Synthesis of Benzo[*d,e*]quinoline-Spiro-Succinimides via Rhodium-Catalyzed C–H Activation/Annulation of 1-Naphthylamides with Maleimides

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Supporting Information

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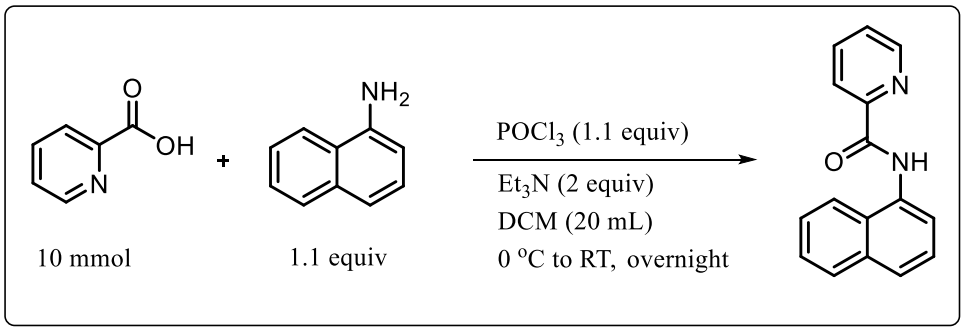
1. General consideration:

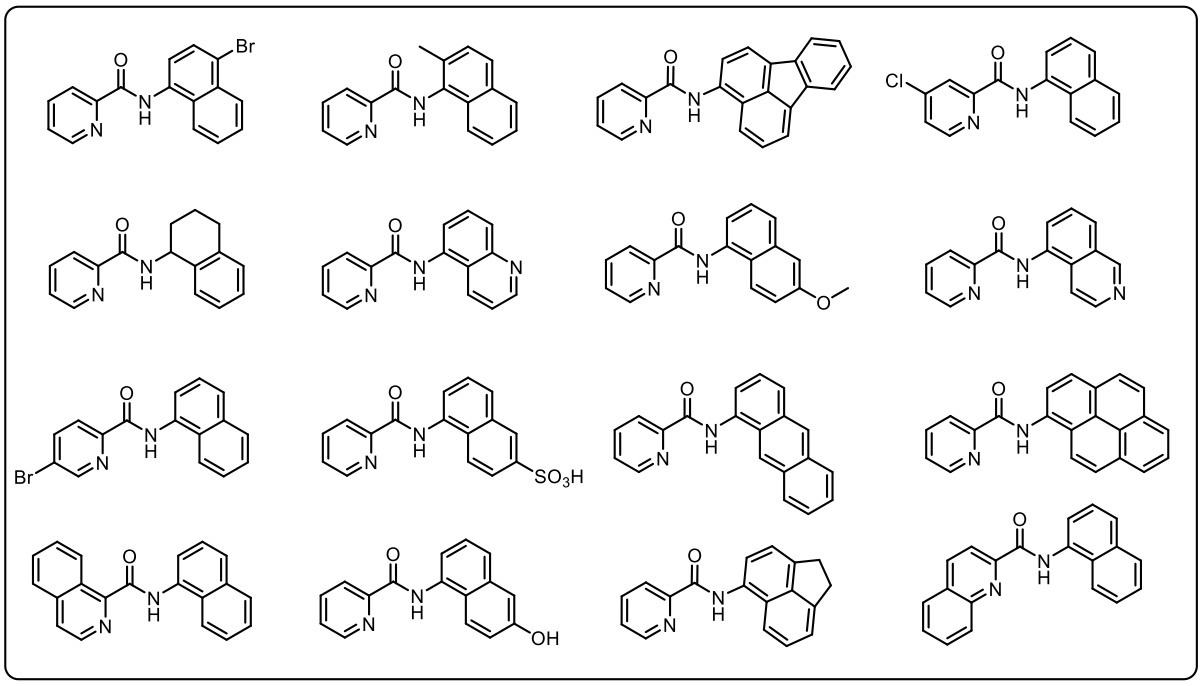
All reactions were carried out in oven-dried glassware under standard reaction conditions. All reagents were purchased from Sigma-Aldirch, SpectrChem, and TCI Chemical and used without further purification unless otherwise noted. All solvents were dried by the standard reported prCedures and stored over activated molecular sieves. Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates. Visualization of the developed plates was performed under UV light (254 nm). Flash column chromatography was performed on silica gel (200-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Jeol Resonance ECZ 600R spectrometer (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 564 MHz for ^{19}F) and Bruker AvanceII 500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR). X-ray structure data was recorded by Bruker D8 Quest. Chemical shifts are reported in ppm referenced to an internal tetramethylsilane standard $CDCl_3$ (δ 7.26) for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.37). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, J, were reported in Hertz unit (Hz). High-resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS Spectrometer.

2. General procedure for the preparation of 1-Naphthylamide & Maleimide Derivatives:

All the amides were synthesized according to the literature procedure[1] as described below:

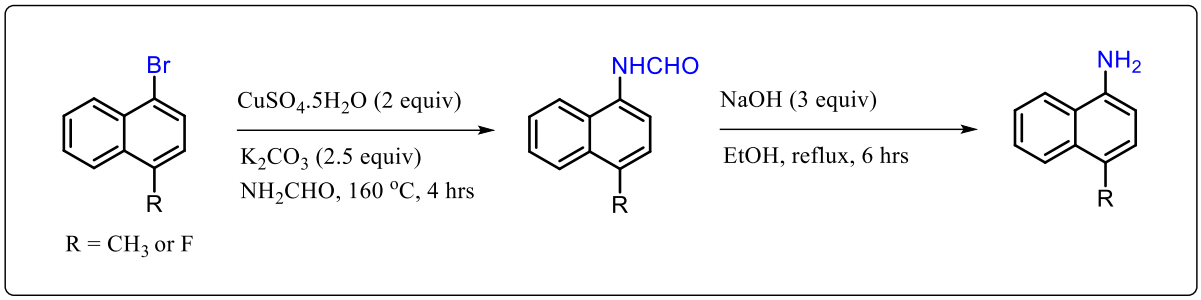


An oven-dried 100 mL round bottom flask was charged with pyridine-2-carboxylic acid (10 mmol, 1231 mg) and 1-naphthyl amine (1.1 equiv, 1575 mg), then DCM (20 mL). Then add Et_3N (2 equiv, 2807 µL) and stir at 0 ºC for 10 minutes. After cooling down to 0 ºC, add $POCl_3$ (1.1 equiv, 1028 µL) dropwise. Then the reaction mixture was stirred at room temperature overnight. The mixture was diluted with DCM (15 mL) and washed with saturated aq. $NaHCO_3$ solution (25 mL), followed by brine solution (25 mL) dried over Na_2SO_4 and evaporated in vacuo. The crude mixture was loaded on a silica gel column chromatography and purified using (Hexane/EtOAc = 5:1) to give the desired product (85%, 2.1 g).



Scheme S1: *Summary of 1-Naphthylamide substrates*

❖ Preparation of 4-fluoronaphthylamine and 4-methylnaphthylamine derivatives:

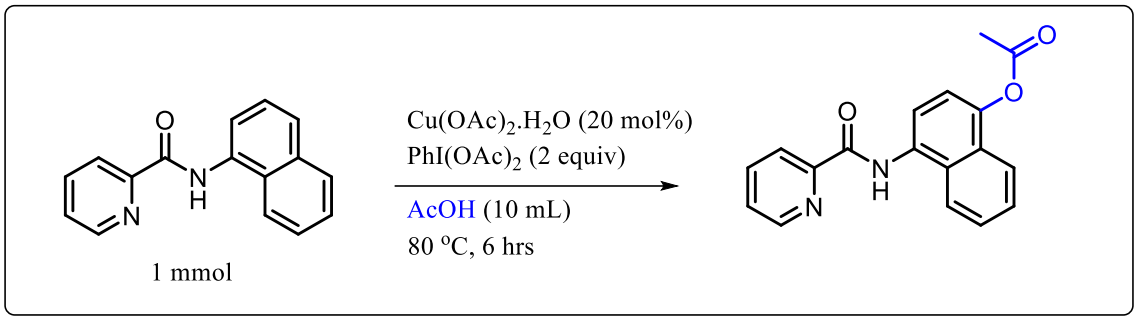


Step 1: An oven-dried 50 mL round bottom flask substituted with 1-bromonapthelene (2.5 mmol), K_2CO_3 (2.5 equiv), and copper(II) sulphate pentahydrate (2 equiv) was taken, and formamide (10 mL) was added. The RBF was fitted with a reflux condenser and heated at 160 ºC for 4 hrs. The reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was mixed with ice-cold water (30 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layers were dried over Na_2SO_4 and evaporated. The crude product was used for the next step without further purification.

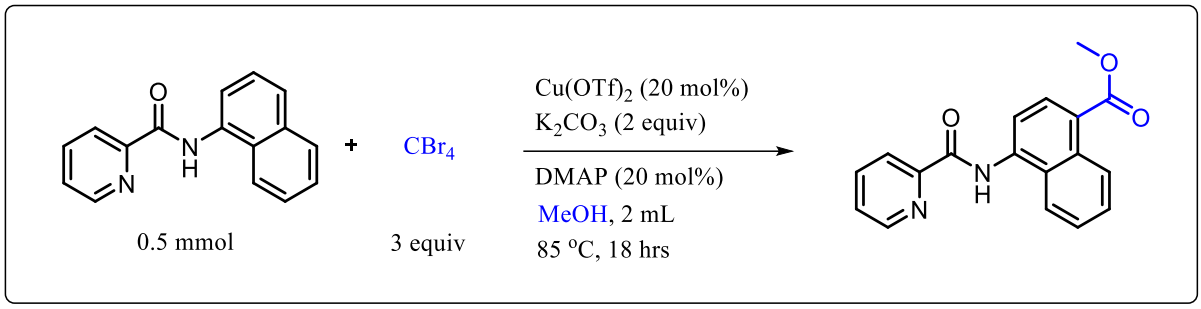
Step 2: Aqueous (2 mL) sodium hydroxide (3.0 equiv) was added to the ethanol (10 mL) solution of N- (naphthalen-1-yl)formamide. The resulting solution was heated to reflux for 6 hrs. Ethanol was evaporated and extracted with ethyl acetate (3×10 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography to obtain naphthylamines[2].

❖ Preparation of 4-(nicotinamide)naphthalen-1-yl acetate:

N-(naphthalen-1-yl)Picolinamide (1 mmol), $Cu(OAc)_2 \cdot H_2O$ (20 mol%), $PhI(OAc)_2$ (2 equiv.), and acetic acid (10 mL) was added into a sealed tube. The mixture was stirred at 80 ºC under air for 6 hrs. After cooling to room temperature, the resulting mixture was filtered through a pad of celite and washed with EtOAc. The filtrate was concentrated under a vacuum and separated on a silica gel column using ethyl acetate/Hexene as eluent to give the product 4-(picolinamido)naphthalen-1-yl acetate[3].



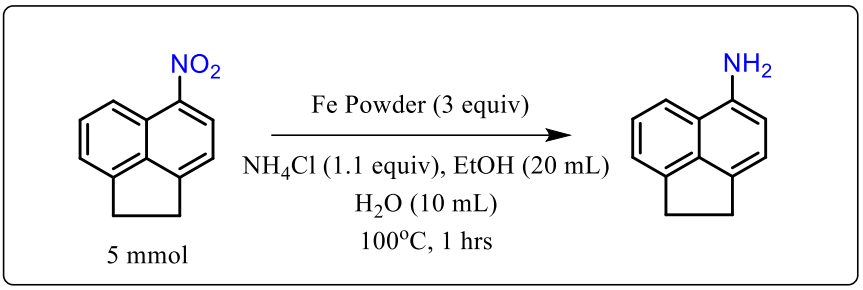
❖ Preparation of methyl 4-(picolinamido)-1-naphthoate:



A mixture of Amide (0.5 mmol), CBr_4 (3 equiv), $Cu(OTf)_2$ (20 mol%), K_2CO_3 (2 equiv), and DMAP (20 mol%) were taken in a carousel screw cap reaction tube equipped with a stirring bar. The reaction tube was evacuated and refilled with nitrogen, and 2 mL dry methanol was added over it and stirred at 85 ºC for 18 h under an N_2 atmosphere. After completion of the reaction, the mixture was cooled to room temperature and filtered through a plug of celite, the filtrate was concentrated and evaporated to dryness in the rotary evaporator. The crude residue was purified by Flash column chromatography (Ethyl acetate: Hexane 5:95) to isolate methyl 4-(picolinamido)-1-naphthoate[4].

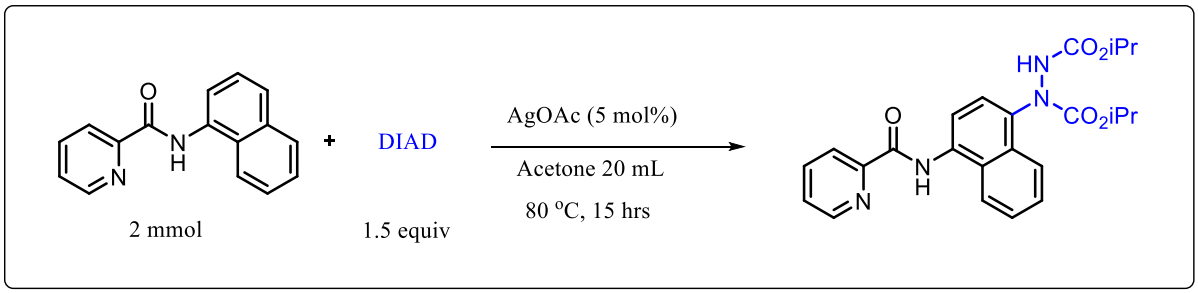
❖ Preparation of 1,2-dihydroacenaphthylen-5-amine:

An oven-dried 50 mL round bottom flask substituted with Fe powder (3 equiv), NH_4Cl (1.1 equiv), and water (10 mL) were taken. The RBF was fitted with a reflux condenser and heated at 100 ºC for 15 to 20 minutes. Then add 5-nitro-1,2-dihydroacenaphthylene and EtOH to the reaction mixture and heated to 100 ºC for 1 hrs. Reaction was continuously monitored by TLC. After completion of the reaction ethanol was evaporated and extracted with ethyl acetate (2×50 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography to obtain 1,2-dihydroacenaphthylen-5-amine.



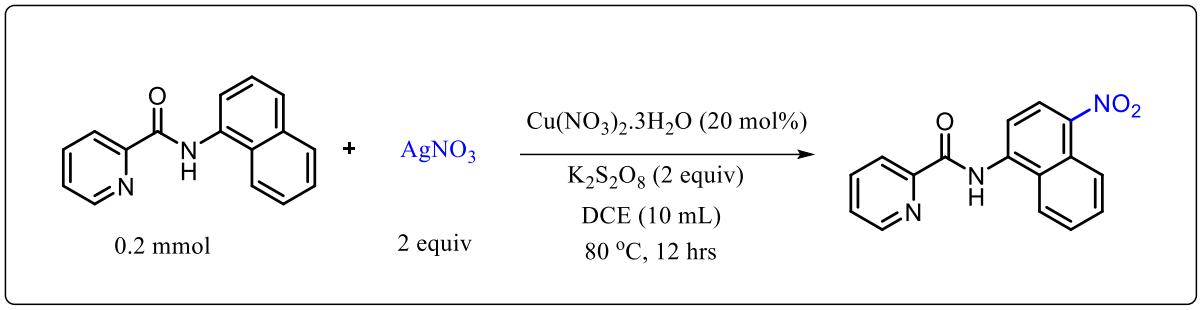
❖ Preparation of di-isopropyl 1-(4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate:

A sealed tube was equipped with a magnetic stir bar and charged with N-(naphthalen-1-yl)Picolinamide (2 mmol), Di-isopropyl azodicarboxylate (1.5 equiv), Silver acetate (5 mol%), and Acetone (20 mL). The mixture was sealed, heated at 80 ºC for 15 h, and cooled to room temperature. After completion of the reaction acetone was evaporated and extracted with ethyl acetate (2×50 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography to obtain the desired product[5].



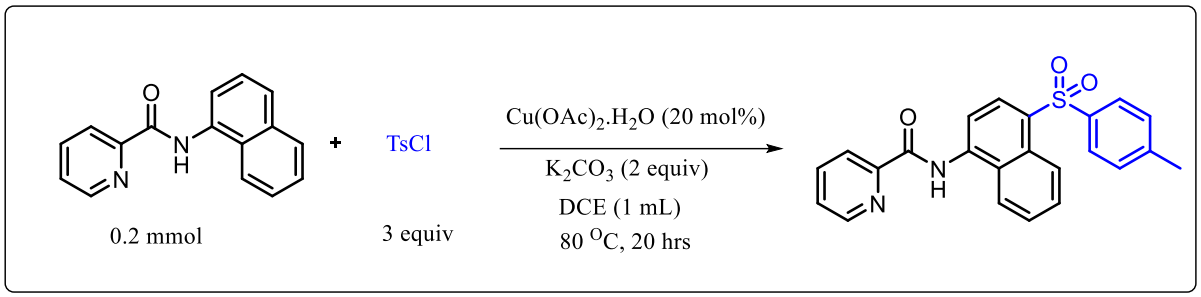
❖ Preparation of N-(4-nitronaphthalen-1-yl)Picolinamide:

A Schlenk tube equipped with a magnetic stir bar was charged with N-(naphthalen-1-yl)Picolinamide (0.2 mmol), silver nitrate (2 equiv), copper nitrate tri hydrate (20 mol%), potassium persulfate (2 equiv), and DCE (10 mL). The resulting mixture was heated at 80 ºC for 12 hrs. After completion of the reaction, DCE was evaporated from the reaction mixture and extracted with ethyl acetate (3×20 mL). The combined organic layer was dried over Na_2SO_4 or $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography to obtain the desired product[6].



