Supplementary Material (ESI) for Chemical Communications

CuI-catalyzed photochemical or thermal reactions of 3-(2-azidobenzylidene)lactams. Application to the synthesis of fused indoles

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Supporting Information

General remark:

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra were recorded in $CDCl_3$, or DMSO-d_6, or CD_3COCD_3. Chemical shifts (δ) are reported in ppm using TMS as internal standard and spin-spin coupling constants (*J*) are given in Hz. EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX Ⅱ 47e spectrometer by ESI.

Experimental procedures:

General procedure for preparation of **1a-1i** [1]:

3-(2-azidobenzylidene)indol-2-one (**1a**): To a 50 mL single-necked flask containing 10 mL water and 10 mL ethanol was added sodium hydroxide (10 mmol, 0.4 g). The reaction mixture was stirred until the solid was dissolved. Then cooled to room temperture, indole-2-one (5.0 mmol) and 2-azidobenzaldehyde (5.5 mmol) was added. The reaction mixture was stirred at room temperture for 1.0 hour. After addition of water (25 mL), the mixture was filtered and washed with water to give the desired products, yield: 85%.

General procedure for preparation of **2a-2b, 4, 5** [2]:

Ethyl-4-(2-azidobenzylidene)-4,5-dihydro-1,2-dimethyl-5-oxo-1*H*-pyrrole-3-carboxyl -ate (**2a**): To a 50 mL single-necked flask containing 8 mL absolute ethanol was added ethyl 4,5-dihydro-1,2-dimethyl-5-oxo-1*H*-pyrrole-3-carboxylate (8.0 mmol), stirred and at 0℃ 2-azidobenzaldehyde (5.0 mmol) and pyrrolidine (10 mmol) which were dissolved in 10 mL absolute ethanol were dropped slowly. Then the mixture was stirred at room temperature for 2.0 hours. After addition of water (25 mL), the mixture was filtered and washed with water to give the desired products, yield: 95%.

General procedure for preparation of **3a-3b** [3]:

4-(2-azidobenzylidene)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**3a**): To a 50 mL single-necked flask containing 10 mL DMF was added 3-Methyl-1-phenyl-5-pyrazolo -ne (5.0 mmol), 2-azidobenzaldehyde (5.5 mmol) and EDDA (0.5 mmol).The reaction mixture was stirred at room temperature for 2.5 hours. After addition of water (25 m L), the mixture was filtered and washed with water to give the desired products , yield: 85%.

Typical experimental procedures for photolysis

(1) **1a** (0.26 g, 1.0 mmol) was dissolved in 200 mL dry dichloromethane in two 100 mL Pyrex flasks. The solution was deaerated by bubbling Ar for 30 min and irradiated at $\lambda \geq 300$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature until the complete conversion of the starting material. The progress of reaction was monitored by TLC at regular intervals. After the solvent was removed under reduced pressure, the residue was separated by column chromatography on silica gel eluted by hexane : acetone 10 : 1 (v/v) to afford product **6a**.

(2) **1a** (0.26 g, 1.0 mmol) and CuI (0.18 g, 1.0 mmol) were dissolved in 200 mL dry acetonitrile in two 100 mL Pyrex flasks. The solution was deaerated by bubbling Ar for 30 min and irradiated at $\lambda \geq 300$ nm with a medium-pressure mercury lamp (500 W) at ambient temperature until the complete conversion of the starting material. The progress of reaction was monitored by TLC at regular intervals. The solution was diluted with an equivalent volume of methylene dichloride and washed 2 × with ice-cold 10% NH_4OH in saturated NH_4Cl (1:4), 3 × with ice-cold H_2O (until the aqueous phase exhibited pH = 7), and 3× with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was separated by column chromatography on silica gel eluted by hexane : acetone 10 : 1 (v/v) to afford product **6a**.

Typical experimental procedures for thermolysis

3-(2-azidobenzylidene) indol-2-one **1a** (0.26 g, 1.0 mmol) was dissolved in 50 mL dry xylene in 100 mL round-bottom flask. The solution was deaerated by bubbling Ar for half an hour and refluxed for 12 hours under the Ar. The progress of reaction was monitored by TLC at regular intervals of time. After the xylene was removed under

reduced pressure, the residue was separated by column chromatography on silica gel eluted by hexane : acetate 10:1(v/v) to afforded product **6a**. The solid was further purified by recrystallization from methanol.

References:

(1) E. P. Kohler, H. M. Chadwell, *Org Synth*., 1922, **2:**1.

(2) K. Ashok, J. K. Saxena, M. S. Prem, *Medicinal Chemistry*, 2008, **4**, 577.

(3)Y. Hu, P. Wei, H. Zhou, *Chinese Chemical Letters*., 2006, **17**, 299.

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Analytical data for compounds (1a-1i, 2a-2c, 3a-3b, 4, 5)

3-(2-azidobenzylidene)indolin-2-one (**1a**): Pale yellow solid; ^{1}H NMR (400 MHz, CD Cl_3): δ = 8.08 (s, 1H, NH), 7.81 (s, 1H, CH), 7.72 (d, 1H, *J* = 7.2 Hz, ArCH), 7.49 (t, 1H, *J* = 7.6 Hz, ArCH), 7.41 (d, 1H, *J* = 7.6 Hz, ArCH), 7.30-7.19 (m, 3H, ArCH), 6. 89 - 6.83 (m, 2H, ArCH).

3-(2-azidobenzylidene)-1-methylindolin-2-one (**1b**): Pale yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.55 (d, 1H, *J* = 8.4 Hz, ArCH), 7.78 (s, 1H, CH), 7.56 (d, 1H, *J* = 6.9 Hz, ArCH), 7.44 (t, 1H, *J* = 8.4 Hz, ArCH), 7.31 (d, 1H, *J* = 7.5 Hz, ArCH), 7.18-7.23 (m, 2H, ArCH), 7.07 (t, 1H, *J* = 7.5 Hz, ArCH), 6.80 (d, 1H, *J* = 7.5 Hz, ArCH), 3.24 (s, 3H, CH_3).

3-(2-azidobenzylidene)-1-phenylindolin-2-one (**1c**): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (s, 1H, CH), 7.74 (d, 1H, *J* = 7.6 Hz, ArCH), 7.54-7.41 (m, 7H, ArC H), 7.29 (d, 1H, *J* = 8.0 Hz, ArCH), 7.24 (t, 1H, *J* = 7.2 Hz, ArCH), 7.18 (t, 1H, *J* = 7. 6 Hz, ArCH), 6.88 (t, 1H, *J* = 7.6 Hz, ArCH), 6.81 (d, 1H, *J* = 7.6 Hz, ArCH).

3-(2-azidobenzylidene)-5-chloroindolin-2-one (**1d**): Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (s, 1H, NH), 7.87 (s, 1H, CH), 7.68 (d, 1H, *J* = 7.6 Hz, ArCH), 7.52 (t, 1H, *J* = 7.6 Hz, ArCH), 7.38 (d, 1H, *J* = 1.6 Hz, ArCH), 7.31-7.24 (m, 2H, Ar CH), 7.19 (dd, 1H, *J* = 8.0 Hz, 2.0Hz, ArCH), 6.86 (d, 1H, *J* = 8.4 Hz, ArCH).

3-(2-azido-4,5-dimethoxybenzylidene)-1-methylindolin-2-one (**1e**): Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.09 (s, 1H, CH), 7.87 (s, 1H, ArCH), 7.54 (d, 1H, *J* = 7.6 Hz, ArCH), 7.29 (d, 1H, *J* = 8.0 Hz, ArCH), 7.06 (t, 1H, *J* = 7.6 Hz, ArCH), 6.9 1 (t, 1H, *J* = 8.0 Hz, ArCH), 6.73 (s, 1H, ArCH), 3.98 (s, 3H, OCH_3), 4.02 (s, 3H, OC H_3), 3.28 (s, 3H, N-CH_3).

3-(2-azido-4,5-dimethoxybenzylidene)-1-phenylindolin-2-one (**1f**): Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 1H, CH), 7.98 (s, 1H, ArCH), 7.64 (d, 1H, *J* = 7.6 Hz, ArCH), 7.53 (t, 2H, *J* = 7. 6 Hz, ArCH), 7.46-7.41 (m, 3H, ArCH), 7.18 (t, 1 H, *J* = 7.6 Hz, ArCH), 7.09 (t, 1H, *J* = 7.6 Hz, ArCH), 6.76 (d, 1H, *J* = 8.0 Hz, ArCH), 6.66 (s, 1H, ArCH), 3.97 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3).

Ethyl 4-azido-3-((1-methyl-2oxoindolin-3-yllidene)methyl)benzoate (**1g**): Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H, CH), 8.13 (d, 1H, *J* = 7.6 Hz, ArC H), 7.78 (s, 1H, ArCH), 7.36-7.27 (m, 3H, ArCH), 6.87 (d, 1H, *J* = 7.6 Hz, ArCH), 6.8 3 (d, 1H, *J* = 8.0 Hz, ArCH), 4.37 (q, 2H, *J* = 7.2 Hz, CH_2), 3.28 (s, 3H, CH_3), 1.37 (t, 3H, *J* = 7.2 Hz, CH_3).

Methyl 4-azido-3-((2-oxo-1-phenylindolin-3-yllidene)methyl)benzoate (**1h**): yellow s olid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, 1H, *J* = 1.6 Hz, ArCH), 8.16 (dd, 1H, *J* = 1.6 Hz, 8.4Hz, ArCH), 7.86 (s, 1H, CH), 7.55 (t, 2H, *J* = 7.6 Hz, ArCH), 7.47-7.34 (m, 5H, ArCH), 7.20 (t, 1H, *J* = 7.6 Hz, ArCH), 6.90 (t, 1H, *J* = 7.6 Hz, ArCH), 6.83 (d, 1H, *J* = 8.0 Hz, ArCH), 3.93 (s, 3H, CH_3).

3-(2-azido-4-chlorobenzylidene)-1-phenylindolin-2-one (**1i**): Pale yellow solid; ^{1}H N MR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1H, CH), 7.77 (d, 1H, *J* = 8.1 Hz, ArCH), 7.56-7.39 (m, 8H, ArCH), 7.19 (t, 2H, *J* = 7.5 Hz, ArCH), 6.82 (d, 1H, *J* = 7.8 Hz, ArCH).

Ethyl-4-(2-azidobenzylidene)-4,5-dihydro-1,2-dimethyl-5-oxo-1*H*-pyrrole-3-carboxyl ate (**2a**): Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (s, 1H, CH), 8.11 (d, 1H, *J* = 8.1 Hz, ArCH), 7.90 (d, 1H, *J* = 7.5 Hz, ArCH), 7.39-7.31 (m, 2H, ArCH), 4.3 3 (q, 2H, *J* = 6.9 Hz, CH_2), 3.12 (s, 3H, N-CH_3), 2.53 (s, 3H, CH_3), 1.40 (t, *J* = 6.9 Hz, 3H, CH_3).

Ethyl-4-(2-azidobenzylidene)-4,5-dihydro-2-methyl-5-oxo-1-phenyl-1*H*-pyrrole-3-car boxylate (**2b**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H, CH), 8.17

(d, 1H, *J* = 7.6 Hz, ArCH), 7.46 (t, 3H, *J* = 8.0 Hz, ArCH), 7.41 (d, 2H, *J* = 7.2 Hz, Ar CH), 7.37 (t, 1H, *J* = 7.6 Hz, ArCH), 7.18 (d, 1H, *J* = 8.0 Hz, ArCH), 7.09 (t, 1H, *J* = 7. 6 Hz, ArCH), 4.37 (q, 2H, *J* = 7.2 Hz, CH_2), 2.35 (s, 3H, CH_3), 1.41 (t, 3H, CH_3).

Ethyl-4-(2-azido-4-chlorobenzylidene)-4,5-dihydro-2-methyl-5-oxo-1-phenyl-1*H*-pyr role-3-carboxylate (**2c**): Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, 1H, J = 8.4 Hz, ArCH), 8.34 (s, 1H, CH), 8.28 (s, 1H, ArCH), 8.20 (d, 1H, *J* = 8.4 Hz, ArC H), 7.50-7.40 (m, 5H, ArCH), 4.37 (q, 2H, *J* = 6.8 Hz, CH_2), 2.34 (s, 3H, CH_3), 1.41 (t, 3H, *J* = 6.8 Hz, CH_3).

