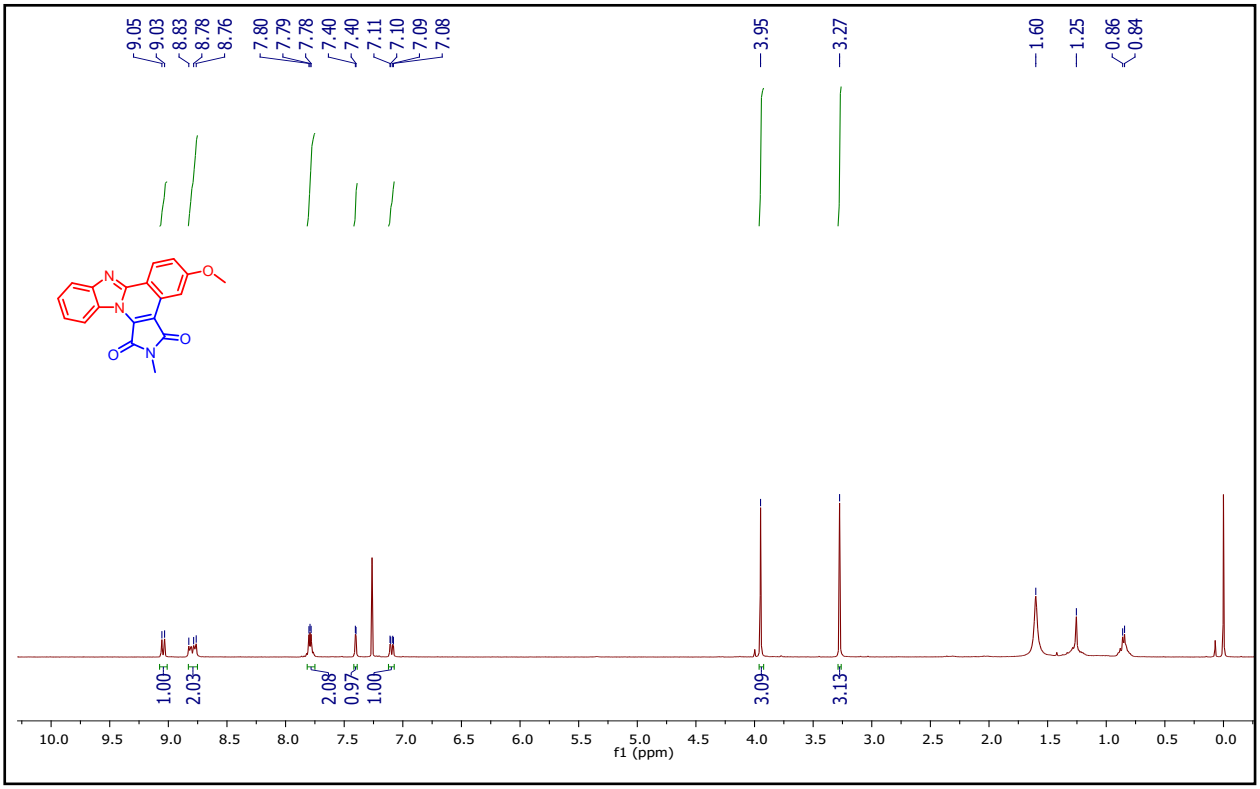
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3t:**



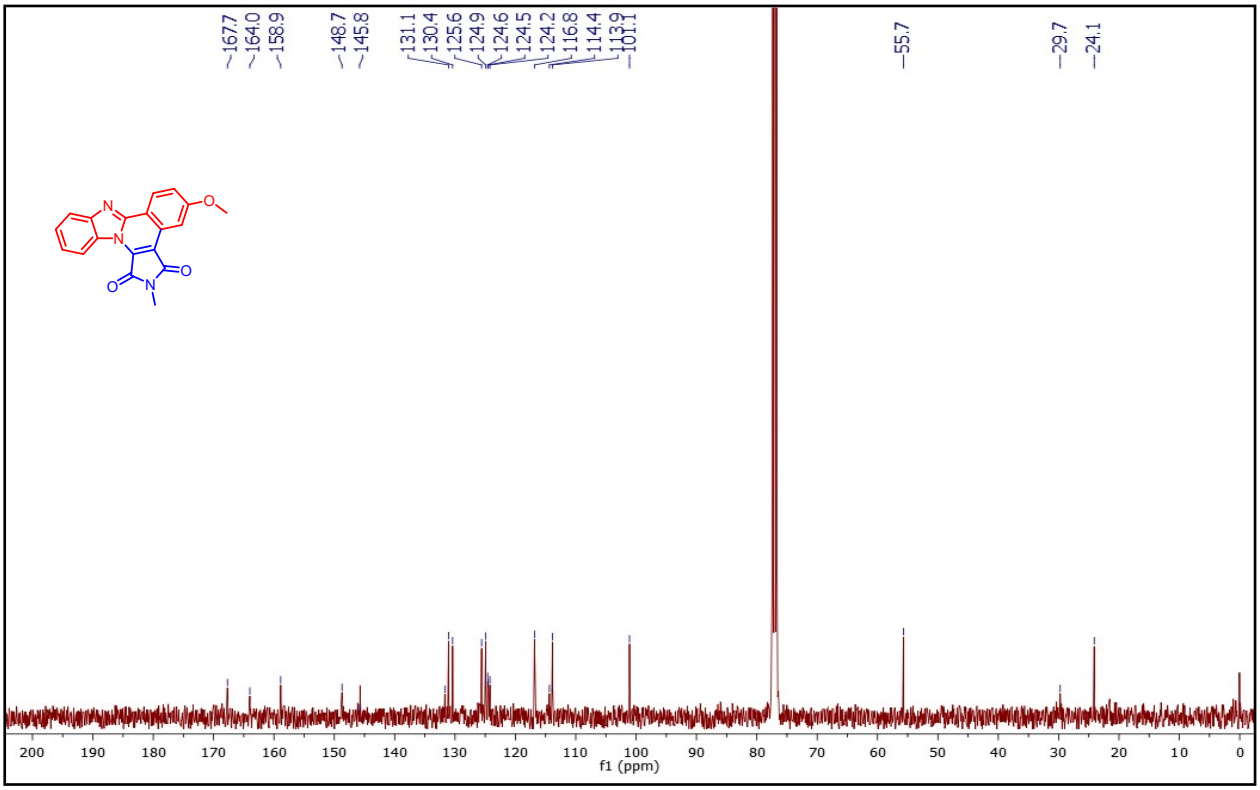
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3t:**



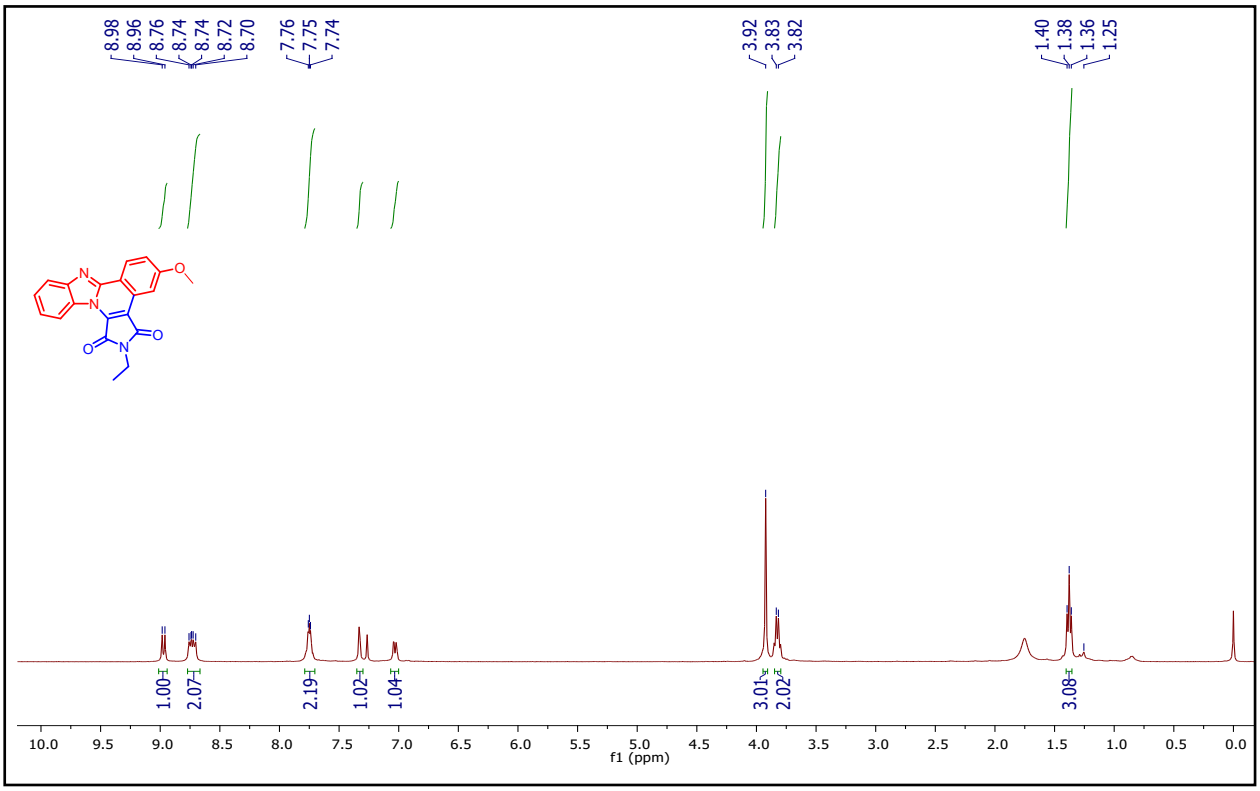
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3u:**



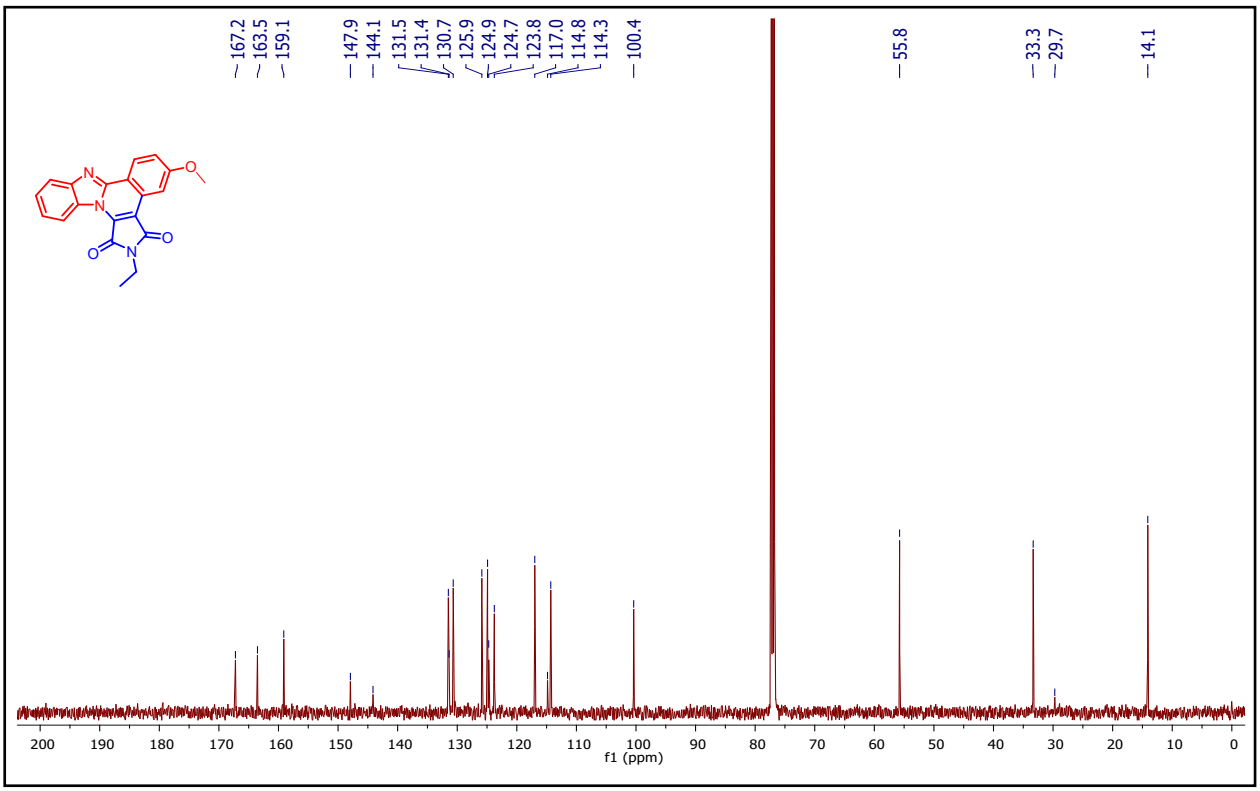
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3u:**



