SUPPLEMENTARY INFORMATION

Catalytic Activity of HKUST-1 for the Synthesis of Fused *N*-heterocycles under Microwave Irradiation and Studies of *In Vitro* Anti-bacterial and Anti-tubercular Activities

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I. General Information

All the chemicals were bought from Alfa Aesar, Spectrochem, Sigma-Aldrich & Merck and were used without any further purification. The purity of the prepared compounds were confirmed by using FT-IR, ^{1}H-NMR, ^{13}C-NMR. The HR-MS data for novel derivatives also provided. FT-IR spectra were recorded in KBr pellets on a Bruker ALPHA II spectrometer and the frequencies are expressed in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance II-400 spectrometer in DMSO-d6 solvent. Mass spectral data of the newly synthesized compounds were recorded on Waters, Xevo G2-XS QT of Mass Spectrometer. Powder XRD analysis was conducted using Powder XRD Make: Rigaku (Model: SmartLab SE). All reactions were monitored by thin layer chromatography (TLC) using pre-coated aluminum sheets (silica gel 60 F 254 0.2 mm thick- ness) and developed in an iodine and UV-light chamber. Melting points were recorded in capillary tubes using OPTICS Technology. TEM were conducted using a transmission electron microscope of JEM-2100 make (JEOL). SEM and EDX analyses were carried out using Zeiss, model: Sigma 300 make scanning electron microscope and Gemini 500 FE-SEM. TGA analysis was conducted on a Perkin Elmer STA-6000. The preparation of the catalyst was carried out by using Monowave 50 reactor (Anton Paar). Microwave synthesis of compounds were done by using Monowave 200 reactor (Anton Paar).

(i) Monowave 50 reactor

The catalyst used here was synthesized by using Monowave 50 (Anton Paar) reactor (**Figure S1**). The G10 glass vial was closed with a stainless-steel heating jacket which offers a homogeneous temperature during the course of the solution. In this apparatus chemical reactions can be carried out to maximum temperature of 220 ℃ and maximum pressure of 18 bar. Furthermore, the temperature as well as the pressure inside the apparatus can be examined in actual attributable to the existence of a temperature as well as pressure sensor. The magnetic stirring can be adjusted from 300 rpm to 1200 rpm and the operation volume is from 2 ml to 6 ml.

Figure S1. Monowave 50 reactor set up

(i) Monowave 200 reactor

All the compounds were synthesized under microwave heating in sealed G10 glass vials with Anton Paar Monowave 200 (**Figure S2**). The glass vial was closed with PTFE septum. This device can accomplish chemical reactions at temperatures up to 300 °C and maximum pressure of 20 bar with maximum power of 850 W magnetron which regulates its unpulsed microwave power automatically to the sample. The power of the microwave reactor is automatically adjusted consistent with the temperature of the reaction system monitored by IR temperature sensor. The magnetic stirring can be adjusted from 300 rpm to 1200 rpm and the operation volume is from 2 ml to 6 ml. The reactions were done under the pressure between 5 to 6 bar.

Figure S2. Monowave 200 reactor set up

II. General methods of compound synthesis

General procedure for the synthesis of 4a-4o and 6a-6j

In a G10 vial, a mixture of 1 mmol of 4-hydroxycoumarin/4-hydroxynaphthoquinone, 1 mmol of corresponding aldehydes, 1 mmol of 3-amino-5-methyl-pyrazole/3-amino-pyrazole and 15 mg of HKUST-1 in 4 mL of ethanol was stirred under monowave 200 reactor at 60 ℃ for appropriate time. The progress of the reaction was monitored by TLC. The catalyst was simply separated from the reaction mixture by simple centrifugation, washed with ethanol, dried at 120 ℃ under vacuum for 12 hours and was re-used for the next runs. Afterwards, the solvent was evaporated under reduced pressure and the pure product was obtained by simple washing with ethanol and by recrystallization from hot ethanol wherever needed.

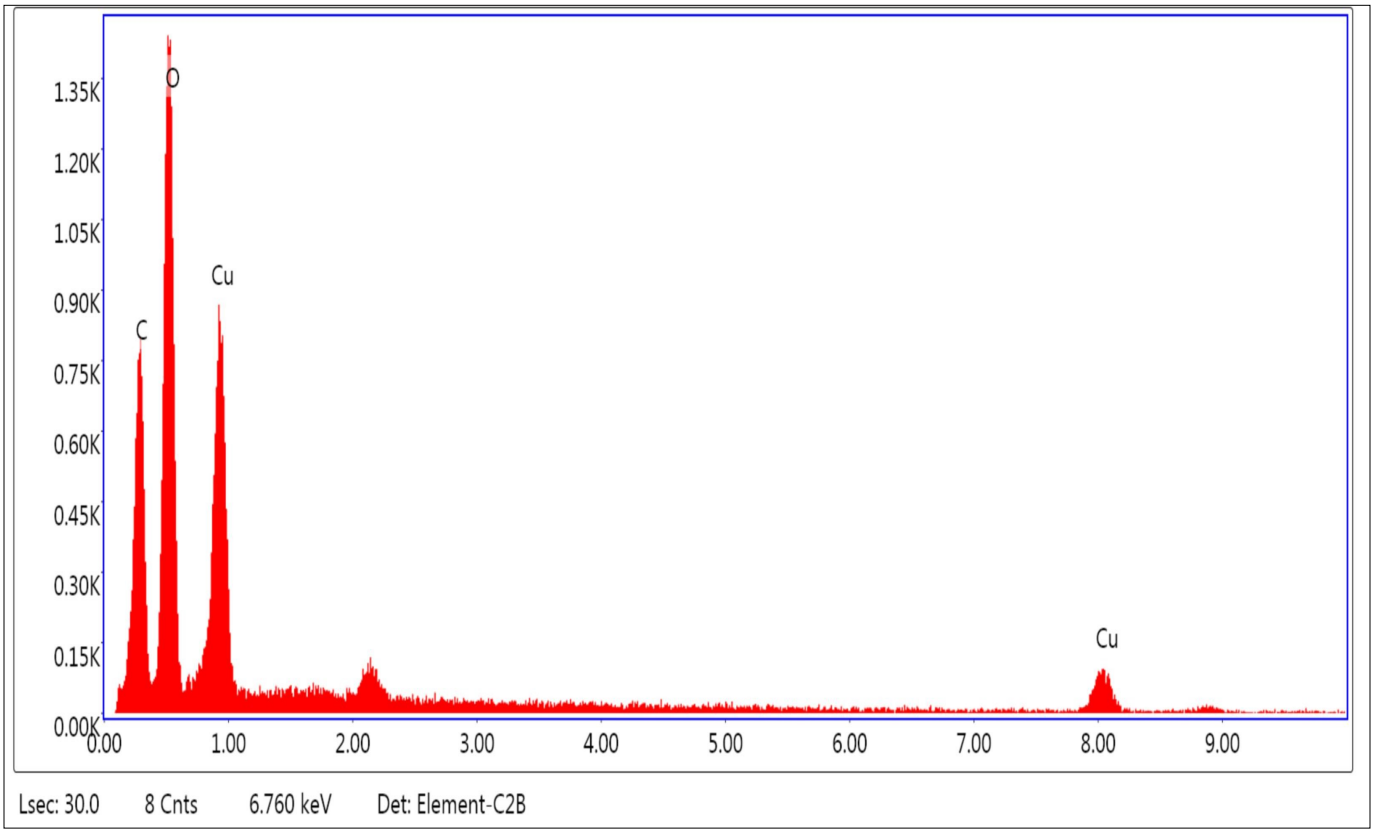
General procedure for the synthesis of 8a-8d and 9a-9e

In a G10 vial, a mixture of 1 mmol of 4-hydroxycoumarin/4-hydroxynaphthoquinone, 1 mmol of corresponding isatins, 1 mmol of 3-amino-5-methyl-pyrazole and 15 mg of HKUST-1 in 4 mL of ethanol was stirred under monowave 200 reactor at 60 ℃ for appropriate time. The progress of the reaction was monitored by TLC. The catalyst was simply separated from the reaction mixture by simple centrifugation, washed with ethanol, dried at 120 ℃ under vacuum for 12 hours and was re-used for the next runs. Afterwards, the solvent was evaporated under reduced pressure and the pure product was obtained by recrystallization from hot ethanol.

III. Recycling procedure

In a round bottom flask, a mixture of 4-hydroxycoumarin (1 mmol), 4-methoxybenzaldehyde (1 mmol) and 3-amino-5-methyl-pyrazole (1 mmol) in 4 mL of ethanol was stirred under monowave 200 reactor in presence of HKUST-1 for 10 min. After completion of the reaction, simple centrifugation method was used to separate the HKUST-1 from the reaction mixture. The recovered catalyst was washed three times with ethanol. The ethanol solution was evaporated and the residue was mixed with internal standard and subjected to ^{1}H NMR quantification. The recovered HKUST-1 was then dried at 120 ℃ under vacuum for 12 hours and used for the next round of reactions. The catalyst can be reused up to six times without significant loss of the catalytic activity.

IV. Characterization of HKUST-1



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	31.38	45.47	268.69	8.73	0.1397	1.0974	0.4057	1.0000
O K	43.90	47.76	491.81	8.80	0.1692	1.0463	0.3684	1.0000
CuK	24.72	6.77	53.18	9.88	0.1896	0.7417	1.0088	1.0249

Figure S3. EDX peaks of the prepared HKUST-1

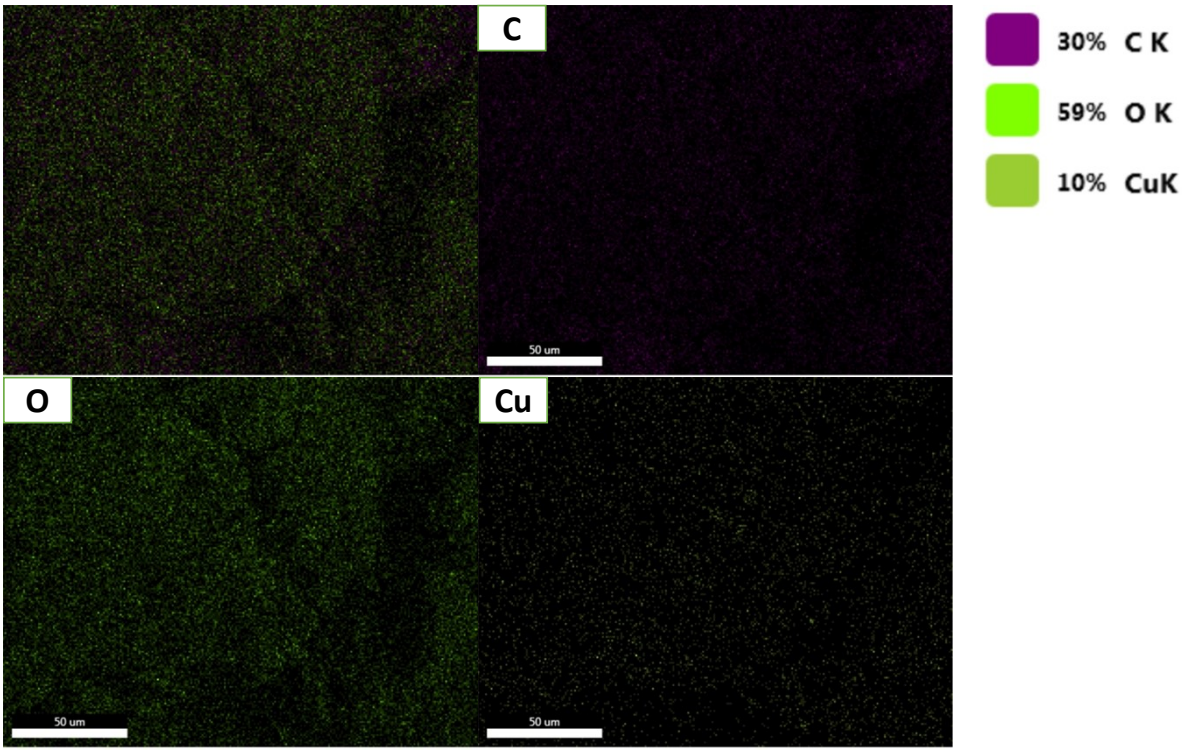
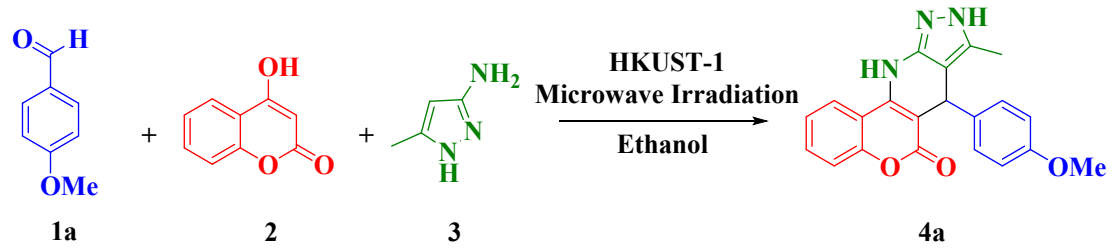


Figure S4. Elementary mapping of the prepared HKUST-1

V. Green chemistry metrics calculations: Green chemistry metrics [S1, S2] has been calculated for our optimized reaction on the basis of following parameters below-

(i) Environmental factor (E-factor)
(ii) Product mass intensity (PMI)
(iii) Atom economy (AE)
(iv) Reaction mass efficiency (RME)
(v) Carbon efficiency (CE)
(vi) Atom efficiency (AE_f)
(vii) Optimum efficiency (OE)

1. For compound 4a



1a 2 3 4a

Compound code	1a	2	3	4a

M. W. (g/mol)	136.15	162.14	97.12	359.39
Chemical formula	$C_8H_8O_2$	$C_9H_6O_3$	$C_4H_7N_3$	$C_{21}H_{17}N_3O_3$
In present work MW (mg)	136.15 x 1 mM = 136.15	162.14 x 1 mM = 162.14	97.12 x 1 mM = 97.12	359.39 x 0.95 mM = 341.42

Solvent: Ethanol (4 ml) = 3.15 mg

(i) E-factor or environmental factor for 4a: E-factor denotes the total amount of waste generated during a chemical reaction. The ideal value of E-factor is zero

$$\text{E-factor} = \frac{Mass\ of\ waste}{Mass\ of\ Product}$$

Where, mass of waste = (total mass of raw materials) – (the total mass of product)

$$E-Factor = \frac{[\{(136.15\ x\ 1) + (162.14\ x\ 1) + (97.12\ x\ 1)\} - 341.42\ ]}{341.42}$$

$$= \frac{[395.41 - 341.42]}{341.42} = \frac{53.99}{341.42} = 0.16$$

(ii) Product mass intensity (PMI) for 4a: PMI can be calculated by the following equation,

$$\text{PMI} = \frac{\Sigma\ (mass\ of\ stoichiometic\ reactants + Solvent)}{mass\ of\ product}$$

$$= \frac{\{(136.15\ x\ 1) + (162.14\ x\ 1) + (97.12\ x\ 1) + 3.15\}}{341.42} =$$

$$\frac{398.53}{341.42} = 1.16$$

(ii) Atom economy (AE) for 4a: Atom economy define the efficacy of a chemical reaction with regard to how many atoms from the starting materials reside within the product. The ideal value of AE factor is 100% which indicates that all atoms from the starting materials reside in the product.

$$\text{AE} = \frac{MW\ of\ the\ Product}{\Sigma\ (MW\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{359.39}{(136.15\ x\ 1) +\ (162.14\ x\ 1) +\ (97.12\ x\ 1)} x\ 100 \quad = \frac{359.39}{395.41}\ \text{x } 100 = 90\ \%$$

(iv) Reaction mass efficiency (RME) for 4a: Reaction mass efficiency is calculated by following equation,

$$\text{RME} = \frac{Mass\ of\ the\ Product}{\Sigma\ (mass\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{341.42}{(136.15\ x\ 1) +\ (162.14\ x\ 1) +\ (97.12\ x\ 1)} x\ 100 \quad = \frac{341.42}{395.41}\ \text{x } 100 = 86.3\ \%$$

(v) Carbon Efficiency (CE) for 4a

CE denotes the percentage of carbon in the reactants that remains in the product.

$$\text{CE} = \frac{Amount\ of\ carbon\ in\ product}{Total\ carbon\ present\ in\ reactants}\ x\ 100$$

$$= \frac{No.\ of\ moles\ of\ product\ x\ no.\ of\ carbons\ in\ product}{moles\ of\ 1a\ x\ carbons\ in\ 1a\ +\ moles\ of\ 2\ x\ carbons\ in\ 2 +\ moles\ of\ 3\ x\ carbons\ in\ 3}\ x\ 100$$

$$= \frac{0.95\ x\ 21}{1\ x\ 8 + 1\ x\ 9 + 1\ x\ 4}\ \text{x } 100 = \frac{19.95}{21}\ \text{x } 100 = 95\ \%$$

(vi) Atom efficiency (AE_f) for 4a:

$$\mathbf{AE_f = AE\ x\ yield\ (\%)}$$

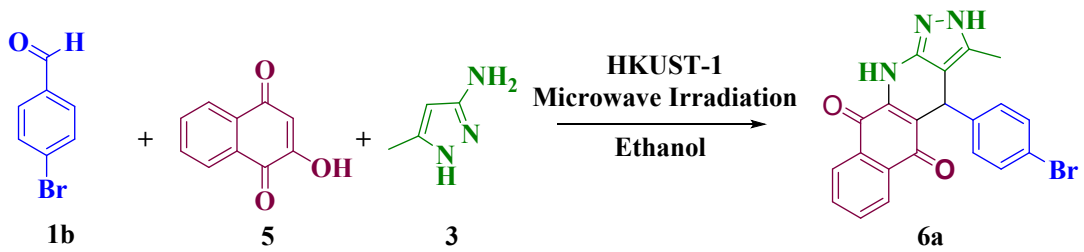
$$= 90\ \text{x } 95\ (\%) = 85.5$$

(vii) Optimum efficiency (OE) for 4a:

$$OE = \frac{RME}{AE} \times 100$$

$$OE = \frac{86.3}{90} \times 100 = 95.8$$

2. For compound 6a



1b + 5 + 3 → 6a

Compound code	1b	5	3	6a
M. W. (g/mol)	180.02	174.15	97.12	420.26
Chemical formula	C_7H_5BrO	$C_{10}H_6O_3$	$C_4H_7N_3$	$C_{21}H_{14}BrN_3O_2$
In present work MW (mg)	180.02 x 1 mM = 180.02	174.15 x 1 mM = 174.15	97.12 x 1 mM = 97.12	420.26 x 0.93 mM = 390.84

Solvent: Ethanol (4 ml) = 3.15 mg

(i) E-factor or environmental factor for 6a:

$$\text{E-factor} = \frac{Mass\ of\ waste}{Mass\ of\ Product}$$

Where, mass of waste = (total mass of raw materials) – (the total mass of product)

$$E-Factor = \frac{[\{(185.02\ x\ 1) + (174.15\ x\ 1) + (97.12\ x\ 1)\} - 390.84\ ]}{390.84}$$

$$= \frac{[456.29 - 390.84]}{390.84} = \frac{65.45}{390.85} = 0.17$$

(ii) Product mass intensity (PMI) for 6a:

$$\text{PMI} = \frac{\Sigma\ (mass\ of\ stoichiometic\ reactants + solvent)}{mass\ of\ product}$$

$$= \frac{\{(185.02\ x\ 1) + (174.15\ x\ 1) + (97.12\ x\ 1) + 3.15\}}{390.84} =$$

$\frac{459.44}{390.84} = 1.17$

(iii) Atom economy (AE) for 6a:

$$AE = \frac{MW\ of\ the\ Product}{\Sigma\ (MW\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{420.26}{(185.02\ x\ 1) + (174.15\ x\ 1) + (97.12\ x\ 1)} x\ 100 = \frac{420.26}{456.29}\ \text{x } 100 = 92.1\ \%$$

(iv) Reaction mass efficiency (RME) for 6a:

$$RME = \frac{Mass\ of\ the\ Product}{\Sigma\ (mass\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{390.84}{(185.02\ x\ 1) + (174.15\ x\ 1) + (97.12\ x\ 1)} x\ 100 = \frac{390.85}{456.29}\ \text{x } 100 = 85.6\ \%$$

(v) Carbon Efficiency (CE) for 6a:

CE denotes the percentage of carbon in the reactants that remains in the product.

$$CE = \frac{Amount\ of\ carbon\ in\ product}{Total\ carbon\ present\ in\ reactants}\ x\ 100$$

$$= \frac{No.\ of\ moles\ of\ product\ x\ no.\ of\ carbons\ in\ product}{moles\ of\ 1b\ x\ carbons\ in\ 1b + moles\ of\ 5\ x\ carbons\ in\ 5 + moles\ of\ 3\ x\ carbons\ in\ 3}\ x\ 100$$

$$= \frac{0.93\ x\ 21}{1\ x\ 7 + 1\ x\ 10 + 1\ x\ 4}\ \text{x } 100 = \frac{19.53}{21}\ \text{x } 100 = 93\ \%$$

(vi) Atom efficiency (AE_f):

$$\mathbf{AE_f} = \text{AE x yield (\%)}$$

$$= 92.1\ \text{x } 93\ (\%)$$

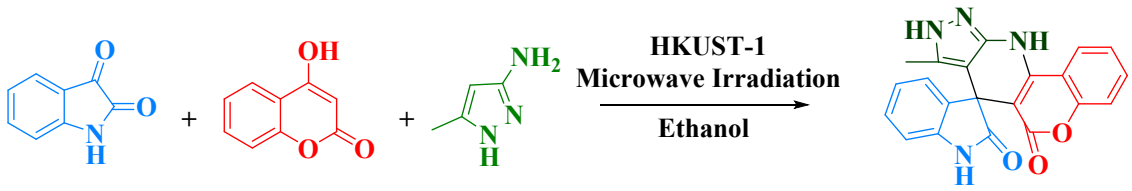
$$= 85.6$$

(vii) Optimum efficiency (OE):

$$OE = \frac{RME}{AE} \times 100$$

$$OE = \frac{85.6}{92.1} \times 100 = 92.9$$

3. For compound 8a



7 2 3 8a

Compound code	7	2	3	8a
M. W. (g/mol)	147.13	162.14	97.12	370.36
Chemical formula	$C_8H_5NO_2$	$C_9H_6O_3$	$C_4H_7N_3$	$C_{21}H_{14}N_4O_3$
In present work MW (mg)	147.13 x 1 mM = 147.13	162.14 x 1 mM = 162.14	97.12 x 1 mM = 97.12	370.36 x 0.96 mM = 355.54

Solvent: Ethanol (4 ml) = 3.15 mg

(i) E-factor or environmental factor for 8a:

$$\text{E-factor} = \frac{Mass\ of\ waste}{Mass\ of\ Product}$$

Where, mass of waste = (total mass of raw materials) – (the total mass of product)

$$E - Factor = \frac{[\{(147.13\ x\ 1) + (162.14\ x\ 1) + (97.12\ x\ 1)\} - 355.54\ ]}{355.54}$$

$$= \frac{[406.39 - 355.54]}{355.54} = \frac{50.85}{355.54} = 0.14$$

(ii) Product mass intensity (PMI) for 8a:

$$\text{PMI} = \frac{\Sigma\ (mass\ of\ stoichiometic\ reactants + solvent\ )}{mass\ of\ product} =$$

$$\frac{\{(147.13\ x\ 1) + (162.14\ x\ 1) + (97.12\ x\ 1) + 3.15\}}{355.54} = \frac{409.54}{355.54} = 1.15$$

(iii) Atom economy (AE) for 8a:

$$\text{AE} = \frac{MW\ of\ the\ Product}{\Sigma\ (MW\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{370.36}{(147.13\ x\ 1) +\ (162.14\ x\ 1) +\ (97.12\ x\ 1)} x\ 100 \quad = \frac{370.36}{406.39}\ \text{x } 100 = 91.1\ \%$$

(iv) Reaction mass efficiency (RME) for 8a:

$$\text{RME} = \frac{Mass\ of\ the\ Product}{\Sigma\ (MW\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{355.54}{(147.13\ x\ 1) +\ (162.14\ x\ 1) +\ (97.12\ x\ 1)} x\ 100 \quad = \frac{355.54}{406.39}\ \text{x } 100 = 87.4\ \%$$

(v) Carbon Efficiency (CE) for 8a:

CE denotes the percentage of carbon in the reactants that remains in the product.

$$\text{CE} = \frac{Amount\ of\ carbon\ in\ product}{Total\ carbon\ present\ in\ reactants}\ x\ 100$$

$$=$$

$$\frac{No.\ of\ moles\ of\ product\ x\ no.\ of\ carbons\ in\ product}{moles\ of\ 7\ x\ carbons\ in\ 7 +\ moles\ of\ 2\ x\ carbons\ in\ 2 +\ moles\ of\ 3\ x\ carbons\ in\ 3} x\ 100$$

$$= \frac{0.96\ x\ 21}{1\ x\ 8 + 1\ x\ 9\ + 1\ x\ 4}\ \text{x } 100 = \frac{20.16}{21}\ \text{x } 100 = 96\ \%$$

(vi) Atom efficiency (AE_f) for 8a:

$$\mathbf{AE_f = AE\ x\ yield\ (\%)}$$

$$= 91.9\ \text{x } 96\ (\%)$$

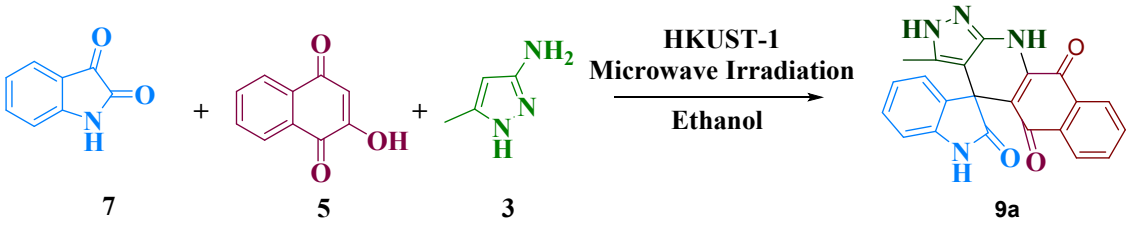
$$= 88.2$$

(vii) Optimum efficiency (OE) for 8a:

$$OE = \frac{RME}{AE} \times 100$$

$$OE = \frac{87.4}{91.9} \times 100 = 95.1$$

4. For compound 9a



7 + 5 + 3 → 9a

Compound code	7	5	3	9a
M. W. (g/mol)	147.13	174.15	97.12	382.37
Chemical formula	$C_8H_5NO_2$	$C_{10}H_6O_3$	$C_4H_7N_3$	$C_{22}H_{14}N_4O_3$
In present work MW (mg)	147.13 x 1 mM = 147.13	174.15 x 1 mM = 174.15	97.12 x 1 mM = 97.12	382.37 x 0.95 mM = 363.25

Solvent: Ethanol (4 ml) = 3.15 mg

(i) E-factor or environmental factor for 9a:

$$\text{E-factor} = \frac{Mass\ of\ waste}{Mass\ of\ Product}$$

Where, mass of waste = (total mass of raw materials) – (the total mass of product)

$$E-Factor = \frac{[\{(147.13\ x\ 1) + (174.15\ x\ 1) + (97.12\ x\ 1)\} - 363.25\ ]}{363.25}$$

$$= \frac{418.40 - 363.25}{363.25} = \frac{55.15}{363.25} = 0.15$$

(ii) Product mass intensity (PMI) for 9a:

$$\text{PMI} = \frac{\Sigma\ (mass\ of\ stoichiometic\ reactants + solvent + solvent)}{363.25}$$

$$= \frac{418.40 + 3.15}{363.25} = 1.16$$

(iii) Atom economy (AE) for 9a:

$$\text{AE} = \frac{MW\ of\ the\ Product}{\Sigma\ (MW\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{382.37}{418.40}\ \text{x}\ 100 = 91.3\ \%$$

(iv) Reaction mass efficiency (RME) for 9a:

$$\text{RME} = \frac{Mass\ of\ the\ Product}{\Sigma\ (mass\ of\ stoichiometric\ reactants)}\ x\ 100$$

$$= \frac{363.25}{418.40}\ \text{x}\ 100 = 86.8\ \%$$

(v) Carbon Efficiency (CE) for 9a:

CE denotes the percentage of carbon in the reactants that remains in the product.

$$\text{CE} = \frac{Amount\ of\ carbon\ in\ product}{Total\ carbon\ present\ in\ reactants}\ x\ 100$$

$$= \frac{No.\ of\ moles\ of\ product\ x\ no.\ of\ carbons\ in\ product}{moles\ of\ 7\ x\ carbons\ in\ 7 +\ moles\ of\ 5\ x\ carbons\ in\ 5 +\ moles\ of\ 3\ x\ carbons\ in\ 3} x\ 100$$

$$= \frac{0.95\ x\ 21}{1\ x\ 8\ +\ 1\ x\ 10 + 1\ x\ 4}\ \text{x}\ 100$$

$$= \frac{19.95}{22}\ \text{x}\ 100 = 90.7\ \%$$

(vi) Atom efficiency (AE_f) for 9a:

AE_f = AE x yield (%)

= 91.3 x 95 (%)

= 86.7

(vii) Optimum efficiency (OE) for 9a:

$$OE = \frac{RME}{AE} \times 100$$

$$OE = \frac{86.8}{91.3} \times 100 = 95.0$$

VI. Calculation of TON and TOF

TON and TOF was calculated by following equations [S1, S3, S4]

$$\text{TON} = \frac{Amnount\ of\ desired\ product\ (in\ mmol)}{Amount\ of\ catalyst\ used\ (in\ mmol)}$$

Cu mmol for catalytic reaction =

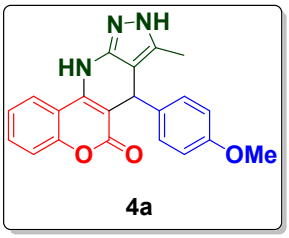
$$\frac{15\ mg\ (catalyst\ used) x\ 0.126\ [Cu\ weight\ ratio\ (12.6\ \%\ by\ ICP) in\ the\ catalyst]}{63.54\ g/mol\ \ (Cu\ atomic\ weight)} = 0.029$$

mmol

TON = $\frac{0.95}{0.029}$ = 32.7 and TOF = 32.7/10 min^{-1} = 3.27 min^{-1}

VII. Analytical and spectroscopic data of the synthesized compounds

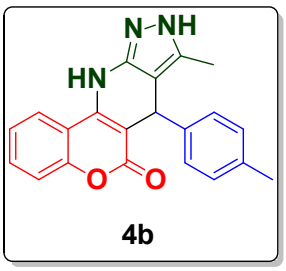
8-methyl-7-(4-methoxyphenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, **4a**



4a

White solid. Melting Point: 252-254 °C. IR (KBr, cm^{-1}): 3334, 3212, 3072, 2904, 1684, 1611, 1546, 1510, 1445, 1386, 1325, 1246, 1204, 1159, 1106, 1043, 960, 757. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.91 (s, 1H), 10.41 (s, 1H), 8.36 (d, J = 7.2 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.08 (t, J = 7.7 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.77 (t, J = 7.8 Hz, 1H), 5.49 (s, 1H), 3.79 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.3, 155.4, 151.9, 145.7, 145.2, 135.3, 134.6, 131.2, 128.2, 126.8, 123.4, 122.7, 120.4, 116.4, 113.8, 110.9, 102.4, 96.6, 55.3, 29.8, 9.0 ppm.