❖ Preparation of N-(4-tosylnaphthalen-1-yl)Picolinamide:

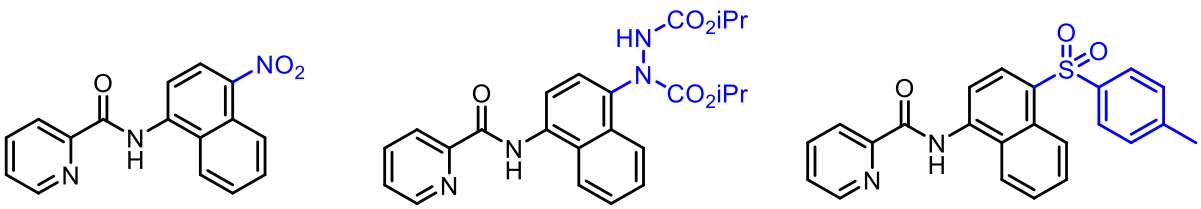
A mixture of amide (0.2 mmol), sulfonyl chloride (3 equiv), $Cu(OAc)_2.H_2O$ (20 mol%), K_2CO_3 (2 equiv), and DCE (1 mL) were taken in a sealed tube. The mixture was stirred at 80 °C under air for 20 hrs. After completion of the reaction, the resulting mixture was filtered through a celite pad and washed with DCM. The filtrate was concentrated under a vacuum and



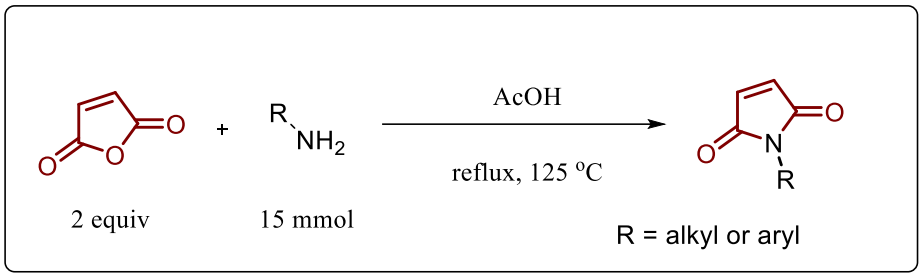
separated on a silica gel column using ethyl acetate/Hexane as eluent to give the desired product[3].

Unreactive substrate:

Substrate N-(4-nitronaphthalen-1-yl)Picolinamide, di-isopropyl 1-(4-(picolinamido)naphthalen-1-yl)hydrazine-1,2-dicarboxylate, and N-(4-tosylnaphthalen-1-yl)Picolinamide were found unreactive under standard reaction condition might be electron withdrawing group present at C4 position makes the electron poor substrate unreactive for the oxidative addition of the C–H bond to a Rh species.



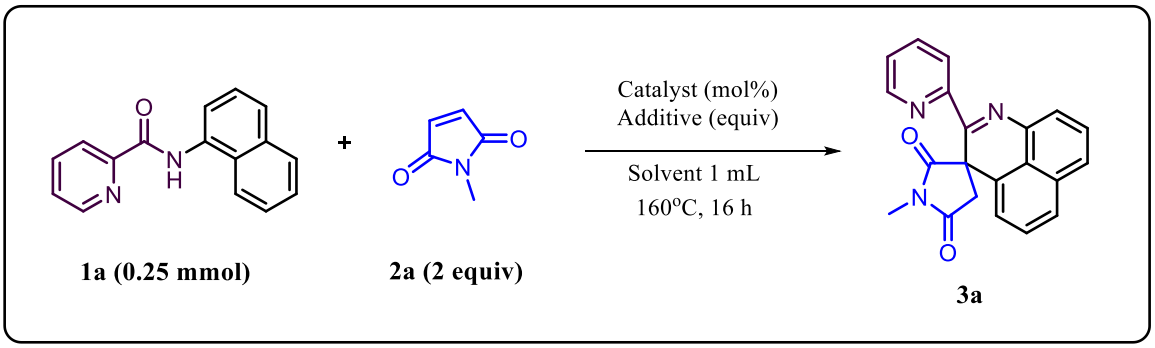
❖ Preparation of maleimide derivatives:



A 50 ml round bottom flask was charged with a magnetic stir bar and was equipped with maleic anhydride (2 equiv., 30 mmol) in acetic acid (15-20 mL), and a suitable amine (15 mmol) was added and the reaction mixture was refluxed for 16 h – 24 h. After completion of the reaction acetic acid was quenched with aq. $NaHCO_3$ solution. Subsequently, the mixture was dissolved in ethyl acetate and the organic layer was washed with saturated aq. NaCl (20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude reaction mixture was further purified by column chromatography on silica gel (Hexane: EtOAc = 5:1), to obtain the desired product.

The aforementioned method of preparation was used to prepare additional substrates of maleimide derivatives[7].

3. Reaction Optimization:



Entry	Catalyst (mol%)	Additive (equiv)	Solvent	Isolated yield
1	$[Rh(OAc)_2]_2$ (5 mol%)	PivOH (2 equiv)	Toluene	15
2	$[Rh(OAc)_2]_2$ (5 mol%)	2-methyl benzoic acid (2 equiv)	Toluene	NR
3	$[Rh(OAc)_2]_2$ (5 mol%)	2-fluorobenzoic acid (2 equiv)	Toluene	NR

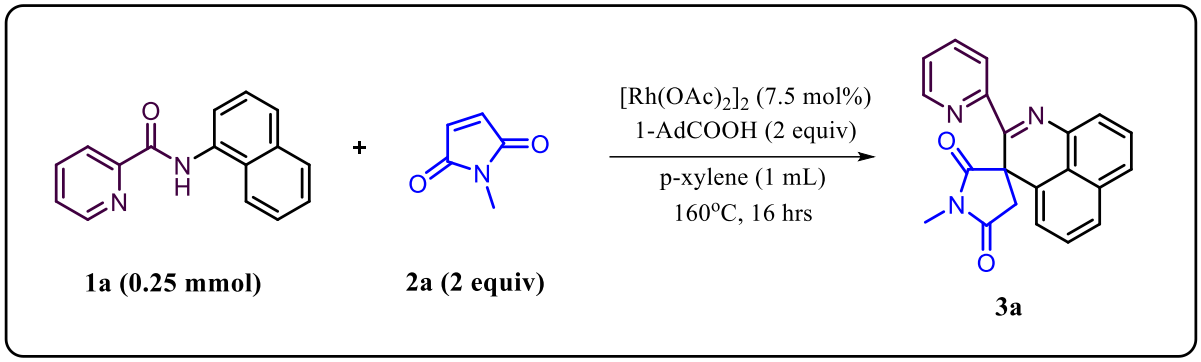
4	$[Rh(OAc)_2]_2$ (5 mol%)	Phenylpropiolic acid (2 equiv)	Toluene	NR
5	$[Rh(OAc)_2]_2$ (5 mol%)	AcOH (2 equiv)	Toluene	Trace
6	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	Toluene	42
7	$[Rh(OAc)_2]_2$ (5 mol%)	2,5-difluorobenzoic acid (2 equiv)	Toluene	NR
8	$[Rh(OAc)_2]_2$ (5 mol%)	1-Methyl-1-cyclohexanecarboxylic Acid (2 equiv)	Toluene	30
9	$[Rh(OAc)_2]_2$ (5 mol%)	MesCOOH (2 equiv)	Toluene	NR
10	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (1 equiv) + NaOAc (1 equiv)	Toluene	NR
11	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (1 equiv) + AgOAc (1 equiv)	Toluene	NR
12	$[Rh(OAc)_2]_2$ (5 mol%)	KOAc (2 equiv)	Toluene	NR
13	$[Rh(OAc)_2]_2$ (5 mol%)	K_2HPO_4 (2 equiv)	Toluene	NR
14	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	DMF	35
15	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	p-xylene	64
16	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	m-xylene	47
17	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	DMA	15
18	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	THF	40
19	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	PhCl	31
20	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	F-Benzene	NR
21	$[Rh(OAc)_2]_2$ (5 mol%)	1-AdCOOH (2 equiv)	mesitylene	49
22	$[RhCl(COD)]_2$ (5 mol%)	1-AdCOOH (2 equiv)	p-xylene	NR
23[a]	$[Rh(OAc)_2]_2$ (7.5 mol%)	1-AdCOOH (2 equiv)	p-xylene	trace
24[b]	$[Rh(OAc)_2]_2$ (7.5 mol%)	1-AdCOOH (2 equiv)	p-xylene	15

25[c]	$[Rh(OAc)_2]_2$ (7.5 mol%)	1-AdCOOH (2 equiv)	p-xylene	80
26[d]	$[Rh(OAc)_2]_2$ (7.5 mol%)	1-AdCOOH (2 equiv)	p-xylene	81
27[b]	$[Cp^*Rh(OAc)_2]$ (7.5 mol%)	1-AdCOOH (2 equiv)	p-xylene	trace
28	**$[Rh(OAc)_2]_2$ (7.5 mol%)**	**1-AdCOOH (2 equiv)**	**p-xylene**	**89**

Reaction conditions: **1a** (0.25 mmol), **2a** (2 equiv), Catalyst (mol%), Additive (equiv), and Solvent (1 mL) at 160 °C in a carousal tube under air..[a]110 ºC and 120 ºC. [b]130 ºC. [c]Under N_2. [d]Under O_2.

Table S1: *Optimization study for spiro annulation of 1-naphthylamide*

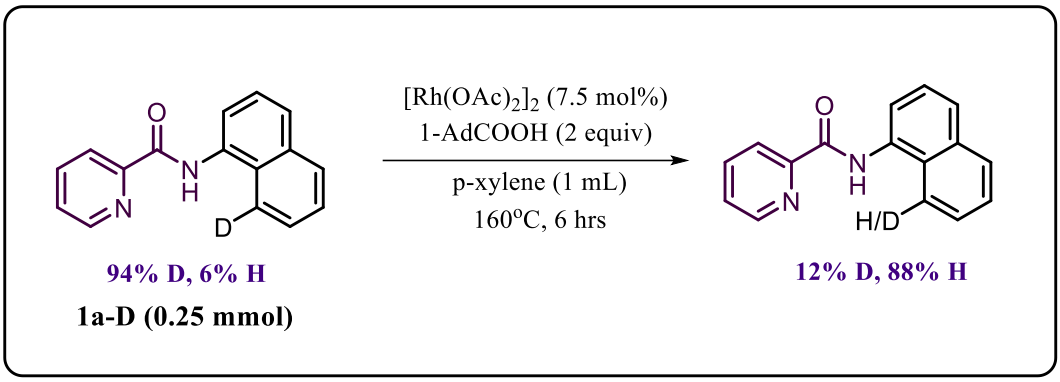
4. Experimental procedure for annulation reaction:

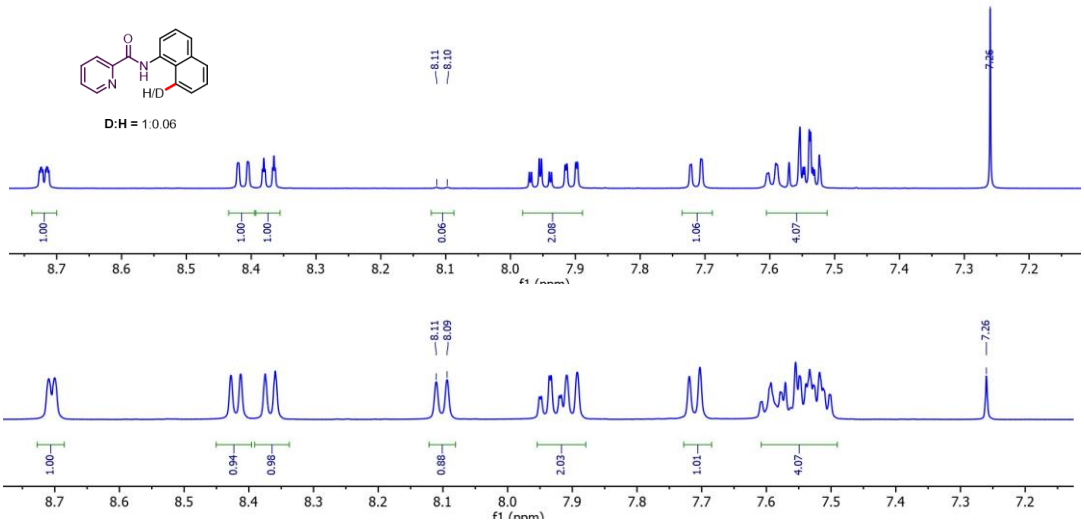


In an oven-dried carousel tube equipped with a magnetic stir bar was charged with appropriate amide **1a** (0.25 mmol, 1.0 equiv), maleimide derivatives **2a** (0.5 mmol, 2.0 equiv), $[Rh(OAc)_2]_2$ (7.5 mol%, 8.3 mg), 1-adamantanecarboxylic acid (2 equiv, 90 mg), and p-xylene (1 mL) as a solvent. The carousel tube was closed with screw cap and stirred at 160 ºC for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and quenched with water (15 mL). Then the reaction mixture was extracted with EtOAc (3 × 20 mL) and the combined organic solvent was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by Flash column chromatography (ethyl acetate/Hexane = 1/4) to give a pure spiro benzo[de]quinoline product **3a.**

5. Control experiments & mechanism study:

❖ Deuterium Labelling study:


[Rh(OAc)2]2 (7.5 mol%)
1-AdCOOH (2 equiv)
p-xylene (1 mL)
160°C, 6 hrs
94% D, 6% H
1a-D (0.25 mmol)
12% D, 88% H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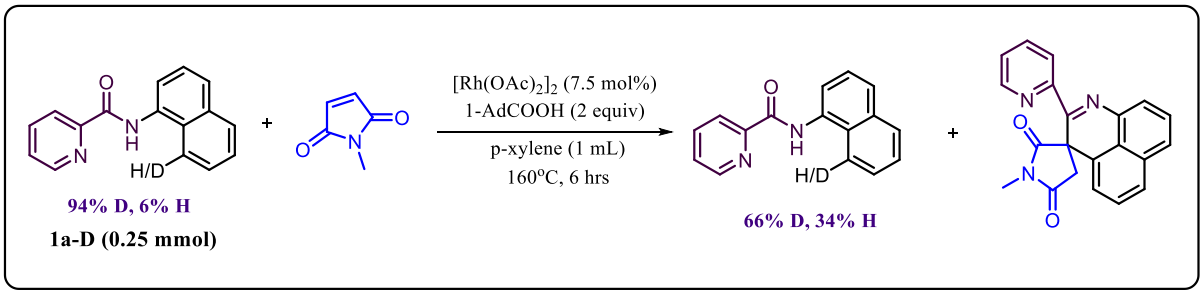
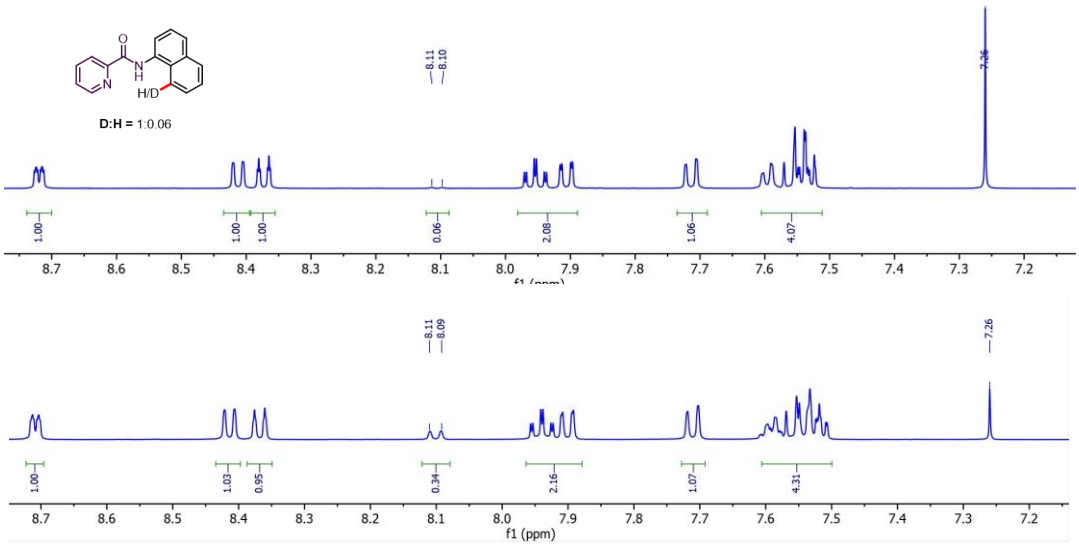
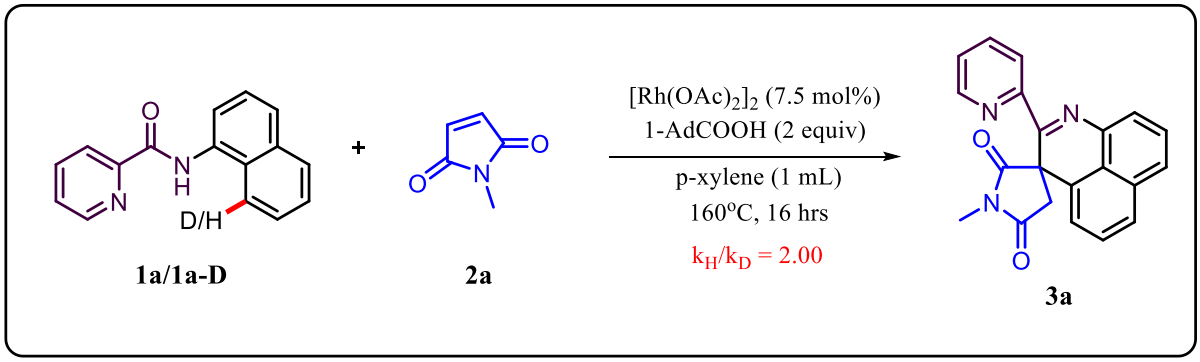

[Rh(OAc)2]2 (7.5 mol%)
1-AdCOOH (2 equiv)
p-xylene (1 mL)
160°C, 6 hrs
94% D, 6% H
1a-D (0.25 mmol)
66% D, 34% H



❖ KIE studies:

Two separate oven-dried carousal tubes were charged with a magnetic stir bar, 1a or 1a-D (1.0 equiv, 0.25 mmol), N-methyl maleimide (2a) (0.5 mmol, 2 equiv), $[Rh(OAc)_2]_2$ (7.5 mol%, 8.3 mg), 1-adamantanecarboxylic acid (2 equiv, 90 mg), and p-xylene (1 mL) as a solvent. The reaction tubes were capped and the reaction mixture was allowed to stir at 160 ºC. Took a sample after a fixed interval of time and filtered it, dissolved it in MeOH to inject the sample into HPLC.