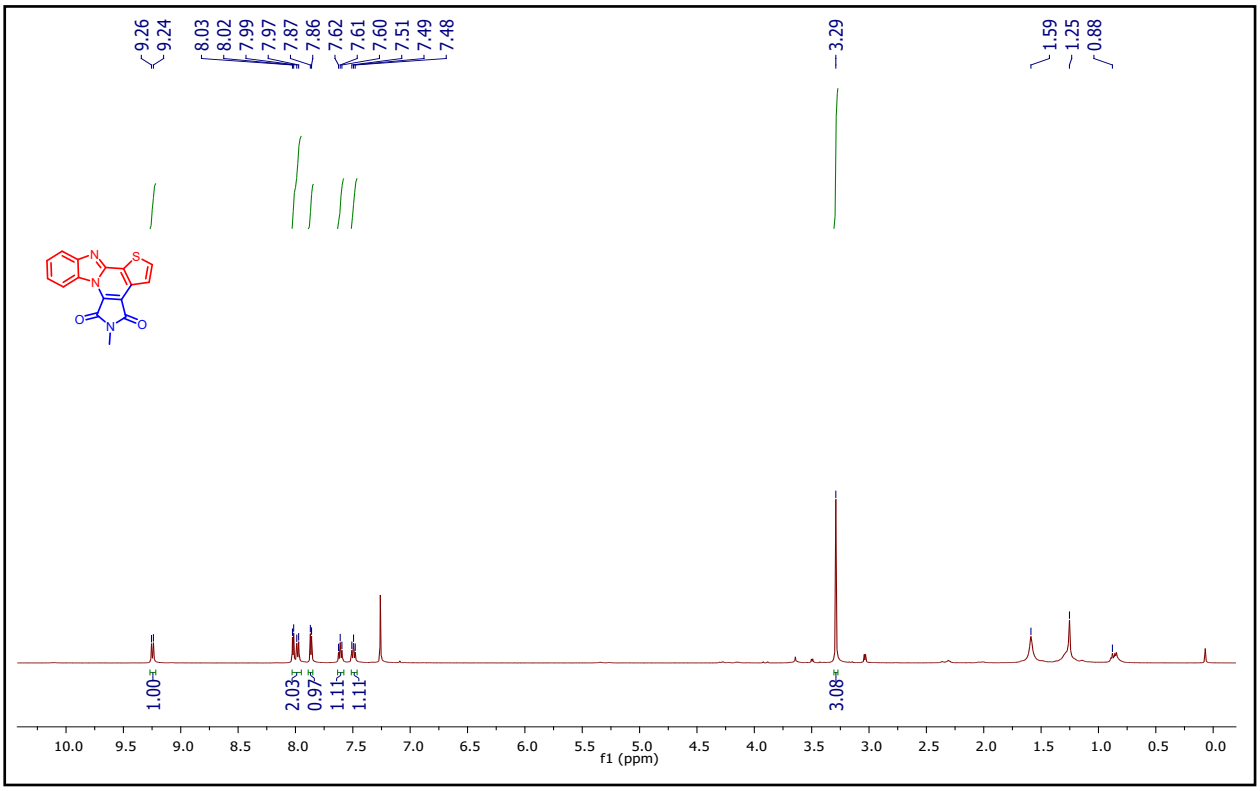
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3v:**



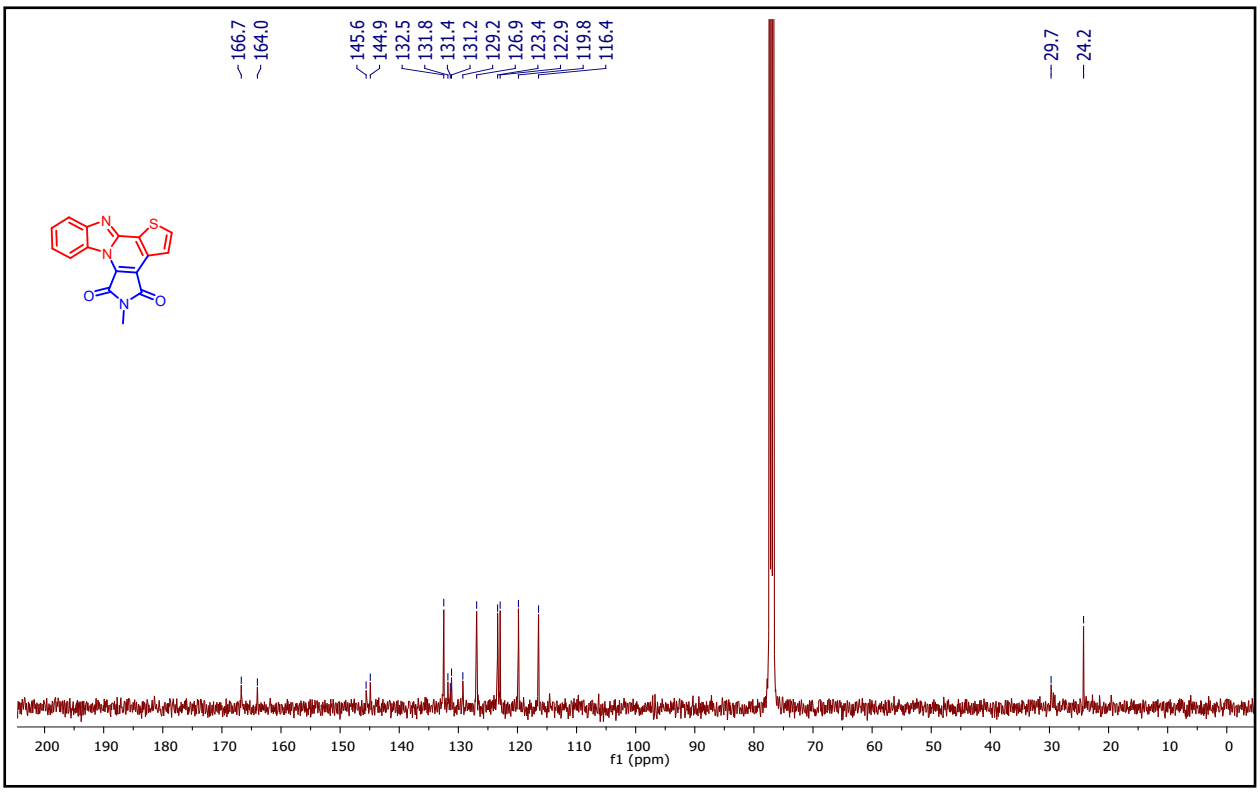
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3v:**



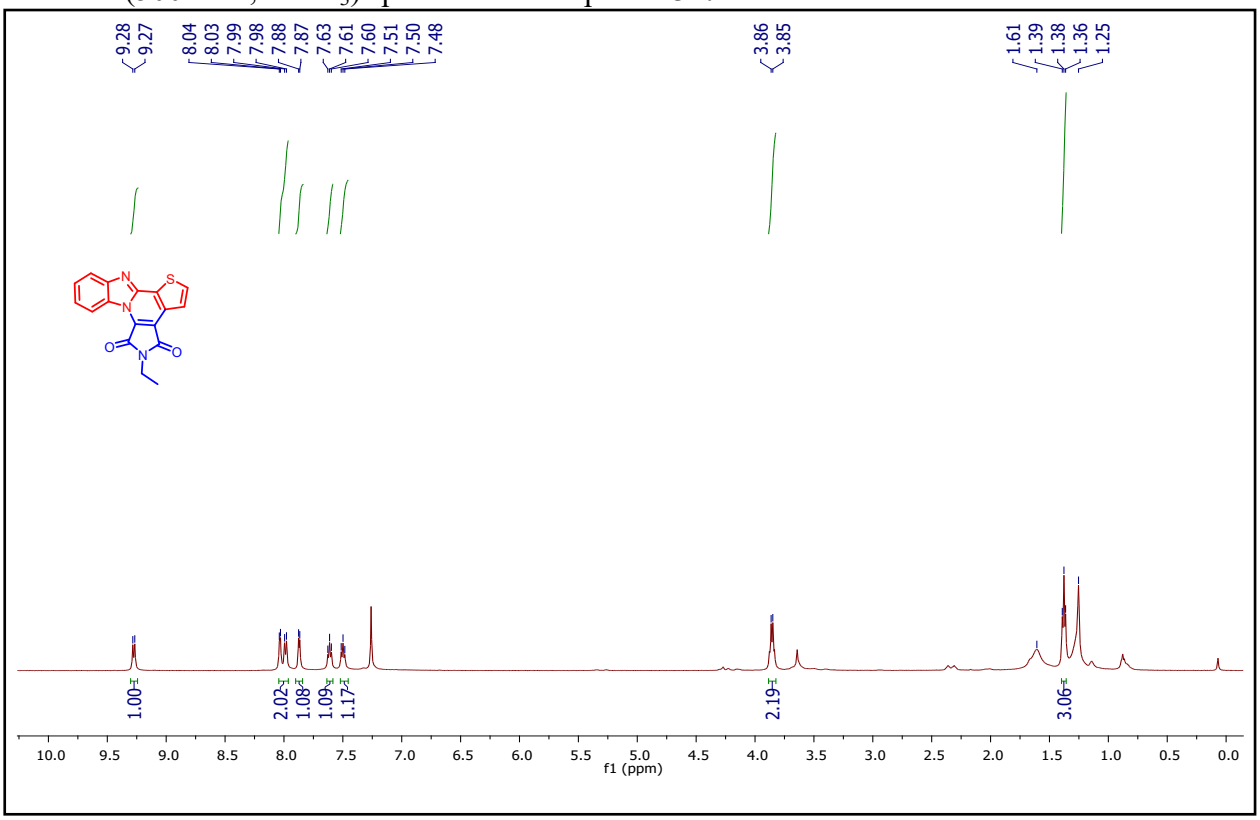
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound **3w:**



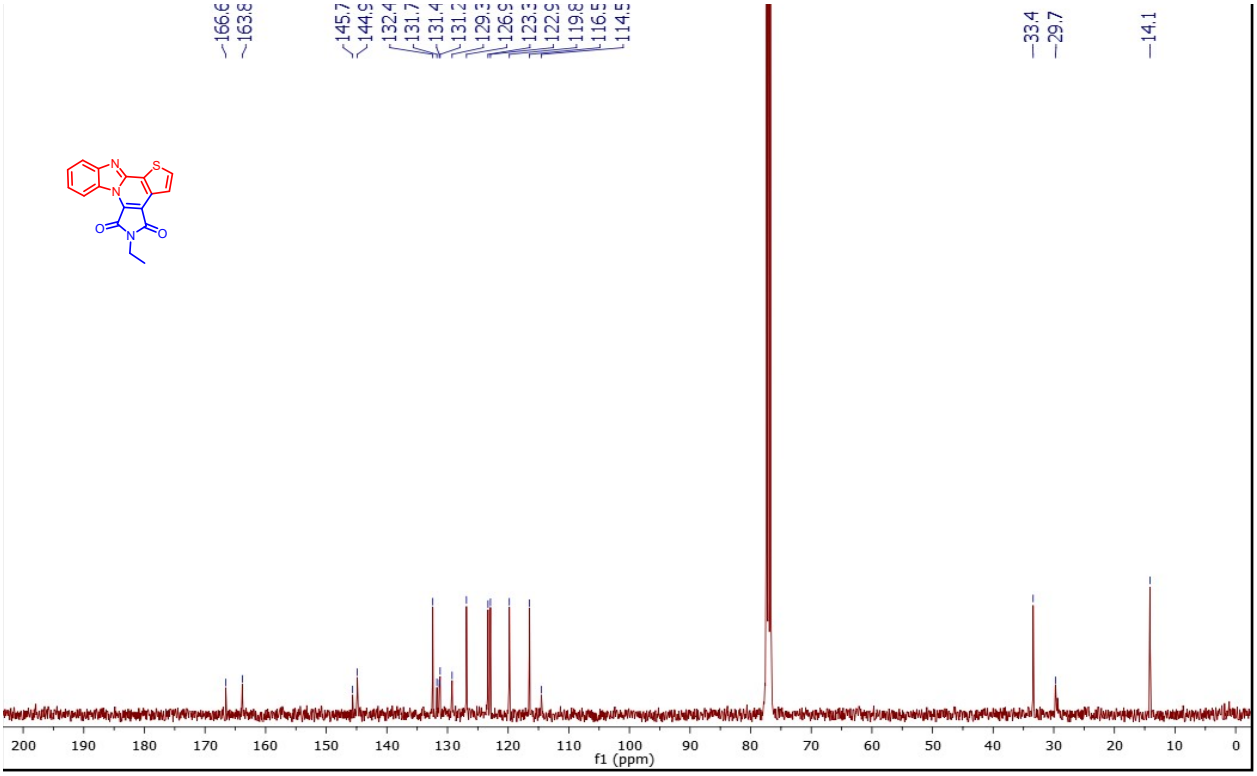
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3w:**



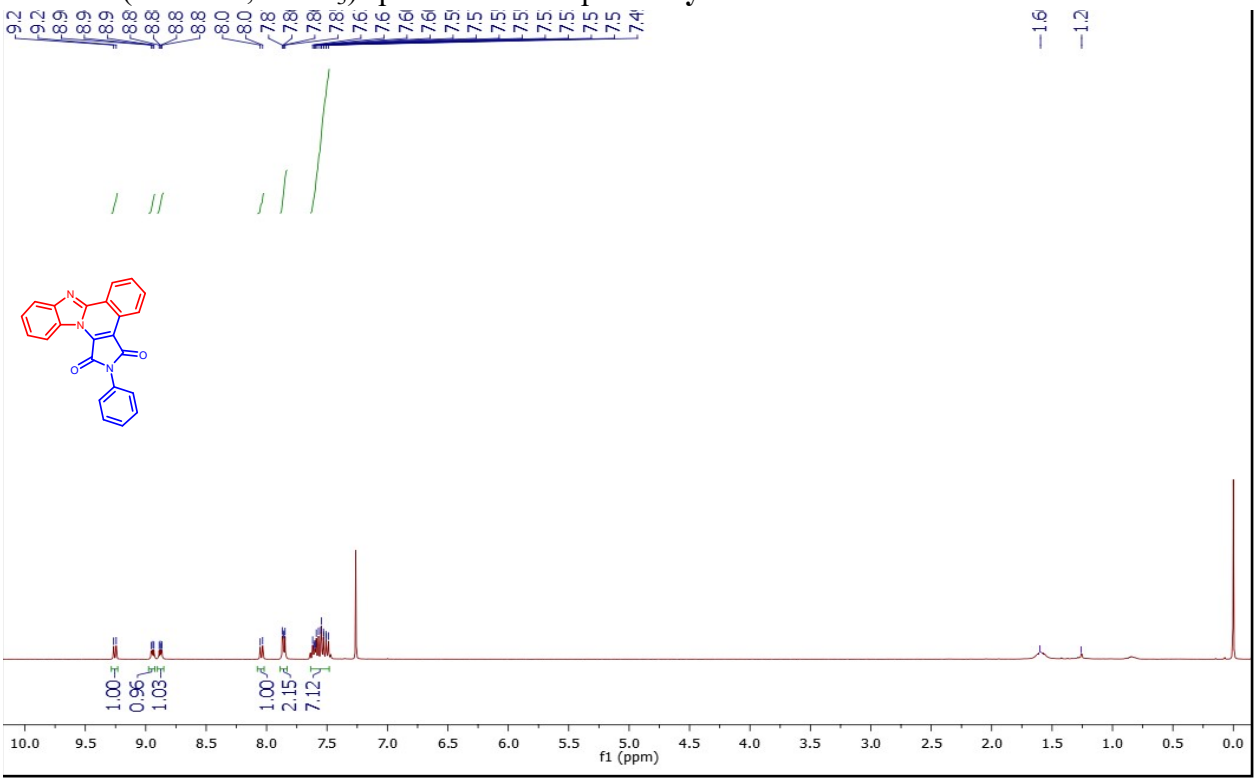
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound **3x:**



