Supporting information

Solvent-Free and Room Temperature Visible Light-Induced C-H Activation: CdS as a Highly Efficient Photo-Induced Reusable Nano-Catalyst for the C-H Functionalization Cyclization of *t*-Amines and C-C Double and Triple bonds

Somayeh Firoozi, [a] Mona Hosseini-Sarvari*[a] and Mehdi Koohgard [a]

[a] Department of Chemistry, Shiraz University, Shiraz 7194684795, I.R. Iran

* Corresponding author, E-mail address: Hossaini@shirazu.ac.ir

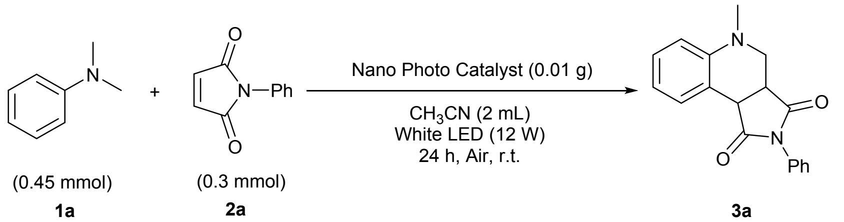
Contents

1. Tests for finding the suitable catalyst for the synthesis of Pyrrolo[3,4-*c*]quinolones

At the first, a model rection was selected in the presence of several photocatalysts in acetonitrile as solvent and under white light radiation for 24 h at atmosphere (Table S1). The main goal of present work was using ZnO or TiO_2 as photocatalyst but since ZnO and TiO_2 have no absorption in visible region, we decided to apply doped ZnO and TiO_2 on graphene to reduce bond gap and increase light adsorption capacity in visible region; but unfortunately, the efficiency of this model was not significant. Therefore, to enhance the photocatalytic activity, CdS was added to dope ZnO on graphene (RGO-ZnO). So, the reaction efficiency was notably increased by finding CdS/ZnO-RGO.

To figure out the effect of CdS/ZnO-RGO composite, CdS-RGO and CdS nano-photocatalysts were synthesized and were used in this reaction and interestingly the same results were observed for all. Herein, we found that an efficiency increment was observed just from CdS and there is no striking difference between using either CdS/ZnO-RGO, CdS-RGO or CdS. As a result, Cds has been applied as a photocatalyst for this process. And also applied Ag/ZnO-RGO as photo catalyst but the reaction efficiency did not change.

Table S1. The effect of various Nano photo-catalyst in the synthesis of pyrrolo[3,4-*c*]quinolones.

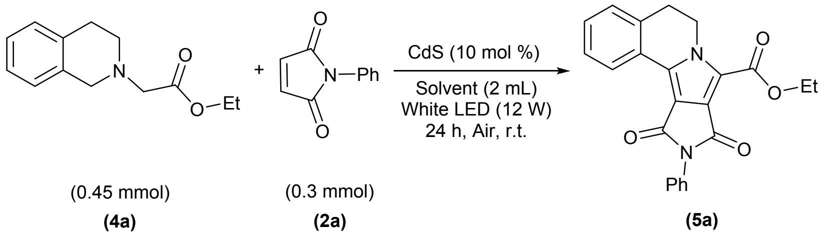


Entry	Nano Photo Catalyst	Yield (%)
1	Non Nano photo catalyst	-
2	GO	5
3	ZnO	20
4	TiO_2	20
5	ZnO-RGO	50
6	TiO_2-RGO	50
7	CdS/ZnO-RGO	92
8	CdS-RGO	92
9	CdS	91
10	Ag/ZnO-RGO	20

2. Tests for finding the suitable catalyst for the synthesis of pyrrolo[2,1-*a*]isoquinoline-8-carboxylates

To achieve the best results, The condensation reaction between ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (**4a**) and *N*-phenylmaleimide (**2a**) was chosen as a model reaction for the synthesis of ethyl 9,11-dioxo-10-phenyl-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5a**). Various reaction conditions were optimized, and this affordable pathway was progressed in the presence of 10 mol% of CdS NPs under sun light or blue light irradiation and air atmosphere, in solvent-free conditions at room temperature. According to Table S2 and S3, various solvents, catalyst quantities different wavelength of irradiation produced from distinct resources as well as different atmospheres were tested. A batch of solvents including H_2O, EtOH, CH_3CN, EtOAc, acetone, $CHCl_3$, CH_2Cl_2, THF, DMF and DMSO in the presence of CdS NPs and under white light as well as solvent-free conditions were checked out. As it can be surveyed in Table S2, the best results have been obtained in solvent-free conditions.

Table S2: The effect of various solvents and different quantities of ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate as a precursor in the synthesis ethyl 9,11-dioxo-10-phenyl-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate.



Entry	Solvent	Yield (%)
1	H_2O	Trace [a]

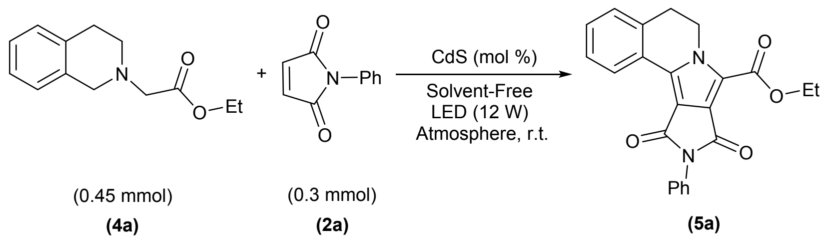
2	EtOH	51 [a]
3	CH_3CN	88 [a]
4	EtOAc	55 [a]
5	Acetone	60 [a]
6	CH_2Cl_2	78 [a]
7	$CHCl_3$	75 [a]
8	THF	32 [a]
9	DMSO	86 [a]
10	DMF	80 [a]
11	Solvent-Free	84 [b]
12	Solvent-Free	88 [c]
13	Solvent-Free	90 [a]
14	Solvent-Free	90 [d]

The condensation reaction of ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (1-2 eq), *N*-phenylmaleimide (0.3 mmol), CdS as nano photo catalyst (10 mol %) and solvent (2 mL) under irradiation white LED 12 W lamp for 24 h at room temperature in the air. [a] ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate 1.5 eq (0.45 mmol), [b] ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate 1 eq (0.3 mmol), [c] ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate 1.2 eq (0.36 mmol) and [d] ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate 2 eq (0.6 mmol).

After finding the solvent-free conditions, diverse amounts of catalyst were tested. The efficiency in catalyst amounts less than 10 mol% was negligible and all amounts more than which showed no increasing in efficiency or reduction in reaction time were observed. The absence of CdS NPs (Table S3, Entry 1) as a photo-catalyst, the reaction is not performed. Effects of light irradiation and different atmospheres were also studied and it was observed that the reaction did not progress in the absence of light (Table 1, Entry 7). This phenomena exhibits that CdS photocatalyst exciting by light radiation. The efficiency slaked using red and green lights, while the same benign efficiency was found for white (Table 1, Entry 3, 11) and blue (Table 1, Entry 8, 12) lights. However, the reaction time reduced from 24 h to 18 h with blue light irradiation. On the other hand, the reaction time decreased to 8 h with Sun light irradiation (Table S3, Entry 15). The same data were obtained for oxygen and air atmosphere but there was no noticeable result under argon atmosphere. So, the air atmosphere was selected as the best conditions.

Therefore, The best reaction conditions were obtained with CdS (10 mol%) as a photocatalyst under the sun light or a blue LED lamp irradiation without any solvent at room temperature and air atmosphere. for the synthesis of different pyrrolo[2,1-*a*]isoquinoline-8-carboxylate derivatives.

Table S3: The optimization of model reaction based on diverse amounts of photocatalyst, wavelengths of light, and atmosphere (gas).



Entry	CdS Amount (mol %)	Light	Atmosphere	Yield (%)
1	Catalyst Free	White	Air	-
2	5	White	Air	78
3	10	White	Air	90 [a]
4	15	White	Air	91
5	20	White	Air	90
6	25	White	Air	90
7	10	Dark	Air	-
8	10	Blue	Air	90 [b]
9	10	Green	Air	44
10	10	Red	Air	35
11	10	White	O_2	90 [a,c]
12	10	Blue	O_2	90 [b,c]
13	10	White	Ar	- [d]

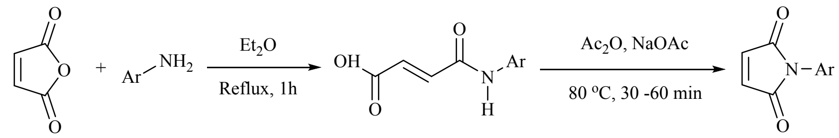
14	10	Blue	Ar	- [d]
15	10	Sun	Air	90 [e]

The condensation reaction of *N*-phenylmaleimide (0.3 mmol), ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (0.45 mmol) and different amount CdS as Nano Photo catalyst (mol %) under different irradiation LED 12 W lamp and solvent-free condition for 24 h at room temperature in the Atmosphere. [a] The completion time of reaction is 24 h, [b] The completion time of reaction is 18 h, [c] oxygen balloon, [d] Argon balloon and [e] The completion time of reaction is 12 h.

3. Experimental for the synthesis of maleimides

N-aryl maleimides and *N*-alky maleimides were synthesized respectively, according to the modified previous reported procedures [1,2].

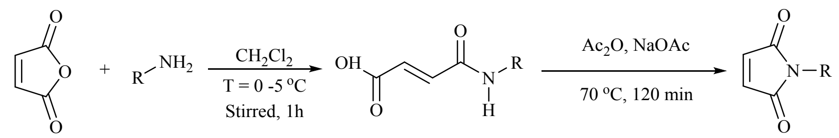
3.1. General procedure for the synthesis of *N*-aryl maleimides



X = H, 4-OH, 4-OEt, 4-OMe, 4-isopropyl, 2-Et, 4-Cl, 4-Br, 3-Cl, 3-Br, 2-CN, 4-NO_2, 3-NO_2

Maleic anhydride (5 mmol) dissolved in diethyl ether (10 mL) and aryl anilin (5 mmol) was dissolved in diethyl ether (5 mL) separately, then aryl anilin solution in diethyl ether drop and drop added to the flask containing the Maleic anhydride solution in diethyl ether and stirred for 1h under reflux. Next, the reaction mixture was cooled to the room temperature, was filtered off and washed with diethyl ether. To the 4-oxo-4-(arylamino)but-2-enoic acid is obtained in step 1, added Acetic anhydride (2mL) and anhydrous sodium acetate (2 mmol) and stirred at 80 °C for 30-60 min. Then the reaction mixture was cooled to the room temperature and added into ice. The product washed with cold water. The *N*-aryl maleimides dried and recrystallized from petroleum ether to obtain pure product.

3.2. General procedure for the synthesis of *N*-alkyl maleimides

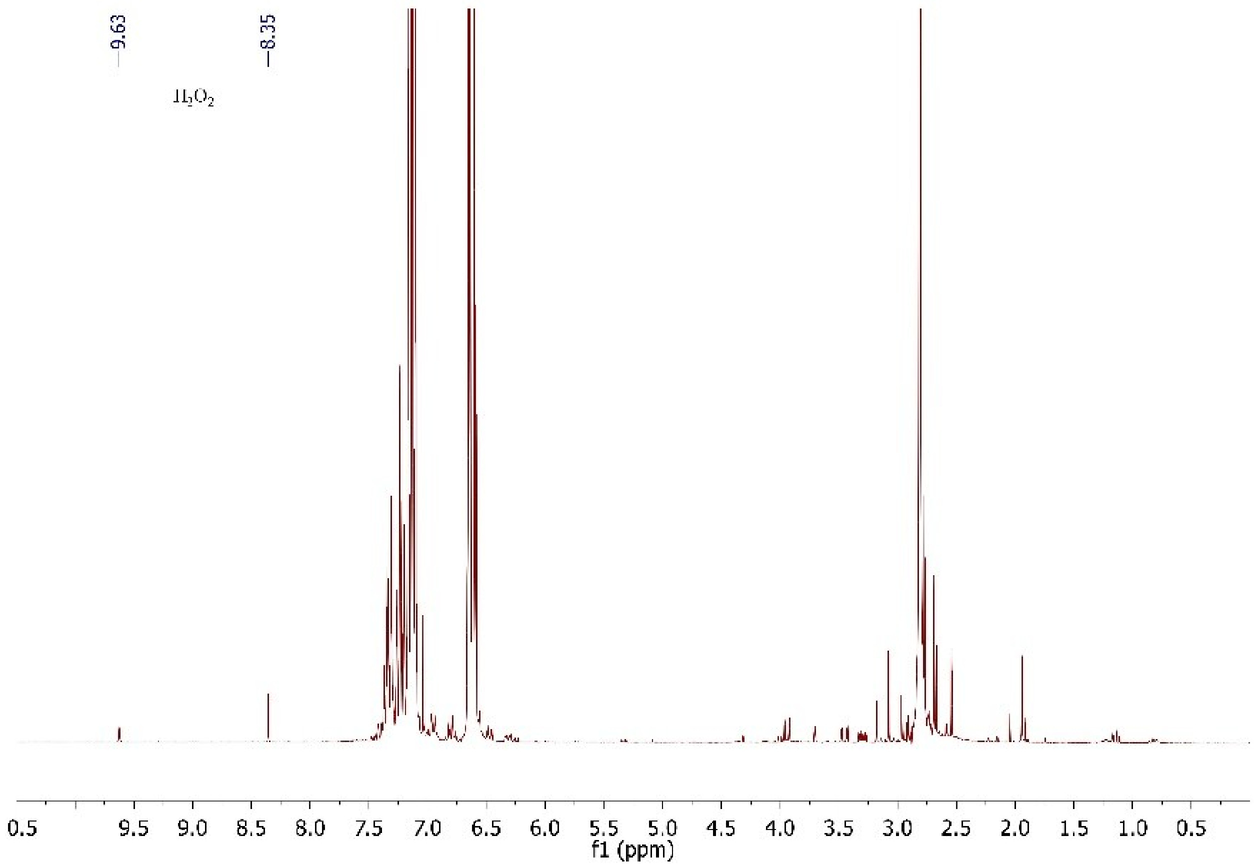


R = cyclohexan, isobutyl

Maleic anhydride (5 mmol) dissolved in dichloromethane (10 mL) and alkyl anilin (5 mmol) was dissolved in dichloromethane (5 mL) separately, then alkyl anilin solution in dichloromethane drop and drop added to the flask containing the Maleic anhydride solution in dichloromethane at 0-5 °C temperature. After that stirred for 1h at room temperature. Next, the reaction mixture was filtered off and washed with dichloromethane. To the 4-oxo-4-(alkylamino)but-2-enoic acid is obtained in step 1, added Acetic anhydride (2mL) and anhydrous sodium acetate (2 mmol) and stirred at 70 °C for 120 min. Then the reaction mixture was cooled to the room temperature and added into ice. The product washed with cold water. The *N*-alkyl maleimides dried and obtained crude products were purified by column chromatography to afford pure *N*-alkyl maleimides products.

4. Indication of H_2O_2 after completing the reaction

For the synthesis of 5-methyl-2-phenyl-3*a*,4,5,9*b*-tetrahydro-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (**3a**), according to optimize conditions, was carried out the reaction of between *N,N*-dimethylaniline (0.45 mmol) and *N*-phenylmaleimide (0.3 mmol) in the presence of CdS NPs (10 mol%) under irradiation of a blue LED 12 W lamp and solvent-free condition for 24 h at room temperature under the air atmosphere, to confirm the formation of H_2O_2 during the reaction, the ^1H NMR spectrum was taken from the reaction mixture (Scheme 3, C). The H_2O_2 representative peak was detected in ^1H NMR spectrum at δ= 9.63 ppm.



Indication of H_2O_2 after completing the reaction

5. Characterization of compounds

5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3a**)
White solid, mp = 203-205 ^oC (202-204 ^oC)[3]. IR (KBr) ν_{max} 2925, 1790, 1715, 1593, 1497, 1390, 1325, 1120, 765, 692 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ(ppm); 2.80 (s, 3H), 3.08 (dd, 1H, *J* = 7.2, 5.0 Hz), 3.48-3.60 (m, 2H), 4.12 (d, 1H, *J* = 7.5), 6.70 (d, 1H, *J* = 7.5 Hz), 6.87 (t, 1H, *J* = 7.5 Hz), 7.17-7.51 (m, 7H). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 39.55, 42.09, 43.46, 50.64, 112.70, 118.60, 119.85, 126.35, 128.53, 128.71, 129.01, 130.35, 131.95, 148.30, 175.72, 177.64. Anal.Calcd for $C_{18}H_{16}N_2O_2$: C 73.95, H 5.52, N 9.58. Found: C 73.89, H 5.57, N 9.60.

2-(4-Hydroxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3b**)
White solid, mp = 147-149 ^oC (146-148 ^oC)[3]. IR (KBr) ν_{max} 3480, 2899, 1768, 1715, 1494, 1375, 1170, 1013, 750 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.78 (s, 3H), 3.07 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.47-3.59 (m, 2H), 4.11 (d, 1H, *J* = 10 Hz), 6.70 (d, 1H, *J* = 10 Hz), 6.86 (td, 1H, *J* = 7.5, 1.0 Hz), 7.10 (d, 2H, *J* = 10 Hz), 7.19-7.22 (m, 1H), 7.26 (d, 2H, *J* = 10.0 Hz), 7.47 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 39.48, 42.14, 43.62, 50.68, 112.61, 118.50, 119.75, 122.17, 127.37, 128.78, 129.42, 130.36, 148.56, 150.28, 175.70, 177.61. Anal.Calcd for $C_{18}H_{16}N_2O_3$: C 70.12, H 5.23, N 9.09. Found: C 70.14, H 5.20, N 9.10.

2-(4-Ethoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3c**)
White solid, mp = 152-154 ^oC (151-153 ^oC)[3]. IR (KBr) ν_{max} 2936, 1770, 1717, 1594, 1513, 1394, 1251, 1205, 1167, 815, 749 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ(ppm); 1.39 (t, 3H, *J* = 7.5 Hz), 2.83 (s, 3H), 3.10 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.50 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.59 (dd, 1H, *J* = 7.5, 2.5 Hz), 4.01 (q, 2H, *J* = 7.5 Hz), 4.13 (d, 1H, *J* = 10.0), 6.73 (d, 1H, *J* = 7.5 Hz), 6.87-6.92 (m, 3H), 7.12-7.26 (m, 3H), 7.52 (d, 1H, *J* = 7.5 Hz,) . ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 14.78, 39.48, 42.09, 43.53, 50.70, 63.71, 112.54, 114.83, 118.68, 119.67, 124.48, 127.59, 128.67, 130.37, 148.54, 158.82, 176.07, 178.02. Anal.Calcd for $C_{20}H_{20}N_2O_3$:C 71.41, H 5.99, N 8.33. Found: C 71.48, H 5.92, N 8.27.

2-(4-Methoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3d**)

White solid, mp = 222-225 ºC (222-224 ºC)[4]. IR (KBr) ν_{max} 2935, 1711, 1596, 1514, 1396, 1250, 1162, 763 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ(ppm); 2.79 (s, 3H), 3.09 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.45-3.59 (m, 2H), 3.75 (s, 3H), 4.10 (d, 1H, *J* = 10 Hz), 6.72 (d, 1H, *J* = 7.5 Hz), 6.84-6.95 (m, 3H), 7.10-7.22 (m, 3H), 7.48 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 39.48, 42.09, 43.53, 50.71, 55.50, 112.55, 114.33, 118.65, 119.68, 124.66, 127.62, 128.68, 130.37, 148.53, 159.42, 176.05, 178.00. Anal.Calcd for $C_{19}H_{18}N_2O_3$: C 70.79, H 5.63, N 8.69. Found: C 7.77, H 5.68, N 8.52.

2-(4-Isopropylphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3e**)
White solid, mp = 158-160 ºC (157-159 ºC)[4]. IR (KBr) ν_{max} 2965, 2860, 1711, 1597, 1509, 1384, 1276, 1193, 751 cm^{-1}. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 1.20 (d, 6H, *J* = 7.5 Hz), 2.80 (s, 3H), 2.83-2.97 (m, 1H), 3.08 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.51-3.60 (m, 2H), 4.11 (d, 1H, *J* = 7.5), 6.71 (d, 1H, *J* = 7.5 Hz), 6.88 (t, 1H, *J* = 7.5 Hz), 7.13-7.27 (m, 5H), 7.50 (d, 1H, *J* = 7.5 Hz) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 23.87, 33.88, 39.42, 42.08, 43.50, 50.66, 112.49, 118.64, 119.61, 126.11, 127.06, 128.62, 129.53, 130.33, 148.48, 149.24, 175.91, 177.86. Anal.Calcd for $C_{21}H_{22}N_2O_2$: C 75.42, H 6.63, N 8.38. Found: C 75.40, H 6.73, N 8.45.

2-(2-Ethylphenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3f**)
White solid, mp = 129-131 ºC (128-130 ºC)[4]. IR (KBr) ν_{max} 2965, 2826, 1717, 1592, 1516, 1393, 1210, 759 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ(ppm); 0.79 (t, 3H, *J* = 7.5 Hz), 2.49 (q, 2H, *J* = 7.5 Hz), 2.84 (s, 3H), 3.08 (dd, 1H, *J*= 7.5, 5.0 Hz), 3.55-3.65 (m, 2H), 4.15 (d, 1H, *J* = 10.0 Hz), 6.75 (dd, 1H, *J* = 7.5, 2.5 Hz), 6.89 (td, 1H, *J*= 7.5, 2.5 Hz), 7.08 (d, 1H, *J*= 7.5 Hz), 7.19-7.36 (m, 4H), 7.48 (d, 1H, *J*=7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 14.20, 24.21, 39.17, 42.90, 44.44, 50.95, 112.25, 119.75, 126.83, 126.87, 128.19, 128.69, 129.11, 129.62, 129.72, 130.29, 141.90, 148.58, 176.25, 178.30. Anal.Calcd for $C_{20}H_{20}N_2O_2$: C 74.98, H 6.29, N 8.74. Found: C 75.11, H 6.28, N 8.71.

2-(4-Chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3g**)
White solid, mp = 187-189 ºC (188-190 ºC)[4] IR (KBr) ν_{max} 2955, 1786, 1714, 1593, 1484, 1398, 1322, 1207, 757 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) *δ* (ppm) 2.85 (s, 3H), 3.10 (dt, 1H, *J* = 7.5, 2.5 Hz), 3.51-3.65 (m, 2H), 4.16 (d, 1H, *J* = 10.0 Hz), 6.77 (dd, 1H, *J* = 75, 2.5 Hz), 6.89-6.96 (m, 1H), 7.22-7.28 (m, 3H), 7.38-7.43 (m, 2H), 7.52 (dd, 1H, *J* = 7.5, 2.0 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) *δ* (ppm) 39.49, 42.10, 43.57, 50.60, 112.64, 118.38, 119.77, 127.58, 128.77, 129.16, 130.28, 130.42, 134.21, 148.45, 175.52, 177.45. Anal.Calcd for $C_{18}H_{15}ClN_2O_2$: C 58.24, H 4.07, N 7.55. Found: C 57.98, H 4.14, N 7.68.

2-(4-Bromophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3h**)
White solid, mp = 218-220 ºC (217-219 ºC)[5]. IR (KBr) ν_{max} 2958, 1783, 1714, 1594, 1483, 1397, 1322, 1211, 754 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) *δ* (ppm) 2.81 (s, 3H), 3.09 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.52-3.61 (m, 2H), 4.13 (d, 1H, *J* = 7.5 Hz), 6.73 (d, 1H, *J* = 7.5 Hz), 6.89 (td, 1H, *J* = 7.5, 1.0 Hz), 7.14-7.25 (m, 3H), 7.51 (t, 3H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) *δ* (ppm) 39.48, 42.16, 43.71, 50.56, 112.75, 118.05, 119.88, 121.54, 123.10, 128.94, 129.75, 130.25, 132.16, 148.49, 175.16, 177.09. Anal.Calcd for $C_{18}H_{15}BrN_2O_2$: C 58.24, H 4.07, N 7.55. Found: C 57.98, H 4.14, N 7.68.

2-(3-Chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3i**)
White solid, mp = 159-161 ºC (158-160 ºC)[5]. IR (KBr) ν_{max} 2841, 1778, 1709, 1589, 1491, 1385, 1187, 789, 739 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$) δ(ppm); 2.89 (s, 3H), 3.19 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.57-3.69 (m, 2H), 4.22 (d, 1H, *J* = 10.0 Hz), 6.84 (d, 1H, *J* = 7.5 Hz), 6.99 (t, 1H, *J*= 7.5 Hz), 7.22-7.44 (m, 5H), 7.57 (d,1H, *J*= 7.5 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$), δ(ppm); 39.60, 42.27, 43.77, 50.75, 112.78, 118.45, 119.90, 124.67, 126.74, 128.85, 128.96, 130.09, 130.43, 133.13, 134.66, 148.65, 175.57, 177.50. Anal.Calcd for $C_{18}H_{15}ClN_2O_2$: C 66.16, H 4.63, N 8.57. Found: C 56.95, H 4.43, N 8.67.

2-(3-Bromophenyl)-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3j**)
White solid, mp = 164-166 ºC (164-166 ºC)[6]. IR (KBr) ν_{max} 2861, 1775, 1715, 1598, 1492, 1387, 1191, 788, 756 cm^{-1}. ^{1}H-NMR (250 MHz, 298K, $CDCl_3$) δ(ppm); 2.86 (s, 3H), 3.13 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.52-3.66 (m, 2H), 4.18 (d, 1H, *J* = 10.0), 6.77 (d, 1H, *J* = 7.5 Hz), 6.93 (td, 1H, *J* = 7.5, 2.5 Hz), 7.23-7.35 (m, 3H), 7.49-7.55(m, 3H) . ^{13}C-NMR (101 MHz, 298K, $CDCl_3$), δ(ppm); 39.47, 42.09, 43.57, 50.58, 112.67, 118.28, 119.81, 122.38, 124.82, 128.80, 129.37, 130.17, 130.26, 131.59, 133.08, 148.40, 175.34, 177.26. Anal.Calcd for $C_{18}H_{15}BrN_2O_2$: C 58.24, H 4.07, N 7.55. Found: C 58.45, H 4.23, N 7.61.

2-(5-Methyl-1,3-dioxo-1,3,3a,4,5,9b-hexahydro-*2H*-pyrrolo[3,4-c]quinolin-2-yl)benzonitrile (**3k**)
White solid, mp = 178-180 ºC (177-179 ºC)[5]. IR (KBr) ν_{max} 2856, 2227, 1722, 1509, 1383, 1189, 762 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) *δ* (ppm) 2.89 (s, 3H), 3.21 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.62-3.73 (m, 2H), 4.30 (d, 1H, *J* = 10.0 Hz), 6.83 (1H, d, *J* = 7.5 Hz), 6.96 (td, 1H, *J* = 7.5, 2.5 Hz), 7.28 (td, 2H, *J* = 7.5, 2.5 Hz), 7.50-7.56 (m, 2H), 7.67 (t, 1H, *J* = 7.5 Hz), 7.78 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) *δ* (ppm) 39.47, 42.61, 44.09, 50.79, 112.74, 119.82, 119.86, 119.88, 128.95, 129.20, 129.22, 129.56, 130.34, 130.37, 133.61, 133.68, 148.67, 174.87, 176.74. Anal.Calcd for $C_{19}H_{15}N_3O_2$: C 71.91, H 4.76, N 13.24. Found: C 71.93, H 4.81, N 13.30.

5-Methyl-2-(4-nitrophenyl)-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3l**)
Yellow solid, mp = 139-141 ºC (138-140 ºC)[5]. IR (KBr) ν_{max} 2923, 1782, 1713, 1596, 1527, 1342, 1180, 765 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.83 (s, 3H), 3.13 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.55-3.65 (m, 2H), 4.20 (d, 1H, *J* = 7.5 Hz), 6.76 (d, 1H, *J* = 7.5 Hz), 6.92 (td, 1H, *J* = 7.5, 1.0 Hz), 7.24 (td, 1H, *J* = 7.5, 1.0 Hz), 7.49-7.59 (m, 3H), 8.27 (dd, 2H, *J* = 7.5, 2.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 39.50, 42.18, 43.80, 50.59, 112.79, 118.04, 119.94, 124.28, 126.84, 129.03, 130.30, 137.50, 146.89, 148.56, 175.16, 177.08. Anal.Calcd for $C_{18}H_{15}N_3O_4$: C 64.09, H 4.48, N 12.46. Found: C 63.89, H 4.57, N 13.04.

5-Methyl-2-(3-nitrophenyl)-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3m**)
Yellow solid, mp = 189-191 ºC (188-190 ºC)[5]. IR (KBr) ν_{max} 2923, 1709, 1528, 1497, 1385, 1352, 1187, 756 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.87 (s, 3H), 3.15 (d, 1H, *J* = 7.5, 2.5), 3.59-3.69 (m, 2H), 4.24 (d, 1H, *J* = 10.0 Hz), 6.78 (1H, d, *J* = 10.0 Hz), 6.94 (td, 1H, *J* = 7.5, 1.0 Hz), 7.24-7.31 (m, 2H), 7.53 (d, 1H, *J* = 7.5 Hz), 7.63 (t, 1H, *J* = 7.5 Hz), 7.70-7.75 (m, 1H), 8.25 (d, 1H, *J* = 10.0 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.53, 42.22, 43.79, 50.62, 112.80, 118.10, 119.93, 121.62, 123.17, 129.01, 129.82, 130.31, 132.23, 133.04, 148.37, 148.59, 175.24, 177.18. Anal.Calcd for $C_{18}H_{15}N_3O_4$: C 64.09, H 4.48, N 12.46. Found: C 63.96, H 4.60, N 12.42.

2-Benzyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3n**)
White solid, mp = 125 -127 ºC (126-128 ºC)[7]. IR (KBr) ν_{max} 2956, 2864, 1781, 1709, 1594, 1493, 1392, 1346, 1167, 758, 707 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.70 (s, 3H), 2.94 (dd, 1H, *J* = 12.5, 5.0 Hz), 3.21-3.28 (m, 1H), 3.40 (dd, 1H, *J* = 12.5, 5.0 Hz), 3.87 (1H, d, *J* = 10.0 Hz), 4.48-4.62 (m, 2H), 6.63 (d, 1H, *J* = 7.5 Hz), 6.81 (td, 1H, *J* = 7.5, 1.0 Hz), 7.09-7.23 (m, 6H), 7.38 (d, 1H, *J* = 7.7 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.40, 42.14, 42.83, 43.71, 50.81, 112.52, 118.93, 119.74, 127.86, 128.40, 128.54, 128.66, 130.29, 135.65, 148.54, 176.48, 178.45. Anal.Calcd for $C_{19}H_{18}N_2O_2$: C 74.49, H 5.92, N 9.14. Found: C 75.02, H 5.60, N 9.23.

2-Cyclohexyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3o**)
Yellowish oil. IR (KBr) ν_{max} 2928, 1710, 1639, 1463, 1379, 1268, 1135, 1082, 756 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.13-1.24 (m, 2H), 1.48-1.75 (m, 8H), 2.73 (s, 3H), 2.96 (dd, 1H, *J* = 10.0, 5.0 Hz), 3.18-3.26 (m, 1H), 3.39 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.81-3.95 (m, 2H), 6.63 (d, 1H, *J* = 7.5 Hz), 6.74-6.85 (m, 1H), 7.14 (t, 1H, *J* = 7.5 Hz), 7.40 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 25.16, 25.93, 28.97, 39.53, 41.84, 43.17, 50.94, 58.86, 112.49, 119,59, 128.54, 129.46, 130.31 148.51, 176.98, 178.86. Anal.Calcd for $C_{18}H_{22}N_2O_2$: C 72.46, H 7.43, N 9.39. Found: C 71.96, H 7.54, N 9.45.

2-Isobutyl-5-methyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3p**)
White solid, mp = 83-85 ºC (82-84 ºC)[5]. IR (KBr) ν_{max} 2950, 1776, 1701, 1602, 1490, 1389, 1213, 1096, 1122, 753 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 0.73 (d, 6H, *J* = 7.5 Hz), 1.83-1.99 (m, 1H), 2.73 (s, 3H), 2.96 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.25 (d, 2H, *J* = 7.5 Hz), 3.28-3.32 (m, 1H), 3.44 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.90 (d, 1H, *J* = 10.0 Hz), 6.63 (d, 1H, *J* = 7.5 Hz), 6.82 (t, 1H, *J* = 7.5 Hz), 7.14 (t, 1H, *J* = 7.5 Hz), 7.39 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 19.76, 26.85, 39.25, 42.00, 43.54, 46.30, 50.86, 112.32, 119.14, 119.58, 128.45, 130.14, 148.45, 176.95, 178.94. Anal.Calcd for $C_{16}H_{20}N_2O_2$: C 70.56, H 7.40, N 10.29. Found: C 70.49, H 7.48, N 10.36.

5-Methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3q**)
White solid, mp = 77-79 ºC (77-79 ºC)[7]. IR (KBr) ν_{max} 3022, 2858, 1770, 1708, 1601, 1502, 1349, 1322, 1117, 789, 752 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.73 (s, 3H), 2.95 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.34 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.42 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.95 (d, 1H, *J* = 10.0 Hz), 6.67 (d, 1H, *J* = 10.0 Hz), 6.82 (td, 1H, *J* = 7.5, 1.5 Hz), 7.10-7.17 (m, 1H), 7.35 (d, 1H, *J* = 7.5 Hz), 8.35 (s, 1H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 39.40, 43.24, 44.79, 50.39, 112.56, 118.39, 119.70 128.71, 130.10, 148.50, 176.97, 178.99. Anal.Calcd for $C_{12}H_{12}N_2O_2$: C 66.65, H 5.59, N 12.96. Found: C 67.02, H 5.51, N 12.89.

5,8-Dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3r**)
White solid, mp = 80-82 ºC. IR (KBr) ν_{max} 3016, 2863, 1765, 1716, 1609, 1504, 1347, 1321, 1114, 792, 749 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.31 (s, 3H), 2.81 (s, 3H), 3.03 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.42 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.50 (dd, 1H, *J* = 7.5, 2.5 Hz), 4.03 (d, 1H, *J* = 10.0 Hz), 6.75 (d, 1H, *J* = 10.0 Hz), 7.22 (t, 1H, *J* = 7.5 Hz), 7.43 (d, 1H, *J* = 7.5 Hz), 8.43 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 22.26, 38.97, 42.80, 44.36, 49.96.39, 112.12, 117.96, 119.27 128.28, 129.67, 148.07, 176.54, 178.55. Anal.Calcd for $C_{13}H_{14}N_2O_2$: C 67.81, H 6.13, N 12.17. Found: C 67.90, H 5.94, N 12.75.

8-Bromo-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3s**)
White solid, mp = 157-159 ºC (158-160 ºC)[5]. IR (KBr) ν_{max} 2931, 1711, 1497, 1393, 1324, 1189, 702, 632 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.75 (s, 3H), 3.06 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.45-3.56 (m, 2H), 4.03 (d, 1H, *J* = 10.0 Hz), 6.58 (1H, d, *J* = 7.5 Hz), 7.16-7.40 (m, 6H), 7.58 (d, 1H, *J* = 2.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 39.48, 41.78, 43.28, 50.37, 111.67, 114.27, 120.41, 126.31, 128.65, 129.07, 131.44, 131.82, 132.71, 147.50, 175.16, 177.28. Anal.Calcd for $C_{18}H_{15}BrN_2O_2$: C 58.24, H 4.07, N 7.55. Found: C 58.78, H 3.98, N 7.72.

5,8-Dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-*1H*-pyrrolo[3,4-c]quinoline-1,3(*2H*)-dione (**3t**)
White solid, mp = 192-194 ºC (193-195ºC)[5]. IR (KBr) ν_{max} 2935, 1710, 1509, 1392, 1268, 1189, 689, 624 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 2.24 (s, 1H), 2.74 (s, 3H), 3.0 (dd, 1H, *J* = 7.5, 5.0 Hz), 3.42-3.55 (m, 2H), 4.06 (d, 1H, *J* = 7.5 Hz), 6.60 (d, 1H, *J* = 7.5 Hz), 6.98 (dd, 1H, *J* = 7.5, 2.5 Hz), 7.19 (t, 1H, *J* = 2.5 Hz), 7.22 (d, 1H, *J* = 2.5 Hz), 7.28-7.40 (m, 4H). ^{13}CNMR (101 MHz, $CDCl_3$) δ (ppm) 20.45, 39.57, 42.18, 43.58, 50.94, 112.54, 118.50, 126.38, 128.50, 128.81, 128.99, 129.24, 130.82, 130.91, 146.37, 175.91, 177.86. Anal.Calcd for $C_{19}H_{18}N_2O_2$: C 74.49, H 5.92, N 9.14. Found: C 77.08, H 5.08, N 8.74.

Ethyl 9,11-dioxo-10-phenyl-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5a**)
White solid, mp = 190-192 ºC (191-192 ºC)[8]. IR (KBr) ν_{max} 3180, 2885, 1762, 1713, 1549, 1375, 1354, 1297, 1108, 943, 872, 865, 757 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.39 (t, 3H, *J* = 7.2 Hz), 3.11 (t, 2H, *J* = 6.7 Hz), 4.35 (q, 2H, *J* = 7.2 Hz), 4.70 (t, 2H, *J* = 7.2 Hz), 7.18-7.23 (m, 1H), 7.29-7.35 (m, 4H), 7.38-7.45 (m, 1H), 8.49-8.52 (m, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.22, 28.36, 43.43, 61.71, 116.24, 118.69, 125.24, 125.57, 127.20, 127.70, 127.83, 127.98, 128.02, 128.95, 130.36, 132.47, 132.60, 133.51, 159.70, 161.65, 163.15. Anal.Calcd for $C_{23}H_{18}N_2O_4$: C 71.49, H 4.70, N 7.25. Found: C 71.52, H 4.65, N 9.08.

Methyl 9,11-dioxo-10-phenyl-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5b**)
Orange solid, mp = 216-218 ºC (117-118 ºC)[8]. IR (KBr) ν_{max} 3103, 2911, 1488, 1392, 1179, 757, 703, 618 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 3.18 (t, 2H, *J* = 6.7 Hz), 3.98 (s, 3H), 4.77 (t, 2H, *J* = 7.2 Hz), 7.26-7.51 (m, 8H), 8.55-8.59 (m, 1H). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 28.31, 43.44, 52.36, 116.27, 118.50, 125.32, 125.49, 127.04, 127.69, 127.76, 127.98, 128.02, 128.87, 130.42, 132.44, 133.65, 160.05, 161.63, 163.00. Anal.Calcd for $C_{22}H_{16}N_2O_4$: C 70.96, H 4.33, N 7.52. Found: C 70.88, H 4.45, N 9.04.

Ethyl 10-(4-methoxyphenyl)-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5c**)
White solid, mp = 167-169 ºC (168-169 ºC)[8]. IR (KBr) ν_{max} 3204, 2990, 1763, 1708, 1512, 1384, 1283, 1255, 1197, 1162, 1113, 1034, 811, 748 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) 1.47 (t, 3H, *J* = 7.2 Hz), 3.19 (t, 2H, *J* = 6.8 Hz), 3.85 (s, 3H), 4.44 (q, 2H, *J* = 7.2 Hz), 4.78 (t, 2H, *J* = 6.8 Hz), 7.01 (d, 2H, *J* = 8.8 Hz), 7.25-7.43 (m, 5H), 8.58 (1H, d, *J* = 7.6 Hz) ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.10, 28.23, 43.24, 55.41, 61.57, 114.21, 116.24, 118.50, 125.19, 125.50, 127.60, 127.80, 128.05, 128.14, 128.41, 130.19, 132.38, 133.30, 158.83, 159.61, 161.95, 163.29. Anal.Calcd for $C_{24}H_{20}N_2O_5$: C 69.22, H 4.84, N 6.73. Found: C 69.26, H 4.81, N 6.69.

Ethyl 10-(4-bromophenyl)-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5d**)
White solid, mp = 190-192 ºC (191-192 ºC)[8]. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) 1.47 (t, 3H, *J* = 7.2 Hz), 3.17 (t, 2H, *J* = 7.2 Hz), 4.42 (q, 2H, *J* = 7.2 Hz), 4.76 (t, 2H, *J* = 7.2 Hz), 7.20-7.42 (m, 5H), 7.57 (d, 2H, *J* = 7.6 Hz), 8.52 (t, 1H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.13, 28.23, 43.43, 61.69, 115.98, 118.80, 121.36, 124.90, 125.37, 127.72, 127.88, 128.00, 128.59, 130.52, 131.66, 131.97, 132.55, 133.60, 159.53, 161.20, 162.66. Anal.Calcd for $C_{23}H_{17}BrN_2O_4$: C 59.37, H 3.68, N 6.02. Found: C 59.29, H 3.91, N 6.11.