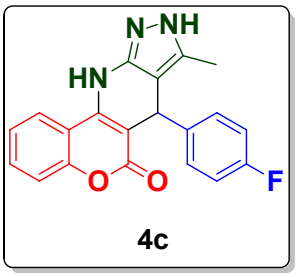
8-methyl-7-(p-tolyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, **4b**



4b

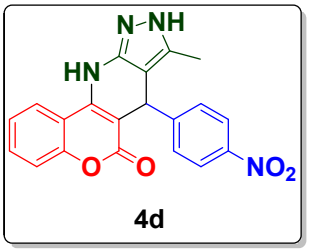
White solid. Melting Point: 272-274 °C. IR (KBr, cm^{-1}): 3226, 3040, 2919, 1672, 1614, 1549, 1515, 1446, 1360, 1302, 1210, 1112, 1087, 1030, 958, 748. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.26 (t, J = 8.2 Hz, 1H), 7.18 (dd, J = 8.2, 2.8 Hz, 1H), 7.06 (dd, J = 8.0, 2.1 Hz, 2H), 6.94 (dd, J = 8.0, 2.5 Hz, 2H), 5.01 (s, 1H), 2.18 (s, 3H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.7, 151.7, 143.5, 134.8, 130.5, 127.9, 126.9, 122.9, 122.6, 115.9, 102.2, 97.0, 78.3, 78.0, 77.7, 36.0, 20.2, 9.0 ppm.

***7-(4-fluorophenyl)-8-methyl-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one,* 4c**



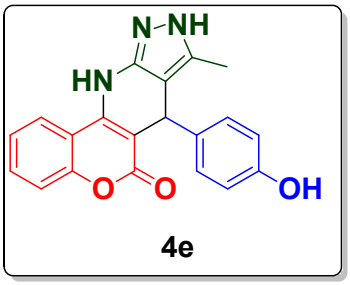
White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3169, 3086, 2919, 1667, 1612, 1560, 1511, 1428, 1378, 1311, 1228, 1096, 1049, 974, 760. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H), 10.42 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.57-7.44 (m, 1H), 7.33-7.27 (m, 1H), 7.24-7.18 (m, 3H), 6.96-6.89 (m, 2H), 5.12 (s, 1H), 1.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 161.0, 159.3, 152.2, 145.8, 144.7, 143.1, 135.2, 131.3, 129.3, 129.2, 123.5, 123.2, 116.5, 114.6, 114.4, 114.2, 102.4, 97.0, 79.2, 78.8, 78.5, 36.2, 9.5 ppm.

***7-(4-nitrophenyl)-8-methyl-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one,* 4d**



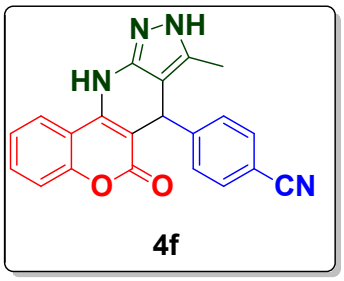
White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3196, 3073, 2913, 1665, 1612, 1554, 1511, 1428, 1382, 1207, 1086, 1055, 908, 964, 750. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 1H), 10.53 (s, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.6 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.2 Hz, 1H), 5.28 (s, 1H), 1.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 154.0, 152.1, 145.5, 145.0, 135.4, 131.3, 128.5, 123.4, 123.1, 123.0, 116.3, 113.8, 101.0, 95.7, 36.9, 9.3 ppm.

8-methyl-7-(4-hydroxyphenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4e



White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3217, 3085, 2872, 1689, 1611, 1545, 1509, 1449, 1379, 1324, 1233, 1203, 1080, 1044, 954, 908, 761. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.98 (s, 1H), 10.41 (s, 1H), 9.10 (s, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.43-7.25 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 8.0 Hz, 2H), 5.02 (s, 1H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.3, 152.0, 145.8, 144.3, 137.7, 134.9, 131.4, 128.3, 123.6, 123.0, 116.5, 114.7, 114.1, 103.0, 97.5, 39.9, 35.7, 9.3 ppm.

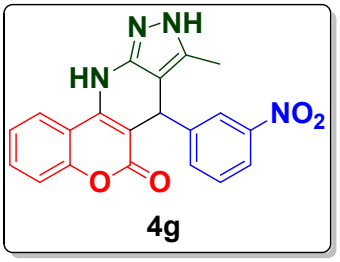
8-methyl-7-(4-cyanophenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4f



4f

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3246, 3071, 2976, 2918, 1714, 1665, 1612, 1554, 1510, 1430, 1385, 1326, 1264, 1207, 1086, 1054, 960, 910, 841, 812, 759. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (s, 1H), 10.62 (s, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.44 – 7.31 (m, 4H), 5.25 (s, 1H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 160.7, 152.3, 152.1, 145. 1356, 145.1,.5, 132.1, 131.8, 128.5, 123.8, 123.2, 118.9, 116.7, 113.8, 108.6, 101.4, 95.9, 37.0, 9.39 ppm

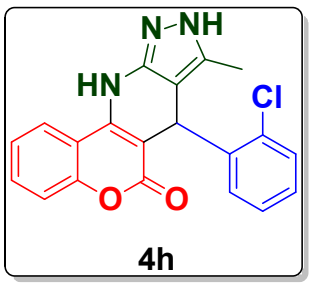
8-methyl-7-(3-nitrophenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4g



4g

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3313, 3185, 3060, 2975, 1660, 1612, 1558, 1518, 1433, 1385, 1340, 1275, 1211, 1150, 1089, 1050, 950, 760. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 1H), 10.66 (s, 1H), 8.39 (d, J = 8.1 Hz, 1H), 8.05 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.39 (t, J = 8.2 Hz, 1H), 7.33 (d, J = 8.3 Hz, 1H), 5.36 (s, 1H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-D_6) δ 160.6, 151.9, 148.8, 147.4, 145.5, 144.9, 135.4, 134.2, 131.7, 129.4, 123.7, 123.0, 121.7, 120.9, 116.5, 113.6, 101.3, 95.8, 36.4, 9.2 ppm

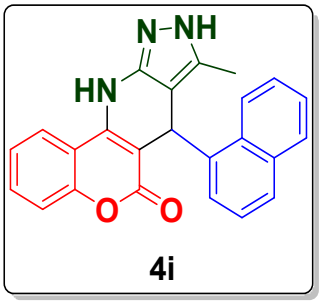
8-methyl-7-(2-chlorophenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4h



4h

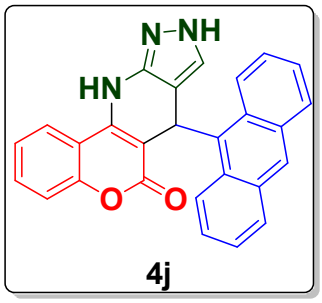
White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3198, 3071, 2974, 1668, 1614, 1555, 1514, 1431, 1386, 1326, 1265, 1205, 1147, 1089, 1049, 964, 750. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H). 10.25 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H), 7.50 – 7.40 (m, 1H), 7.29 – 7.14 (m, 4H), 7.09 – 6.97 (m, 2H), 5.58 (s, 1H), 1.92 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-D_6) δ 160.8, 152.0, 145.5, 145.0, 143.8, 143.6, 135.6, 135.5, 131.5, 131.4, 130.8, 130.8, 130.3, 130.3, 128.4, 126.7, 126.5, 123.1, 122.7, 116.1, 113.8, 101.6, 96.6, 34.0, 9.3 ppm.

8-methyl-7-(naphthalen-1-yl)-9,11-dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-one, 4i



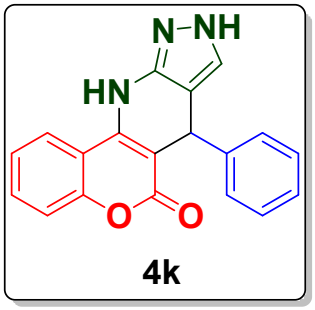
White solid. Melting Point: 275 °C. IR (KBr, cm^{-1}): 3297, 3176, 2963, 1669, 1612, 1554, 1512, 1429, 1383, 1325, 1262, 1225, 1153, 1111, 1046, 955, 765. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 10.60 (s, 1H), 8.42 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.63-7.56 (m, 1H), 7.47 (s, 2H), 7.43 – 7.34 (m, 2H), 7.31 (dd, J = 8.3, 1.1 Hz, 1H), 5.99 (s, 1H), 4.35 (s, 1H), 1.69 (s, 3H) ppm.

7-(anthracen-9-yl)-9,11-dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-one, 4j



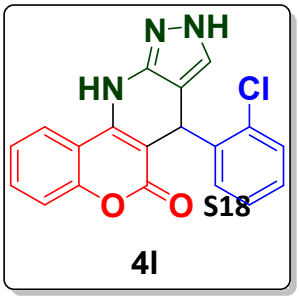
White solid. Melting Point: 263-265 °C. IR (KBr, cm^{-1}): 3240, 3133, 3089, 2922, 1675, 1632, 1576, 1529, 1446, 1359, 1338, 1255, 1235, 1158, 1089, 1036, 932, 750. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 10.98 (s, 1H), 8.51 (s, 1H), 8.31 (d, J = 7.9 Hz, 2H), 8.03 (dd, J = 17.3, 8.6 Hz, 2H), 7.50 – 7.42 (m, 4H), 7.37 (d, J = 7.5 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 6.72 (d, J = 8.3 Hz, 1H), 6.58 (t, J = 7.6 Hz, 1H), 6.32 (d, J = 12.1 Hz, 1H), 5.79 (d, J = 12.0 Hz, 1H) ppm.

7-phenyl-9,11-dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-one, 4k



White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3177, 3063, 2951, 1666, 1606, 1562, 1506, 1452, 1351, 1322, 1241, 1200, 1158, 1110, 1056, 968, 752. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 10.59 (s, 1H), 8.38 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.43 (s, 1H), 7.41 – 7.33 (m, 2H), 7.24 – 7.18 (m, 4H), 7.13 – 7.06 (m, 1H), 5.25 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 160.7, 152.1, 147.8, 145.5, 145.0, 131.6, 128.1, 126.8, 126.1, 125.8, 123.7, 123.0, 116.6, 113.9, 105.2, 96.2, 36.7 ppm. HRMS (ESI) calcd for $C_{19}H_{13}N_3O_2$ $(M + H)^+$ 316.1086, found 316.1083.

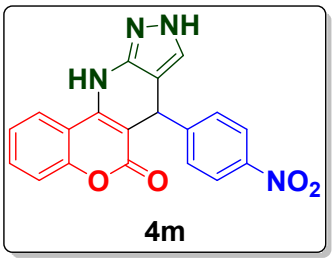
7-(2-chlorophenyl)-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4l



White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3169, 3053, 2954, 1667, 1608, 1562, 1512, 1443, 1323, 1238, 1204, 1164, 1114, 1055, 950, 747. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H), 10.66 (s, 1H), 8.39 (d,

J = 7.6 Hz, 1H), 7.63 (t, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.43-7.34 (m, 3H), 7.18-7.08 (m, 3H), 5.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.7, 152.3, 146.1, 144.8, 131.9, 131.0, 129.3, 128.6, 127.6, 127.6, 123.9, 123.2, 116.8, 113.8, 103.8, 95.0, 34.3 ppm. HRMS (ESI) calcd for $C_{19}H_{12}ClN_3O_2$ $(M + H)^+$ 350.0678, found 350.0696

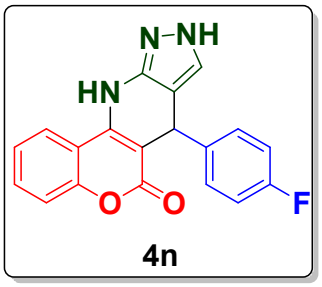
7-(4-nitrophenyl)-9,11-dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-one, 4m



4m

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3188, 3071, 2954, 1666, 1606, 1564, 1510, 1456, 1347, 1284, 1246, 1238, 1158, 1110, 1058, 967, 759. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.35 (s, 1H), 10.61 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 7.59 ‘(t, J = 8.3 Hz, 1H), 7.43 (s, 1H), 7.40 – 7.31 (m, 2H), 7.25 – 7.18 (m, 2H), 7.06 – 6.98 (m, 2H), 5.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 155.1, 152.2, 145.7, 145.5, 145.3, 131.9, 128.2, 123.9, 123.6, 123.2, 116.8, 113.8, 103.9, 95.1, 37.0 ppm. HRMS (ESI) calcd for $C_{19}H_{12}N_4O_4$ $(M + H)^+$ 360.0928, found 360.0937

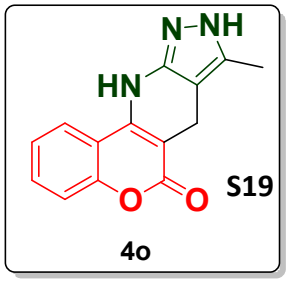
7-(4-fluorophenyl)-9,11-dihydrochromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridin-6(7*H*)-one, 4n



4n

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3173, 3070, 2953, 1662, 1606, 1562, 1506, 1407, 1354, 1324, 1286, 1207, 1158, 1112, 1058, 969, 756. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.35 (s, 1H), 10.61 (s, 1H), 8.37 (d, J = 7.9 Hz, 1H), 7.59 (t, J = 8.3 Hz, 1H), 7.43 (s, 1H), 7.40 – 7.31 (m, 2H), 7.25 – 7.18 (m, 2H), 7.06 – 6.98 (m, 2H), 5.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 160.8, 152.1, 145.5, 145.1, 144.1, 144.1, 131.8, 128.7, 128.7, 126.3, 123.8, 123.1, 116.7, 114.9, 114.7, 114.0, 105.1, 96.2, 36.1 ppm. HRMS (ESI) calcd for $C_{19}H_{12}FN_3O_2$ $(M + H)^+$ 333.0978, found 333.0992

8-methyl-9,11-dihydrochromeno[4,3-b]pyrazolo[4,3-e]pyridin-6(7H)-one, 4o

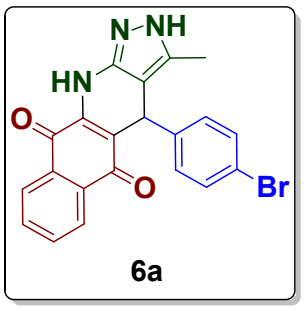


4o

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3230, 3146, 2989, 1682, 1607, 1552, 1497, 1466, 1318, 1250, 1218, 1159, 1119, 1054, 937, 743. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 10.32 (s, 1H), 7.54 –

7.27 (m, 2H), 7.08 – 6.89 (m, 2H), 5.99 (s, 1H), 5.77 (s, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.2, 155.0, 152.0, 148.1, 142.3, 131.8, 129.9, 119.9, 119.4, 116.4, 95.6, 88.8, 14.1 ppm. HRMS (ESI) calcd for $C_{14}H_{11}N_3O_2$ $(M + H)^+$ 254.0929, found 254.0927.

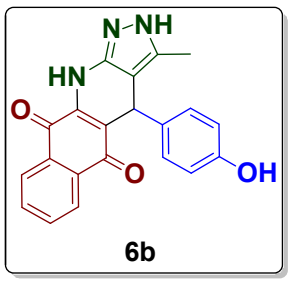
4-(4-bromophenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6a



6a

Purple solid. Melting Point: 285-287 °C. IR (KBr, cm^{-1}): 3420, 3164, 3023, 2921, 1705, 1670, 1606, 1536, 1466, 1382, 1304, 1251, 1224, 1151, 1096, 958, 783. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.11 (s, 1H), 10.25 (s, 1H), 8.00 (d, J = 7.3 Hz, 1H), 7.84 (d, J = 7.2 Hz, 1H), 7.81 – 7.70 (m, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 5.35 (s, 1H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 180.5, 146.6, 141.1, 134.8, 132.6, 132.5, 131.0, 130.3, 129.8, 125.8, 125.4, 118.9, 113.7, 102.6, 35.6, 9.5 ppm.

4-(4-hydroxyphenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6b

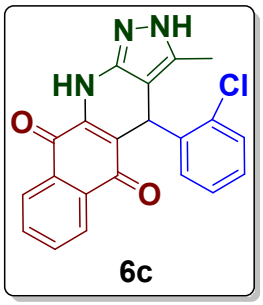


6b

Purple solid. Melting Point: 275-277 °C. IR (KBr, cm^{-1}): 3446, 3275, 3035, 2982, 1666, 1592, 1565, 1511, 1469, 1353, 1243, 1149, 1098, 1063, 957, 777. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H), 10.02 (s, 1H), 9.09 (s, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.86 (dd, J = 7.6, 1.1 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.74 (t, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 6.6 Hz, 2H), 5.24 (s, 1H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 180.5, 155.3, 140.5, 137.8, 134.6, 132.5, 132.4, 130.2, 128.3, 125.6, 125.3, 114.7, 34.8, 30.6, 9.3 ppm

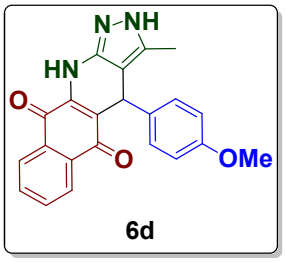
4-(2-chlorophenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6c

Purple Solid. Melting point: 275-278 °C . IR (KBr, cm^{-1}): 3440, 3237, 3067, 1677, 1600, 1532, 1439, 1384, 1306, 1274, 1225, 1157, 1040, 957, 753. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.18 (s, 1H), 10.29 (s, 1H), 8.01 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 7.82 (t, J = 7.1 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 4.3 Hz, 1H), 6.84 (d, J = 4.3 Hz, 2H), 5.72 (s, 1H), 2.10 (s, 3H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.6, 180.4, 144.5, 141.5, 134.8, 132.5, 132.4, 130.9, 130.8, 130.3, 128.9, 125.7, 125.4, 113.7, 102.3, 33.5, 9.6 ppm. HRMS (ESI) calcd for $C_{21}H_{14}ClN_3O_2$ $(M + H)^+$ 376.0853, found 376.0837.



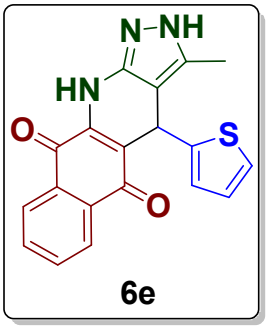
4-(4-methoxyphenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6d

Purple solid. Melting Point: 271-273 °C. IR (KBr, cm^{-1}): 3430, 3159, 3025, 1713, 1665, 1598, 1512, 1465, 1345, 1304, 1268, 1227, 1148, 1093, 958, 768. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (s, 1H), 10.09 (s, 1H), 7.99 (d, J = 7.4 Hz, 1H), 7.85 (d, J = 7.4 Hz, 1H), 7.77 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.3 Hz, 1H), 7.14 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 5.29 (s, 1H), 3.66 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 180.6, 157.3, 140.7, 139.5, 134.7, 132.5, 132.5, 130.3, 128.5, 125.7, 125.4, 114.6, 113.4, 103.3, 54.9, 35.0, 9.4 ppm.



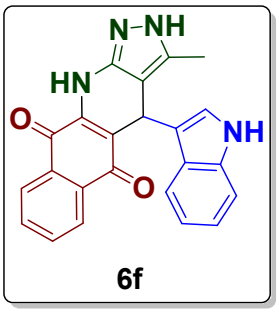
4-(2-thienyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6e

Purple solid. Melting Point: 280-282 °C. IR (KBr, cm^{-1}): 3437, 3162, 3099, 1665, 1606, 1567, 1512, 1465, 1347, 1305, 1248, 1148, 1058, 950, 783. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.18 (s, 1H), 10.29 (s, 1H), 8.01 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 7.82 (t, J = 7.1 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 4.3 Hz, 1H), 6.84 (d, J = 4.3 Hz, 2H), 5.72 (s, 1H), 2.10 (s, 3H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.8, 180.5, 151.0, 140.4, 134.8, 132.6, 132.5, 130.2, 126.5, 125.8, 125.5, 124.0, 123.5, 113.6, 102.5, 30.3, 9.5 ppm. HRMS (ESI) calcd for $C_{19}H_{13}N_3O_2S$ $(M + H)^+$ 348.0806, found 348.0847.



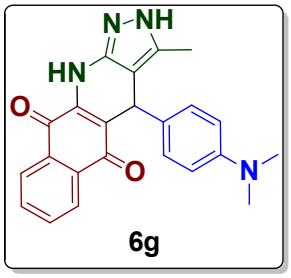
4-(3-indolyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, *6f*

Purple solid. Melting Point: 285-287 °C. IR (KBr, cm^{-1}): 3348, 3165, 3097, 2854, 1672, 1611, 1596, 1512, 1464, 1383, 1347, 1251, 1223, 1147, 1061, 949, 743. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 10.77 (s, 1H), 10.15 (s, 1H), 7.98 (d, J = 7.2 Hz, 1H), 7.81 (d, J = 7.2 Hz, 1H), 7.77 – 7.63 (m, 2H), 7.33 – 7.20 (m, 3H), 6.94 (t, J = 7.3 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 5.65 (s, 1H), 1.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.7, 180.4, 140.1, 136.0, 134.4, 132.3, 132.1, 129.9, 125.4, 125.3, 125.1, 122.3, 120.2, 119.6, 118.3, 118.0, 114.1, 111.2, 102.5, 27.0, 9.1 ppm. HRMS (ESI) calcd for $C_{23}H_{16}N_4O_2$ $(M + H)^+$ 381.1351, found 381.1352.



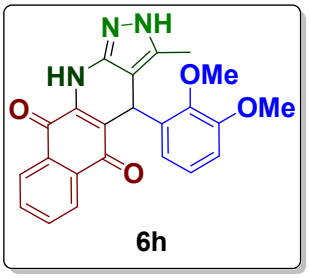
4-(4-N,N-dimethylphenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, *6g*

Purple solid. Melting Point: 275-277 °C. IR (KBr, cm^{-1}): 3451, 3234, 3027, 2920, 1665, 1607, 1568, 1517, 1446, 1348, 1305, 1267, 1222, 1157, 1097, 951, 743. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.00 (s, 1H), 10.03 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.77 (t, J = 7.4 Hz, 1H), 7.72 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 6.56 (d, J = 8.5 Hz, 2H), 5.22 (s, 1H), 2.78 (s, 6H), 1.97 (s, 3H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6) δ 180.8, 180.6, 148.6, 140.4, 135.4, 134.6, 132.5, 132.4, 130.2, 127.9, 125.6, 125.3, 115.0, 112.2, 103.5, 34.6, 9.4 ppm. HRMS (ESI) calcd for $C_{23}H_{20}N_4O_2$ $(M + H)^+$ 385.1664, found 385.1658

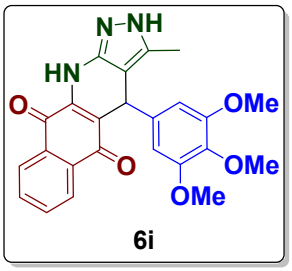


4-(2,3-dimethoxyphenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6h

Purple solid. Melting Point: 282-284 C. IR (KBr, cm^{-1}): 3427, 3235, 2934, 1663, 1594, 1536, 1463, 1382, 1347, 1247, 1216, 1147, 1114, 1089, 957, 751. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 10.06 (s, 1H), 8.01 (d, J = 7.4 Hz, 1H), 7.85 – 7.70 (m, 3H), 6.87 (d, J = 8.8 Hz, 1H), 6.65 (dd, J = 8.8, 2.6 Hz, 1H), 6.57 (s, 1H), 5.63 (s, 1H), 3.78 (s, 3H), 3.56 (s, 3H), 1.96 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.6, 153.3, 149.6, 141.7, 137.1, 134.7, 132.4, 130.3, 125.7, 125.4, 115.4, 114.2, 112.3, 110.5, 103.0, 56.2, 55.1, 9.3 ppm. HRMS (ESI) calcd for $C_{23}H_{19}N_3O_4$ $(M + H)^+$ 402.1454, found 402.1414



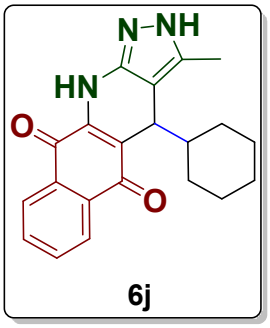
4-(3,4,5-trimethoxyphenyl)-3-methyl-1*H*-benzo[*g*]pyrazolo[3,4-*b*]-quinoline-5,10(4*H*,11*H*)-dione, 6i



6i

Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3349, 3323, 3062, 1673, 1594, 1508, 1461, 1381, 1326, 1266, 1232, 1186, 1126, 1056, 975, 724. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.06 (s, 1H), 10.11 (s, 1H), 8.01 (d, J = 7.2 Hz, 1H), 7.88 (d, J = 7.2 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.74 (t, J = 7.4 Hz, 1H), 6.52 (s, 2H), 5.31 (s, 1H), 3.67 (s, 6H), 3.57 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 180.5, 179.5, 175.3, 169.6, 157.2, 156.9, 152.6, 146.1, 143.1, 142.9, 135.6, 134.8, 132.6, 130.4, 125.5, 104.7, 102.9, 59.9, 55.8, 36.34, 30.77, 5.77 ppm. HRMS (ESI) calcd for $C_{24}H_{21}N_3O_5$ $(M + H)^+$ 432.1559, found 432.1540

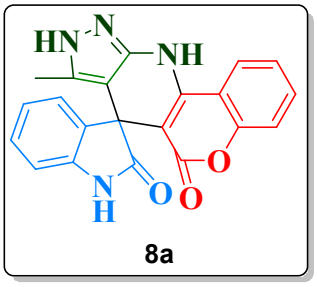
4-cyclohexyl-3-methyl-4,11-dihydro-2H-benzo[g]pyrazolo[3,4-b]quinoline-5,10-dione, 6j



6j

Brown solid. Melting Point: 190-192 °C. IR (KBr, cm^{-1}): 3335, 3223, 2926, 2853, 1668, 1607, 1570, 1506, 1303, 1245, 1213, 1162, 1118, 1034, 939, 722. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 9.47 (s, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 7.3 Hz, 1H), 7.88 – 7.80 (m, 1H), 7.79 – 7.73 (m, 1H), 7.39 (s, 1H), 6.06 (s, 1H), 2.21 (s, 3H), 1.72 – 0.93 (m, 10H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.9, 181.2, 172.7, 148.5, 142.8, 134.4, 132.2, 132.1, 130.0, 129.0, 125.7, 124.8, 106.1, 95.8, 28.5, 25.6, 24.0, 21.6, 20.4, 10.1 ppm. HRMS (ESI) calcd for $C_{21}H_{21}N_3O_2$ $(M + H)^+$ 348.1712, found 348.1707

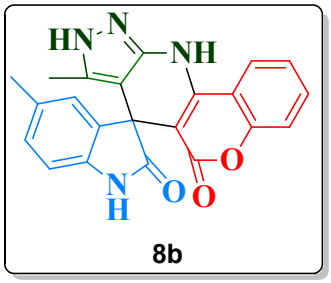
8-Methyl-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3′-indoline]-2′,6(9*H*,11*H*)-dione, 8a



8a

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3361, 3224, 3070, 1692, 1613, 1550, 1515, 1469, 1384, 1326, 1221, 1110, 1069, 987, 761. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H), 10.80 (s, 1H), 10.50 (s, 1H), 8.40 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.14 (t, J = 7.3 Hz, 1H), 6.89 – 6.83 (m, 3H), 1.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.9, 177.7, 166.8, 159.9, 148.7, 142.3, 136.2, 134.1, 131.6, 131.5, 128.7, 125.3, 123.5, 122.1, 119.3, 117.6, 111.0, 99.9, 56.4, 47.6, 8.8 ppm. HRMS (ESI) calcd for $C_{21}H_{14}N_4O_3$ $(M + H)^+$ 371.1144, found 371.1160.

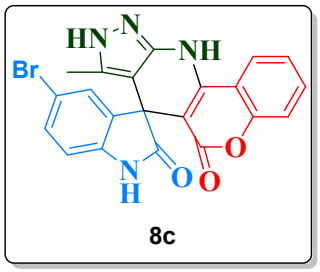
5′-Methyl-8-methyl-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]-pyridine-7,3′-indoline]-20,6(9*H*,11*H*)-dione, 8b



8b

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3367, 3191, 3096, 1676, 1610, 1558, 1512, 1427, 1384, 1324, 1226, 1200, 1150, 1106, 1072, 992, 758. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 10.74 (s, 1H), 10.36 (s, 1H), 8.35 (d, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.39 – 7.30 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.8 Hz, 1H), 6.66 (s, 1H), 2.08 (s, 3H), 1.60 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.6, 178.3, 157.9, 152.3, 139.1, 135.7, 129.9, 124.5, 124.3, 123.4, 122.0, 116.3, 113.2, 108.0, 99.7, 95.7, 47.9, 20.2, 8.3 ppm. HRMS (ESI) calcd for $C_{21}H_{13}BrN_4O_3$ $(M + H)^+$ 449.0249, found 449.0268

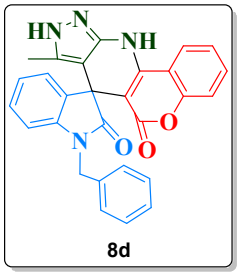
5′-Bromo-8-methyl-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]-pyridine-7,3′-indoline]-20,6(9*H*,11*H*)-dione, 8c



8c

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3359, 3255, 3081, 2924, 1672, 1610, 1548, 1503, 1473, 1380, 1324, 1250, 1221, 1150, 1107, 1048, 950, 757. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 10.85 (s, 1H), 10.67 (s, 1H), 8.39 (d, J = 8.6 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.47 – 7.28 (m, 3H), 7.08 (s, 1H), 6.83 (d, J = 8.7 Hz, 1H), 1.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.8, 159.9, 152.2, 146.6, 141.1, 138.9, 134.9, 132.5, 130.6, 126.3, 124.2, 123.5, 116.9, 113.7, 111.1, 99.7, 8.8 ppm. HRMS (ESI) calcd for $C_{21}H_{13}BrN_4O_3$ $(M + H)^+$ 449.0249, found 449.0268

1'-benzyl-8-methyl-9,11-dihydro-6*H*-spiro[chromeno[4,3-*b*]pyrazolo[4,3-*e*]pyridine-7,3'-indoline]-2',6-dione, 8d

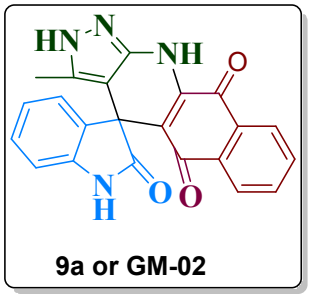


8d

White solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3382, 3255, 3068, 2923, 1681, 1608, 1545, 1504, 1464, 1362, 1323, 1289, 1218, 1144, 1111, 1060, 965, 755. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.22 (s, 1H), 10.91 (s, 1H), 8.44 (d, J = 8.4 Hz, 1H), 7.69 -7.62 (m, 1H), 7.57 (d, J = 6.8 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.39 – 7.32 (m, 3H), 7.29 (d, J = 6.6 Hz, 1H), 7.15 (t, J = 6.8 Hz, 1H), 7.00 – 6.86 (m, 3H), 5.10 (d, J = 15.6 Hz, 1H), 4.86 (d, J = 15.6 Hz, 1H), 1.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 177.5, 159.5, 152.0, 146.4, 145.6, 142.3, 136.5, 135.6, 134.7, 132.3,

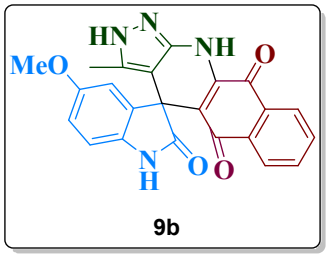
132.1, 128.3, 127.8, 127.6, 127.2, 124.0, 123.3, 123.2, 122.58, 116.74, 113.6, 108.3, 100.0, 94.4, 48.7, 43.4, 8.6 ppm. HRMS (ESI) calcd for $C_{28}H_{20}BrN_4O_3$ $(M + H)^+$ 461.1613, found 461.1609.