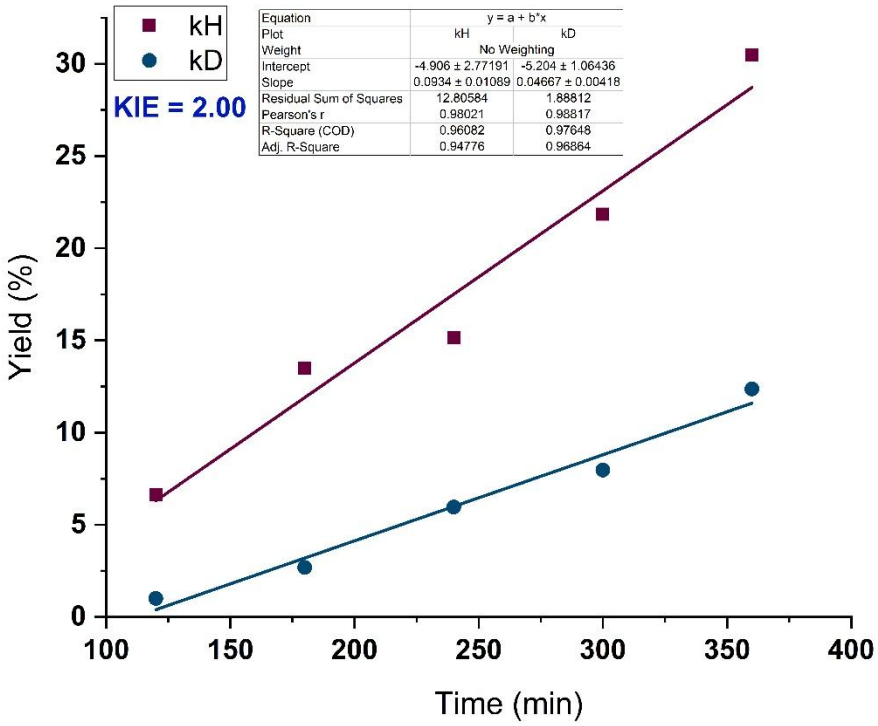


Figure S1: *KIE studies*

❖ Determination of Order of reaction:

The kinetics of annulation reactions were investigated using standard reaction conditions where amide **1a** reacts with maleimide **2a**. The progress of the reaction was examined after each 30 min time interval by HPLC.

Initially, it was assumed that the rate of the reaction depended on the starting materials (i.e., amide and maleimide) and the catalyst.

The rate law is;

Rate of reaction = $k[\text{amide}]^x[\text{maleimide}]^y[\text{catalyst}]^z$……. (1)

x = Order of the reaction with respect to amide

y = Order of the reaction with respect to maleimide

z = Order of the reaction with respect to catalyst

❖ Determination of order with respect to amide:

Run	*N-(naphthalen-1-yl)Picolinamide (mmol)*	*N-methyl maleimide (mmol)*	*$[Rh(OAc)_2]_2$*	*1-AdCOOH (mmol)*	*p-Xylene (mL)*
1	0.2	0.4	7.5 mol%	0.4	1
2	0.1	0.4	7.5 mol%	0.4	1

From the different sets of experiments (run 1 and run 2) the following product formation plot was observed:

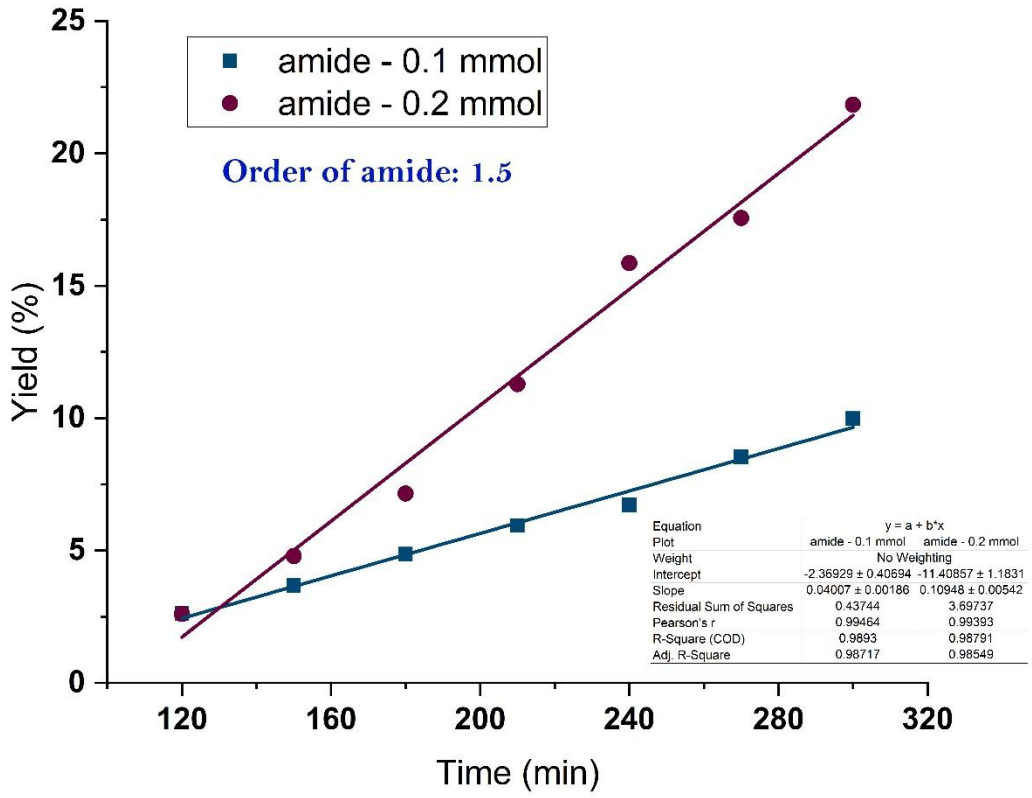


Figure S2: *Product formation plot in runs 1 and 2 with respect to amide*

The rate of the reaction was evaluated by calculating the initial progress of the reaction.

Rate of the 1st experiment (for Run 1) = $k[amide]^x[maleimide]^y[catalyst]^z$

$6.569 = k[0.2]^x[0.4]^y[0.015]^z$…….(2)

Rate of the 2st experiment (for Run 2) = $k[amide]^x[maleimide]^y[catalyst]^z$

$2.404 = k[0.1]^x[0.4]^y[0.015]^z$…….(3)

Hence, from the equations (2) and (3)

We get. $6.569/2.404 = [0.2]^x/[0.1]^x$

or, $2.7325 = [2]^x$

or, $\ln(2.7325) = x\ln(2)$

or, $x = \sim 1.45$

So, the order of reaction to amide derivative is ~ 1.5

❖ Determination of order with respect to maleimide:

Run	***N-(naphthalen-1-yl)Picolinamide (mmol)***	***N-methyl maleimide (mmol)***	***$[Rh(OAc)_2]_2$***	***1-AdCOOH (mmol)***	***p-Xylene (mL)***
1	0.2	0.4	7.5 mol%	0.4	1
2	0.2	0.6	7.5 mol%	0.4	1

From the different sets of experiments (run 1 and run 2) the following product formation plot was observed:

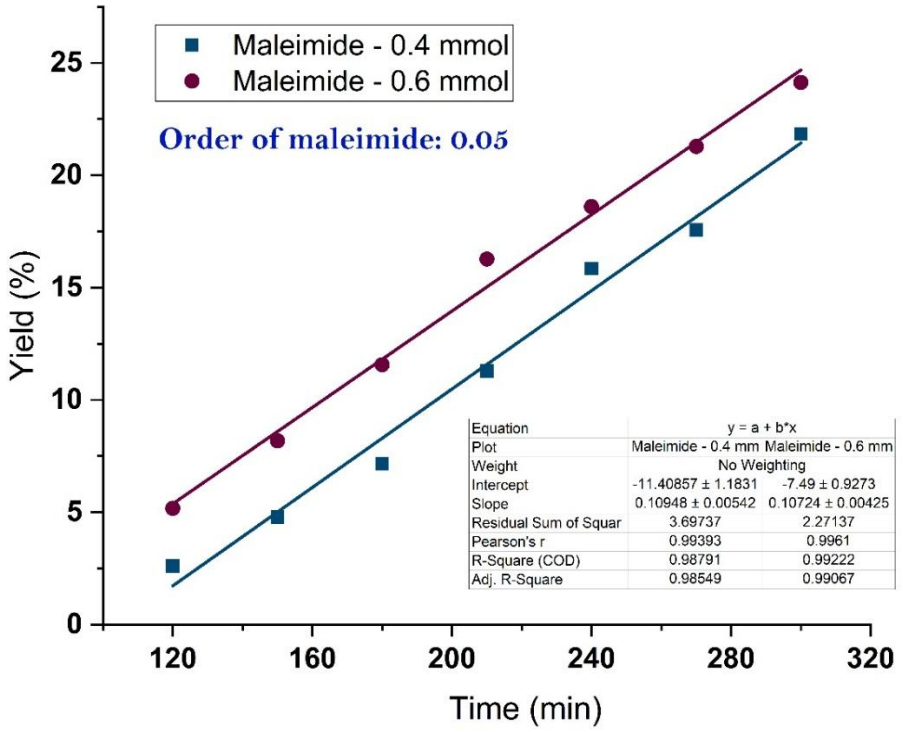


Figure S3*: Product formation plot in runs 1 and 2 with respect to maleimide*

The rate of the reaction was evaluated by calculating the initial progress of the reaction.

Rate of the 1st experiment (for Run 1) = k[amide]^{x}[maleimide]^{y}[catalyst]^{z}

6.569 = k[0.2]^{x}[0.4]^{y}[0.015]^{z}…….(2)

Rate of the 2st experiment (for Run 2) = k[amide]^{x}[maleimide]^{y}[catalyst]^{z}

6.434 = k[0.2]^{x}[0.6]^{y}[0.015]^{z}…….(4)

Hence, from the equations (2) and (4)

We get. 6.434/6.569 = [0.6]^{y}/[0.4]^{y}

or, 0.9794 = [1.5]^{y}

or, ln(0.9794) = yln(1.5)

or, y = ~0.051

So, the order of reaction to the maleimide derivative is ~ 0.05

❖ Determination of order with respect to Catalyst:

Run	***N-(naphthalen-1-yl)picolinamide(mmol)***	***N-methyl maleimide (mmol)***	***$[Rh(OAc)_2]_2$***	***1-AdCOOH (mmol)***	***p-Xylene (mL)***
1	0.2	0.4	3.75 mol%	0.4	1
2	0.2	0.4	7.5 mol%	0.4	1

As a part of the mechanistic investigation the reaction profile of the transformation has been monitored with the different catalyst loading. The kinetics data sets have been plotted in the form of Product concentration vs normalized time scale.[8-10] The processed data reflected a catalytic order of 1.8 for the $[Rh(OAc)_2]$

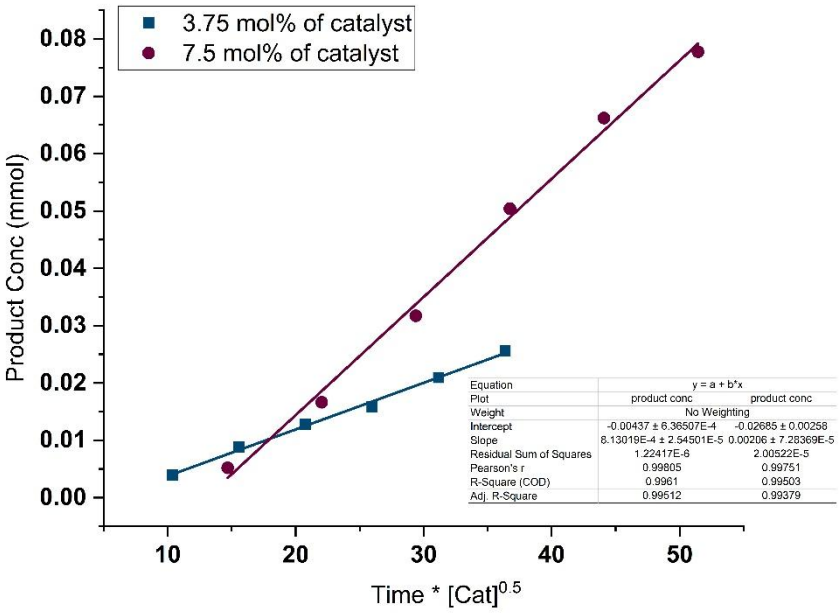


Figure S4: *Representative plot of concentration of product (mmol) vs. time (min) for the reaction of N-methyl maleimide and amide, in different concentration of catalyst. Determination of catalyst order with normalized time axis (n = 0.5).*

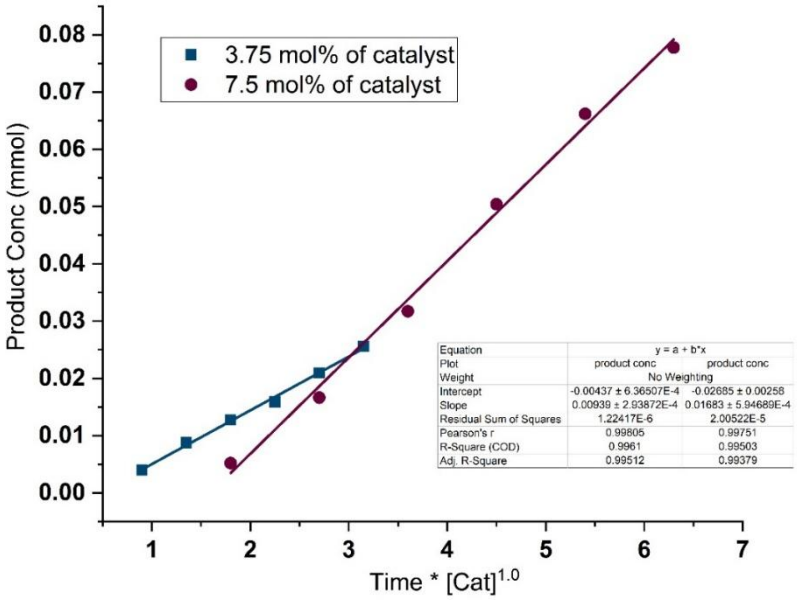


Figure S5: *Representative plot of concentration of product (mmol) vs. time (min) for the reaction of N-methyl maleimide and amide, in different concentration of catalyst. Determination of catalyst order with normalized time axis (n = 1.0).*

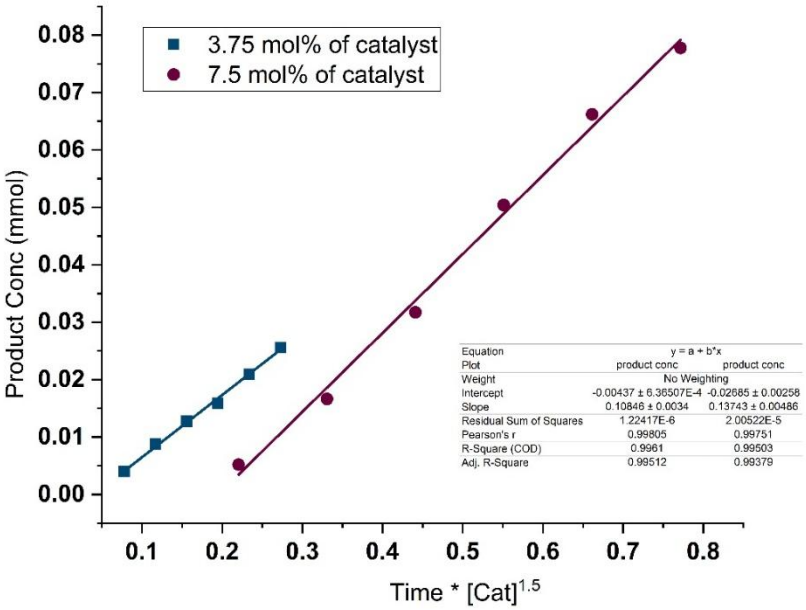


Figure S6: *Representative plot of concentration of product (mmol) vs. time (min) for the reaction of N-methyl maleimide and amide, in different concentration of catalyst. Determination of catalyst order with normalized time axis (n = 1.5).*