Ethyl 10-(4-nitrophenyl)-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5e**)
Yellow solid, mp = 205-207 ºC (206-207 ºC)[8]. IR (KBr) ν_{max} 3126, 2984, 1765, 1719, 1523, 1387, 1327, 1261, 1208, 1145, 1118, 1057, 886, 859, 804, 763 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) 1.50 (t, 3H, *J* = 7.2 Hz), 3.21 (t, 2H, *J* = 6.8 Hz), 4.45 (q, 2H, *J* = 7.2 Hz), 4.81 (t, 2H, *J* = 6.8 Hz), 7.33 (d, 1H, *J* = 6.4 Hz), 7.41 (t, 1H, *J* = 6.8 Hz), 7.50 (t, 1H, *J* = 6.8 Hz), 7.72 (d, 2H, *J* = 8.8 Hz), 8.36 (d, 2H, *J* = 8.8 Hz), 8.55 (1H, d, *J* = 6.4 Hz) ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.18, 28.20, 43.49, 61.83, 115.55, 119.22, 124.12, 124.39, 125.17, 126.79, 127.85, 128.06, 128.52, 130.70, 132.50, 134.03, 138.50, 145.95, 159.36, 160.58,162.10. Anal.Calcd for $C_{23}H_{17}N_3O_6$: C 64.04, H 3.97, N 9.74. Found: C 64.13, H 3.89, N 9.67.

Methyl 10-cyclohexyl-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5f**)
yellow oil. IR (KBr) ν_{max} 3029, 2864, 2857, 1685, 1676, 1645, 1450, 1231, 1082 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.18-1.36 (m, 4H), 1.55-1.81 (m, 4H), 2.08-2.23(m, 2H), 3.07 (t, 2H, *J* = 7.0 Hz), 3.91 (s, 1H), 3.99-4.06 (m, 1H), 4.65 (t, 2H, *J* = 7.0 Hz), 7.18-7.21 (m, 1H), 7.25-7.37 (m, 2H), 8.46 (dd, 1H, *J* = 7.0, 2.0 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 24.23, 25.14, 27.32, 28.85, 42.21, 50.02, 51.25, 115.68, 116.33, 124.61, 124.75, 126.57, 126.81, 126.87, 129.10, 131.31, 131.88, 159.17, 161.88, 163.13 Anal.Calcd for $C_{22}H_{22}N_2O_4$: C 69.83, H 5.86, N 7.40. Found: C 69.55, H 5.87, N 8.17.

Ethyl 10-benzyl-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5g**)
White solid, mp = 200-202 ºC (200-201 ºC)[8]. ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm) 1.48 (t, 3H, *J* = 7.2 Hz), 3.14 (t, 2H, *J* = 6.8 Hz), 4.43 (q, 2H, *J* = 7.2 Hz), 4.73 (t, 2H, *J* = 6.8 Hz), 4.79 (s, 2H), 7.26 (d, 1H, *J* = 8.0 Hz), 7.31 (t, 2H, *J* = 7.6 Hz), 7.35-7.41 (m, 3H), 7.45 (d, 2H, *J* = 7.6 Hz) 8.52 (1H, d, *J* = 7.6 Hz) ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.19, 28.17, 41.71, 43.15, 61.49, 116.31, 118.50, 125.37, 125.49, 127.40, 127.55, 127.68, 127.81, 128.41, 128.46, 130.10, 132.30, 132.88, 137.05, 159.54, 162.23, 163.70. Anal.Calcd for $C_{24}H_{20}N_2O_4$: C 71.99, H 5.03, N 7.0. Found: C 71.78, H 5.15, N 7.12.

Methyl 10-isobutyl-9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5h**)
IR (KBr) ν_{max} 3082, 2985, 1774, 1723, 1597, 1490, 1165, 1094, 764 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 0.84 (d, 6H, *J* = 6.7 Hz), 1.93-2.10 (m, 1H), 3.05 (t, 2H, *J* = 7.0 Hz), 3.31 (d, 1H, *J* = 7.2 Hz), 3.87 (s, 3H), 4.61 (t, 2H, *J* = 7.0 Hz), 7.14-7.32 (m, 3H), 8.41 (d, 1H, *J* = 6.7 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 20.21, 27.87, 28.22, 43.21, 45.59, 52.27, 116.50, 117.44, 125.49, 125.65, 127.57, 127.77, 130.14, 132.34, 132.89, 160.03, 162.87, 164.15. Anal.Calcd for $C_{20}H_{10}N_2O_4$: C 68.17, H 5.72, N 7.95. Found: C 68.22, H 5.62, N 8.09.

Ethyl 9,11-dioxo-5,9,10,11-tetrahydro-6H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]isoquinoline-8-carboxylate (**5i**)
IR (KBr) ν_{max} 3112, 2969, 1765, 1712, 1602, 1513, 1354, 1308, 1156, 772, 765 cm^{-1}. ^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.34 (t, 3H, *J* = 7.0 Hz), 3.13 (t, 2H, *J* = 6.7 Hz), 4.32 (q, 2H, *J* = 7.0 Hz), 4.60 (t, 2H, *J* = 6.7 Hz), 7.38-7.42 (m, 3H), 8.33 (t, 1H, *J* = 4.5 Hz), 10.71 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 14.49, 27.86, 44.03, 60.19, 117.21, 117.69, 125.30, 126.23, 126.88, 127.43, 128.36, 130.56, 131.91, 133.24, 158.95, 163.11, 164.89. Anal.Calcd for $C_{17}H_{14}N_2O_4$: C 65.80, H 4.55, N 9.03. Found: C 66.08, H 4.19, N 8.89.

Diethyl 1-methyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7a**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.01 (t, 3H, *J* = 7.5 Hz), 1.16 (t, 3H, *J* = 7.5 Hz), 3.15 (s, 3H), 4.00-4.09 (m, 4H), 4.73 (s, 2H), 7.13-7.22 (m, 3H), 7.26 (d, 1H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 12.60, 13.41, 39.80, 58.43, 60.74, 87.55, 119.47, 120.79, 125.80, 126.35, 128.32, 128.48, 143.66, 153.14, 163.71, 166.25. Anal.Calcd for $C_{16}H_{19}NO_4$: C 66.42, H 6.62, N 4.84. Found: C 67.04, H 6.44, N 4.73.

Diethyl 1,6-dimethyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7b**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 1.01 (t, 3H, *J* = 7.5 Hz), 1.15 (t, 3H, *J* = 7.5 Hz), 2.24 (s, 3H), 3.14 (s, 3H), 3.98-4.12 (m, 4H), 4.72 (s, 2H), 6.88 (d, 1H, *J* = 7.5 Hz), 7.01 (t, 3H, *J* = 7.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 12.76, 13.57, 22.33, 39.96, 58.60, 60.90, 87.72, 121.70, 125.91, 126.53, 127.35, 127.94, 128.25, 143.77, 153.08, 163.85, 166.36. Anal.Calcd for $C_{17}H_{21}NO_4$: C 67.31, H 6.98, N 4.62. Found: C 67.83, H 6.56, N 4.49.
Diethyl 6-bromo-1-methyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7c**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 0.97 (t, 3H, *J* = 7.5 Hz), 1.09 (t, 3H, *J* = 7.5 Hz), 3.10 (s, 3H), 3.96-4.08 (m, 4H), 4.68 (s, 2H), 7.57-7.88 (m, 3H).). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 12.67, 13.46, 39.86, 58.52, 60.81, 87.59, 119.41, 120.67, 125.84, 126.32, 128.38, 128.54, 143.53, 153.18, 163.75, 166.29. Anal.Calcd for $C_{16}H_{18}BrNO_4$: C 52.19, H 4.93, N 3.80. Found: C 52.61, H 4.73, N 4.02.

Dimethyl 1-methyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7d**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 3.15 (s, 3H), 3.57 (s, 3H), 3.60 (s, 3H), 4.73 (s, 2H), 7.11-7.14 (m, 1H), 7.14-7.17 (m, 1H), 7.26 (t, 1H, *J* = 2.5 Hz), 7.29 (t, 1H, *J* = 2.5 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 40.82, 50.94, 52.61, 88.15, 122.38, 126.53, 127.44, 129.46, 129.64, 135.20, 144.55, 154.20, 165.33, 167.84. Anal.Calcd for $C_{14}H_{15}NO_4$: C 64.36, H 5.79, N 5.36. Found: C 64.02, H 6.11, N 5.28.

Dimethyl 1,6-dimethyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7e**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 3.65 (s, 3H), 4.06 (s, 3H), 4.09 (s, 3H), 4.79 (s, 2H), 7.65-7.90 (m, 3H). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 22.41, 40.74, 50.87, 52.53, 88.07, 122.03, 126.24, 126.87, 127.69, 128.27, 128.60, 144.53, 154.21, 165.35, 167.85. Anal.Calcd for $C_{15}H_{17}NO_4$: C 65.44, H 6.22, N 5.09. Found: C 65.50, H 6.17, N 5.13.

Dimethyl 6-bromo-1-methyl-1,2-dihydroquinoline-3,4-dicarboxylate (**7f**)
^{1}HNMR (250 MHz, $CDCl_3$) δ (ppm) 3.65 (s, 3H), 4.06 (s, 3H), 4.09 (s, 3H), 4.79 (s, 2H), 7.65-7.90 (m, 3H). ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 40.86, 50.93, 52.63, 88.17, 119.54, 120.69, 125.85, 126.35, 128.39, 128.56, 144.60, 154.24, 165.36, 167.87. Anal.Calcd for $C_{14}H_{14}BrNO_4$: C 49.43, H 4.15, N 4.12. Found: C 49.13, H 3.96, N 4.32.

1-methyl-4-phenyl-1,2-dihydroquinoline (**7g**)
IR (KBr) ν_{max} 3045, 3030, 2969, 1632, 1614, 1587, 1573 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.99 (s, 3H), 4.00 (d, 2H, *J* = 7.2 Hz), 6.09 (t, 1H, *J* = 7.6 Hz), 6.78 (t, 1H, *J* = 7.2 Hz), 6.89 (d, 1H, *J* = 6.8 Hz), 7.10 (t, 1H, *J* = 7.6 Hz), 7.30 (t, 1H, *J* = 8.0 Hz) 7.37-7.47 (m, 3H), 7.59 (t, 2H, *J* = 7.6 Hz). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 38.69, 47.03, 119.81, 120.56, 121.10, 121.43, 122.89, 124.37, 126.63, 127.16, 127.44, 133.24, 133.77, 145.29. Anal.Calcd for $C_{16}H_{15}N$: C 86.84, H 6.83, N 6.33. Found: C 86.79, H 6.91, N 6.45.

1-methyl-4-(p-tolyl)-1,2-dihydroquinoline (**7h**)
IR (KBr) ν_{max} 3122, 3084, 2958, 1645, 1618, 1577, 1562 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.47 (s, 3H), 3.25 (s, 3H), 4.35 (d, 2H, *J* = 8.0 Hz), 6.22 (t, 1H, *J* = 7.6 Hz), 6.86 (t, 1H, *J* = 7.6 Hz), 6.99 (d, 1H, *J* = 7.6 Hz), 7.24-7.33 (m, 4H), 7.50-7.55 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 20.68, 39.02, 47.11, 120.24, 121.15, 121.99, 122.21, 123.31, 124.88, 127.25, 128.18, 131.75, 133.92, 137.56, 148.48. Anal.Calcd for $C_{17}H_{17}N$: C 86.77, H 7.28, N 5.95. Found: C 86.74, H 7.23, N 6.03.

1,6-dimethyl-4-phenyl-1,2-dihydroquinoline (**7i**)

IR (KBr) ν_{max} 3073, 3042, 2957, 1641, 1610, 1582, 1569 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.99 (s, 3H), 4.00 (d, 2H, *J* = 7.2 Hz), 6.09 (t, 1H, *J* = 7.6 Hz), 6.78 (t, 1H, *J* = 7.2 Hz), 6.89 (d, 1H, *J* = 6.8 Hz), 7.10 (t, 1H, *J* = 7.6 Hz), 7.30 (t, 1H, *J* = 8.0 Hz) 7.37-7.47 (m, 3H), 7.59 (t, 2H, *J* = 7.6 Hz). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 21.72, 39.20, 47.53, 115.81, 122.13, 124.93, 125.10, 127.11, 127.61, 127.83, 127.88, 128.13, 133.72, 134.09, 144.47. Anal.Calcd for $C_{17}H_{17}N$: C 86.77, H 7.28, N 5.95. Found: C 86.55, H 7.41, N 6.04.

1,6-dimethyl-4-(p-tolyl)-1,2-dihydroquinoline (**7j**)

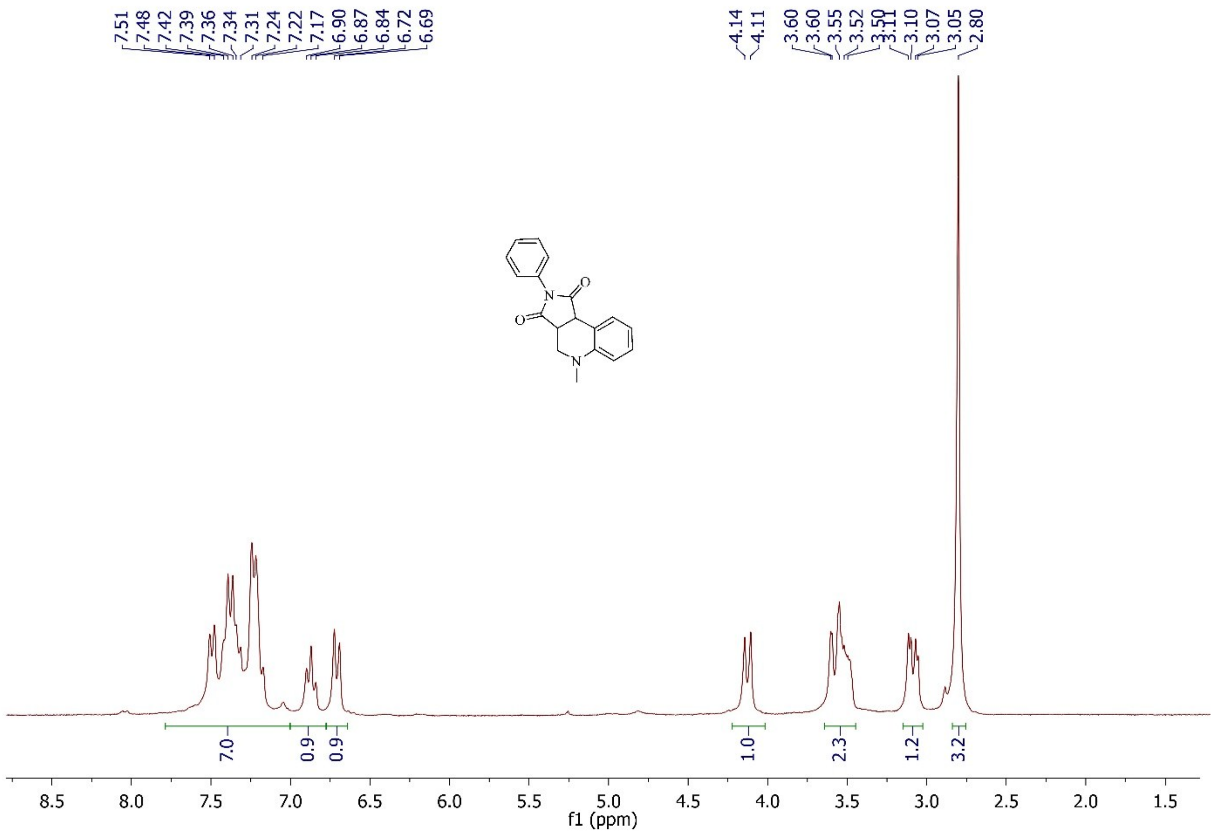
IR (KBr) ν_{max} 3038, 3052, 2965, 1644, 1609, 1567, 1579 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.35 (s, 3H), 2.37 (s, 3H), 3.20 (s, 3H), 3.98 (d, 2H, *J* = 7.2 Hz), 6.18 (t, 1H, *J* = 7.6 Hz), 6.79 (d, 1H, *J* = 7.6 Hz), 6.91 (d, 1H, *J* = 7.6 Hz), 7.15-7.21 (m,3H), 7.38 (t, 2H, *J* = 7.6 Hz). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 20.94, 21.50, 39.72, 48.31, 115.76, 122.83, 125.59, 125.77, 128.03, 128.60, 128.80, 129.25, 132.31, 134.79, 138.33, 145.44. Anal.Calcd for $C_{18}H_{19}N$: C 86.70, H 7.68, N 5.62. Found: C 86.75, H 7.76, N 5.49.

6-bromo-1-methyl-4-phenyl-1,2-dihydroquinoline (**7k**)

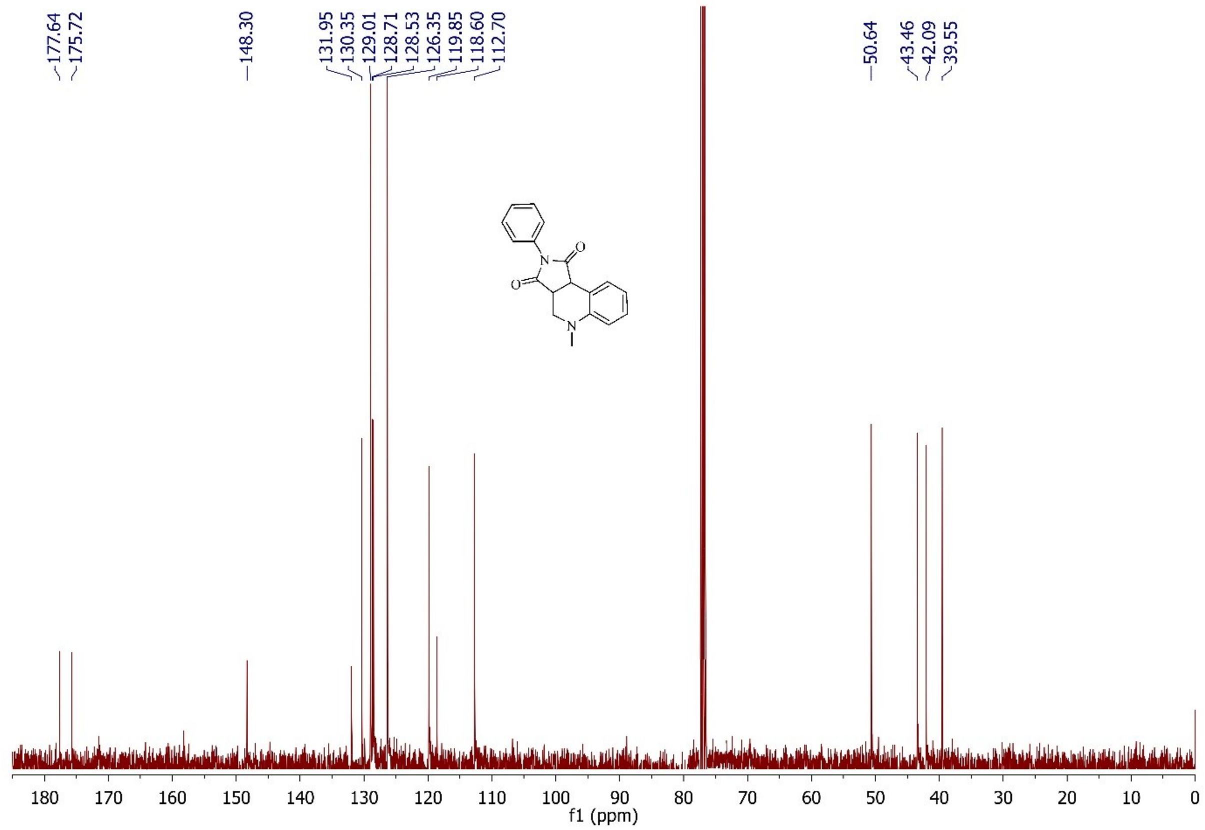
IR (KBr) ν_{max} 3029, 3011, 2975, 1638, 1624, 1592, 1575 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.93 (s, 3H), 3.89 (d, 2H, *J* = 8.8 Hz), 5.87 (t, 1H, *J* = 8.8 Hz), 6.40 (d, 1H, *J* = 8.8 Hz), 7.04 (dd, 1H, *J* = 6.0, 3.2 Hz), 7.12 (t, 1H, *J* = 8.4 Hz), 7.20-7.27 (m, 2H) 7.45-7.54 (m, 3H). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 42.54, 50.74, 115.02, 118.67, 124.93, 126.85, 127.75, 128.49, 128.86, 129.55, 130.82, 134.42, 134.93, 147.02. Anal.Calcd for $C_{16}H_{14}BrN$: C 64.02, H 4.70, N 4.67. Found: C 64.11, H 4.64, N 4.60.

6-bromo-1-methyl-4-(p-tolyl)-1,2-dihydroquinoline (**7l**)

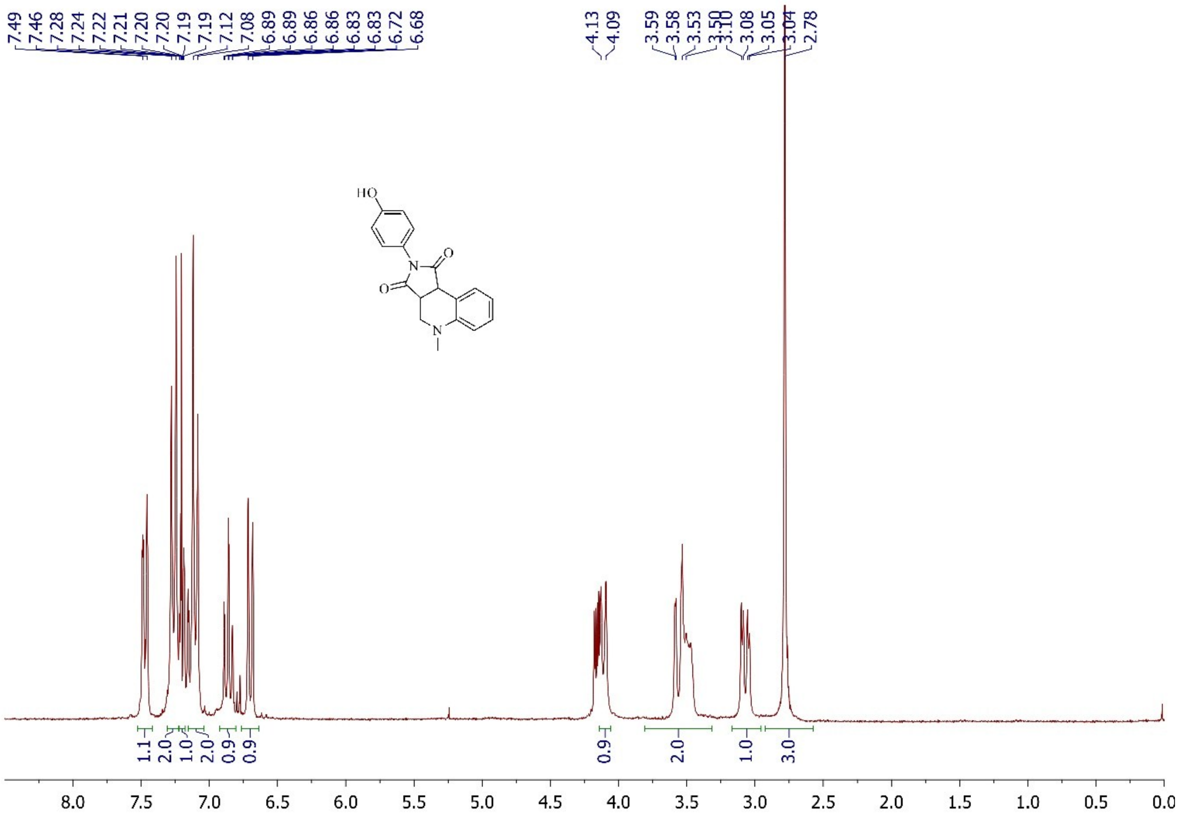
IR (KBr) ν_{max} 3045, 3030, 2969, 1632, 1614, 1587, 1573 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$) δ(ppm); 2.37 (s, 3H), 3.20 (s, 3H), 4.07 (d, 2H, *J* = 8.8 Hz), 6.13 (t, 1H, *J* = 8.8 Hz), 6.64 (d, 1H, *J* = 8.0 Hz), 7.14-7.23 (m, 3H), 7.39 (d, 2H, *J* = 8.0 Hz), 7.68 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$), δ(ppm); 22.46, 42.77, 49.92, 115.22, 118.82, 123.54, 125.97, 128.90, 129.87, 130.25, 131.55, 133.21, 135.63, 39.14, 146.98. Anal.Calcd for $C_{17}H_{16}BrN$: C 64.98, H 5.13, N 4.46. Found: C 64.88, H 5.17, N 4.51.