4-(2-azidobenzylidene)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**3a**): Red solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.09 (d, 1H, *J* = 8.0 Hz, ArCH), 7.93 (d, 2H, *J* = 8.0 Hz, ArCH), 7.77 (s, 1H, CH), 7.54 (t, 1H, *J* = 7.6 Hz, ArCH), 7.39 (t, 2H, *J* = 7.6 Hz, ArC H), 7.27-7.16 (m, 3H, ArCH), 2.35 (s, 3H, CH_3).

4-(2-azidobenzylidene)-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (**3b**): Red solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, 1H, *J* = 8.0 Hz, ArCH), 8.01-8.04 (m, 3H, ArCH), 7. 69-7.72 (m, 2H, ArCH), 7.52-7.56 (m, 3H, ArCH), 7.42 (t, 2H, *J* = 8.0 Hz, ArCH), 7. 35 (s, 1H, CH), 7.25 (d, 1H, *J* = 6.4 Hz, ArCH), 7.20 (t, 2H, *J* = 4 Hz, ArCH).

4-(2-azidobenzylidene)-2-phenylisoquinoline-1,3(2*H*,4*H*)-dione (**4**): Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, 1H, *J* = 7.8 Hz, ArCH), 8.21 (s, 1H, CH), 7. 55 - 7.41 (m, 6H, ArCH), 7.36 (t, 2H, *J* = 6.9 Hz, ArCH), 7.34-7.25 (m, 3H, ArCH), 7. 12 (t, 1H, *J* = 7.5 Hz, ArCH).

5-(2-azidobenzylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (**5**): Pale y ellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1H, CH), 7.88 (d, 1H, *J* = 7.8 H z, ArCH), 7.52 (t, 1H, *J* = 7.8 Hz, ArCH), 7.25 (t, 1H, *J* = 7.5 Hz, ArCH), 7.18 (d, 1H, *J* = 7.5 Hz, ArCH), 3.31 (s, 3H, CH_3), 3.33 (s, 3H, CH_3).

Analytical data for compounds (6a-6i, 8a-8b, 7a-7c, 9, 10)

5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6a**): Yellow solid; mp > 360 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.56 (s, 1H, NH), 11.43 (s, 1H, NH), 8.18 (d, 2H, *J* = 7.5 Hz, ArCH), 7.60 (d, 2H, *J* = 7.8 Hz, ArCH), 7.22-7.52 (m, 4H, ArCH); ^{13}C NMR (100 M Hz, DMSO-d_6): δ = 160.3, 141.2, 138.4, 138.2, 129.6, 124.8, 124.4, 122.6, 122.0, 12 1.5, 12 1.2, 116.5, 112.4, 112.1, 106.9; MS (EI-*m/z*): 234 (M^+, 100); HRMS Calcd for $C_{15}H_{10}N_2O$ $(M+1)^+$ 235.0866, Found 235.0860.

5-methyl-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6b**): Yellow solid; mp > 360 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.59 (s, 1H, NH), 8.22-8.30 (m, 2H, ArCH), 7.6 1-7.66 (m, 3H, ArCH), 7.35-7.40 (m, 2H, ArCH), 7.27 (t, 1H, *J* = 7.5 Hz, ArCH), 3. 73 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.5, 140.1, 139.1, 138.2, 13 0.1, 125.0, 124.6, 12 3.0, 122.1, 121.6, 121.3, 116.1, 113.3, 112.1, 106.3, 28.9; MS (EI-*m/z*): 248 (M^+, 100); HR MS Calcd for $C_{16}H_{12}N_2O$ $(M+1)^+$ 249.1022, Found 24 9.1025.

5-phenyl-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6c**): Yellow solid; mp > 360 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.85 (s, 1H, NH), 8.31 (dd, 1H, *J* = 1.2, 7.6 Hz, Ar CH), 8.17 (d, 1H, *J* = 8.4 Hz, ArCH), 7.64-7.70 (m, 4H, ArCH), 7.59 (d, 1H, *J* = 7.6 Hz, ArCH), 7.30-7.44 (m, 5H, ArCH), 6.64 (d, 1H, *J* = 8.4 Hz, ArCH); ^{13}C NMR (10 0 MHz, DMSO-d_6): δ = 158.6, 139.7, 139.4, 137.8, 137.4,129.4, 129.4, 12 9. 3, 129.3, 128.7, 127.9, 124.1, 123.7, 122.1, 12 1.4, 120.7, 120.2, 115.9, 11 2.2, 111.3, 105.4; M S (EI-*m/z*): 310 (M^+, 100); HRMS Calcd for $C_{21}H_{14}N_2O$ $(M+1)^+$ 31 1.1179, Found 31 1.1175.

2-chloro-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6d**): Dark yellow solid; mp: 293-295 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 12.64 (s, 1H, NH), 11.60 (s, 1H, NH), 8.33 (s, 1H, ArCH), 8.20 (d, 1H, *J* = 7.5 Hz, ArCH), 7.63 (d, 1H, *J* = 7.8 Hz, ArCH), 7.54 (d,

1H, *J* = 8.7 Hz, ArCH), 7.46 (d, 1H, *J* = 8.7 Hz, ArCH), 7.39 (t, 1H, *J* = 7.5 Hz, ArC H), 7.28 (t, 1H, *J* = 7.5 Hz, ArCH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.1, 139. 9, 138.2, 137.1, 129.4, 125.9, 124.8, 124.6, 121.9, 121.7, 121.3, 118.3, 113.7, 112.3, 107.5; MS (EI-*m/z*): 268 (M^+, 100); HRMS Calcd for $C_{15}H_9ClN_2O$ $(M+1)^+$ 269.0476, Found 269.0481.

8,9-dimethoxy-5-methyl-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6e**): Yellow solid mp: 230-232 °C; ^{1}H NMR (400 Hz, DMSO-d_6): δ = 12.31 (s, 1H, NH), 8.20 (d, 1H, J = 7.6 Hz, ArCH), 7.70 (s, 1H, ArCH), 7.56-7.58 (m, 2H, ArCH), 7.35 (t, 1H, ArCH), 7.10 (s, 1 H, ArCH), 3.87 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.72 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.1, 148.2, 145.6, 138.1, 137.9, 132.3, 128.7, 122.0, 12 1.6, 11 7.2, 115.6, 113.3, 106.1, 102.7, 95.2, 55.8, 55.7, 28.4; MS (EI-m/z): 308 (M^+, 100); HRMS Calcd for $C_{18}H_{16}N_2O_3$ $(M+1)^+$ 309.1234, Found 309.1228.

8,9-dimethoxy-5-phenyl-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6f**): Dark yellow so lid; mp: 200-203 °C; ^{1}H NMR (400 Hz, DMSO-d_6): δ = 12.50 (s, 1H, NH), 8.25 (m, 1 H, ArCH), 7.65 (m, 3H, ArCH), 7.57 (t, 1H, *J* = 7.2 Hz, ArCH), 7.35 (m, 4H, ArCH), 7.17 (s, 1H, ArCH), 6.62 (d, 1H, *J* = 8.0 Hz, ArCH), 3.90 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.7, 147.8, 145.3, 138.7, 138.1, 137. 9, 131.9, 129.4, 129.4, 129.3, 129.3, 127.9, 127.8, 121.4, 121.3, 116.7, 115.9, 112.6, 105.7, 102.1, 94.8, 55.2, 55.2; MS (EI-m/z): 370 (M^+, 100); HRMS Ca lcd for $C_{23}H_{18}$ N_2O_3 $(M+1)^+$ 371.1390, Found 371.1395.

Ethyl6, 11-dihydro-5-methyl-6-oxo-5*H*-indolo[3,2-c]quinoline-8-carboxylate (**6g**) : White solid; mp: 310-312 °C; ^{1}H NMR (400 Hz, CD_3COCD_3): δ = 8.98 (d, 1H, *J* = 1.2 Hz, ArCH), 8.34 (d, 1H, *J* = 7.6 Hz, ArCH), 8.03 (dd, 1H, *J* = 8.8, 1.6 Hz, ArCH), 7. 73 (d, 1H, *J* = 8.8 Hz, ArCH), 7.42-7.70 (m, 3H, ArCH), 4.40 (q, 2H, *J* = 7.2 Hz, CH_2), 3.81 (s, 3 H, CH_3), 1.42 (t, 3H, *J* = 7.2 Hz, CH_2CH_3); ^{13}C NMR (100 MHz, $CD_3C OD_3$): δ = 176.1, 16 8.6, 150.8, 150.2, 148.8, 139.8, 134.8, 134.0, 132.6, 132.5,

13 1.4, 125.3, 122.4, 121.1, 116.2, 70.0, 38.8, 23.7; MS (EI-*m/z*): 320 (M^+, 100); HRMS Calcd for $C_{19}H_{16}N_2O_3$ $(M+1)^+$ 321.1234, Found 321.1241.

Methyl6,11-dihydro-6-oxo-5-phenyl-5*H*-indolo[3,2-c]quinoline-8-carboxylate (**6h**): White solid; mp: 338-340 °C; ^{1}H NMR (400Hz, CD_3COCD_3): δ = 8.95 (d, 1H, *J* = 1. 2Hz, Ar CH), 8.39 (dd, 1H, *J* = 8.0, 1.2Hz, ArCH), 8.06 (dd, 1H, *J* = 8.8, 1.6Hz, Ar CH), 7.80 (d, 1H, *J* = 8.4Hz, ArCH), 7.70 (t, 2H, *J* = 8.0Hz, ArCH), 7.62 (t, 1H, *J* = 7.2Hz, Ar CH), 7.41-7.51 (m, 4H, ArCH), 3.92 (s, 3H, CH_3); ^{13}C NMR (100MHz, C D_3COCD_3): δ = 166.8,153.4,104.5,140.2,138.1,129.8, 129.8,129.4, 129.4,129.3, 129.3, 128.3, 125.0, 122.9, 122.7, 122.5, 121.8, 121.8, 116.4, 112.4, 111.5, 107.1, 51.3; MS (EI-*m/z*): 368 (M^+, 26); HRMS Calcd for $C_{23}H_{16}N_2O_3$ $(M+1)^+$ 369.1234, Found 369.1239.

9-chloro-5-phenyl-5*H*-indolo[3,2-c]quinolin-6(11*H*)-one (**6i**): Yellow solid; mp: 225 - 227 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 12.85 (s, 1H, NH), 8.32 (dd, 1H, *J* = 7.6, 1.2 Hz, ArCH), 8.13 (d, 1H, *J* = 8.4Hz, ArCH), 7.69-7.66 (m, 3H, ArCH), 7.59 (d, 1H, *J* = 7.6Hz, ArCH), 7.44-7.42 (m, 1H, ArCH), 7.38 (d, 3H, *J* = 7.6Hz, ArCH), 7.31 (dd, 1H, *J* = 8.4, 2.0Hz, ArCH), 6.64 (d, 1H, *J* = 8.4Hz, ArCH); ^{13}C NMR (100MHz, DM SO-d_6): δ = 158.4, 140.6, 139.6, 38.0, 137.7, 129.5, 129.5 ,129.3, 129.3, 129.1, 128.3, 128.1, 123.0, 122.2, 121.6, 121.4, 121.2, 116.1, 112.1, 111.1, 105.4; MS (EI-*m/z*): 34 4 (M^+,60); HRMS Calcd for $C_{21}H_{13}ClN_2O$ $(M+1)^+$ 345.0789, Found 345.0783.

Ethyl.2, 5-dihydro-2,3-dimethyl-1-oxo-1*H*-pyrido[4,3-b]indole-4-carboxylate (**7a**): W hite solid; mp: 162-164 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 11.27 (s, 1H, NH), 8. 13 (d, 1H, *J* = 7.6Hz, ArCH), 7.65 (d, 1H, *J* = 8.0Hz, ArCH), 7.33-7.29 (m, 1H, ArC H), 7. 21 (t, 1H, *J* = 7.6Hz, ArCH), 4.44 (q, 2H, *J* = 7.2Hz, CH_2), 3.62 (s, 3H, N-CH $_3$), 2.76 (s, 3H, CH_3), 1.38 (t, 3H, *J* = 7.2Hz, CH_3); ^{13}C NMR (100MHz, DM SO-d_6): δ = 165.0, 158.1, 150.4, 140.7, 137.1, 123.3, 123.1, 120.3, 119.6, 111.5, 103.6, 98.7, 6 0.4, 29.8, 18.0, 13.7; MS (EI-*m/z*): 284 (M^+, 64); HRMS Calcd for $C_{16}H_{16}N_2O_3$ (M+ 1)$^+$ 285.1234, Found 285.1236.