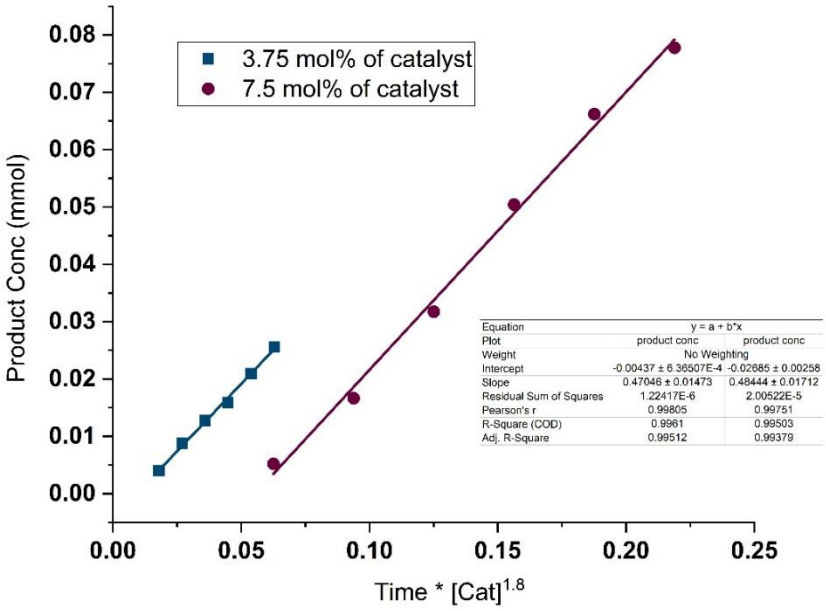


Figure S7: *Representative plot of concentration of product (mmol) vs. time (min) for the reaction of N-methyl maleimide and amide, in different concentration of catalyst. Determination of catalyst order with normalized time axis (n = 1.8).*

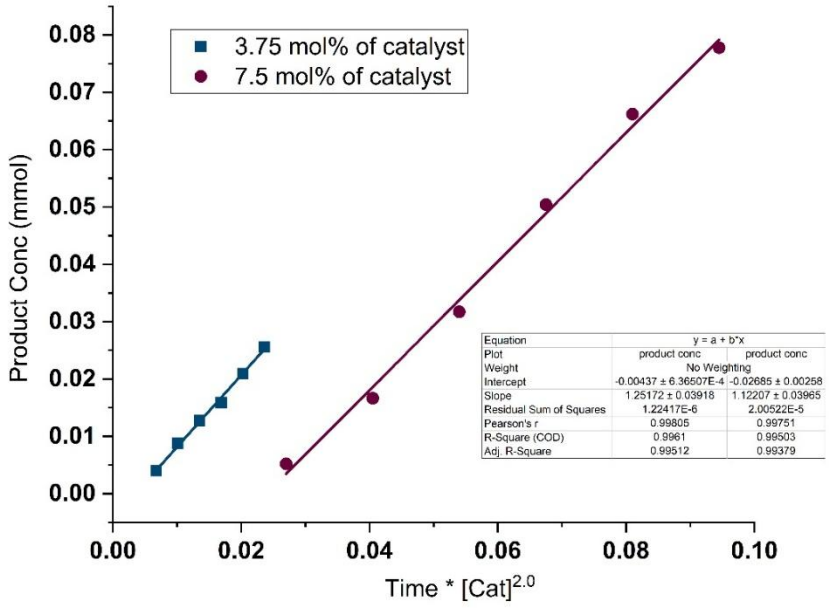
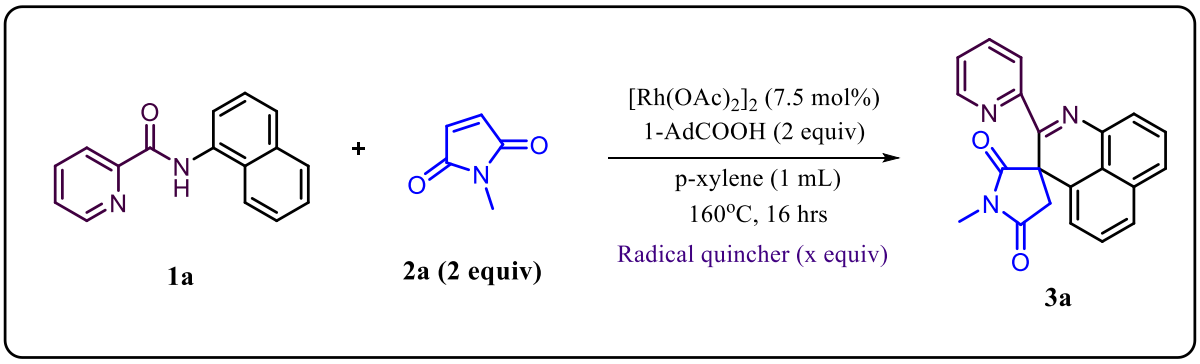


Figure S8: *Representative plot of concentration of product (mmol) vs. time (min) for the reaction of N-methyl maleimide and amide, in different concentration of catalyst. Determination of catalyst order with normalized time axis (n = 2.0).*

❖ Control experiments:

The radical quenching experiment was carried out with a very well-known radical quencher. However, it was observed that the yield of the product remained unchanged, thus involvement of any radical species in the reaction may be ruled out.



1a + **2a (2 equiv)** → **3a**

Entry	*Radical Quencher*	*Yield*
1	BHT (2 equiv.)	78%
2	TEMPO (1 equiv.)	69%
3	TEMPO (2 equiv.)	61%

Table S2: *Control experiments*

❖ Intermediate identification:

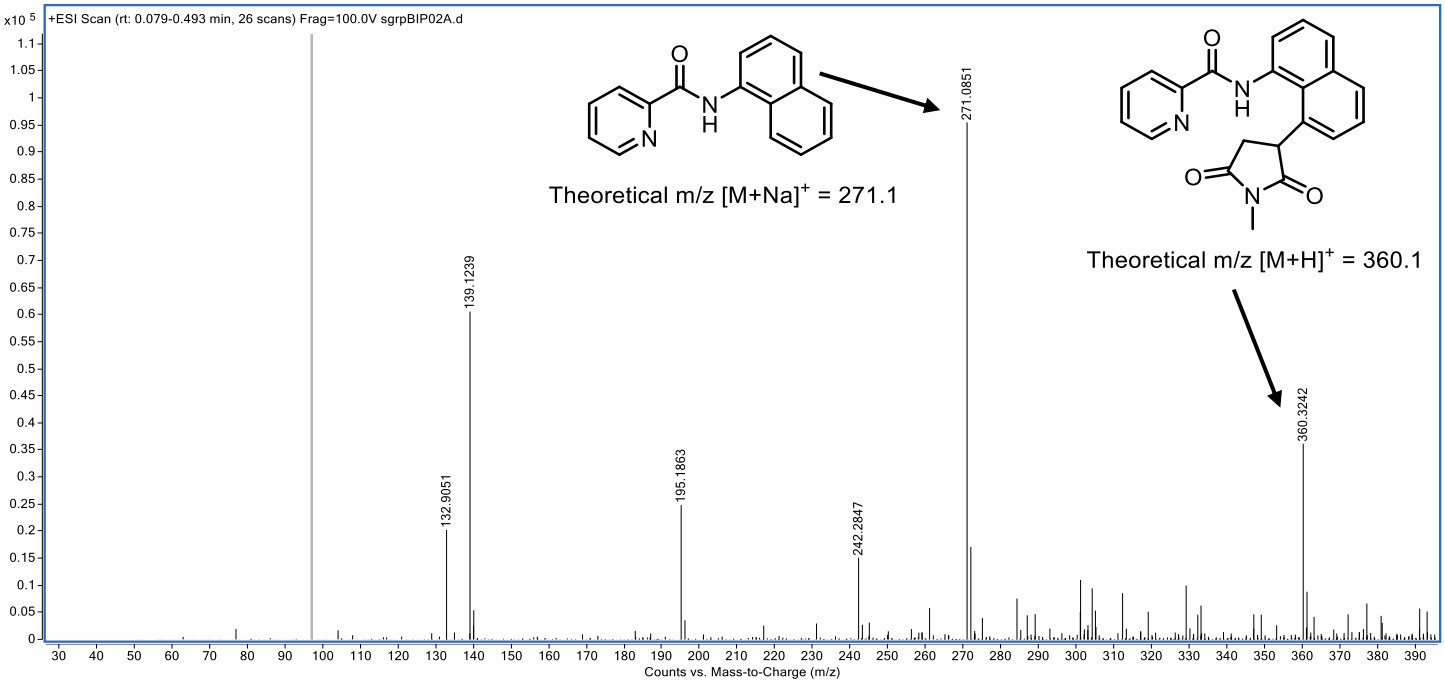


Figure S9 *: ESI MS data for crude reaction mixture to identify the intermediate*

6. Photophysical Studies of benzo[*de*]quinoline product (Quantum yield):

Sr No.	Compound[a]	Absorption λ_{max}(abs) (nm)	Emission λ_{max}(em)[b] (nm)	Quantum Yield[d] (ϕ)
1	3a	365	466	0.0998514
2	3b	369	463	0.01460789
3	3c	363	454	0.16914304
4	3d	370	469	0.33993223
5	3k	300	520	0.0065846
6	3l	372	475	0.00483021
7	3n	366	469	0.11544247
8	3o	366	469	0.29163464
9	3q	366	469	0.28970887
10	3u	366	466	0.1403963
11	3v	365	469	0.27315717

[a]Recorded in EtOH at 25 °C. [b]Excited at the longest wavelength of the absorption maxima. [d]The fluorescence quantum yield was calculated using Anthracene as a standard (ϕ_{std} = 0.27 for 10^{-3} M solution).

Table S3: *Quantum yield calculation of benzo[de]quinoline product*

7. Crystal data and structure:

I. Crystal data and structure for 3a	
Name of compound	1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione
Identification code	3a
Empirical Formula	$C_{21}H_{15}N_3O_2$
Formula weight	341.36
Temperature/K	298
Crystal system	monoclinic
Space group	P21/n
a/Å	8.9088(4)
b/Å	10.2842(5)
c/Å	18.4632(8)
α/°	90
β/°	95.650(2)
γ/°	90
Volume/Å3	1683.38(13)
Z	4
ρcalcg/cm3	1.347
μ/mm-1	0.089
F(000)	712.0
Crystal size/mm3	0.44 × 0.29 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.434 to 72.9
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -30 ≤ l ≤ 30
Reflections collected	98263

Independent reflections	8220 [Rint = 0.0932, Rsigma = 0.0395]
Data/restraints/parameters	8220/0/236
Goodness-of-fit on F2	1.077
Final R indexes [I>=2σ (I)]	R1 = 0.0624, wR2 = 0.1738
Final R indexes [all data]	R1 = 0.0991, wR2 = 0.2031
Largest diff. peak/hole / e Å-3	0.47/-0.35

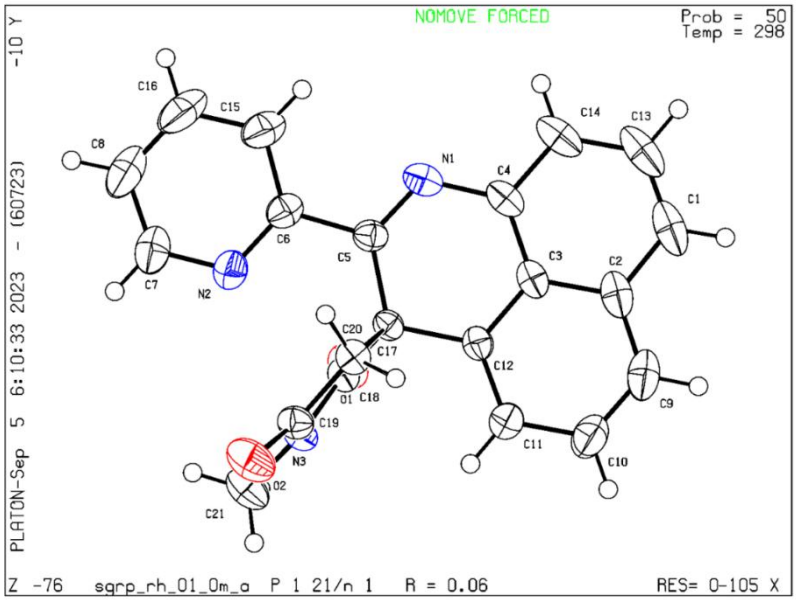


Figure S10 : *ORTEP diagram of the organic compound **3a***

ORTEP diagram of the organic compound **3a** with atom numbering scheme (50% probability factor for the thermal ellipsoids CCDC No.: 2292900 is shown in Figure S10.

II. Crystal data and structure 3q	
Name of compound	1'-(4-methoxyphenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione
Identification code	3q
Empirical Formula	$C_{27}H_{19}N_3O_3$
Formula weight	433.45
Temperature/K	100

Crystal system	monoclinic
Space group	P21/n
a/Å	8.401(3)
b/Å	10.392(4)
c/Å	24.781(9)
α/°	90
β/°	96.749(13)
γ/°	90
Volume/Å3	2148.5(14)
Z	4
ρcalcg/cm3	1.340
μ/mm-1	0.089
F(000)	904.0
Crystal size/mm3	0.13 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.968 to 54.984
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -32 ≤ l ≤ 32
Reflections collected	111901
Independent reflections	4898 [Rint = 0.0965, Rsigma = 0.0274]
Data/restraints/parameters	4898/0/299
Goodness-of-fit on F2	1.066
Final R indexes [I>=2σ (I)]	R1 = 0.0425, wR2 = 0.0943
Final R indexes [all data]	R1 = 0.0735, wR2 = 0.1158
Largest diff. peak/hole / e Å-3	0.15/-0.18

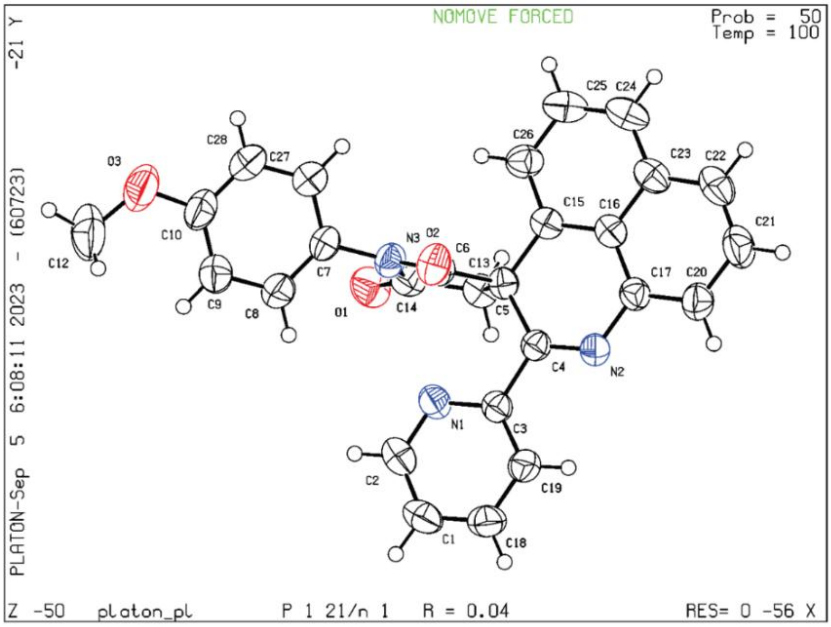


Figure S11 : *ORTEP diagram of the organic compound **3q***

ORTEP diagram of the organic compound **3q** with atom numbering scheme (50% probability factor for the thermal ellipsoids. CCDC No.: 2292974 is shown in Figure S11.