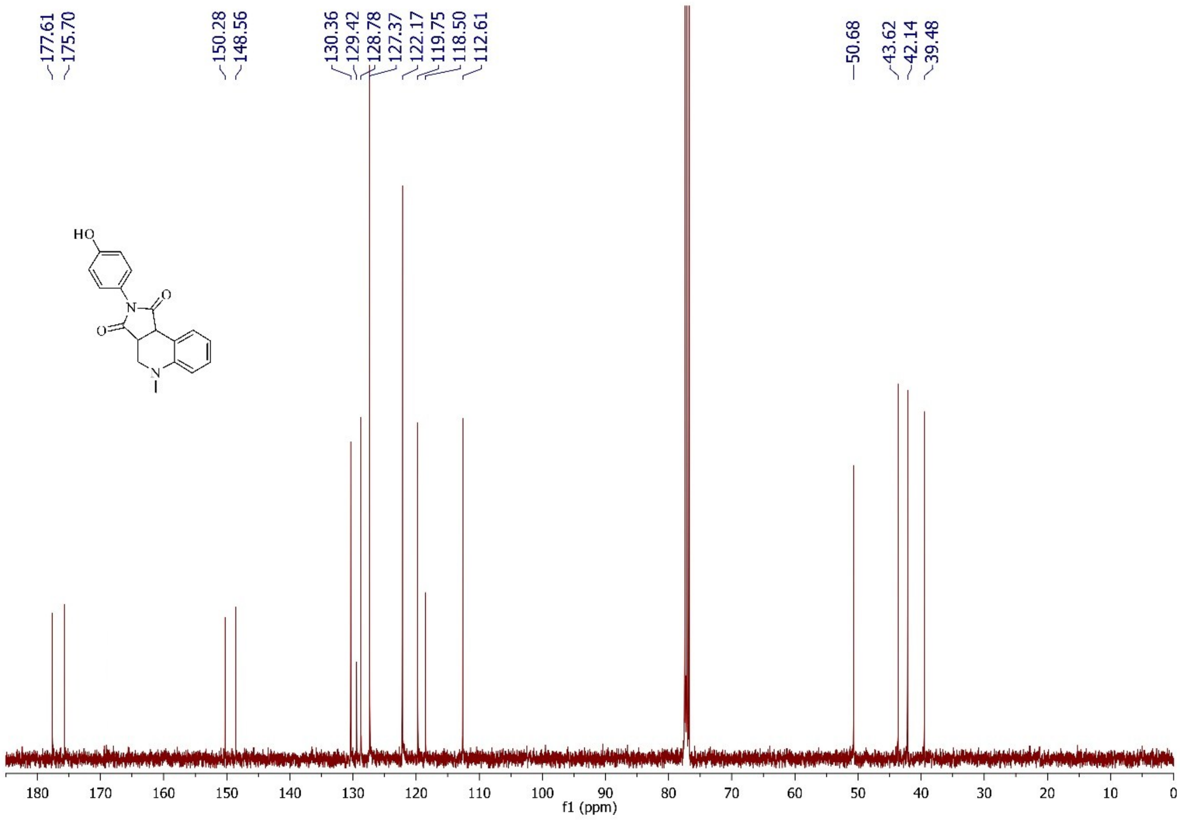
^{1}HNMR 3a



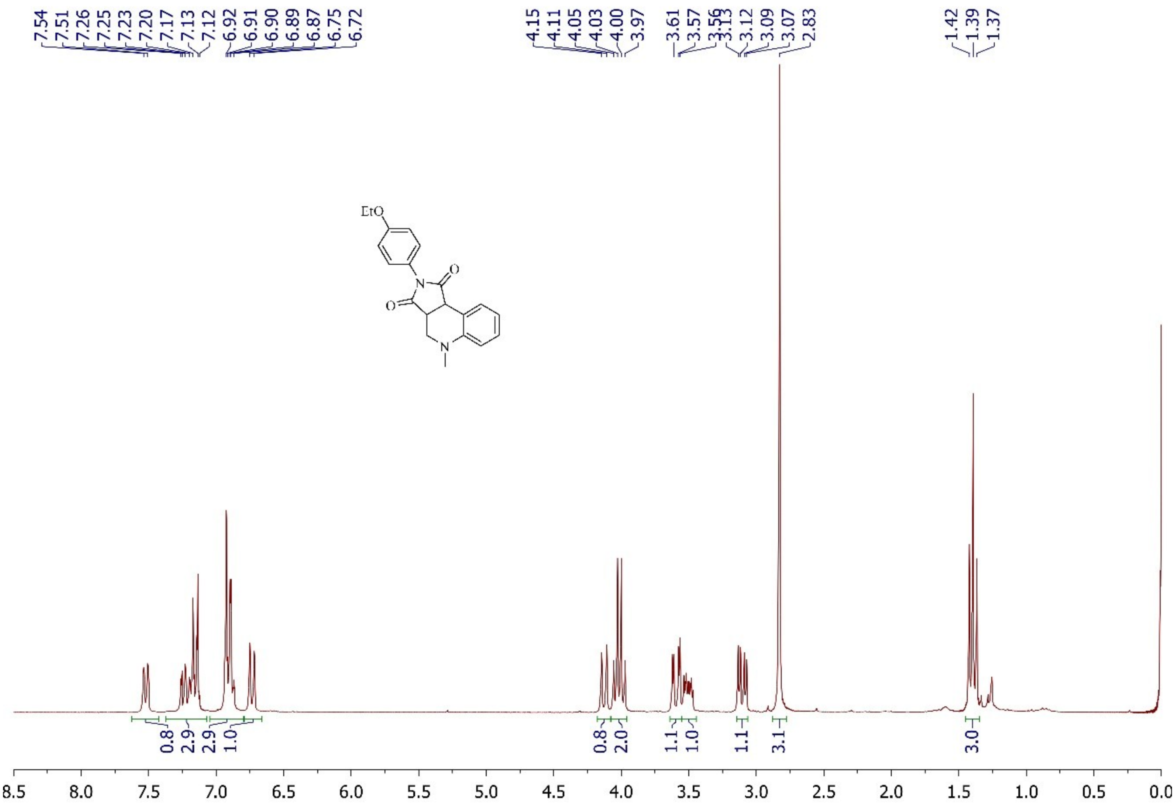
^{13}CNMR 3a



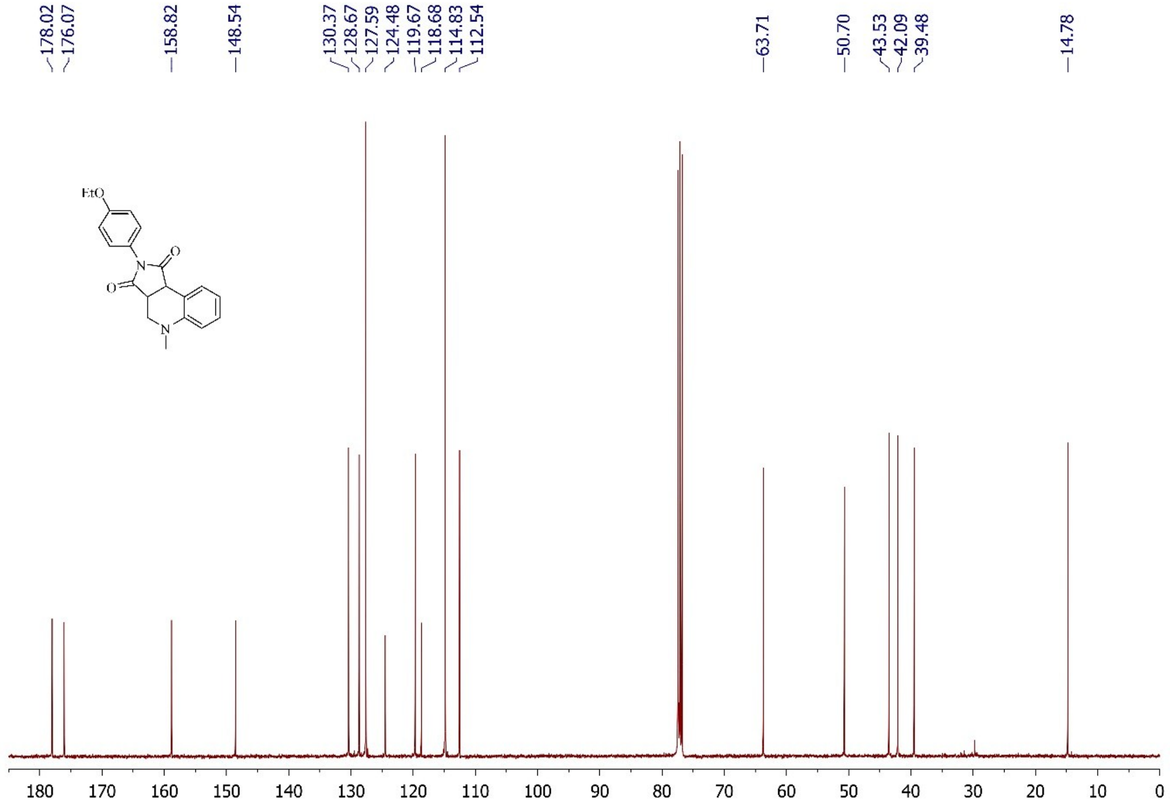
[1]HNMR 3b



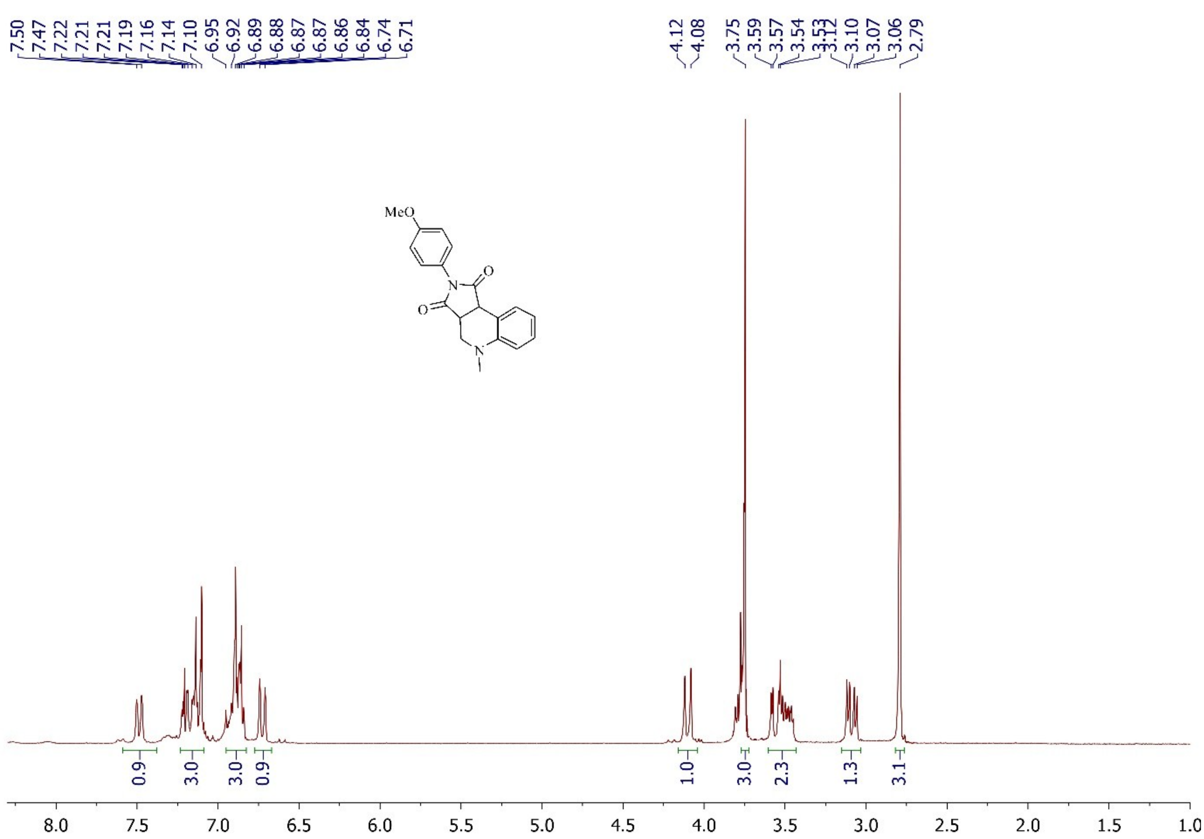
[13]CNMR 3b



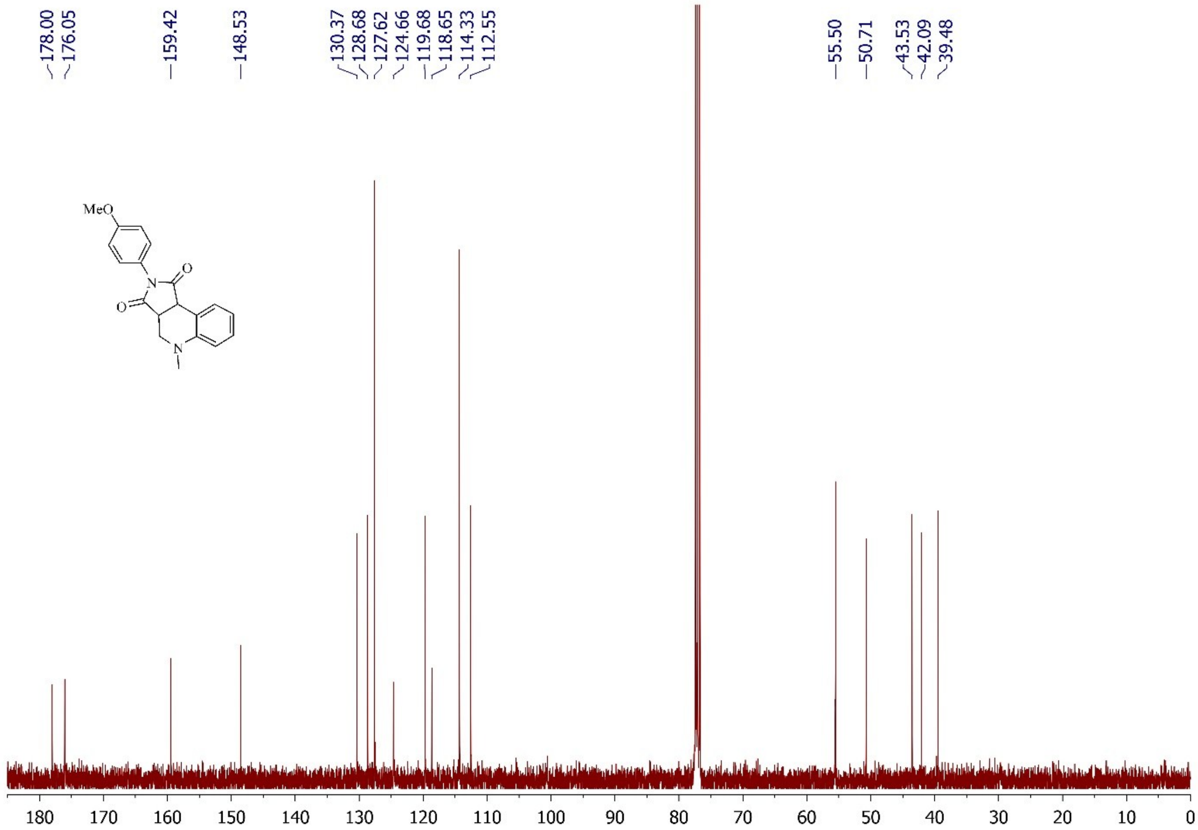
^{1}HNMR 3c



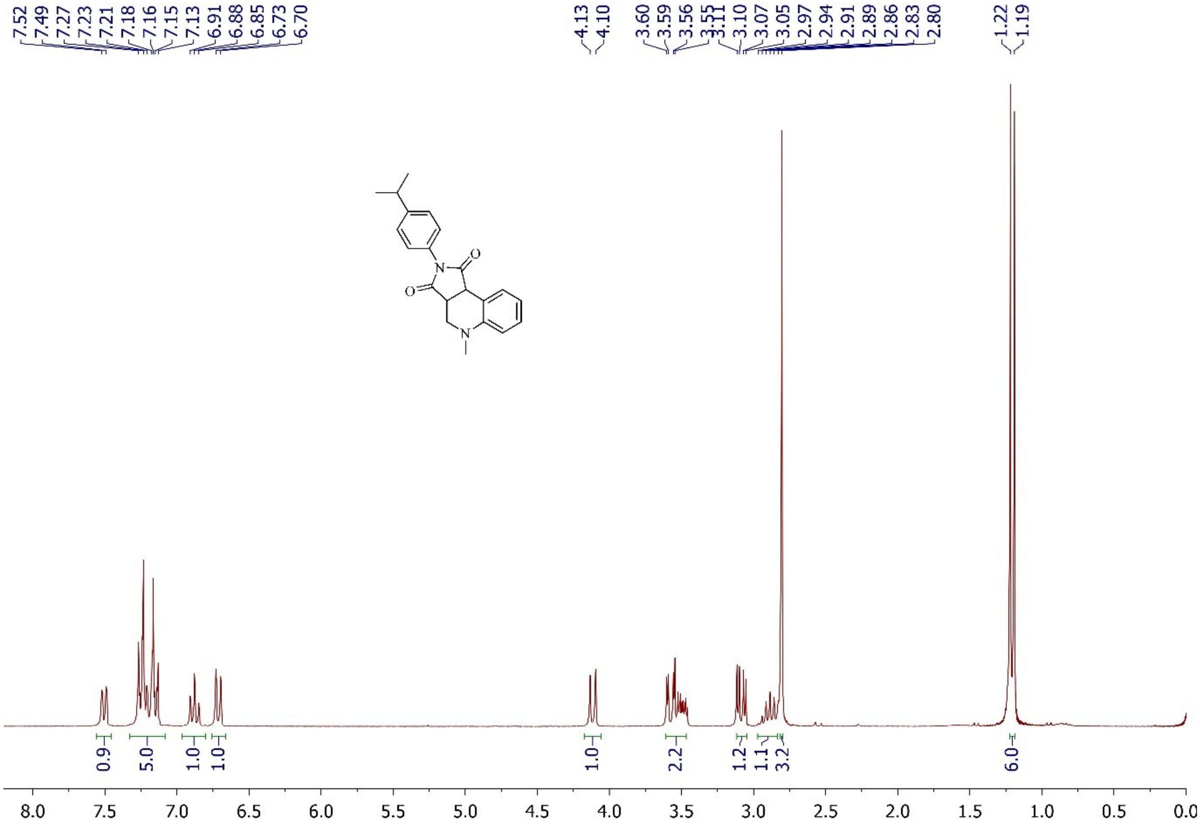
^{13}CNMR 3c



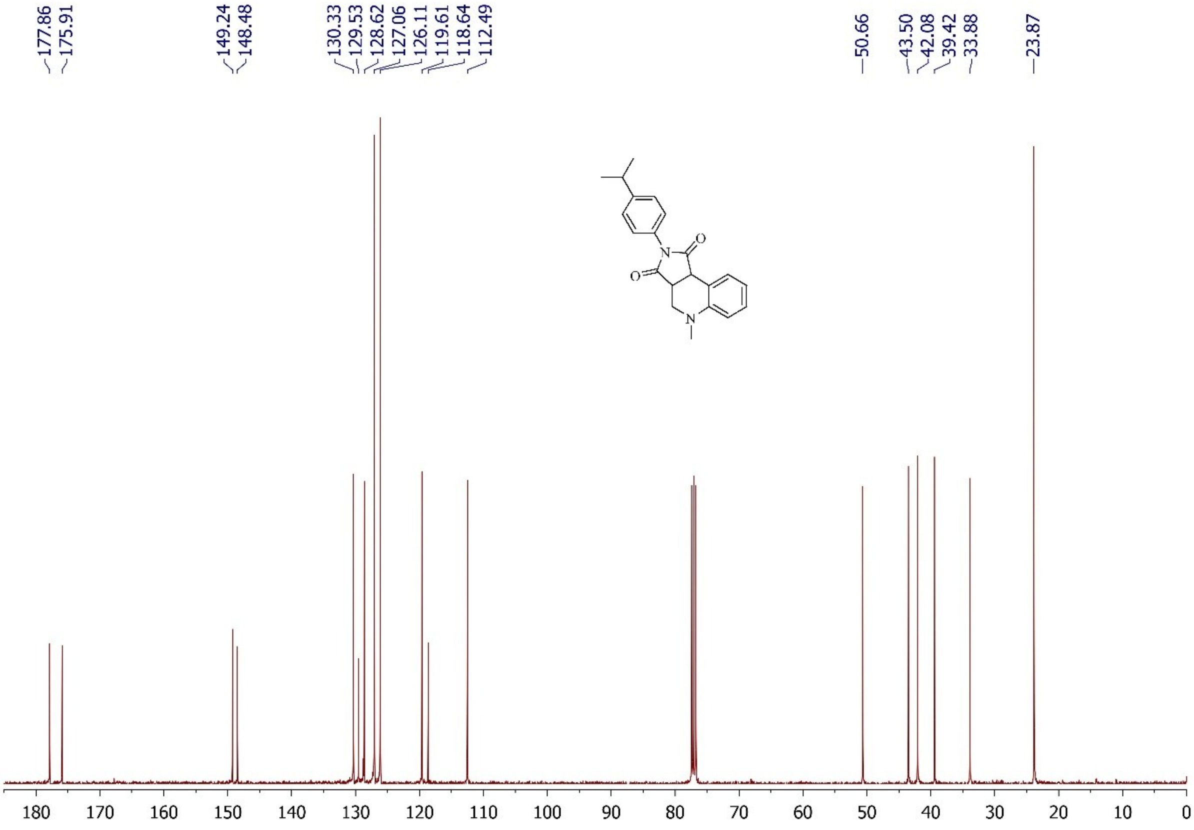
^{1}HNMR 3d



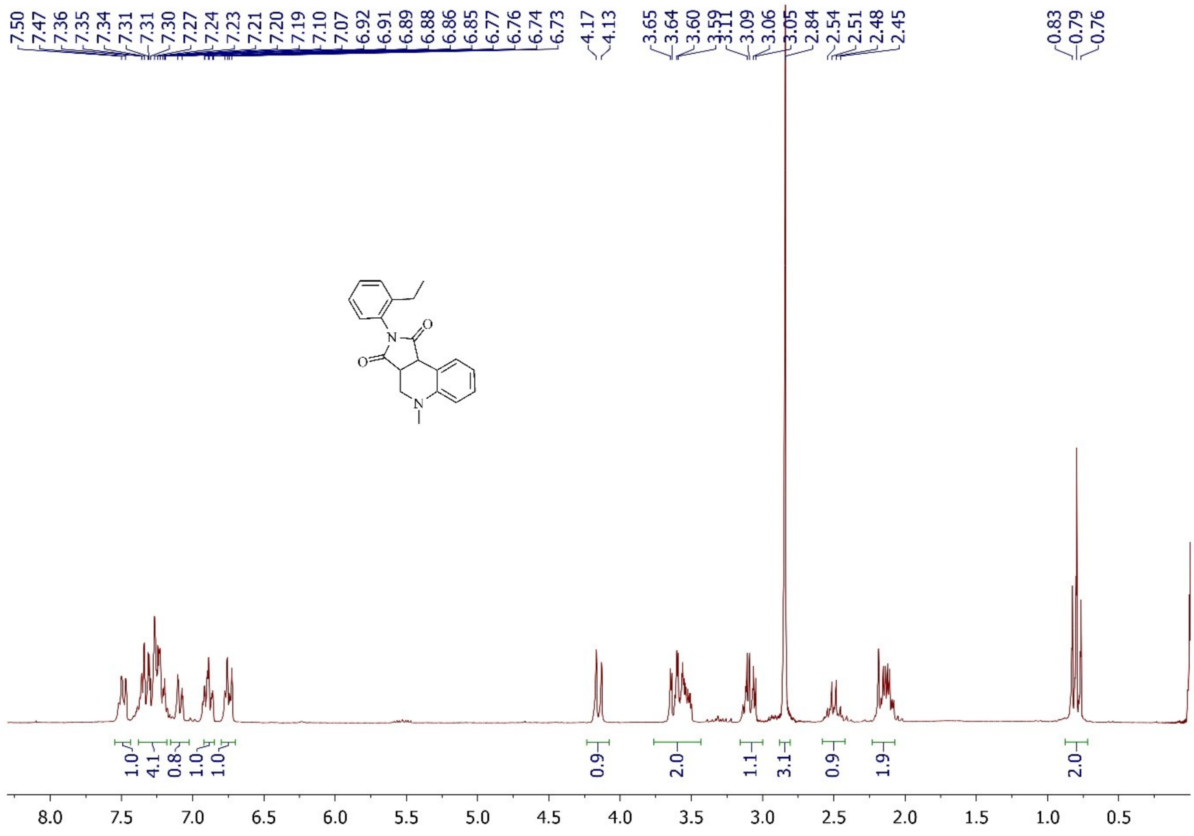
^{13}CNMR 3d



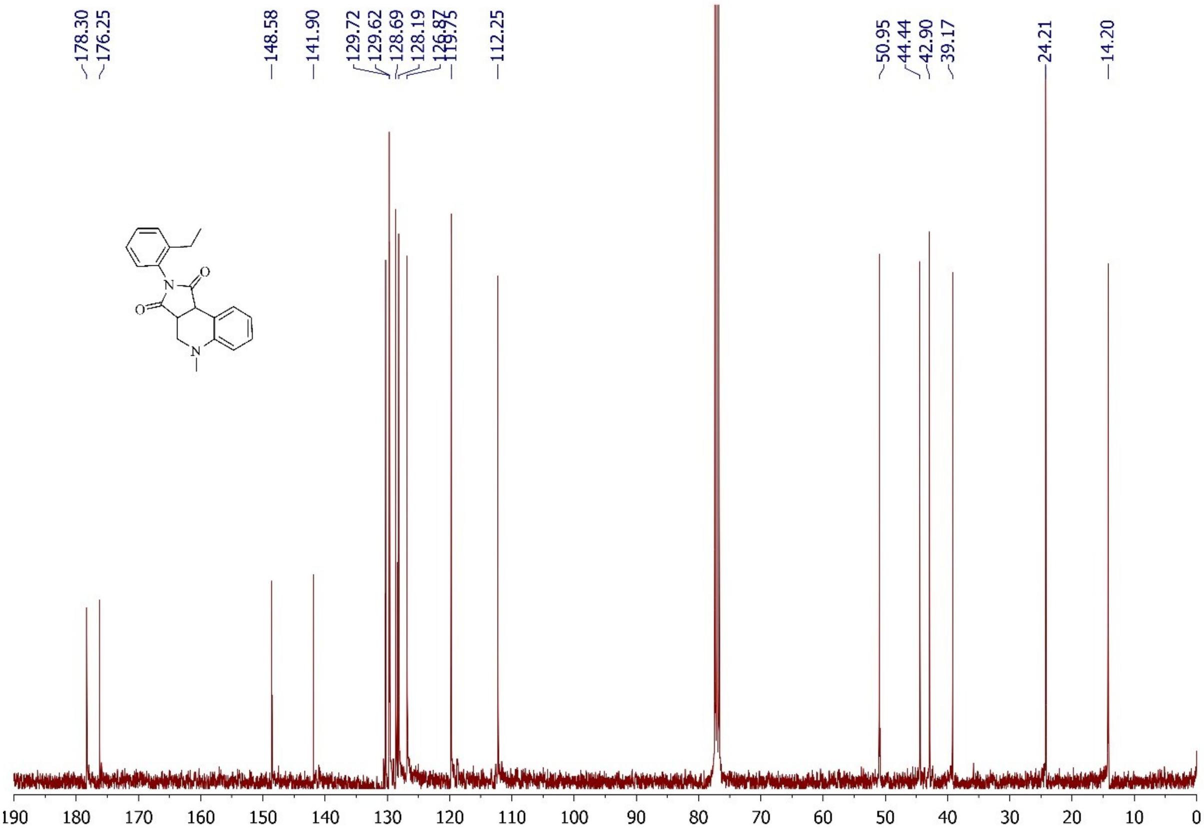
^{1}HNMR 3e



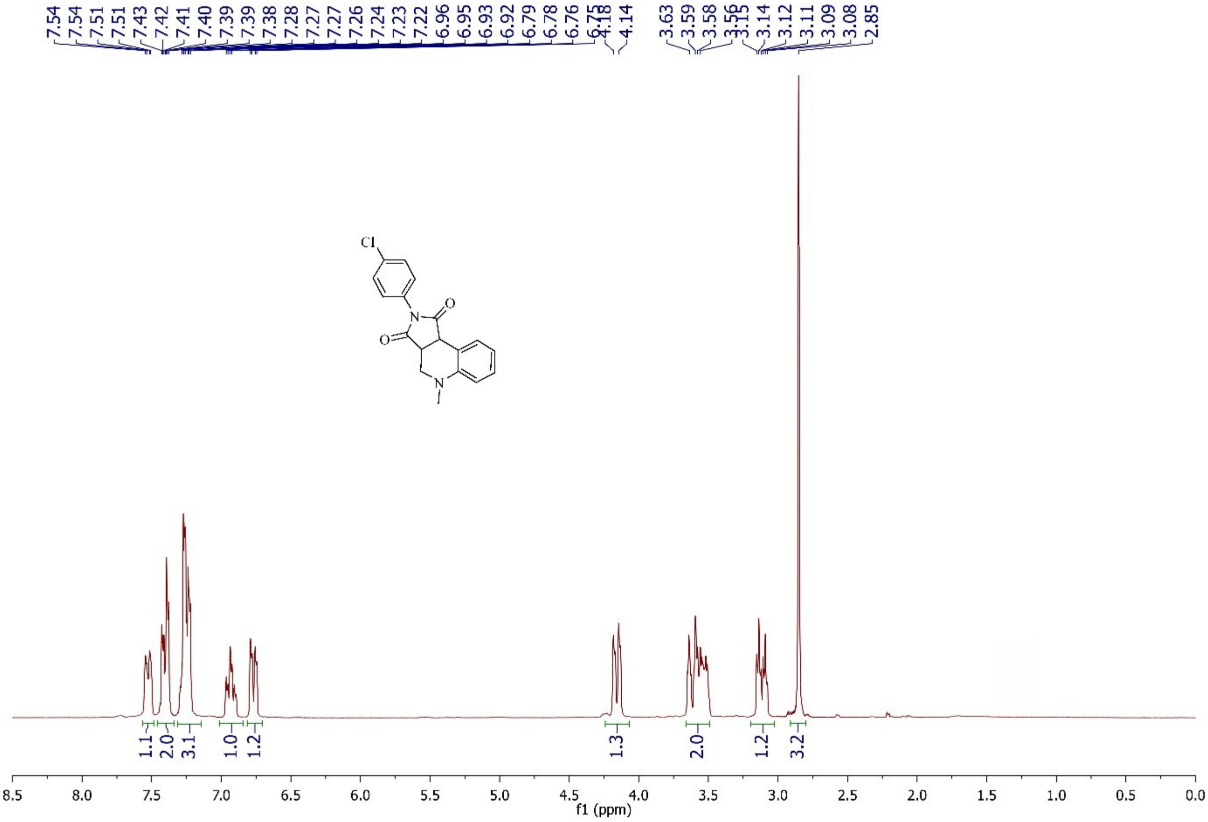
^{13}CNMR 3e



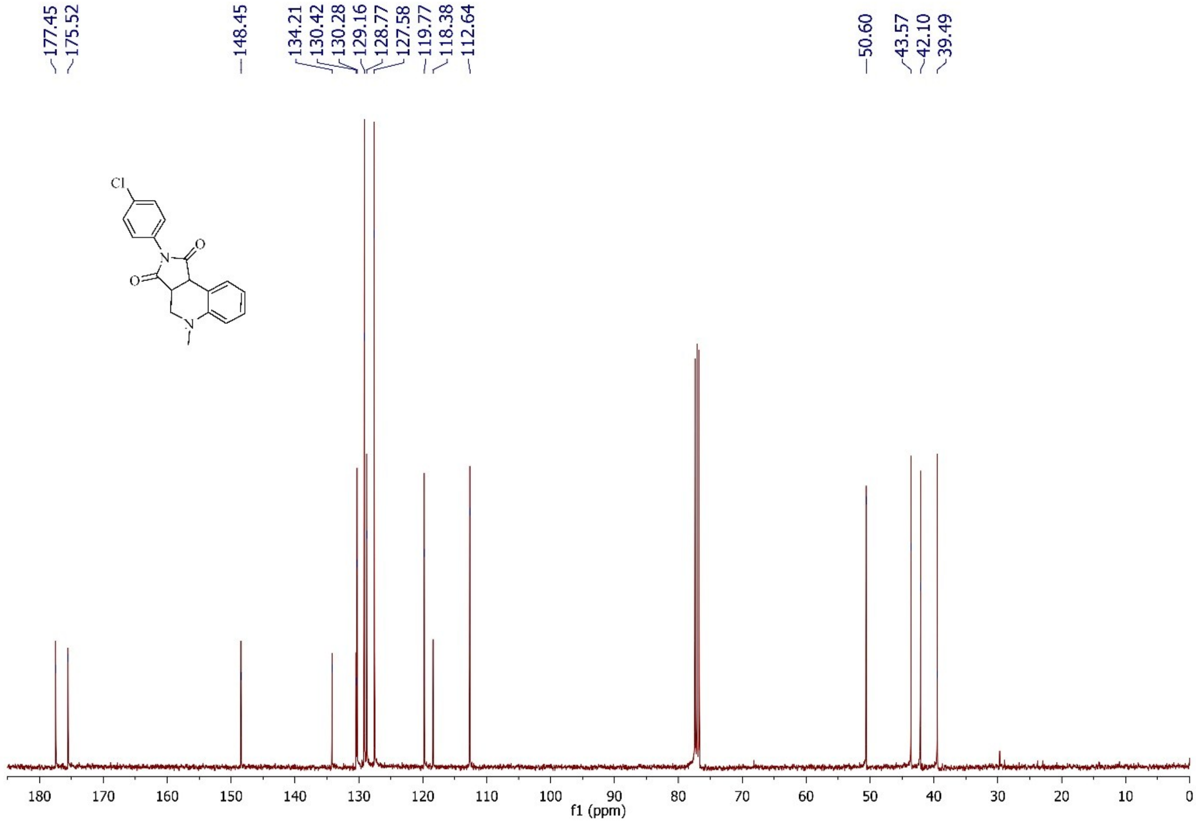
^{1}HNMR 3f



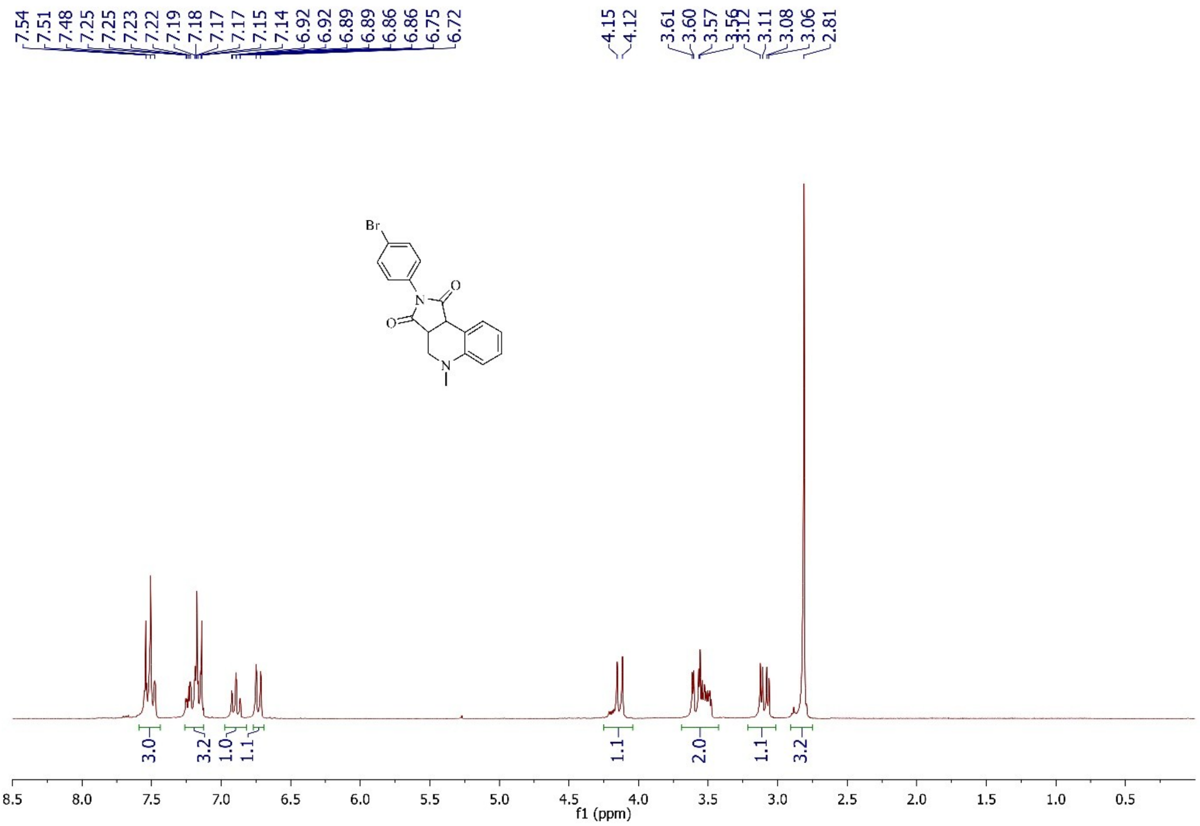
^{13}CNMR 3f



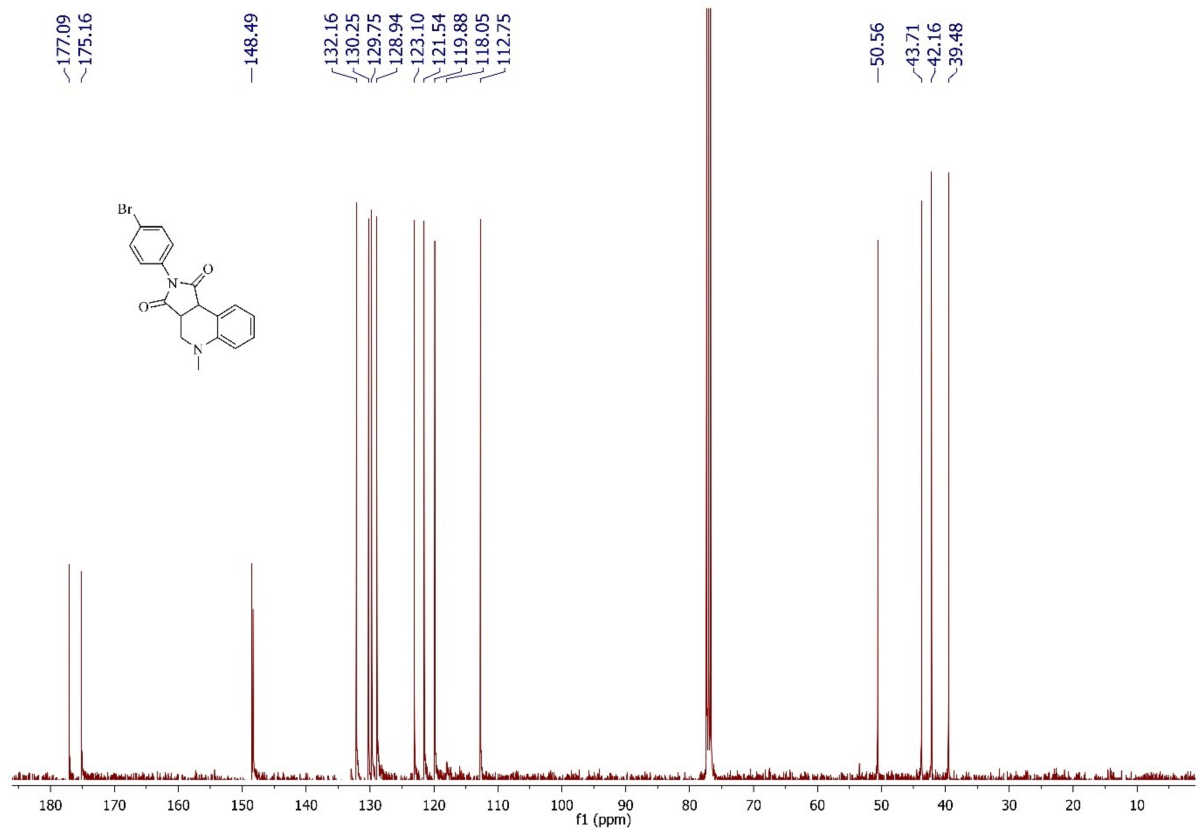
[1]HNMR 3g



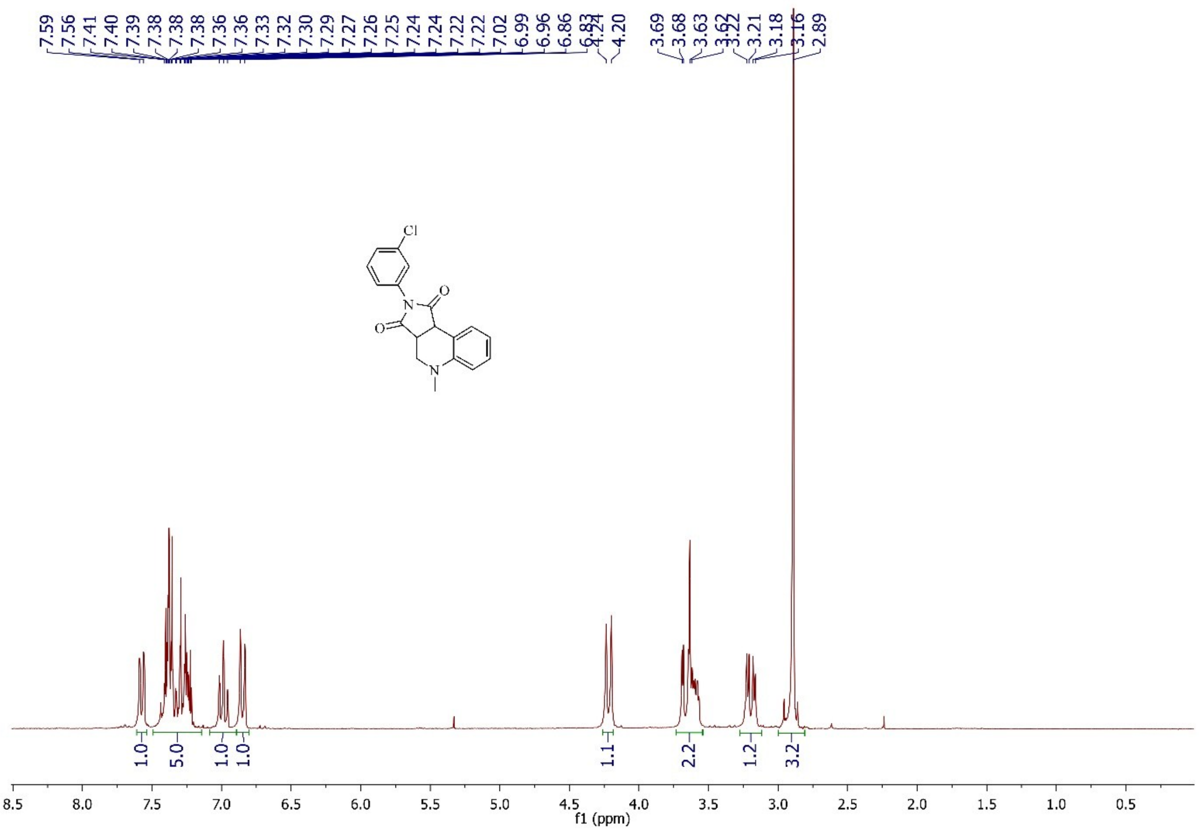
[13]CNMR 3g



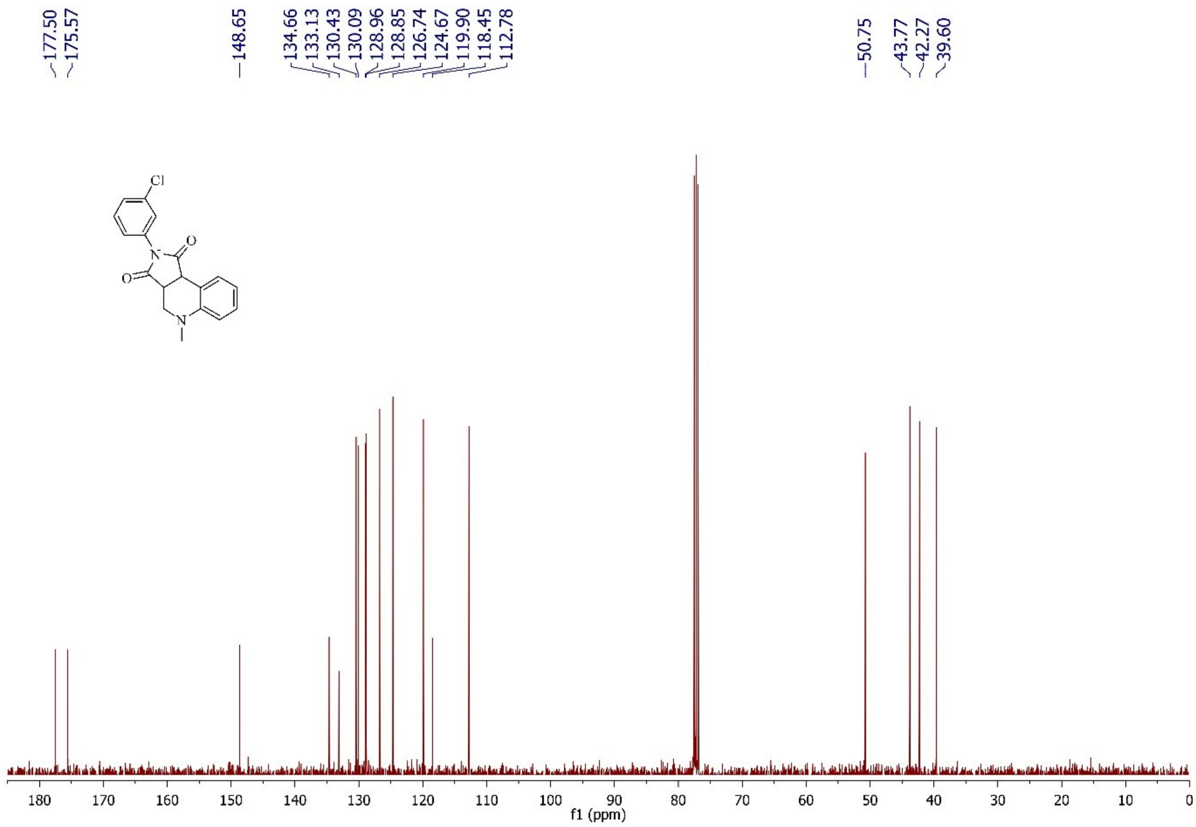
[1]HNMR 3h



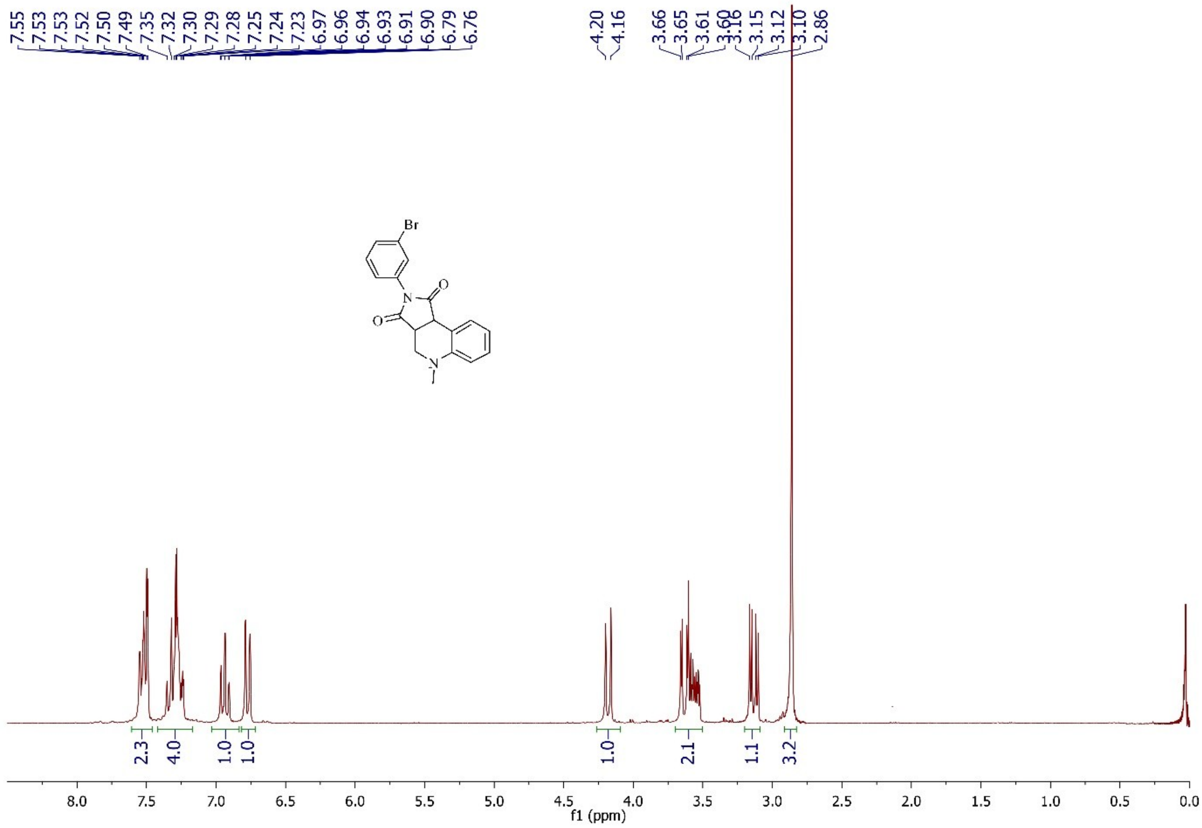