3-methyl-2,11-dihydrospiro[benzo[*g*]pyrazolo[3,4-*b*]quinoline-4,3'-indoline]-2',5,10-trione, 9a



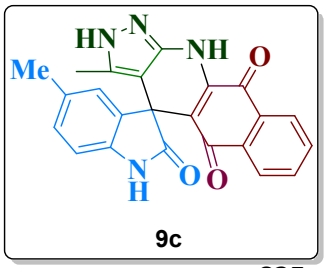
Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3428, 3296, 3084, 1735, 1666, 1596, 1532, 1513, 1470, 1352, 1303, 1275, 1222, 1168, 1066, 932, 757. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 10.58 (s, 1H), 10.55 (s, 1H), 8.03 (d, J = 7.0 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.82 (t, J = 7.4 Hz, 1H), 1.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.3, 180.1, 179.4, 172.3, 142.5, 141.3, 137.4, 135.2, 132.9, 132.3, 130.1, 127.8, 126.1, 125.7, 123.6, 121.9, 112.1, 109.1, 101.1, 49.4, 30.8, 21.2, 8.8 ppm. HRMS (ESI) calcd for $C_{22}H_{14}N_4O_3$ $(M + H)^+$ 383.1144, found 383.1164.

5'-methoxy-3-methyl-2,11-dihydrospiro[benzo[g]pyrazolo[3,4-b]quinoline-4,3'-indoline]-2',5,10-trione, 9b



Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3296, 3084, 1666, 1596, 1546, 1513, 1470, 1381, 1352, 1275, 1222, 1148, 1092, 1066, 932, 757. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 10.54 (s, 1H), 10.37 (s, 1H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.81 – 7.73 (m, 3H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.55 (s, 1H), 3.50 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.3, 180.1, 179.3, 155.2, 142.5, 138.7, 135.2, 134.7, 132.9, 132.4, 130.2, 126.1, 125.7, 112.3, 112.0, 110.5, 109.4, 101.1, 55.4, 49.9, 8.9 ppm. HRMS (ESI) calcd for $C_{23}H_{16}N_4O_4$ $(M + H)^+$ 413.1250, found 413.1237

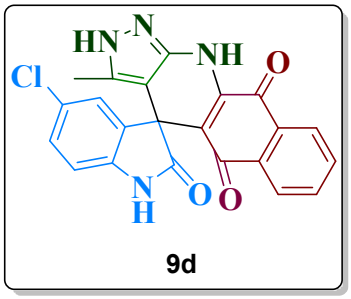
3,5'-dimethyl-2,11-dihydrospiro[benzo[g]pyrazolo[3,4-b]quinoline-4,3'-indoline]-2',5,10-trione, 9c



Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3234, 3096, 1669, 1585, 1550, 1512, 1475, 1385, 1355, 1265, 1221, 1149, 1089, 1055, 950, 755. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 10.57 (s, 1H), 10.43 (s, 1H), 8.03 (d, *J* = 7.1 Hz, 1H), 7.82 – 7.74 (m, 3H), 6.93 (d, *J* =

7.6 Hz, 1H), 6.77 – 6.74 (m, 2H), 2.11 (s, 3H), 1.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.7, 179.5, 178.7, 141.9, 138.4, 137.0, 134.6, 132.3, 131.8, 130.1, 129.6, 127.4, 125.5, 125.2, 123.6, 108.2, 48.8, 20.2, 8.3 ppm. HRMS (ESI) calcd for $C_{23}H_{16}N_4O_3$ $(M + H)^+$ 397.1300, found 397.1300.

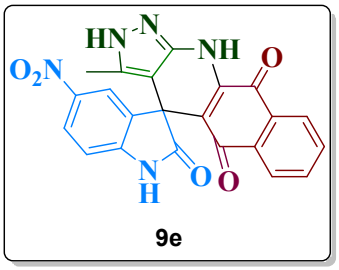
5'-chloro-3-methyl-2,11-dihydrospiro[benzo[*g*]pyrazolo[3,4-*b*]quinoline-4,3'-indoline]-2',5,10-trione, 9d



9d

Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3340, 3033, 2854, 1738, 1667, 1597, 1534, 1473, 1434, 1350, 1301, 1279, 1219, 1155, 1105, 1067, 990, 727. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 10.68 (s, 1H), 10.67 (s, 1H), 8.04 (d, J = 7.2 Hz, 1H), 7.82 – 7.74 (m, 3H), 7.19 (d, J = 8.2 Hz, 1H), 7.03 (s, 1H), 6.89 (d, J = 8.2 Hz, 1H), 1.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.6, 179.6, 178.5, 142.2, 139.8, 138.7, 134.5, 132.3, 131.8, 129.7, 127.1, 125.5, 125.2, 125.2, 123.3, 110.8, 109.8, 100.0, 49.9, 8.3 ppm. HRM S (ESI) calcd for $C_{22}H_{13}N_4O_3$ $(M + H)^+$ 417.0754, found 417.0766

3-methyl-5'-nitro-2,11-dihydrospiro[benzo[*g*]pyrazolo[3,4-*b*]quinoline-4,3'-indoline]-2',5,10-trione, 9e

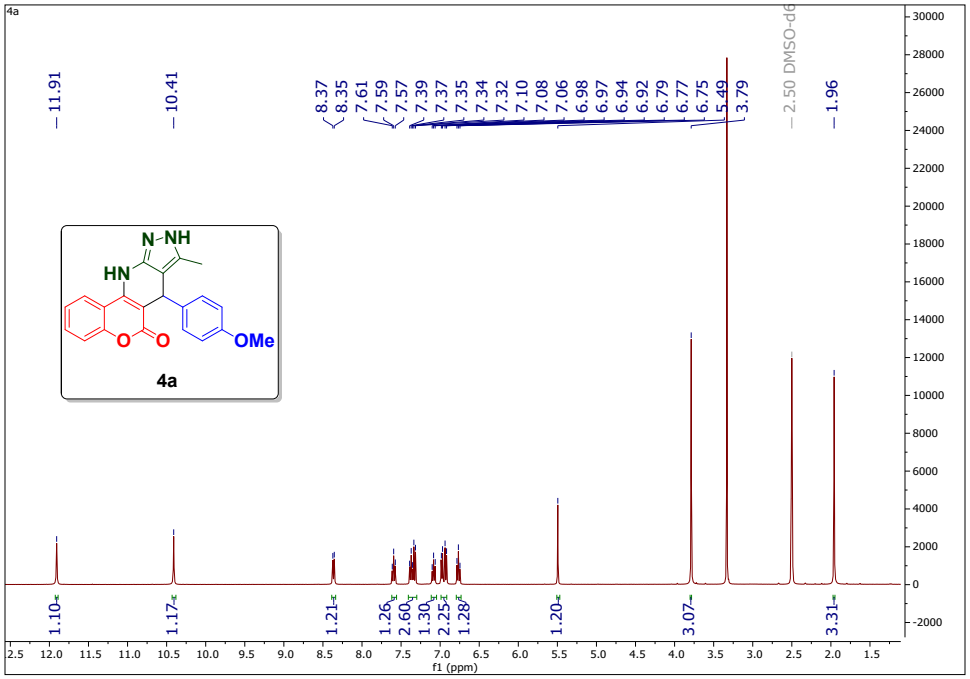


9e

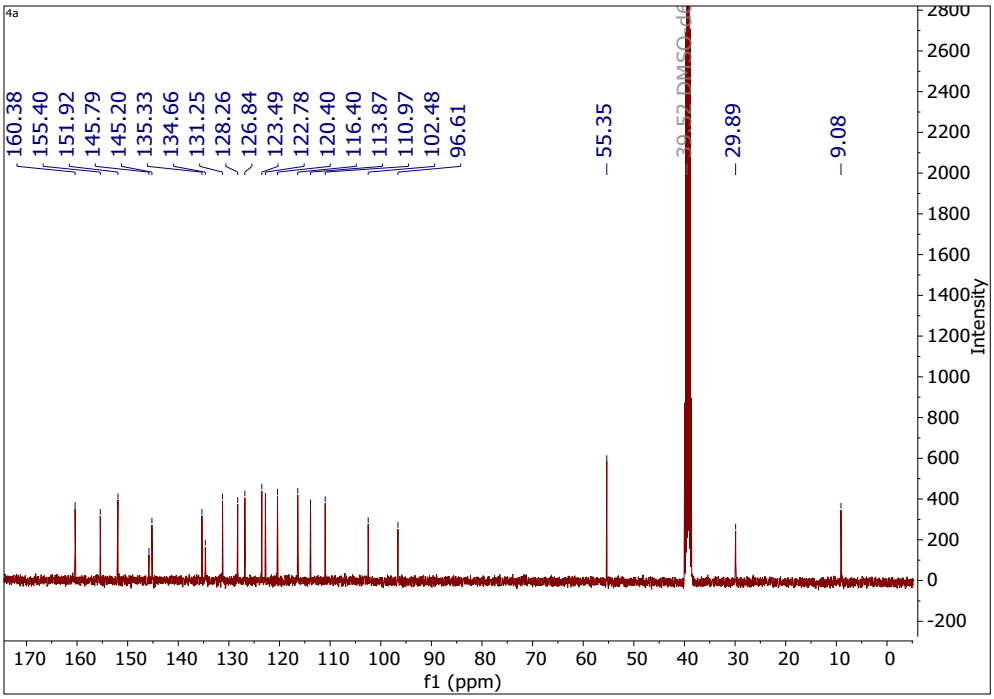
Purple solid. Melting Point: > 300 °C. IR (KBr, cm^{-1}): 3306, 2854, 1745, 1690, 1599, 1534, 1514, 1473, 1336, 1305, 1275, 1216, 1157, 1120, 1069, 996, 724. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.39 (s, 1H), 11.30 (s, 1H), 10.80 (s, 1H), 8.13 (dd, J = 16.8, 7.6 Hz, 1H), 8.04 (d, J = 6.5 Hz, 1H), 7.87 (d, J = 6.4 Hz, 2H), 7.78 (s, 2H), 7.10 (d, J = 8.3 Hz, 1H), 1.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.4, 150.6, 148.0, 142.7, 138.1, 135.1, 133.0, 132.3, 130.5, 129.1, 126.5, 125.8, 119.5, 115.7, 111.9, 110.8, 109.3, 100.0, 49.4, 29.9, 9.1 ppm. HRMS (ESI) calcd for $C_{22}H_{13}N_5O_5$ $(M + H)^+$ 428.0995, found 428.0995.