III. Crystal data and structure 3v	
Name of compound	1'-mesityl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione
Identification code	3v
Empirical Formula	$C_{29}H_{23}N_3O_2$
Formula weight	445.50
Temperature/K	273.15
Crystal system	monoclinic
Space group	P21
a/Å	11.6874(5)
b/Å	7.3297(3)
c/Å	15.2220(7)
α/°	90
β/°	100.470(2)
γ/°	90
Volume/Å3	1282.28(10)

Z	2
ρcalcg/cm3	1.154
μ/mm-1	0.074
F(000)	468.0
Crystal size/mm3	0.21 × 0.11 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.056 to 49.996
Index ranges	-13 ≤ h ≤ 13, -8 ≤ k ≤ 8, -18 ≤ l ≤ 18
Reflections collected	43802
Independent reflections	4510 [Rint = 0.0596, Rsigma = 0.0284]
Data/restraints/parameters	4510/1/310
Goodness-of-fit on F2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0330, wR2 = 0.0884
Final R indexes [all data]	R1 = 0.0391, wR2 = 0.0931
Largest diff. peak/hole / e Å-3	0.10/-0.13
Flack parameter	0.4(5)

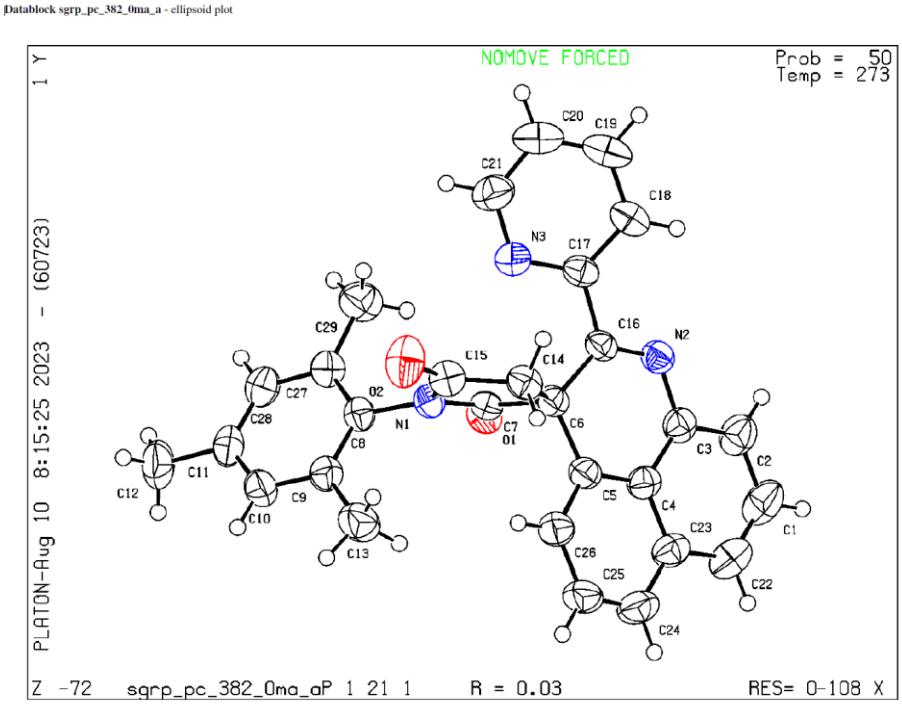


Figure S12 : *ORTEP diagram of the organic compound **3v***

ORTEP diagram of the organic compound **3v** with atom numbering scheme (50% probability factor for the thermal ellipsoids, CCDC No.: 2292898 is shown in Figure S12.

8. References:

[1] S. Sarkar, T. Sahoo, C. Sen, S. C. Ghosh, *Chem. Comm.* 2021, **57**, 8949.

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[5] H. Zhu, S. Sun, H. Qiao, F. Yang, J. Kang, Y. Wu, Y. Wu, *Org. Lett.* 2018, **20**, 620.

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[7] R. Mandal, B. Emayavaramban, B. Sundararaju, *Org. Lett.* 2018, **20**, 2835.

[8] Bures, J. *Angew. Chem. Int. Ed*. 2016, **55**, 2028

[9] S. Maity, R. Kancherla, U. Dhawa, E. Hoque, S. Pimparkar, D. Maiti, *ACS Catal.* 2016, **6**, 5493.

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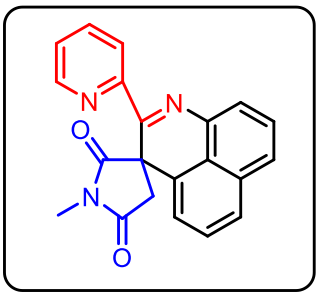
9. NMR Characterization Data:

1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3a)

Yellowish white (76 mg, 89%) (n-Hexane: EtOAc = 4:1). M.P. = 215-216 ºC



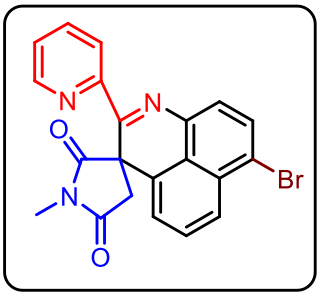
^{1}H NMR (600 MHz, Chloroform-d): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.53 (ddd, *J* = 18.8, 8.2, 7.2 Hz, 2H), 7.31 – 7.26 (m, 2H), 3.50 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 2.84 (d, *J* = 18.2 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.2, 177.1, 160.9, 153.8, 148.0, 138.7, 137.1, 134.8, 132.0, 129.0, 127.6, 127.4, 126.6, 125.2, 122.9, 122.6, 120.5, 51.2, 50.6, 26.0.

HRMS-ESI: calcd. For $C_{21}H_{16}N_3O_2$ $[M+H]^+$: 342.1243 Found: 342.1242

7-bromo-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3b)

Brown solid (92 mg, 88%) (n-Hexane: EtOAc = 4:1). M.P. = 265-266 ºC



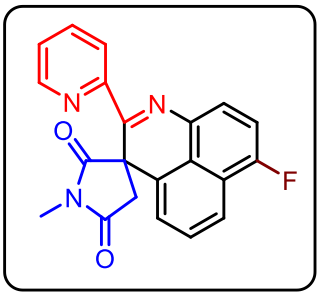
^{1}H NMR (600 MHz, Chloroform-d): δ 8.51 (d, *J* = 8.1 Hz, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 6.1 Hz, 1H), 3.50 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 2.83 (d, *J* = 18.1 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.0, 176.9, 161.4, 153.6, 148.1, 138.5, 137.2, 135.3, 131.6, 131.5, 128.8, 127.2, 126.9, 125.4, 123.6, 123.1, 123.0, 121.5, 51.0, 50.6, 26.1.

HRMS-ESI: calcd. For $C_{21}H_{15}BrN_3O_2$ $[M+H]^+$: 420.0348 Found: 420.0348

7-fluoro-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3c)

White solid (63 mg, 71%) (n-Hexane: EtOAc = 4:1). M.P. = 235-236 ºC



1H NMR (600 MHz, Chloroform-d): δ 8.51 (d, *J* = 7.9 Hz, 1H), 8.41 (d, *J* = 5.1 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 5.1 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.23 (dd, *J* = 10.1, 8.0 Hz, 1H), 3.50 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 2.83 (d, *J* = 18.0 Hz, 1H).

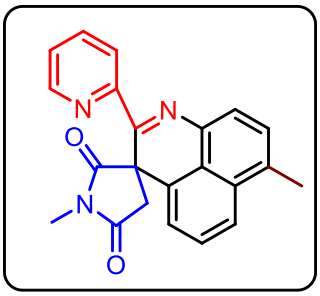
^{13}C NMR (151 MHz, Chloroform-d): δ 178.1, 177.0, 160.1, 159.6, 157.8 (C−F, $^{1}J_{C-F}$ = 258 Hz), 153.8, 148.0, 137.2, 135.2 (C−F, $^{3}J_{C-F}$ = 7.5 Hz), 128.0, 126.7 (C−F, $^{3}J_{C-F}$ = 8.4 Hz), 125.2, 123.8, 123.2 (C−F, $^{2}J_{C-F}$ = 19.63 Hz), 122.8, 121.5, 120.7, 111.2 (C−F, $^{2}J_{C-F}$ = 21.14 Hz), 51.0, 50.2, 26.0.

^{19}F {^{1}H} NMR (564 MHz, $CDCl_3$): δ -119.0

HRMS-ESI: calcd. For $C_{21}H_{14}FN_3O_2Na$ $[M+Na]^+$: 382.0968 Found: 382.0981

1',7-dimethyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3d)

Yellow solid (71 mg, 80%) (n-Hexane: EtOAc = 4:1). M.P. = 212-213 ºC



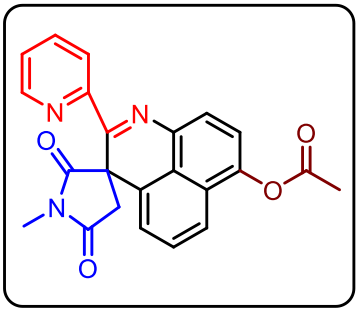
^{1}H NMR (600 MHz, Chloroform-d): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.1 Hz, 2H), 3.49 (d, *J* = 18.1 Hz, 1H), 3.27 (s, 3H), 2.83 (d, *J* = 18.1 Hz, 1H), 2.69 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.4, 177.2, 159.8, 153.9, 148.0, 137.3, 137.1, 136.3, 135.3, 132.1, 128.1, 127.4, 126.5, 125.0, 124.1, 122.7, 122.5, 120.5, 51.1, 50.7, 26.0, 19.8.

HRMS-ESI: calcd. For $C_{22}H_{17}N_3O_2Na$ $[M+Na]^+$: 378.1218 Found: 378.1222

1'-methyl-2',5'-dioxo-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidin]-7-yl acetate (3e)

Yellow solid (76 mg, 76%) (n-Hexane: EtOAc = 4:1). M.P. = 252-254 ºC



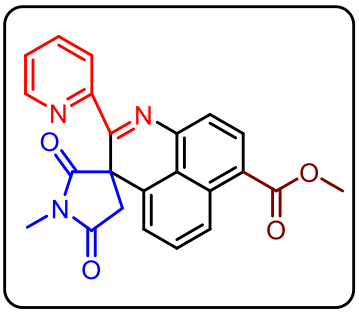
^{1}H NMR (600 MHz, Chloroform-d): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 4.7 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.30 (m, 2H), 3.49 (d, *J* = 18.1 Hz, 1H), 3.27 (s, 3H), 2.83 (d, *J* = 18.1 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.1, 177.0, 169.3, 160.7, 153.7, 148.0, 146.9, 137.2, 136.8, 135.4, 128.1, 126.4, 126.3, 125.3, 123.4, 122.9, 121.4, 121.3, 119.8, 51.0, 50.4, 26.0, 21.2.

HRMS-ESI: calcd. For $C_{23}H_{18}N_3O_4$ $[M+H]^+$: 400.1297 Found: 400.1299

methyl 1'-methyl-2',5'-dioxo-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-7-carboxylate (3f)

Yellow solid (62 mg, 65%) (n-Hexane: EtOAc = 4:1). M.P. =260-262 ºC



^{1}H NMR (600 MHz, Chloroform-d): δ 8.95 (d, *J* = 8.6 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 4.4 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.35 (t, *J* = 6.3 Hz, 2H), 4.02 (s, 3H), 3.51 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 2.85 (d, *J* = 18.2 Hz, 1H).

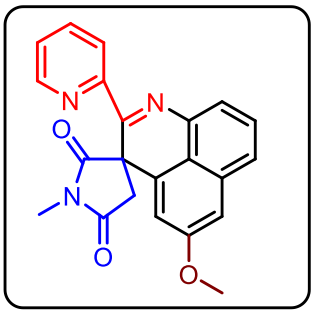
^{13}C NMR (151 MHz, Chloroform-d): δ 177.9, 176.9, 167.3, 163.6, 153.5, 148.2, 142.1, 137.3, 135.0, 132.4, 131.4, 129.0, 127.4, 126.2, 125.7, 125.4, 123.2, 123.1, 120.9, 52.4, 51.1, 29.8, 26.1.

HRMS-ESI: calcd. For $C_{23}H_{17}N_3O_4$ Na $[M+Na]^+$: 422.1117 Found: 422.1109

5-methoxy-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3h)

Brown solid (60 mg, 64%) (n-Hexane: EtOAc = 4:1). M.P. = 245-247 ºC

^{1}H NMR (600 MHz, Chloroform-d): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 3.7 Hz, 1H), 7.81 (t, *J* = 6.9 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 6.7 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.32



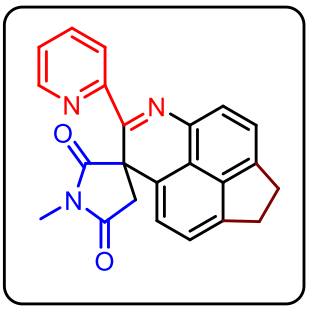
– 7.28 (m, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 3.91 (s, 3H), 3.47 (d, *J* = 18.1 Hz, 1H), 3.25 (s, 3H), 2.84 (d, *J* = 18.1 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.0, 176.8, 160.6, 158.8, 153.8, 148.0, 138.8, 137.1, 136.6, 134.5, 128.3, 128.1, 125.2, 124.6, 122.9, 115.9, 115.1, 105.9, 55.6, 51.0, 50.7, 26.0.

HRMS-ESI: calcd. For $C_{22}H_{17}N_3O_3Na$ $[M+Na]^+$: 394.1168 Found: 394.1146

1'-methyl-2-(pyridin-2-yl)-6,7-dihydrospiro[indeno[6,7,1-def]quinoline-3,3'-pyrrolidine]-2',5'-dione (3i)

Yellow solid (55 mg, 59%) (n-Hexane: EtOAc = 4:1). M.P. = 260-261 ºC



^{1}H NMR (600 MHz, Chloroform-d): δ 8.51 (d, *J* = 8.1 Hz, 1H), 8.39 (d, *J* = 4.3 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 11.6, 7.2 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 3.49 (d, *J* = 18.1 Hz, 1H), 3.42 (s, 4H), 3.25 (s, 3H), 2.83 (d, *J* = 18.1 Hz, 1H).

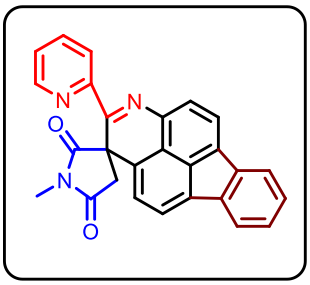
^{13}C NMR (151 MHz, Chloroform-d): δ 178.4, 177.4, 160.3, 154.3, 147.9, 147.5, 145.4, 138.8, 137.0, 136.0, 130.6, 127.3, 124.9, 123.6, 122.9, 121.7, 120.8, 118.3, 51.3, 50.2, 31.3, 31.1, 25.9.

HRMS-ESI: calcd. For $C_{23}H_{17}N_3O_2Na$ $[M+Na]^+$: 390.1218 Found: 390.1199

1'-methyl-2-(pyridin-2-yl)spiro[fluoreno[2,1,9-def]quinoline-3,3'-pyrrolidine]-2',5'-dione (3j)

Yellow solid (44 mg, 42%) (n-Hexane: EtOAc = 3:1). M.P. = 265-267 ºC

^{1}H NMR (600 MHz, Chloroform-d): δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 4.6 Hz, 1H), 8.01 (d, *J* = 6.9 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.81



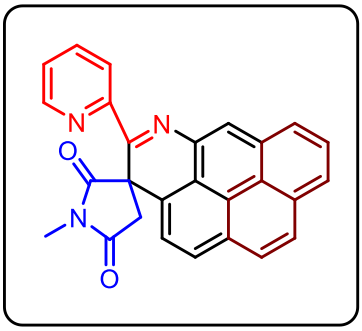
(d, *J* = 7.6 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.35 – 7.31 (m, 1H), 3.55 (d, *J* = 18.3 Hz, 1H), 3.30 (s, 3H), 2.92 (d, *J* = 18.3 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 177.9, 177.2, 162.7, 154.1, 148.1, 140.1, 139.2, 139.2, 137.5, 137.2, 136.1, 135.0, 131.6, 128.1, 128.1, 127.1, 125.3, 123.3, 123.3, 122.3, 122.3, 122.3, 121.8, 117.0, 50.3, 49.2, 26.2.

HRMS-ESI: calcd. For $C_{27}H_{18}N_3O_2$ $[M+H]^+$: 416.1399 Found: 416.1418

1'-methyl-4-(pyridin-2-yl)spiro[phenanthro[3,4,5-defg]quinoline-3,3'-pyrrolidine]-2',5'-dione (3k)

Brown solid (60 mg, 58%) (n-Hexane: EtOAc = 3:1). M.P. = 269-271 ºC



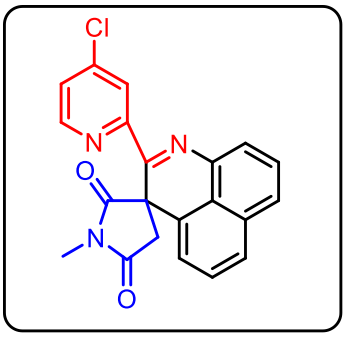
^{1}H NMR (600 MHz, Chloroform-d): δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 4.7 Hz, 1H), 8.23 (q, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.07 – 7.98 (m, 3H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.34 (dd, *J* = 7.3, 4.5 Hz, 1H), 3.61 (d, *J* = 18.3 Hz, 1H), 3.38 (s, 3H), 3.02 (d, *J* = 18.3 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.4, 177.3, 161.1, 153.9, 148.1, 137.2, 136.4, 134.7, 132.2, 131.4, 128.3, 127.5, 127.0, 126.9, 126.7, 126.2, 125.7, 125.3, 124.3, 124.0, 123.8, 123.0, 116.8, 51.7, 51.2, 26.2.

HRMS-ESI: calcd. For $C_{27}H_{20}N_3O_2$ $[M+H]^+$: 418.1556 Found: 418.3928

2-(4-chloropyridin-2-yl)-1'-methylspiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3l)

Brown solid (52 mg, 55%) (n-Hexane: EtOAc = 4:1). M.P. = 218-220 ºC



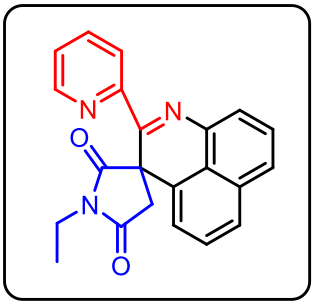
^{1}H NMR (600 MHz, Chloroform-d): δ 8.56 (d, *J* = 2.0 Hz, 1H), 8.32 (d, *J* = 5.2 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.56 (dt, *J* = 24.0, 7.8 Hz, 2H), 7.32 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 3.47 (d, *J* = 18.3 Hz, 1H), 3.25 (s, 3H), 2.85 (d, *J* = 18.3 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.0, 176.9, 159.6, 155.4, 148.9, 145.5, 138.4, 134.5, 133.0, 129.5, 127.7, 127.6, 127.0, 125.4, 123.2, 122.7, 120.5, 51.1, 50.7, 26.0.