[13]CNMR 3h



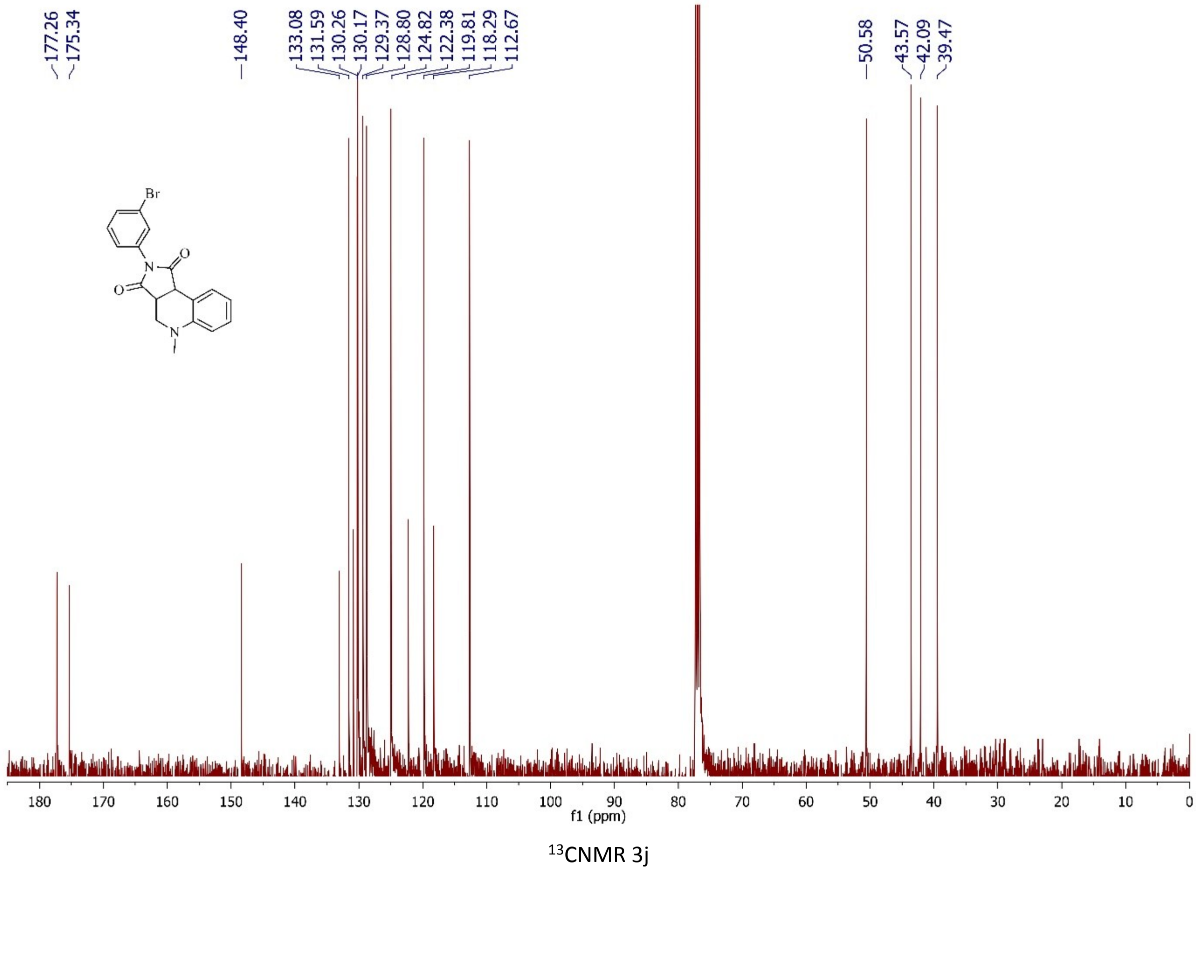
^{1}HNMR 3i



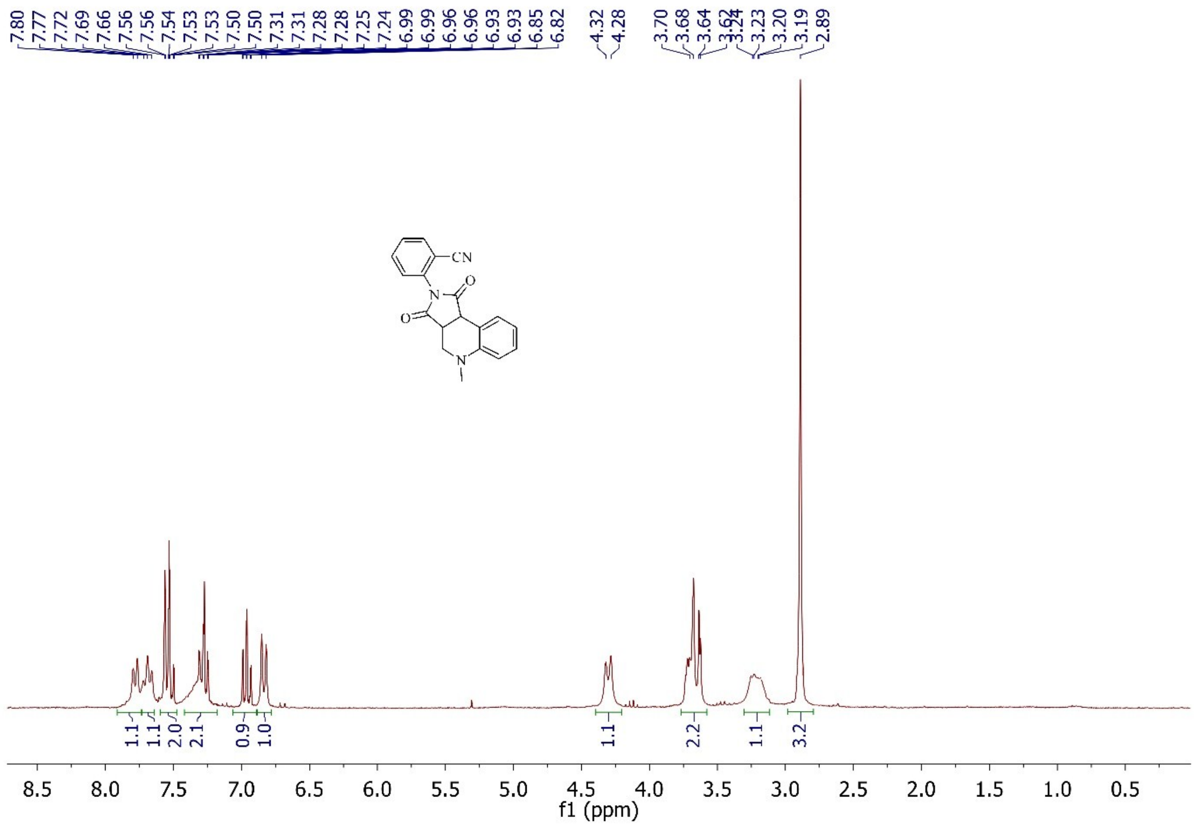
^{13}CNMR 3i



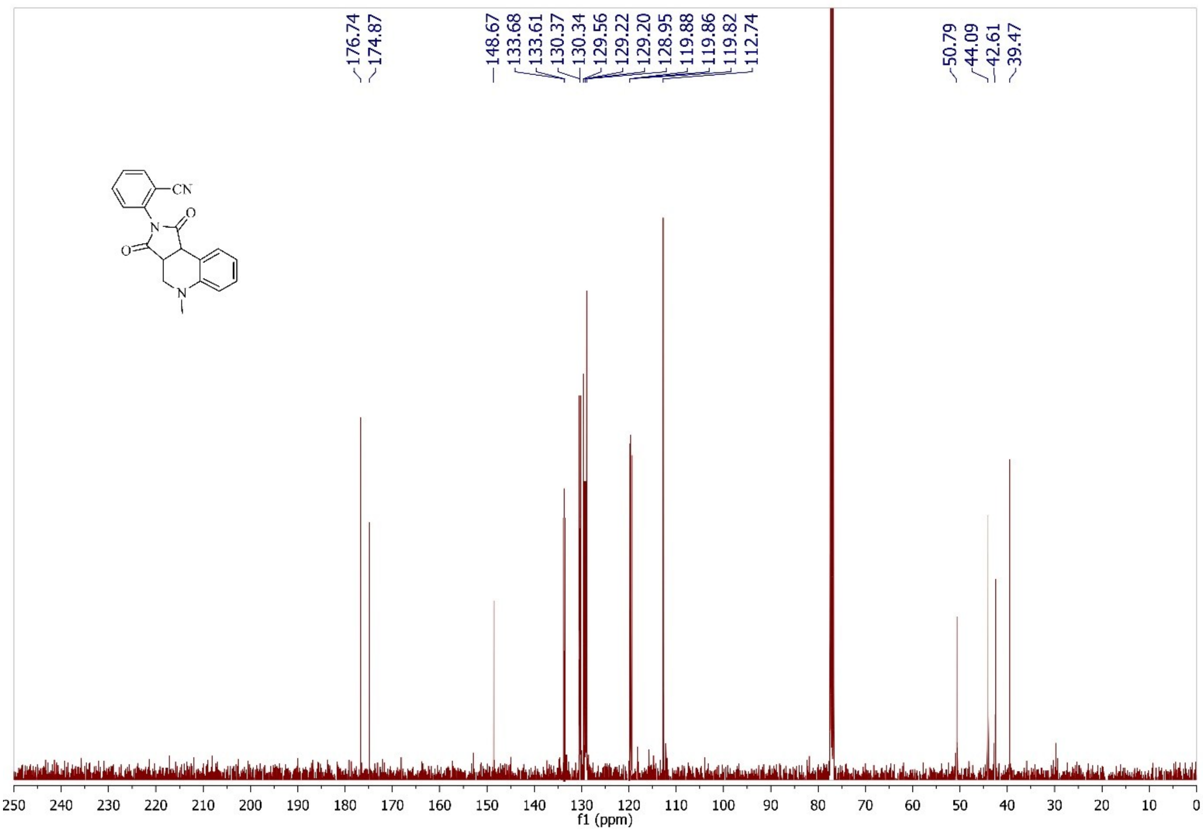
^{1}HNMR 3j



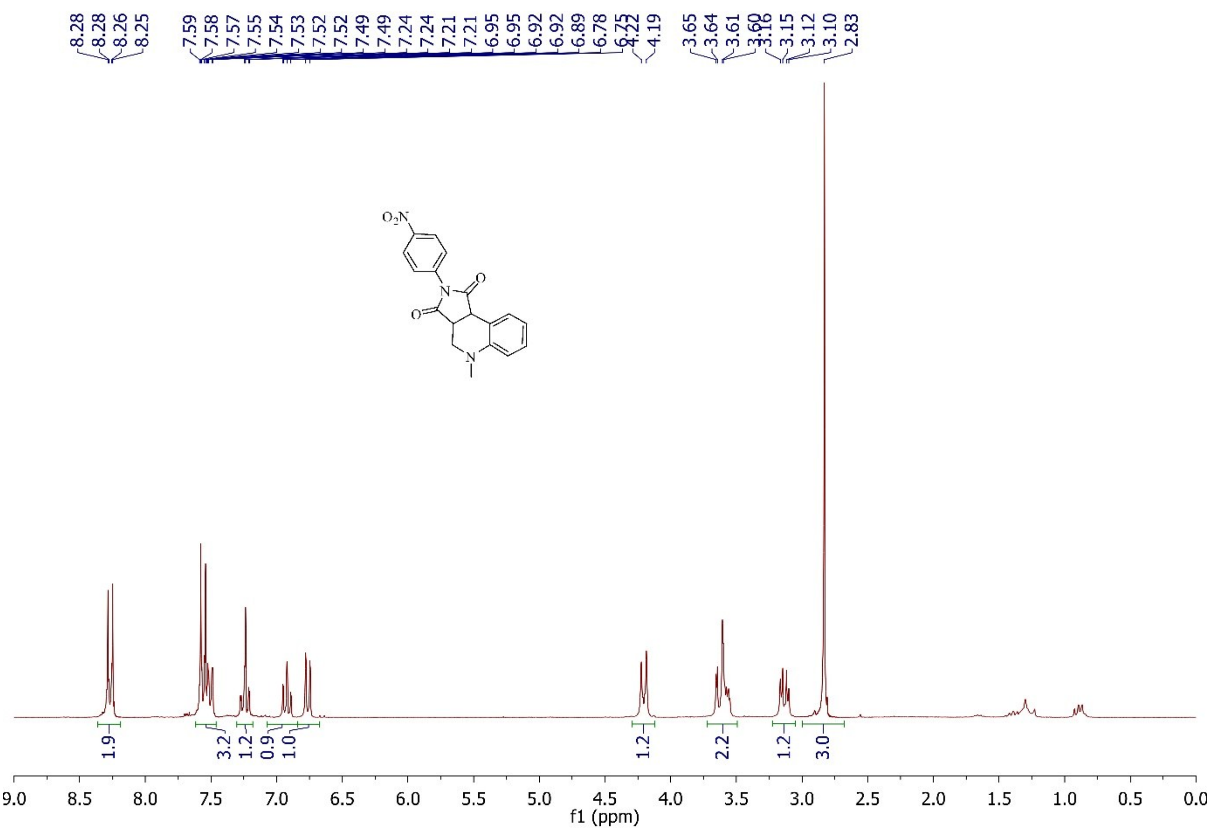
^{13}CNMR 3j



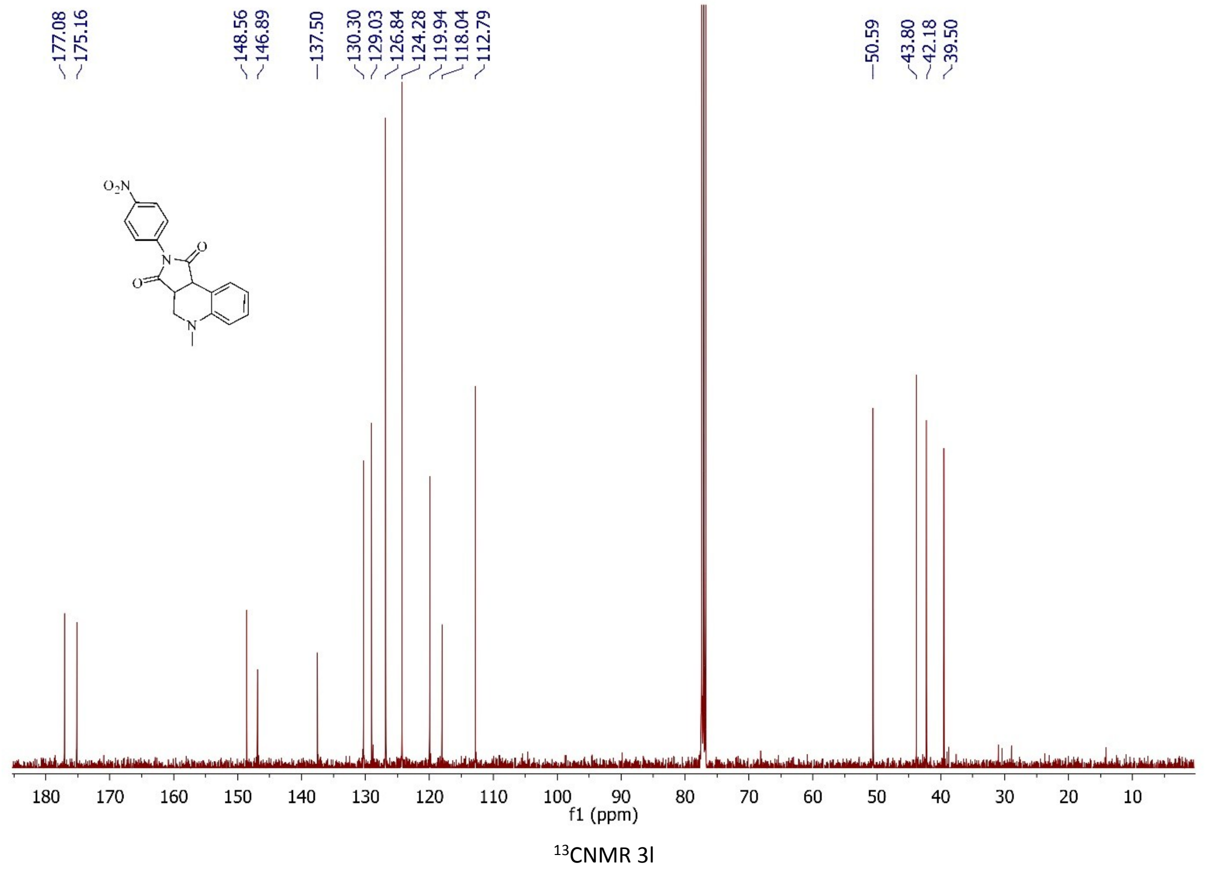
^{1}HNMR 3k



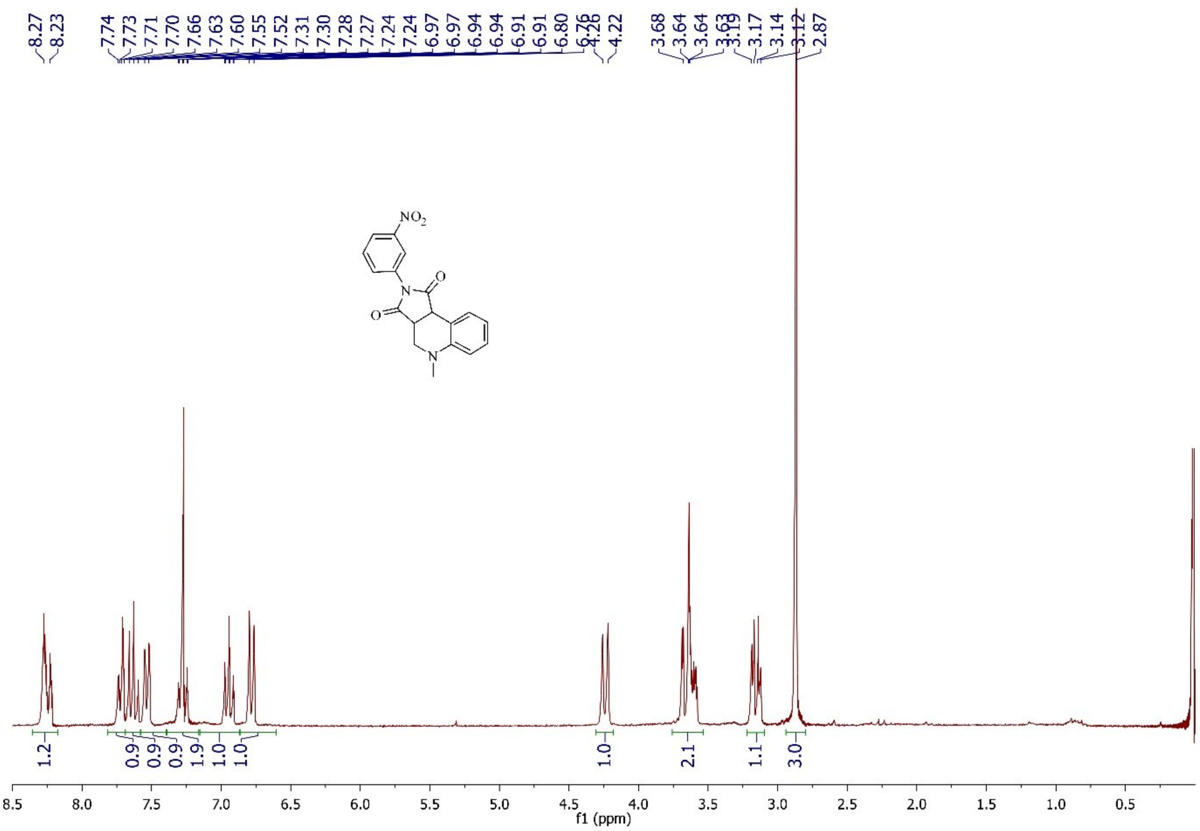
^{13}CNMR 3k



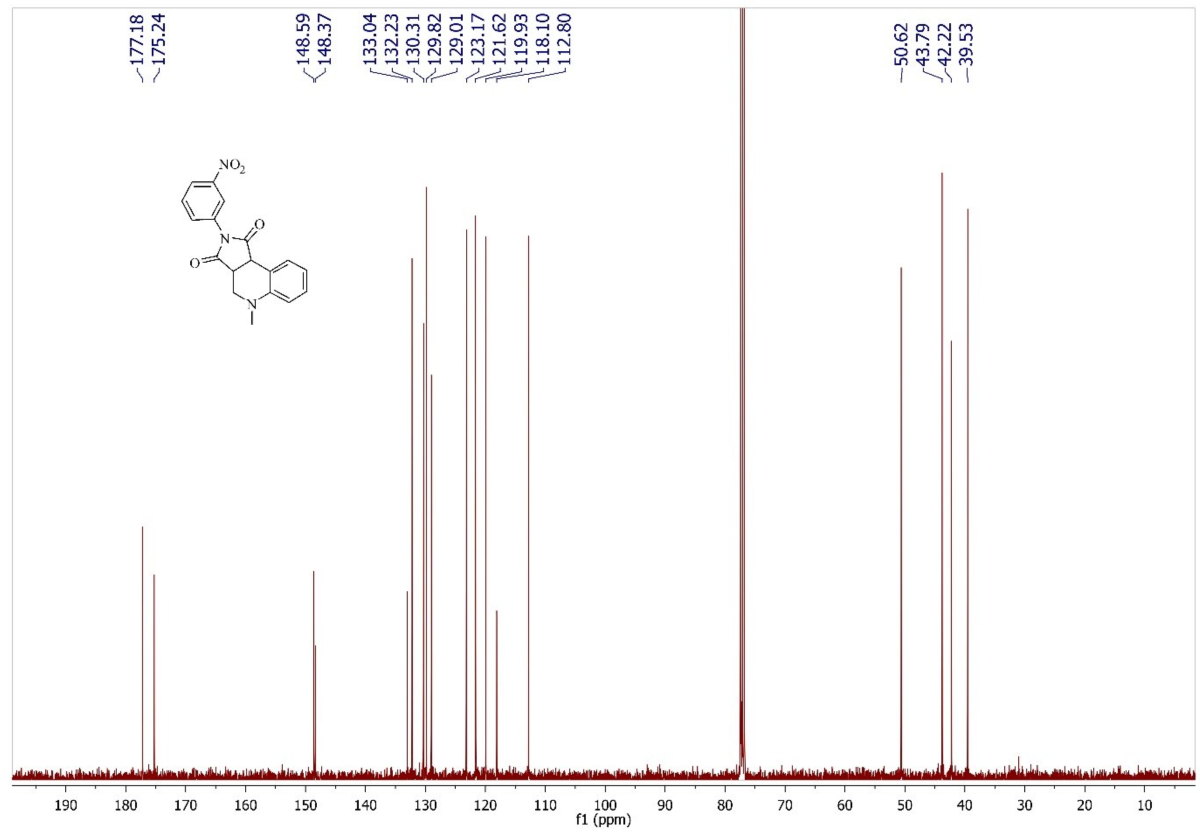
^{1}HNMR 3l



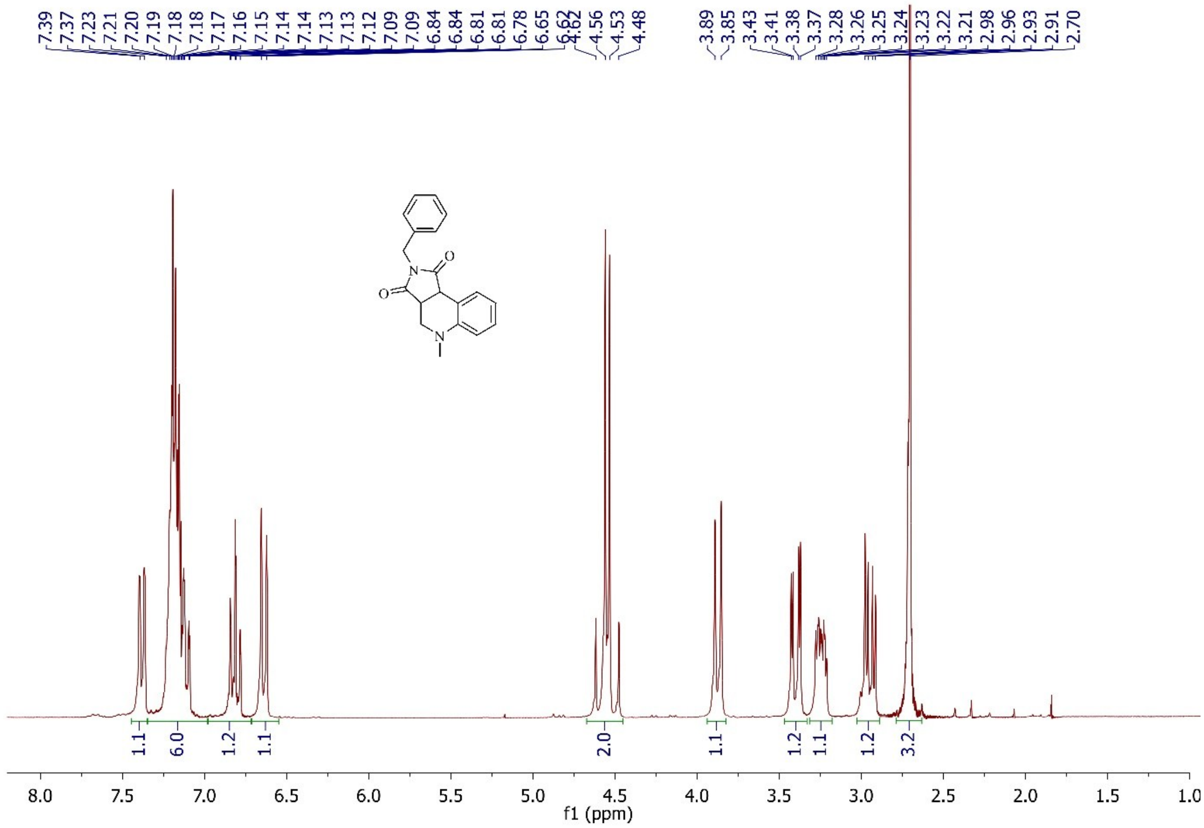
^{13}CNMR 3l



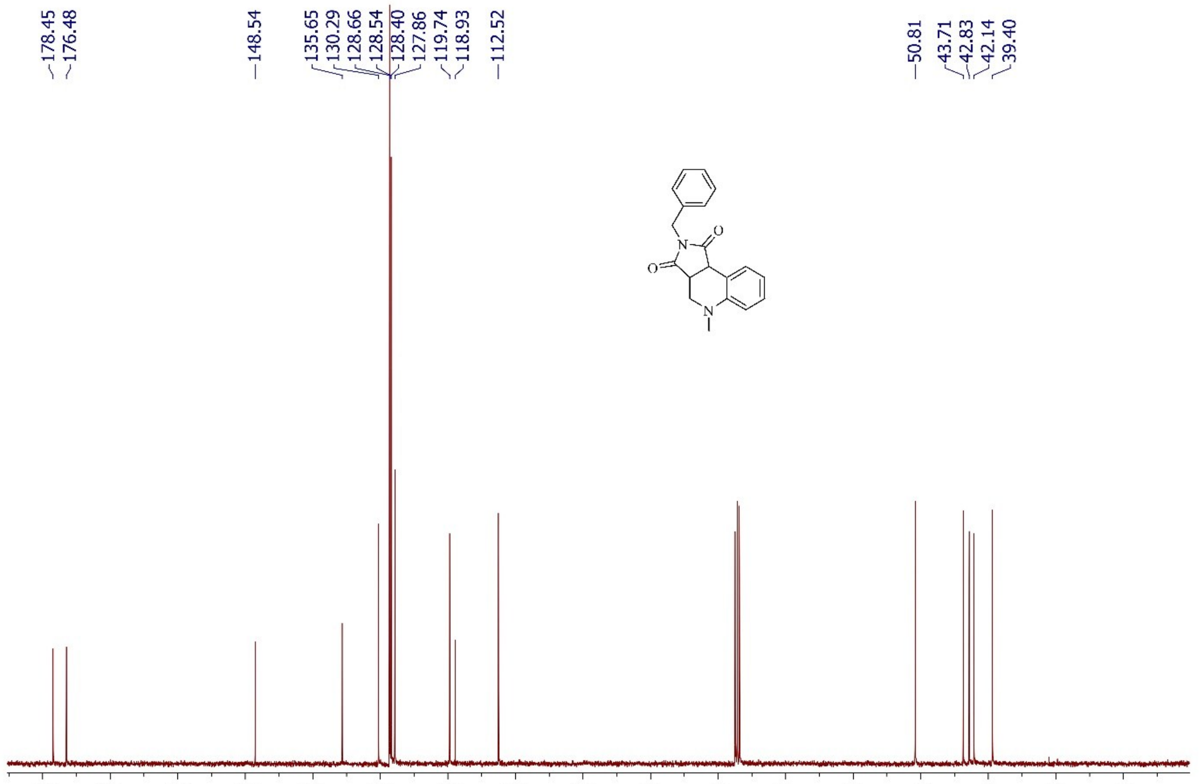
^{1}HNMR 3m



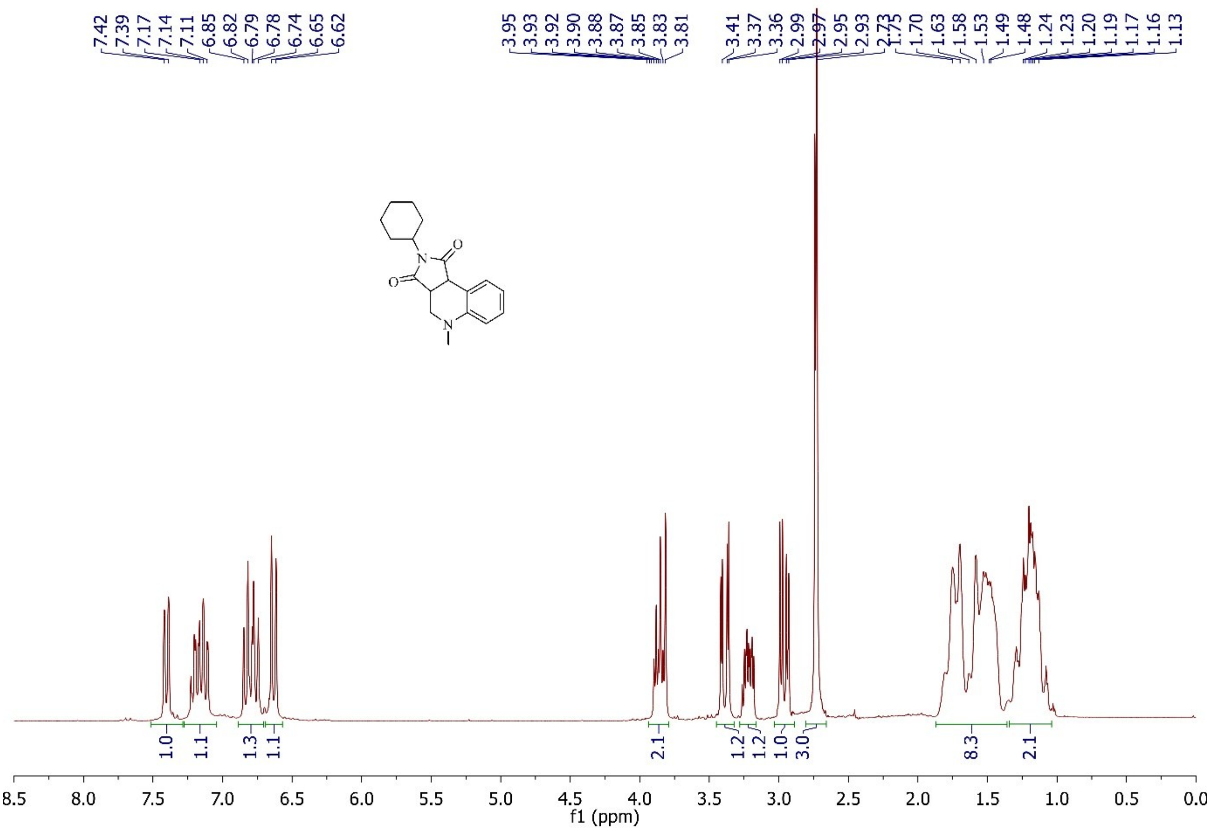
^{13}CNMR 3m



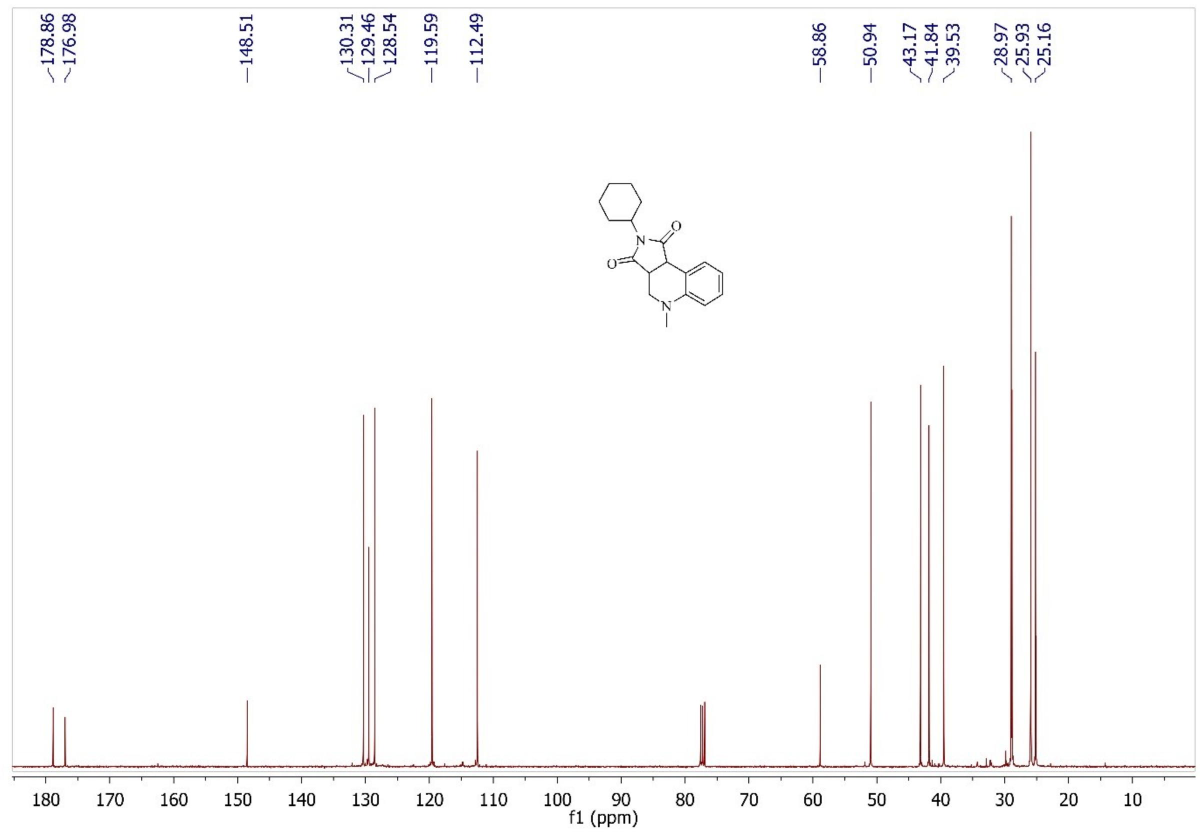
^{1}HNMR 3n



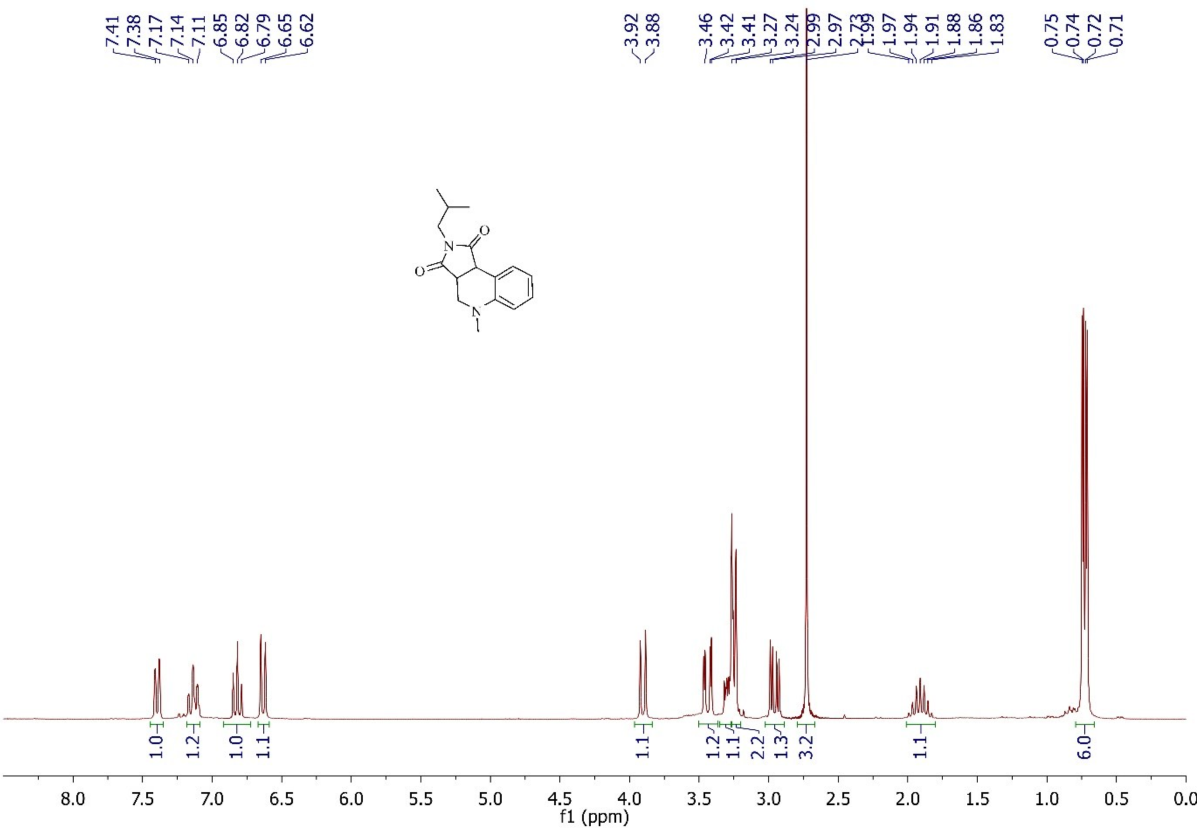
^{13}CNMR 3n



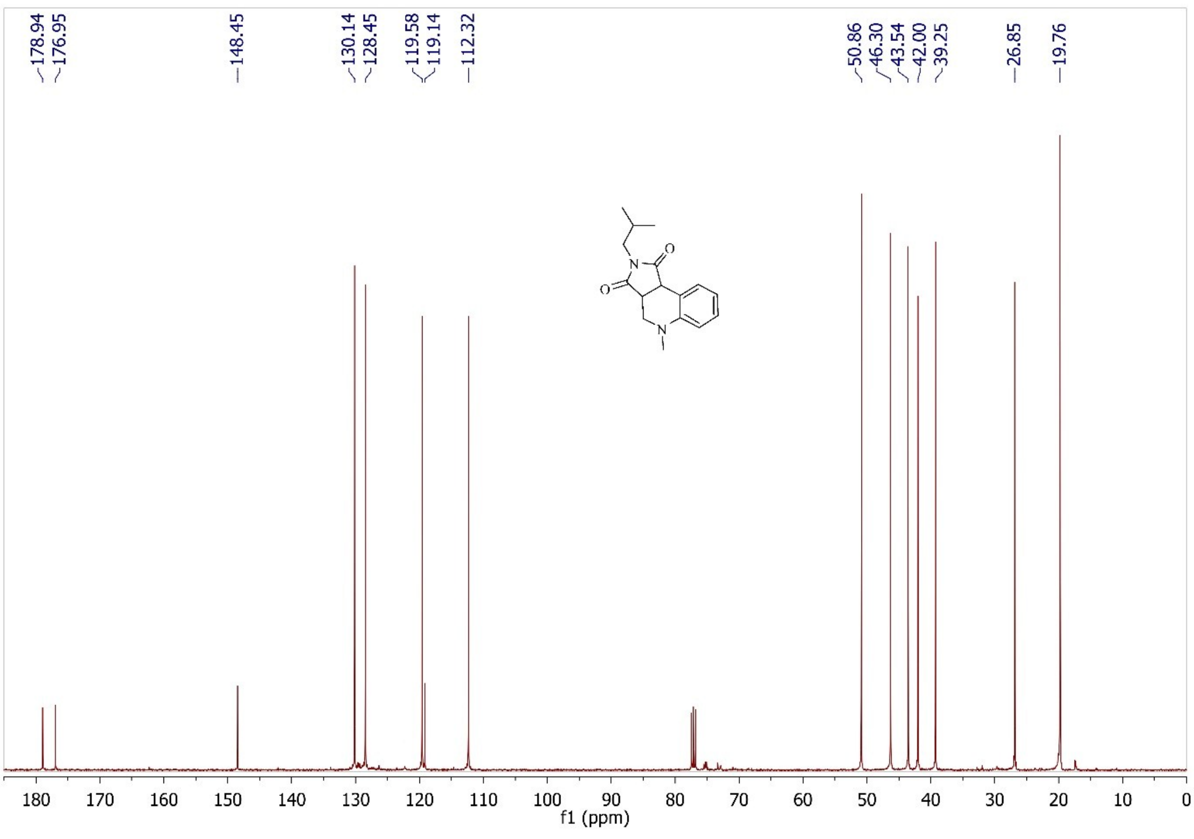
^{1}HNMR 3o



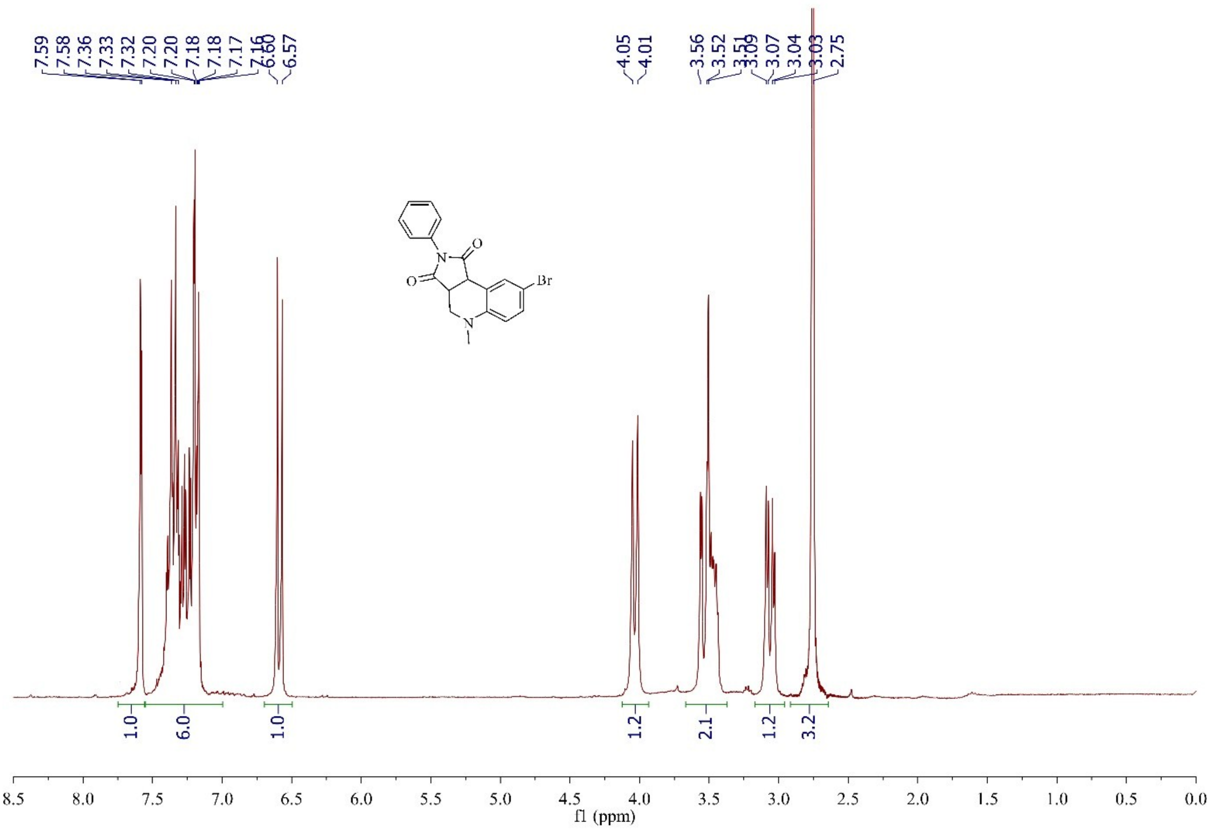
^{13}CNMR 3o



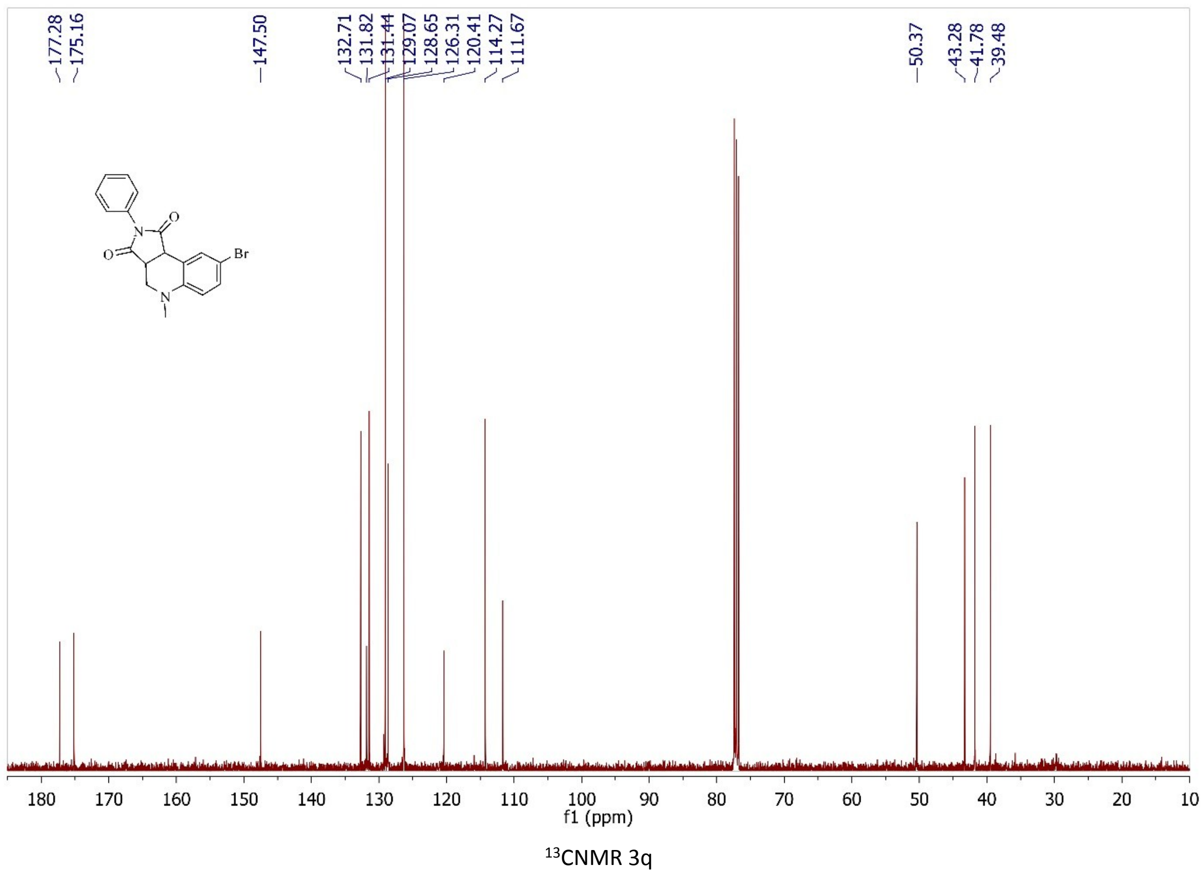
^{1}HNMR 3p



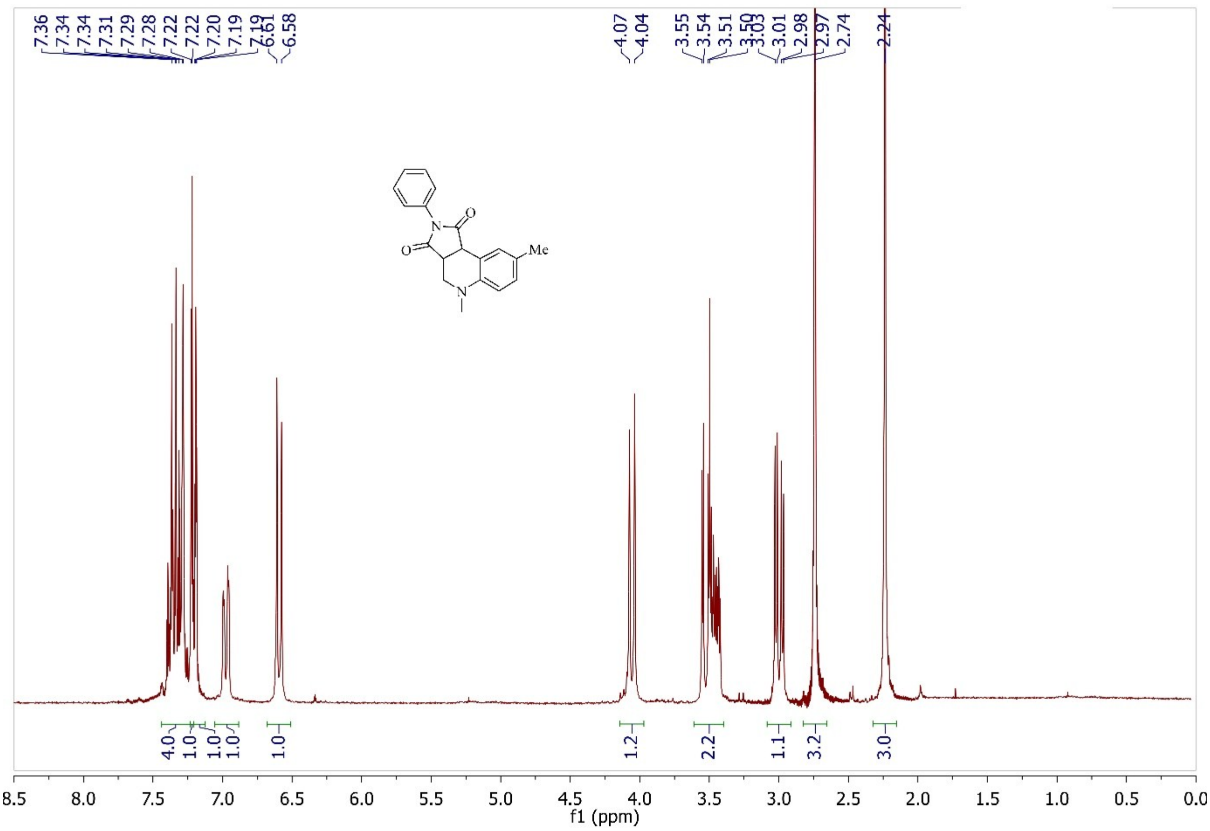