Ethyl.2,5-dihydro-3-methyl-1-oxo-2-phenyl-1*H*-pyrido[4,3-b]indole-4-carboxylate (**7b**): White solid; mp: 216-219 °C; ^{1}H NMR (300MHz, $CDCl_3$): δ = 10.07 (s, 1H, N H), 8.28 (d, 1H, *J* = 10.5Hz, ArCH), 7.53 (d, 2H, *J* = 8.1Hz, ArCH), 7.50-7.45 (m, 2H, ArCH), 7.35 (t, 1H, *J* = 6.9Hz, ArCH), 7.30 (dd, 2H, *J* = 6.9, 8.1Hz, ArCH), 7.24 (d, 1H, *J* = 6.0Hz, ArCH), 4.47 (q, 2H, *J* = 7.2Hz, CH_2), 2,47 (s, 3H, CH_3), 1.45 (t, 3 H, *J* = 7. 2Hz, CH_3); ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.6, 160.0, 151.5, 142.8, 139.1, 1 36.9, 130.0, 128.8, 128.6, 124.5, 124.2, 121.8, 121.5, 110.8, 105.9, 99.4, 61.4, 21.2, 1 4.4; MS (EI-*m/z*): 346 (M^+, 28); HRMS Calcd for $C_{21}H_{18}N_2O_3$ $(M+1)^+$ 347.1390, Found 347.1393.

Ethyl.7-chloro-2,5-dihydro-3-methyl-1-oxo-2-phenyl-1*H*-pyrido[4,3-b]indole-4-carbo -xylate (**7c**): White solid; mp: 167-169 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 11.57 (s, 1 H, NH), 8.00 (d, 1H, *J* = 8.4Hz, ArCH), 7.73 (d, 1H, *J* = 1.6Hz, ArCH), 7.60-7. 56 (m, 2H, ArCH), 7.53-7.50 (m, 1H, ArCH), 7.35 (d, 2H, *J* = 7.2Hz, ArCH), 7.27- 7. 24 (m, 1 H, ArCH), 4.46 (q, 2H, *J* = 7.2Hz, CH_2), 2.34 (s, 3H, CH_3), 1.38 (t, 3H, *J* = 7.2Hz, CH_3); ^{13}C NMR (100MHz, DMSO-d_6): δ = 164.7, 158.2, 150.5, 142.0, 138.3, 137.7, 12 9.0, 129.0, 128.4, 128.4, 128.1, 127.8, 122.0, 120.9, 120.6, 111.5, 104.0, 9 8.7, 60.6, 2 0.0, 13.7; MS (EI-*m/z*): 380 (M^+, 5); HRMS Calcd for $C_{21}H_{17}ClN_2O_3$ $(M+1)^+$ 381.1000, Found 381.1005.

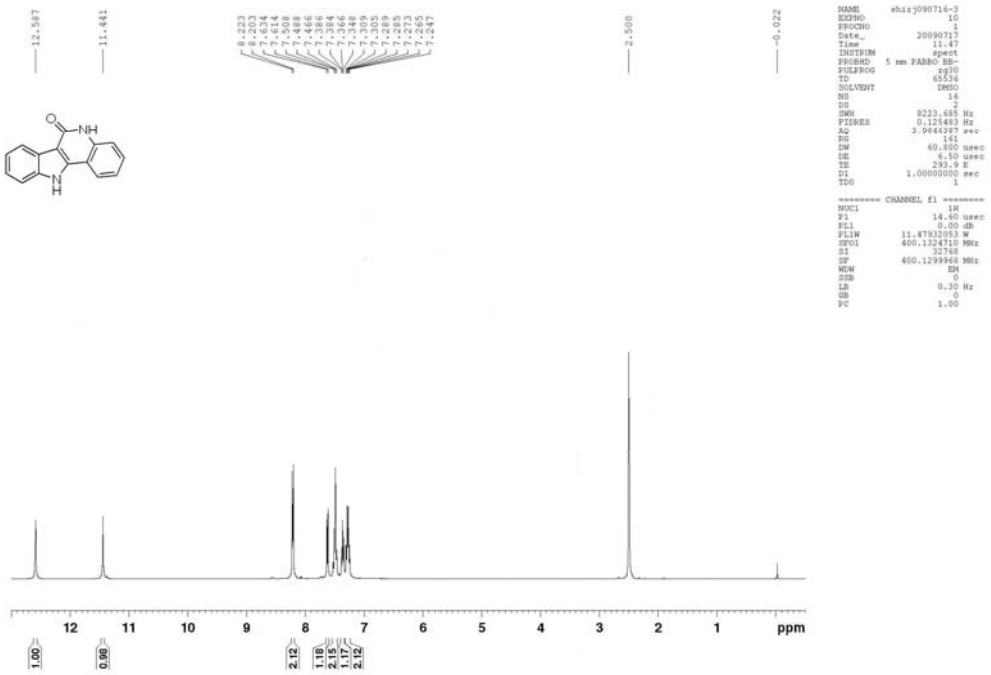
4-methyl-2-phenyl-2*H*-pyridazino[4,5-b]indol-1(5*H*)-one (**8a**); Pale yellow solid; mp: 280-282 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 12.50 (s, 1H, NH), 8.22 (d, 1H, *J* = 8.0 Hz, ArCH), 7.71 (d, 1H, *J* = 8.0Hz, ArCH), 7.60 (d, 2H, *J* = 7.6Hz, ArCH), 7.51 (t, 3H,*J* = 7.6Hz, ArCH), 7.42-7.34 (m, 2H, ArCH), 2.63 (s, 3H, CH_3); ^{13}C NMR (100 M Hz, DMSO-d_6): δ = 157.4, 141.6, 137.8, 136.0, 135.4, 127.8, 127.8, 126.6, 125.9, 12 5.9, 125.8, 122.3, 121.3, 121.1, 112.2, 110.4, 16.9; MS (EI-*m/z*): 275 (M^+, 87); HRM S Calcd for $C_{17}H_{13}N_3O$ $(M+1)^+$ 276.1131, Found 276.1127.

2,4-diphenyl-2*H*-pyridazino[4,5-b]indol-1(5*H*)-one (**8b**): Yellow solid; mp: 229-232 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 12.28 (s, 1H, NH), 8.28 (d, 1H, *J* = 7.6Hz, Ar CH), 7. 93 -7.90 (m, 2H, ArCH), 7.74-7.71 (m, 3H, ArCH), 7.63-7.59 (m, 3H, ArCH), 7.53 (t, 3H, *J* = 7.6Hz, ArCH), 7.44 (d, 1H, *J* = 7.6Hz, ArCH), 7.37 (d, 1H, *J* = 8.0Hz, ArCH); ^{13}C NMR (100MHz, DMSO-d_6): δ = 157.2, 141.5, 138.5, 137.0, 134.2, 133.2, 129.0, 12 8.5, 128.5, 127.9, 127.9, 127.8, 127.8, 126.9, 126.0, 125.9, 125.9 , 122.3, 12 1.5, 121.0, 112.6, 111.6; MS (EI-*m/z*): 337 (M^+, 39); HRMS Calcd for $C_{22}H_{15}N_3O$ (M +1)$^+$ 338.1288, Found 338.1285.

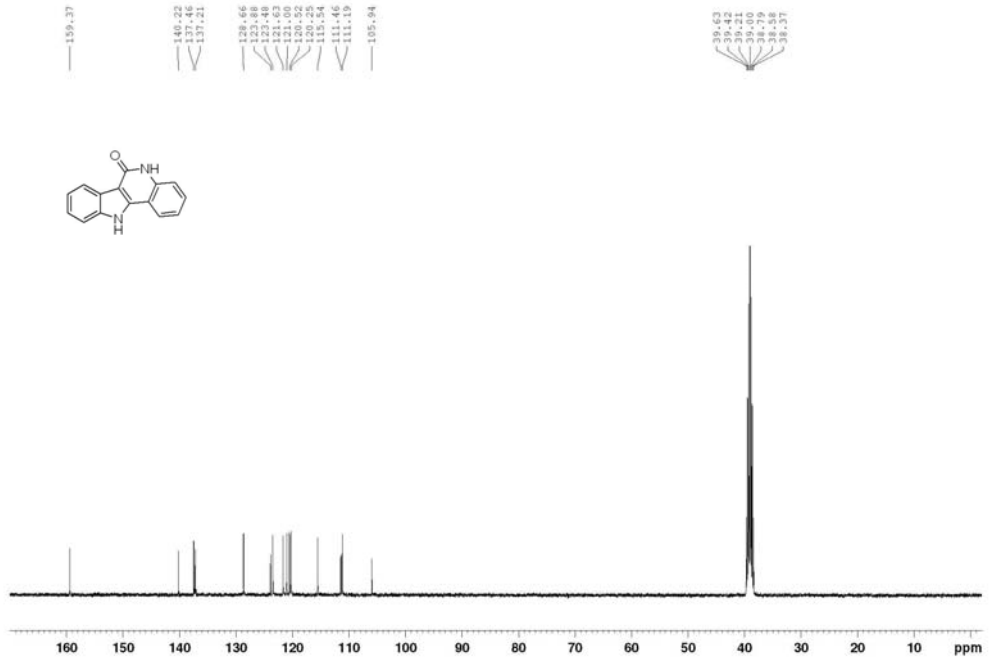
2-phenylbenzo[e]azepino[4,3-b]indole-1,3(2*H*,6*H*)-dione (**9**): White solid; mp: 180 -182 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ = 10.05 (s, 1H, NH), 8.39 (d, 1H, *J* = 8.0Hz, ArCH), 8.24 (dd, 1H, *J* = 8.0, 1.2Hz, ArCH), 7.79 (d, 1H, *J* = 7.6Hz, ArCH), 7.60 - 7. 56 (m, 1H, ArCH), 7.50-7.20 (m, 9H, ArCH); ^{13}C NMR (100MHz, $CDCl_3$): δ = 168.9, 163.8, 140.3, 136.9, 136.1, 134.1, 132.8, 132.8, 132.5, 129.6,129.4, 129.4, 12 8.4, 12 8.4, 128.3, 128.1, 127.1, 125.1, 125.0, 122.7, 111.3, 109.3; MS (EI-*m/z*): 338 (M^+, 65); HRMS Calcd for $C_{22}H_{14}N_2O_2$ (M +1)$^+$ 339.1128, Found 339.1122.

2,4-dimethyl-[1,3]diazepino[5,6-b]indole-1,3,5(2*H*,4*H*,6*H*)-trione (**10**): White solid; mp: 267-269 °C; ^{1}H NMR (400MHz, DMSO-d_6): δ = 12.86 (s, 1H, NH), 8.37 (d, 1H, *J* = 8.0Hz, ArCH), 7.60 (d, 1H, *J* = 8.0Hz, ArCH), 7.46-7.43 (m,1H,ArCH), 7.33 (t, 1 H, *J* = Hz, ArCH), 3.44 (s, 3H, CH_3), 3,43 (s, 3H, CH_3); ^{13}C NMR (100MHz, DMSO -d_6) : δ = 160.4, 157.4, 150.5, 136.0, 132.1, 129.3, 126.0, 125.9, 122.6, 112.6, 108.4, 34.1, 34.0; MS (EI-*m/z*): 257 (M^+,60); HRMS Calcd for $C_{13}H_{11}N_3O_3$ (M +1)$^+$ 258.08 73, Found 258.0878.

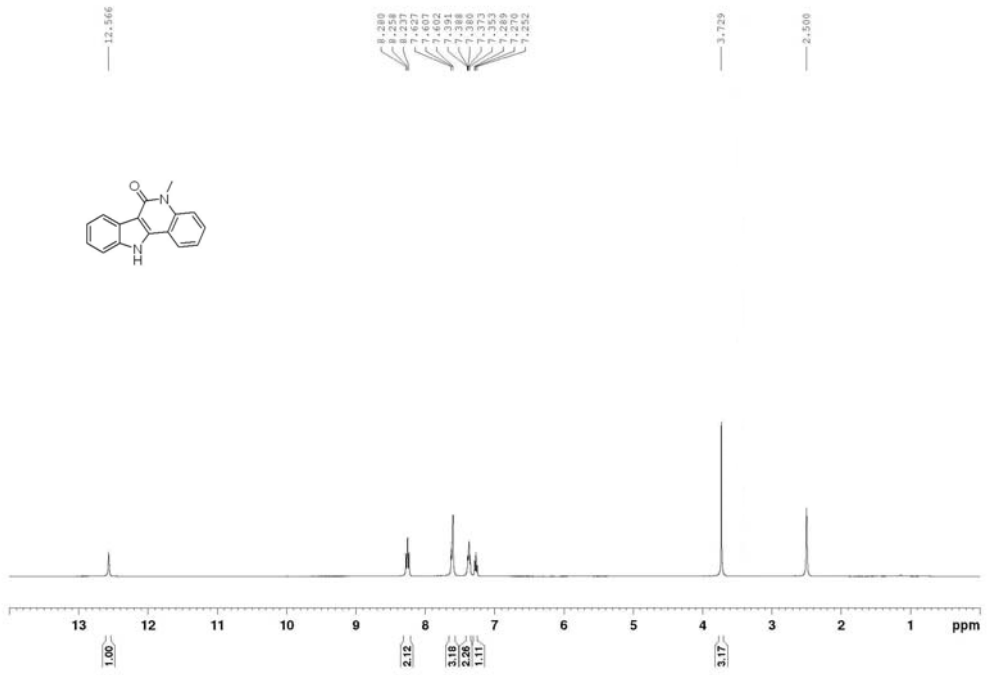
^{1}H NMR of **6a**.