HRMS-ESI: calcd. For $C_{21}H_{14}N_3ClO_2Na[M+Na]^+$: 398.0672 Found: 398.0662

1'-ethyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3m)

Brown solid (74 mg, 80%) (n-Hexane: EtOAc = 4:1). M.P. = 215-217 ºC



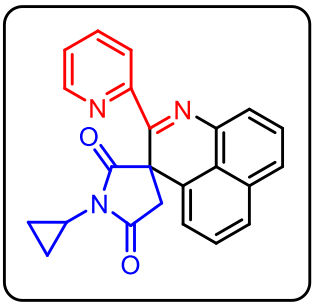
^{1}H NMR (600 MHz, Chloroform-d): δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 4.6 Hz, 1H), 7.83 – 7.75 (m, 3H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.53 (dt, *J* = 19.1, 7.8 Hz, 2H), 7.30 (dd, *J* = 7.5, 4.8 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 1H), 3.90 – 3.77 (m, 2H), 3.50 (d, *J* = 18.2 Hz, 1H), 2.80 (d, *J* = 18.2 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 177.7, 176.8, 161.0, 153.9, 147.5, 138.7, 137.0, 134.9, 133.0, 129.0, 127.6, 127.4, 126.5, 125.2, 122.9, 122.3, 120.5, 51.1, 50.5, 34.7, 12.5.

HRMS-ESI: calcd. For $C_{22}H_{18}N_3O_2$ $[M+H]^+$: 356.1399 Found: 356.1375

1'-cyclopropyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3n)

Brown solid (73 mg, 80%) (n-Hexane: EtOAc = 4:1). M.P. = 205-206 ºC



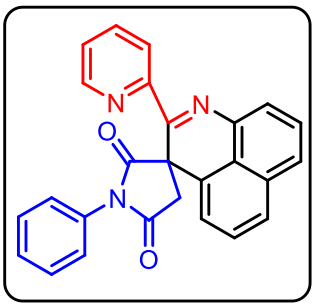
^{1}H NMR (600 MHz, Chloroform-d): δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 4.7 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.54 (dt, *J* = 19.6, 7.8 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 3.43 (d, *J* = 18.2 Hz, 1H), 2.86 (dt, *J* = 6.8, 3.0 Hz, 1H), 2.77 (d, *J* = 18.2 Hz, 1H), 1.16 (d, *J* = 8.4 Hz, 1H), 1.12 – 1.04 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 178.3, 177.4, 161.1, 153.8, 147.5, 138.7, 137.1, 135.0, 132.9, 129.0, 127.6, 127.6, 127.4, 126.5, 125.2, 122.9, 122.2, 120.4, 50.7, 50.0, 22.9, 5.3, 5.2.

HRMS-ESI: calcd. For $C_{23}H_{18}N_3O_2$ $[M+H]^+$: 368.1399 Found: 368.1395

1'-phenyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3o)

Yellow solid (79 mg, 78%) (n-Hexane: EtOAc = 4:1). M.P. = 222-223 ºC



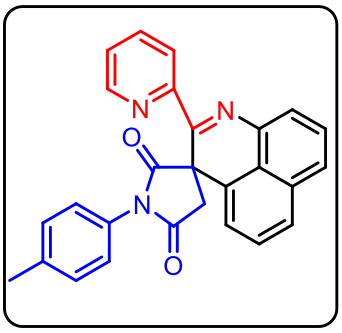
^{1}H NMR (600 MHz, Chloroform-d): δ 8.59 (d, *J* = 8.1 Hz, 1H), 8.55 (d, *J* = 4.7 Hz, 1H), 7.85 (dd, *J* = 12.3, 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 6.9 Hz, 2H), 7.56 (d, *J* = 4.5 Hz, 4H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.46 (q, *J* = 4.3 Hz, 1H), 7.38 – 7.34 (m, 1H), 3.67 (d, *J* = 18.1 Hz, 1H), 3.01 (d, *J* = 18.1 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.8, 175.9, 160.9, 153.8, 147.9, 138.7, 137.3, 135.0, 133.00, 133.0, 132.9, 129.4, 129.1, 128.8, 127.7, 127.6, 126.7, 126.6, 125.4, 123.0, 122.6, 120.5, 51.1, 50.5.

HRMS-ESI: calcd. For $C_{26}H_{18}N_3O_2$ $[M+H]^+$: 404.1399 Found: 404.1398

2-(pyridin-2-yl)-1'-(p-tolyl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3p)

Yellow solid (74 mg, 71%) (n-Hexane: EtOAc = 4:1). M.P. = 223-224 ºC



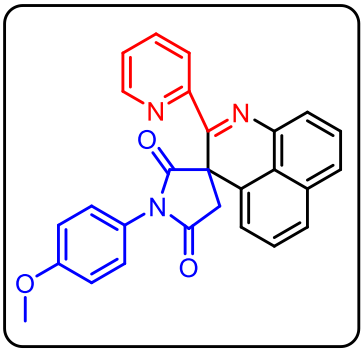
^{1}H NMR (600 MHz, Chloroform-d): δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 4.8 Hz, 1H), 7.85 (dd, *J* = 15.1, 7.5 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 3H), 3.66 (d, *J* = 18.4 Hz, 1H), 3.00 (d, *J* = 18.4 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.9, 176.1, 161.0, 153.9, 148.0, 138.8, 138.7, 137.2, 135.1, 133.0, 130.3, 130.1, 129.1, 127.7, 127.7, 127.6, 126.7, 126.4, 125.4, 123.1, 122.6, 120.5, 51.1, 50.5, 21.4.

HRMS-ESI: calcd. For $C_{27}H_{20}N_3O_2$ $[M+H]^+$: 418.1556 Found: 418.1563

1'-(4-methoxyphenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3q)

Yellow solid (90 mg, 83%) (n-Hexane: EtOAc = 3:1). M.P. = 230-231 ºC



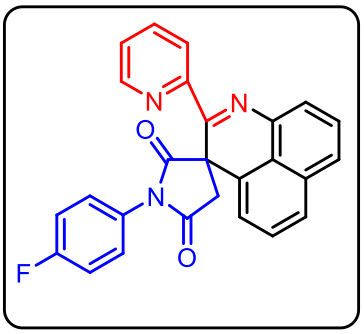
^{1}H NMR (600 MHz, Chloroform-d): δ 8.58 (d, *J* = 8.1 Hz, 1H), 8.54 (d, *J* = 4.7 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.57 (q, *J* = 7.8 Hz, 2H), 7.49 (dd, *J* = 18.4, 8.0 Hz, 3H), 7.36 – 7.32 (m, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.66 (d, *J* = 18.3 Hz, 1H), 3.00 (d, *J* = 18.3 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 177.0, 176.1, 160.9, 159.7, 153.8, 147.9, 137.2, 135.0, 132.9, 129.0, 127.7, 127.6, 127.5, 126.6, 125.5, 125.3, 123.0, 122.5, 120.4, 114.7, 55.6, 51.0, 50.4.

HRMS-ESI: calcd. For $C_{27}H_{20}N_3O_2$ $[M+H]^+$: 434.1505 Found: 434.1509

1'-(4-fluorophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3r)

Brown solid (74 mg, 70%) (n-Hexane: EtOAc = 4:1). M.P. = 243-244 ºC



^{1}H NMR (600 MHz, Chloroform-d): δ 8.58 (d, *J* = 8.0 Hz, 1H), 8.50 (d, *J* = 4.0 Hz, 1H), 7.83 (dd, *J* = 13.2, 7.1 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.53 (dd, *J* = 9.0, 4.9 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.25 – 7.21 (m, 2H).

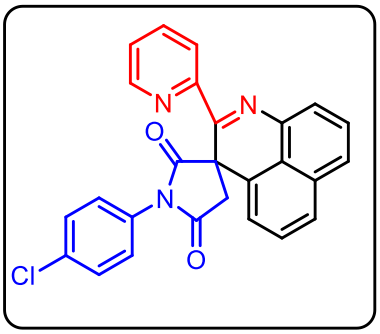
^{13}C NMR (151 MHz, Chloroform-d): δ 176.7, 175.8, 163.2 (C−F, $^{1}J_{C-F}$ = 249.15 Hz), 160.6, 153.8, 147.9, 138.6, 137.3, 134.8, 133.0, 129.1, 128.8, 128.4 (C−F, $^{3}J_{C-F}$ = 8.65 Hz), 127.7 (C−F, $^{3}J_{C-F}$ = 7.55 Hz), 127.6, 126.8, 125.4, 123.1, 122.5, 120.4, 116.5 (C−F, $^{2}J_{C-F}$ = 24.16 Hz), 51.0, 50.4.

^{19}F {^{1}H} NMR (564 MHz, $CDCl_3$): δ -112.2

HRMS-ESI: calcd. For $C_{26}H_{17}FN_3O_2$ $[M+H]^+$: 422.1305 Found: 422.1301

1'-(4-chlorophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3s)

Yellow solid (82 mg, 75%) (n-Hexane: EtOAc = 4:1). M.P. = 250-251 ºC



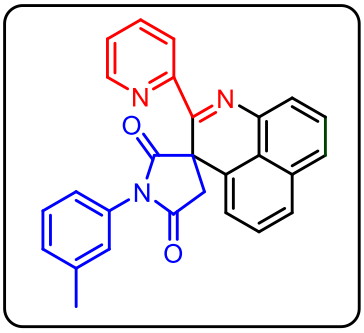
^{1}H NMR (600 MHz, Chloroform-d): δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.50 (d, *J* = 4.7 Hz, 1H), 7.86 (dd, *J* = 16.0, 8.5 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.54 – 7.49 (m, 4H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.35 (m, 1H), 3.65 (d, *J* = 18.4 Hz, 1H), 3.01 (d, *J* = 18.4 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.6, 175.6, 160.6, 153.7, 147.9, 138.6, 137.3, 134.8, 134.5, 134.4, 133.0, 131.4, 129.6, 129.2, 127.8, 127.8, 126.8, 125.4, 123.1, 122.5, 120.4, 51.0, 50.4.

HRMS-ESI: calcd. For $C_{26}H_{16}ClN_3O_2Na$ $[M+Na]^+$: 460.0829 Found: 460.0849

2-(pyridin-2-yl)-1'-(m-tolyl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3t)

Yellow solid (80 mg, 77%) (n-Hexane: EtOAc = 4:1). M.P. = 220-221 ºC



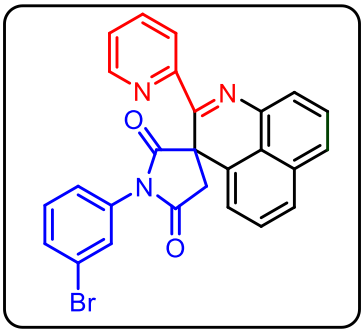
^{1}H NMR (600 MHz, Chloroform-d): δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 4.6 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.0 Hz, 1H), 7.59 (q, *J* = 9.3, 8.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 3.66 (d, *J* = 18.3 Hz, 1H), 3.00 (d, *J* = 18.3 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.9, 176.0, 160.9, 153.9, 147.9, 139.4, 138.7, 137.2, 135.1, 133.0, 132.8, 129.7, 129.2, 129.1, 127.7, 127.6, 127.2, 126.7, 125.4, 123.7, 123.1, 122.5, 120.5, 51.1, 50.5, 21.6.

HRMS-ESI: calcd. For $C_{27}H_{19}N_3O_2Na[M+Na]^+$: 440.1375 Found: 440.1371

1'-(3-bromophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3u)

Yellow solid (96 mg, 80%) (n-Hexane: EtOAc = 4:1). M.P. = 196-198 ºC



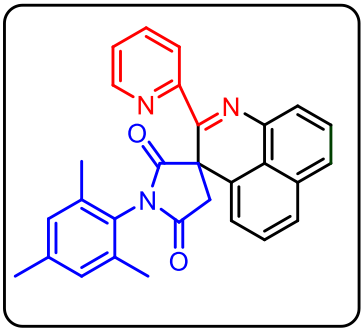
^{1}H NMR (600 MHz, Chloroform-d): δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 4.8 Hz, 1H), 7.86 (dd, *J* = 14.8, 7.9 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.74 (d, *J* = 2.8 Hz, 2H), 7.60 (d, *J* = 2.4 Hz, 3H), 7.52 (d, *J* = 6.3 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.39 – 7.36 (m, 1H), 3.64 (d, *J* = 18.3 Hz, 1H), 3.01 (d, *J* = 18.3 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.4, 175.4, 160.6, 153.7, 148.0, 138.6, 137.4, 134.8, 134.2, 133.0, 131.9, 130.6, 129.7, 129.2, 127.8, 127.8, 127.7, 126.9, 125.5, 125.3, 123.1, 122.7, 122.6, 120.4, 51.0, 50.4.

HRMS-ESI: calcd. For $C_{26}H_{17}N_3O_2[M+H]^+$: 482.0504 Found: 482.0509

1'-mesityl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3v)

Yellow solid (69 mg, 62%) (n-Hexane: EtOAc = 3:1). M.P. = 233-235 ºC



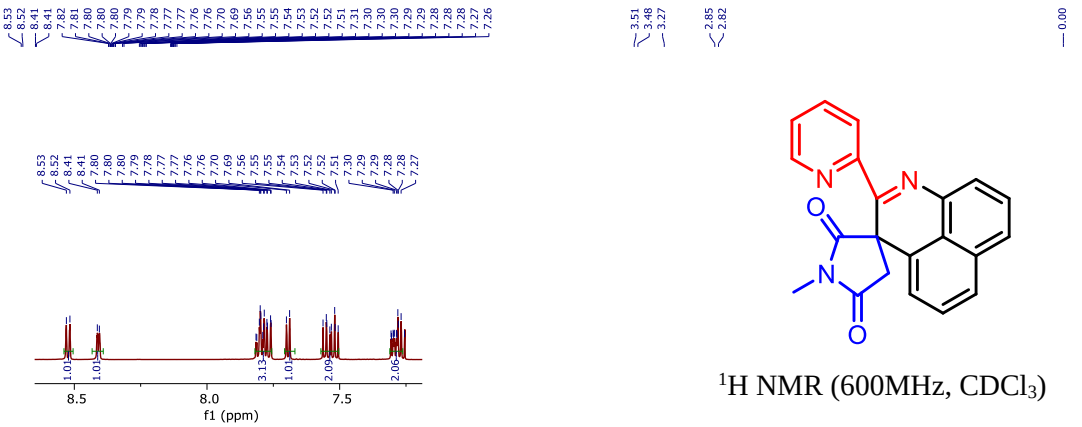
^{1}H NMR (600 MHz, Chloroform-d): δ 8.51 (d, *J* = 7.8 Hz, 2H), 7.89 – 7.82 (m, 2H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.00 (s, 1H), 6.91 (s, 1H), 4.22 (d, *J* = 18.2 Hz, 1H), 3.19 (d, *J* = 18.2 Hz, 1H), 2.48 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d): δ 176.3, 174.5, 160.3, 154.8, 147.6, 139.4, 139.0, 137.2, 137.0, 136.1, 133.7, 133.1, 129.9, 129.7, 128.9, 127.8, 127.8, 127.7, 126.8, 126.8, 125.1, 123.6, 123.5, 121.0, 52.1, 49.4, 21.1, 19.0, 18.6.