^{13}CNMR 3p



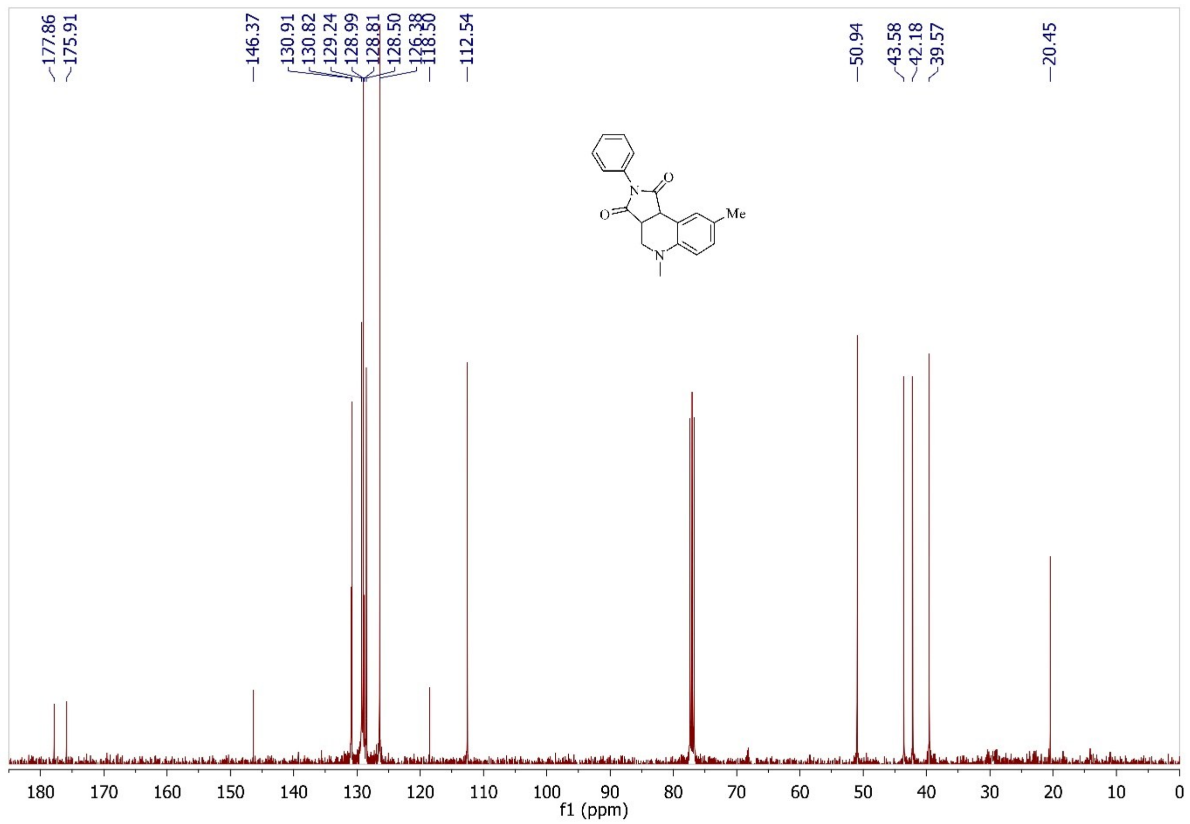
^{1}HNMR 3q



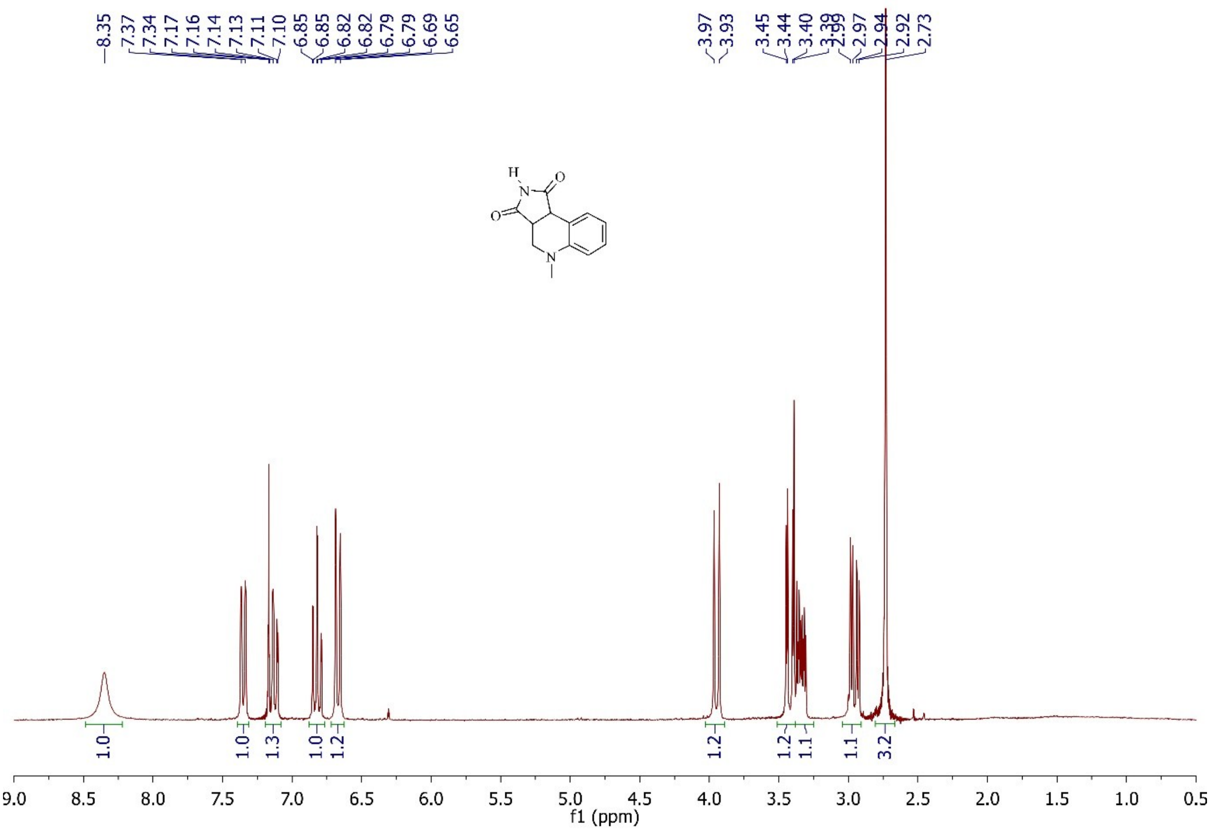
^{13}CNMR 3q



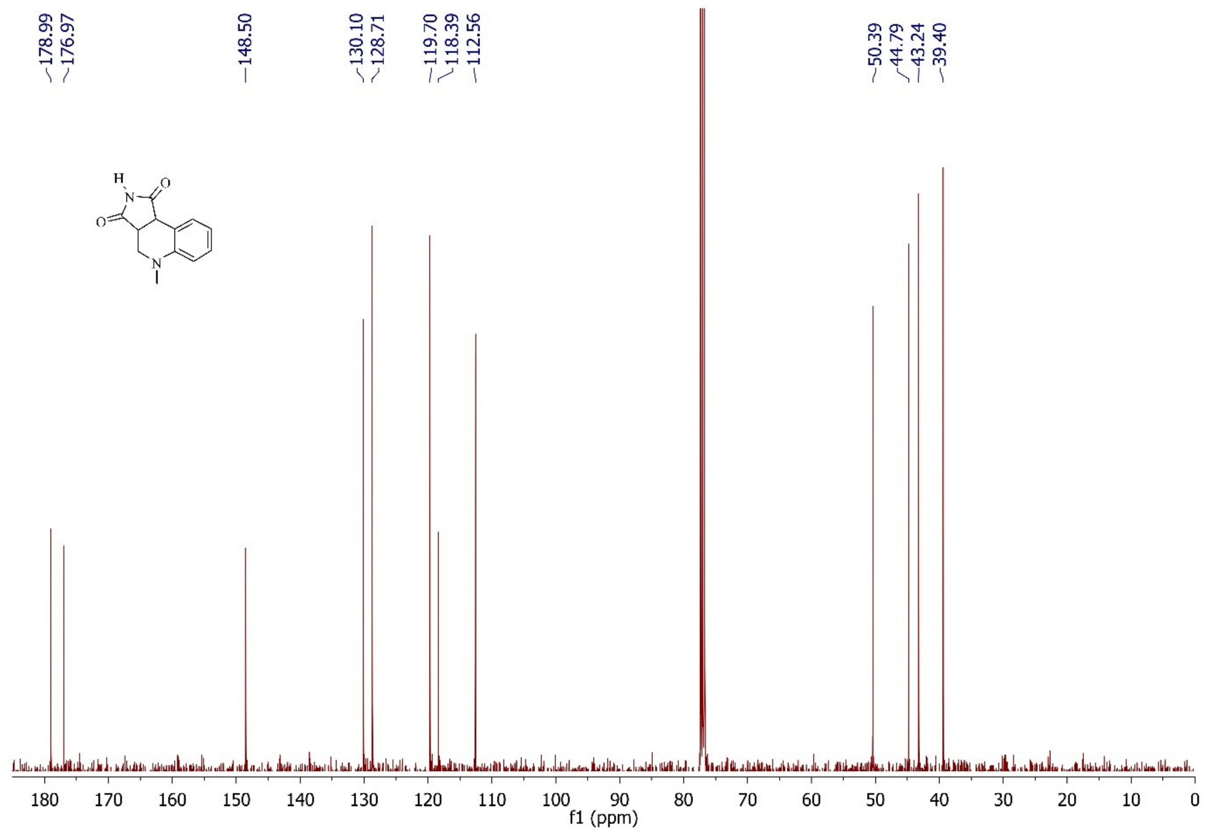
^{1}HNMR 3r



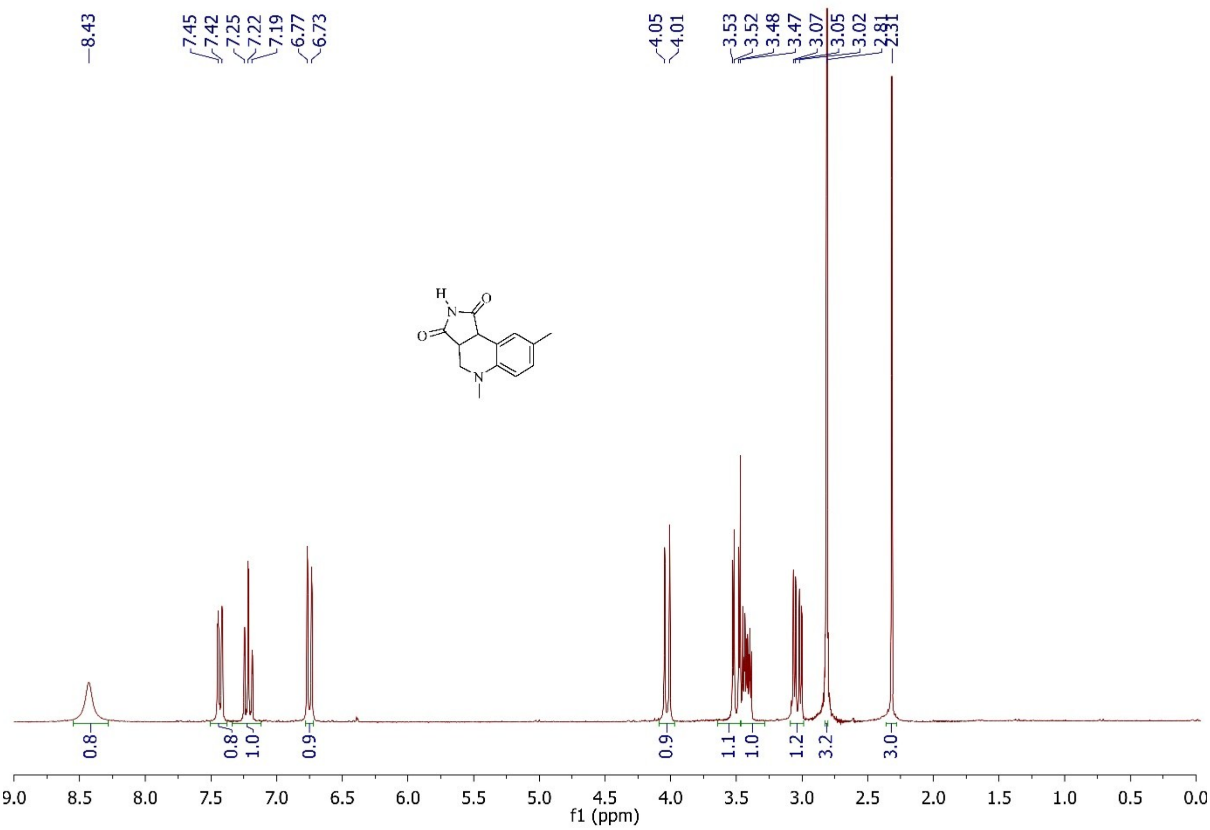
^{13}CNMR 3r



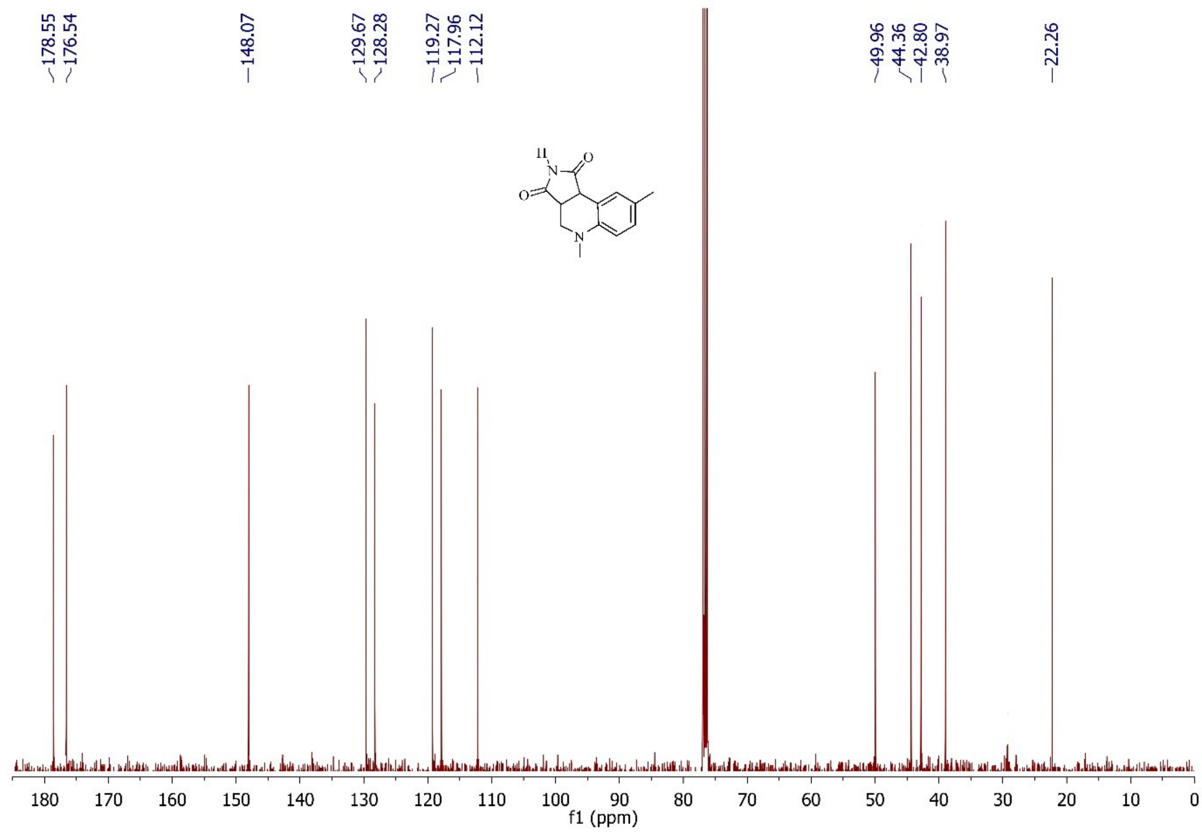
^{1}HNMR 3t



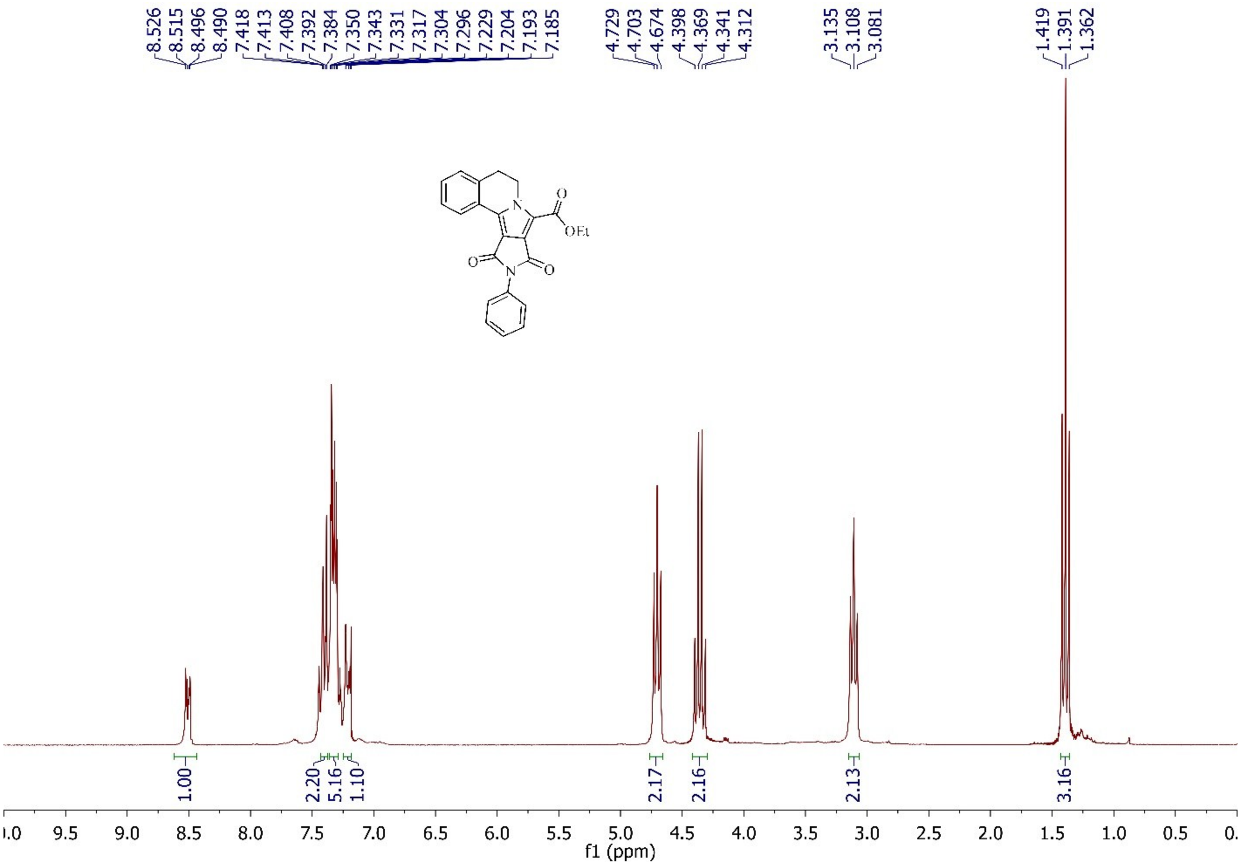
^{13}CNMR 3t



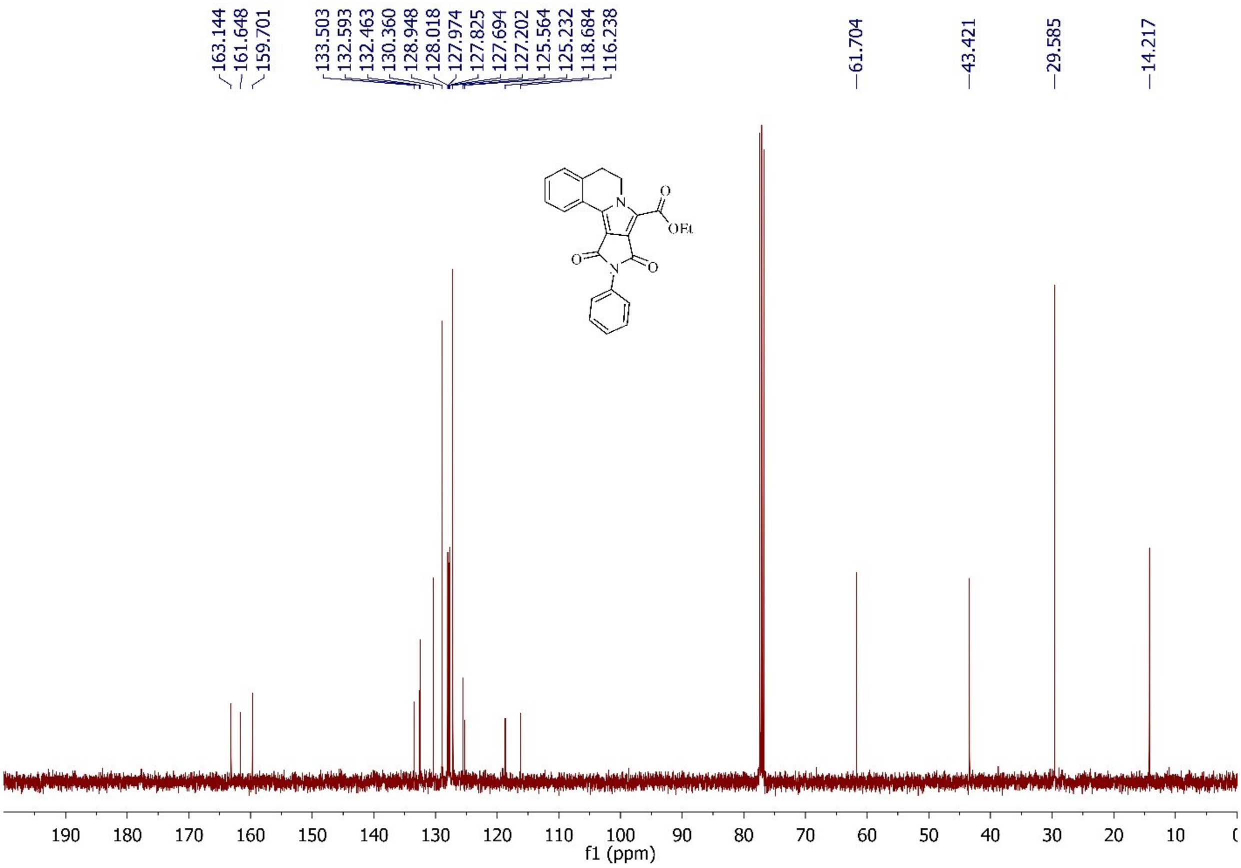
^{1}HNMR 3u



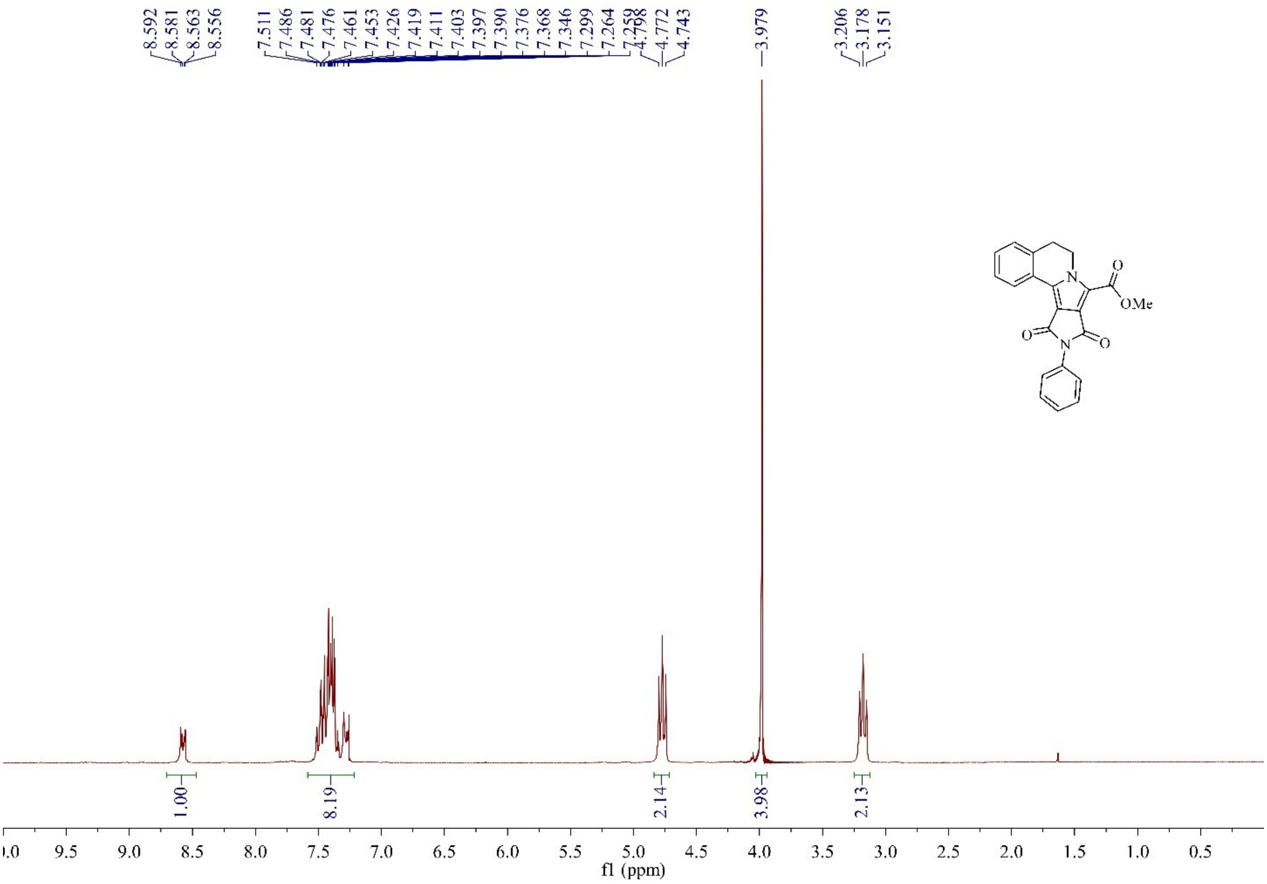
^{13}CNMR 3u



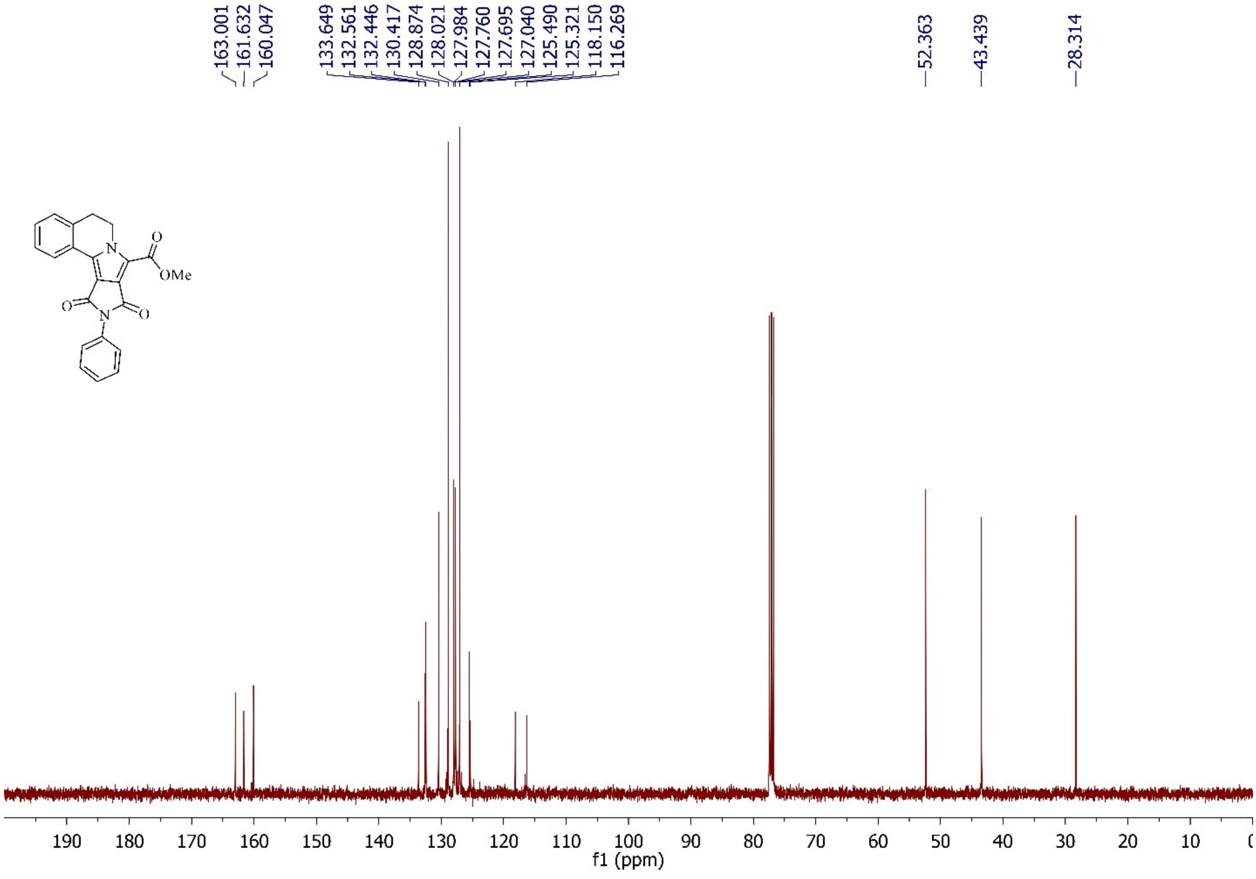
^{1}HNMR 5a



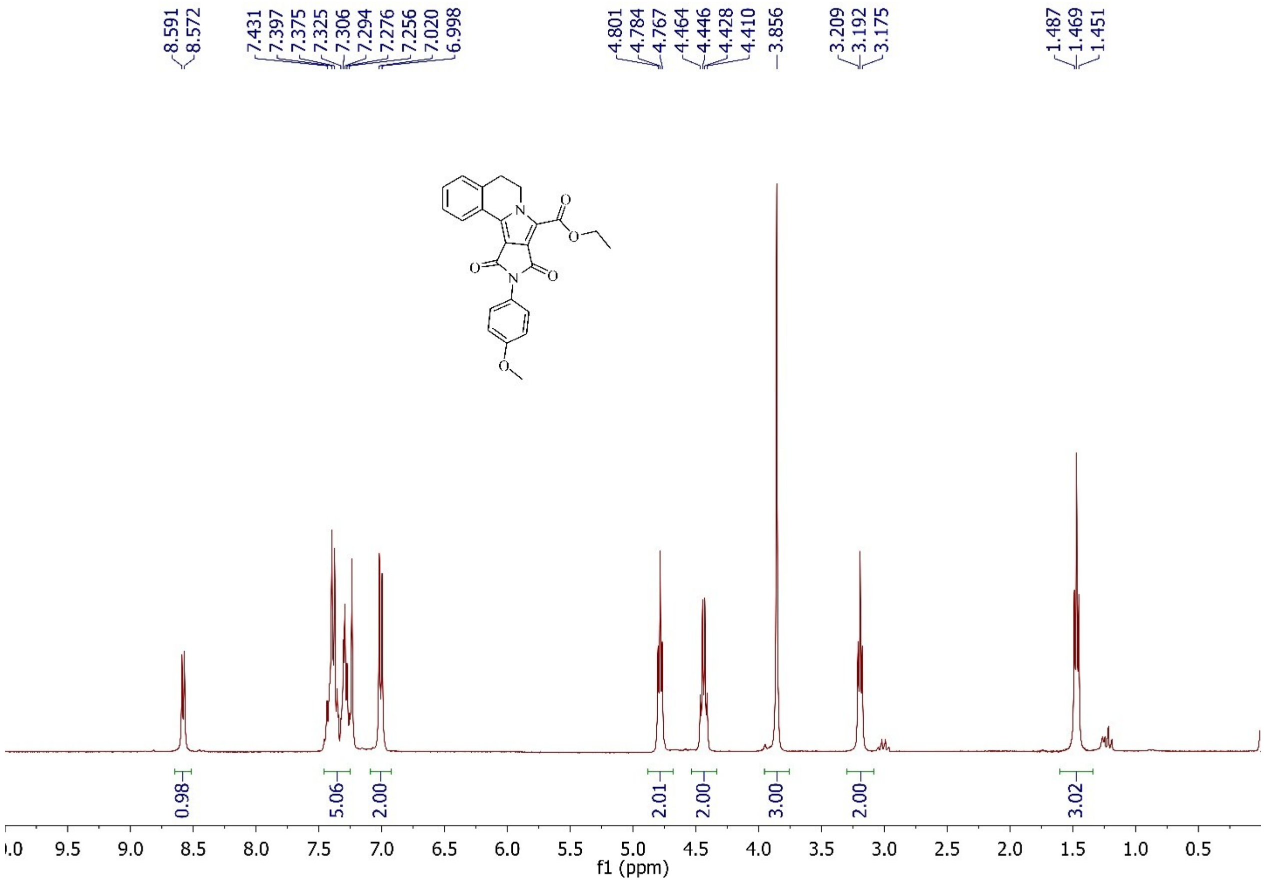
^{13}CNMR 5a



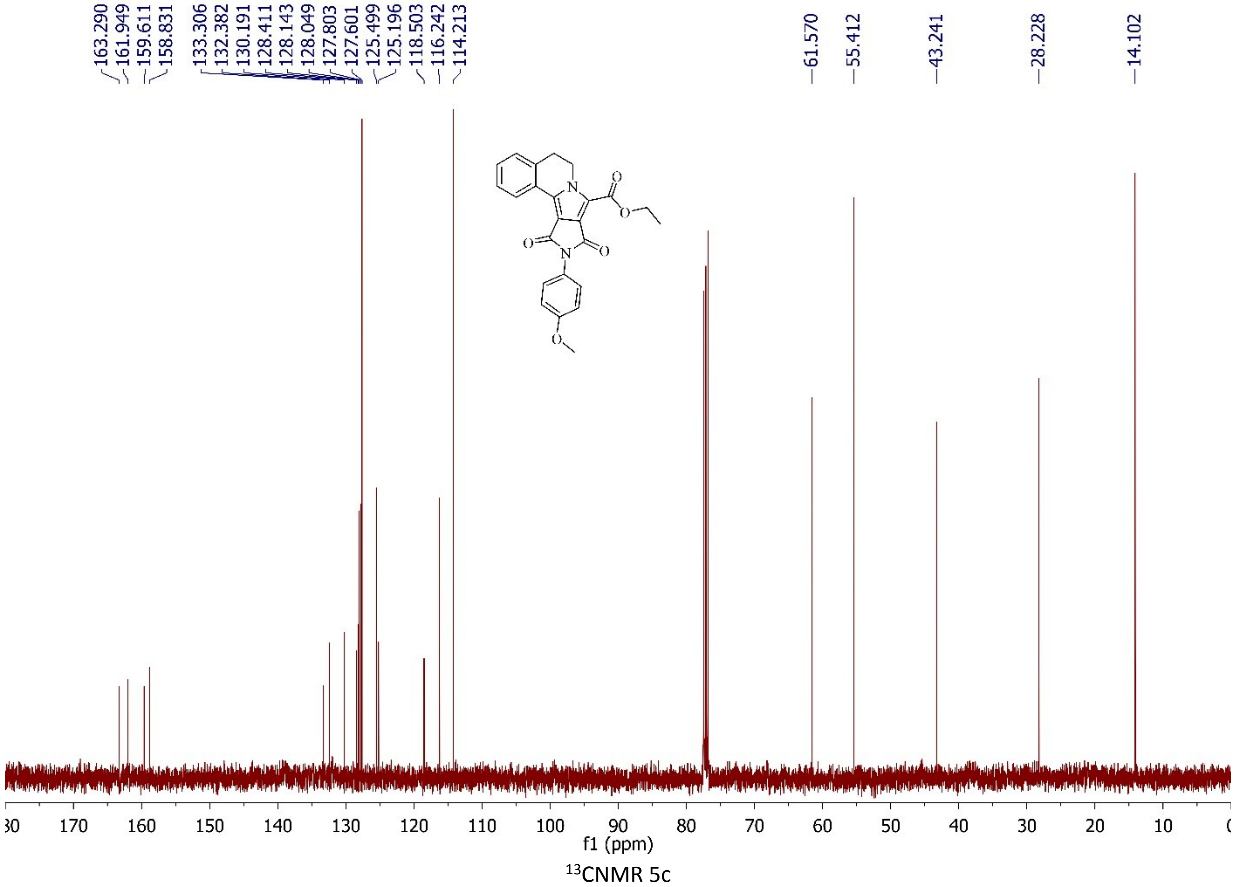
^{1}HNMR 5b



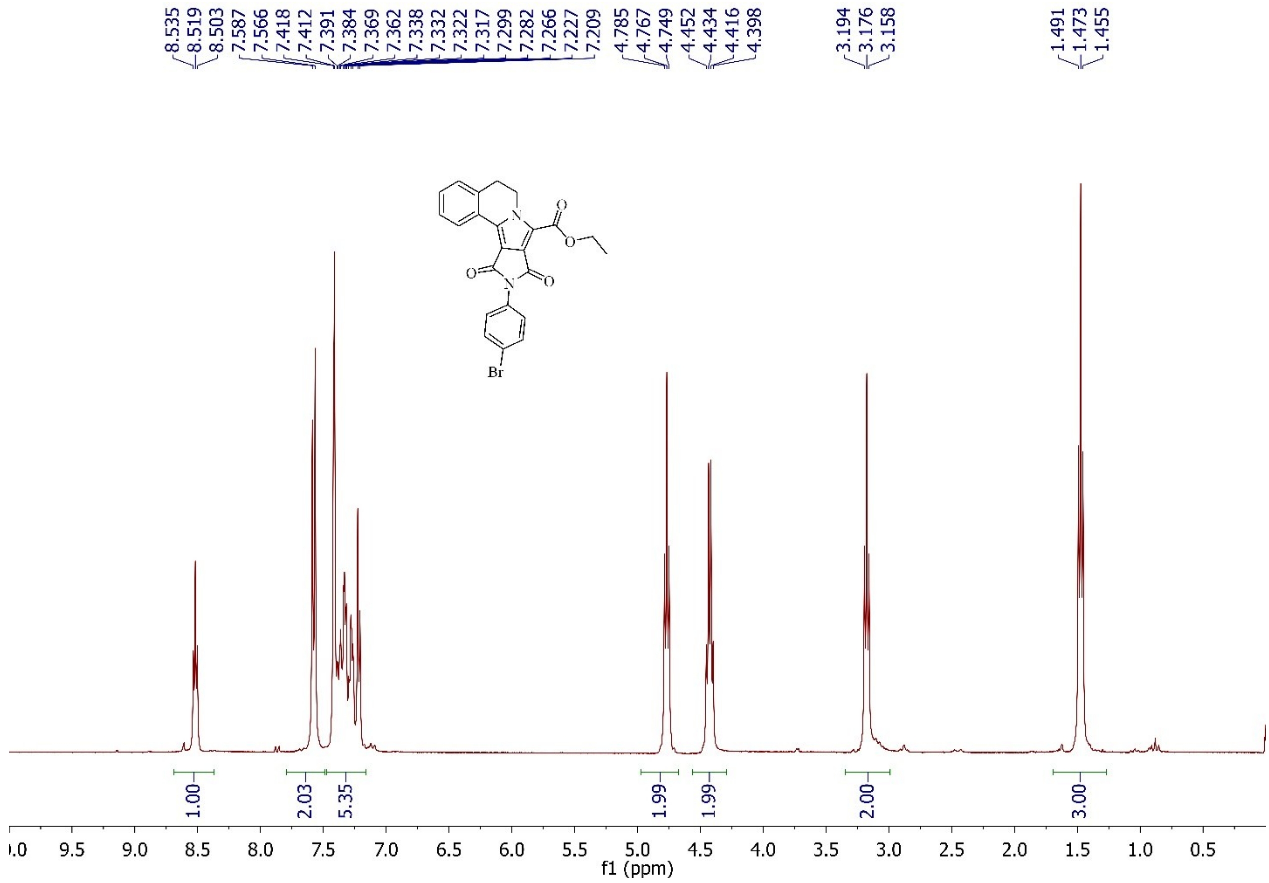
^{13}CNMR 5b



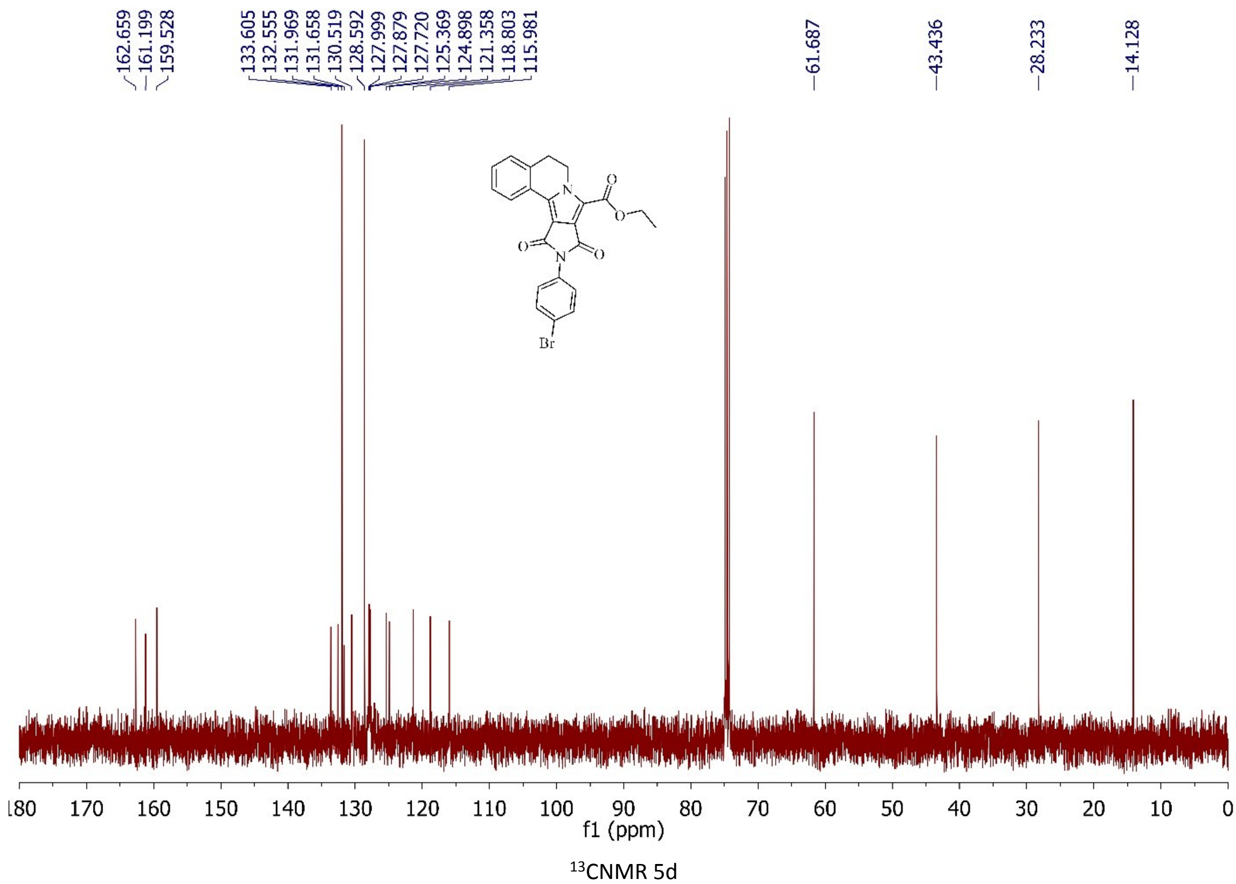
[1]HNMR 5c



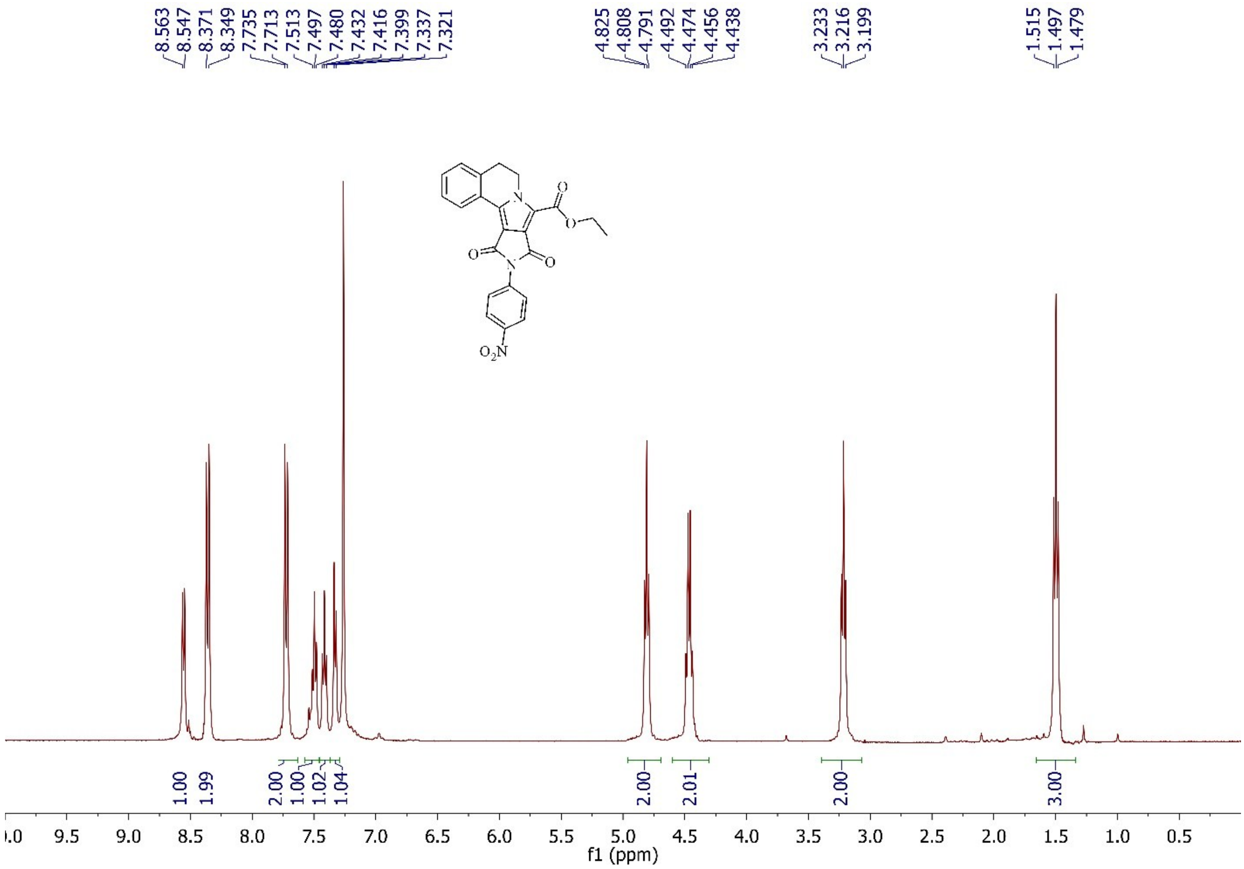
[13]CNMR 5c



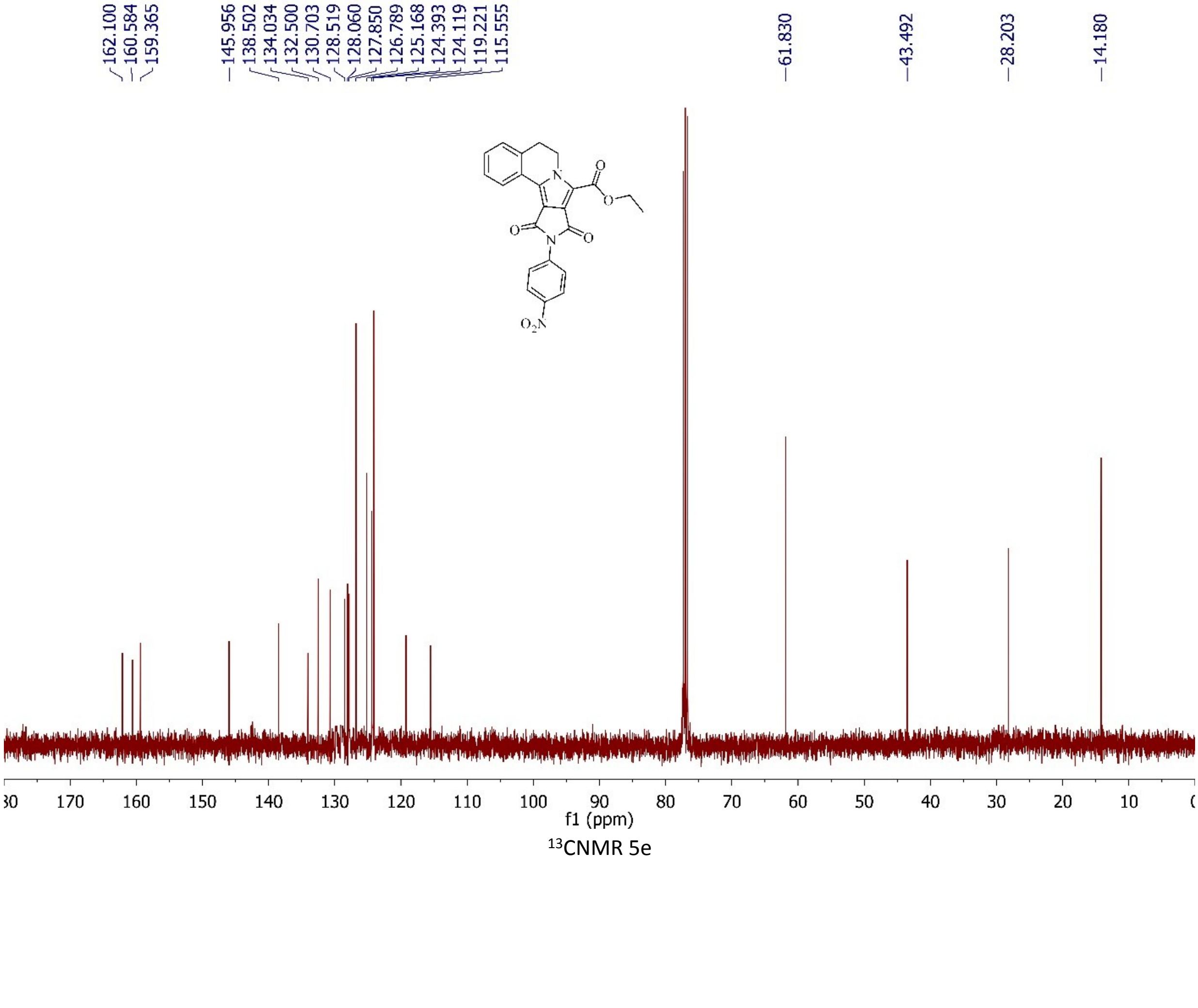
^{1}HNMR 5d