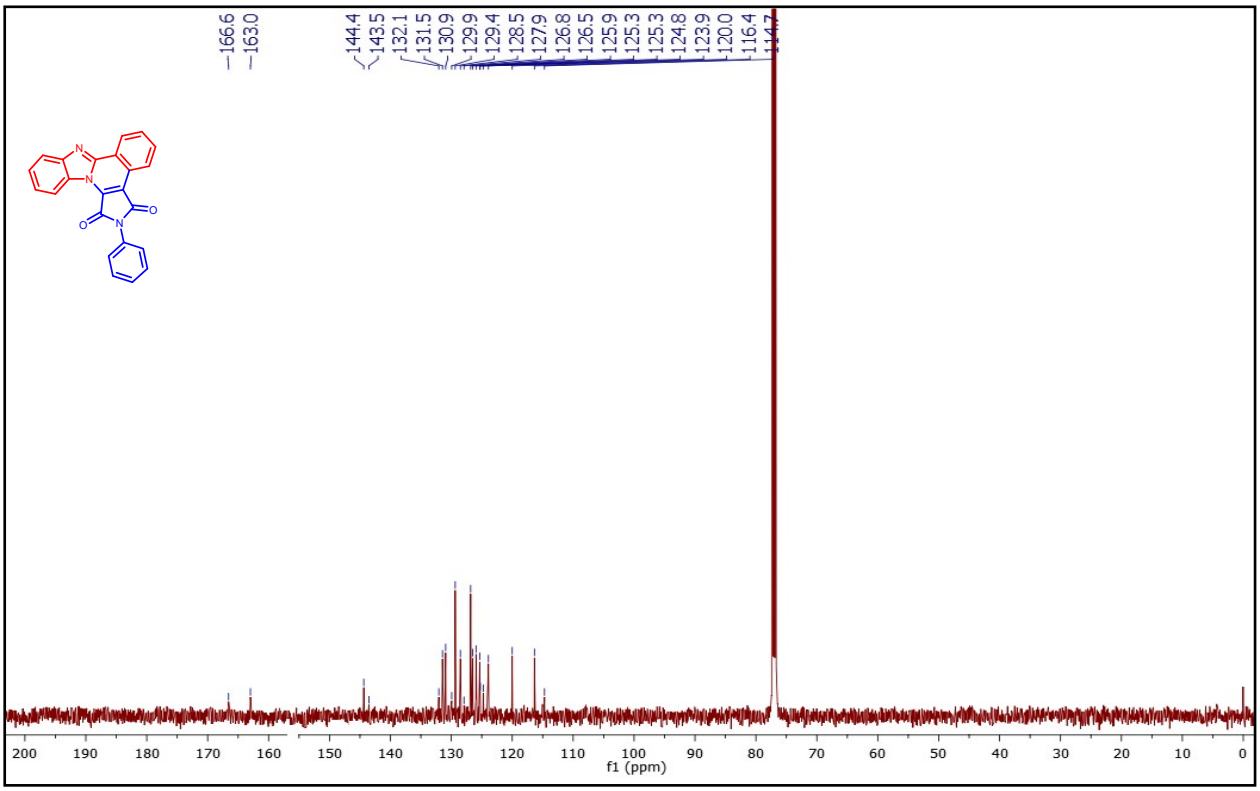
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3x**:



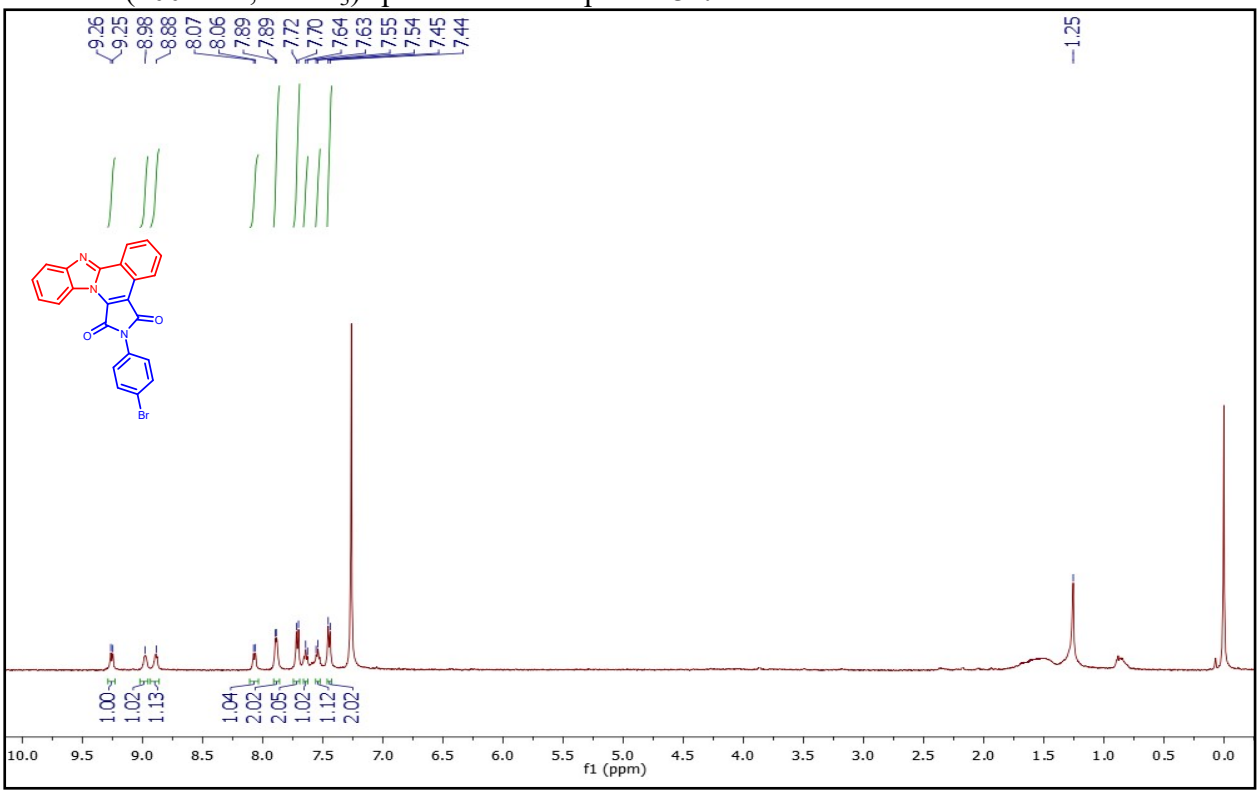
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3y:**



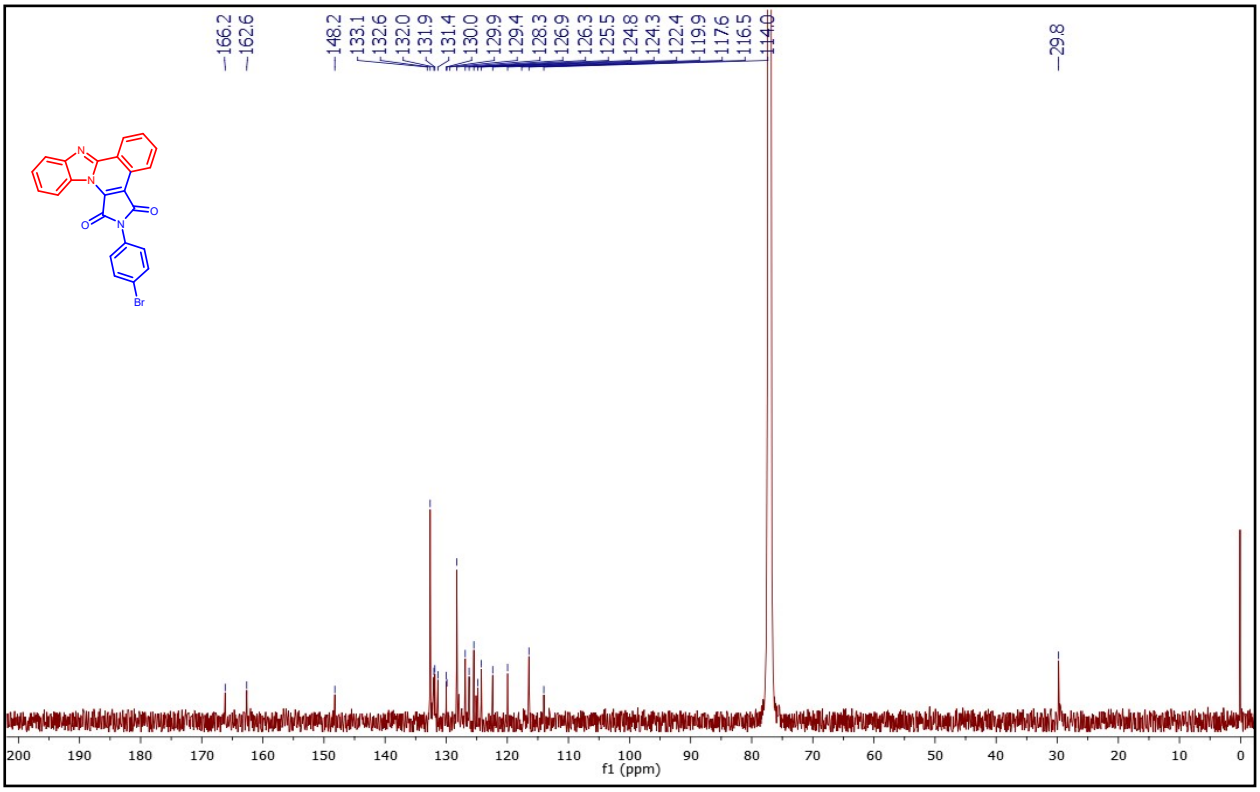
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **3y**:



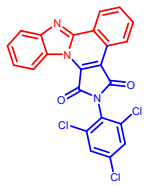
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3z:**

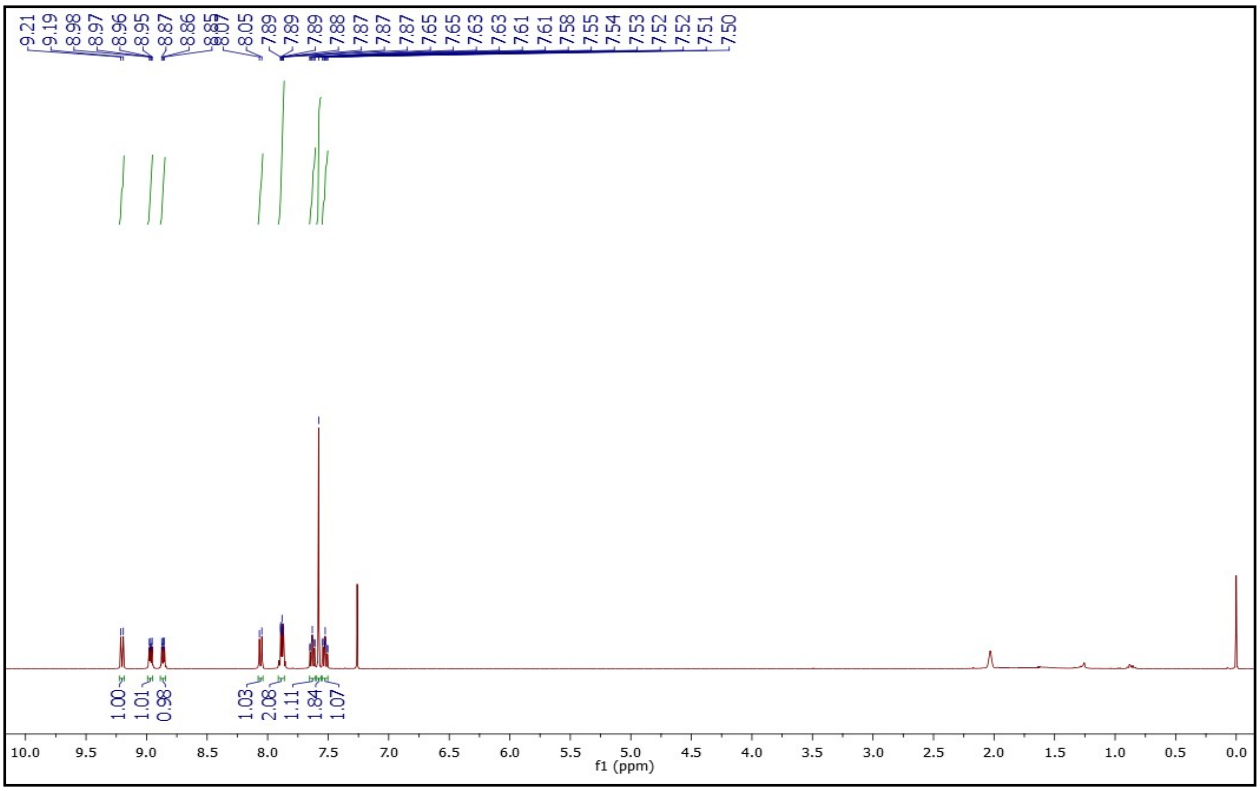


^{13}C NMR (154 MHz, $CDCl_3$) spectrum of compound **3z**:

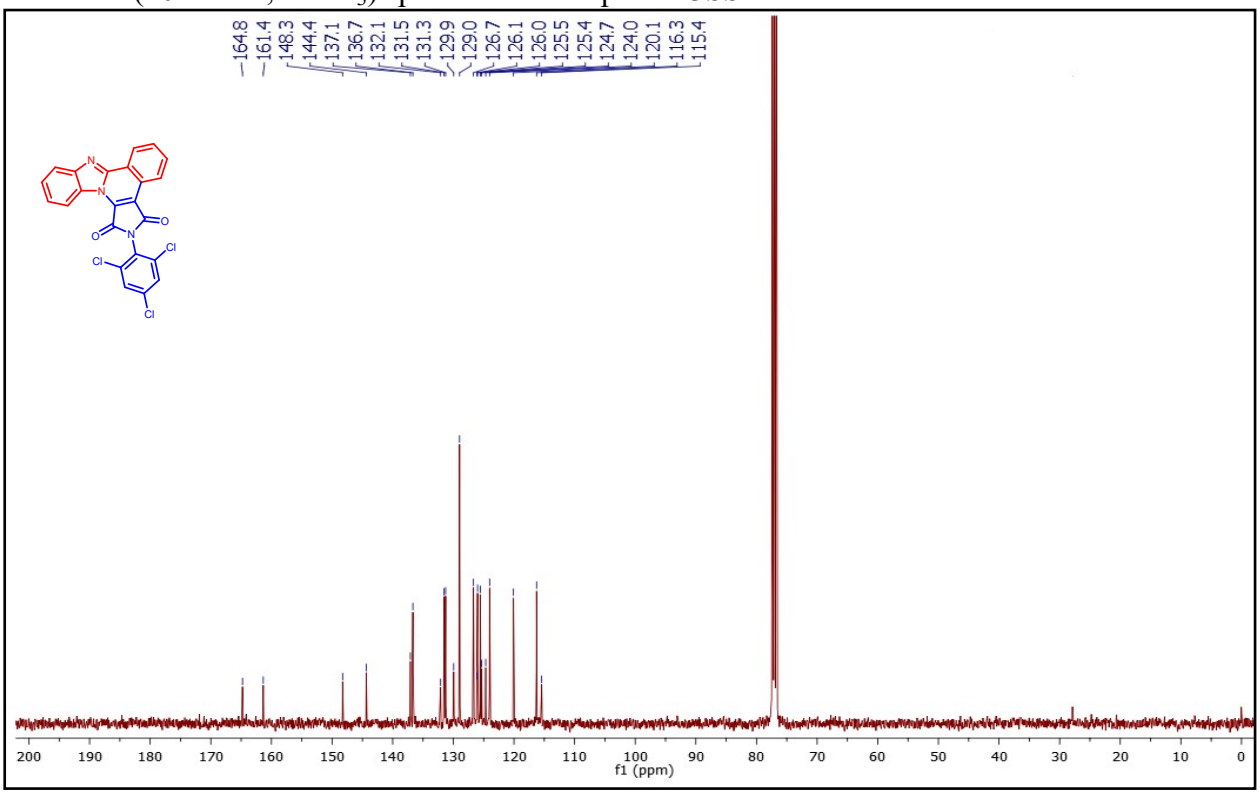


^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3bb**

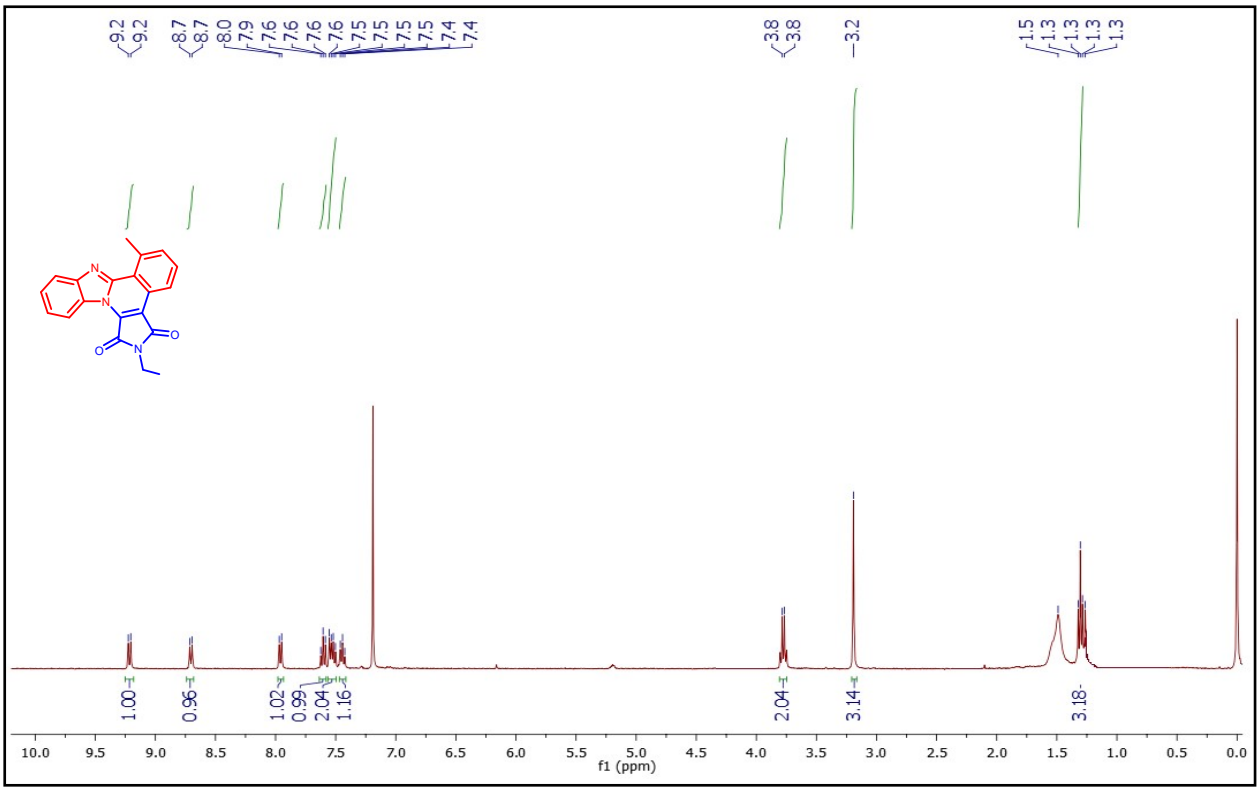




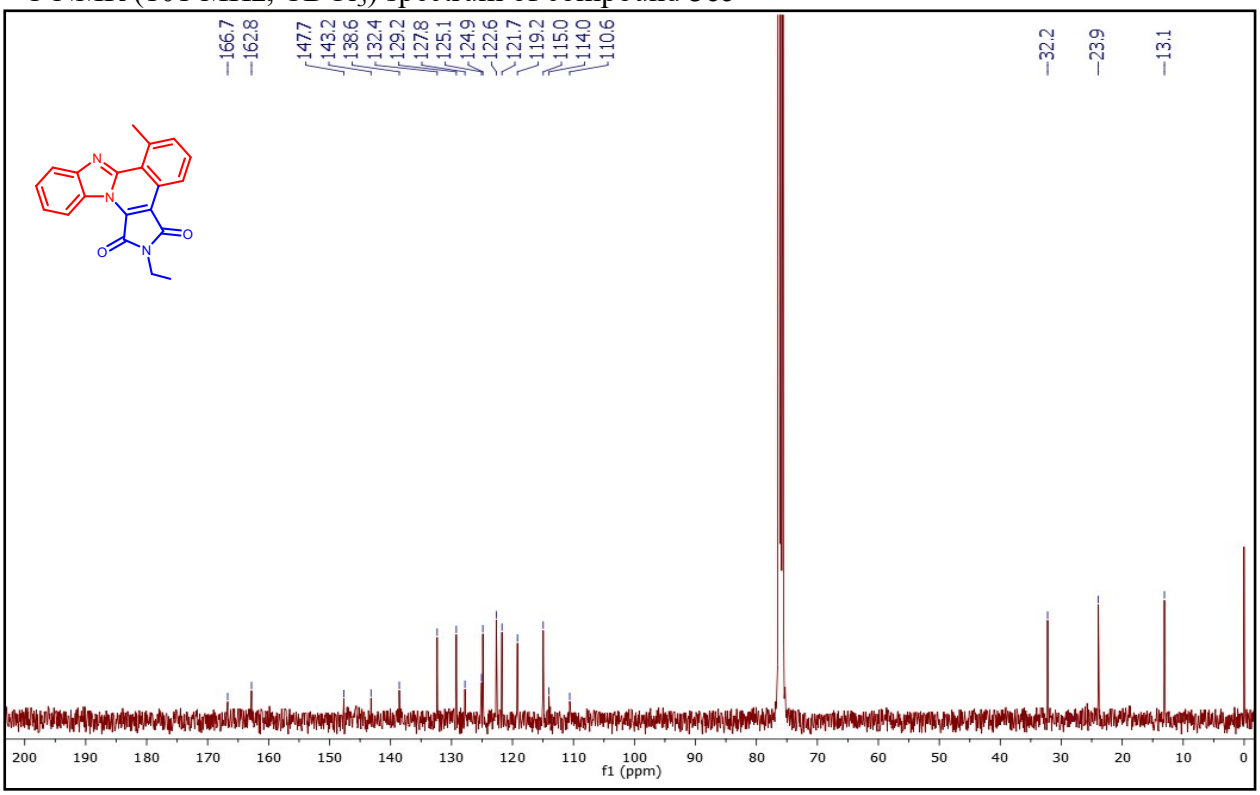
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3bb**



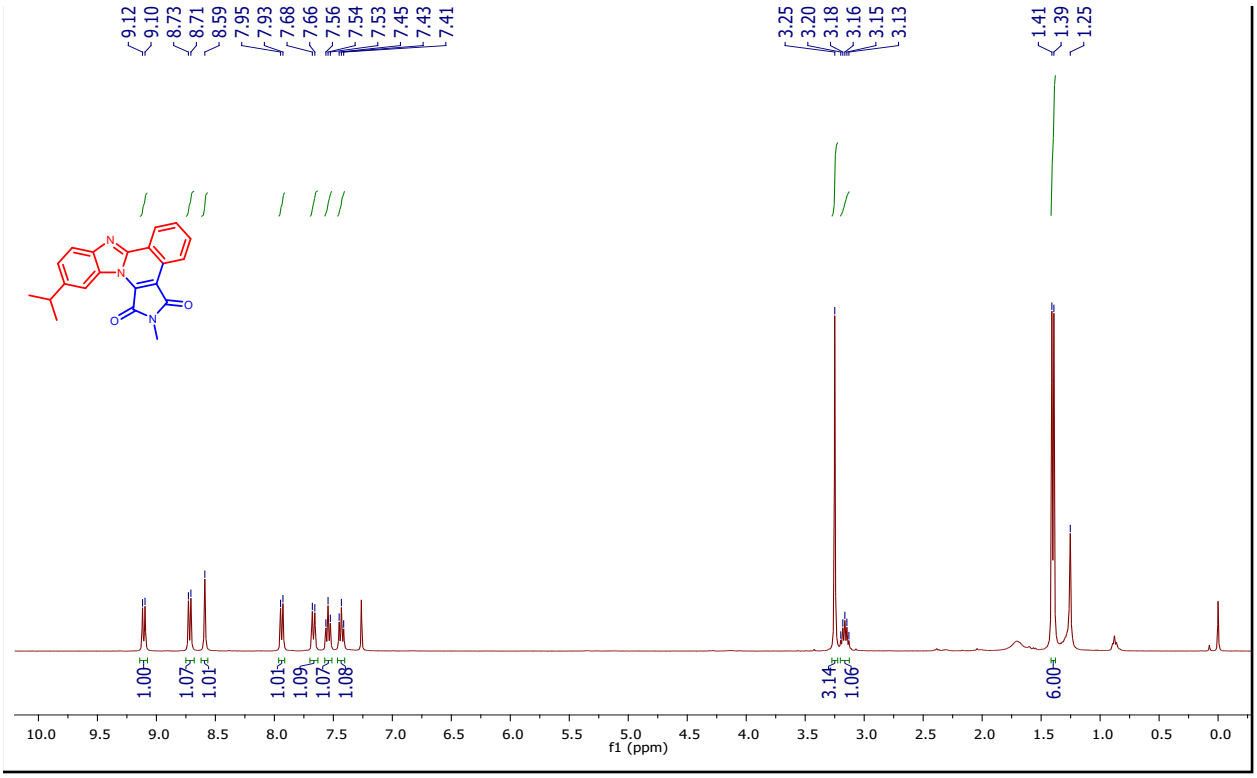
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3cc**