VIII. ^{1}H & ^{13}C NMR spectra of the synthesized compounds

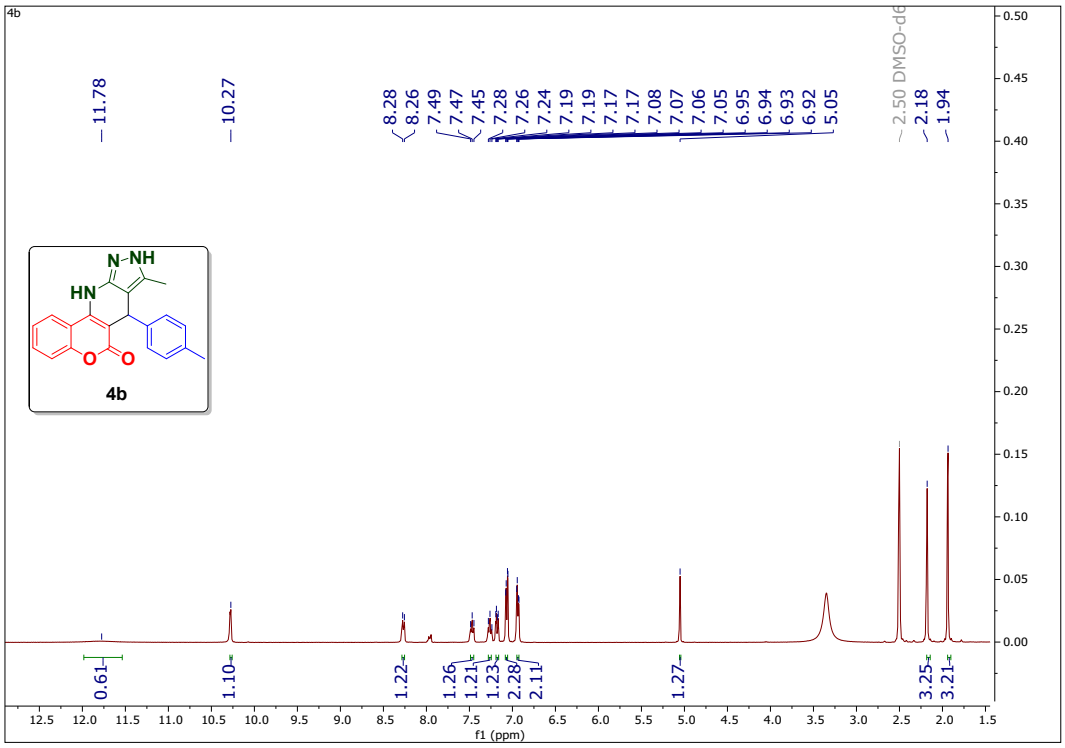
^{1}H NMR spectrum of 4a



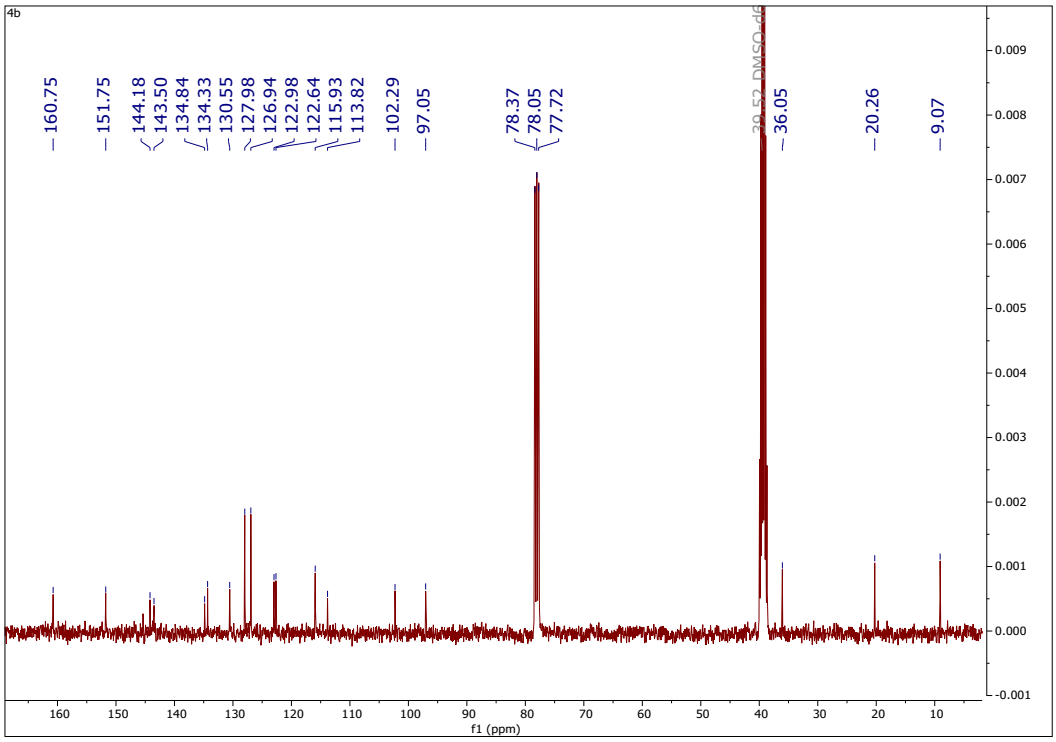
^{13}C NMR Spectrum of 4a



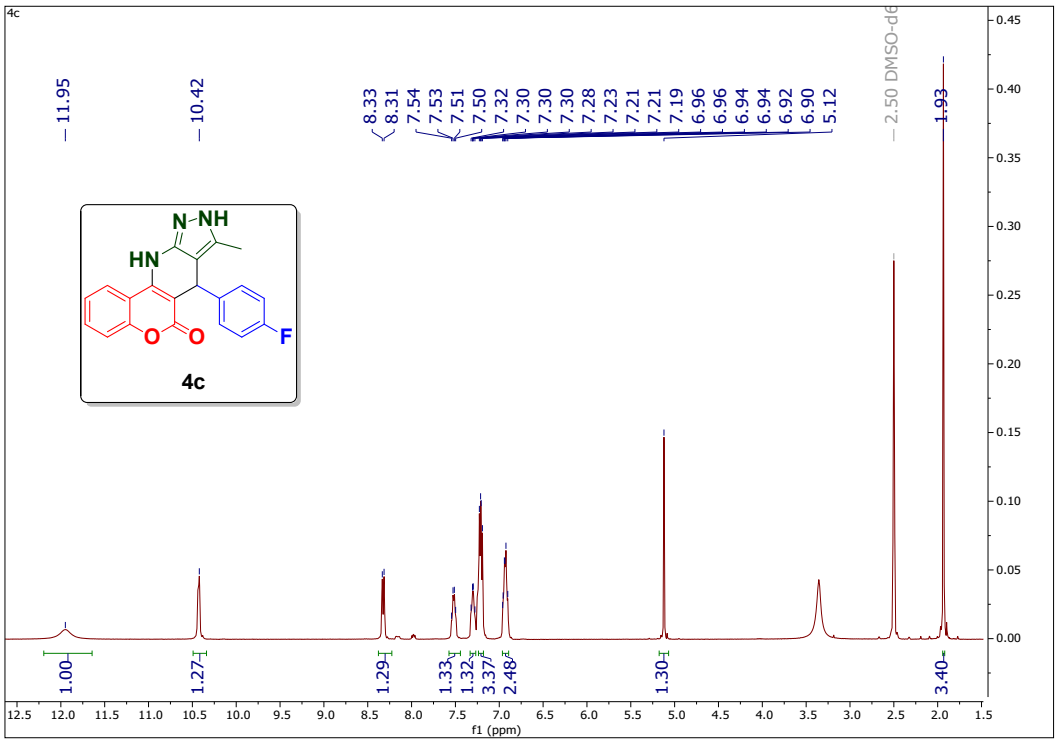
^{1}H NMR spectrum of 4b



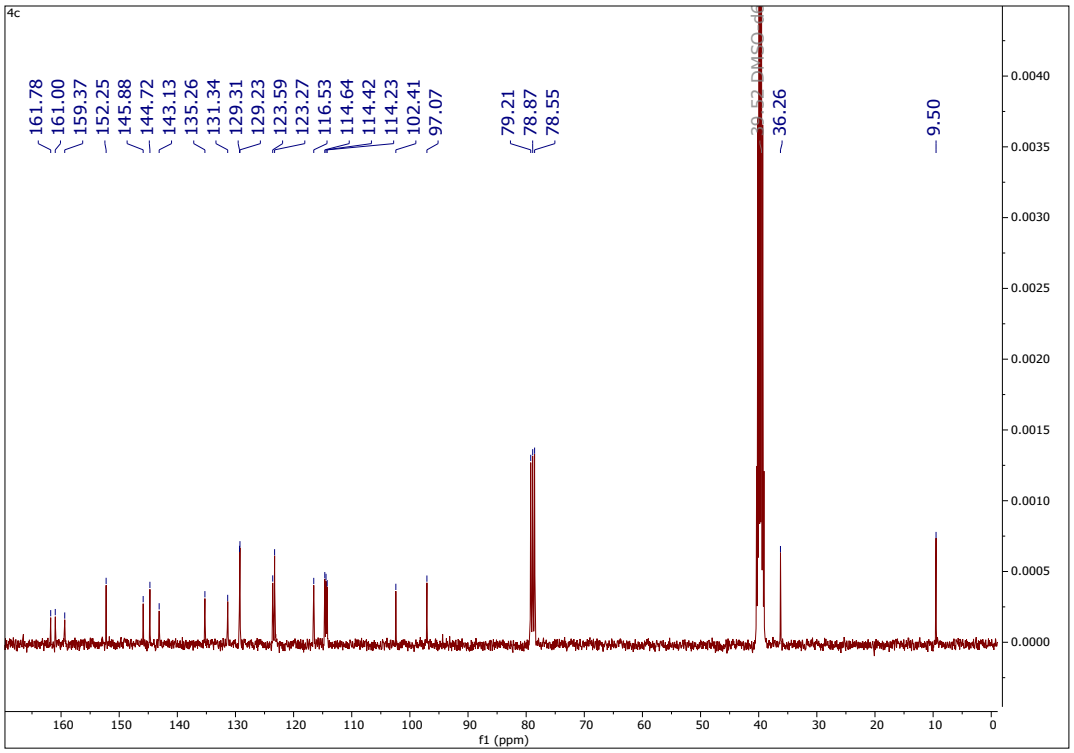
^{13}C NMR Spectrum of 4b



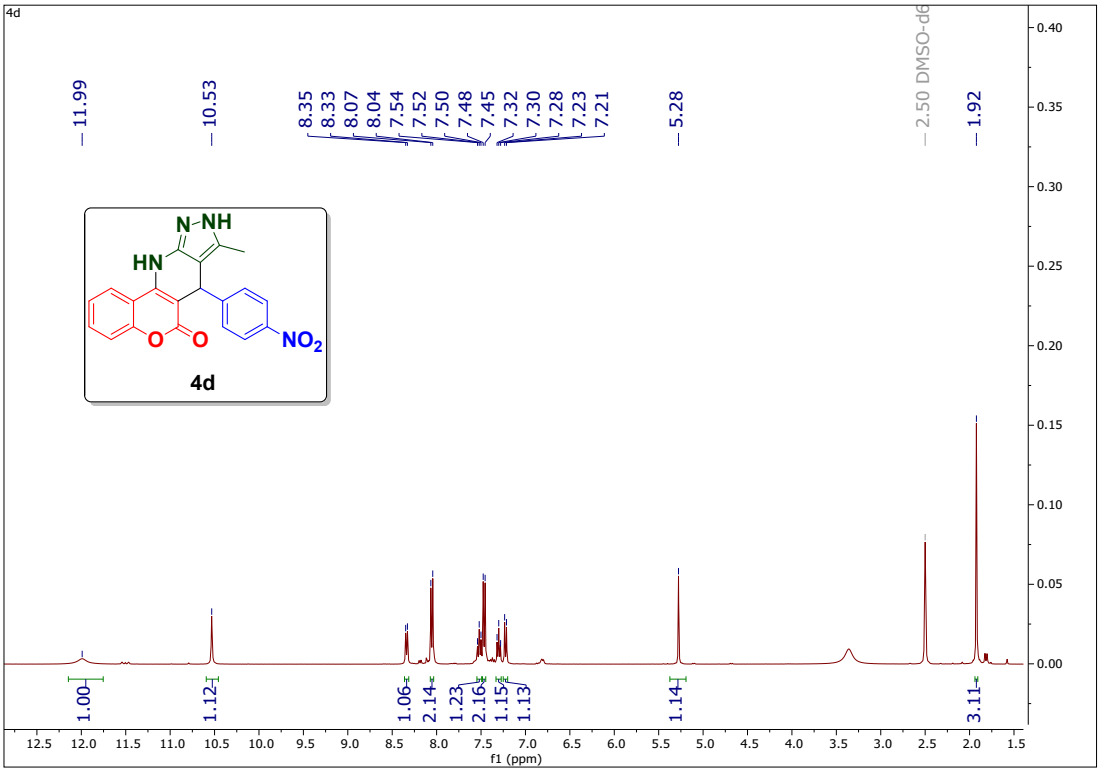
^{1}H NMR spectrum of 4c



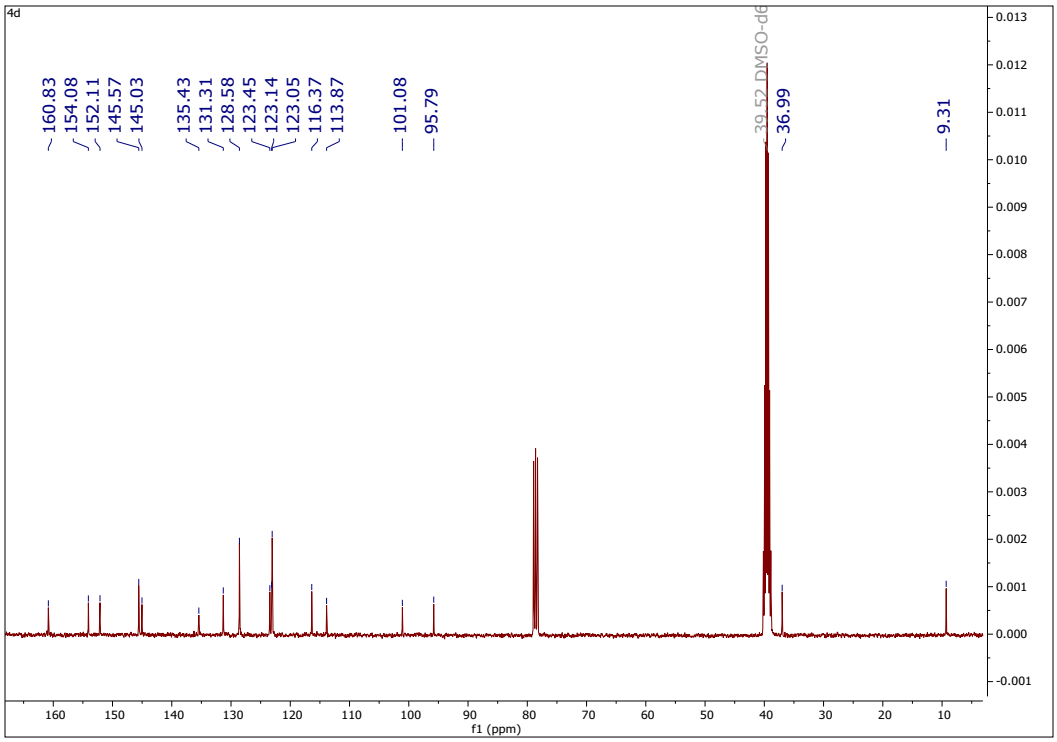
^{13}C NMR Spectrum of 4c



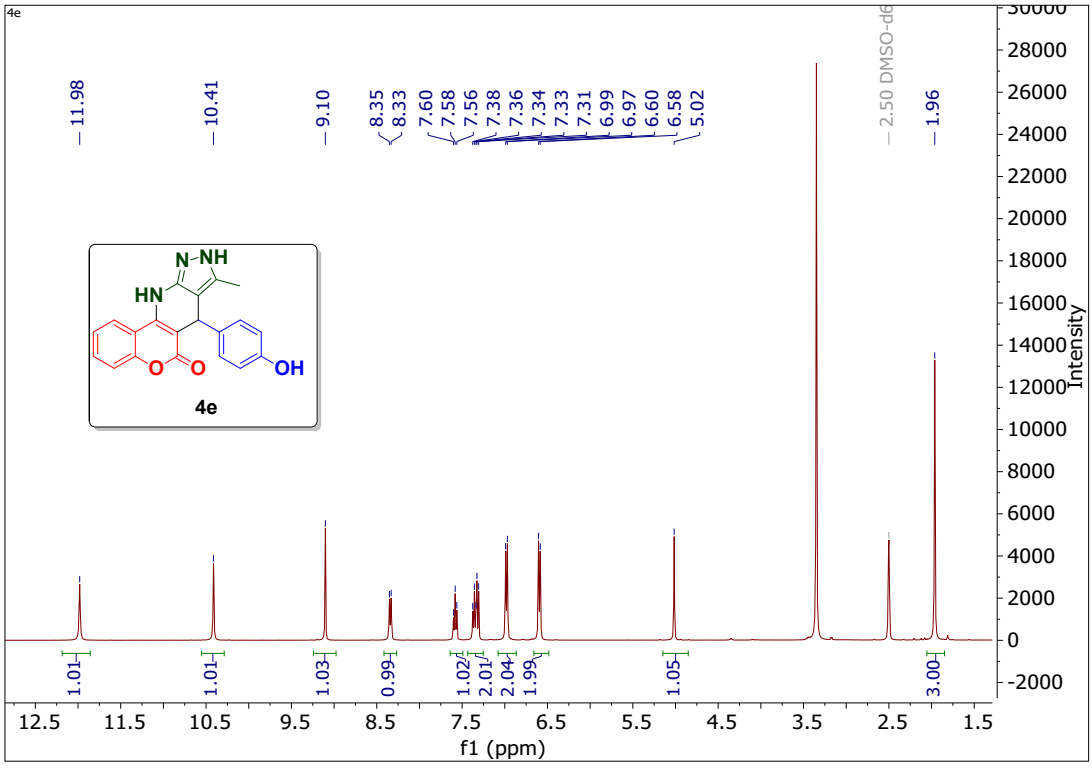
[1]H NMR spectrum of 4d



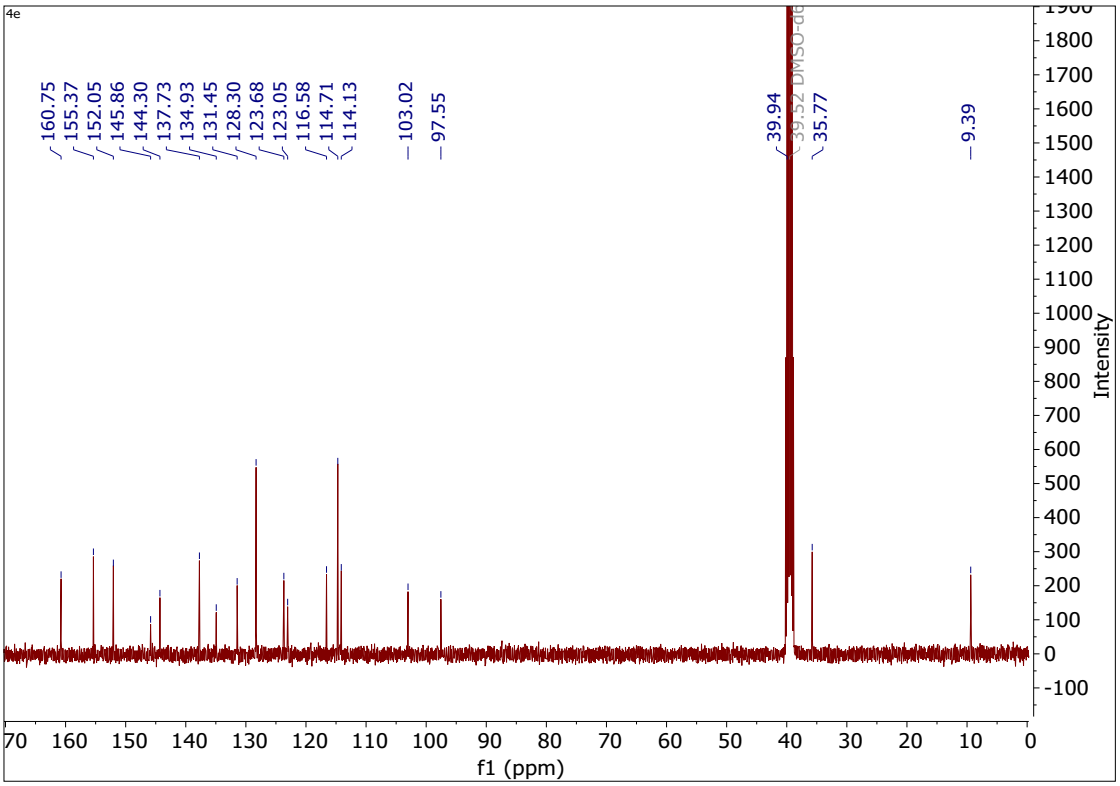
[13]C NMR Spectrum of 4d



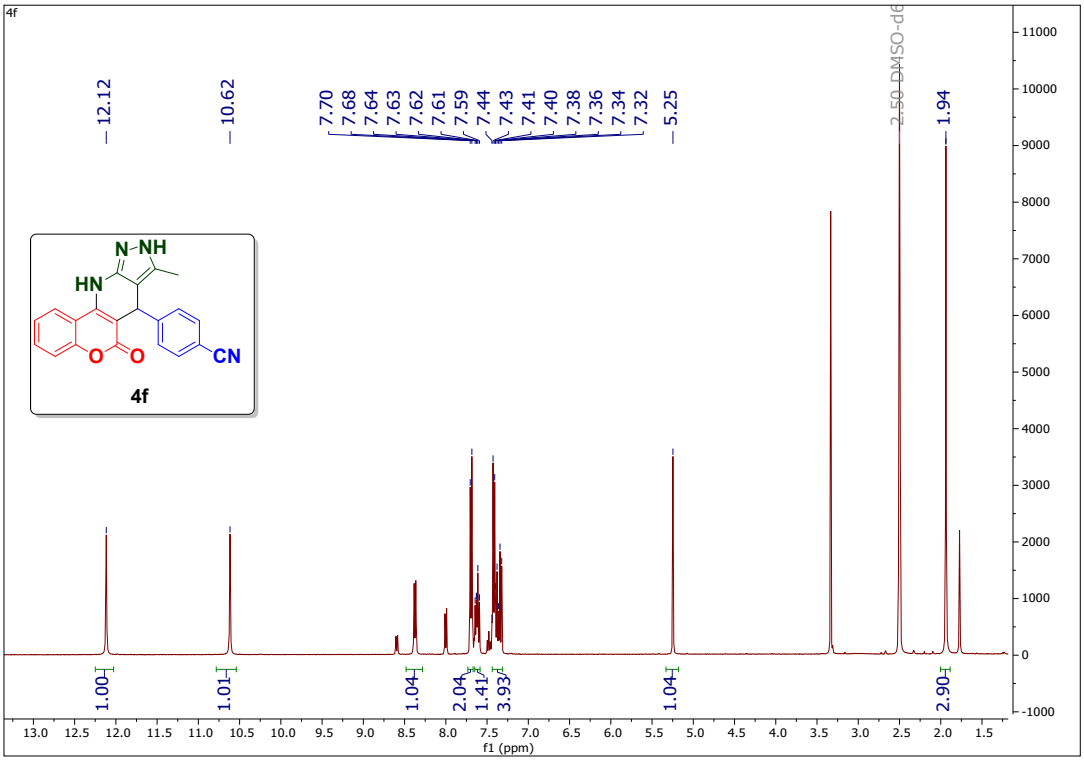
[1]H NMR spectrum of 4e



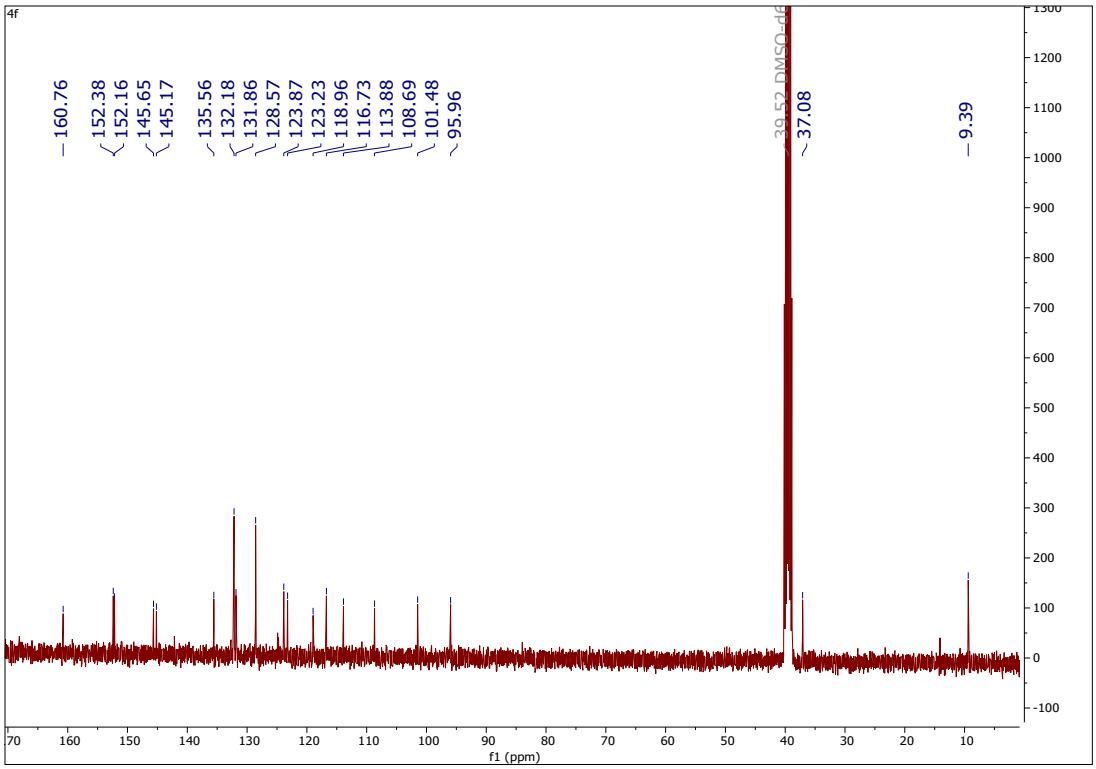
[13]C NMR Spectrum of 4e



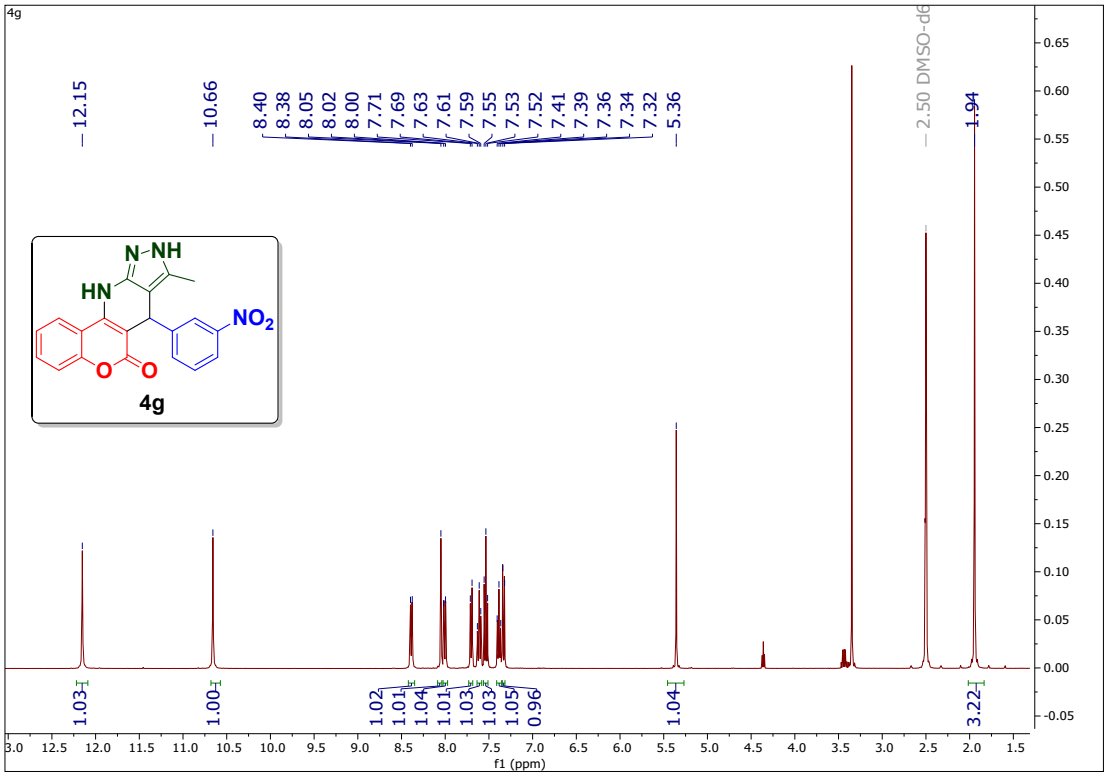
[1]H NMR spectrum of 4f



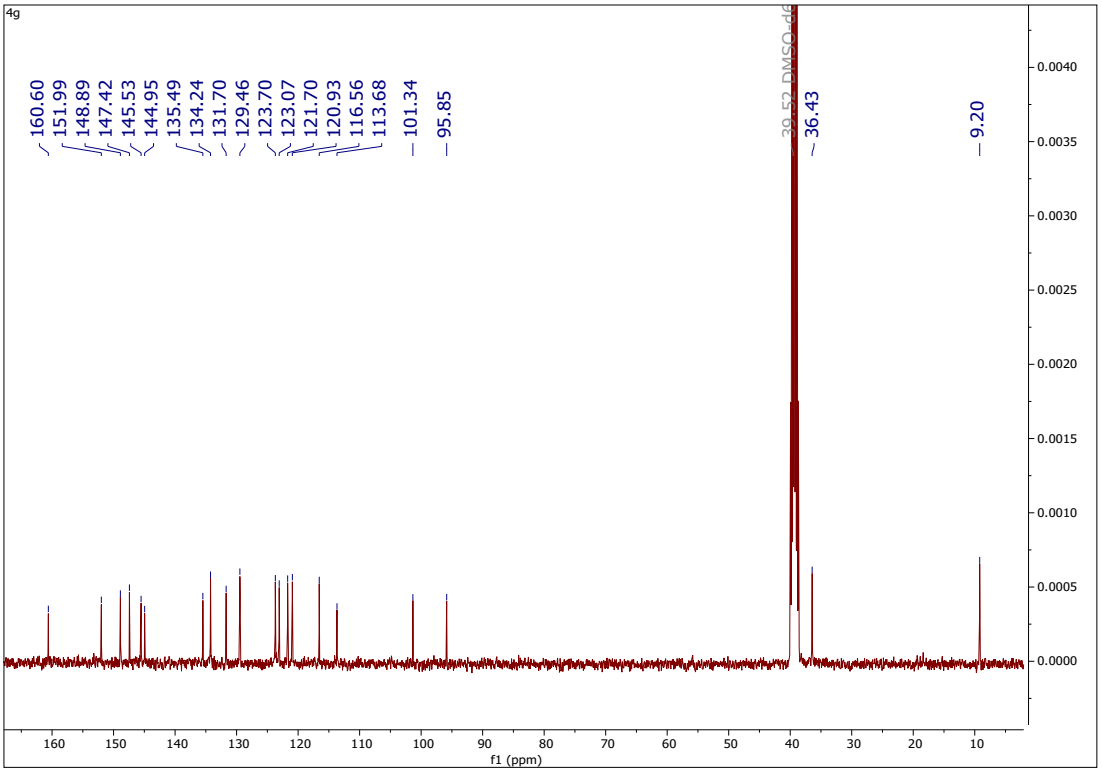
[13]C NMR Spectrum of 4f



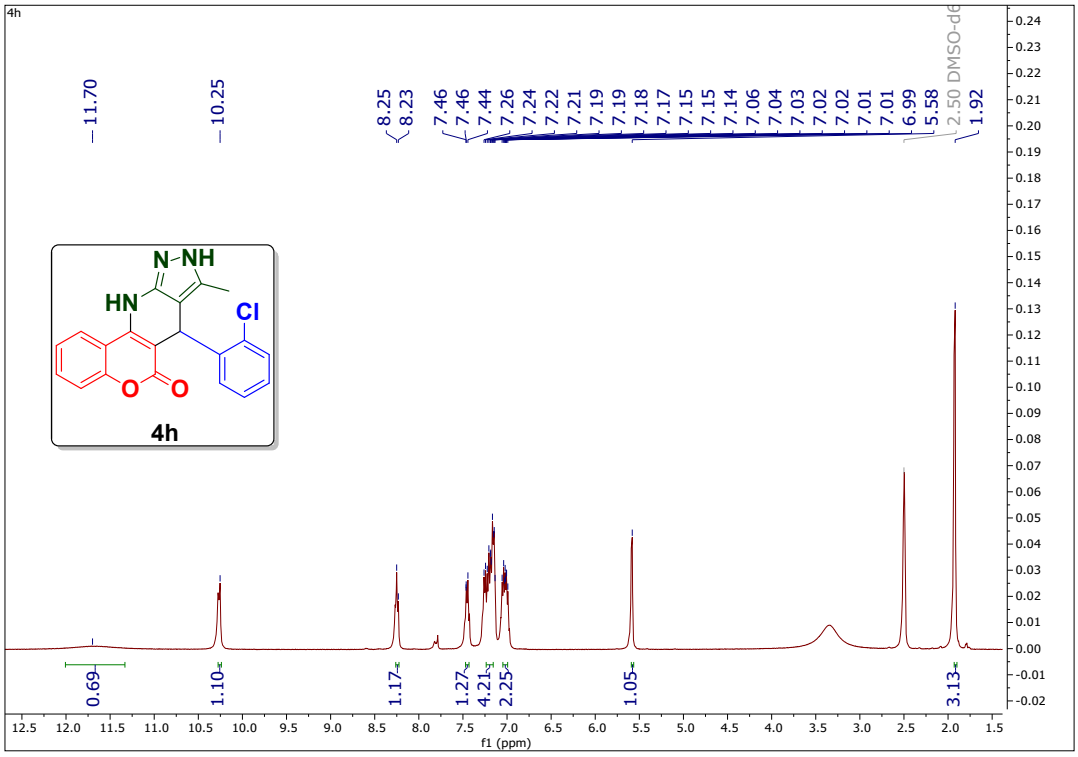
[1]H NMR spectrum of 4g



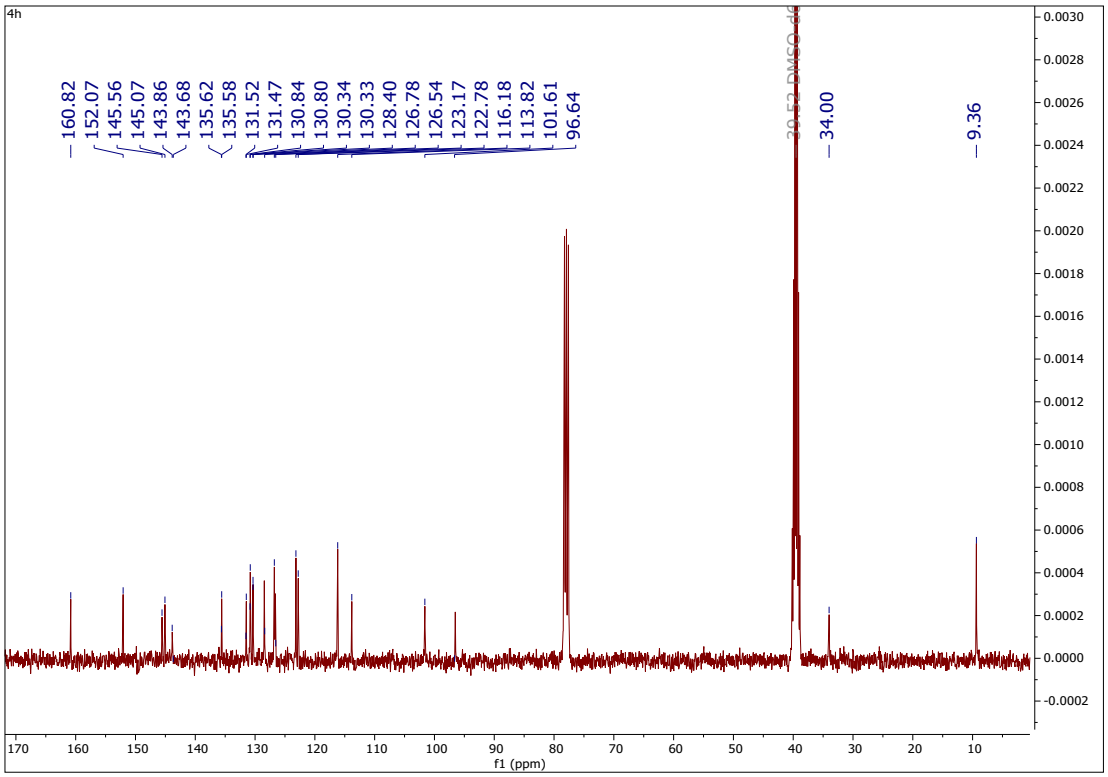
[13]C NMR Spectrum of 4g



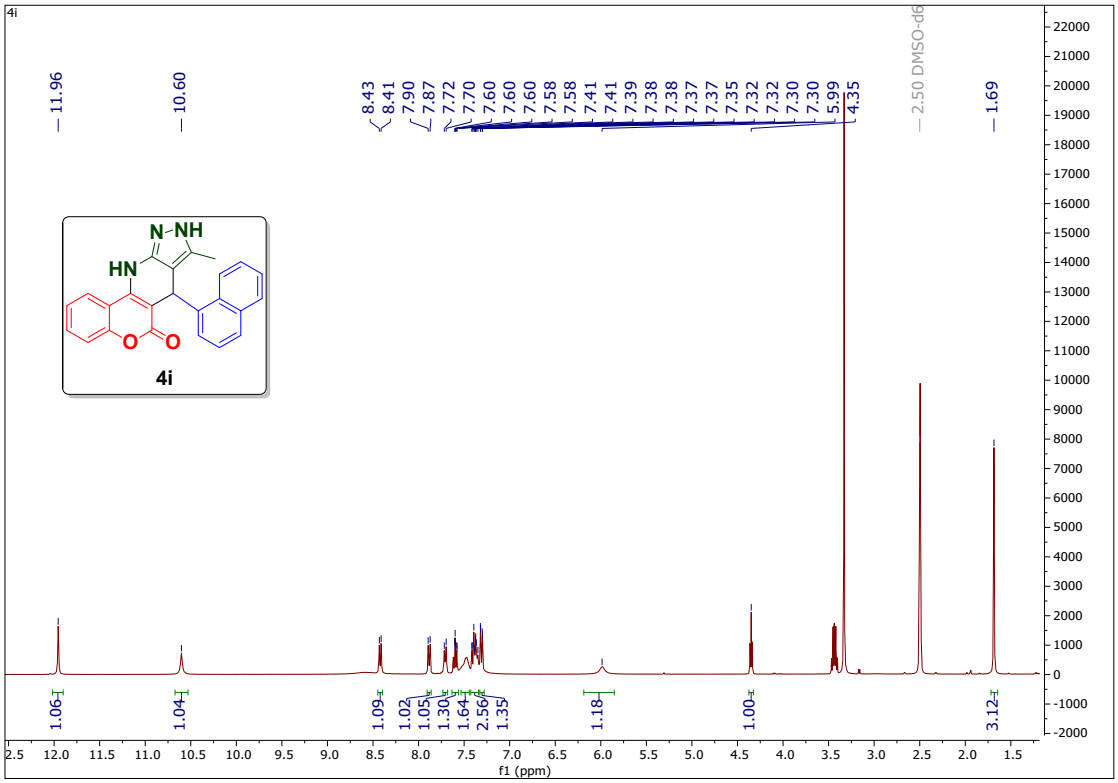
[1]H NMR spectrum of 4h



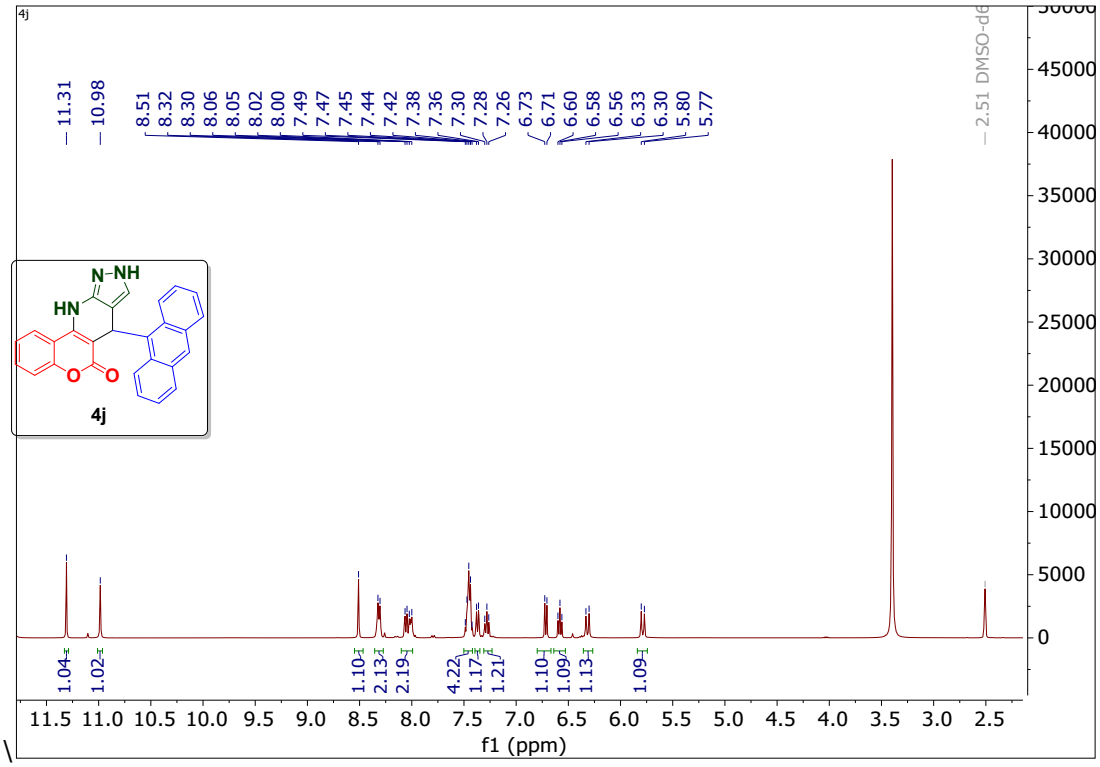
[13]C NMR Spectrum of 4h



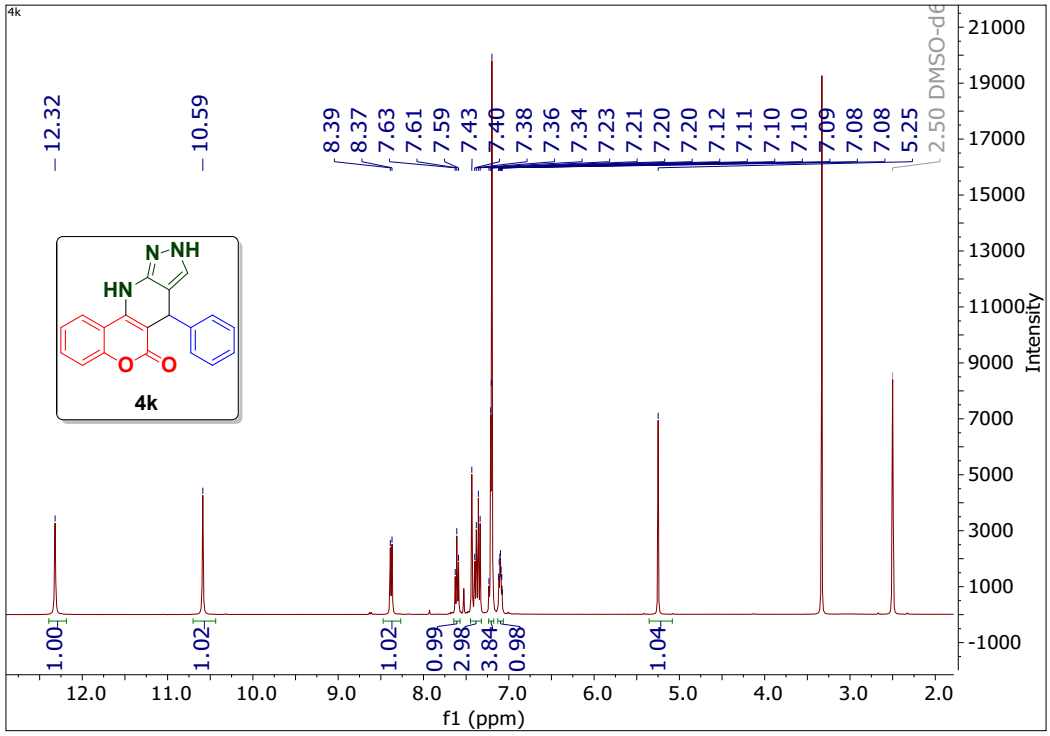
^{1}H NMR Spectrum of 4i



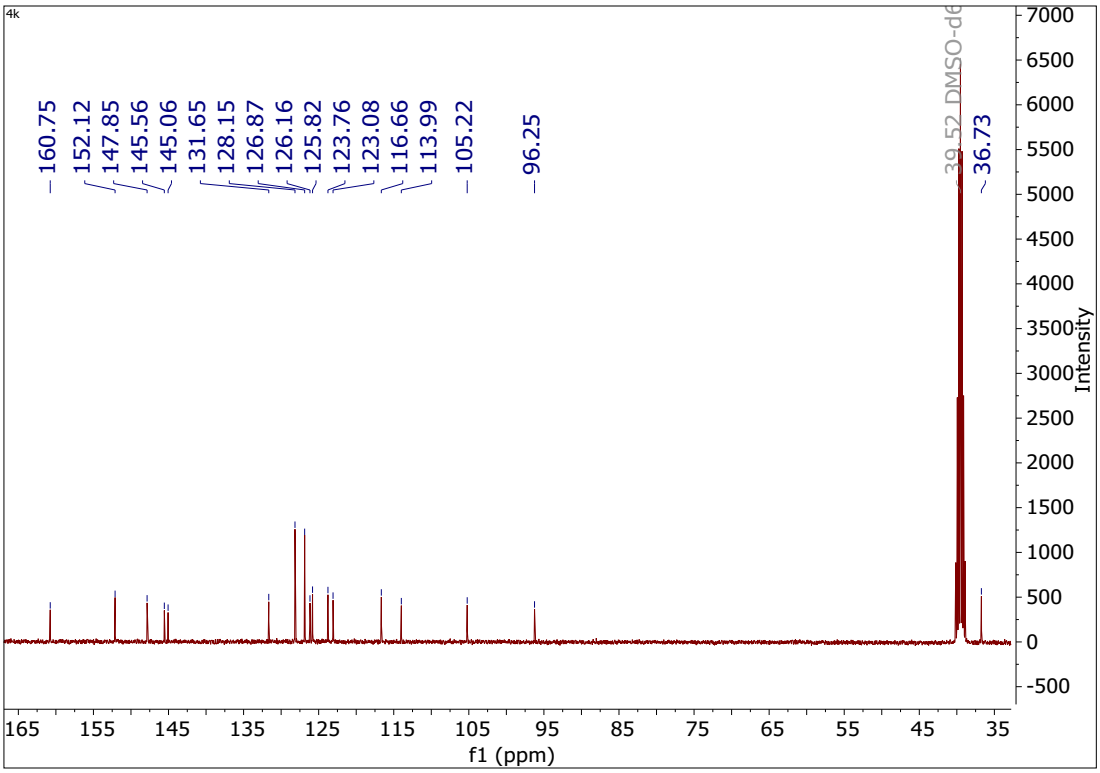
^{1}H NMR Spectrum of 4j



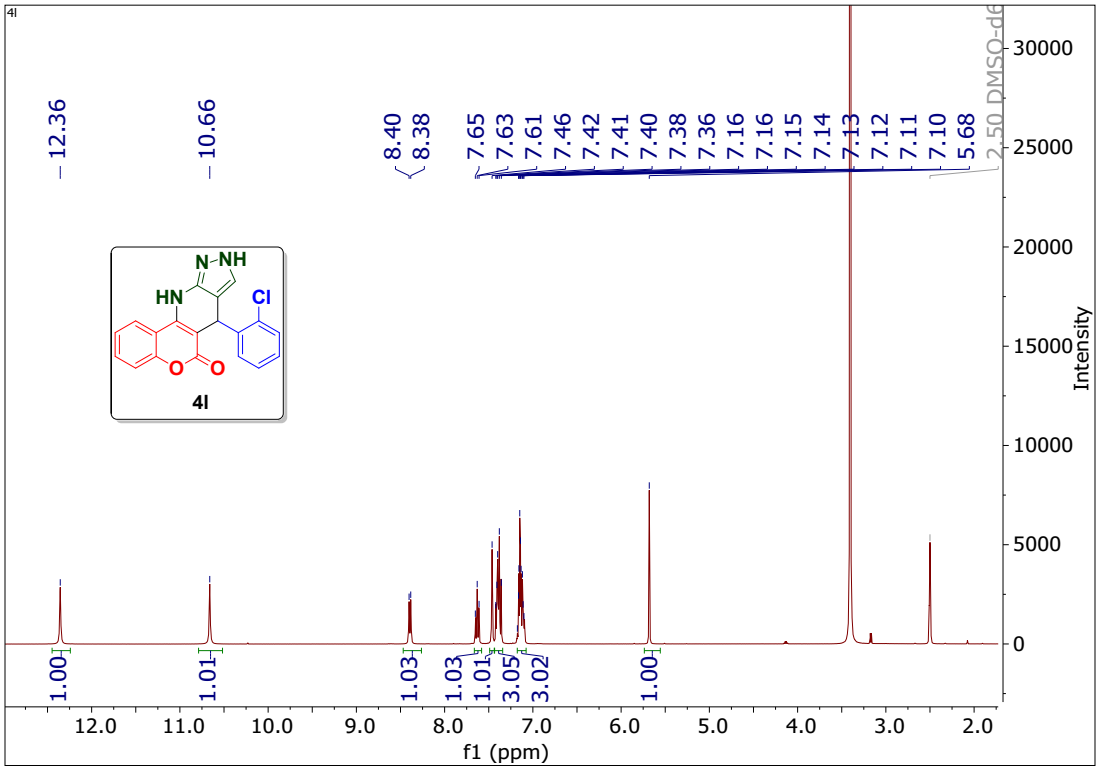
^{1}H NMR Spectrum of 4k



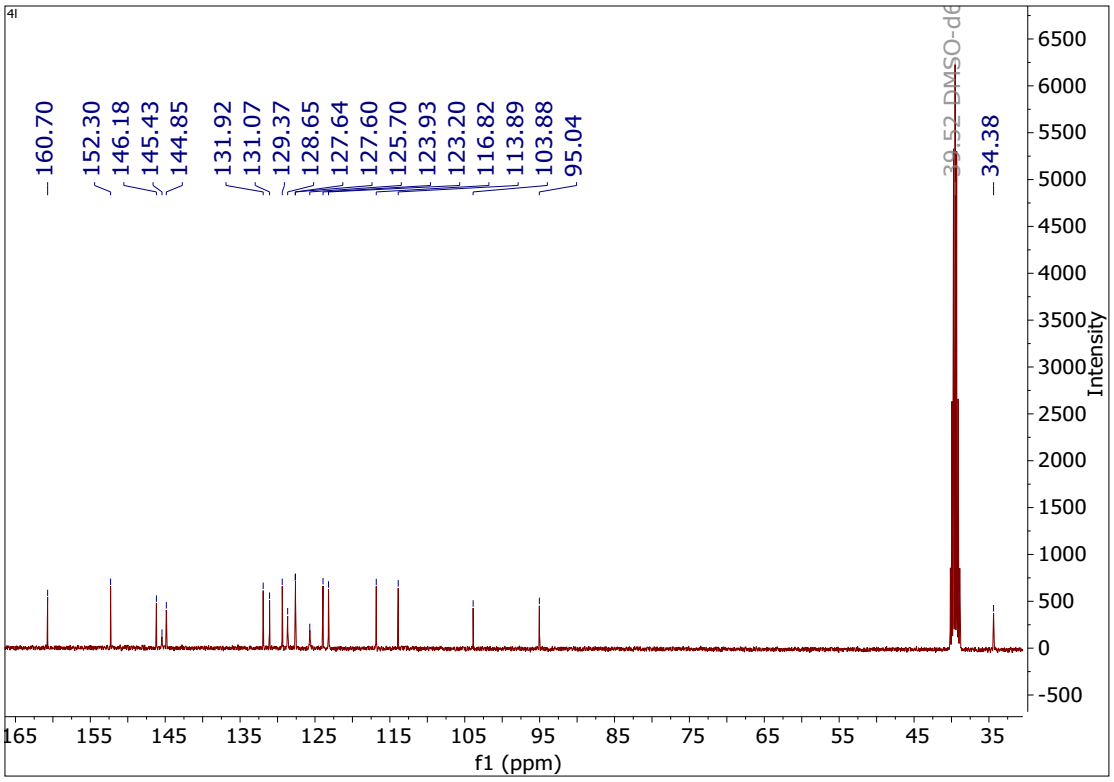