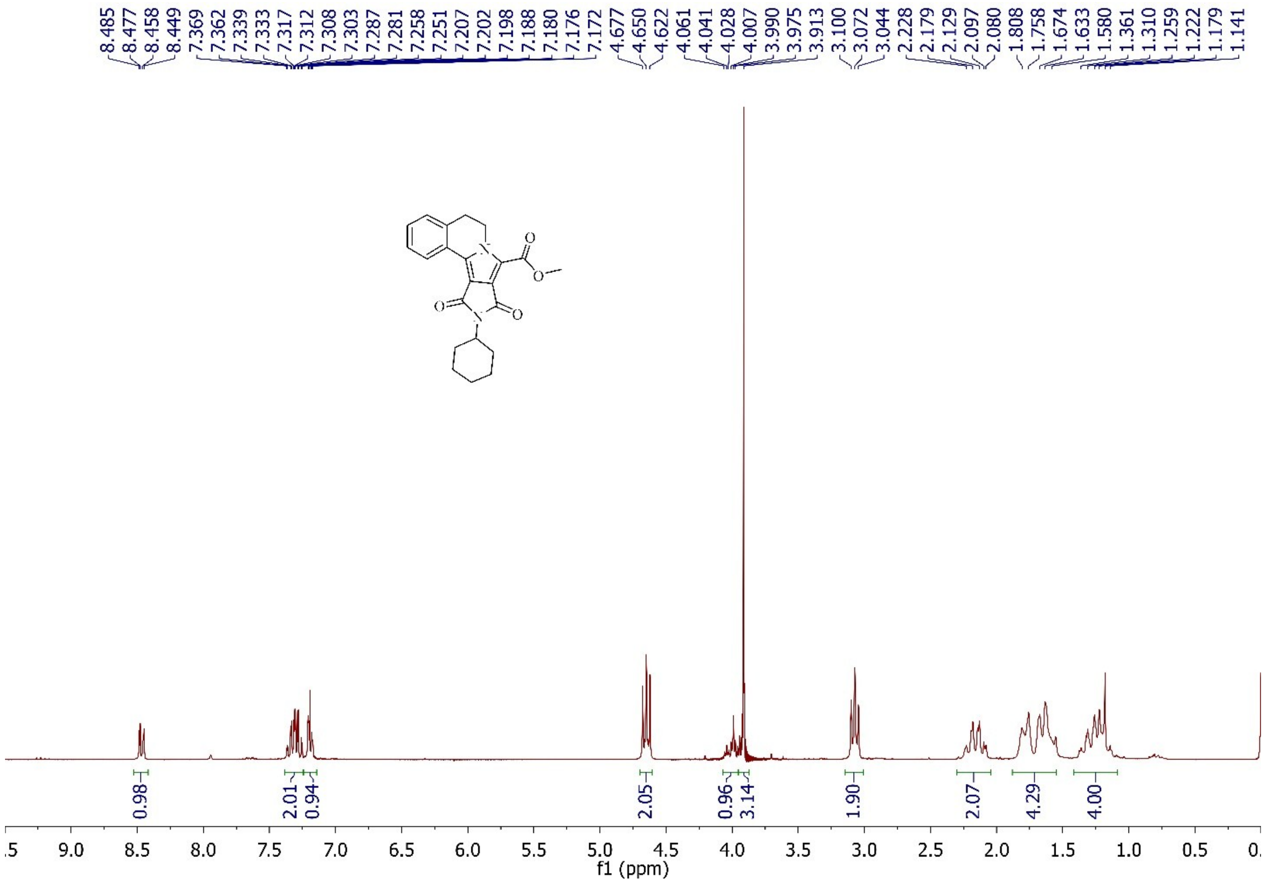
^{13}CNMR 5d



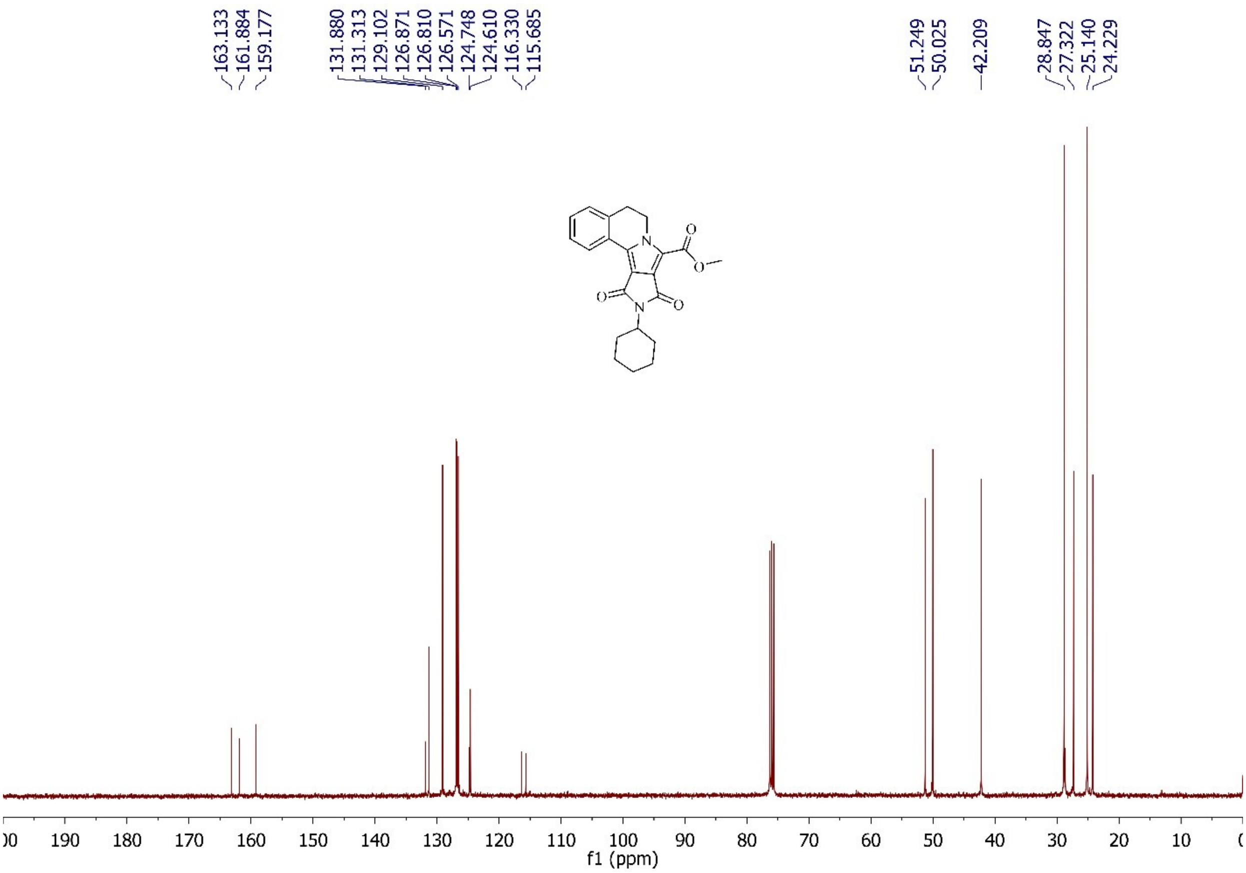
[1]HNMR 5e



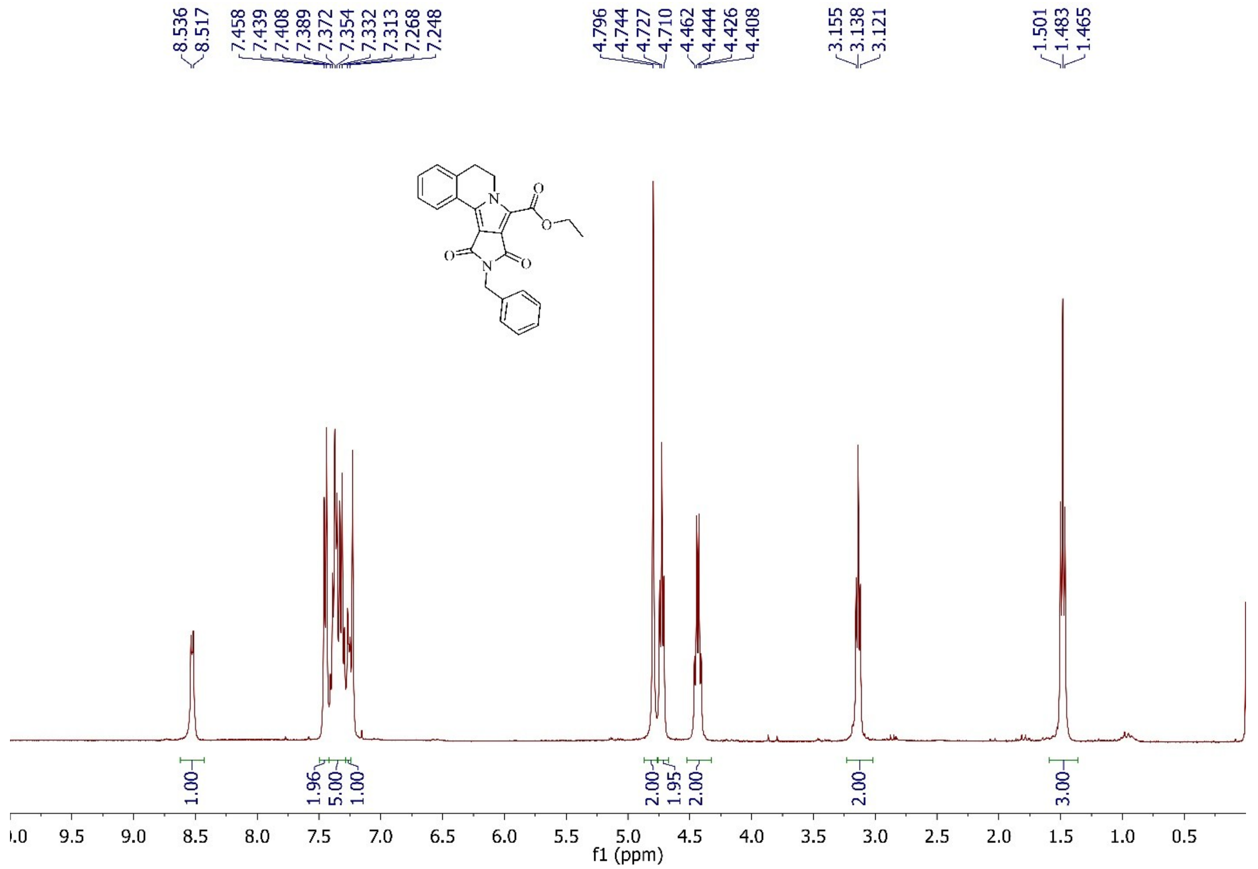
[13]CNMR 5e



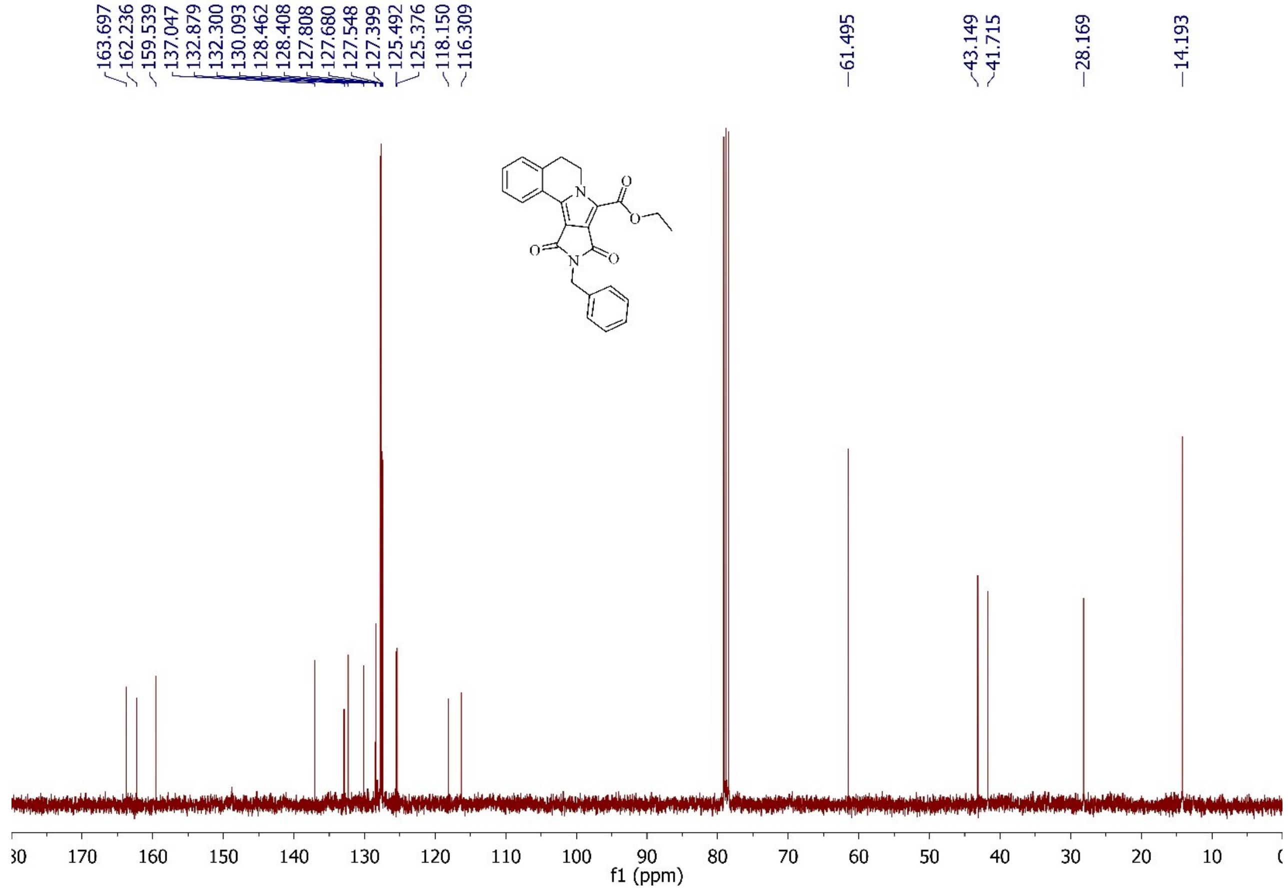
[1]HNMR 5f



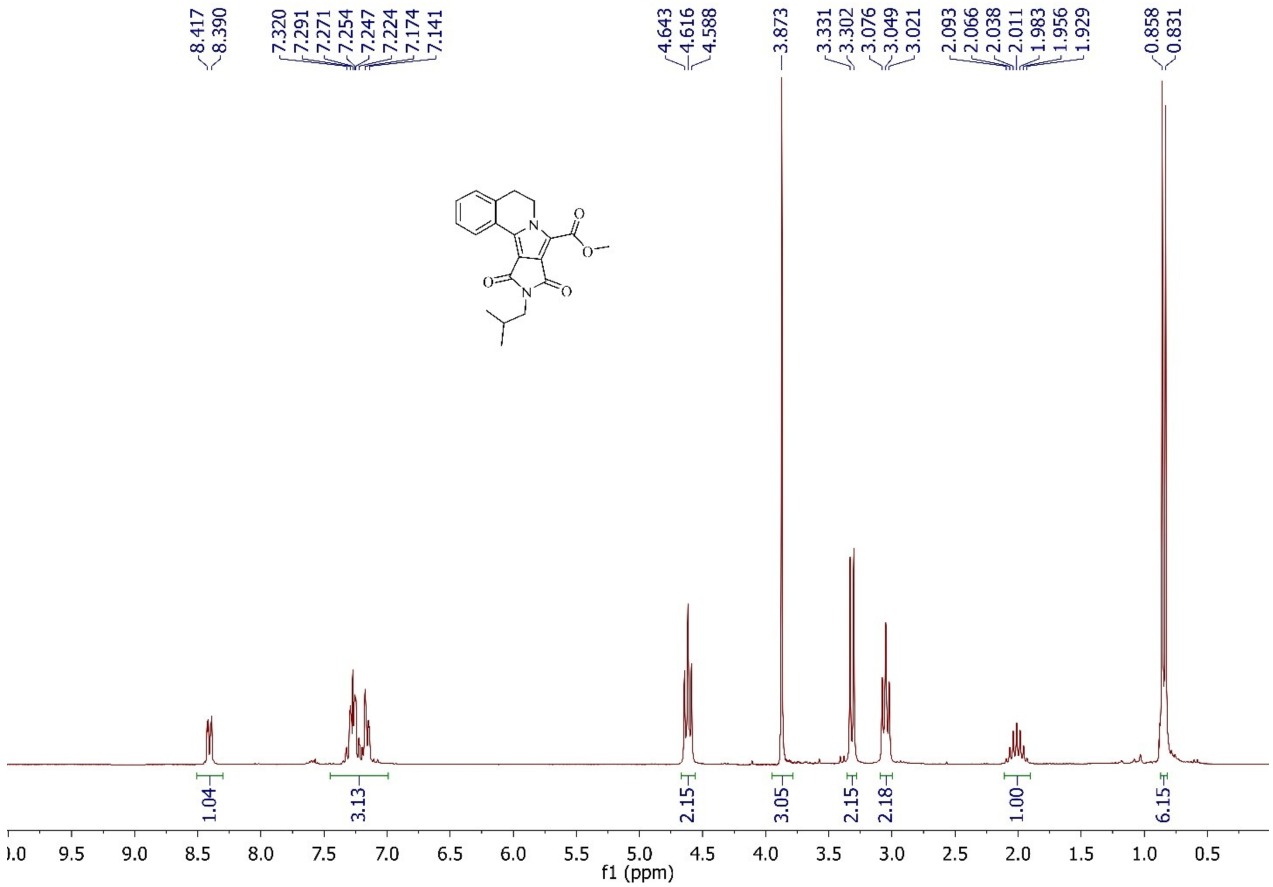
[13]CNMR 5f



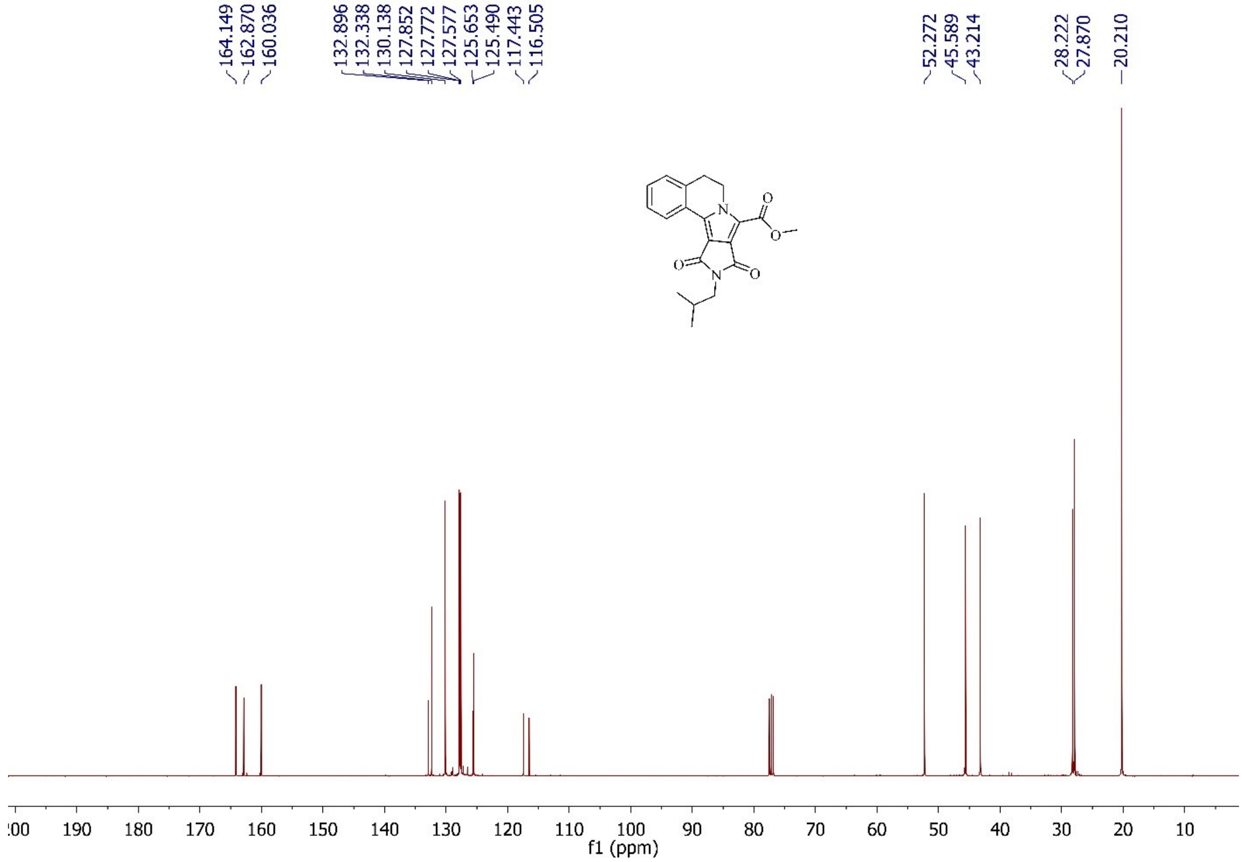
^{1}HNMR 5g



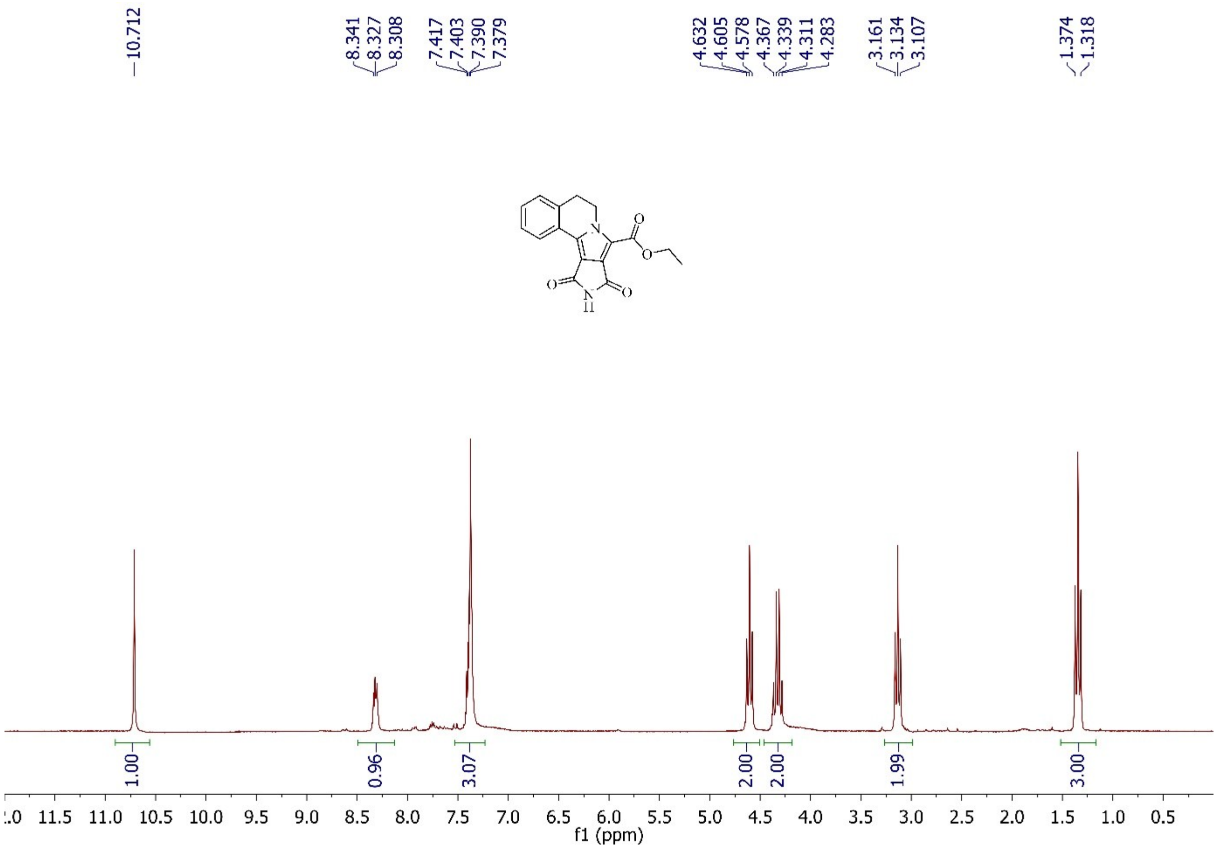
^{13}CNMR 5g



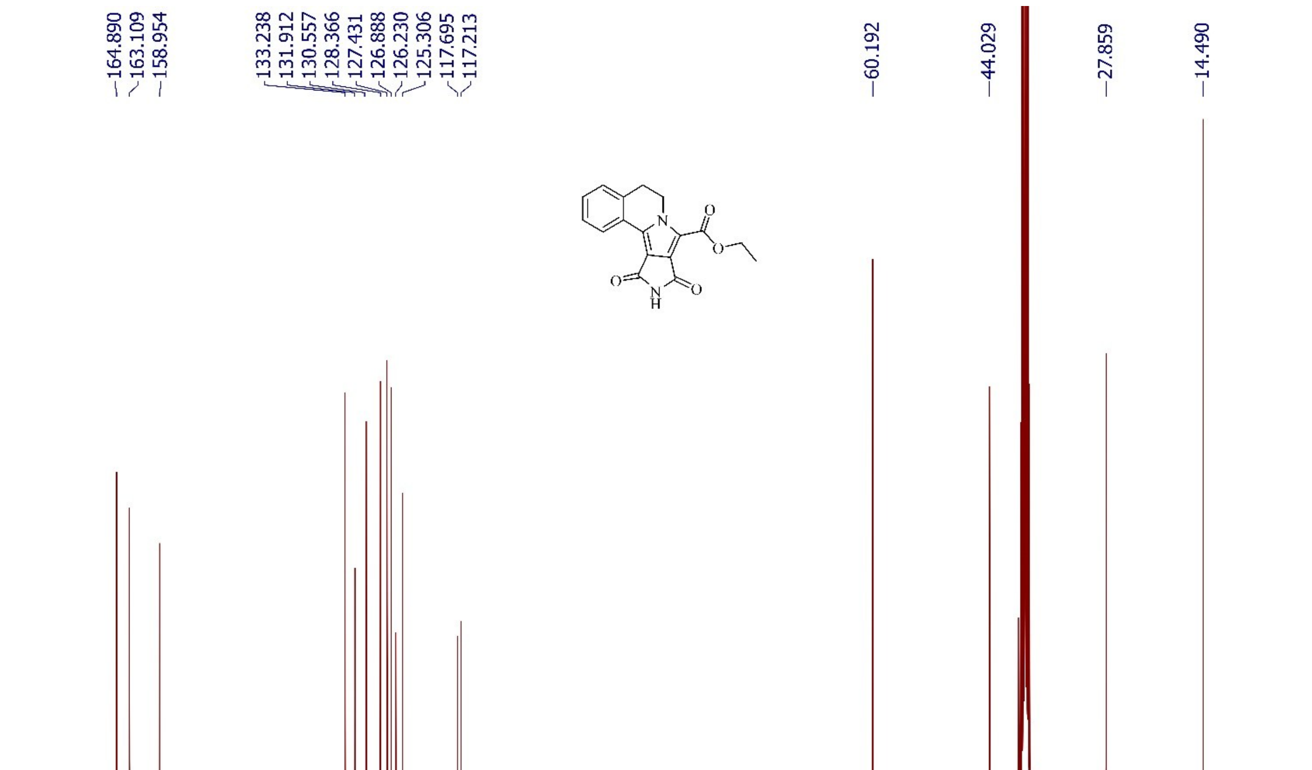
^{1}HNMR 5h



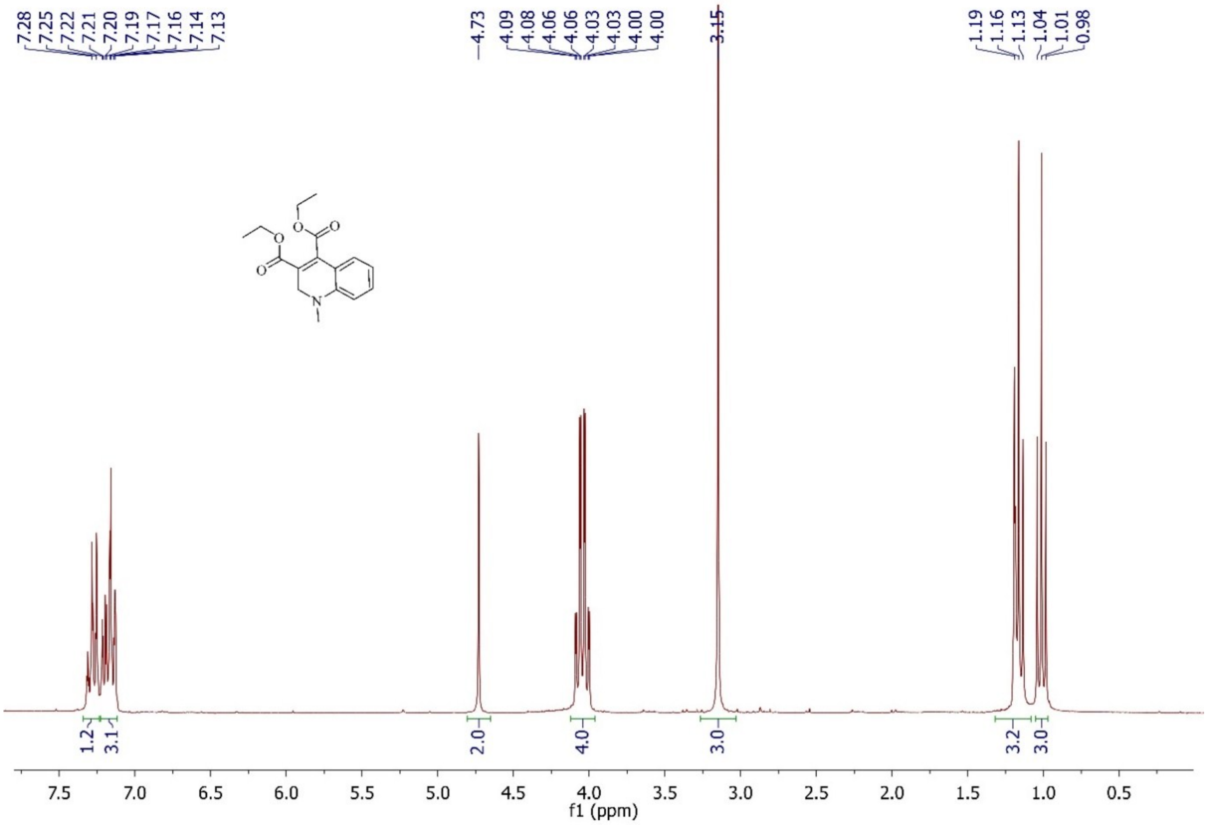
^{13}CNMR 5h



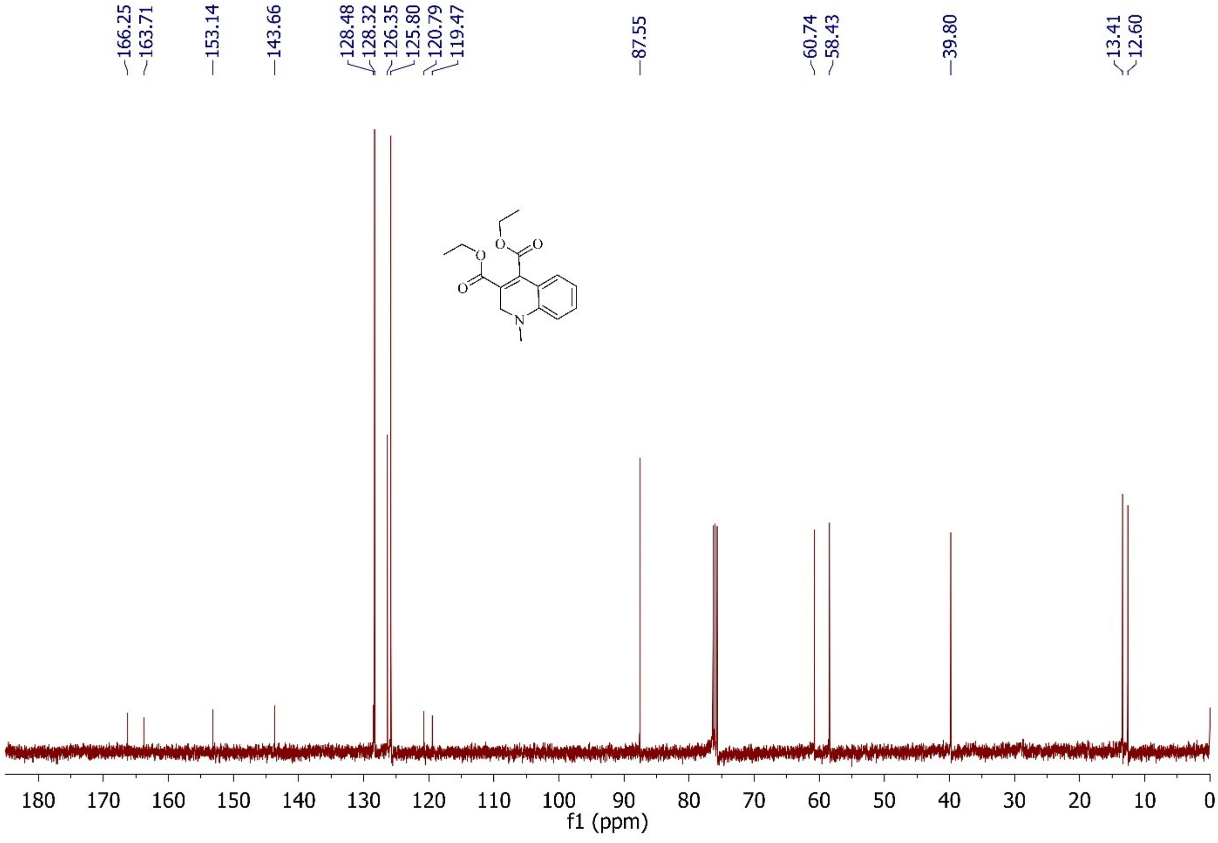
^{1}HNMR 5i



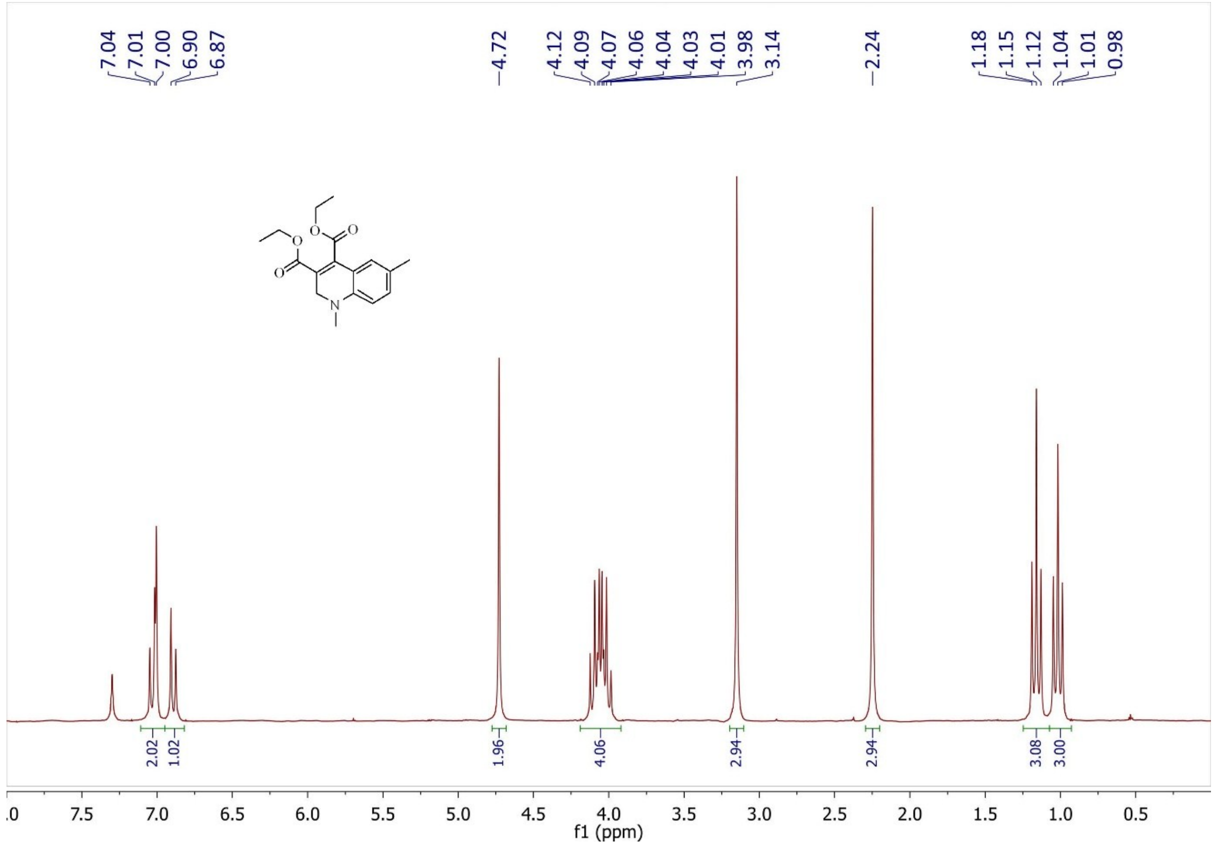
^{13}CNMR 5i



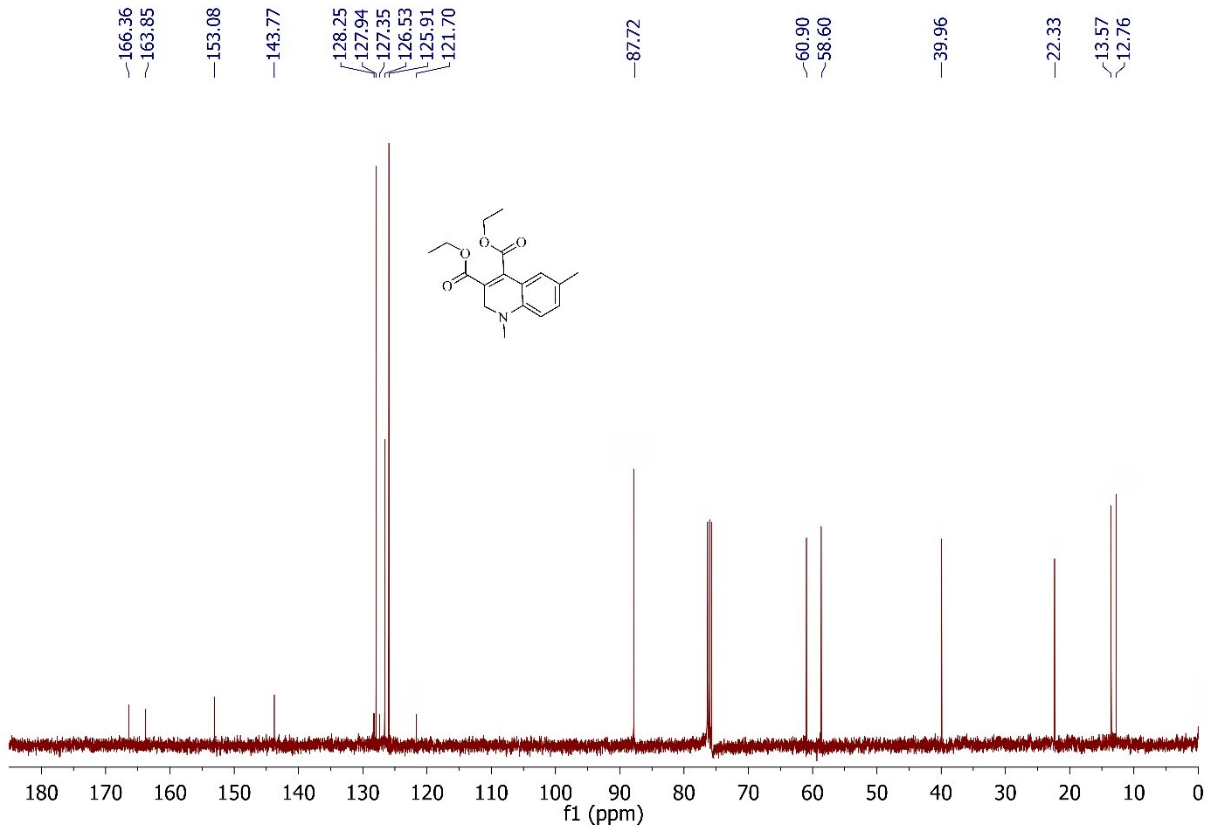
^{1}HNMR 7a



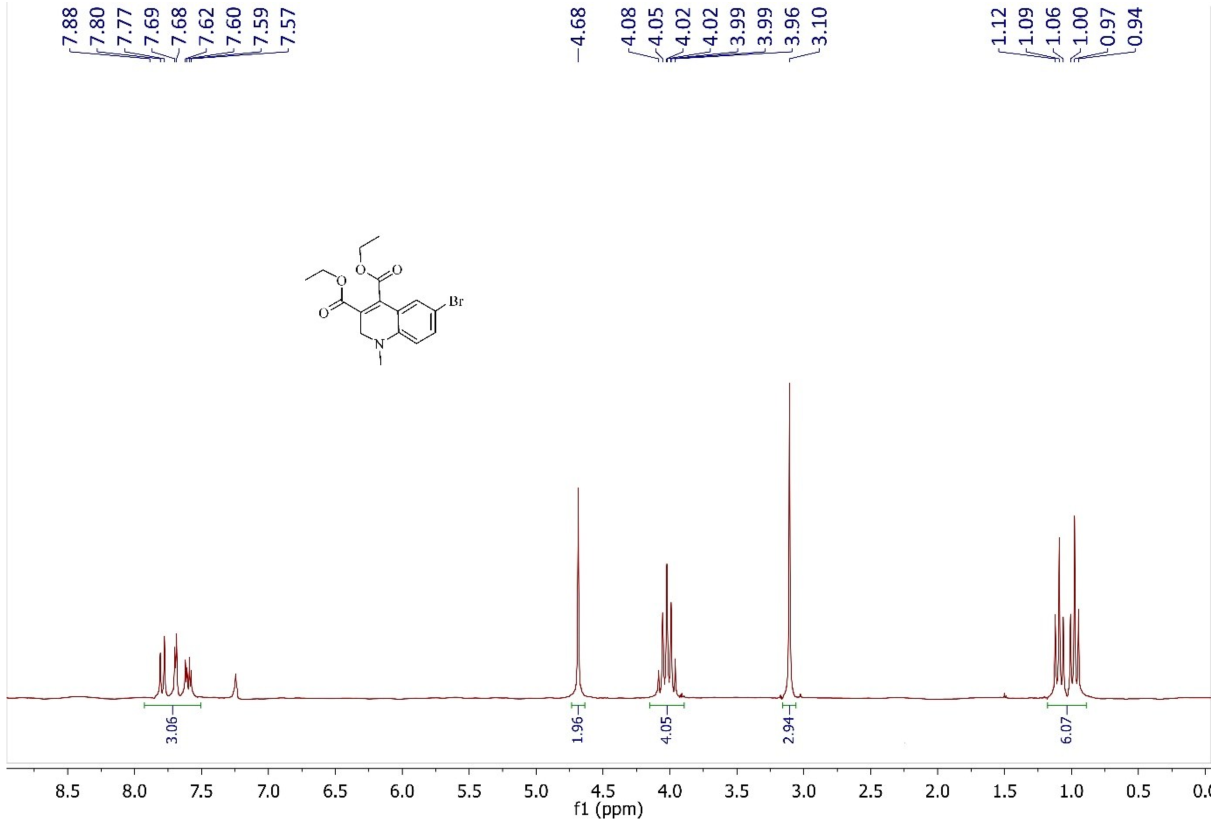
^{13}CNMR 7a



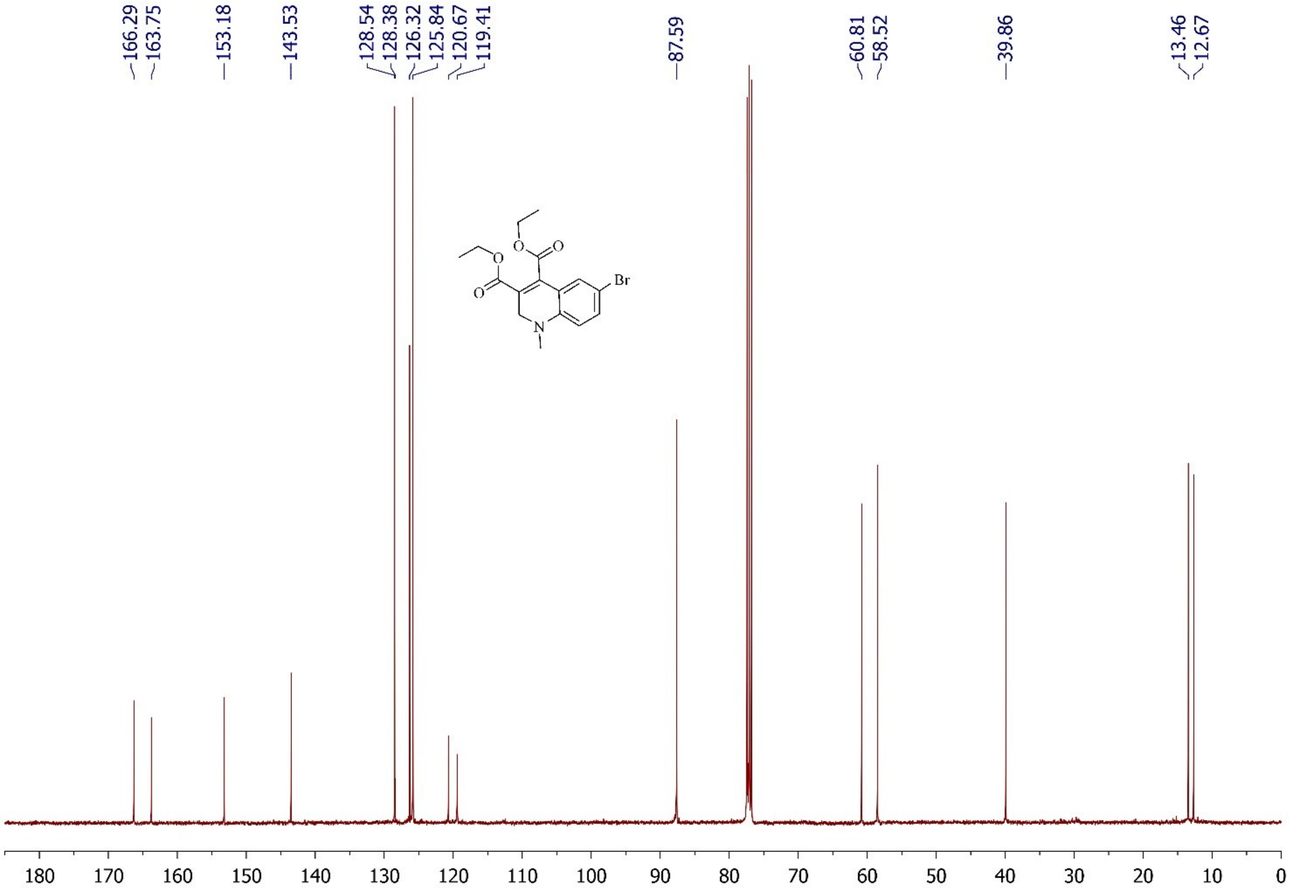
^{1}HNMR 7b



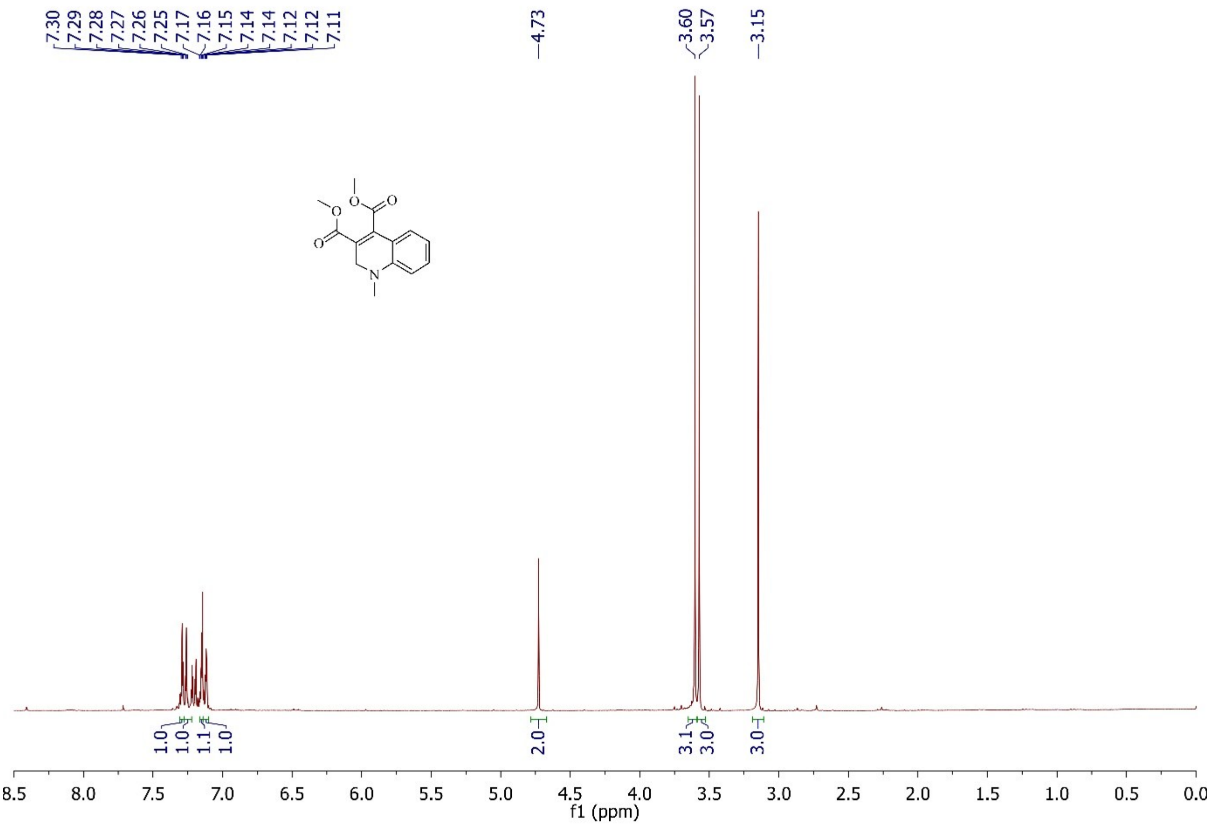
^{13}CNMR 7b



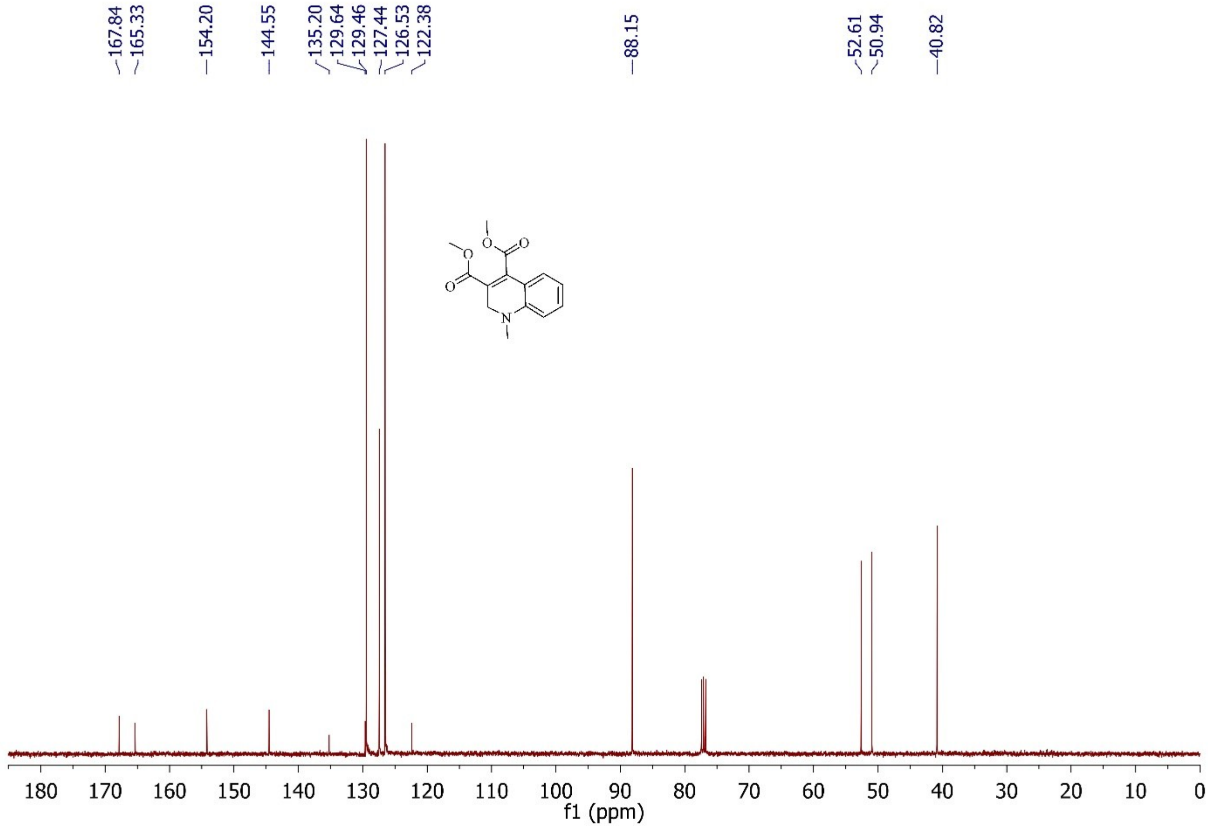
^{1}HNMR 7c