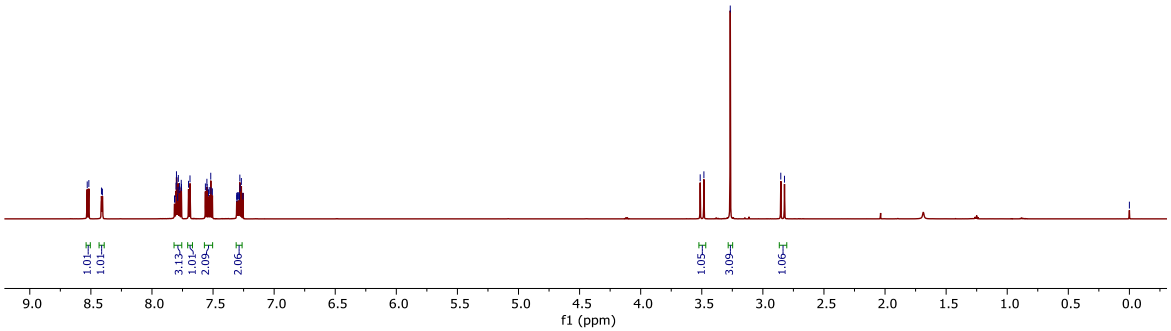
HRMS-ESI: calcd. For $C_{29}H_{23}N_3O_2Na[M+Na]^+$: 468.1688 Found: 468.1683

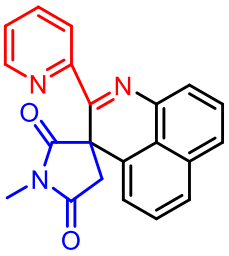
10. Copies of NMR Spectra

1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3a)

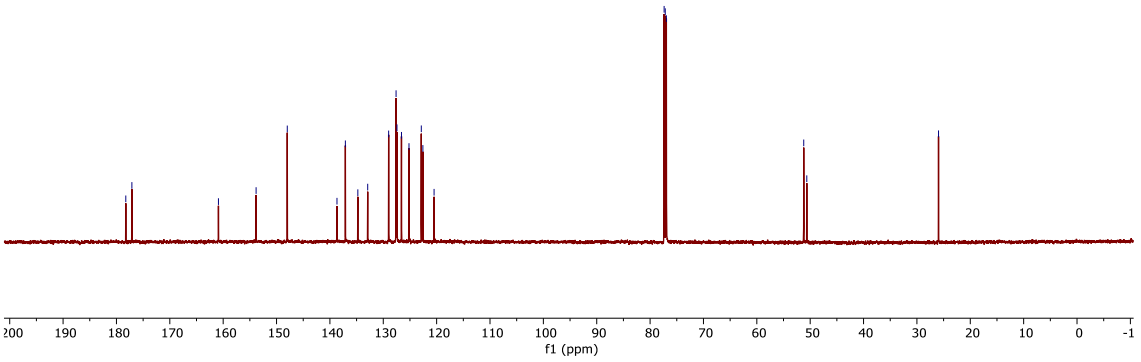


^{1}H NMR (600MHz, $CDCl_3$)

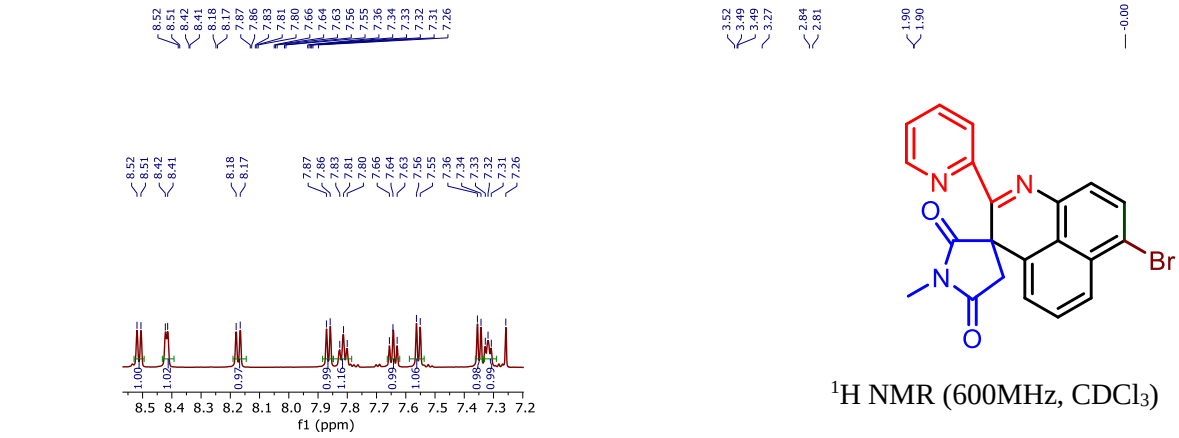




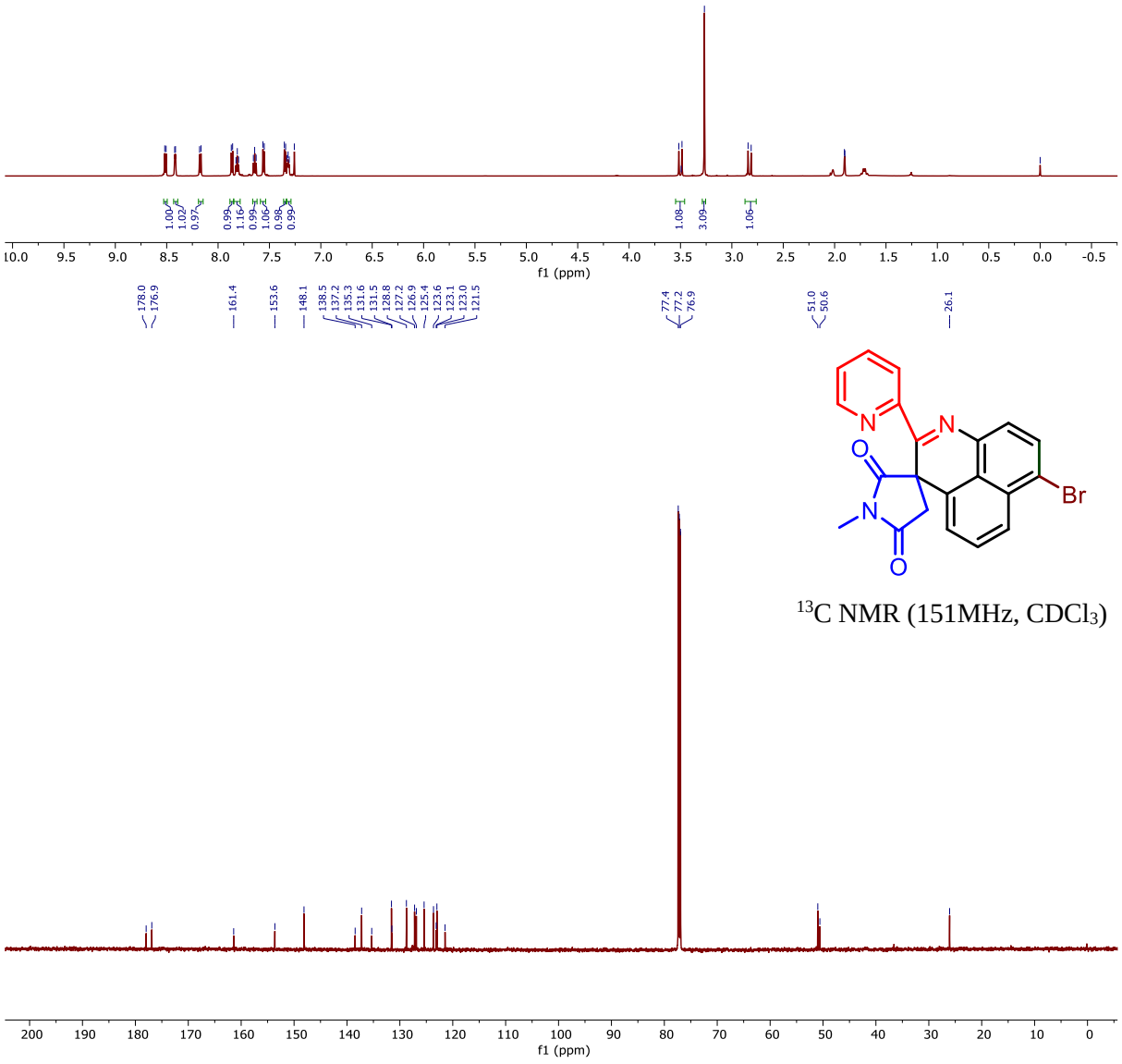
^{13}C NMR (151MHz, $CDCl_3$)



7-bromo-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3b)

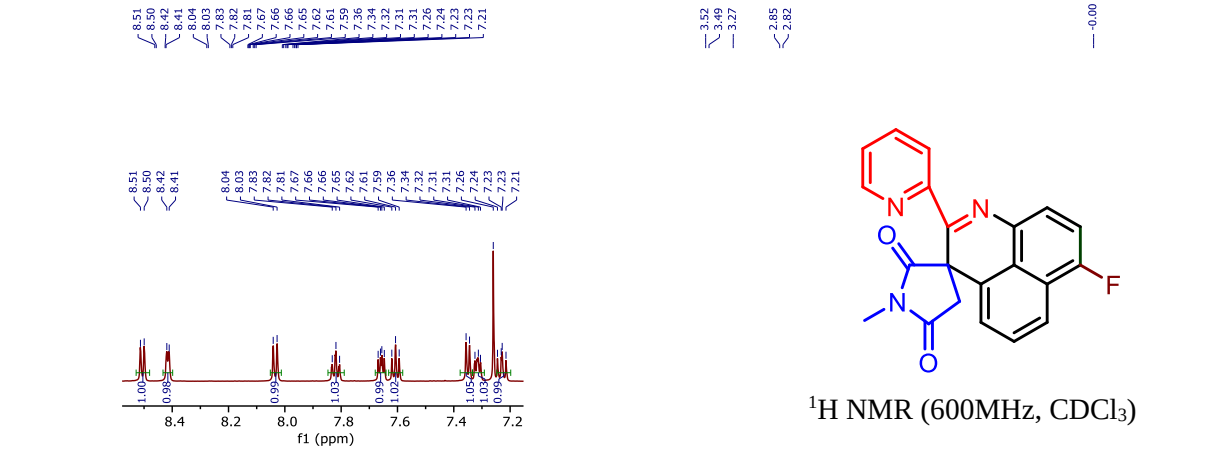


^{1}H NMR (600MHz, $CDCl_3$)

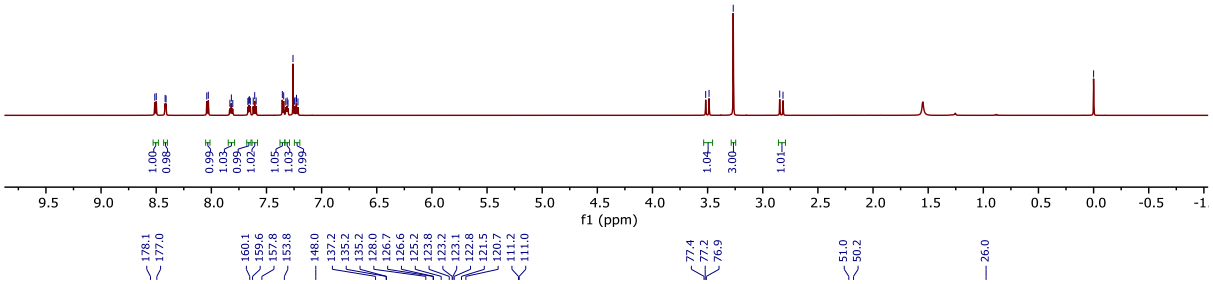


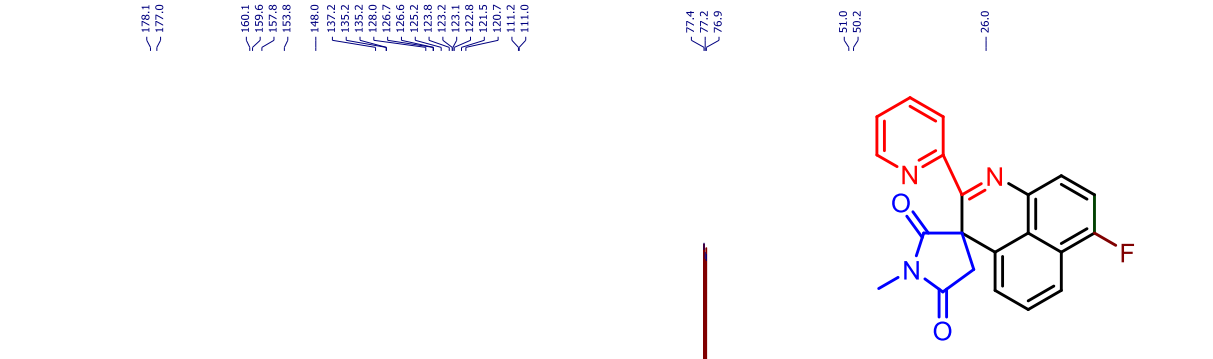
^{13}C NMR (151MHz, $CDCl_3$)

7-fluoro-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3c)

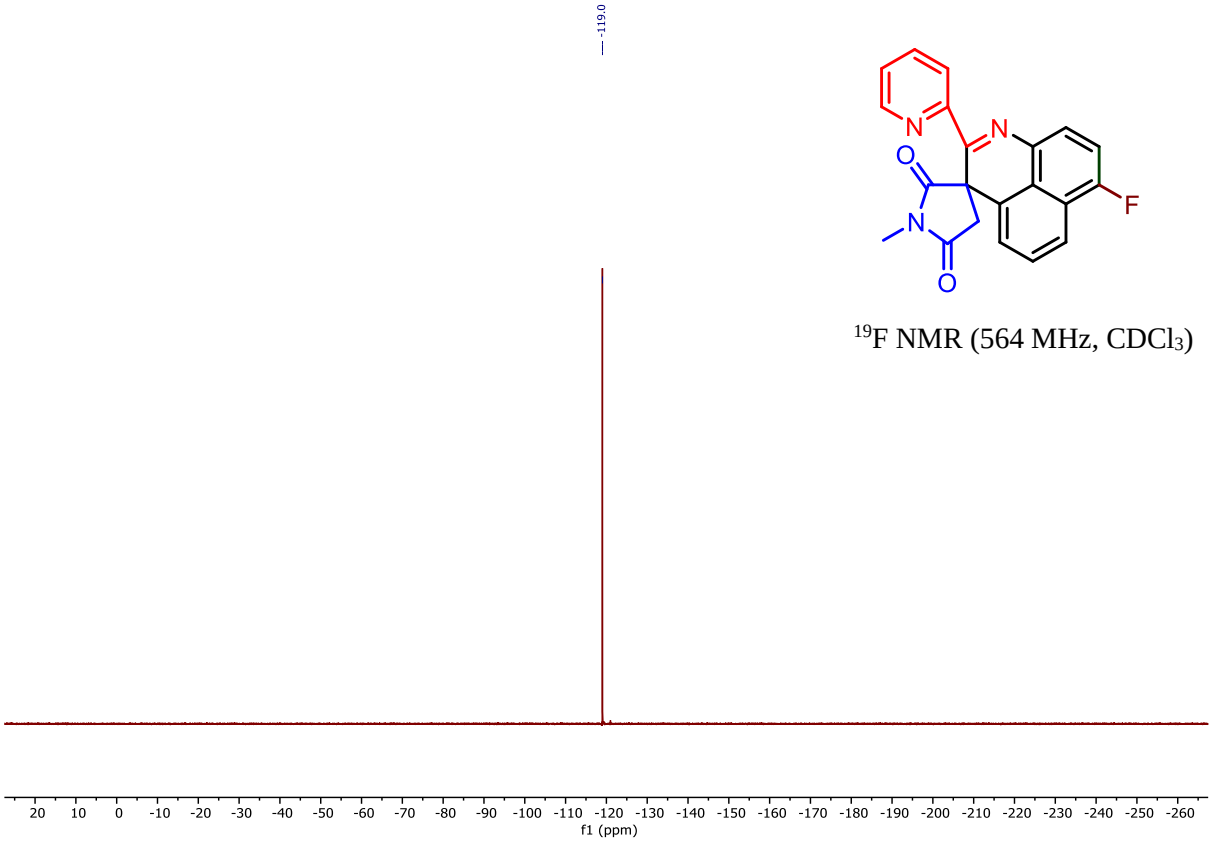


^{1}H NMR (600MHz, $CDCl_3$)



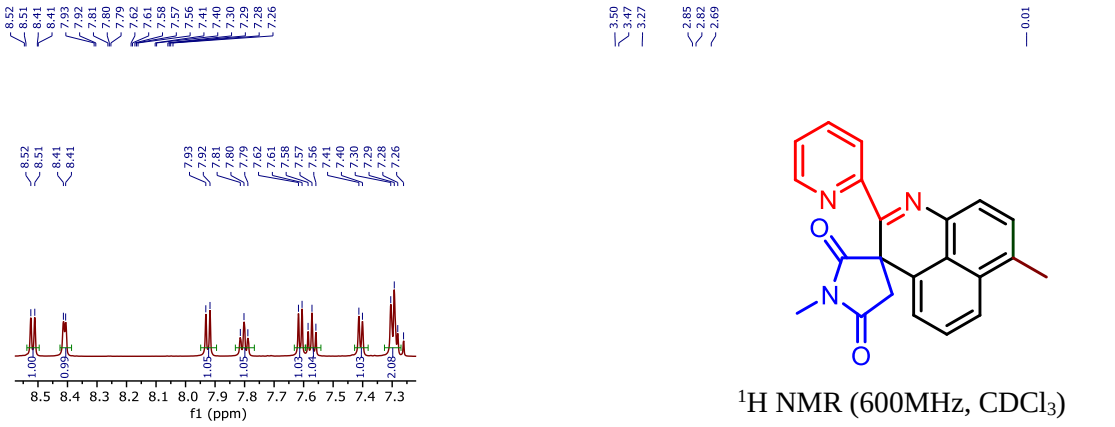


^{13}C NMR (151MHz, $CDCl_3$)

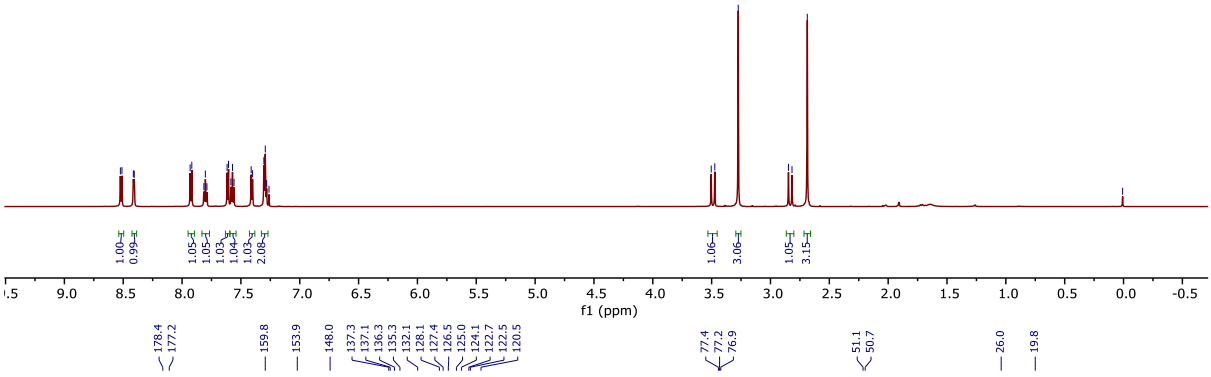


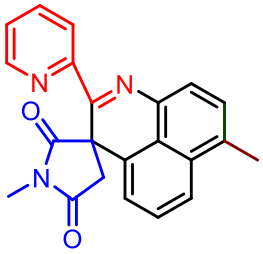
^{19}F NMR (564 MHz, $CDCl_3$)