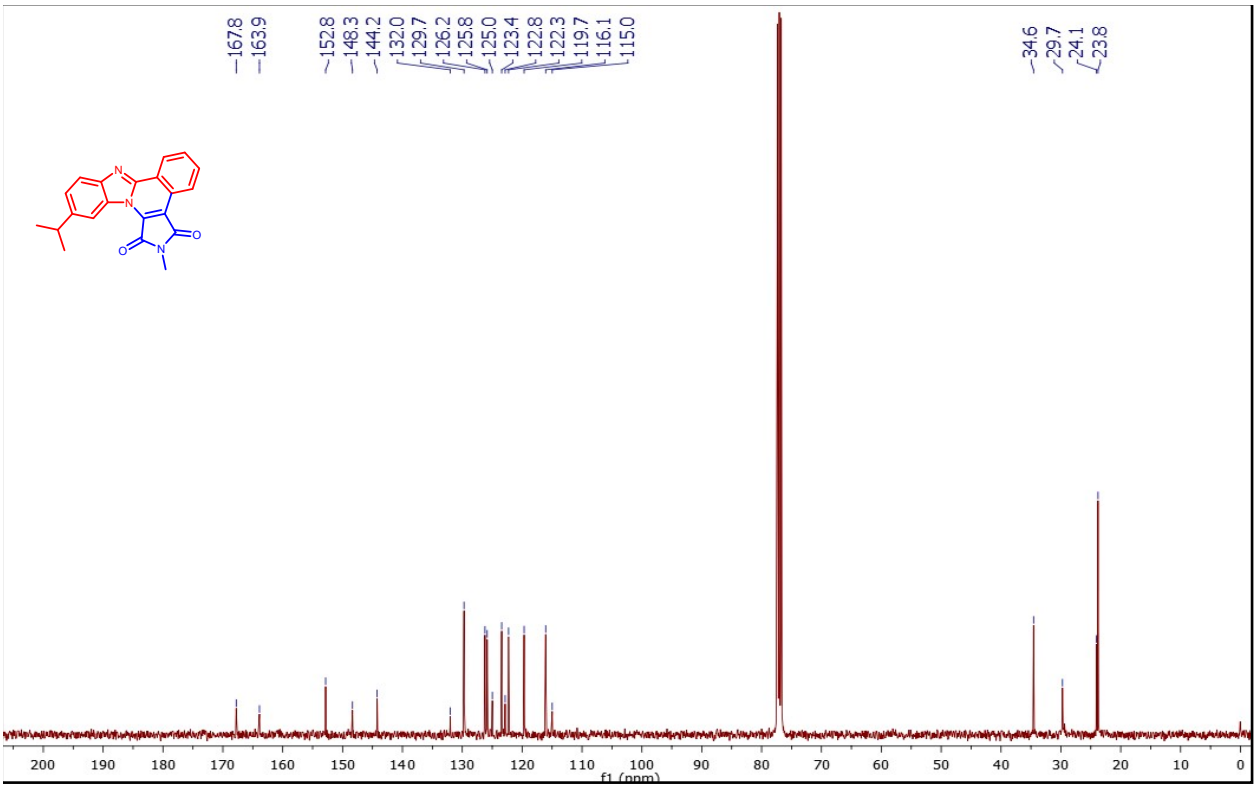
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3cc**



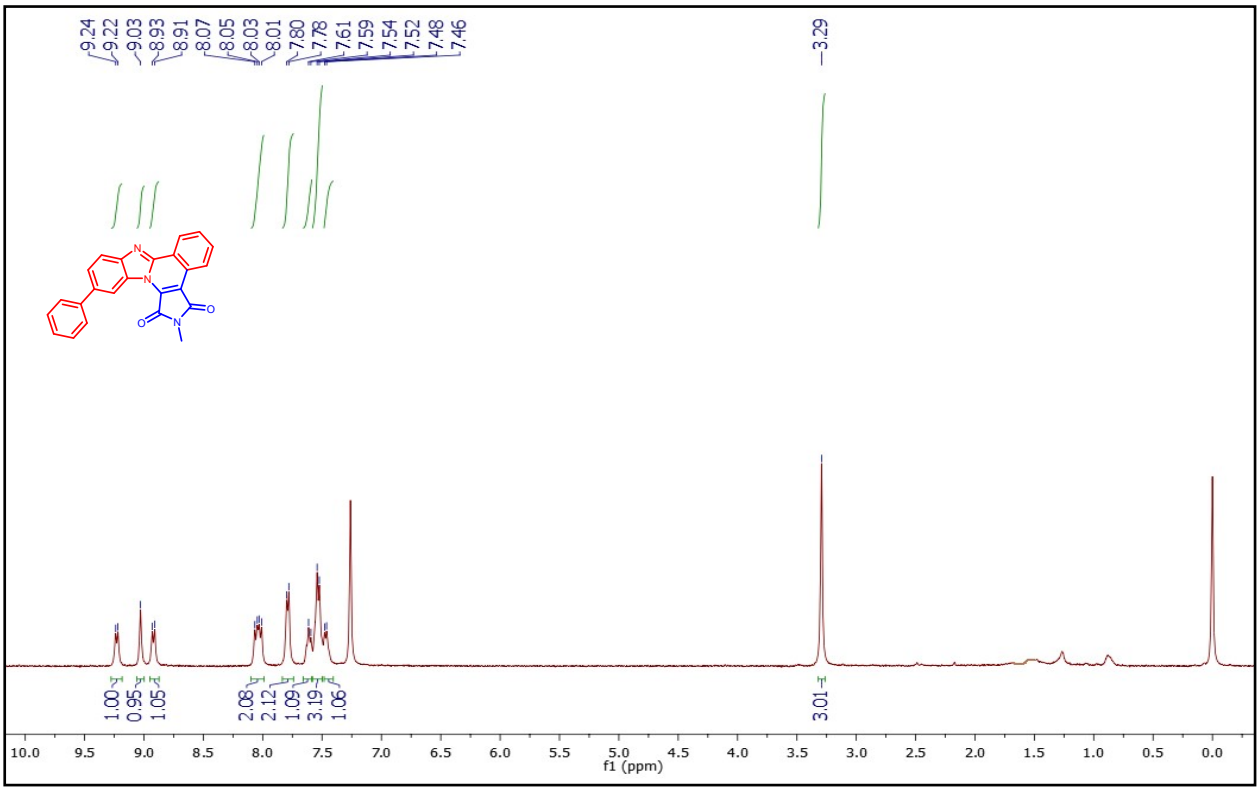
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3dd**



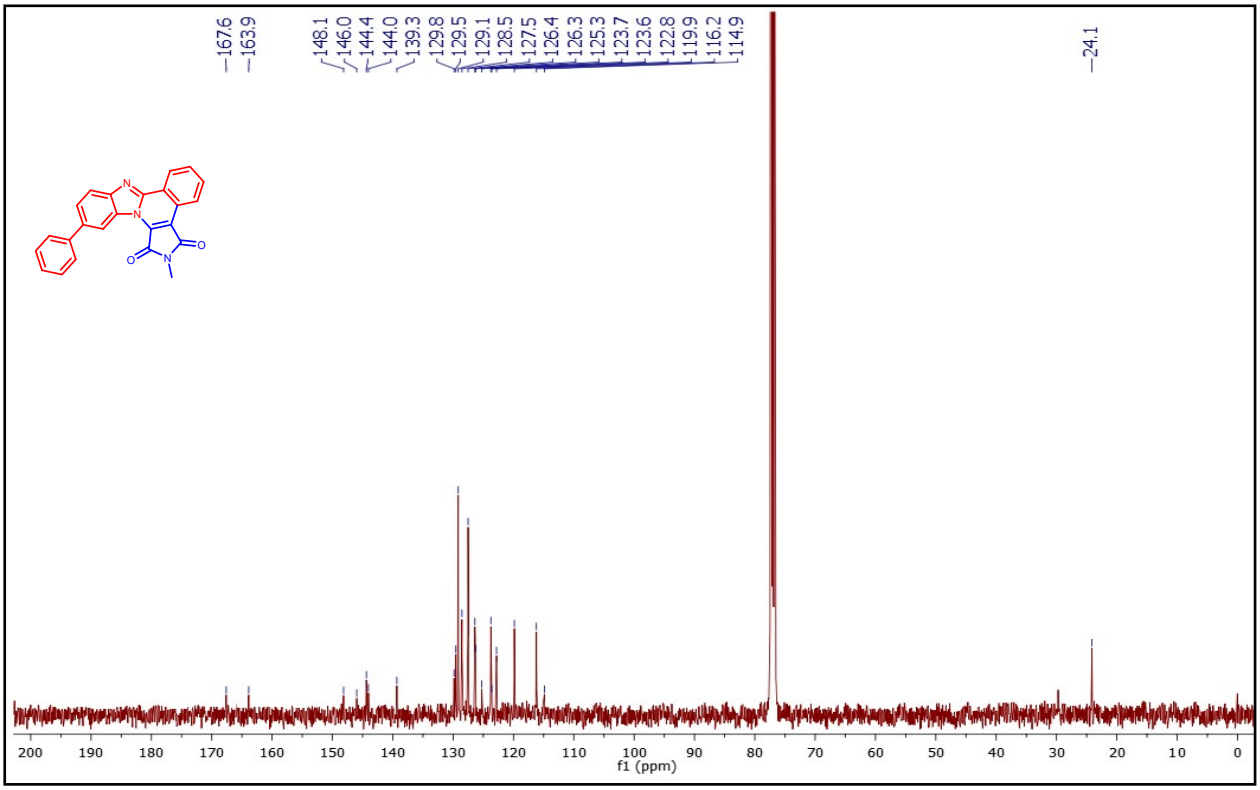
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3dd**



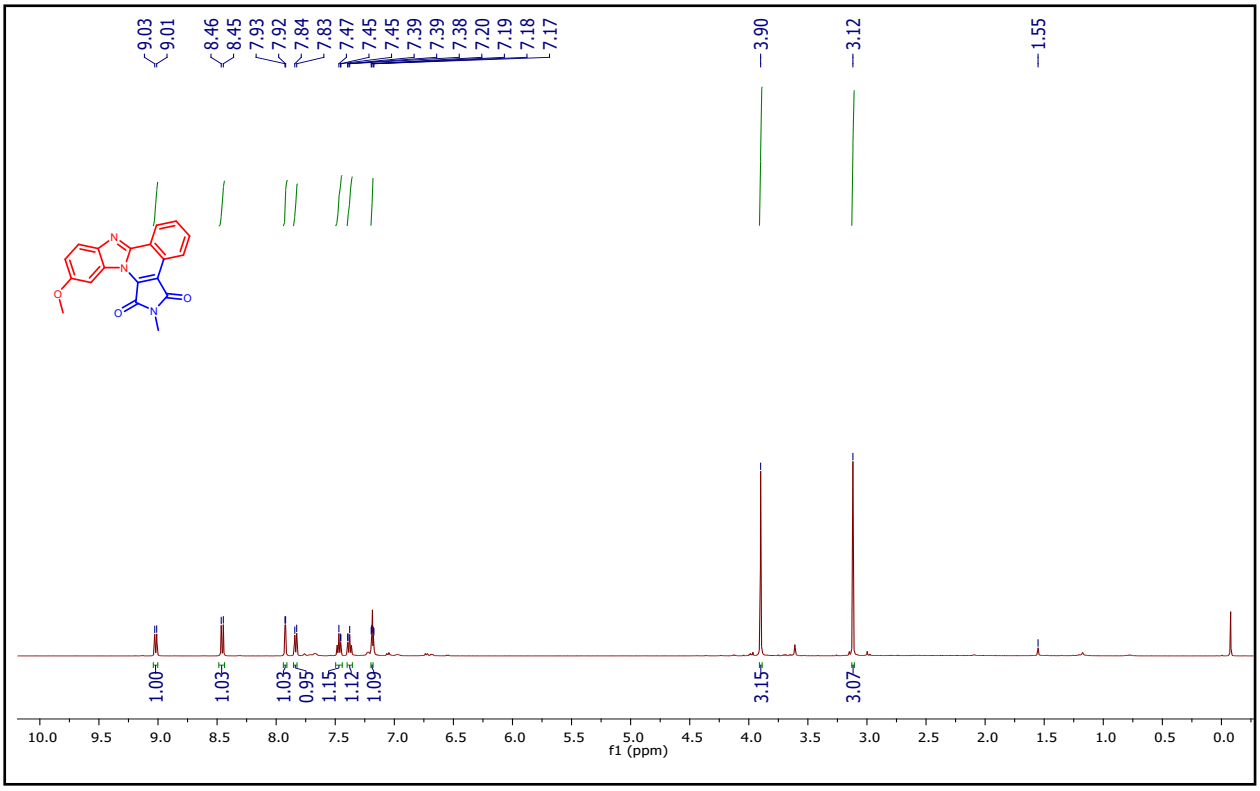
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3ee**



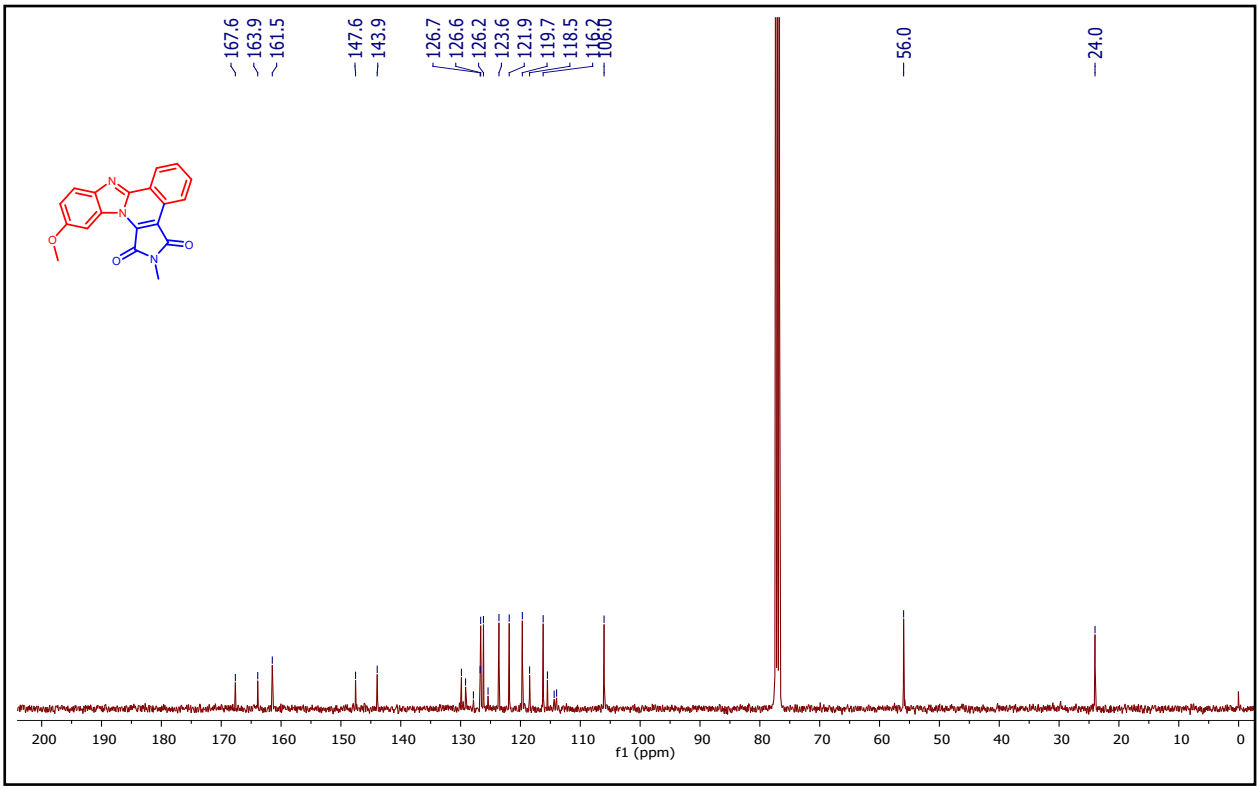
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ee**