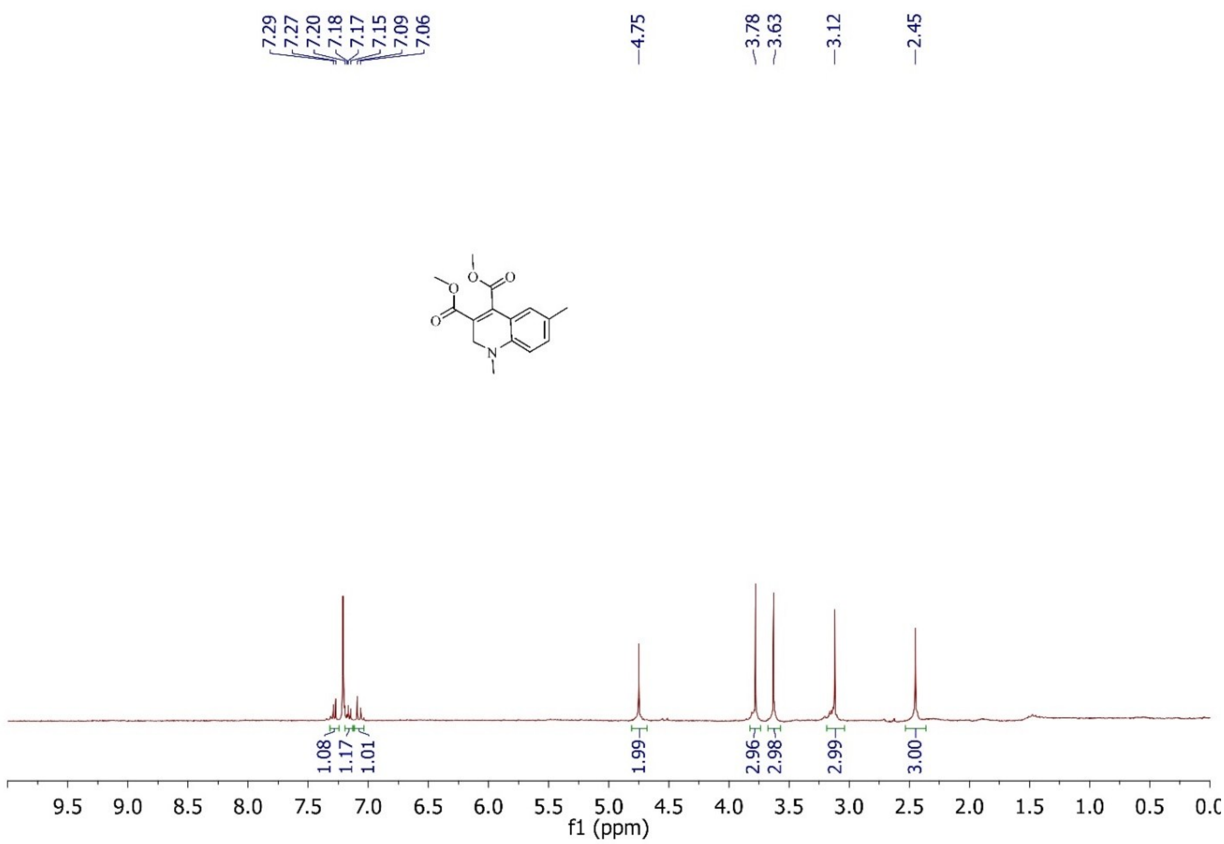
^{13}CNMR 7c



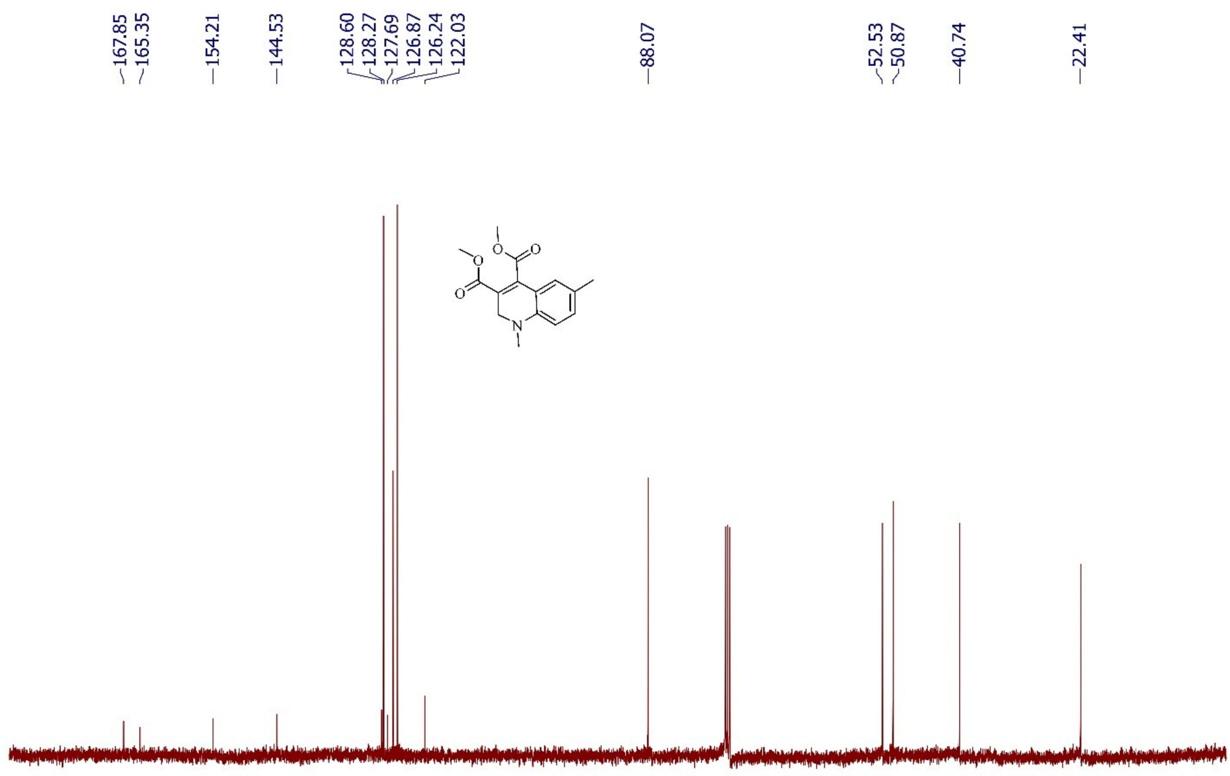
^{1}HNMR 7d



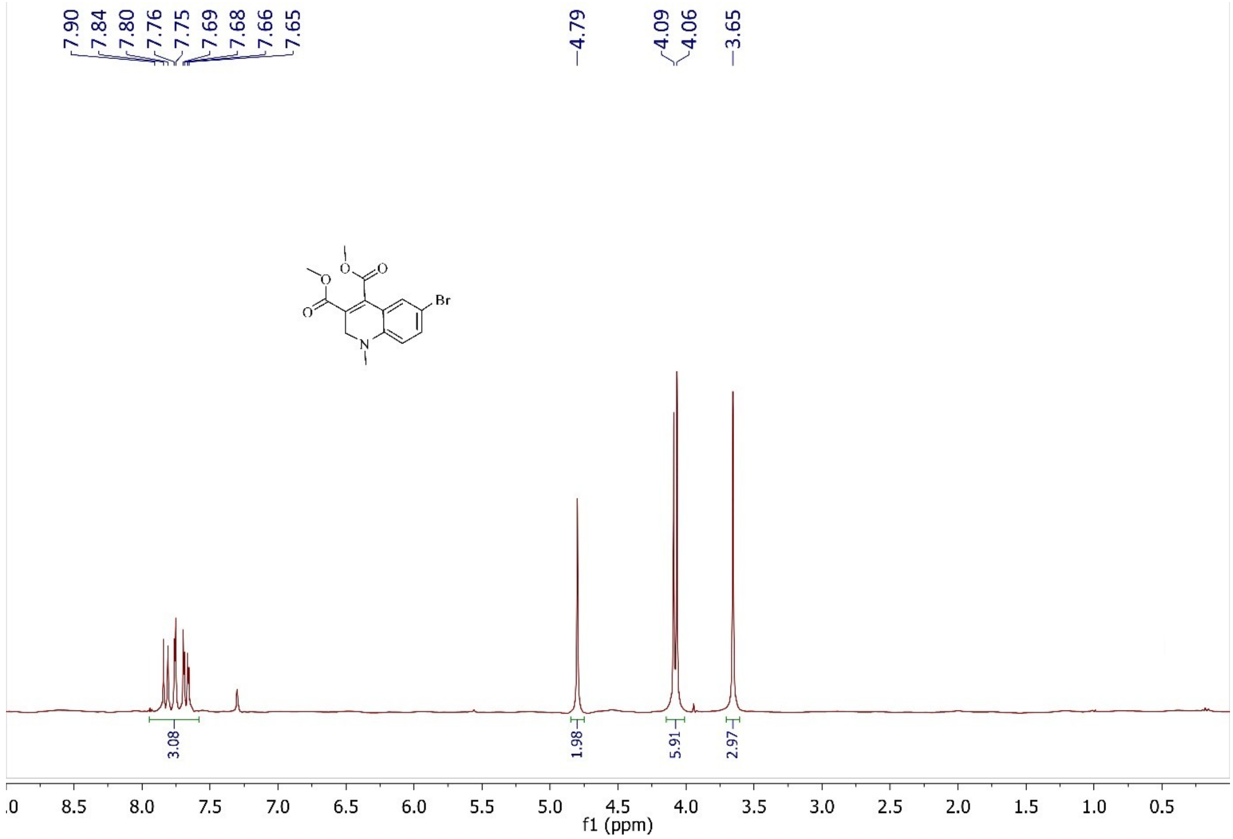
^{13}CNMR 7d



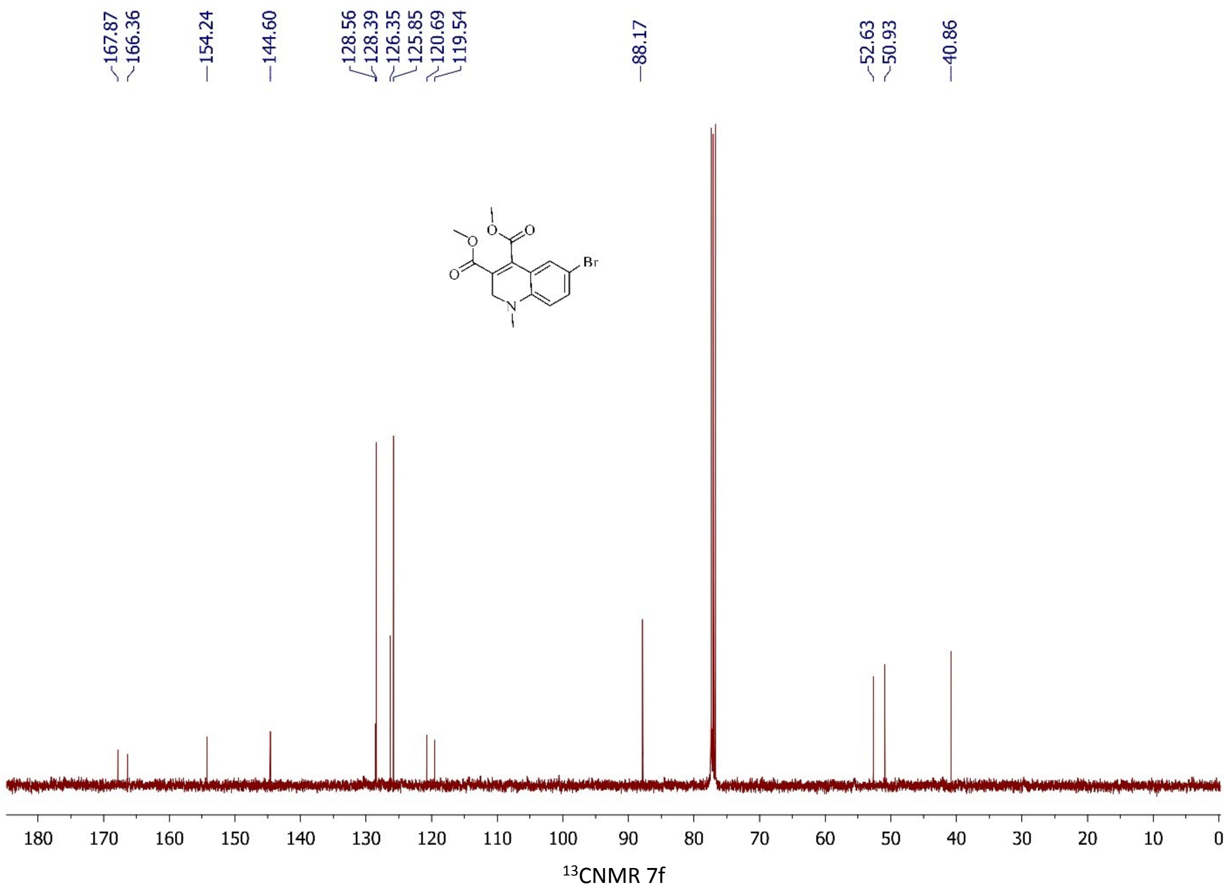
^{1}HNMR 7e



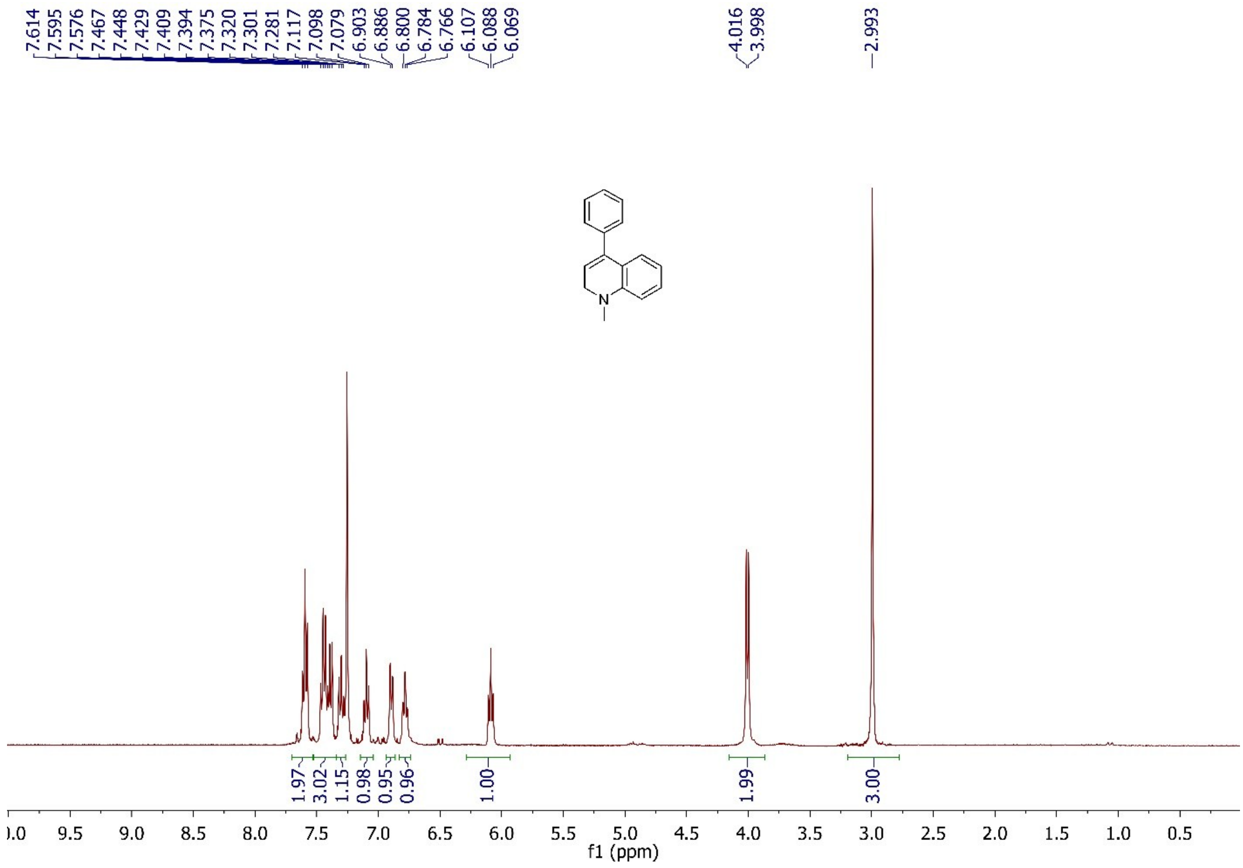
^{13}CNMR 7e



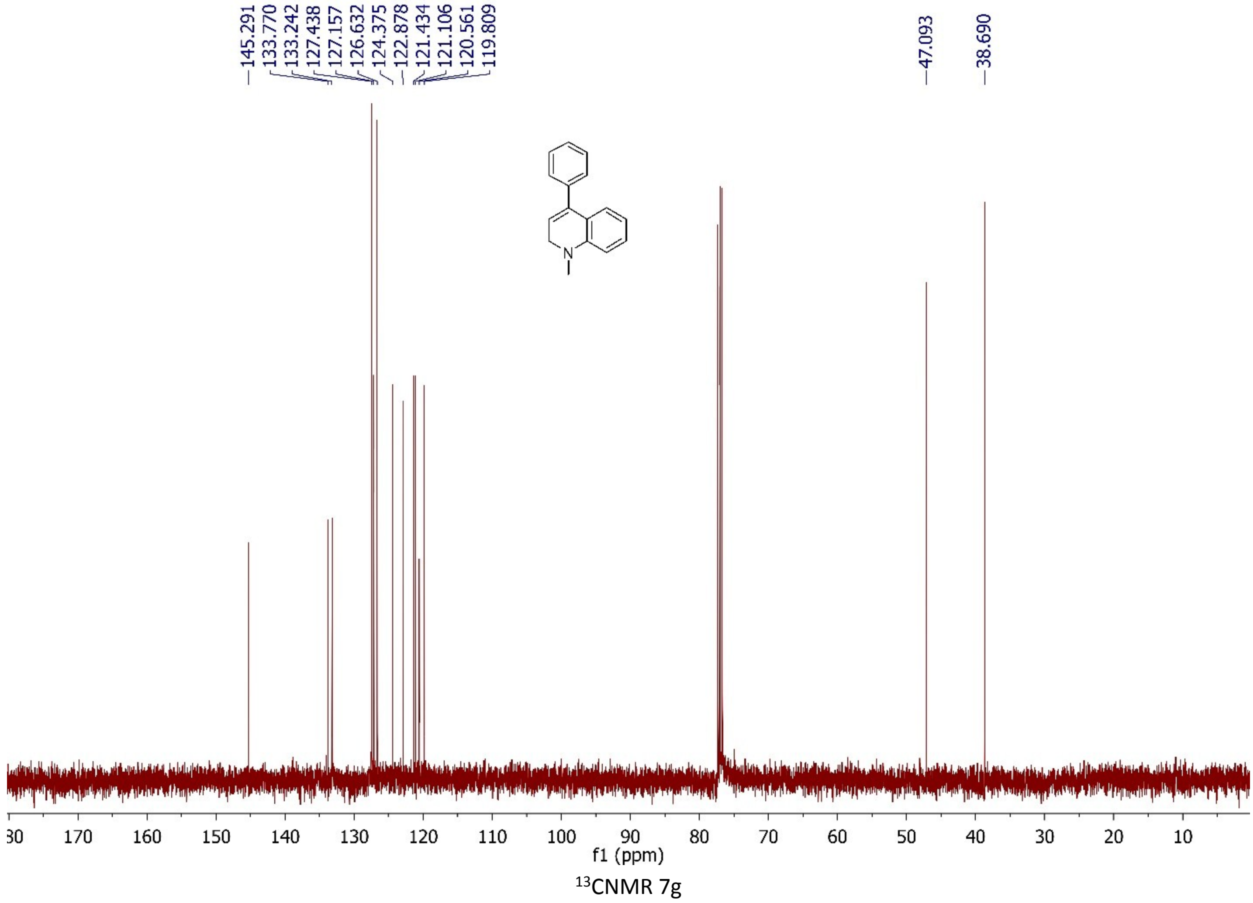
^{1}HNMR 7f



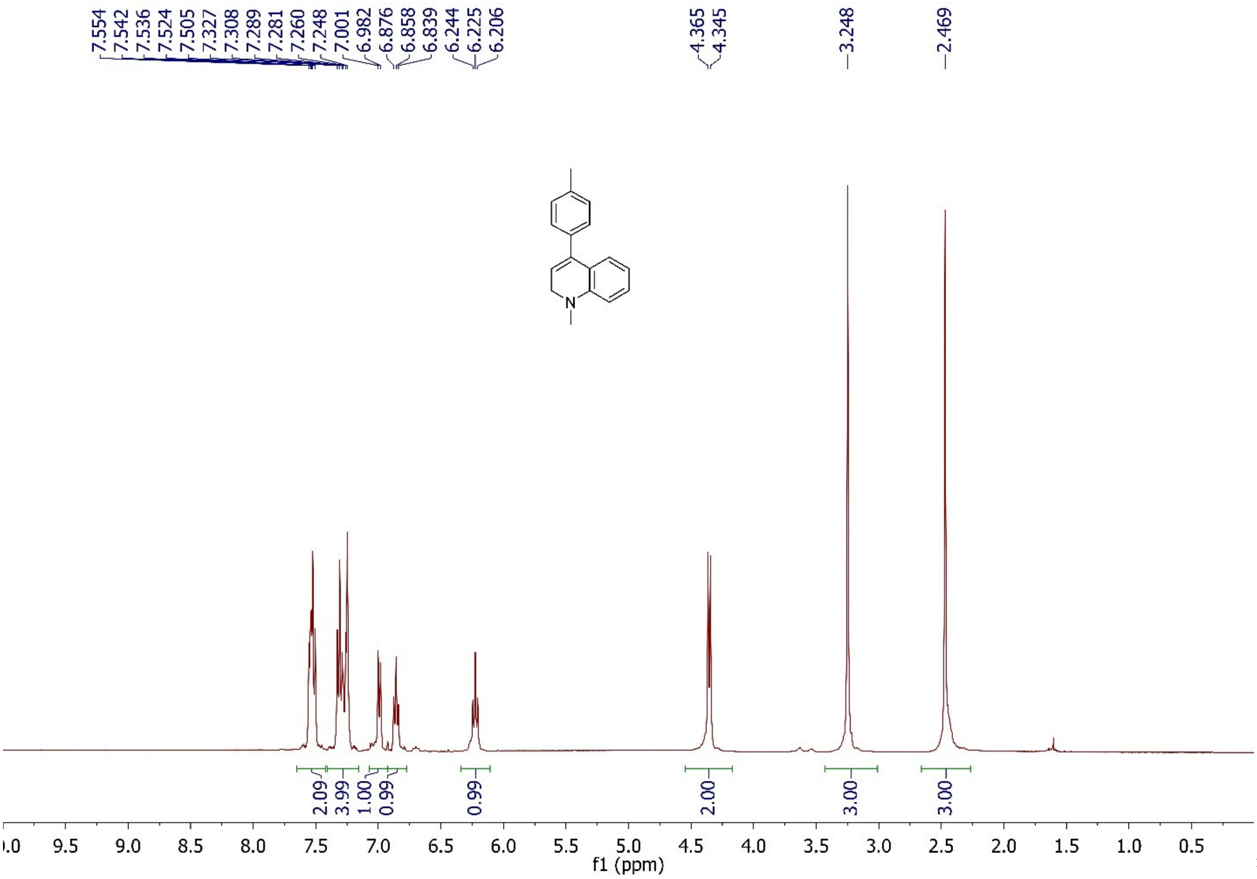
^{13}CNMR 7f



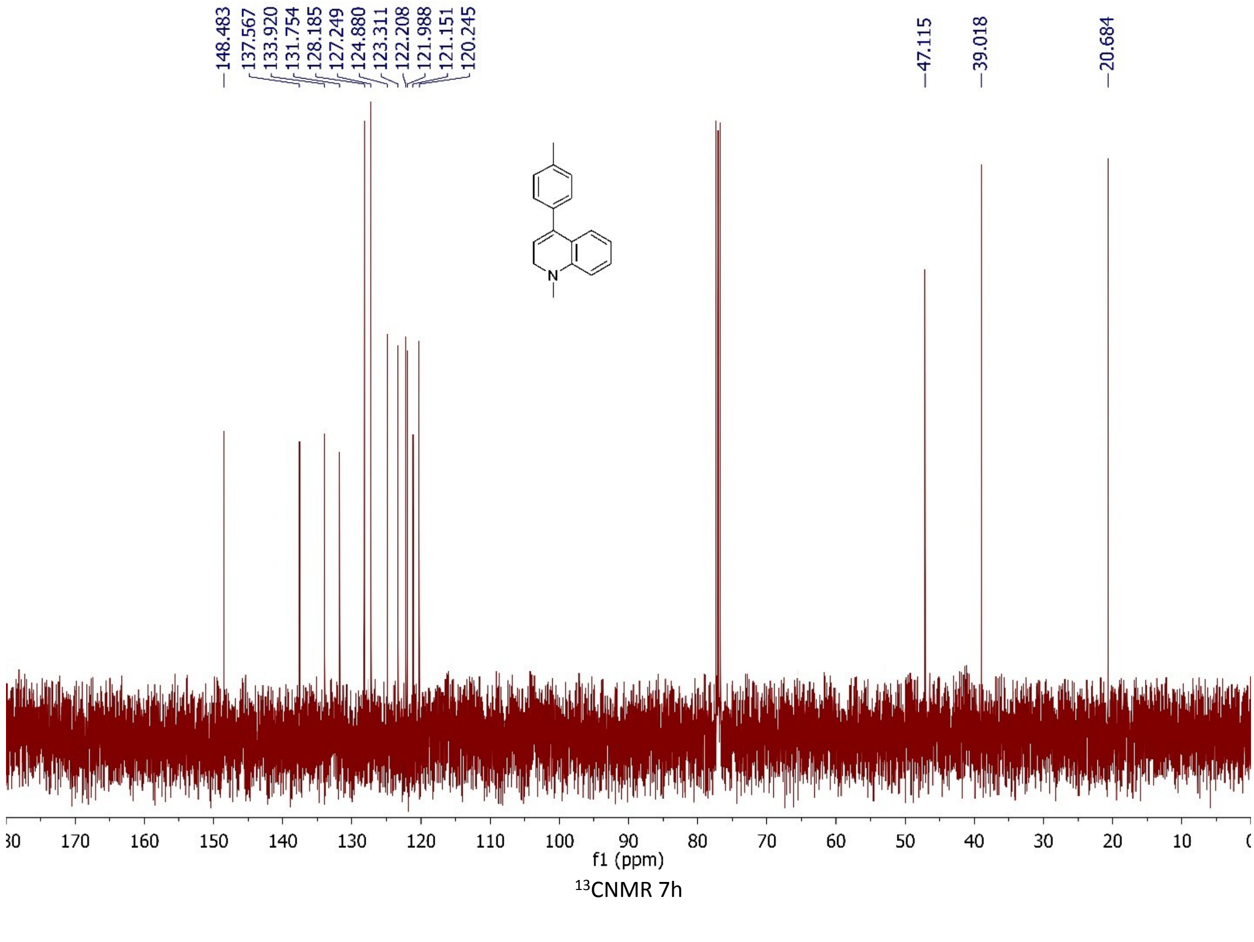
^{1}HNMR 7g



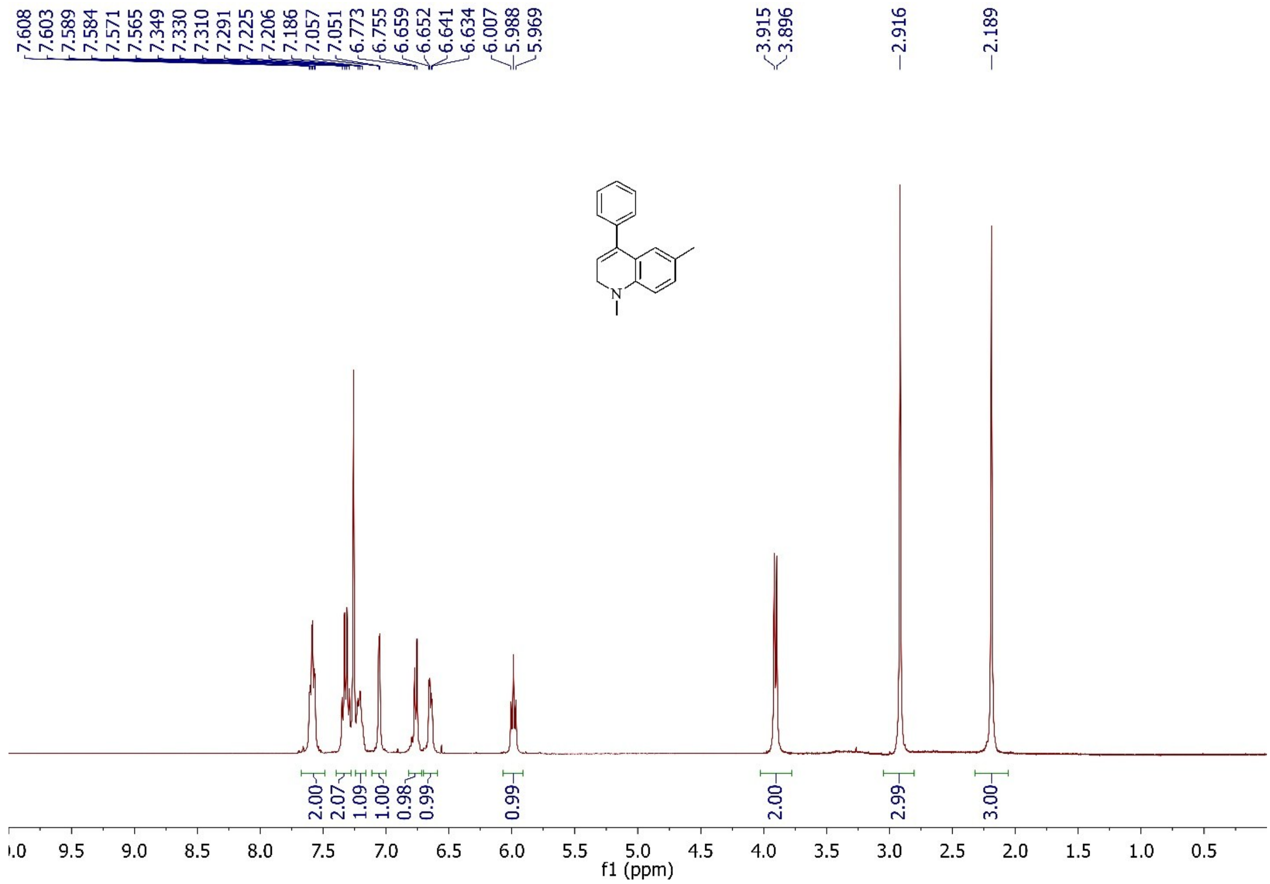
^{13}CNMR 7g



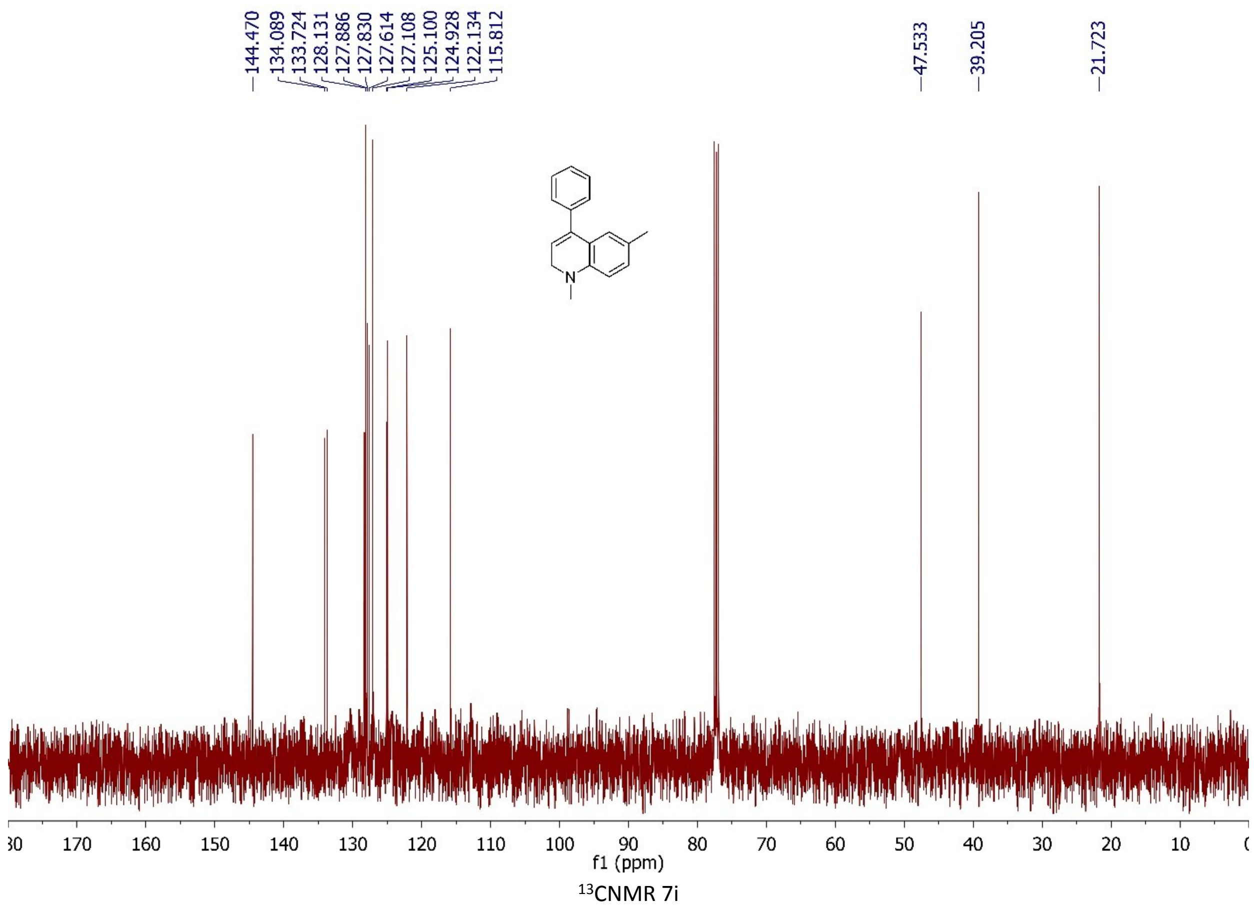
^{1}HNMR 7h



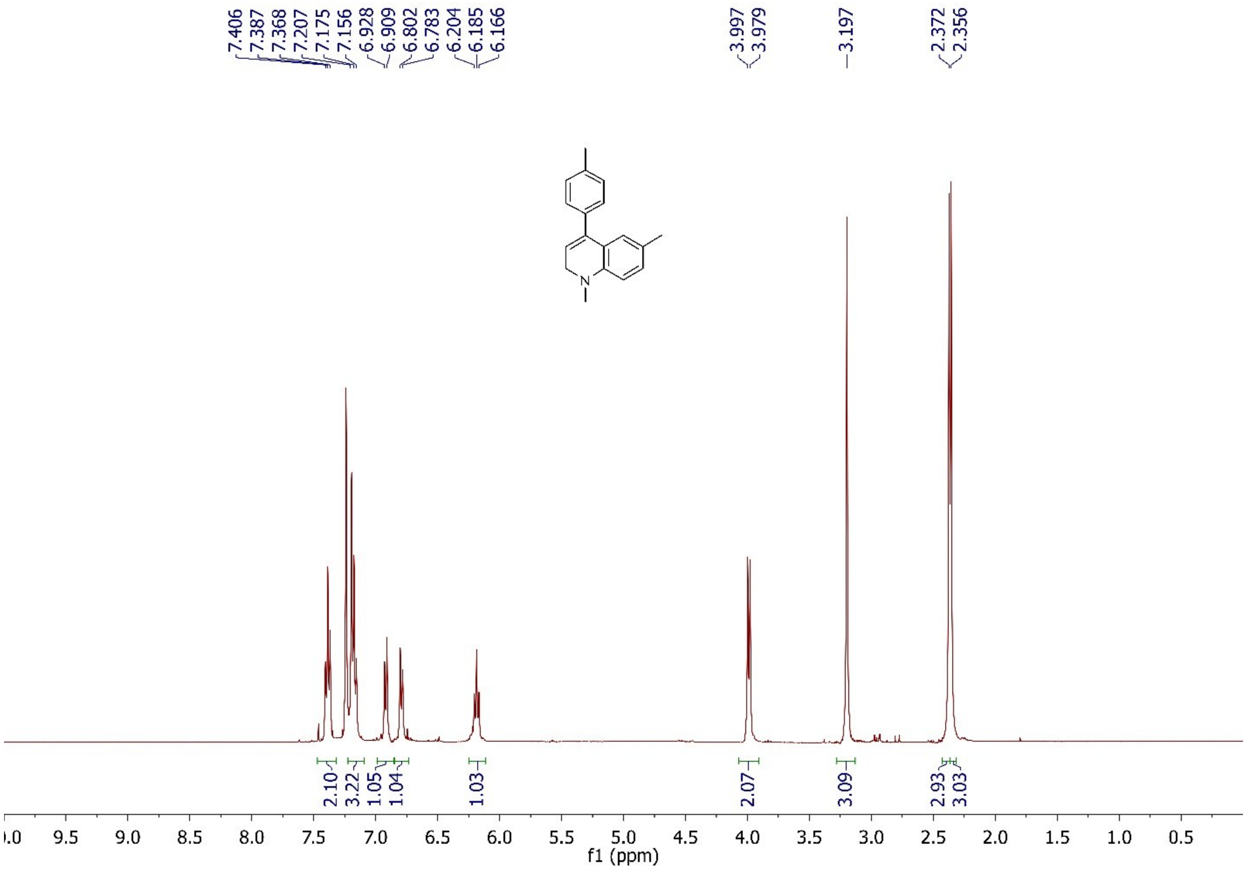
^{13}CNMR 7h



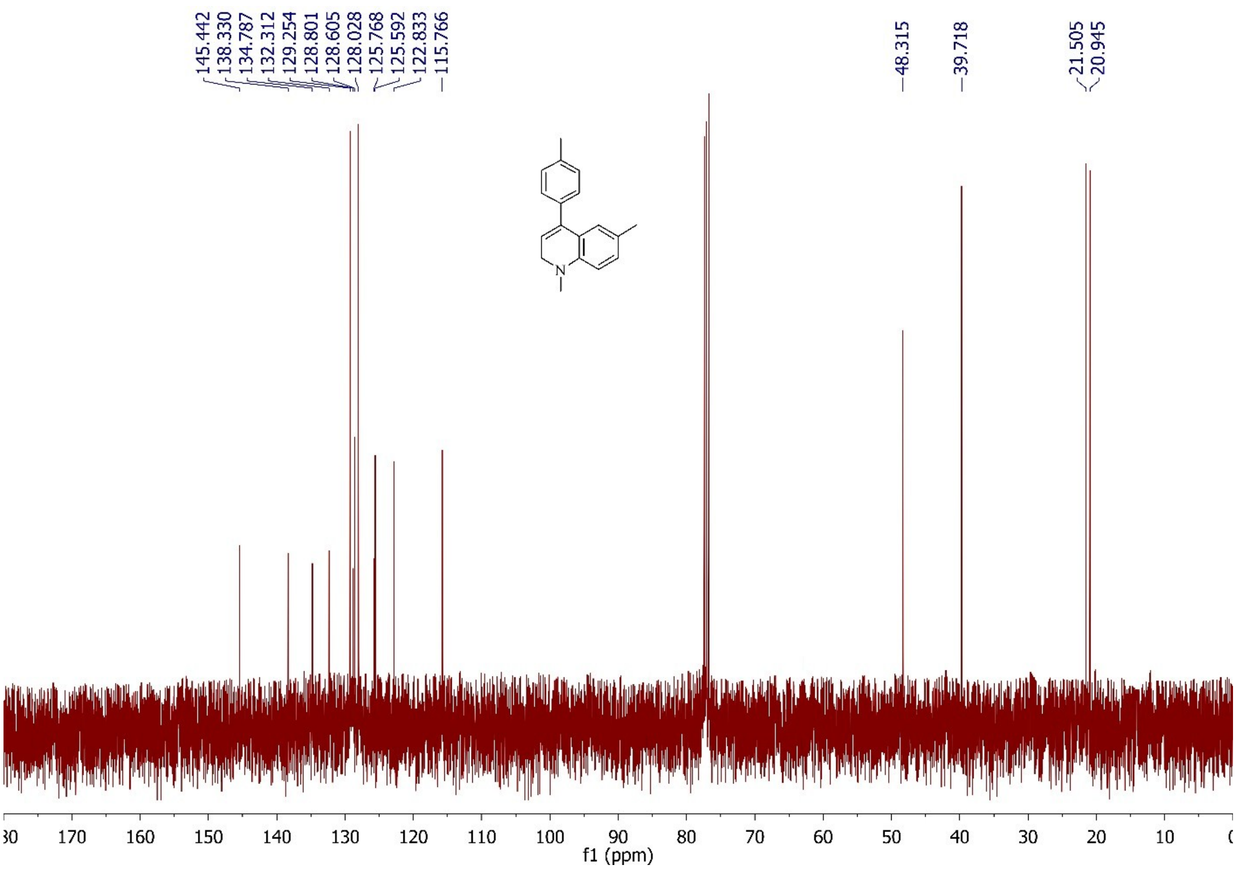
[1]HNMR 7i



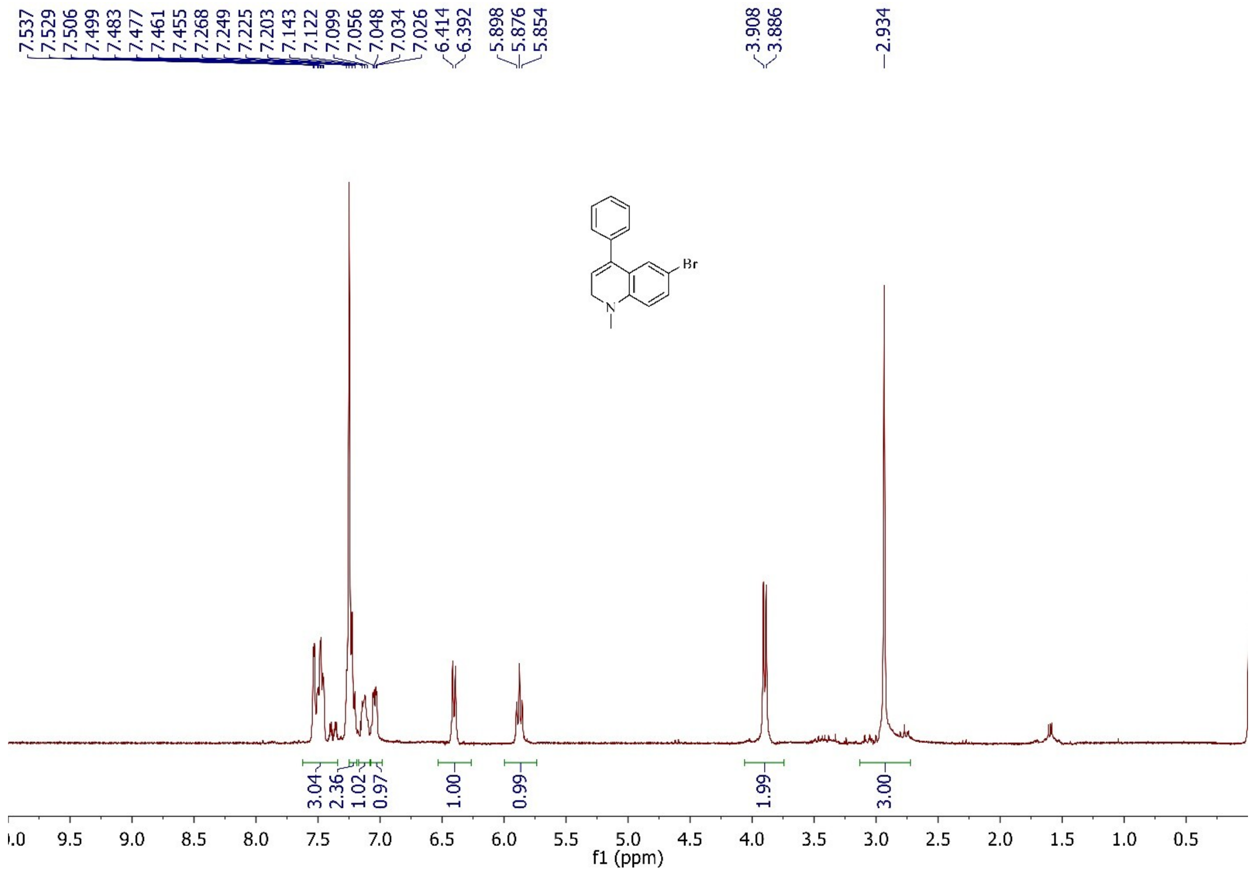
[13]CNMR 7i



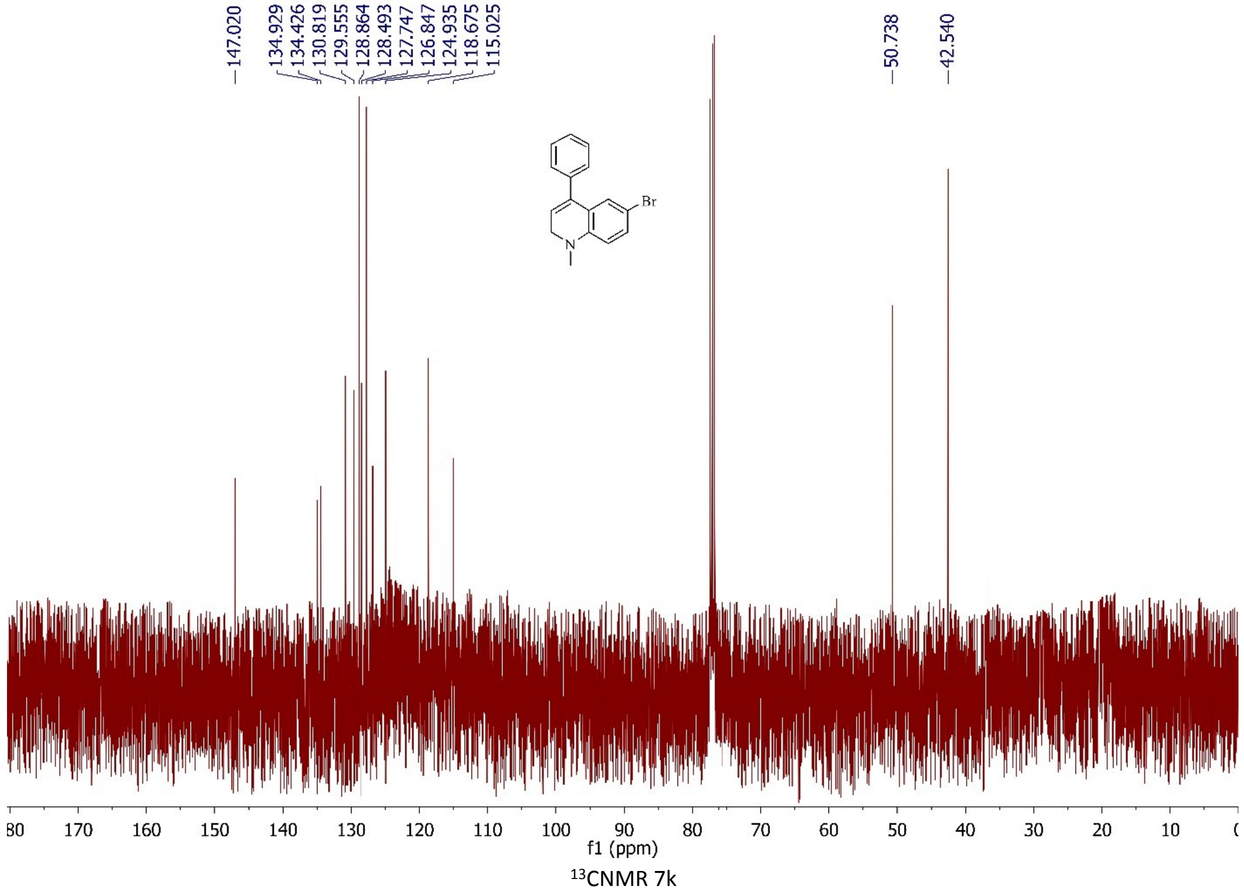
^{1}HNMR 7j



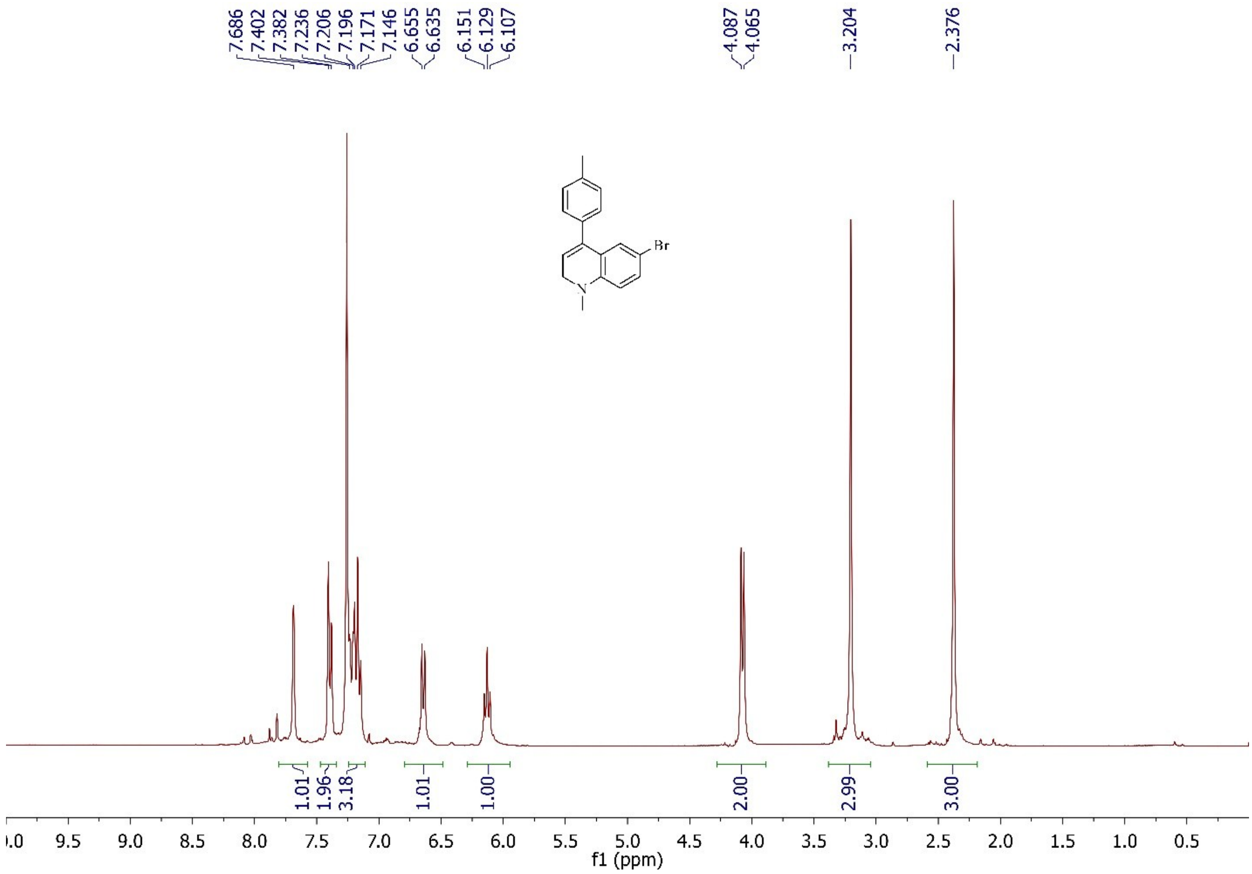
^{13}CNMR 7j



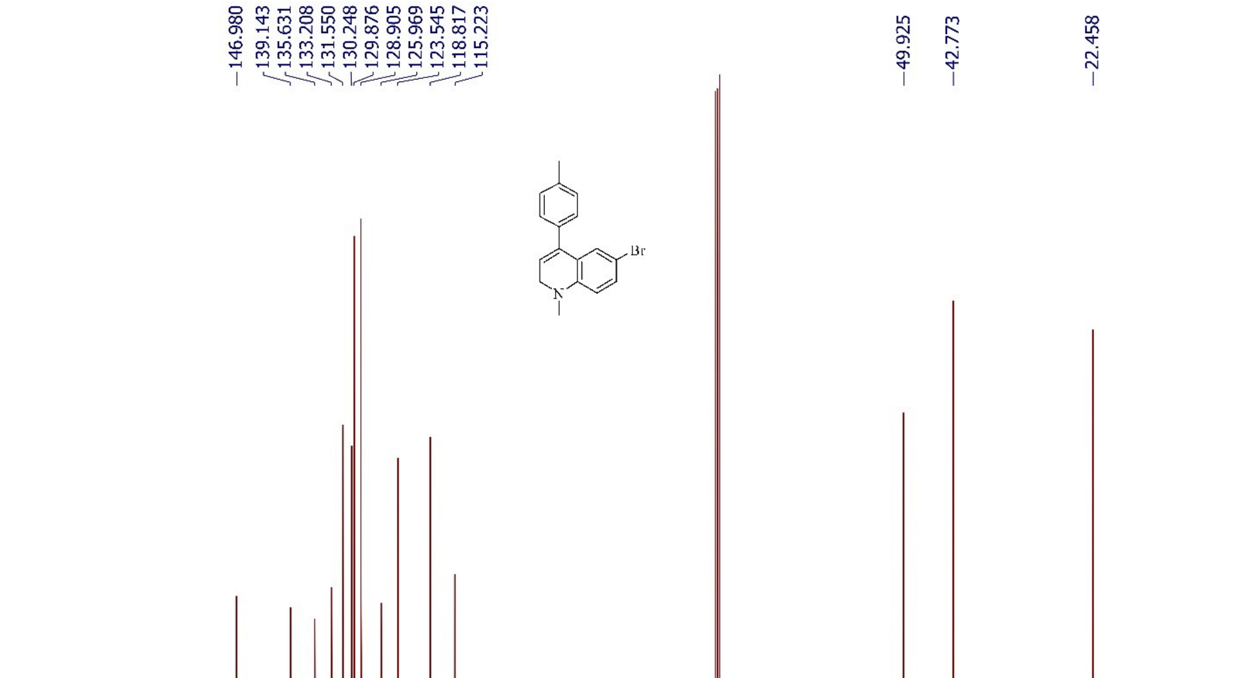