^{13}C NMR Spectrum of 4k



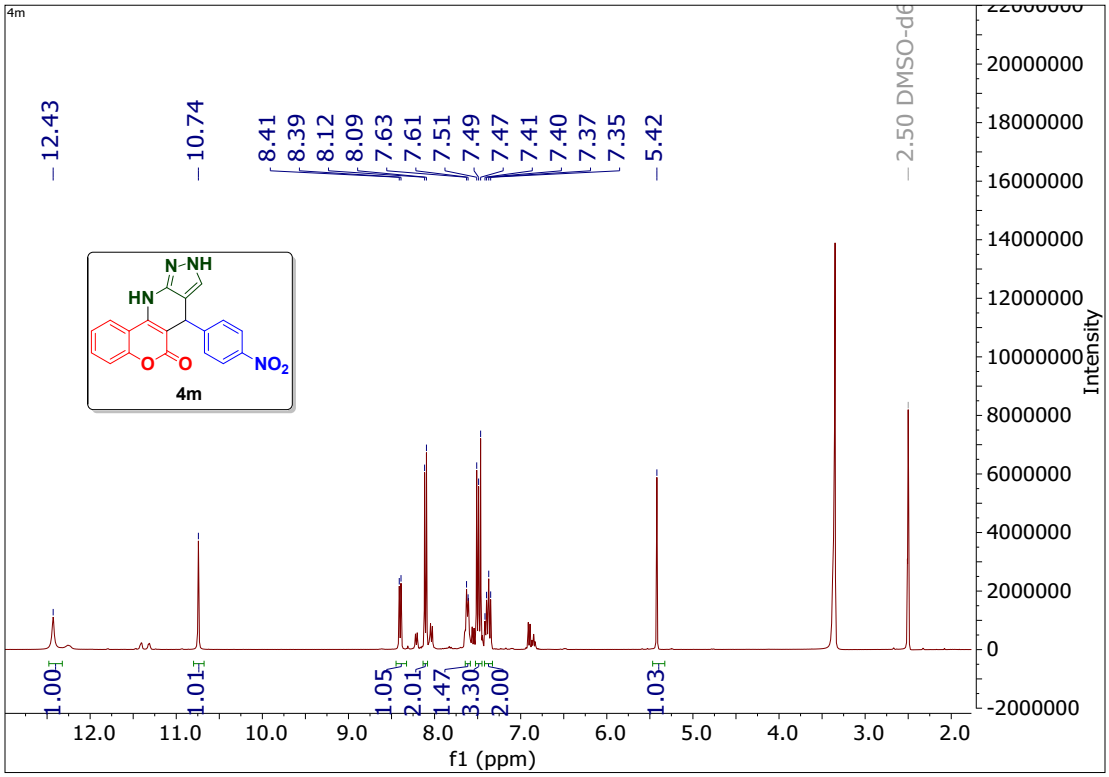
^{1}H NMR Spectrum of 4l



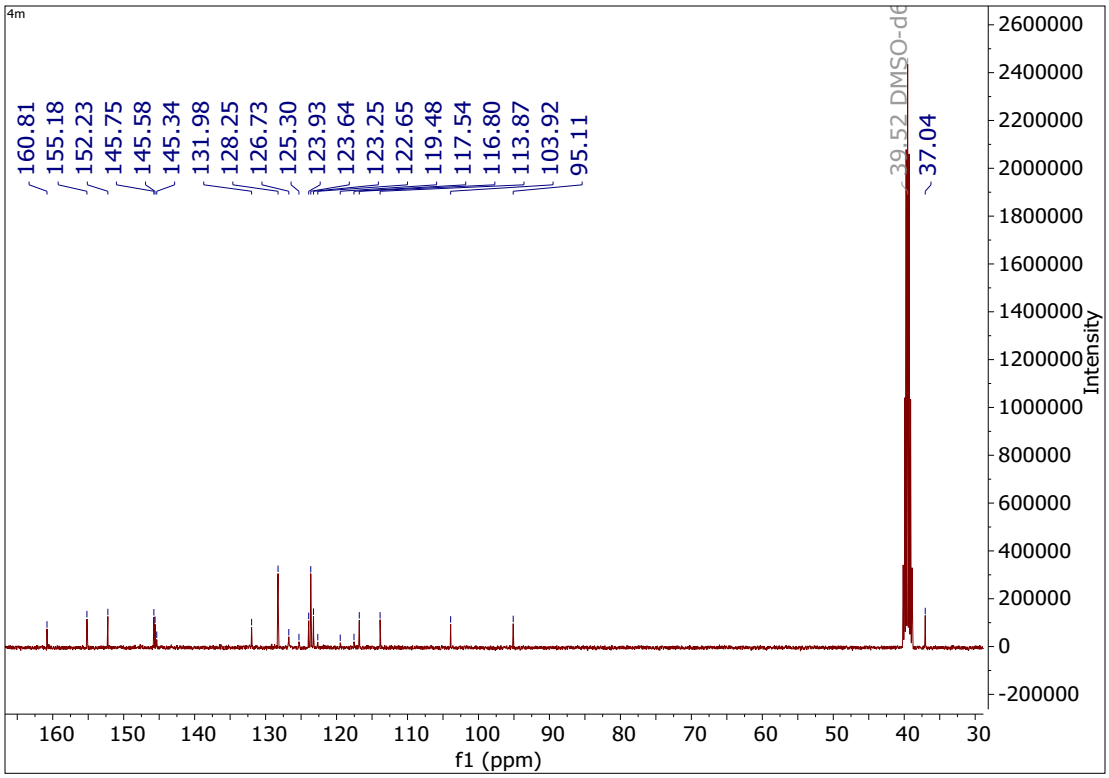
^{13}C NMR Spectrum of 4l



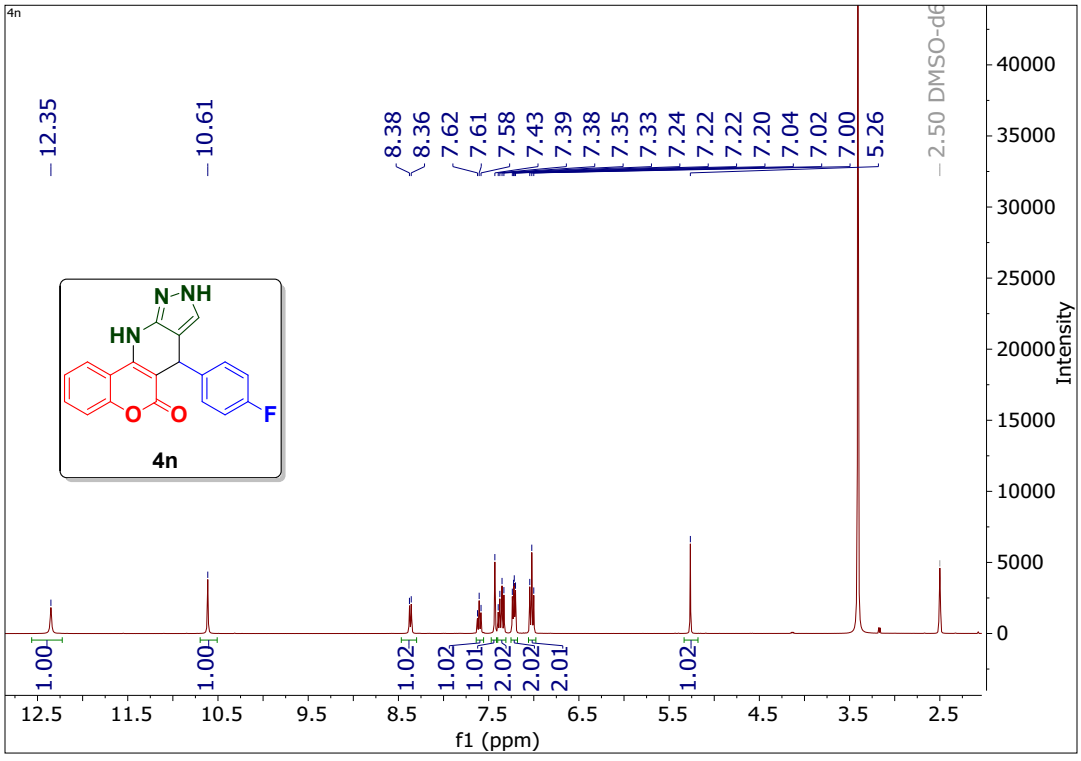
[1]H NMR Spectrum of 4m



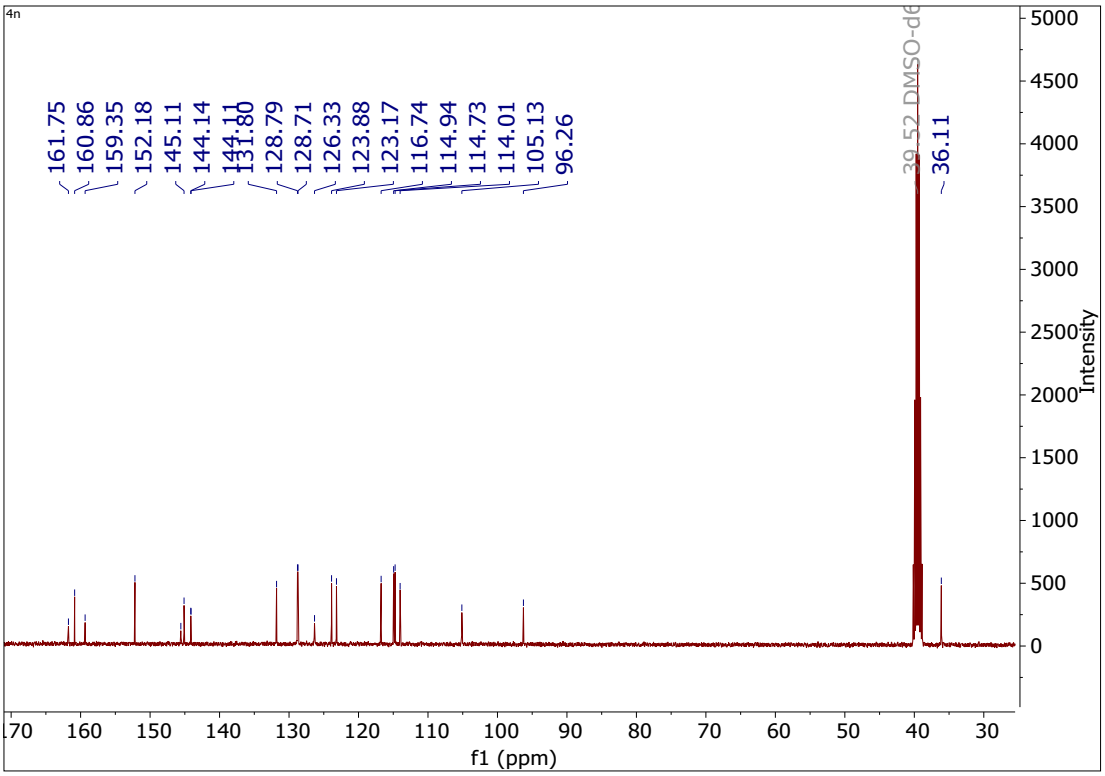
[13]C NMR Spectrum of 4m



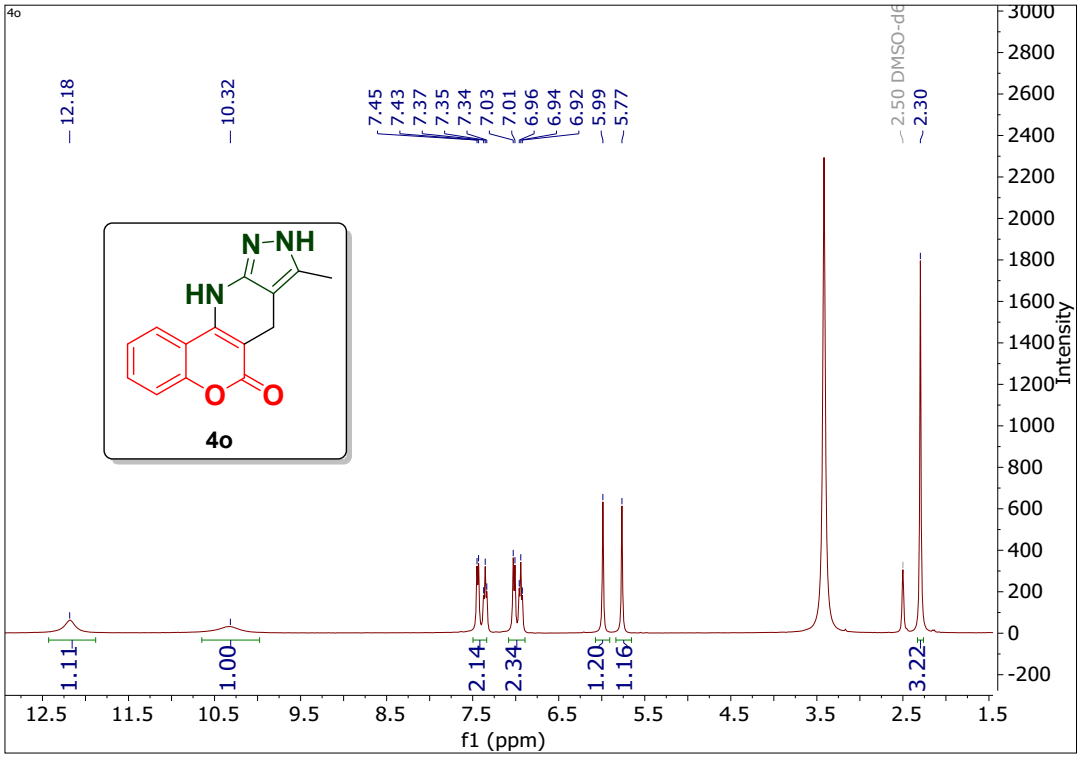
[1]H NMR Spectrum of 4n



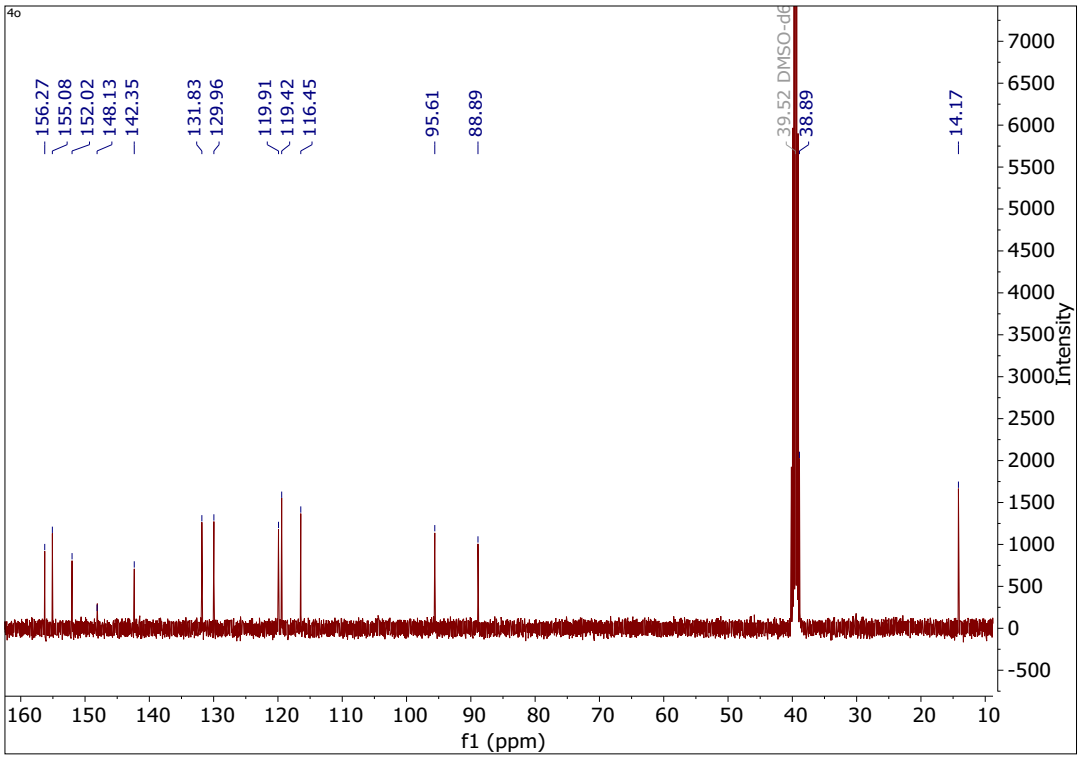
[13]C NMR Spectrum of 4n



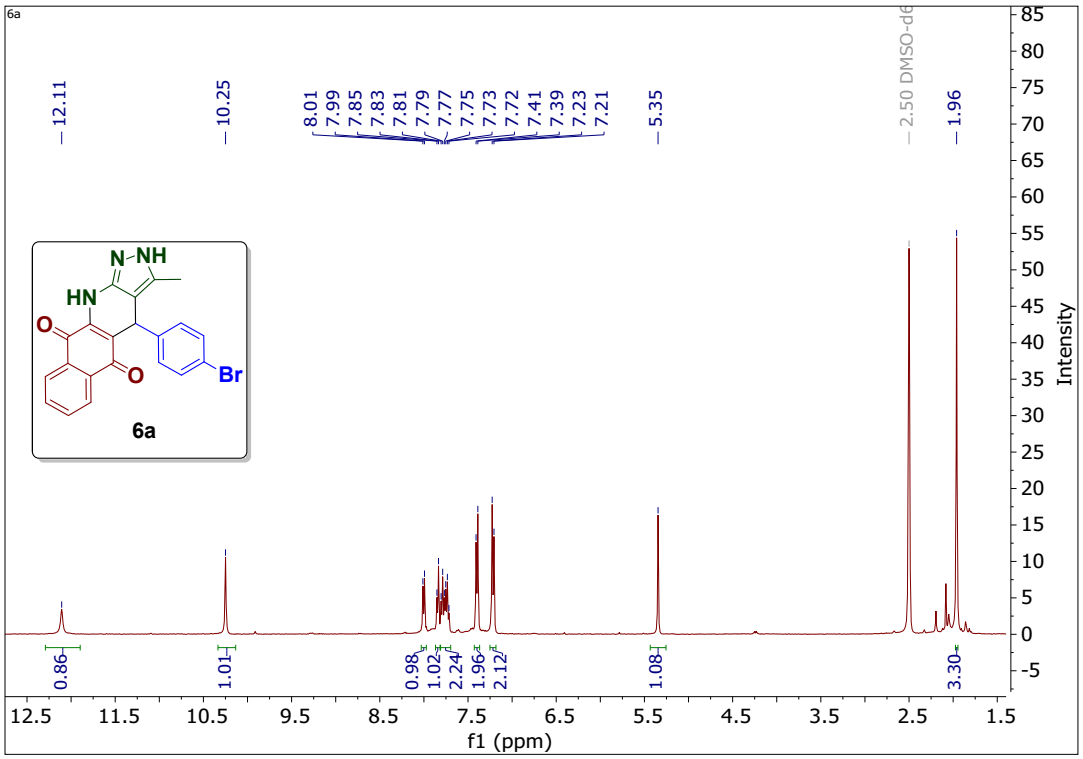
[1]H NMR Spectrum of 4o



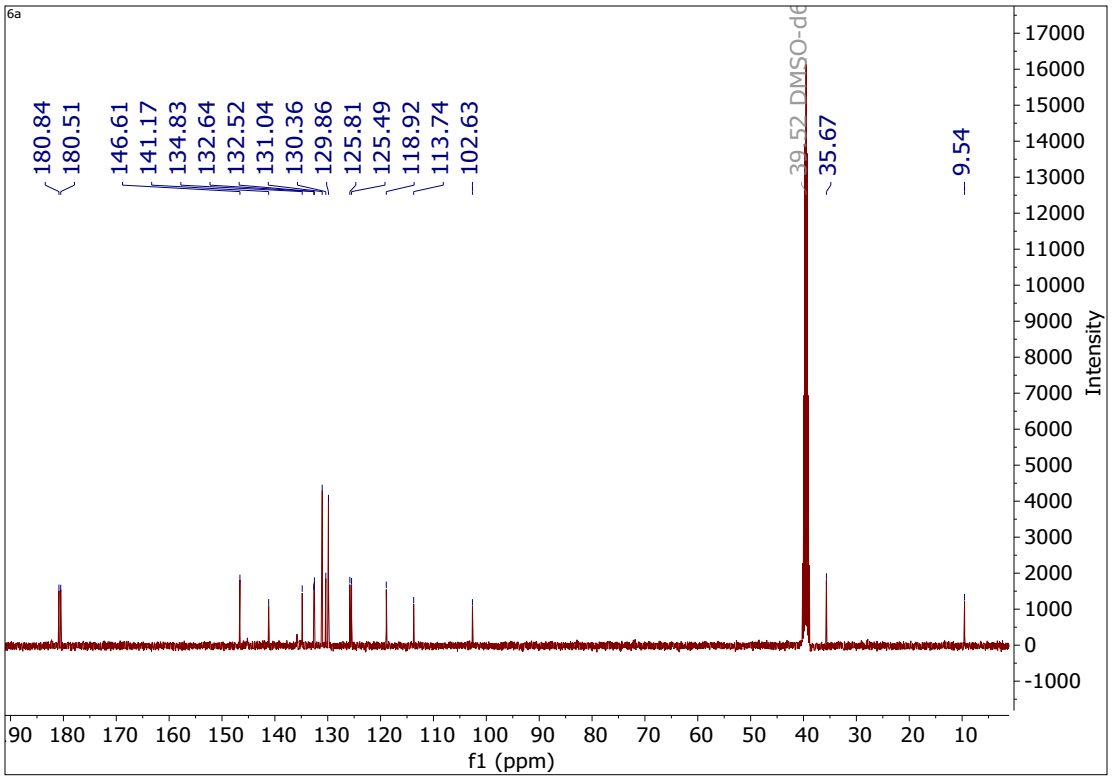
[13]C NMR Spectrum of 4o



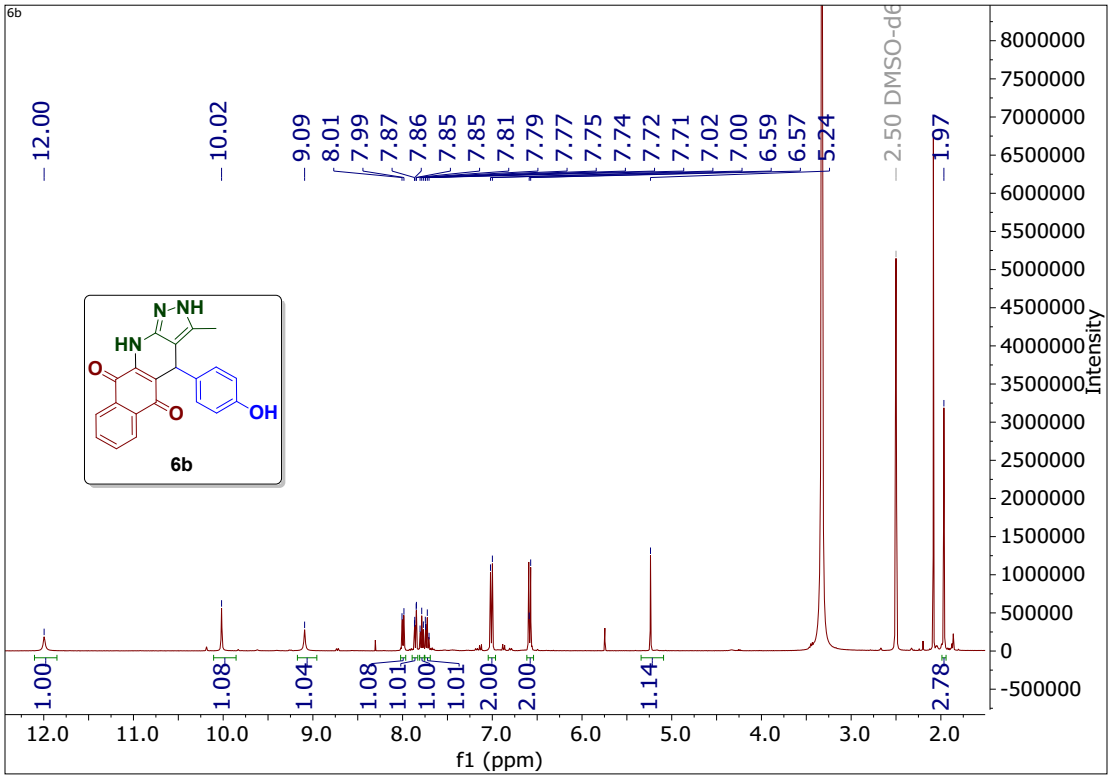
^{1}H NMR Spectrum of 6a



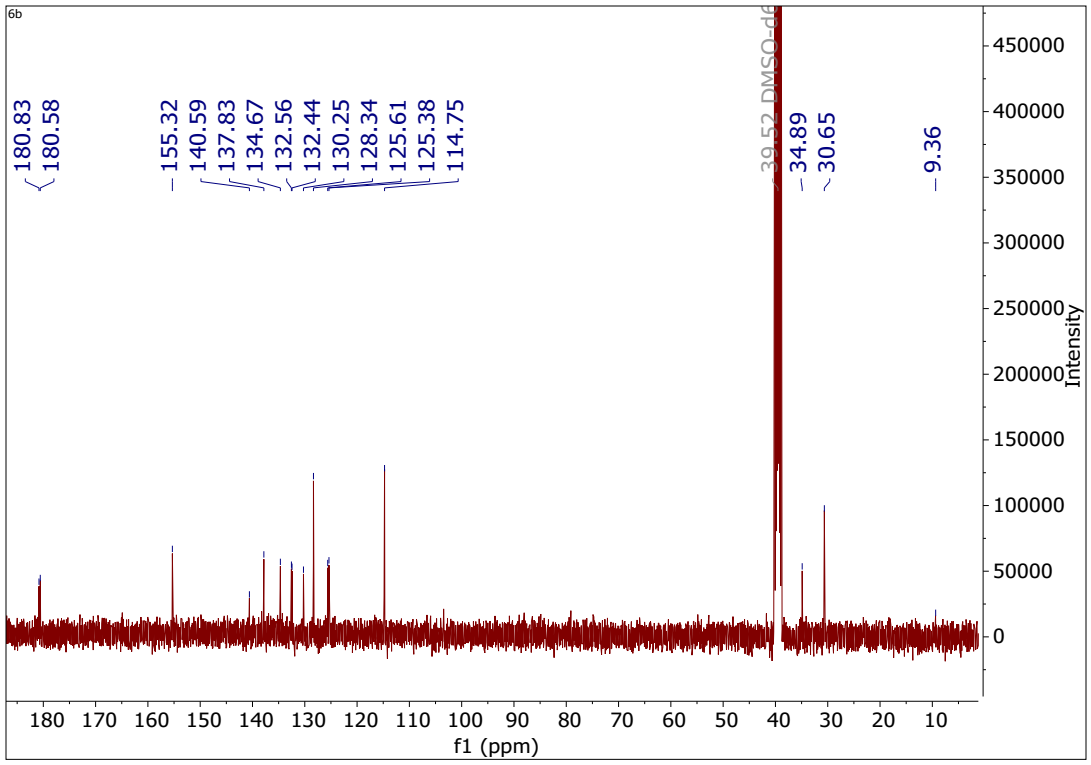
^{13}C NMR Spectrum of 6a



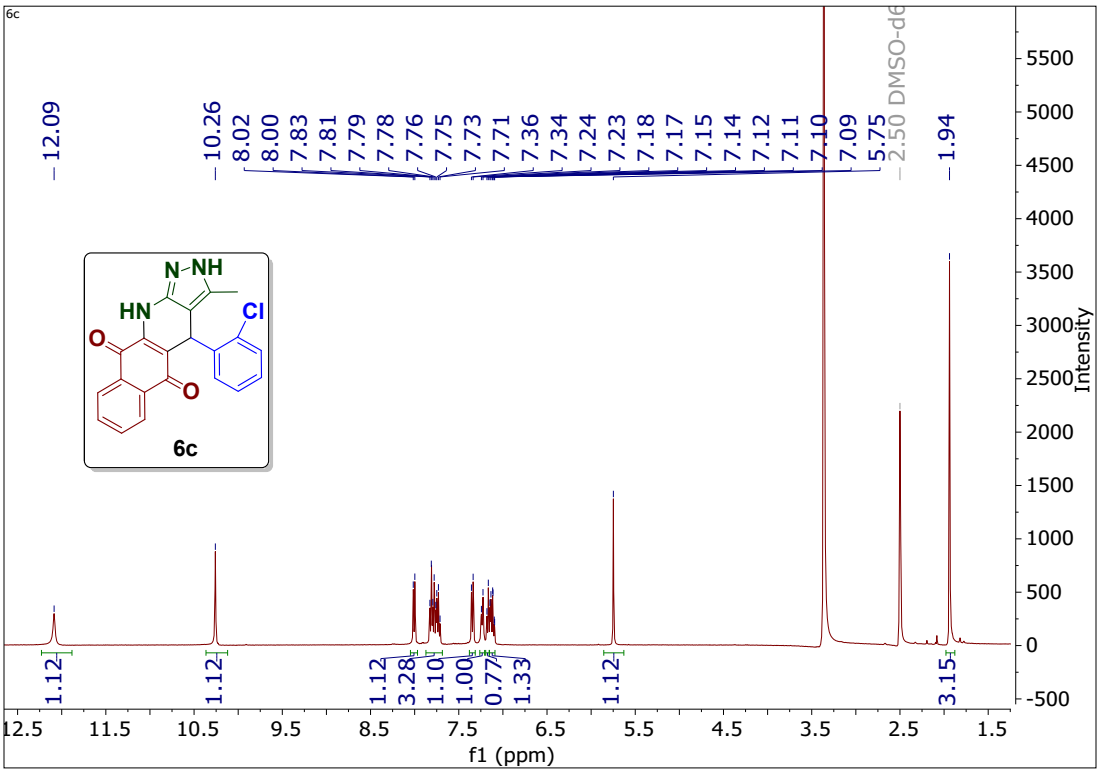
[1]H NMR Spectrum of 6b



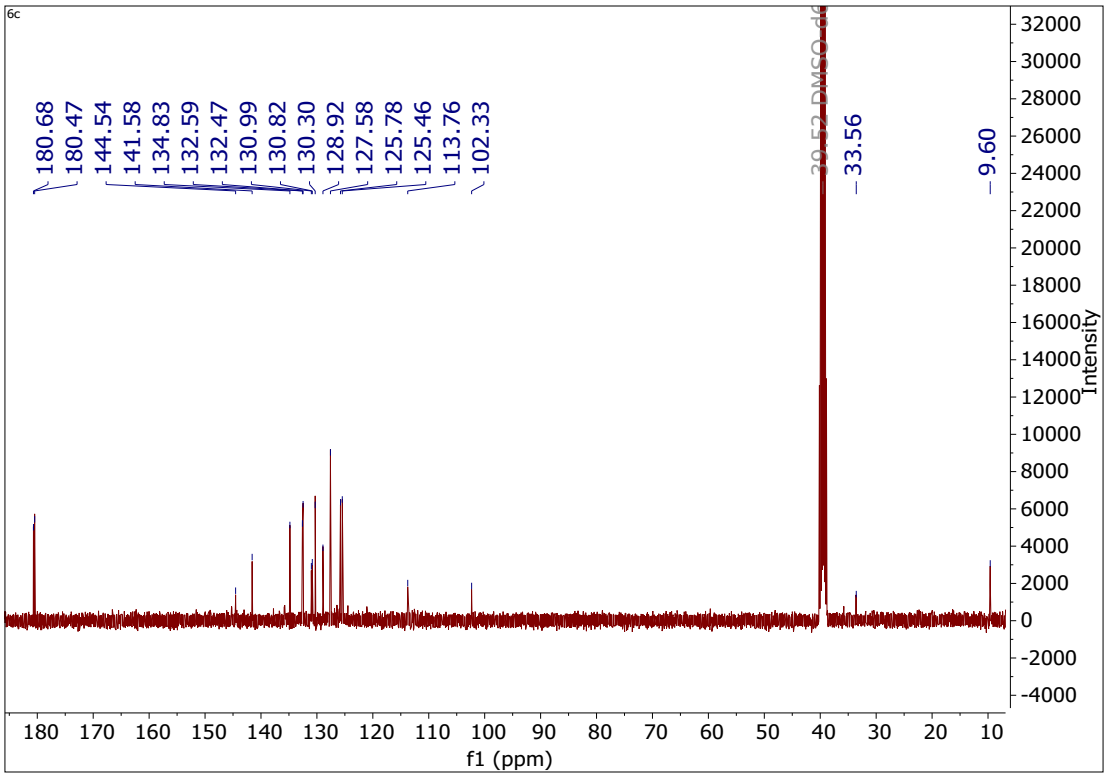
[13]C NMR Spectrum of 6b



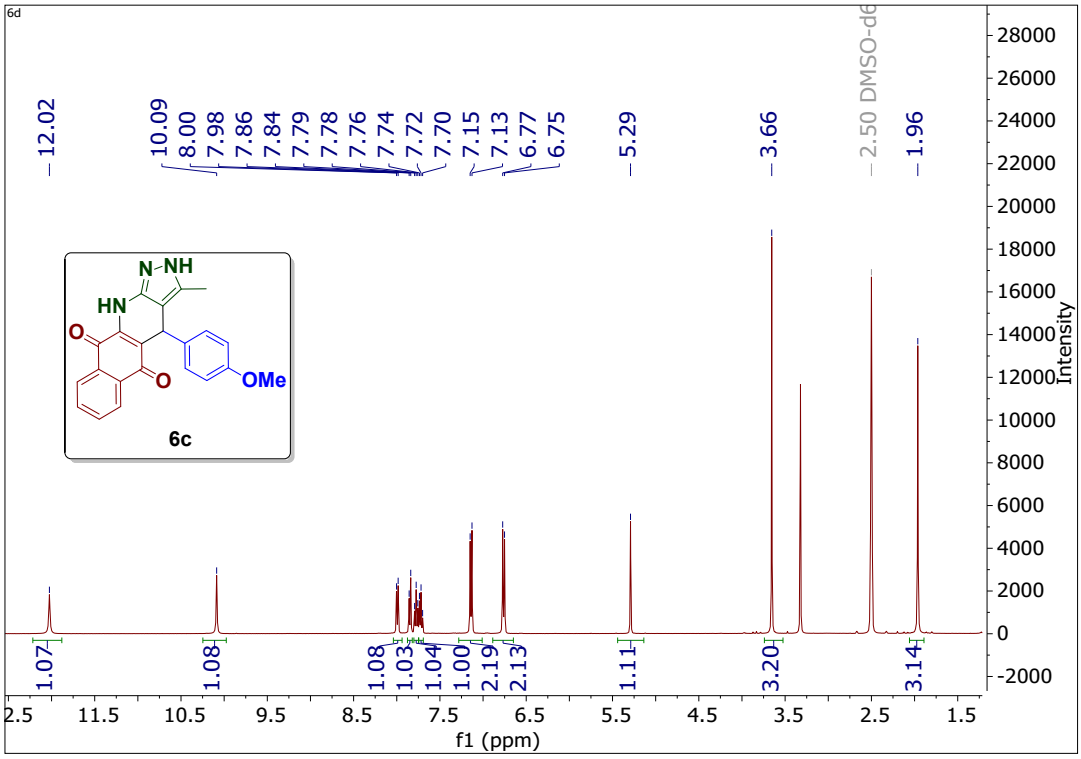
[1]H NMR Spectrum of 6c



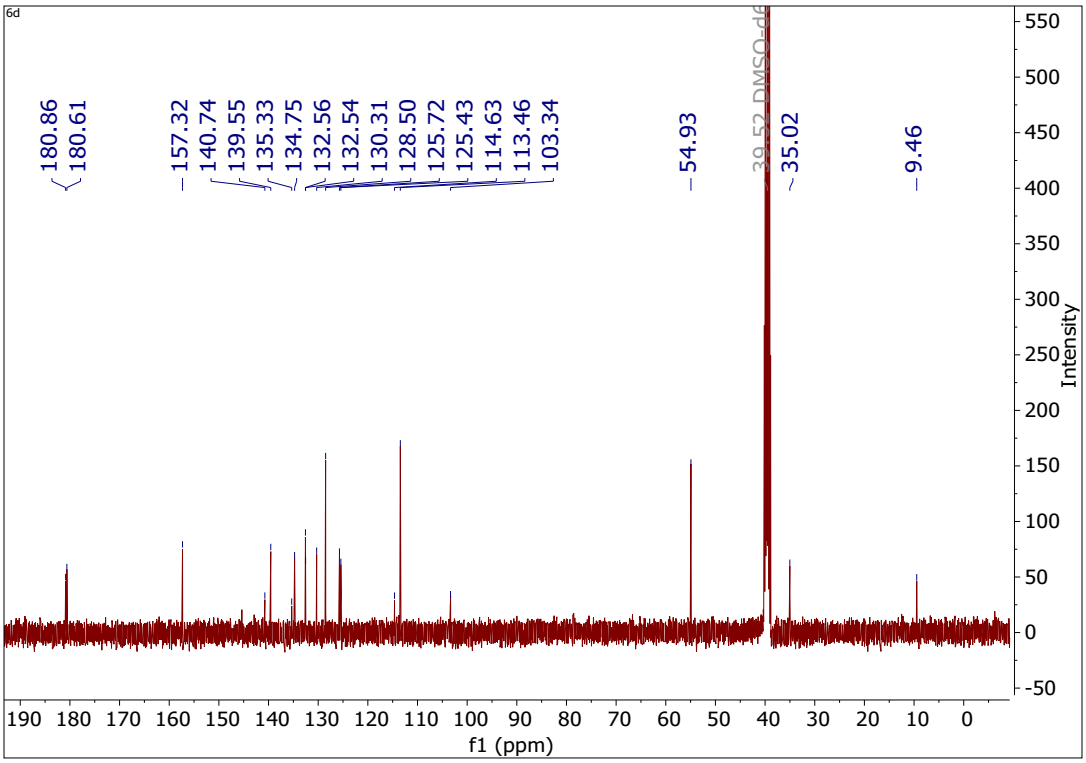
[13]C NMR Spectrum of 6c



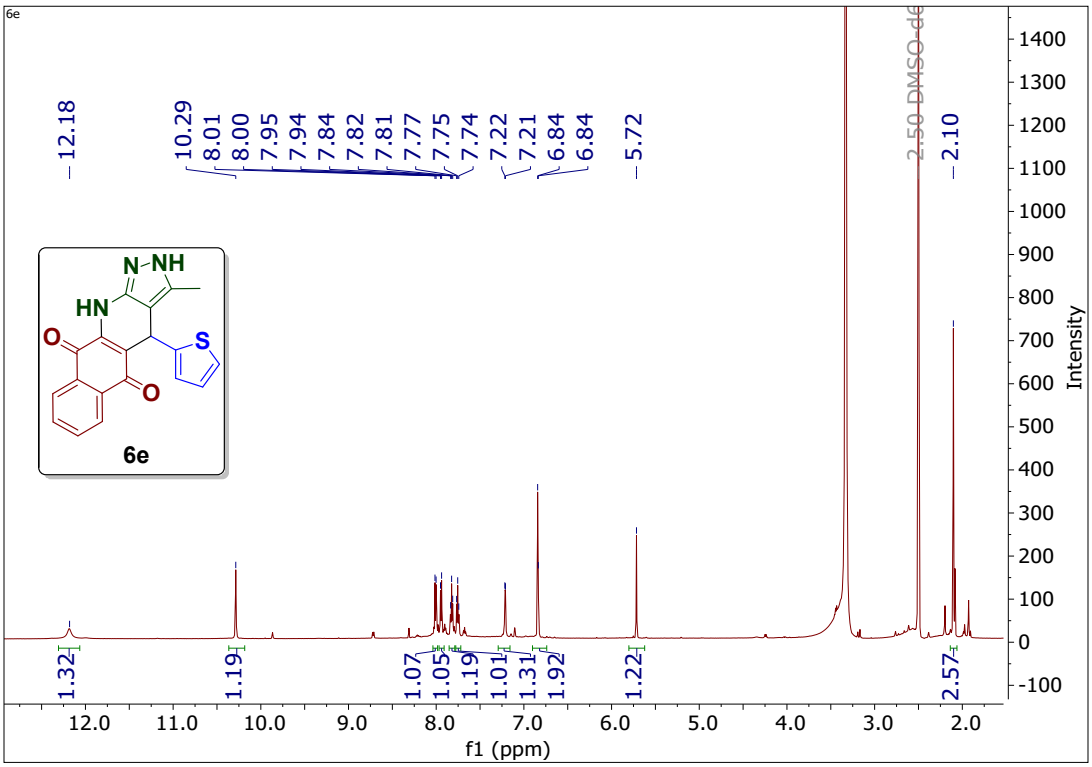
[1]H NMR Spectrum of 6d



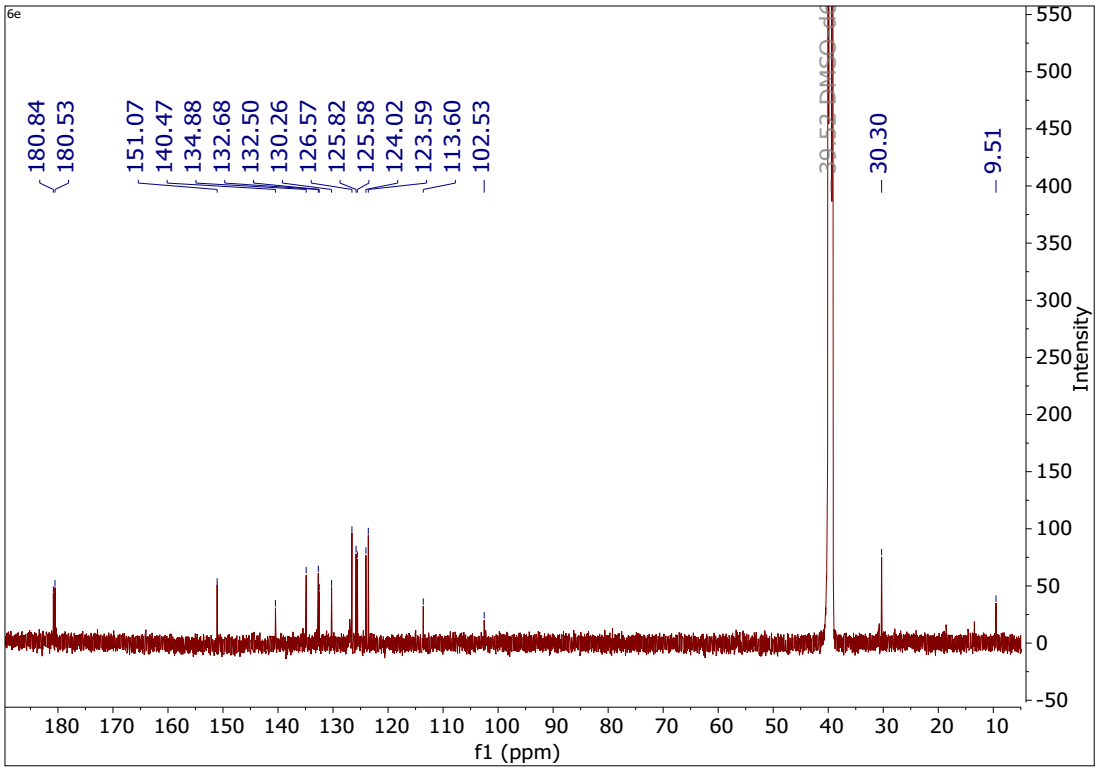
[13]C NMR Spectrum of 6d



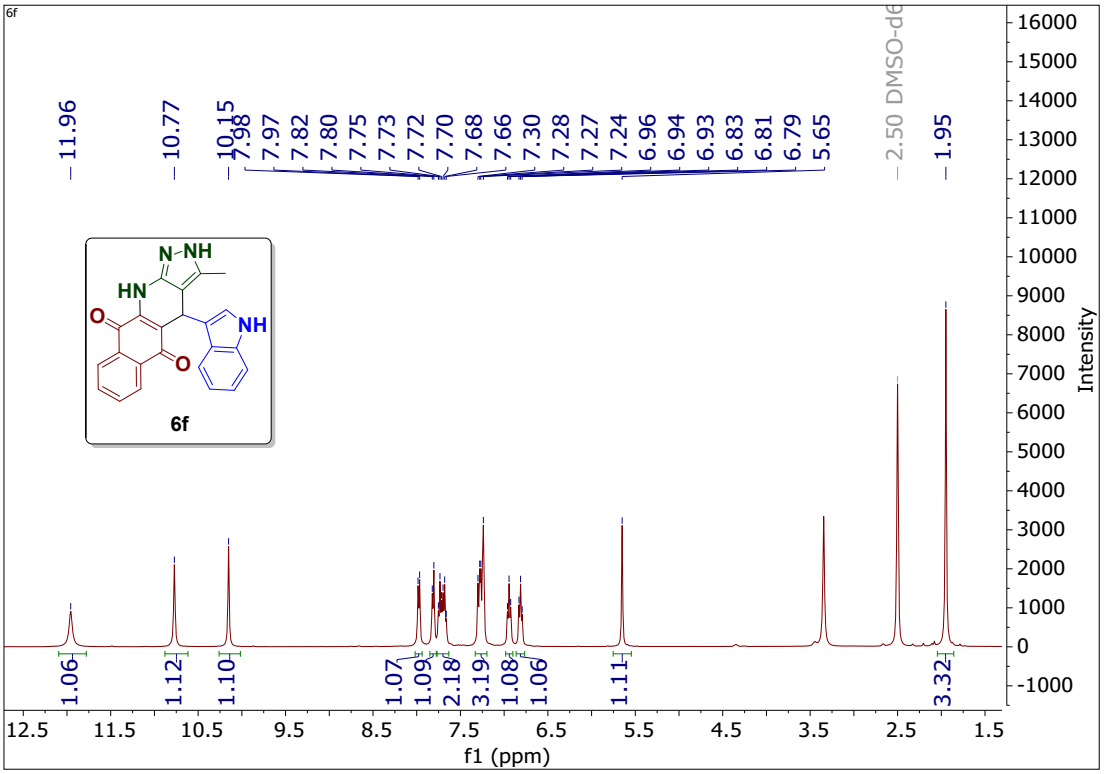
[1]H NMR Spectrum of 6e



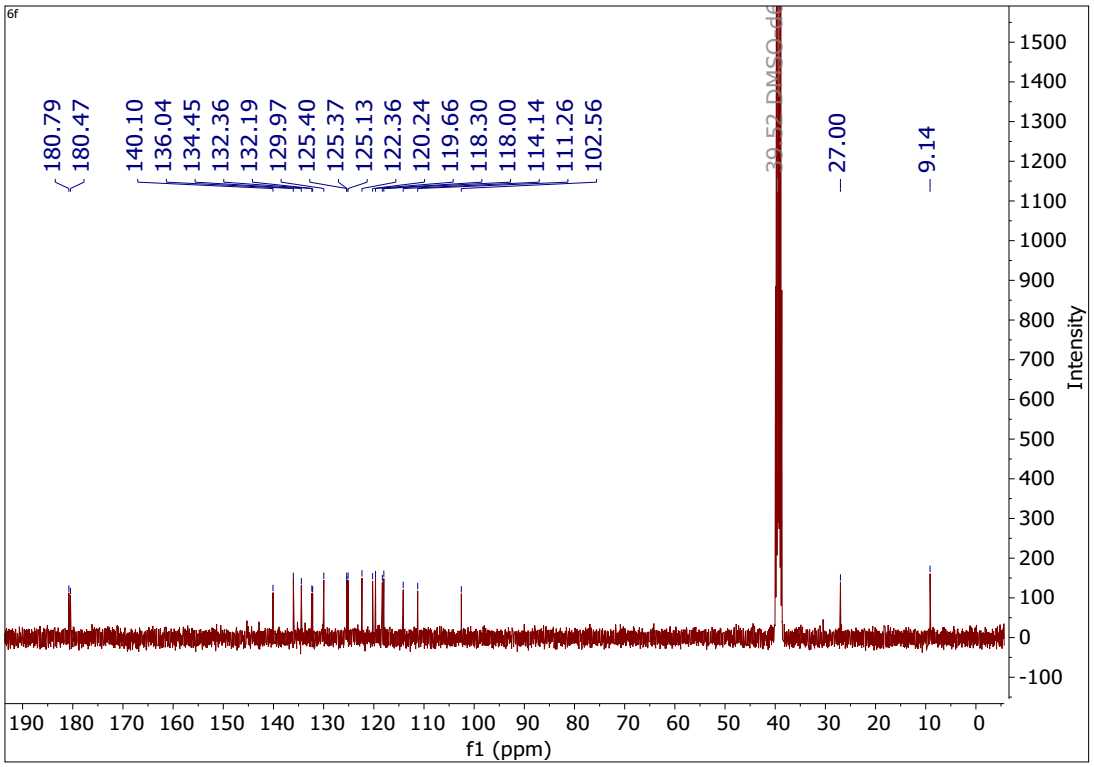
[13]C NMR Spectrum of 6e



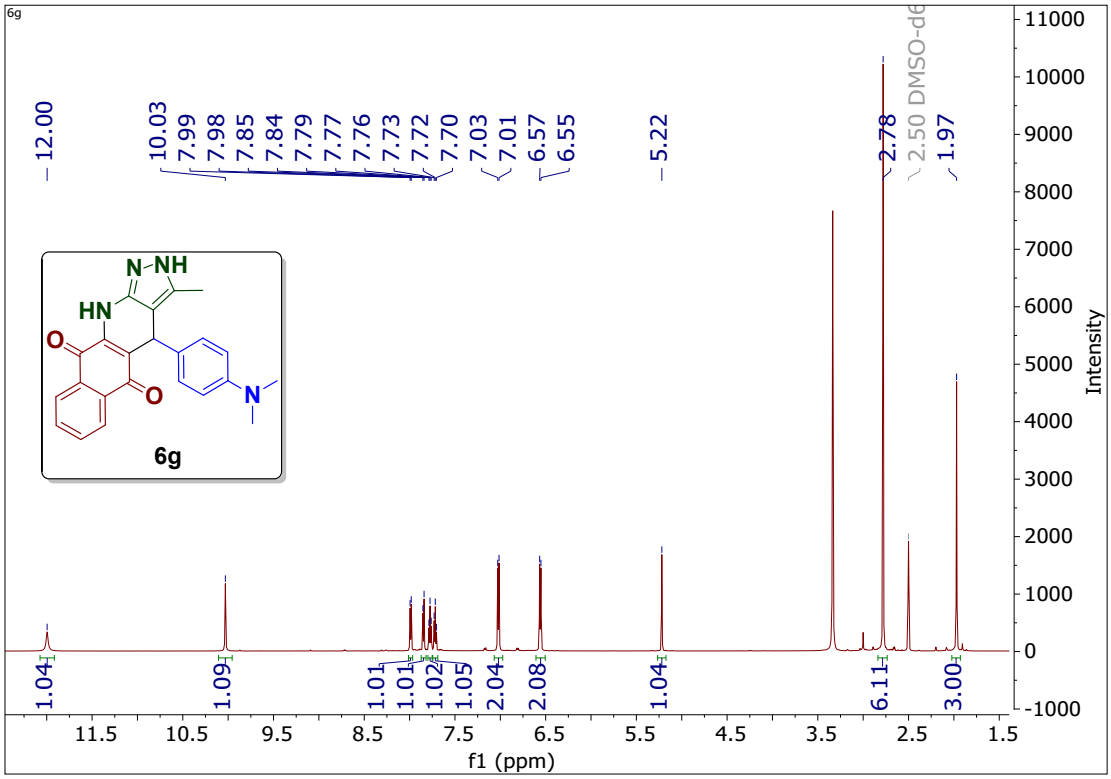
[1]H NMR Spectrum of 6f



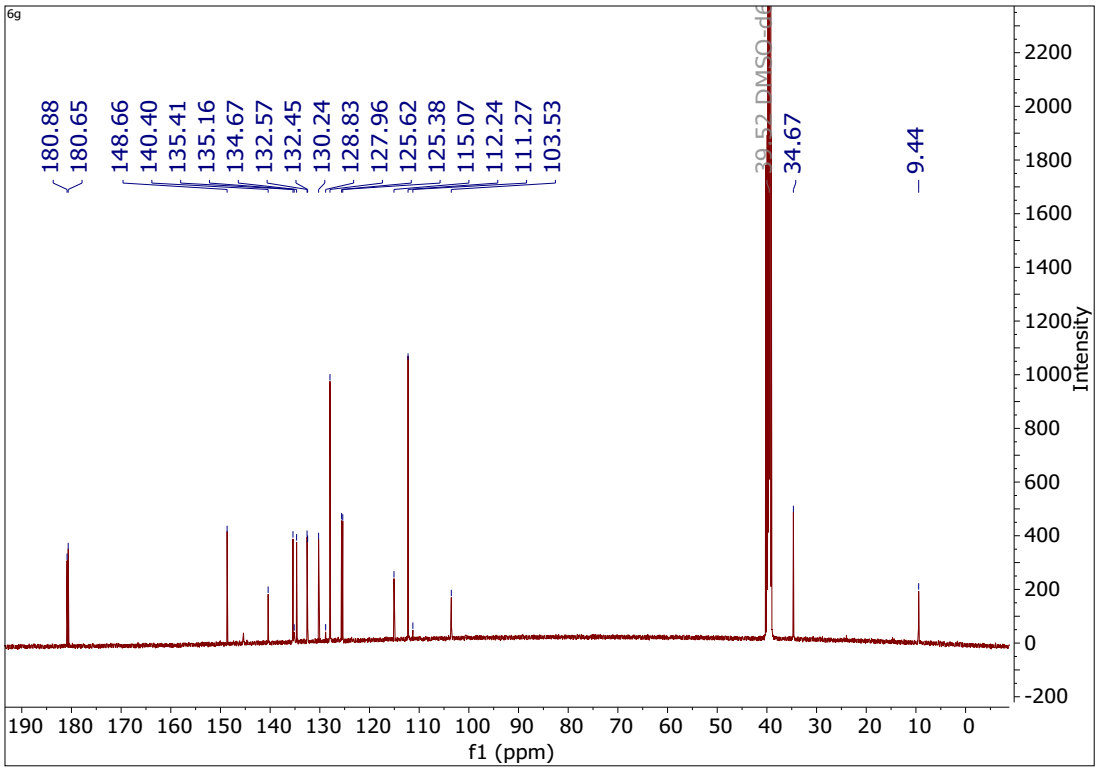
[13]C NMR Spectrum of 6f