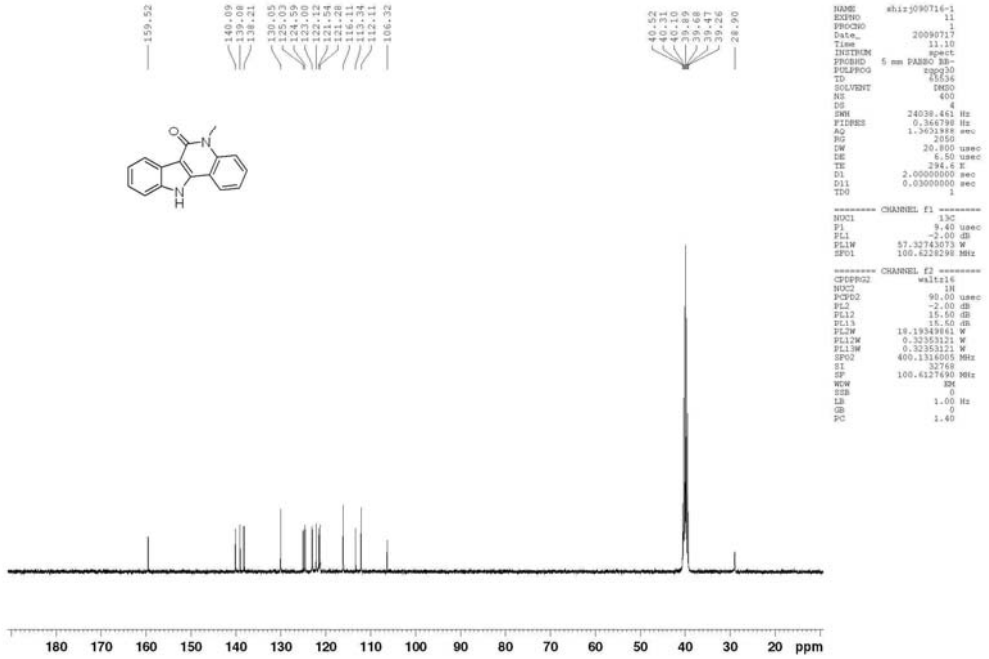
^{13}C NMR of **6a**



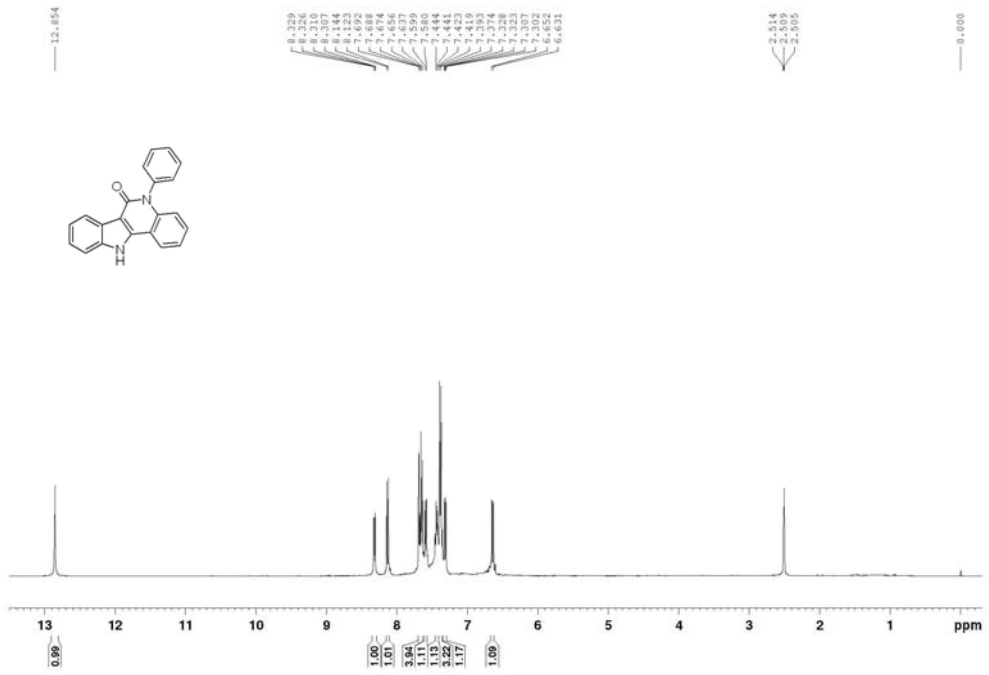
^{1}H NMR of **6b**.



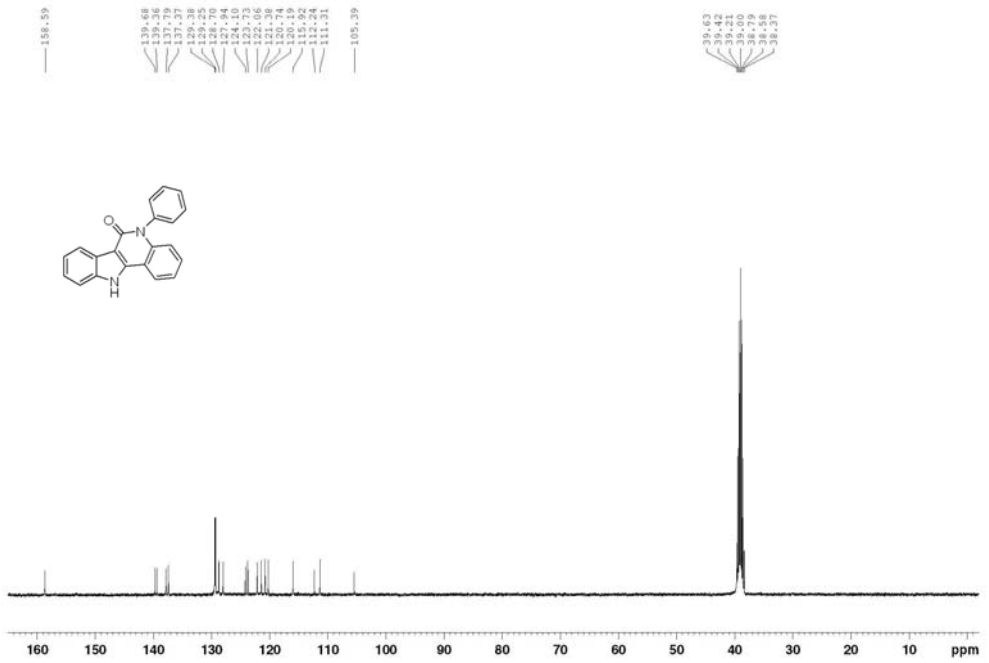
^{13}C NMR of **6b**



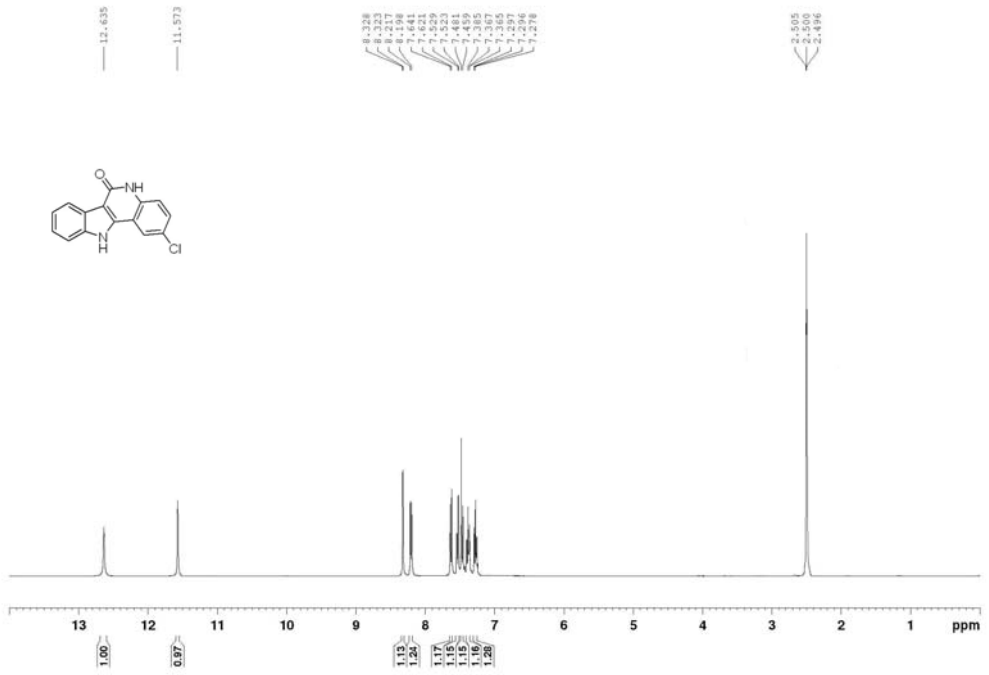
^{1}H NMR of **6c**.



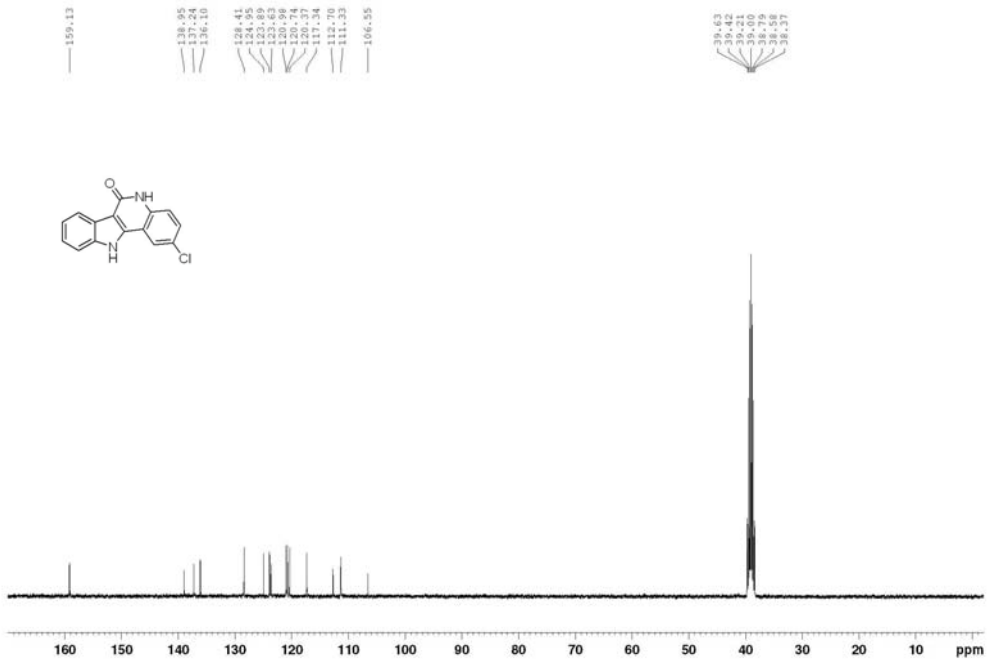
^{13}C NMR of **6c**



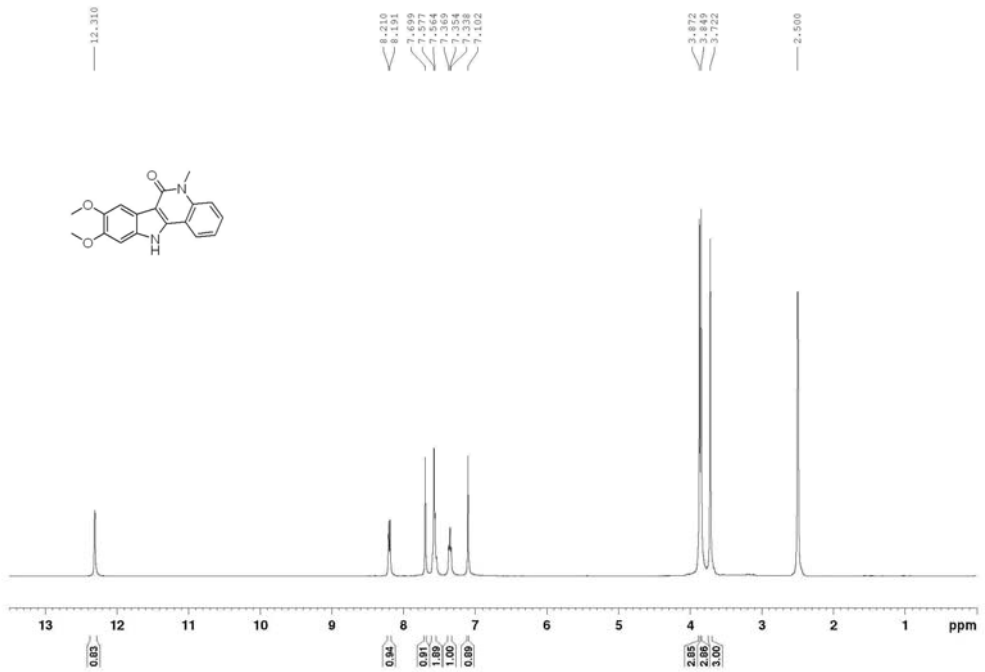
^{1}H NMR of **6d**.