^{1}HNMR 7k



^{13}CNMR 7k



^{1}HNMR 7l



^{13}CNMR 7l

7. References

1. N. Matuszak, G. G. Muccioli, G. Labar, D. M. Lambert, *J. med. chem*, 2009, **52**, 7410.
2. M. Sortino, F. Garibotto, V. Cechinel Filho, M. Gupta, R. Enriz, S. Zacchino, *Bioorg. Med. chem*, 2011, **19**, 2823.
3. X. Ju, D. Li, W. Li, W. Yu, F. Bian, *Adv. Syn. Cat*, 2012, **354**, 3561.
4. J. Tang, G. Grampp, Y. Liu, B.-X. Wang, F.-F. Tao, L.-J. Wang, X.-Z. Liang, 7. H.-Q. Xiao, Y.-M. Shen, *J. org. chem*, 2015, **80**, 2724.
5. M. Hosseini-Sarvari, M. Koohgard, S. Firoozi, A. Mohajeri, H. Tavakolian, *New J. Chem*, 2018, **42**, 6880.
6. Z. Liang, S. Xu, W. Tian, R. Zhang, *Beilstein j. org. chem*, 2015, **11**, 425.
7. J.-T. Guo, D.-C. Yang, Z. Guan, Y.-H. He, *J. Org. Chem*, 2017, **82**, 1888.
8. H. M. Huang, F. Huang, Y. J. Li, J. H. Jia, Q. Ye, L. Han, J. R. Gao, *RSC Adv*, 2014, **4**, 27250.