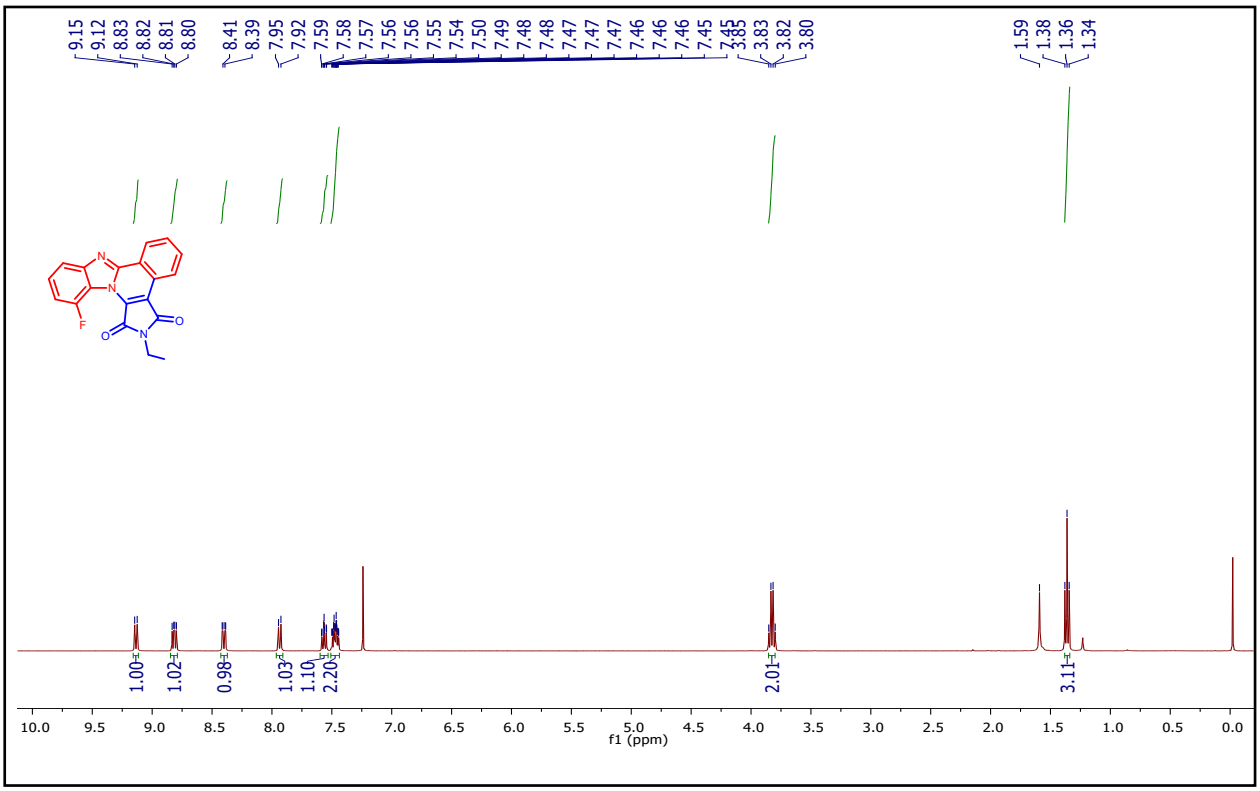
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound **3ff**



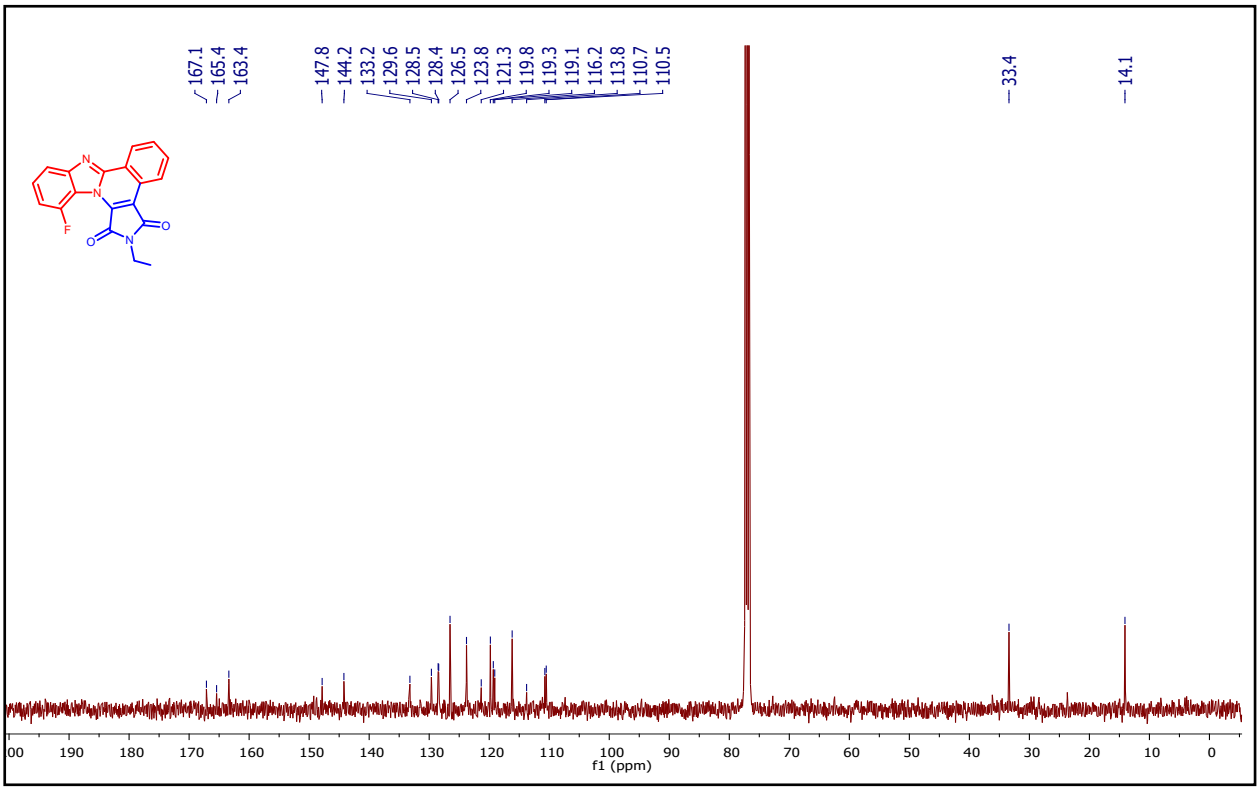
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ff**



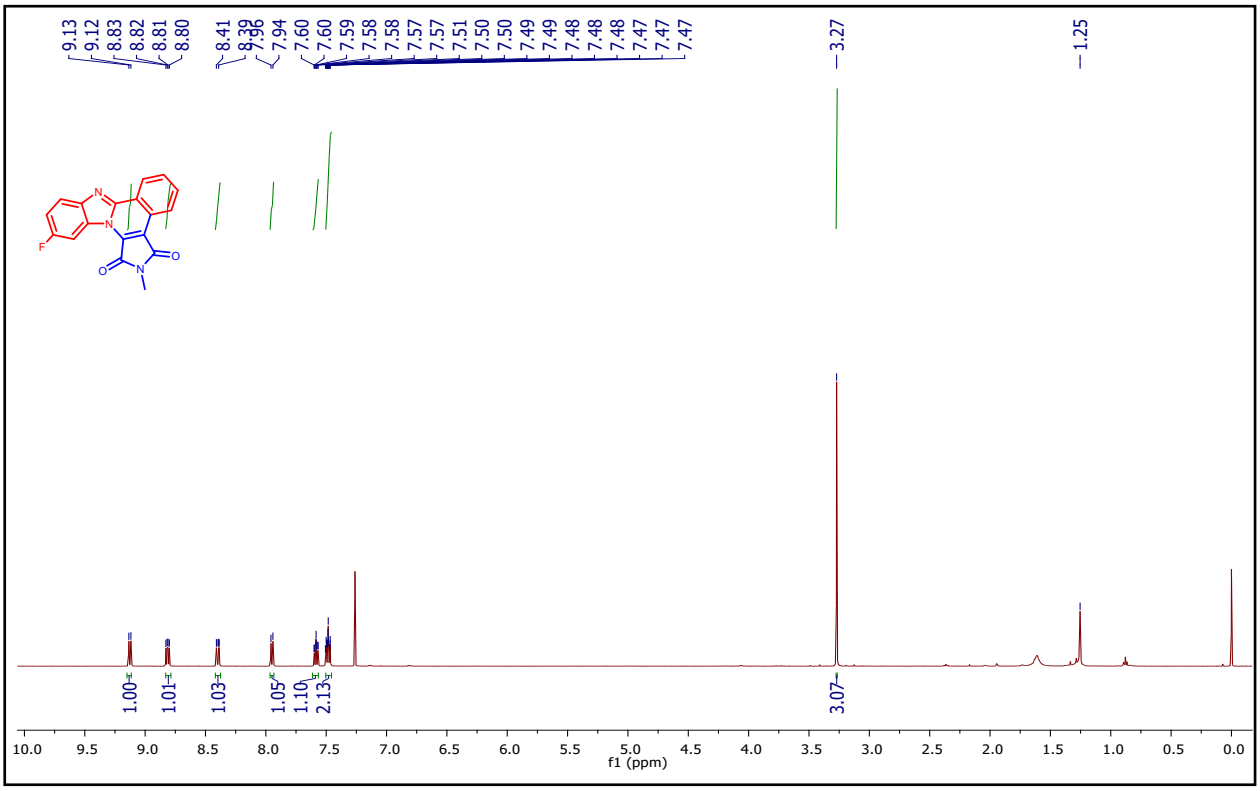
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3gg**



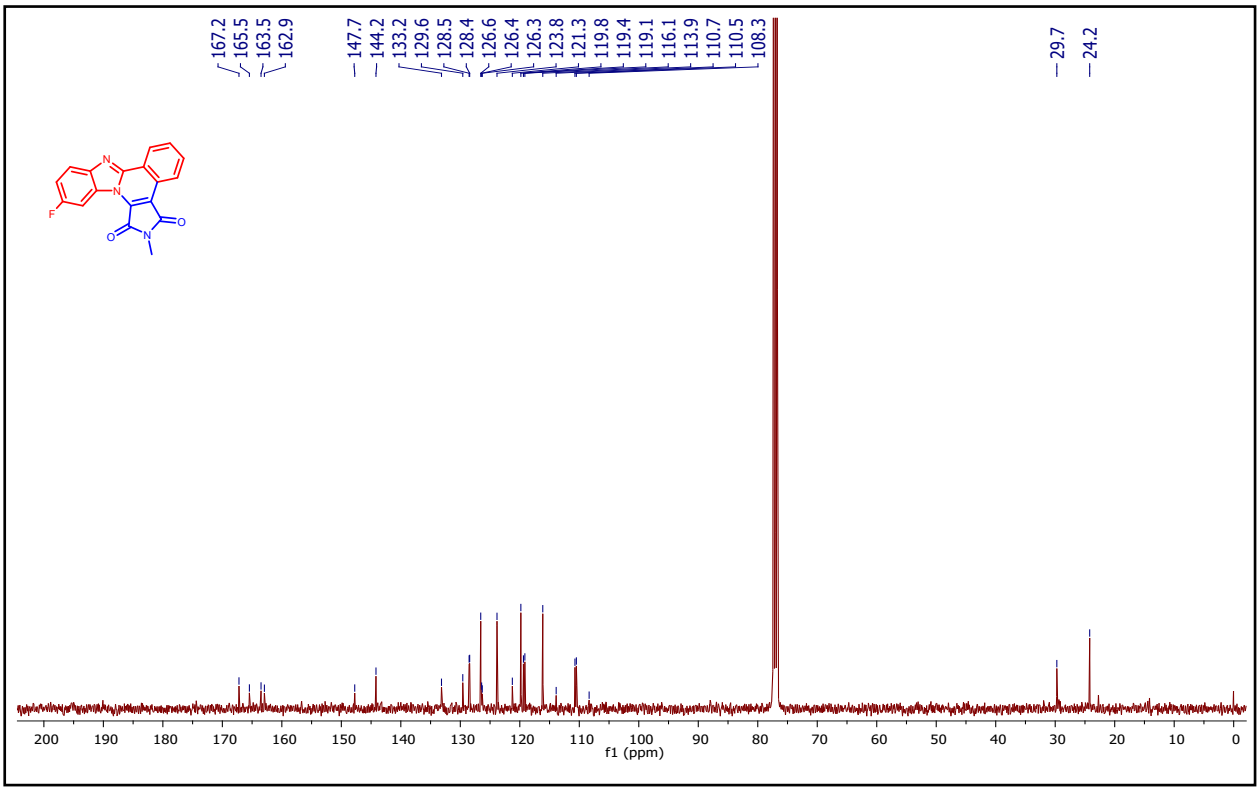
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3gg**