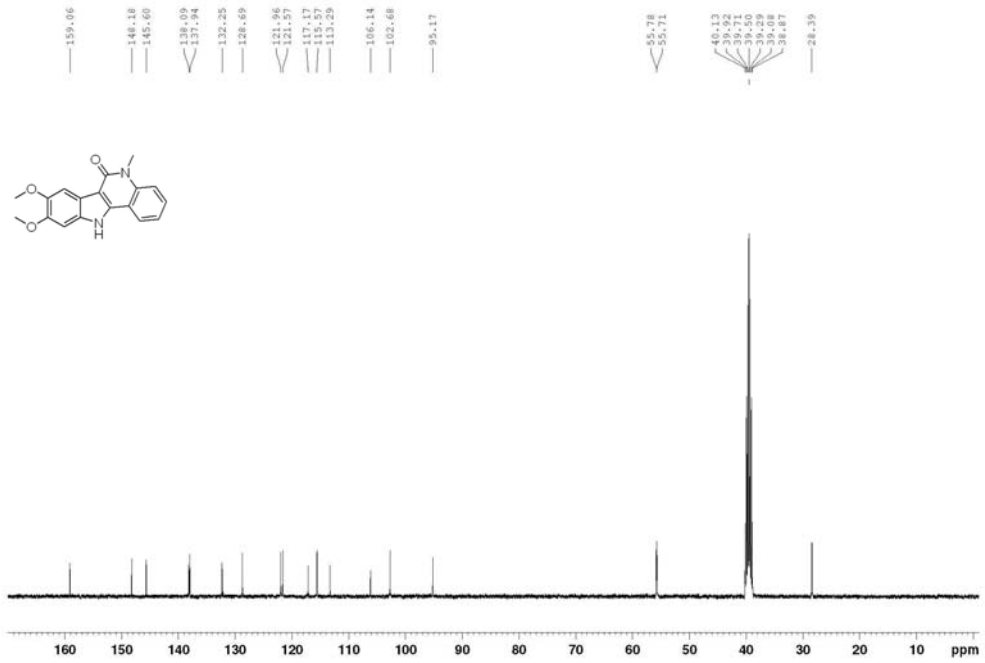
^{13}C NMR of **6d**



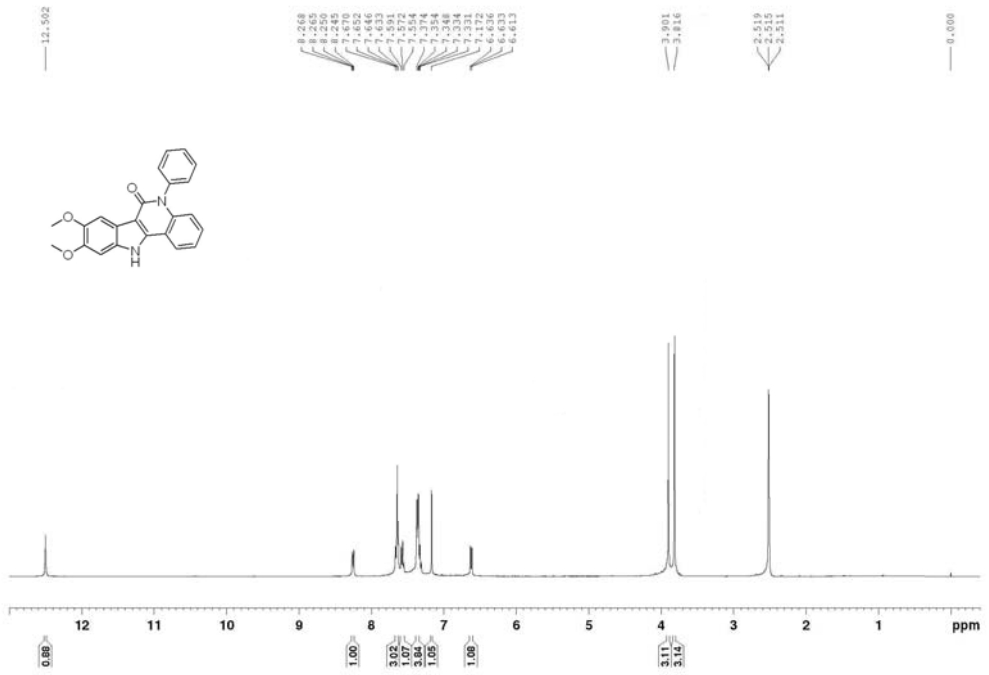
^{1}H NMR of **6e**.



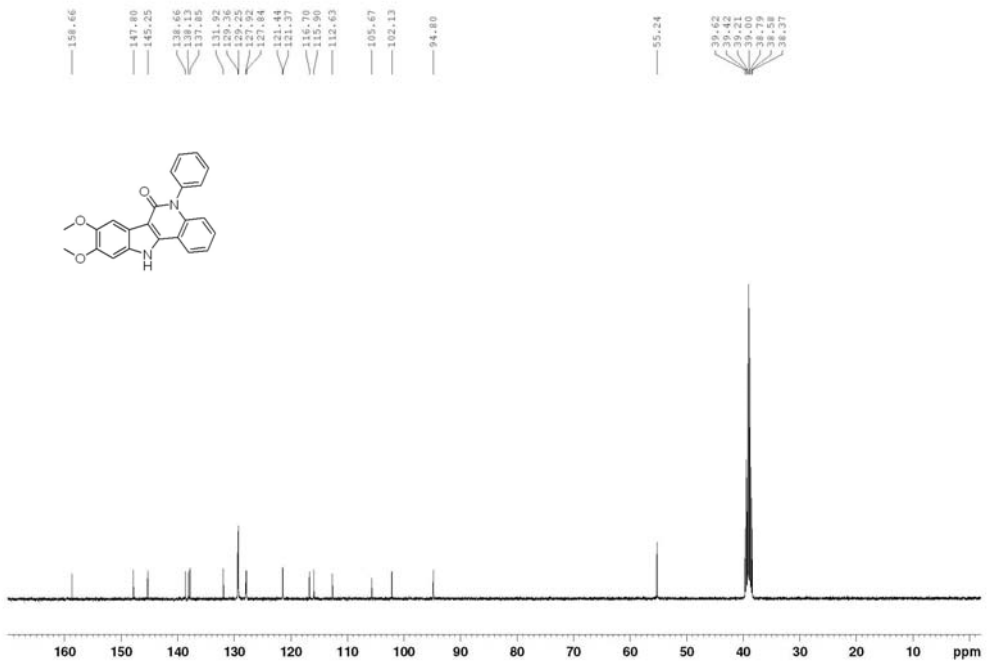
^{13}C NMR of **6e**



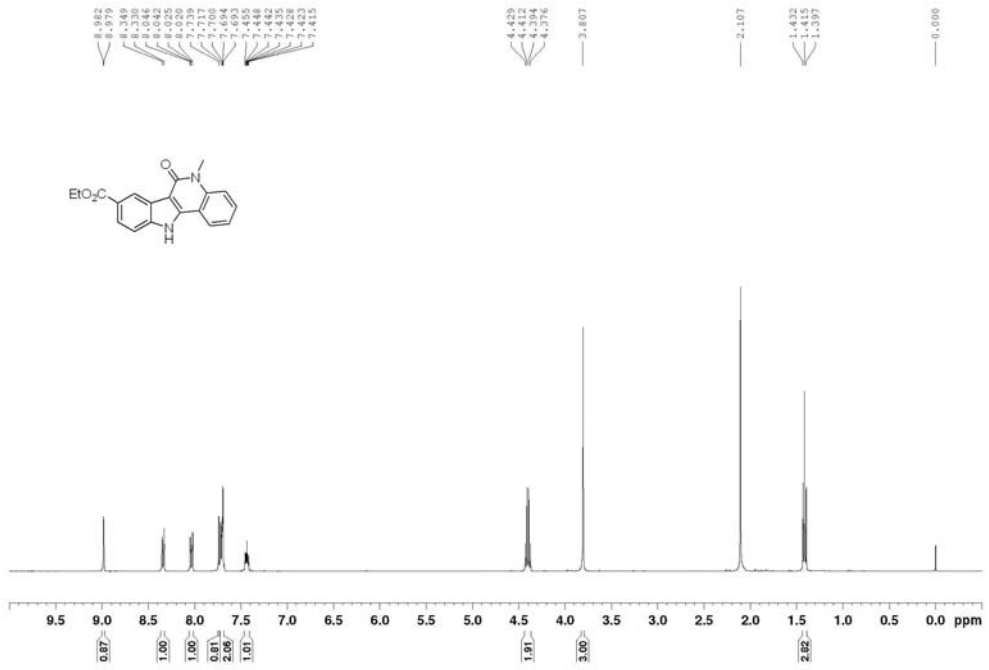
^{1}H NMR of **6f**.