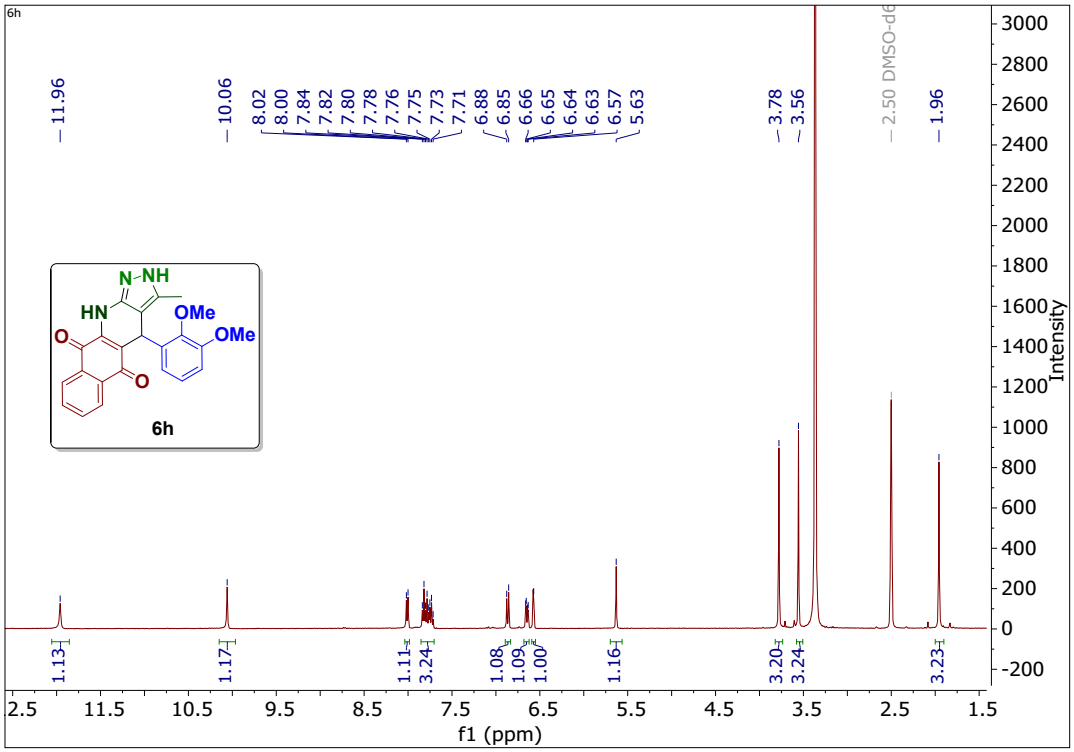
[1]H NMR Spectrum of 6g



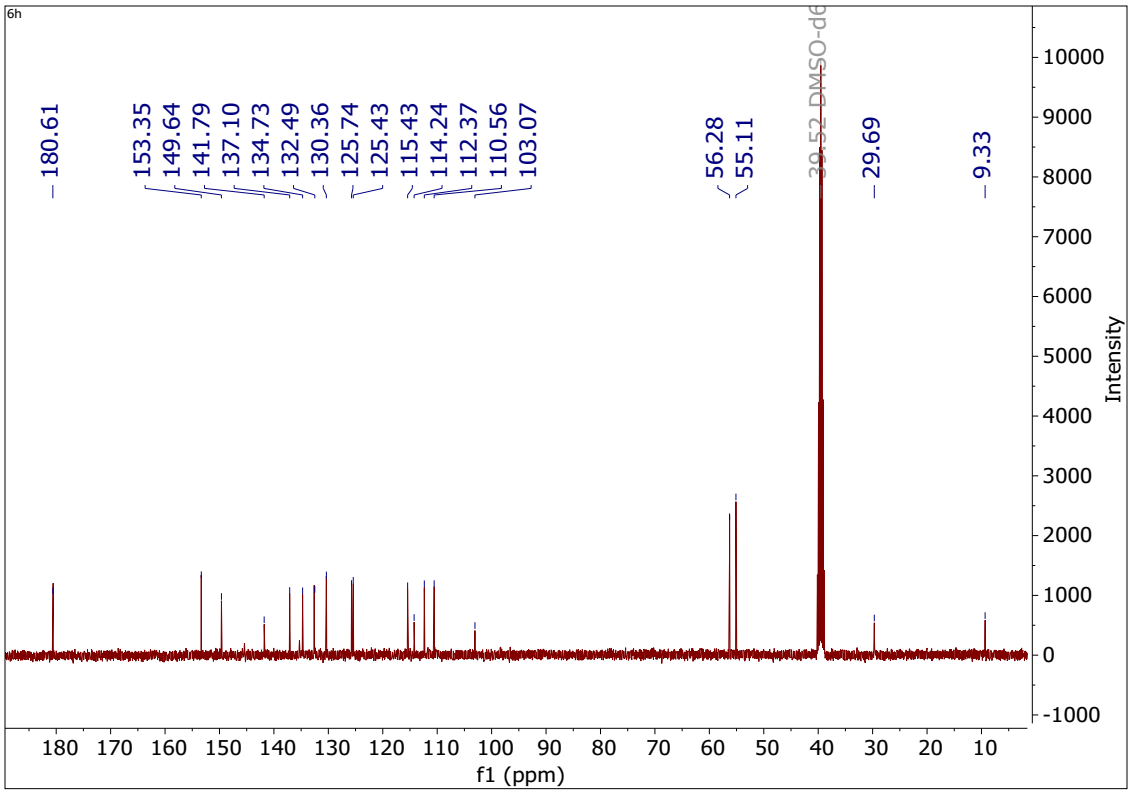
[13]C NMR Spectrum of 6g



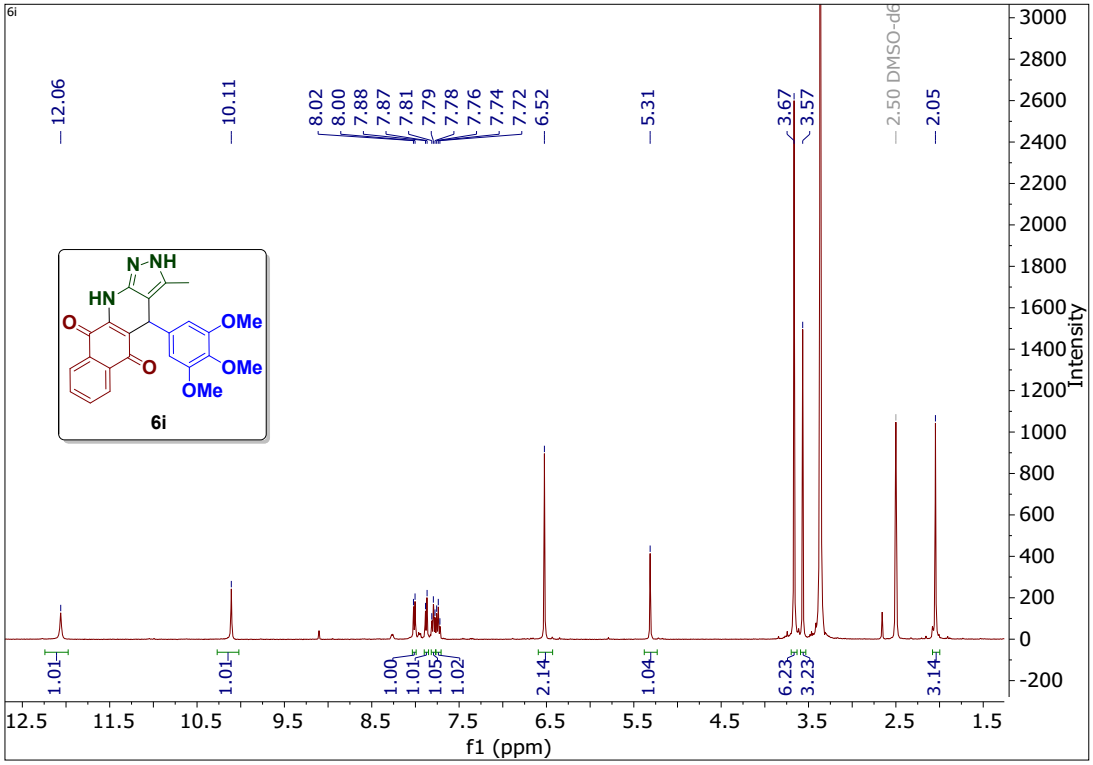
[1]H NMR Spectrum of 6h



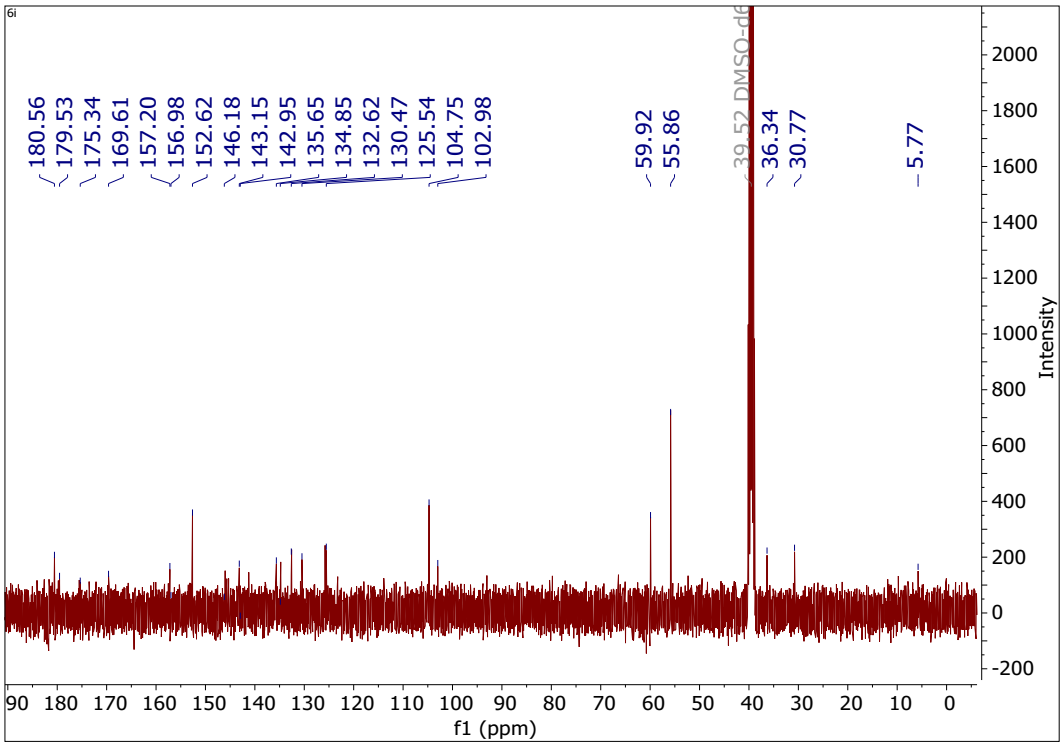
[13]C NMR Spectrum of 6h



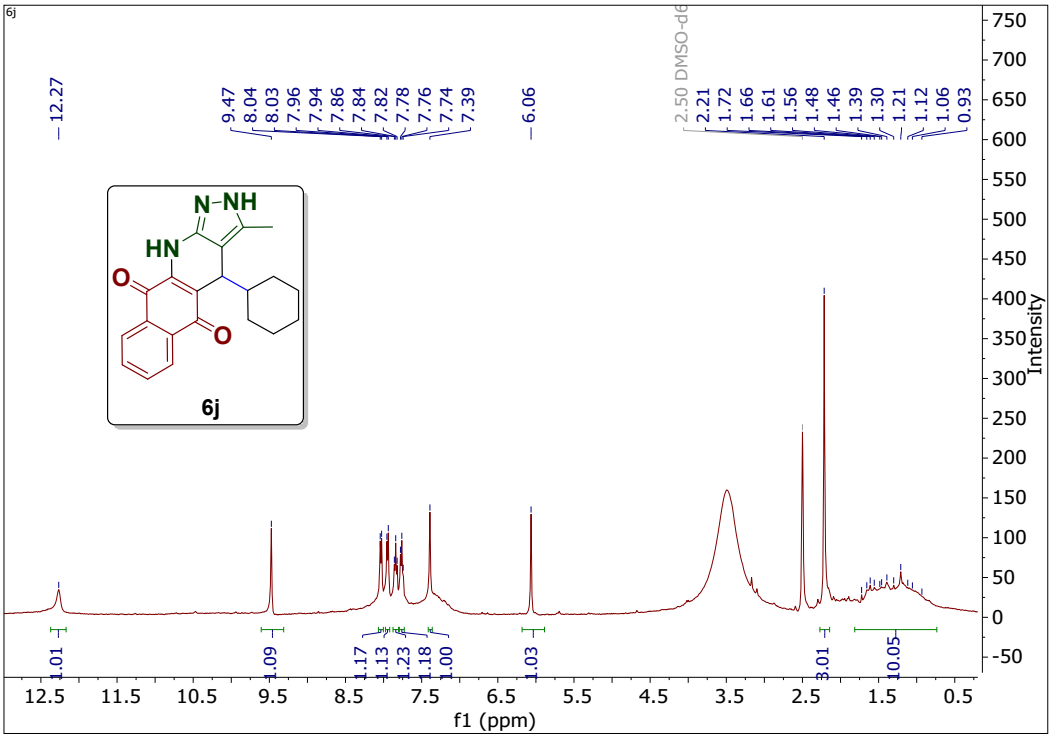
[1]H NMR Spectrum of 6i



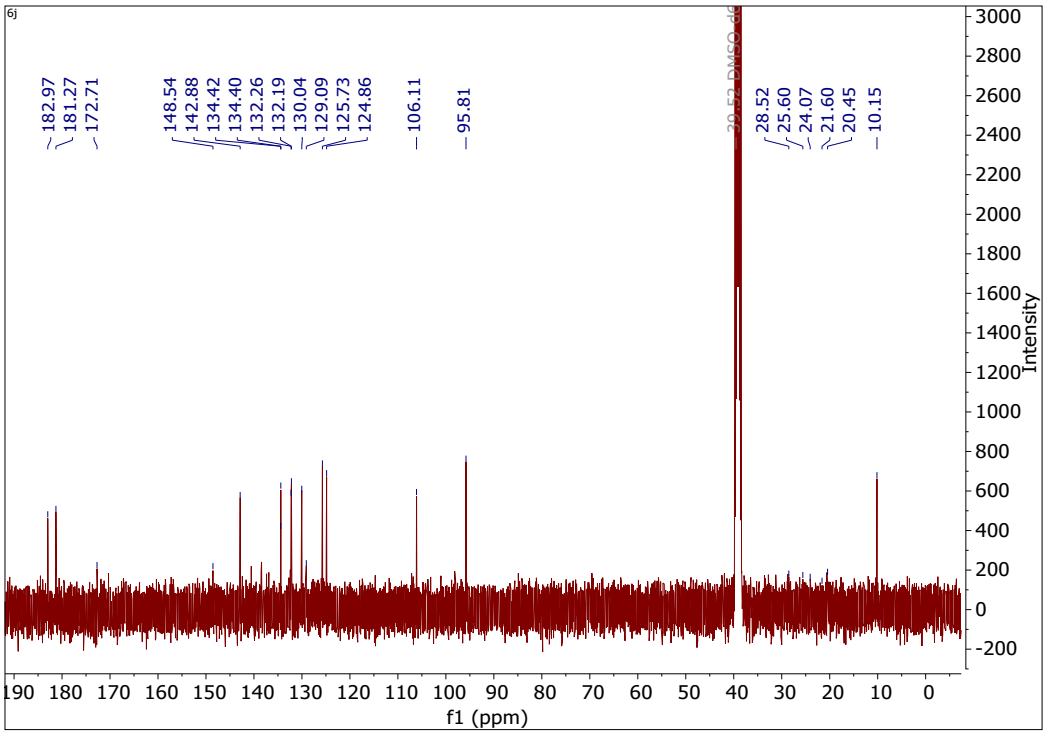
[13]C NMR Spectrum of 6i



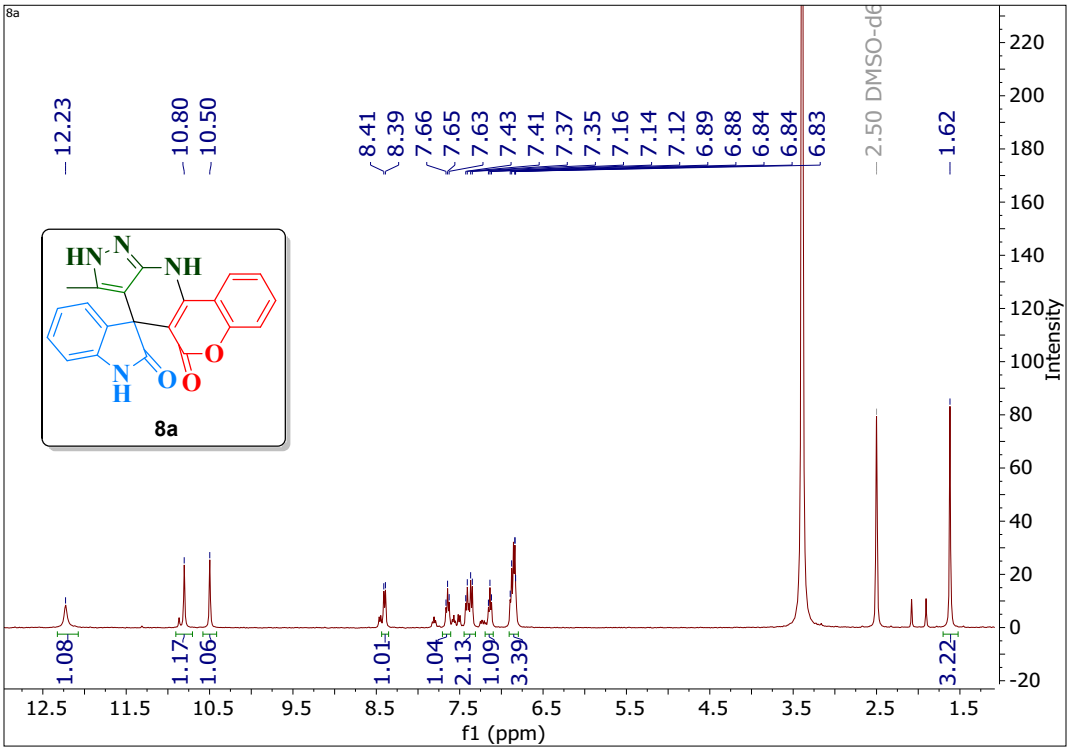
^{1}H NMR Spectrum of 6j



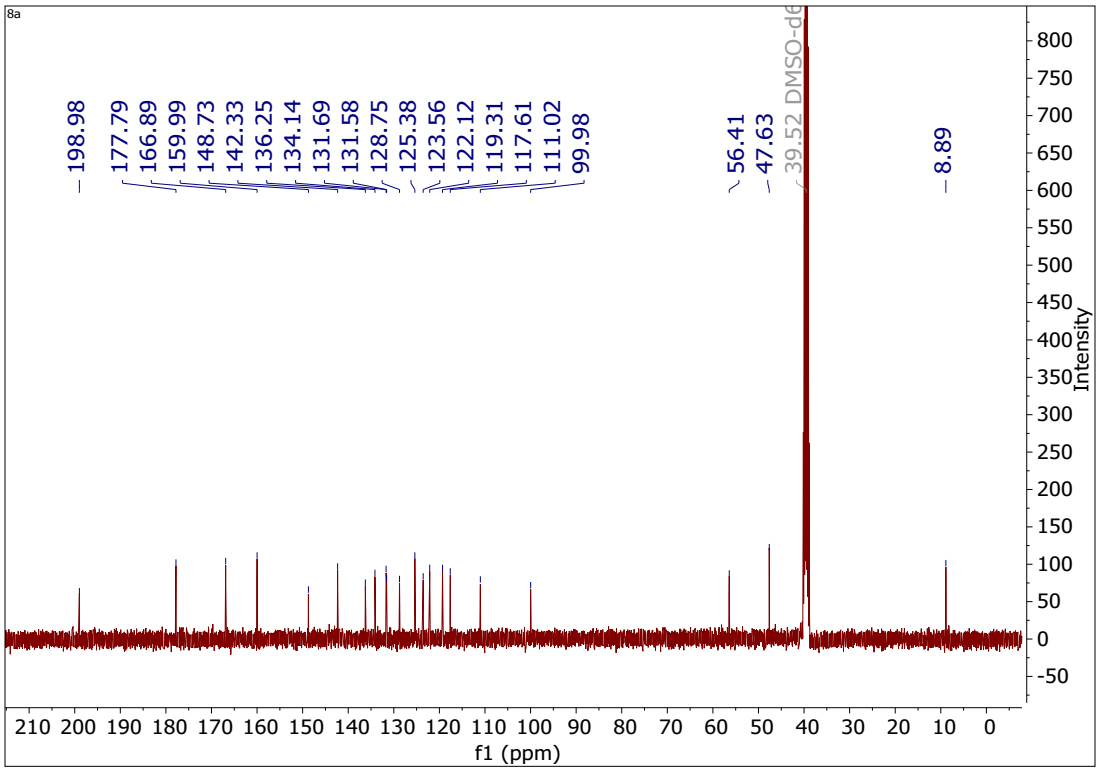
^{13}C NMR Spectrum of 6j



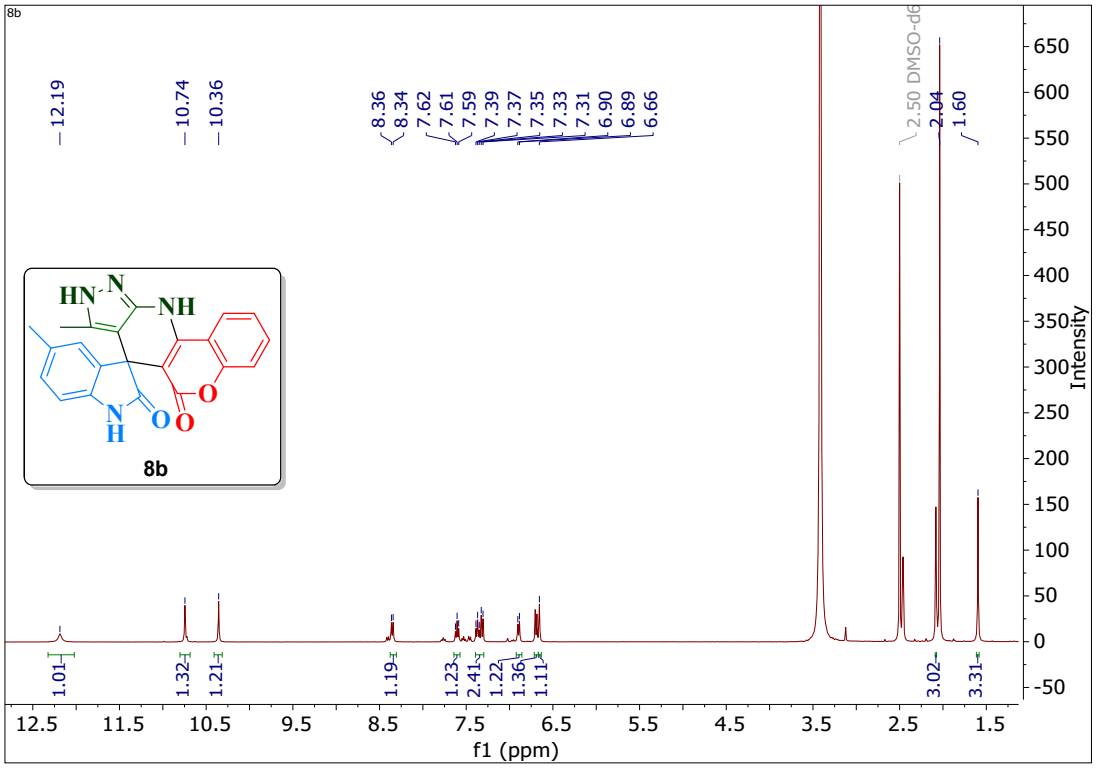
[1]H NMR Spectrum of 8a



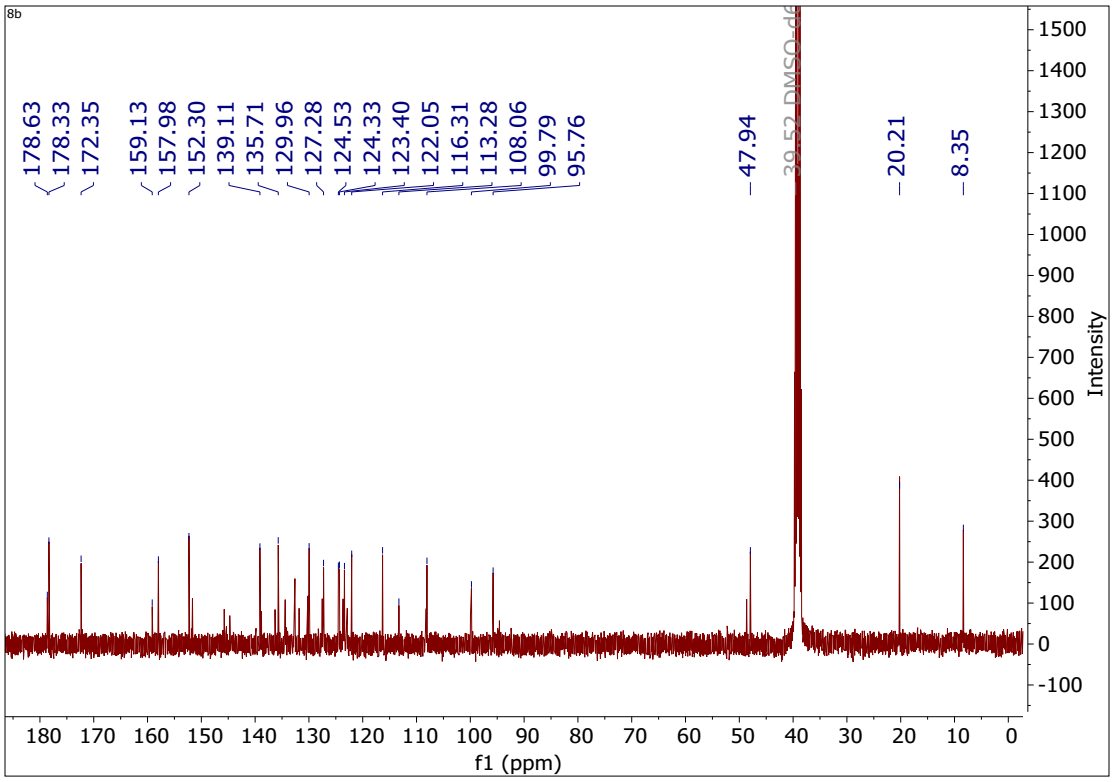
[13]C NMR Spectrum of 8a



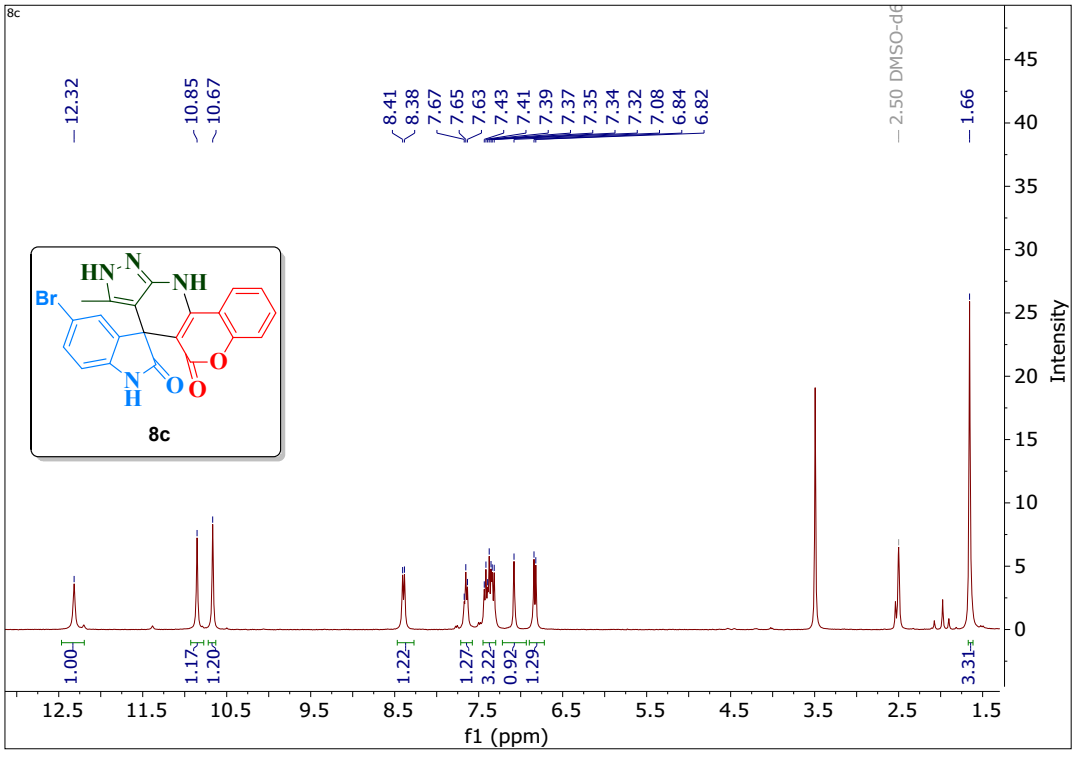
^{1}H NMR Spectrum of 8b



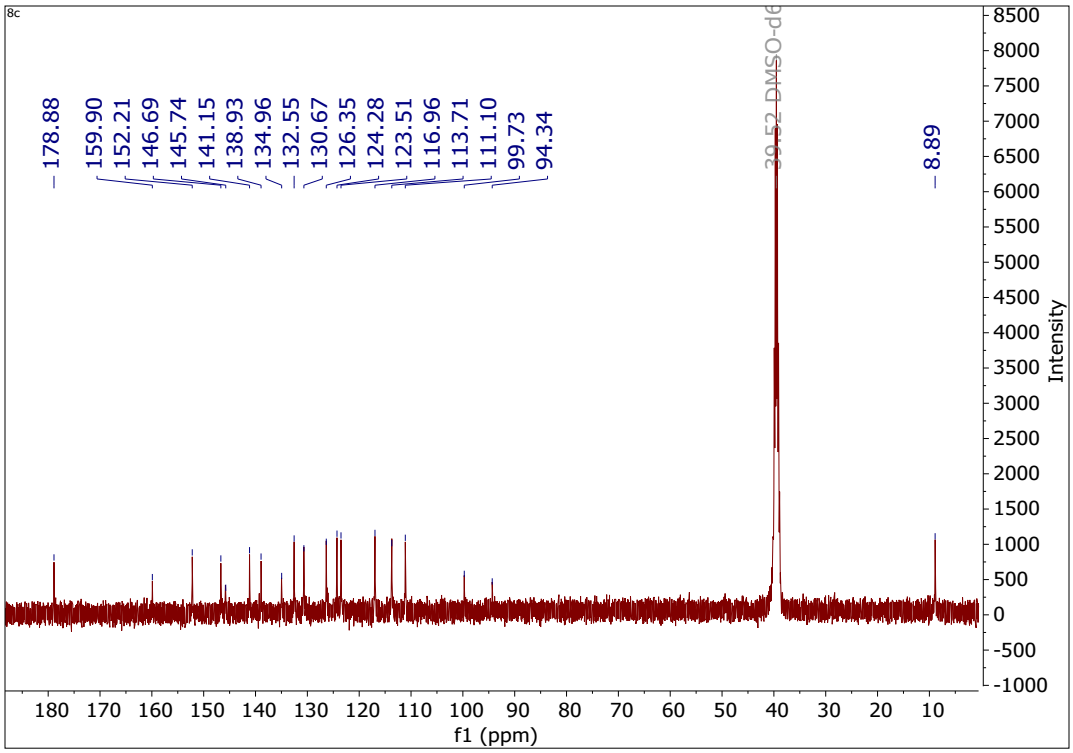
^{13}C NMR Spectrum of 8b



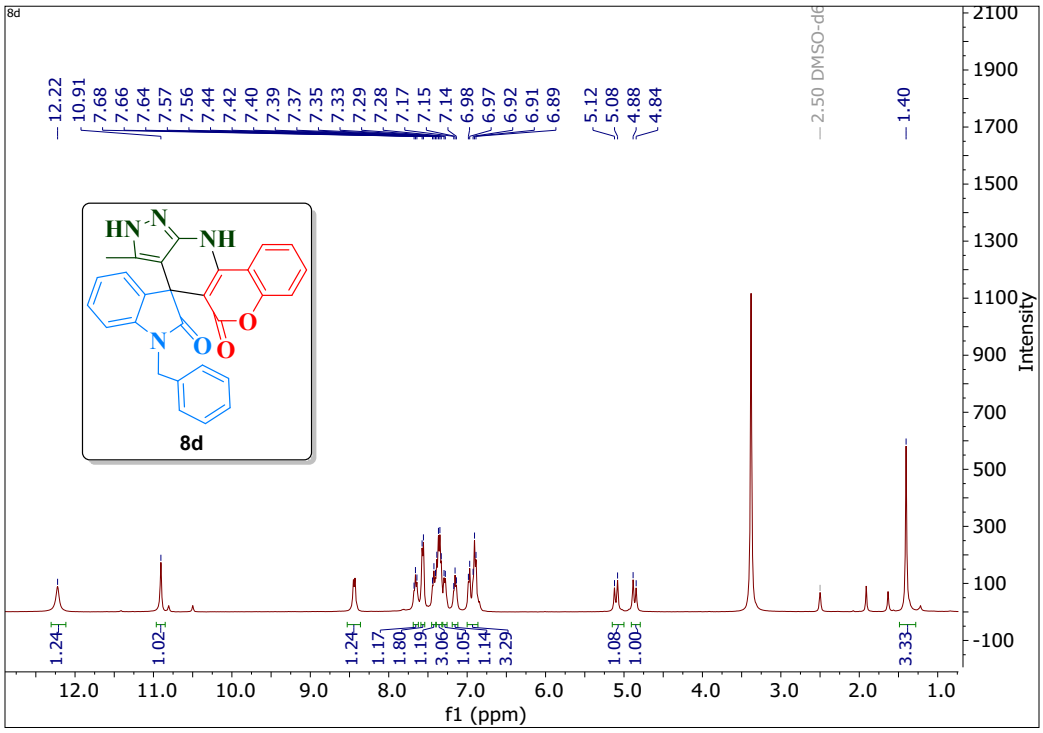
^{1}H NMR Spectrum of 8c



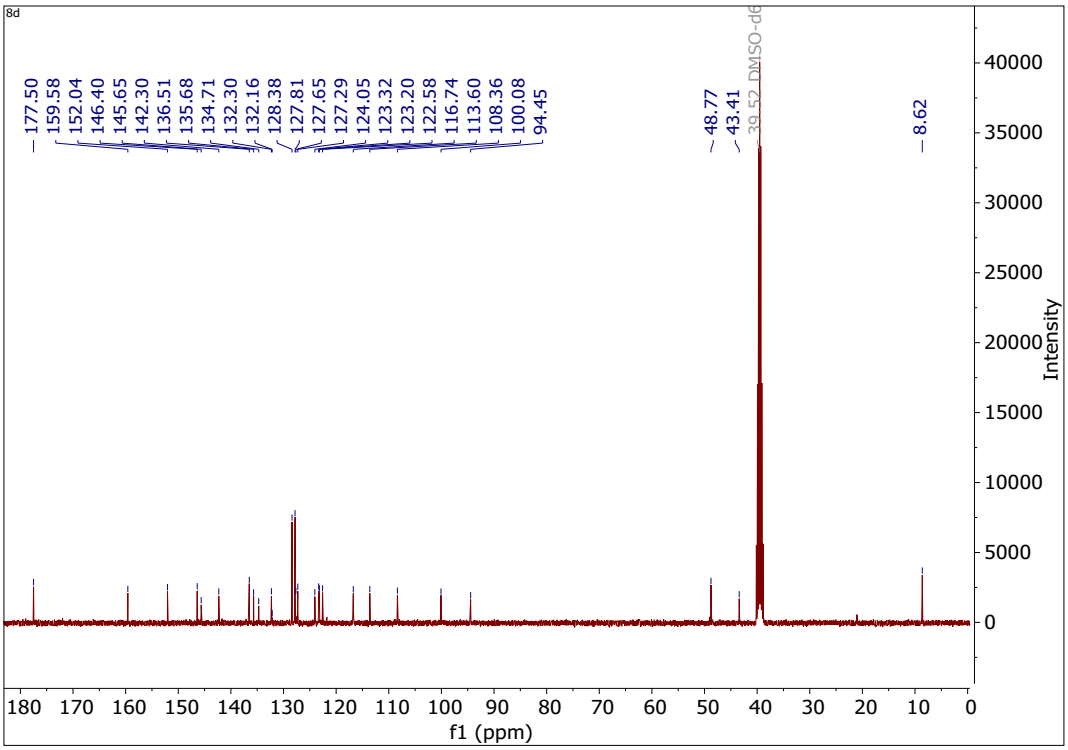
^{13}C NMR Spectrum of 8c



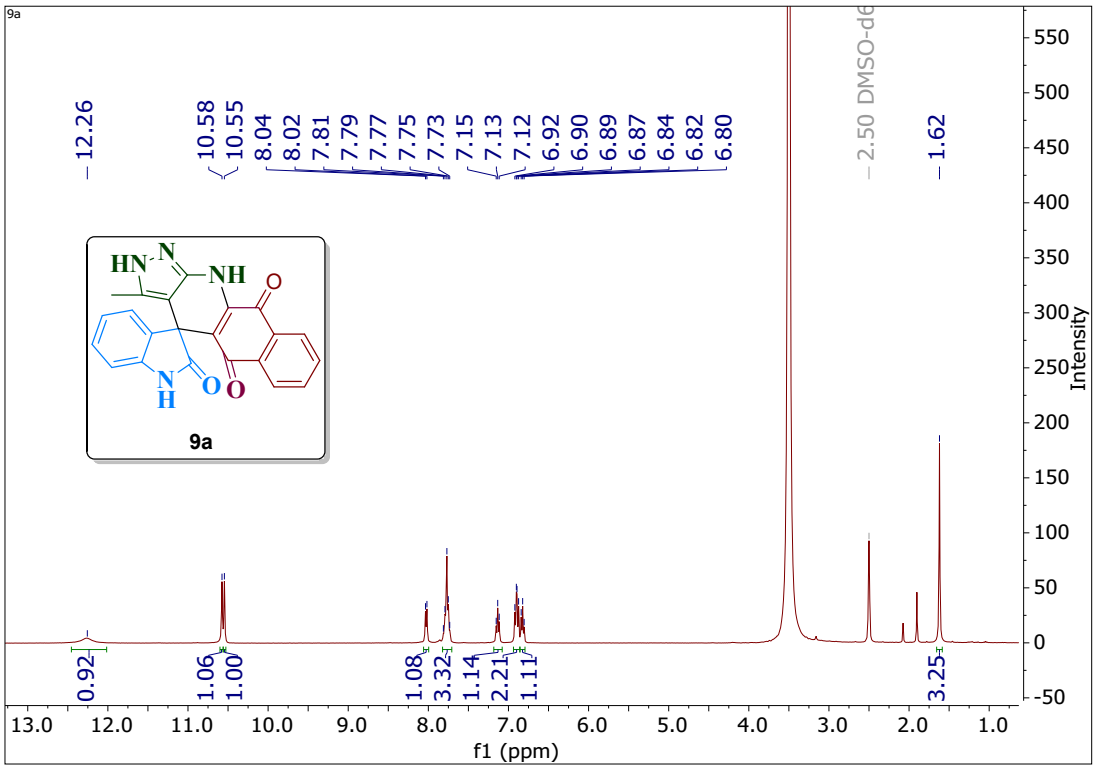
[1]H NMR Spectrum of 8d



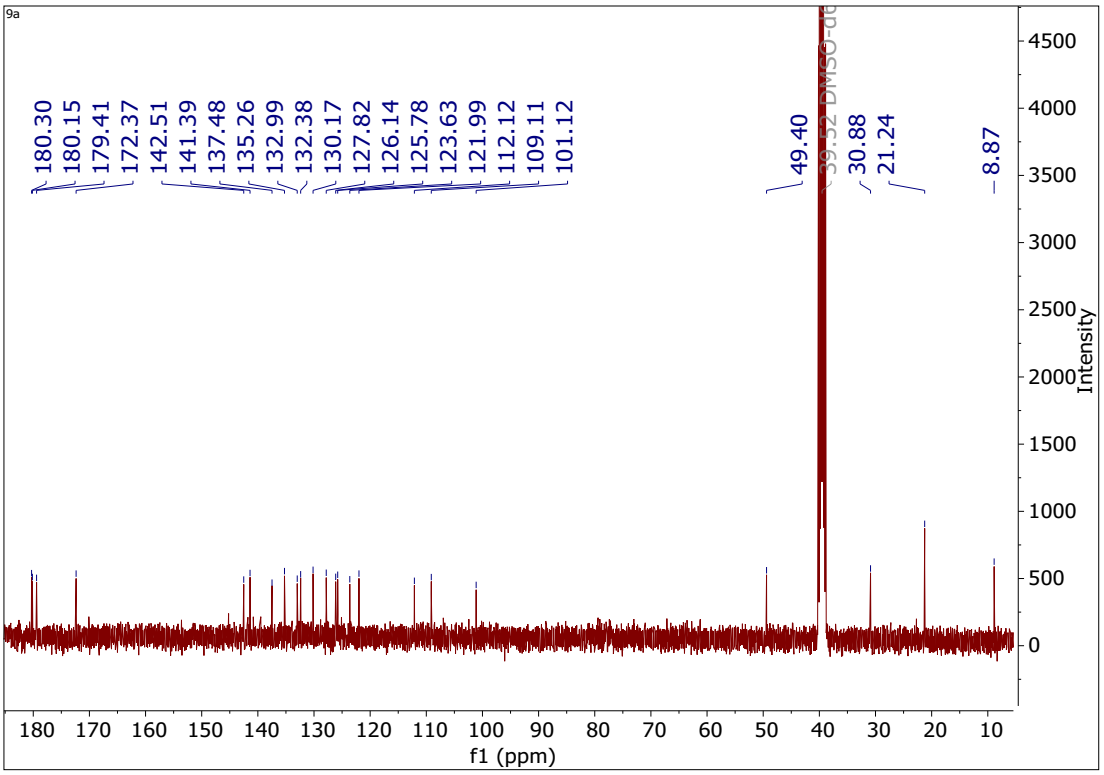
[13]C NMR Spectrum of 8d



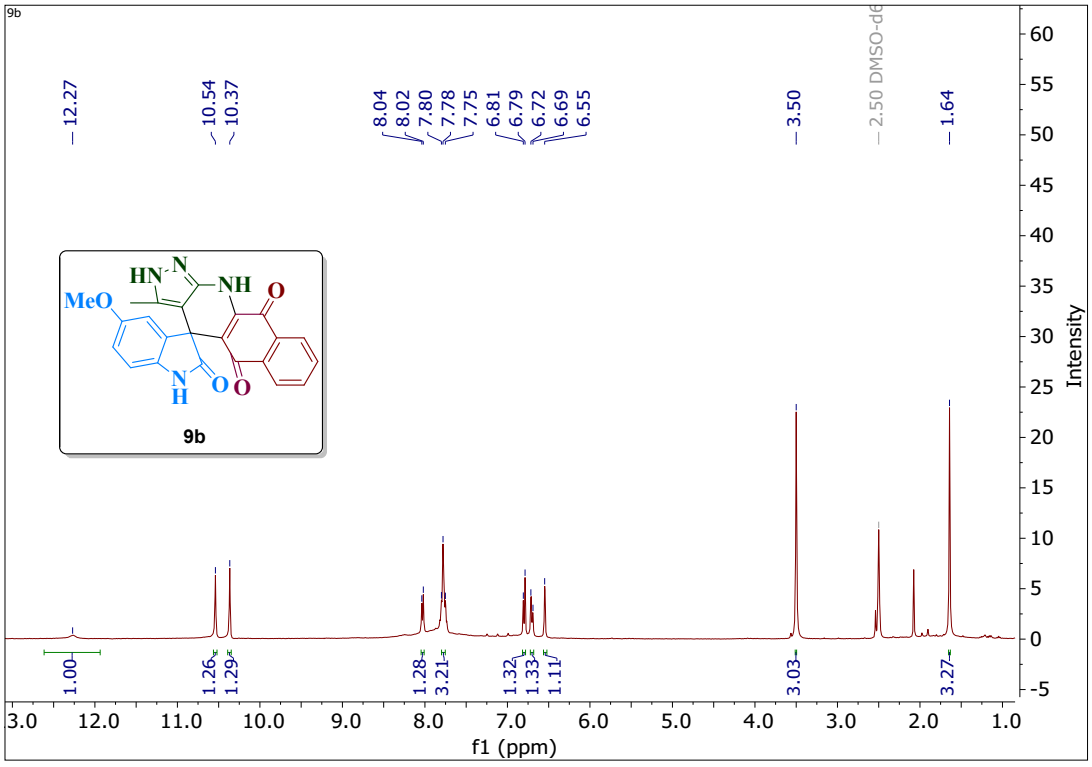
[1]H NMR Spectrum of 9a



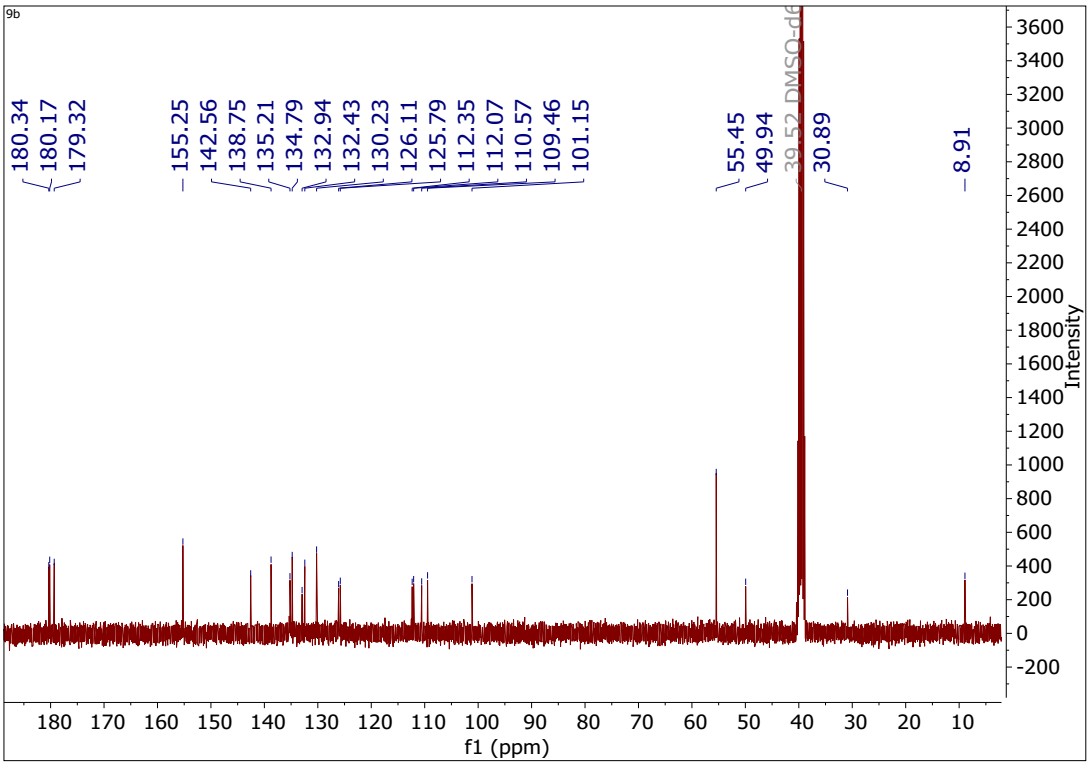
[13]C NMR Spectrum of 9a



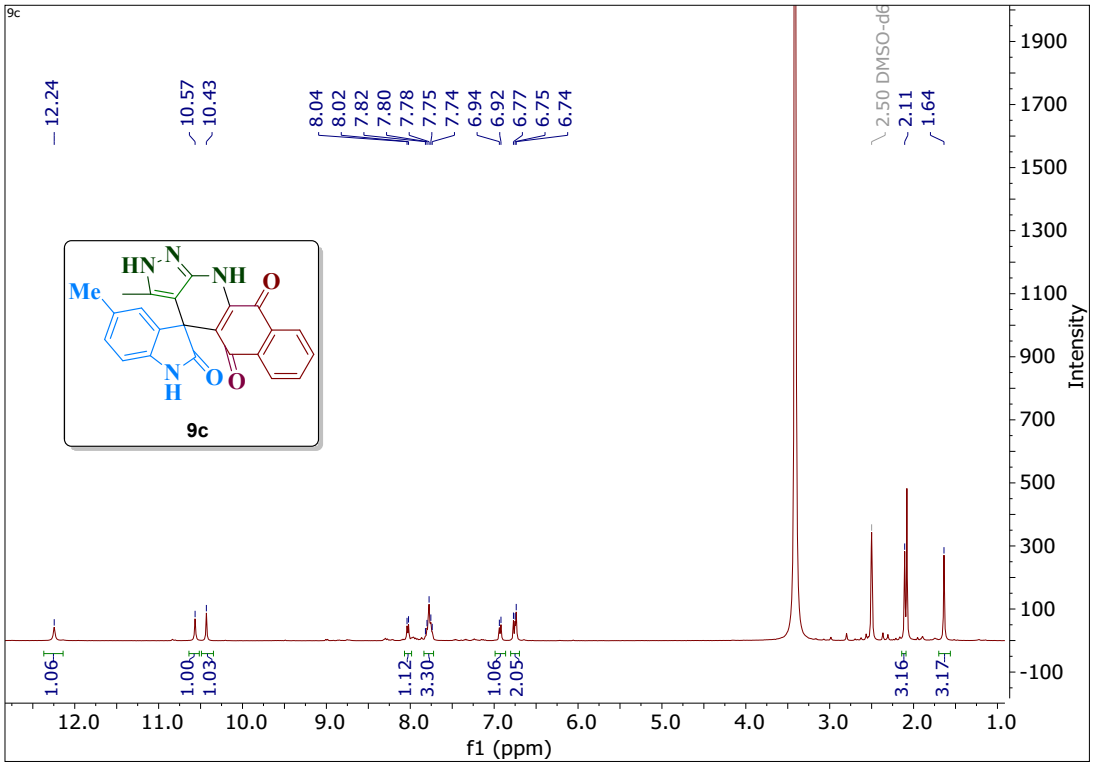
^{1}H NMR Spectrum of 9b



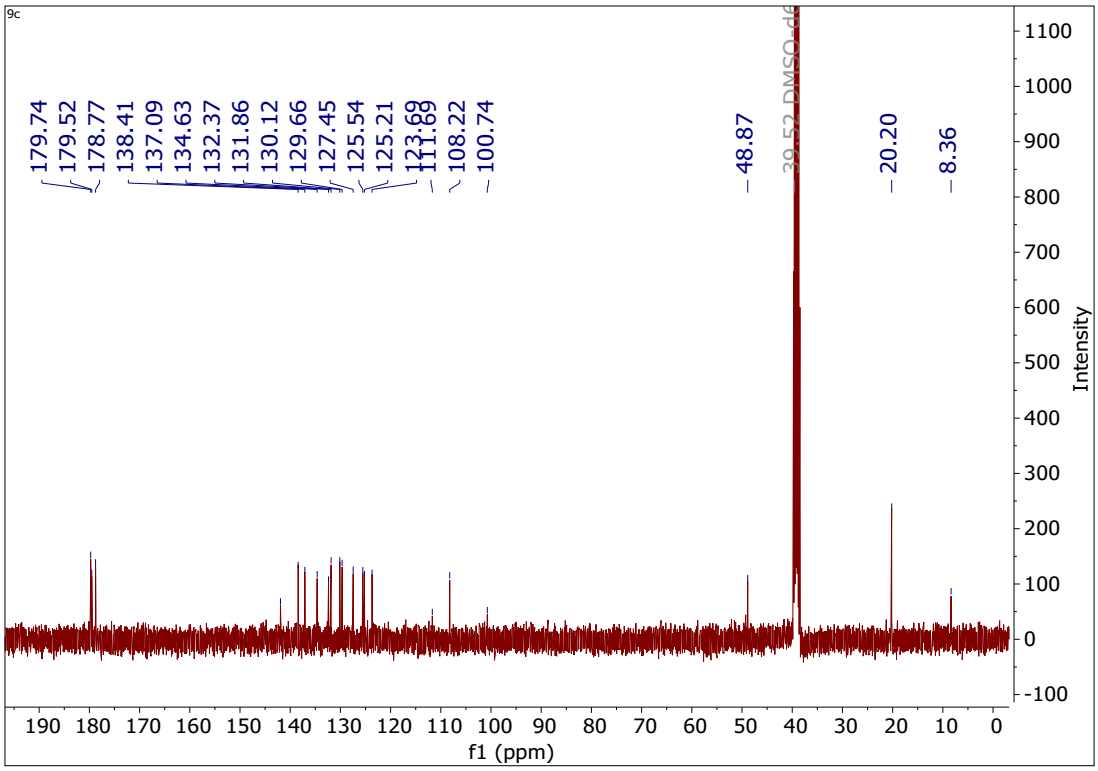
^{13}C NMR Spectrum of 9b