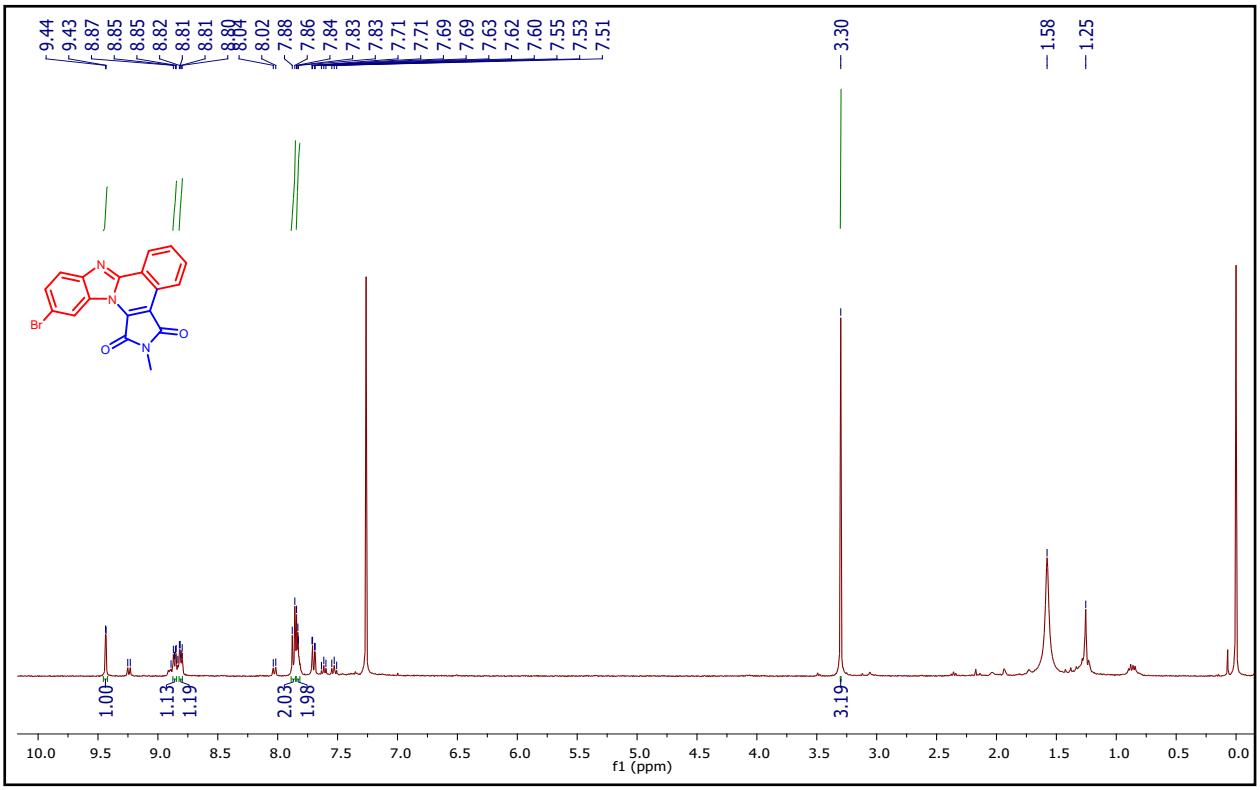
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound **3hh**



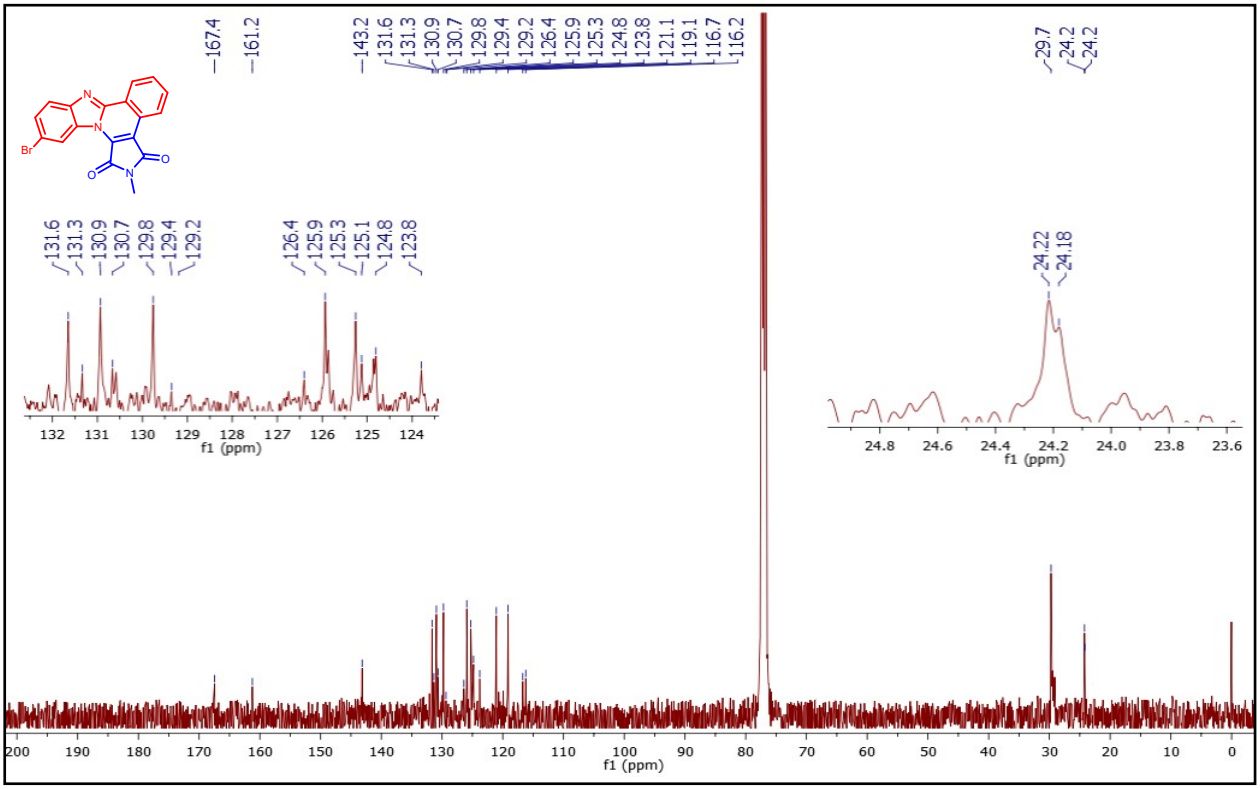
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3hh**



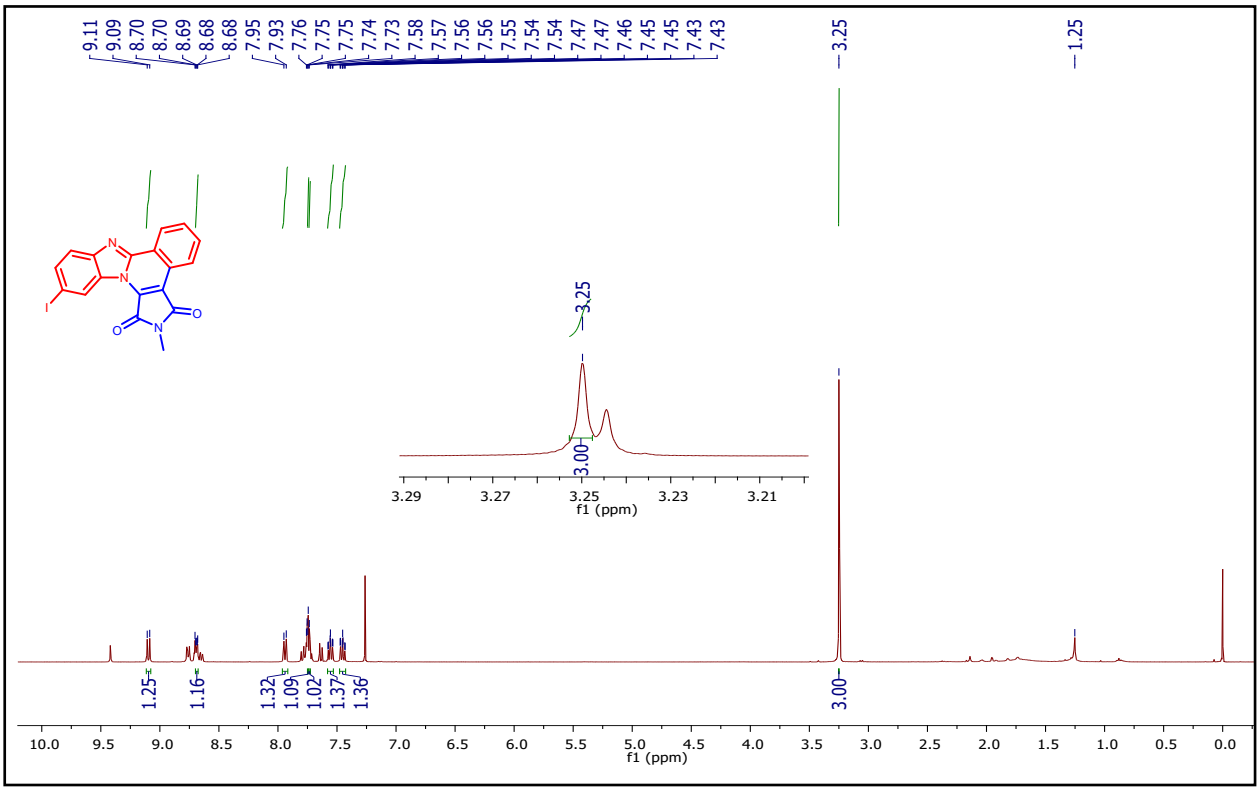
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3ii**



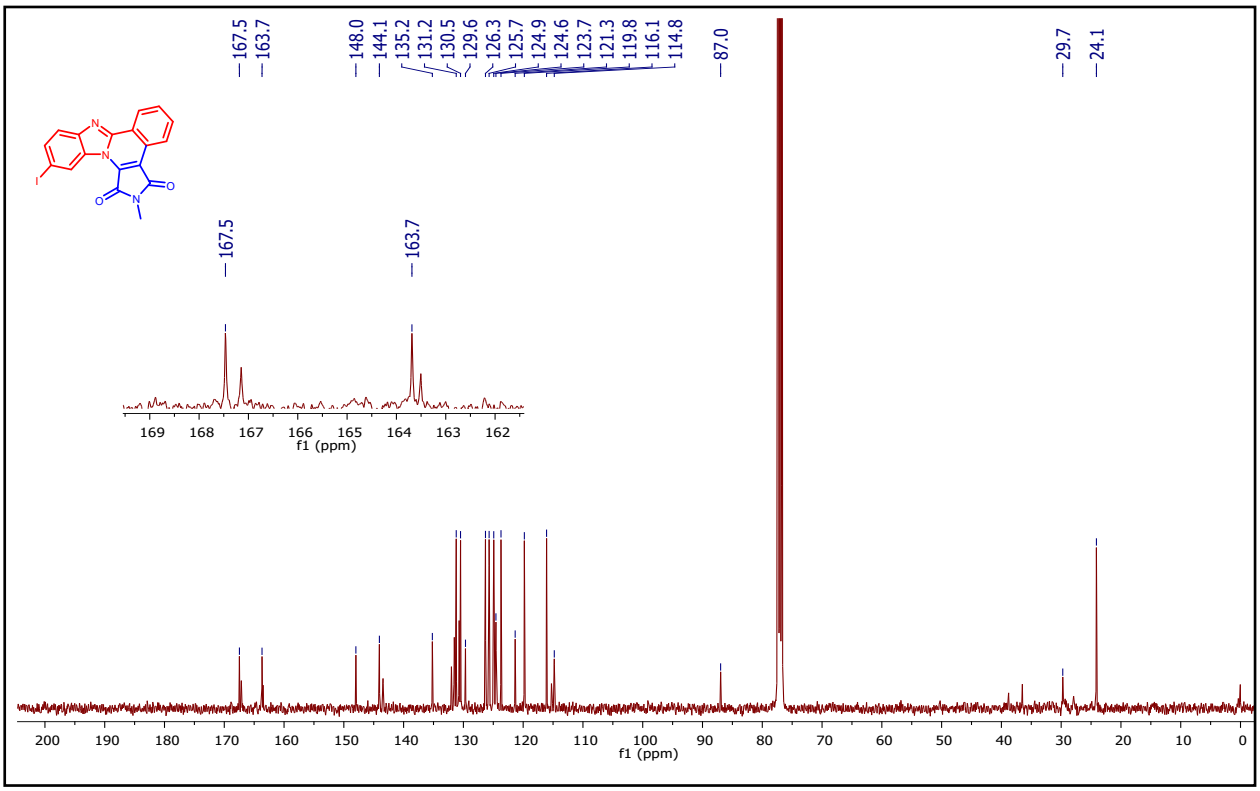
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3ii**