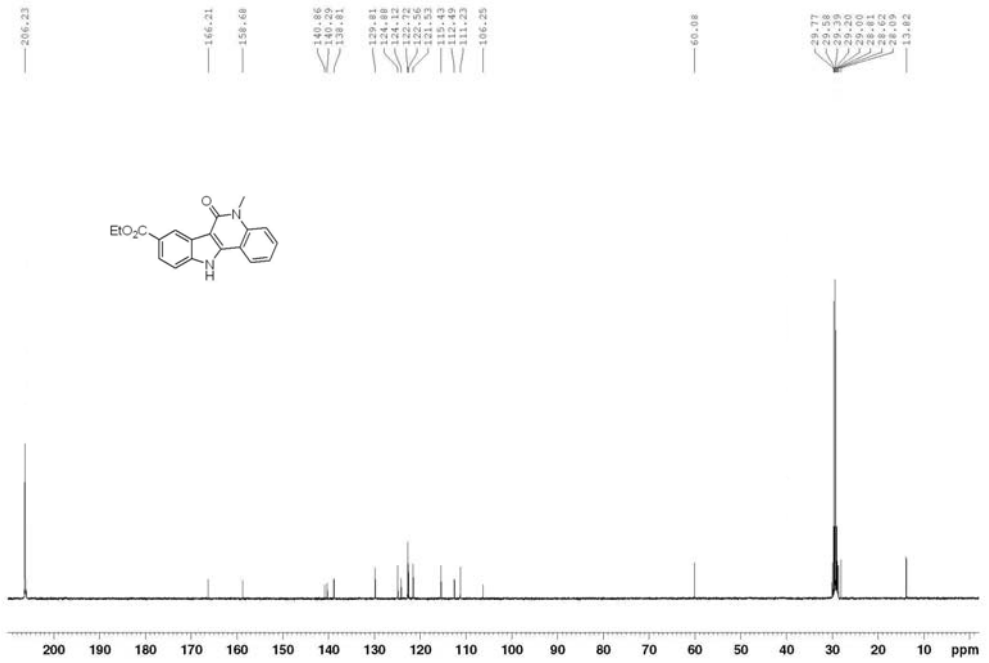
^{13}C NMR of **6f**



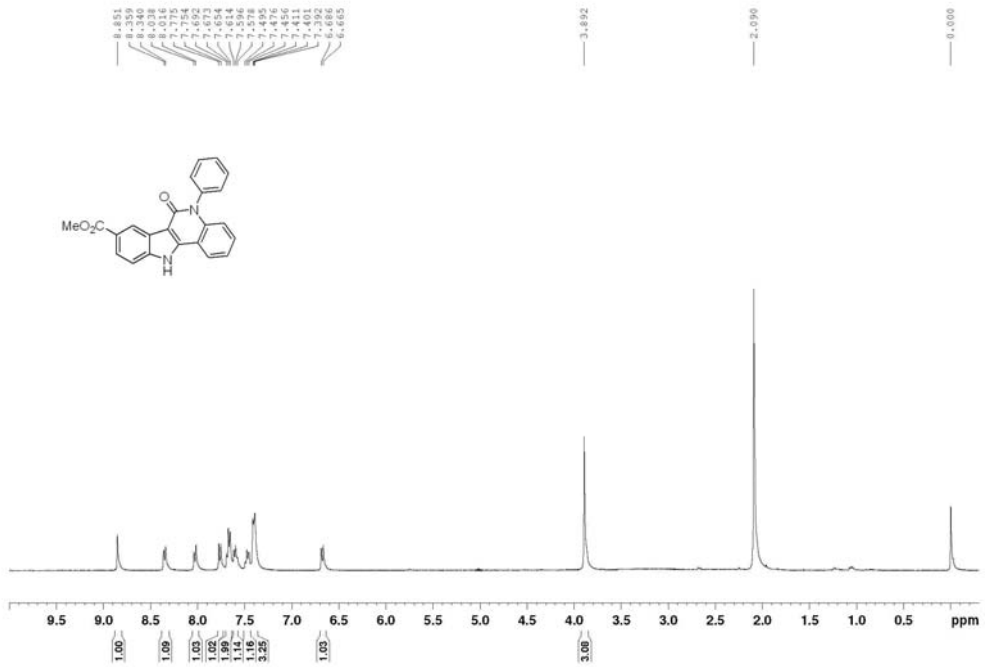
^{1}H NMR of **6g**.



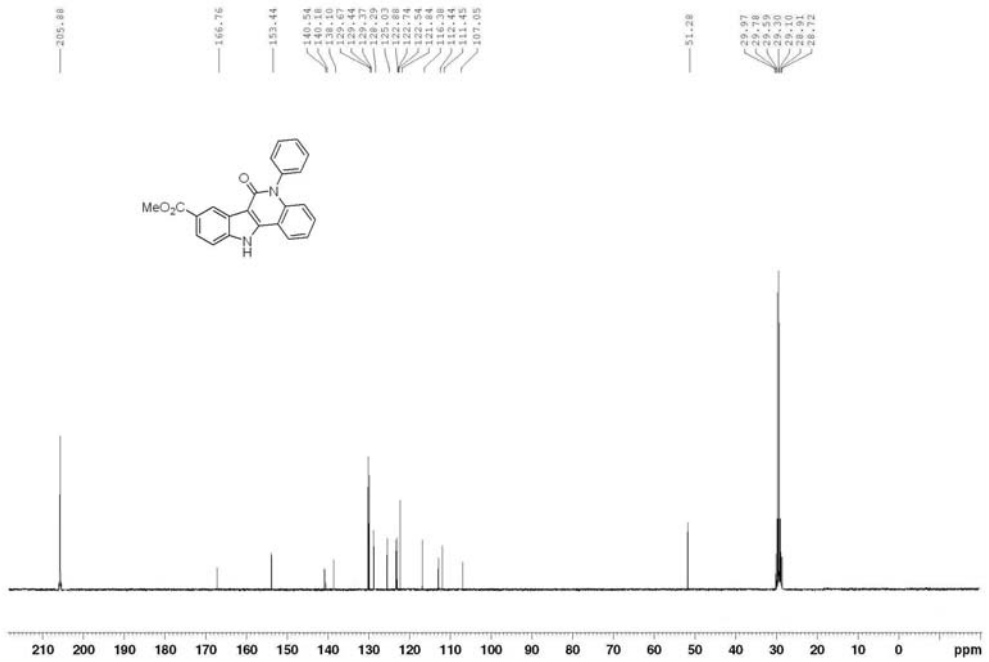
^{13}C NMR of **6g**



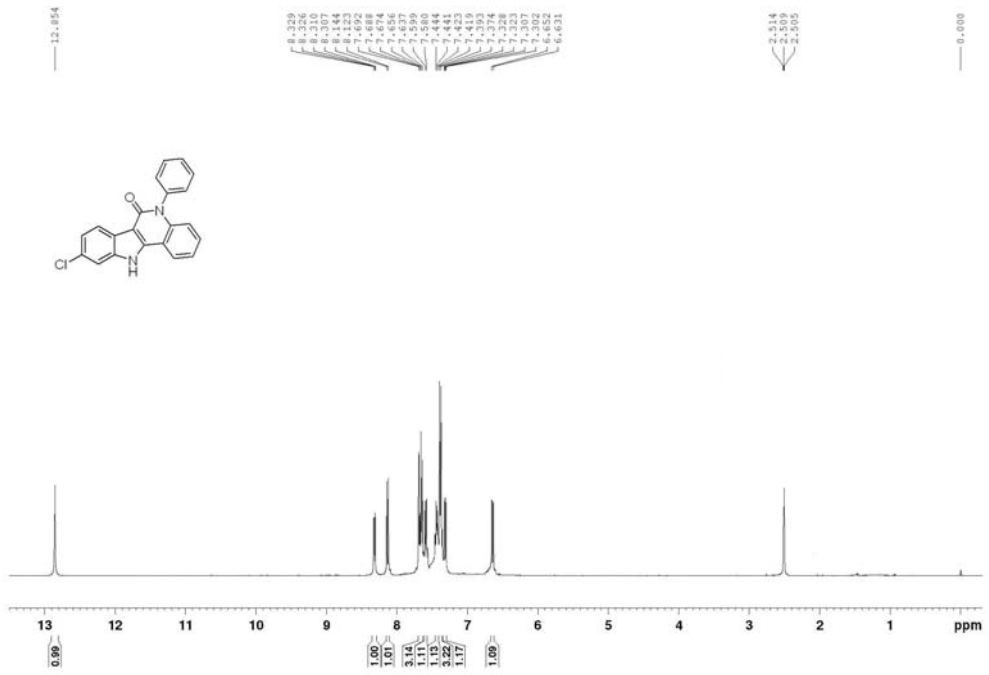
^{1}H NMR of **6h**.



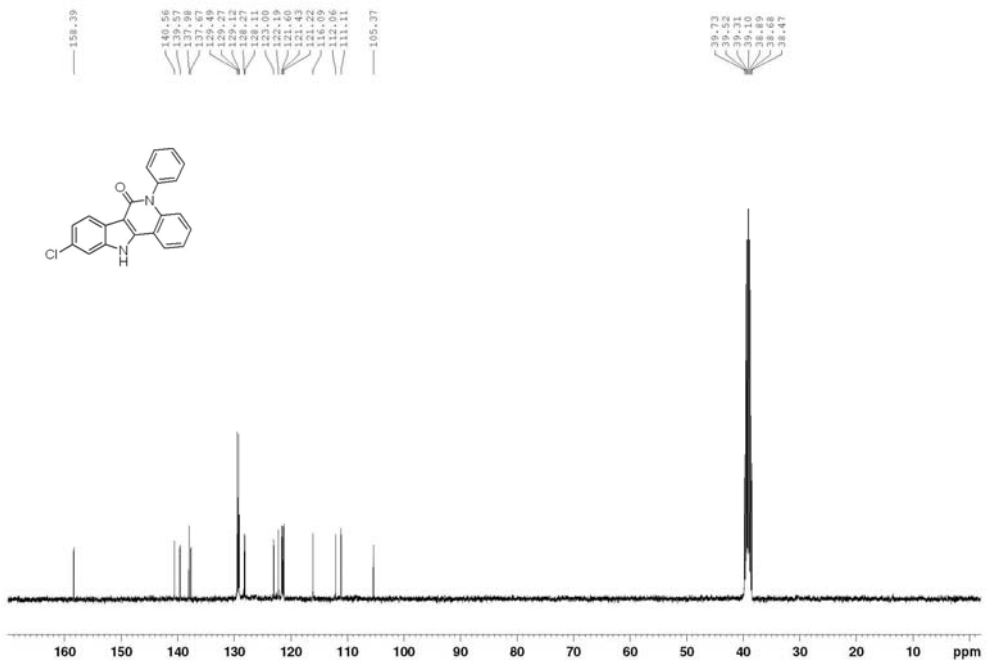
^{13}C NMR of **6h**



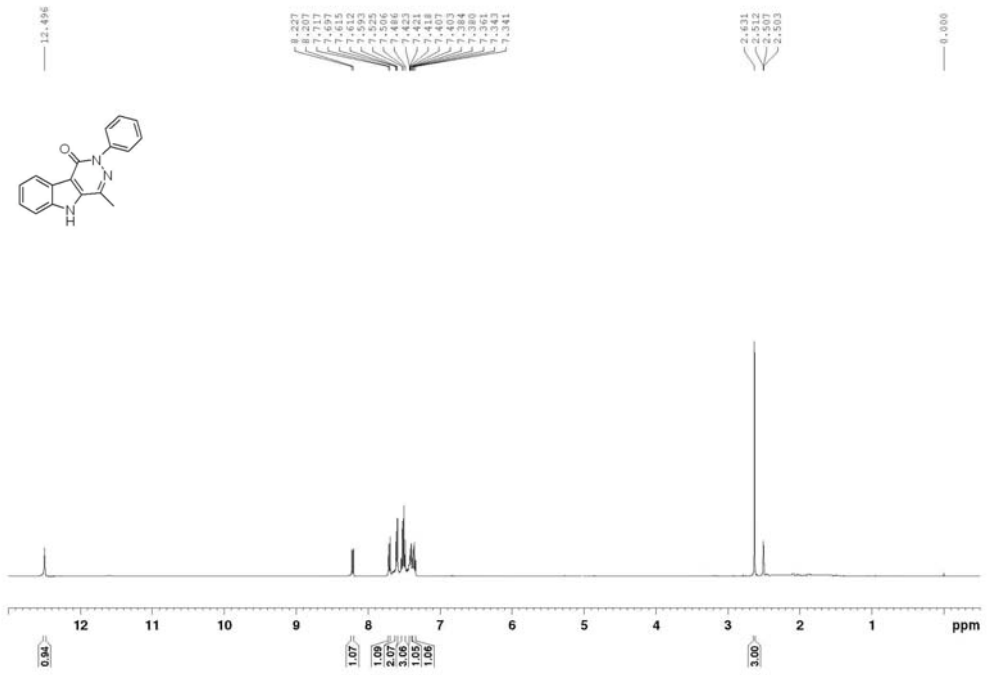
^{1}H NMR of **6i**.