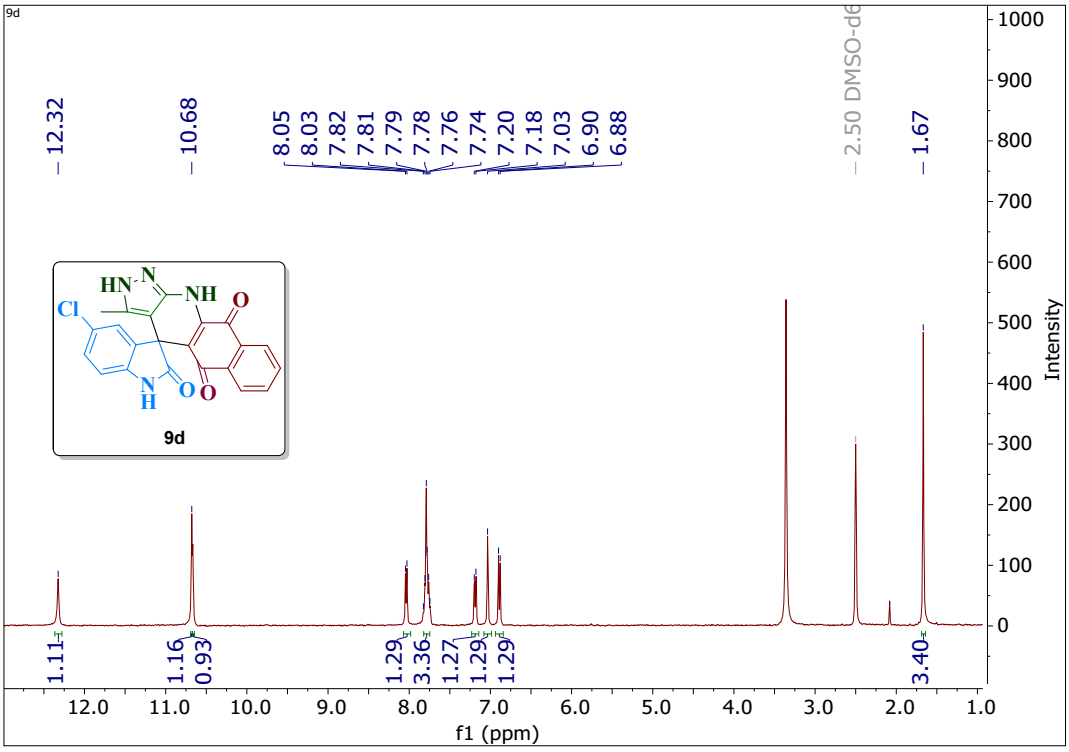
^{1}H NMR Spectrum of 9c



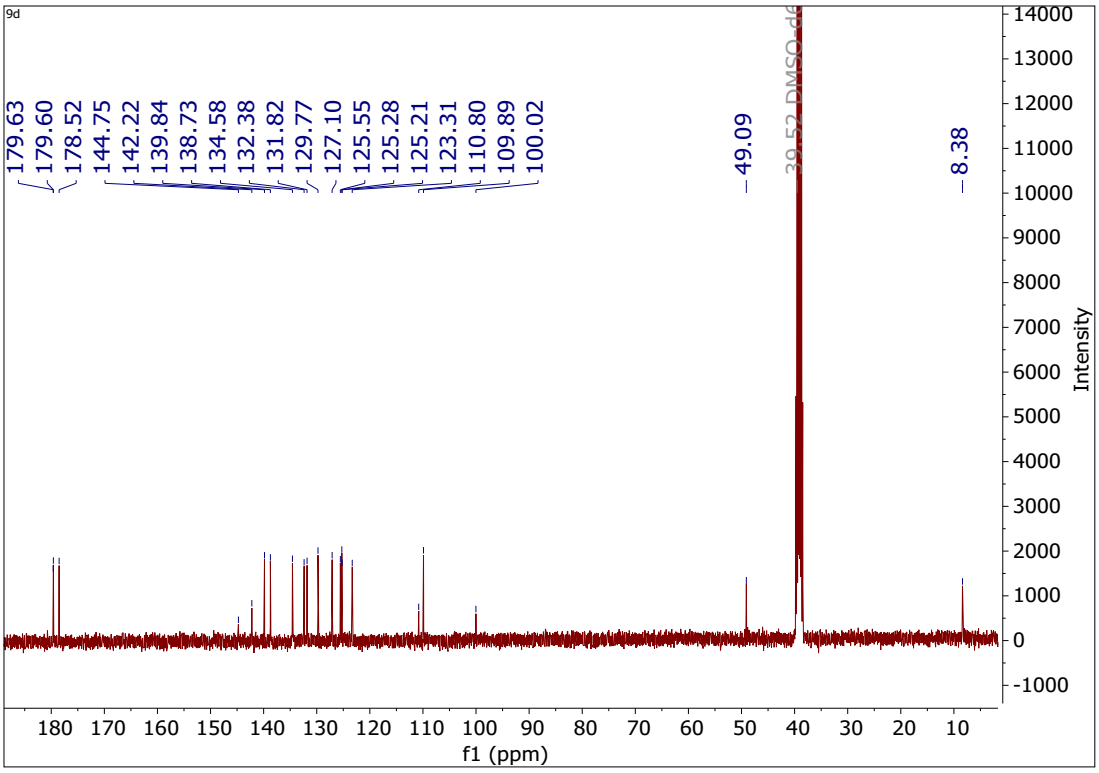
^{13}C NMR Spectrum of 9c



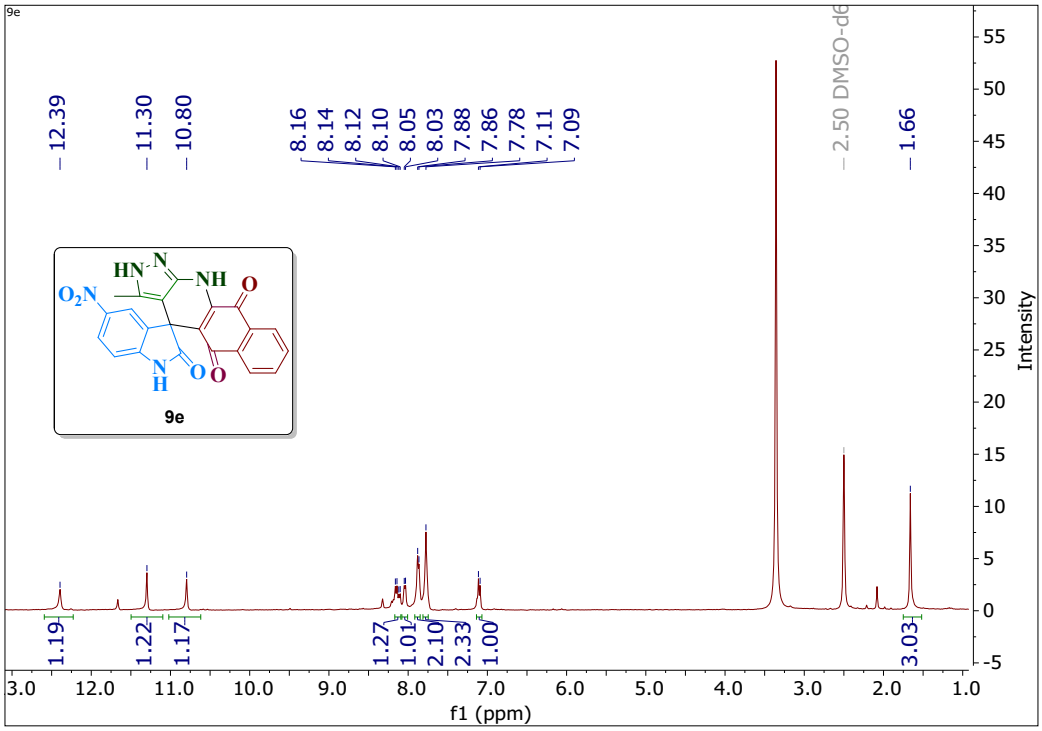
[1]H NMR Spectrum of 9d



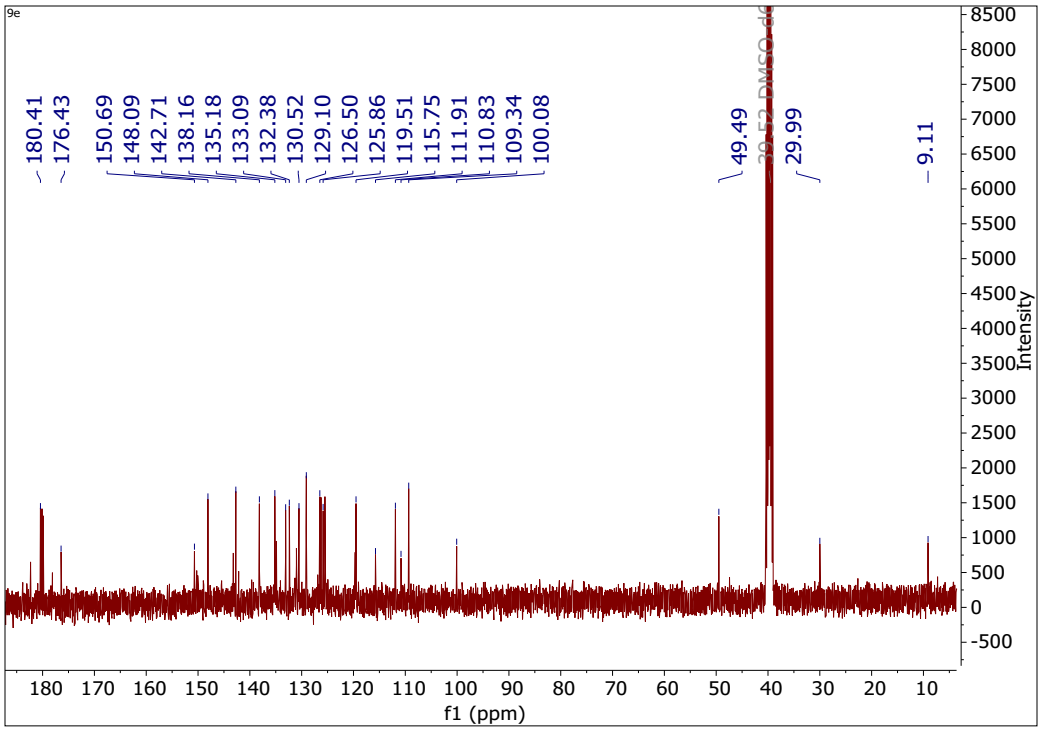
[13]C NMR Spectrum of 9d



[1]H NMR Spectrum of 9e



[13]C NMR Spectrum of 9e



IX. Evaluation of Anti-bacterial and anti-tubercular activities

Anti-bacterial study

Antimicrobial activity of the organic extract was determined by agar well diffusion method (S5, S6) against three bacterial pathogens namely *Escherichia coli* (MTCC730) as gram negative and *Staphylococcus aureus* (MTCC96) as gram positive bacteria. For determination of antimicrobial activity, Muller Hinton Agar (MHA) culture media plates were used. The cups were filled with 100 µL of the extracts (1 mg/ mL in DMSO). The plates were then incubated at 35±1 ^{0}C for 24 hours. Overnight cultures of each bacterial suspension (Optical density - 0.5 at 600 nm) were evenly spread out on separate MHA plates with the help of sterile cotton swabs. 6 mm wells were dug into the media by scooping out the media with the help of a sterile cork borer (6 mm) Antimicrobial activity was determined as zone of inhibition of the target bacteria around the well as appearance of clear zones. DMSO solvent which is used to dissolve the compounds was used as negative control and antibacterial discs were used as a positive control.