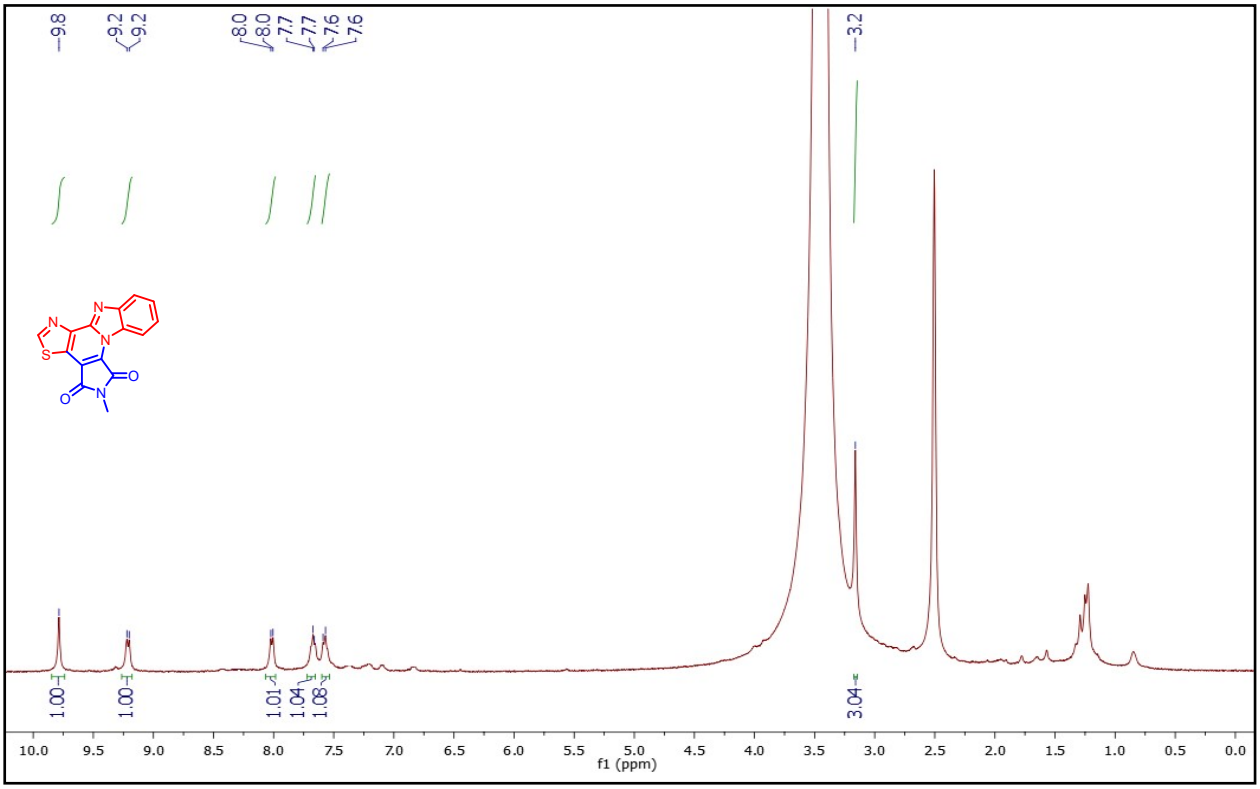
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **3jj**



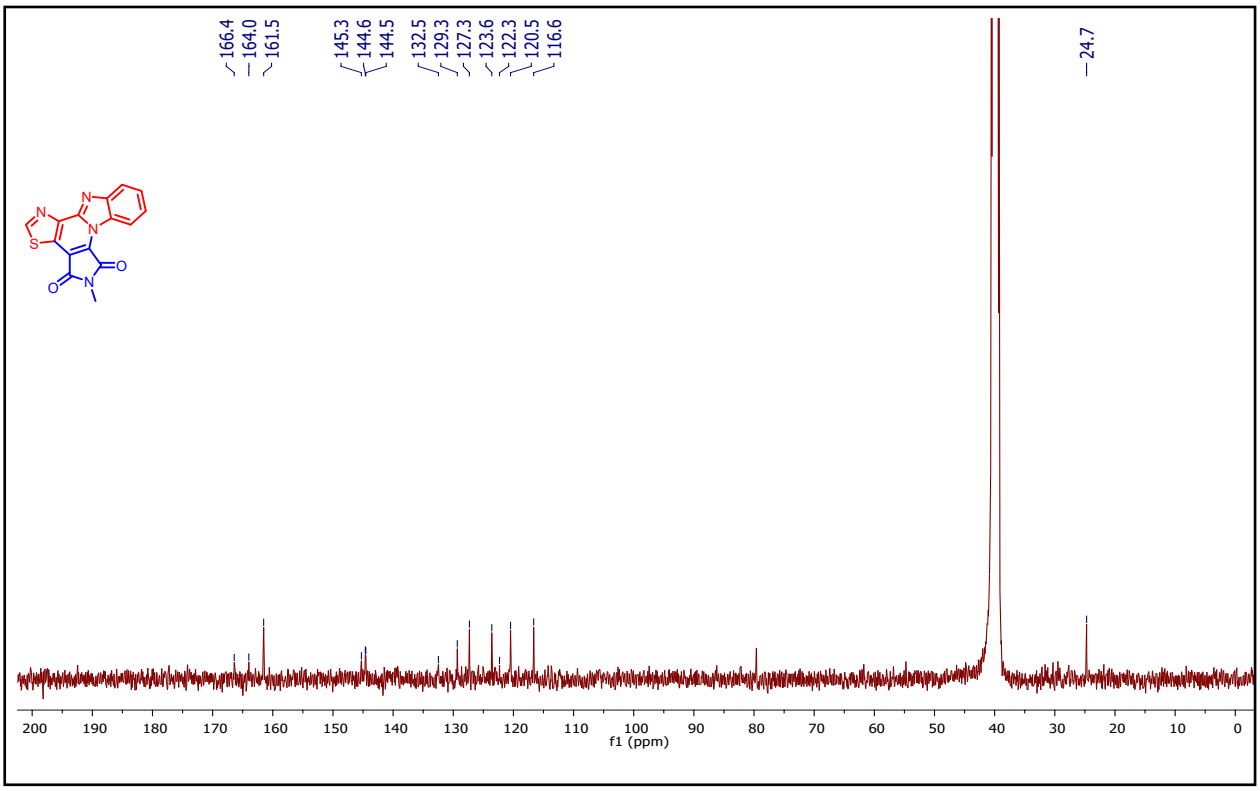
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3jj**



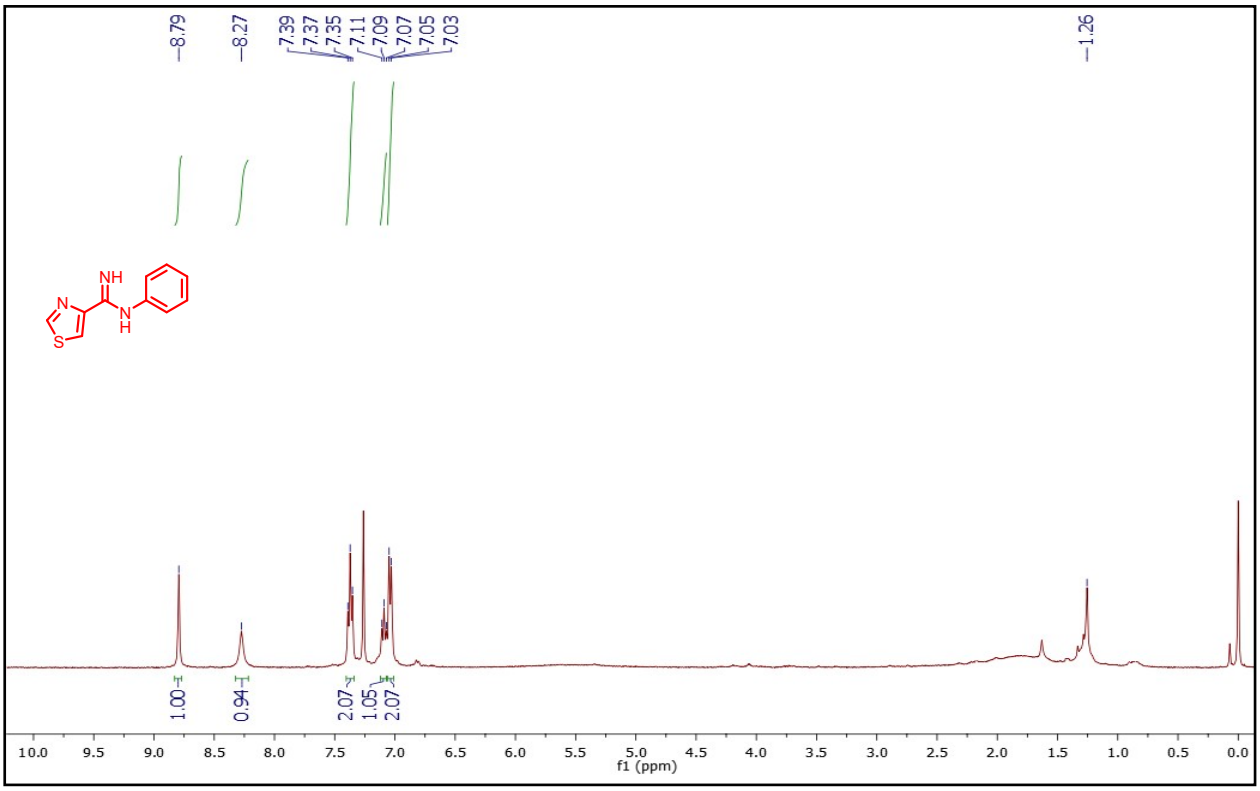
^{1}H NMR (400MHz, DMSO) spectrum of compound **3aa**



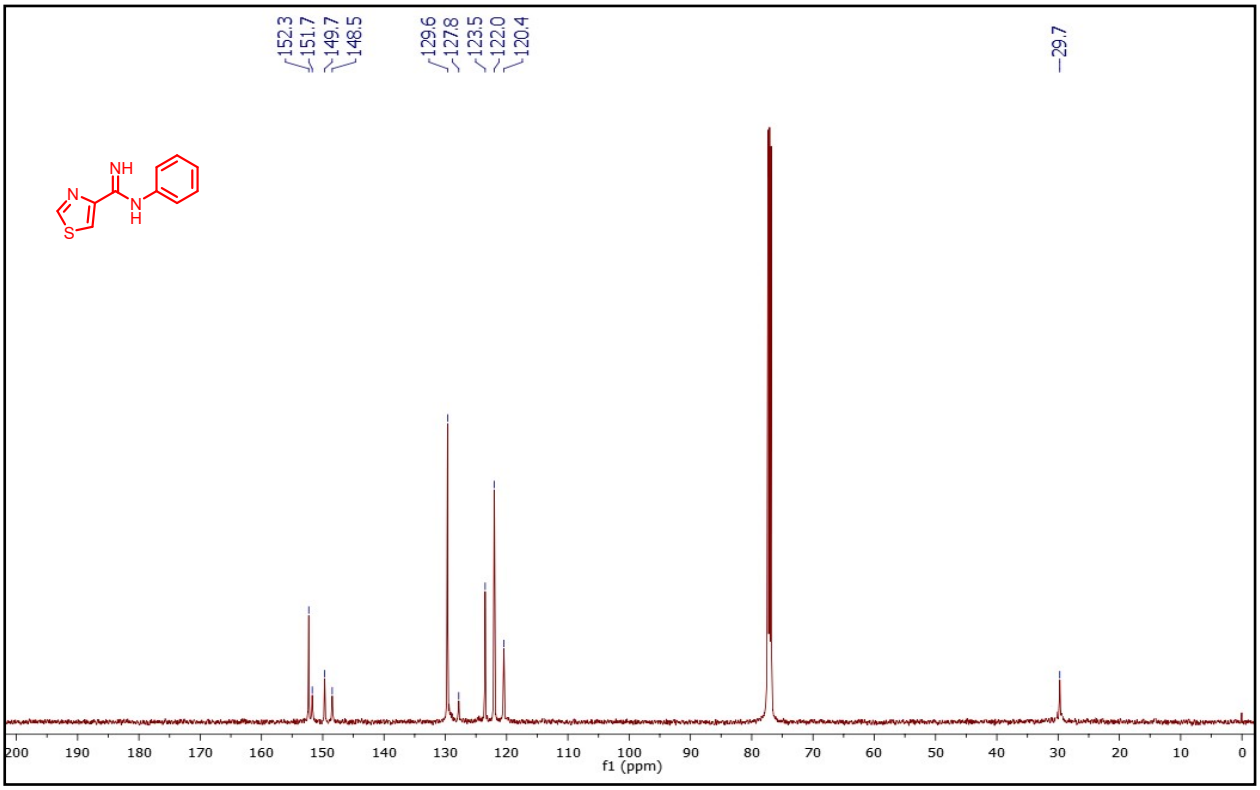
^{13}C NMR (101 MHz, DMSO) spectrum of compound **3aa**



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



^{13}C NMR (126MHz, $CDCl_3$) spectrum of compound **3aa'**



3. X-ray Crystallography.

X-ray data for the compounds **3a** and **3n** were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for other H atoms].

Crystal structure determination of 3a

Crystal Data for $C_{20}H_{15}N_3O_2$ (*M* =329.35 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 7.6673(18) Å, *b* = 10.263(2) Å, *c* = 20.044(4) Å, *β* = 95.911(5)°, *V* = 1568.9(6) Å^3, *Z* = 4, *T* = 294.15 K, μ(MoKα) = 0.093 mm^{-1}, *Dcalc* = 1.394 g/cm^3, 28297 reflections measured (5.342° ≤ 2Θ ≤ 60.95°), 4559 unique (R_{int} = 0.0681, R_{sigma} = 0.0456) which were used in all calculations. The final R_1 was

0.0494 (I > 2σ(I)) and wR_2 was 0.1420 (all data).CCDC2213298contains supplementary Crystallographic data for the structure.

Crystal structure determination of 3n

Crystal Data for $C_{18}H_{11}N_3O_2$ (*M* =301.30 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 18.464(2) Å, *b* = 7.3813(9) Å, *c* = 21.180(2) Å, *β* = 110.522(5)°, *V* = 2703.4(6) Å^3, *Z* = 8, *T* = 294.15 K, μ(MoKα) = 0.100 mm^{-1}, *Dcalc* = 1.481 g/cm^3, 48117 reflections measured (5.774° ≤ 2Θ ≤ 61.036°), 8237 unique (R_{int} = 0.0402, R_{sigma} = 0.0366) which were used in all calculations. The final R_1 was 0.0598 (I > 2σ(I)) and wR_2 was 0.1732 (all data).CCDC 2213299contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** ActaCrystallogrC71:3-8.