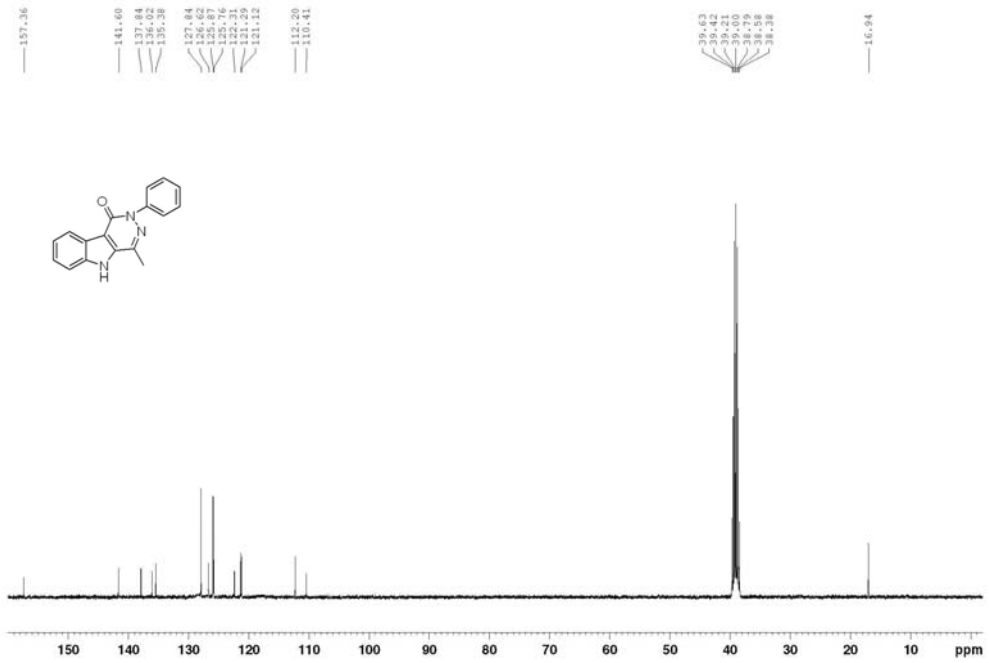
^{13}C NMR of **6i**



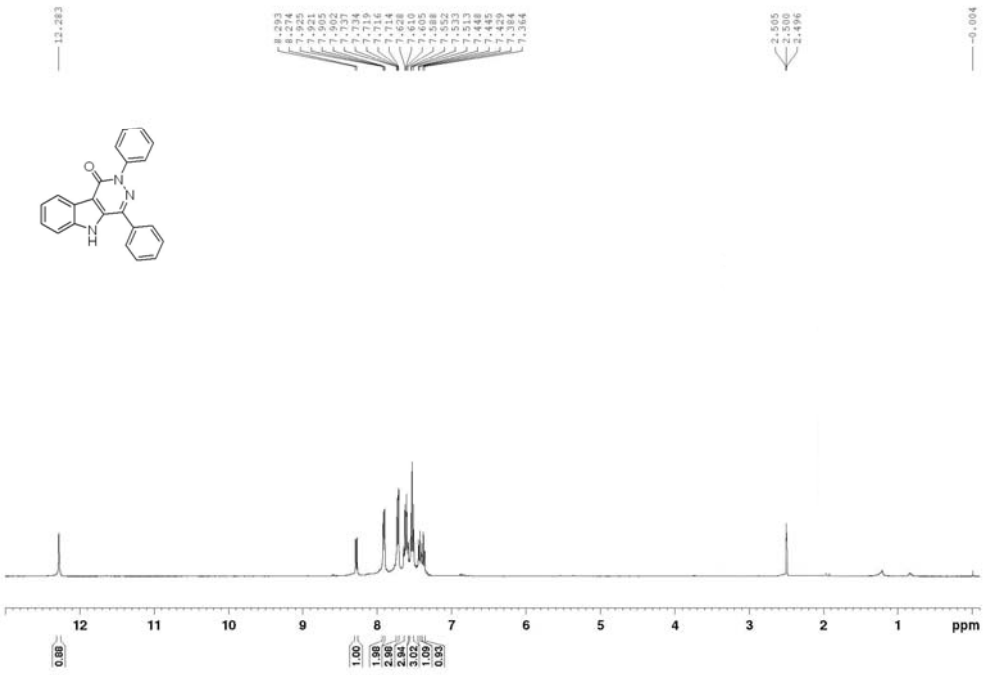
^{1}H NMR of **8a**.



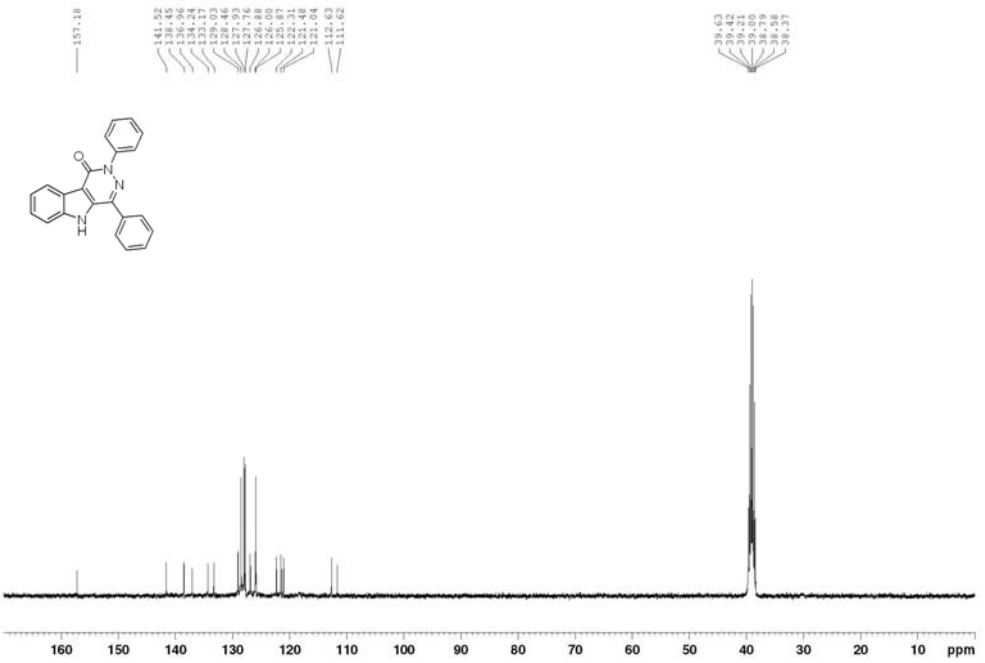
^{13}C NMR of **8a**



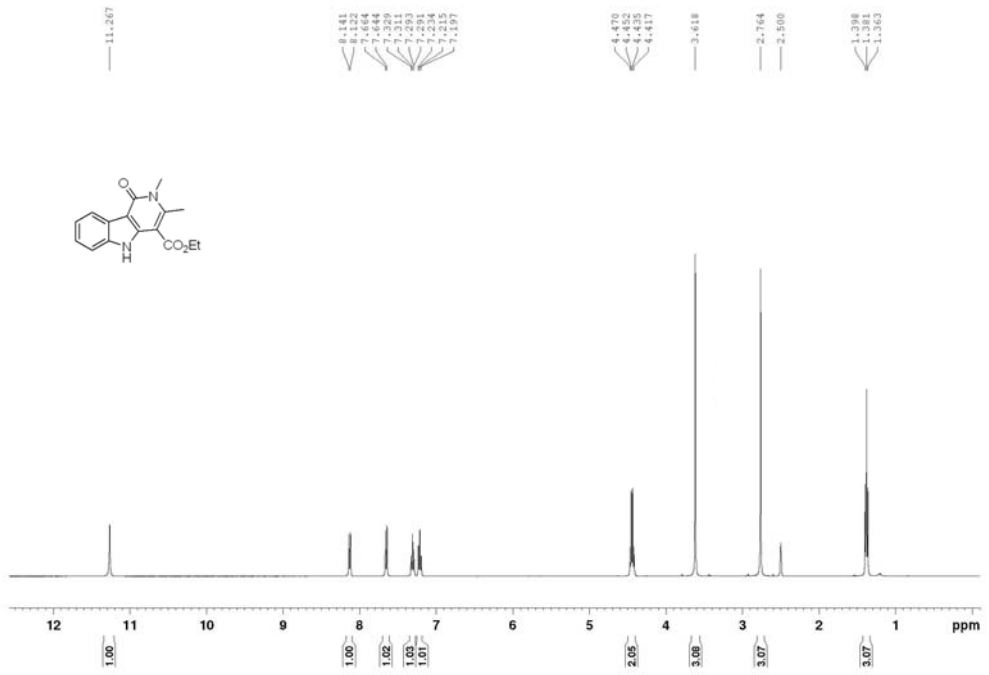
^{1}H NMR of **8b**



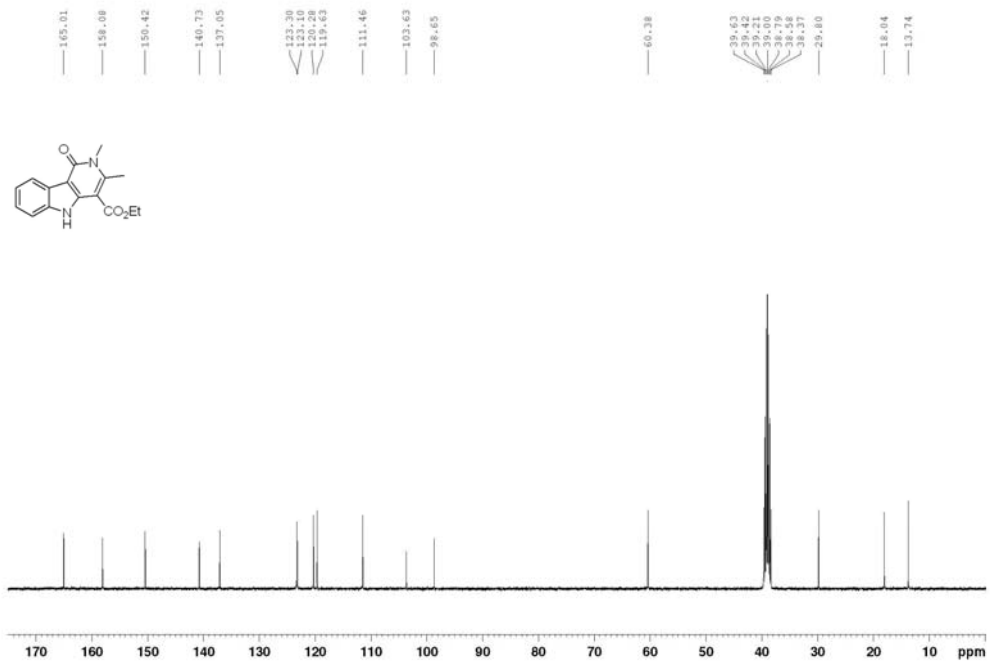
^{13}C NMR of **8b**



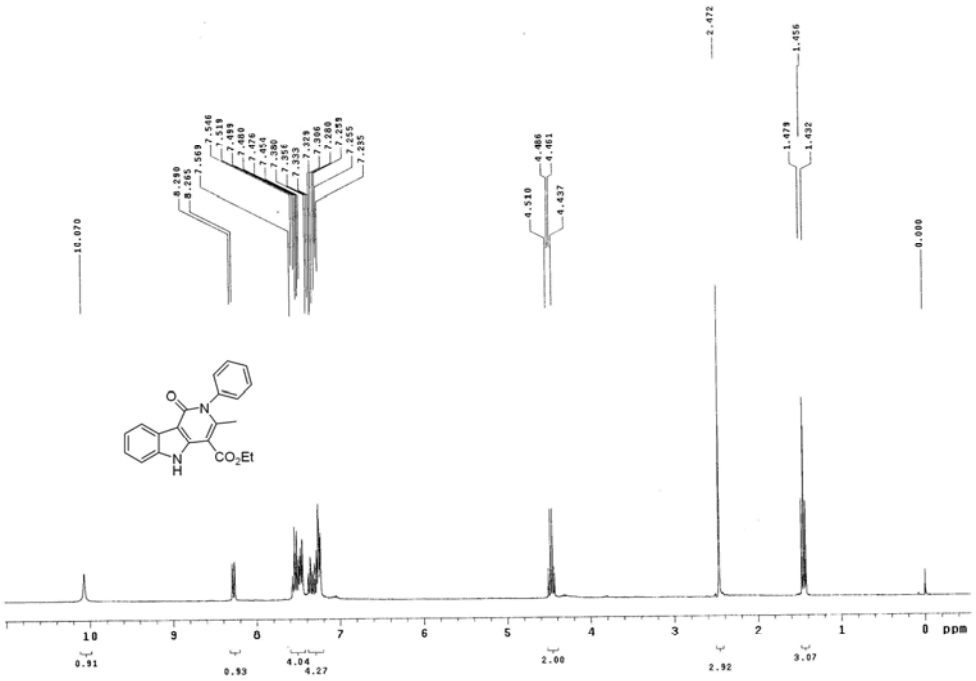
^{1}H NMR of **7a**.