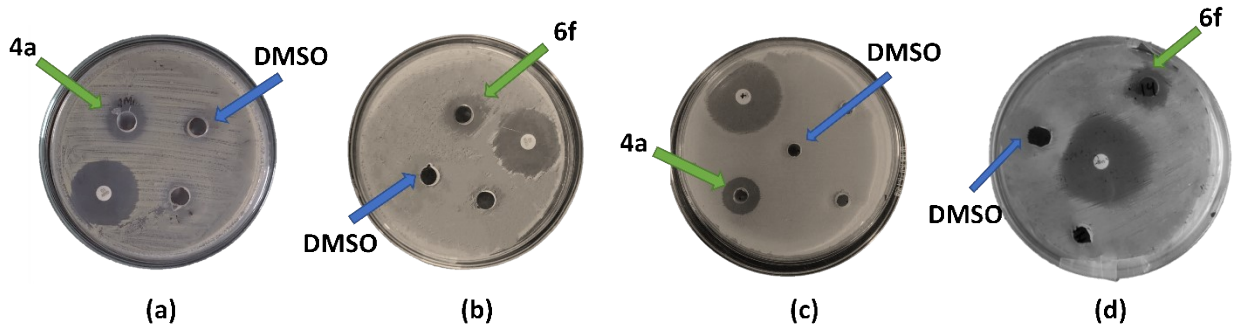


Figure S3. Photo plates showing antibacterial activity of **4a** and **6f** against (a), (b) *E. coli* and (c), (d) *B. cereus* respectively.

Anti-tubercular studies

Briefly, the inoculum was prepared from fresh LJ medium re-suspended in 7H9-S medium (7H9 broth, 0.1% casitone, 0.5% glycerol, supplemented oleic acid, albumin, dextrose, and catalase [OADC]), adjusted to a OD_{590} 1.0, and diluted 1:20; 100 µl was used as inoculum. Each drug stock solution was thawed and diluted in 7H9-S at four-fold the final highest concentration tested. Serial two-fold dilutions of each drug were prepared directly in a sterile 96-well microtiter plate using 100 µl 7H9-S. A growth control containing no antibiotic and a sterile control were also prepared on each plate. Sterile water was added to all perimetre wells to avoid evaporation during the incubation. The plate was covered, sealed in plastic bags and incubated at 37°C in normal atmosphere. After 7 days incubation, 30 µl of alamar blue solution was added to each well, and the plate was re-incubated overnight. A change in color from blue (oxidised state) to pink (reduced) indicated the growth of bacteria, and the MIC was defined as the lowest concentration of drug that prevented this change in color [S7, S8].

X. References

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