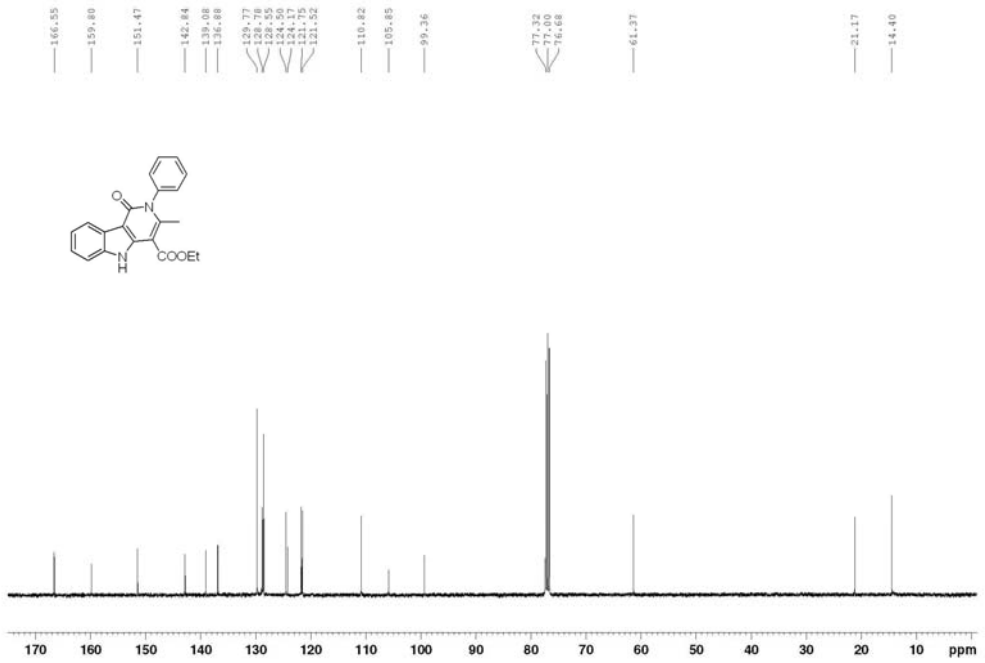
^{13}C NMR of **7a**



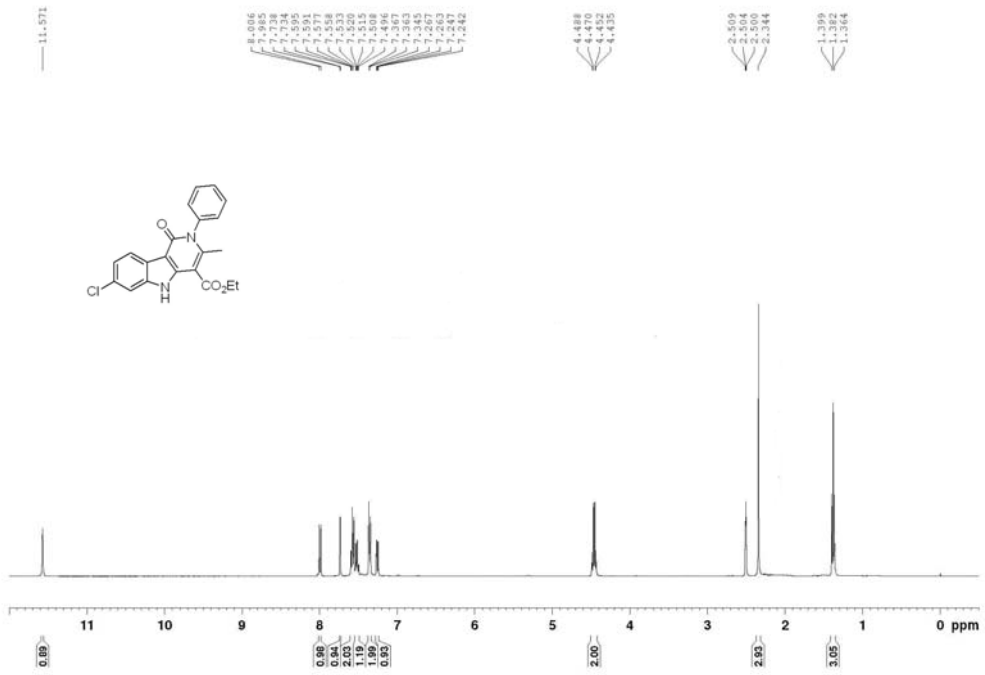
^{1}H NMR of **7b**.



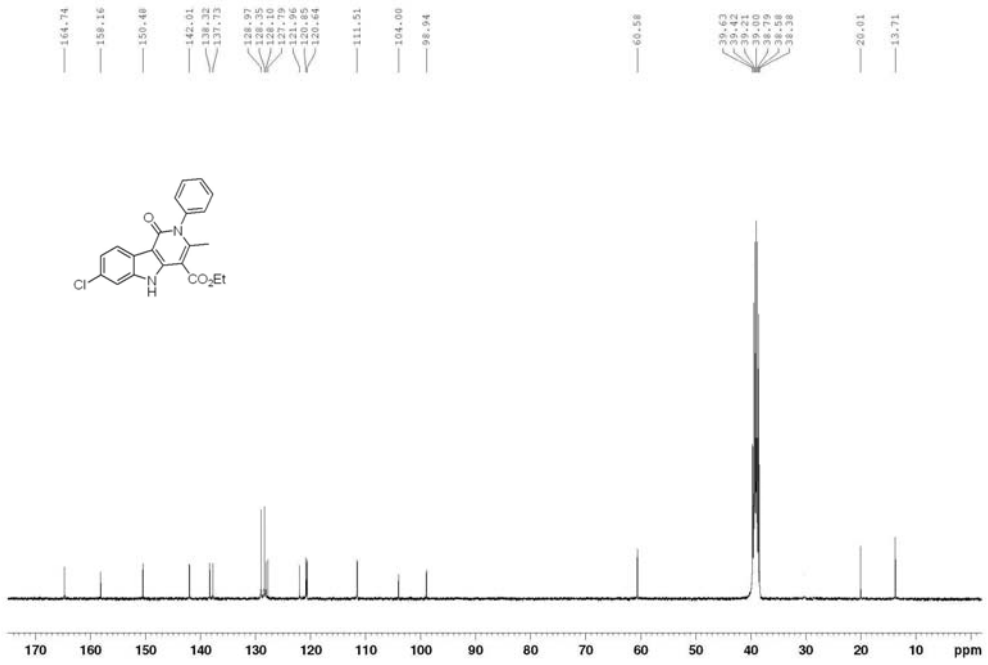
^{13}C NMR of **7b**



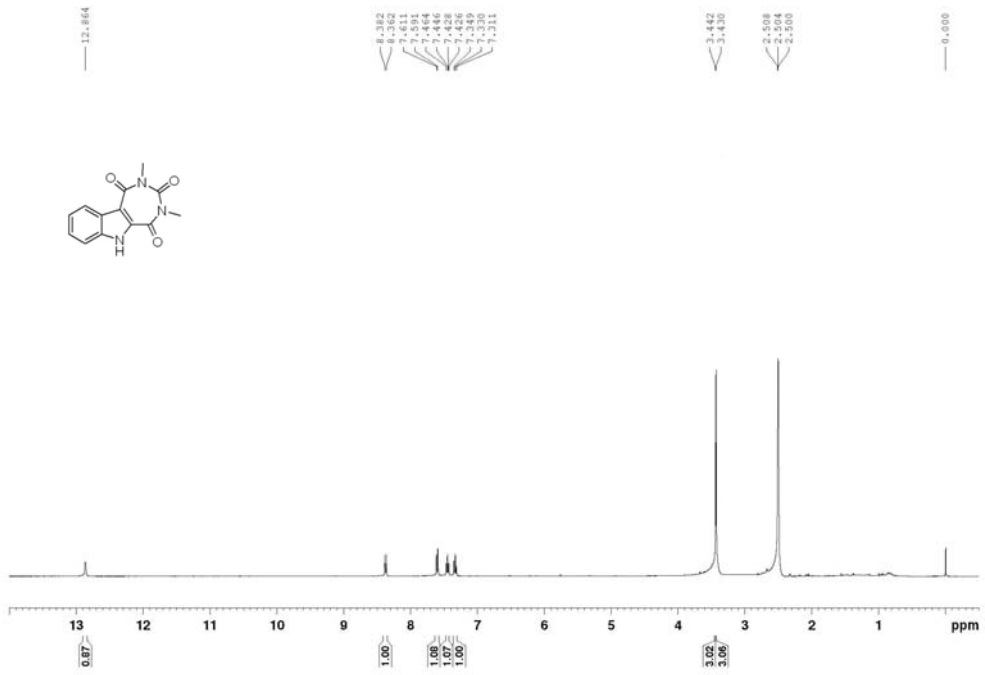
^{1}H NMR of **7c**.



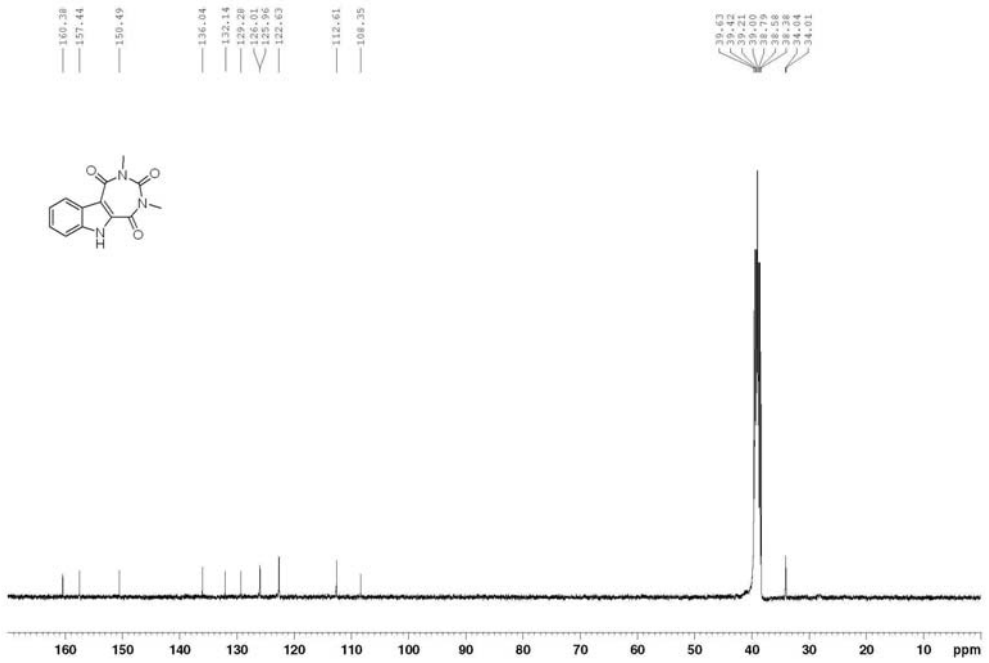
^{13}C NMR of **7c**



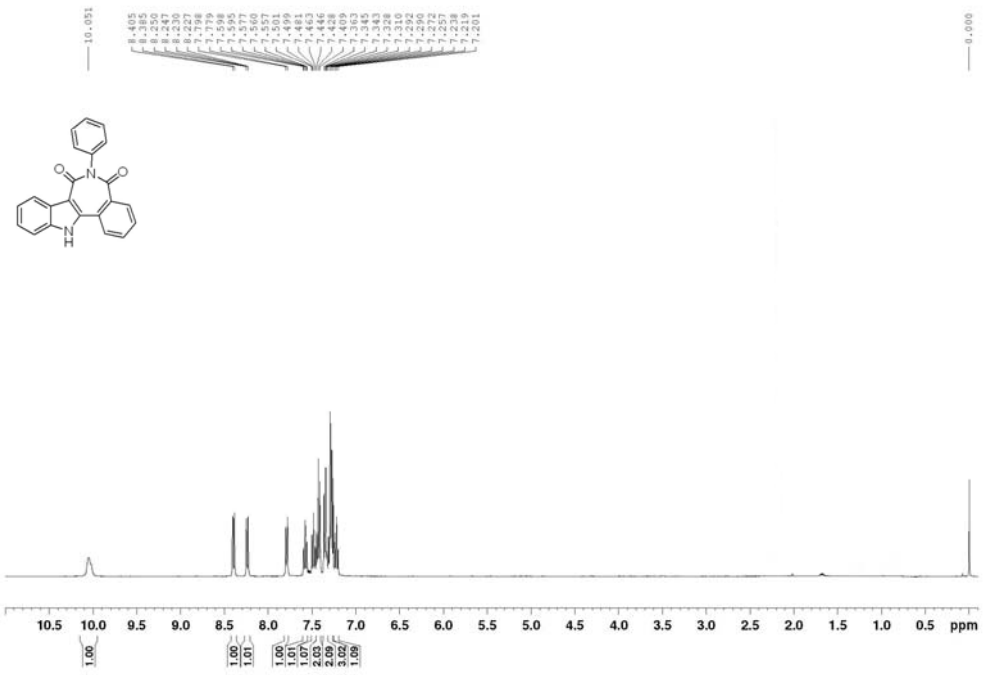
^{1}H NMR of **10**.



^{13}C NMR of **10**



^{1}H NMR of **9**.



^{13}C NMR of **9**