1',7-dimethyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3d)

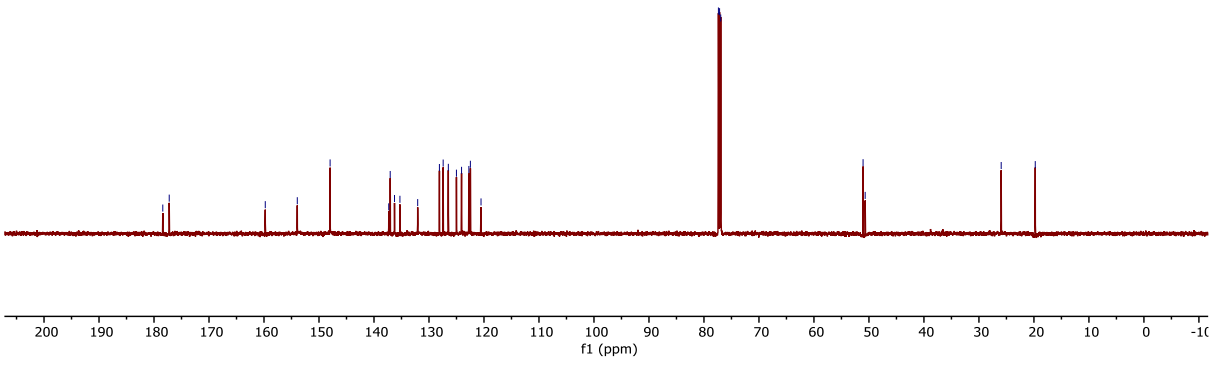


^{1}H NMR (600MHz, $CDCl_3$)

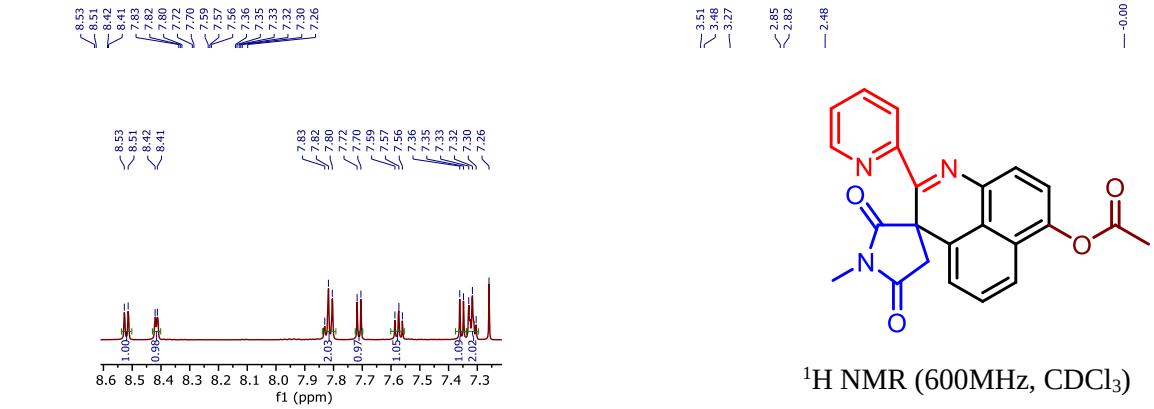




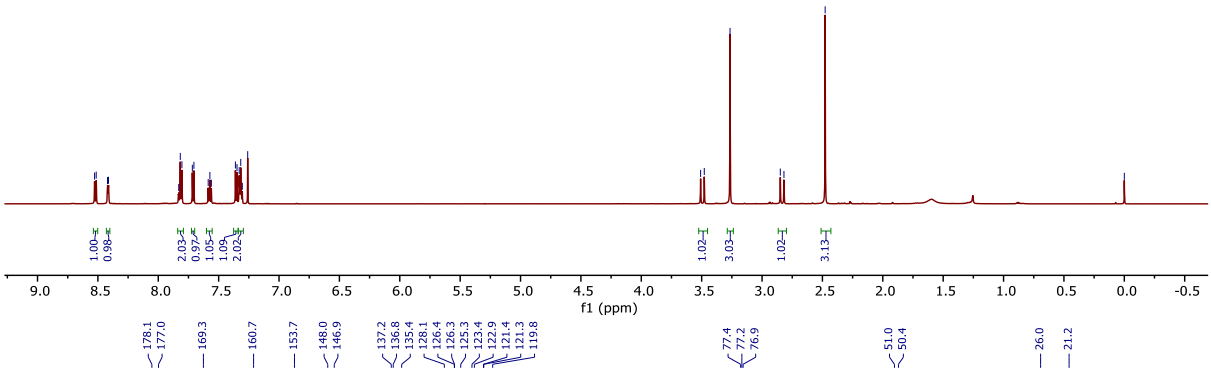
^{13}C NMR (151MHz, $CDCl_3$)

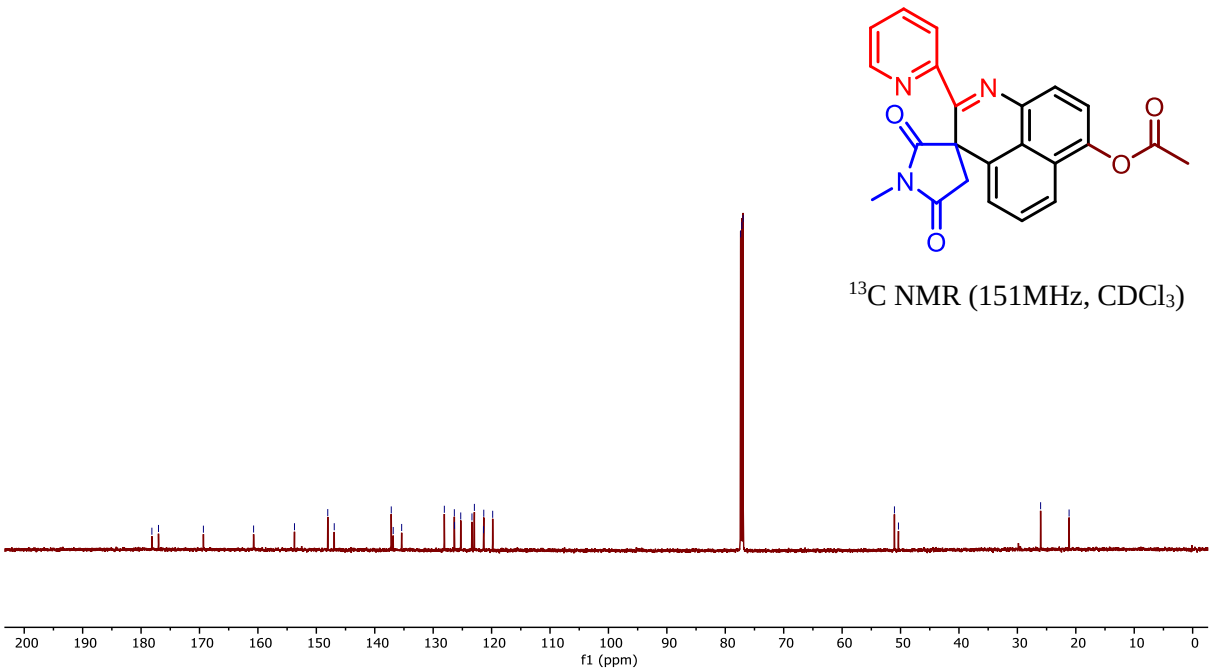


1'-methyl-2',5'-dioxo-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidin]-7-yl acetate (3e)



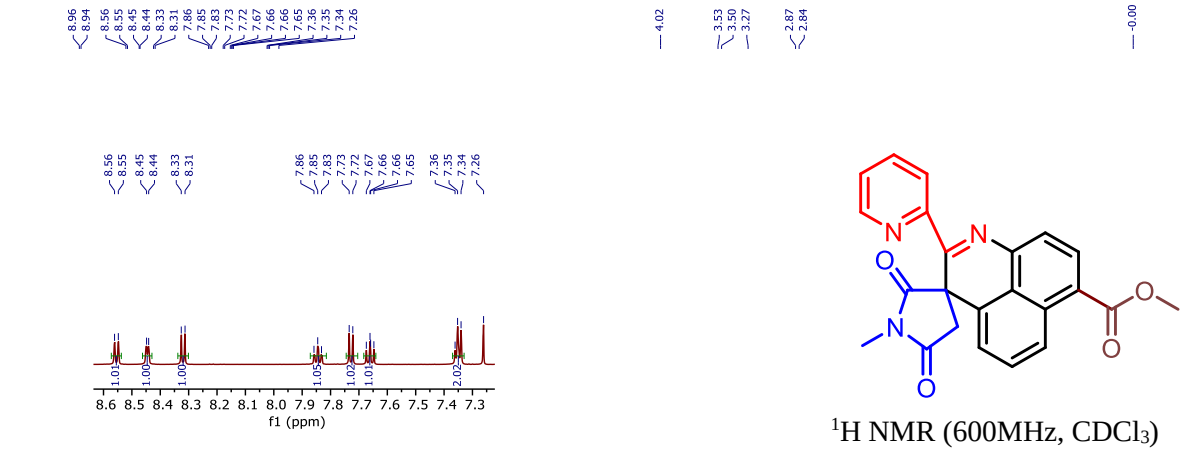
^{1}H NMR (600MHz, $CDCl_3$)



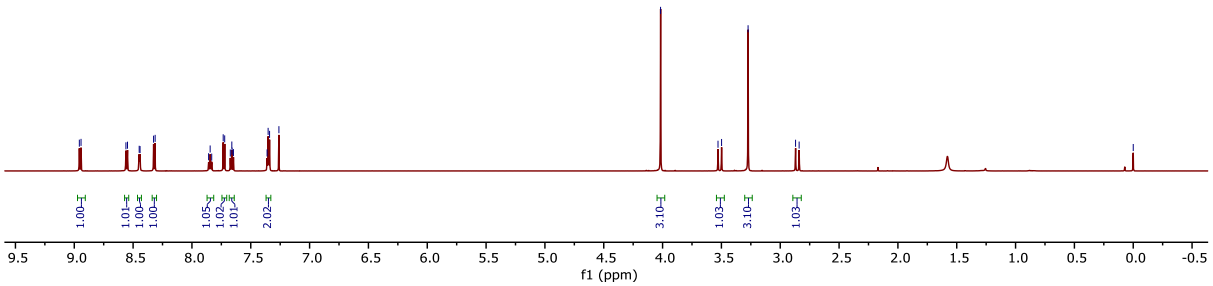


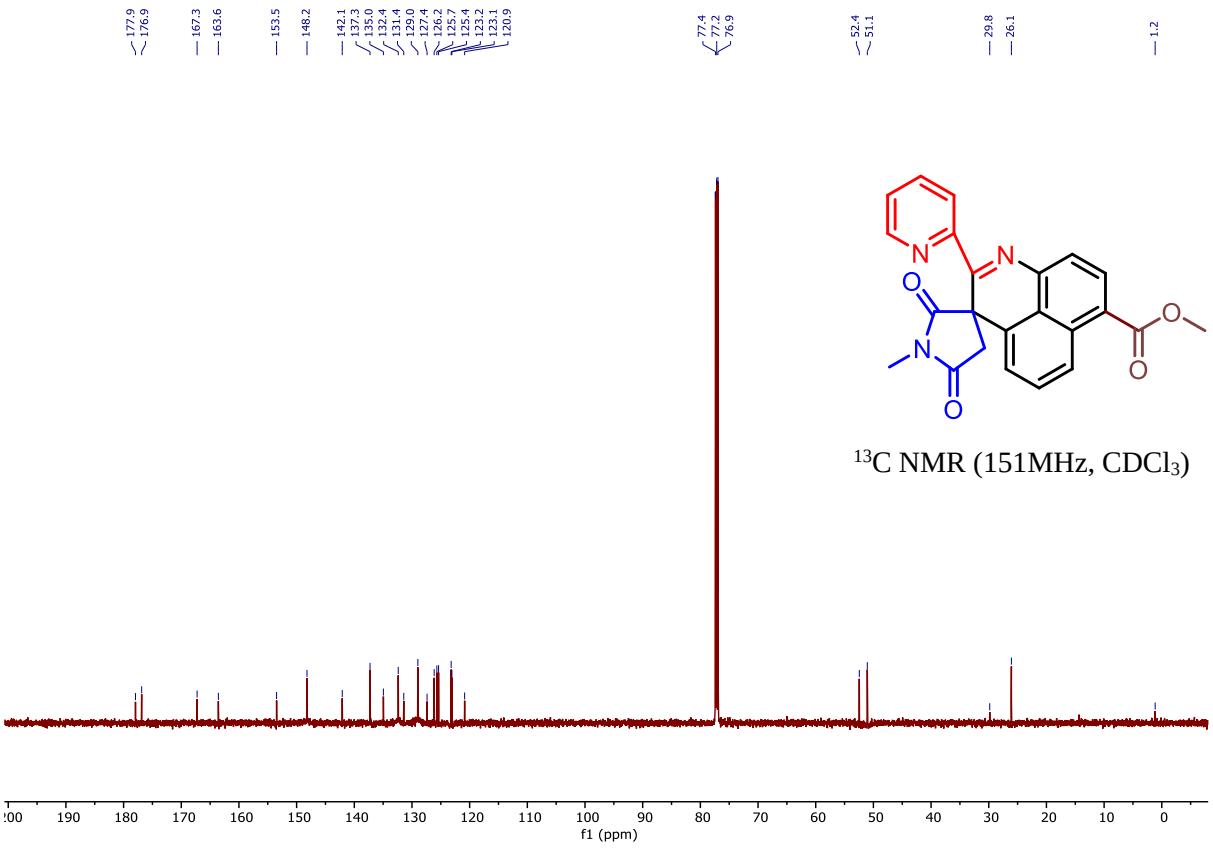
^{13}C NMR (151MHz, $CDCl_3$)

methyl 1'-methyl-2',5'-dioxo-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-7-carboxylate (3f)



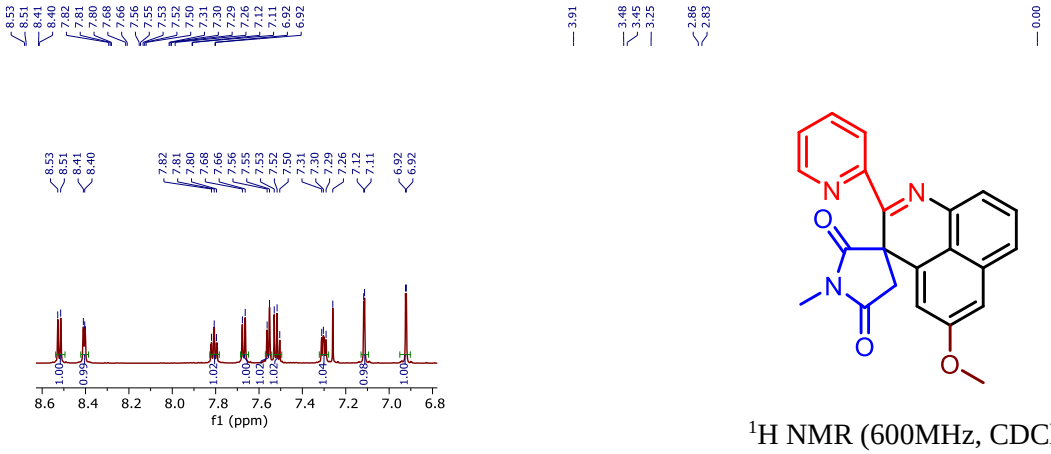
^{1}H NMR (600MHz, $CDCl_3$)



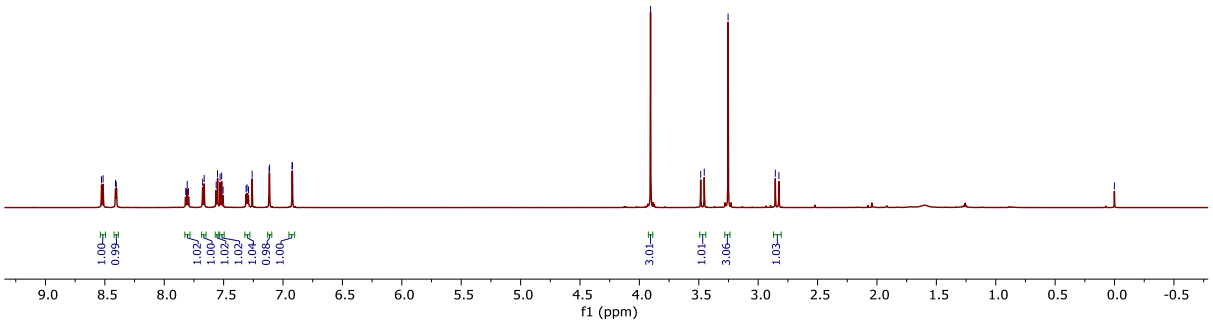


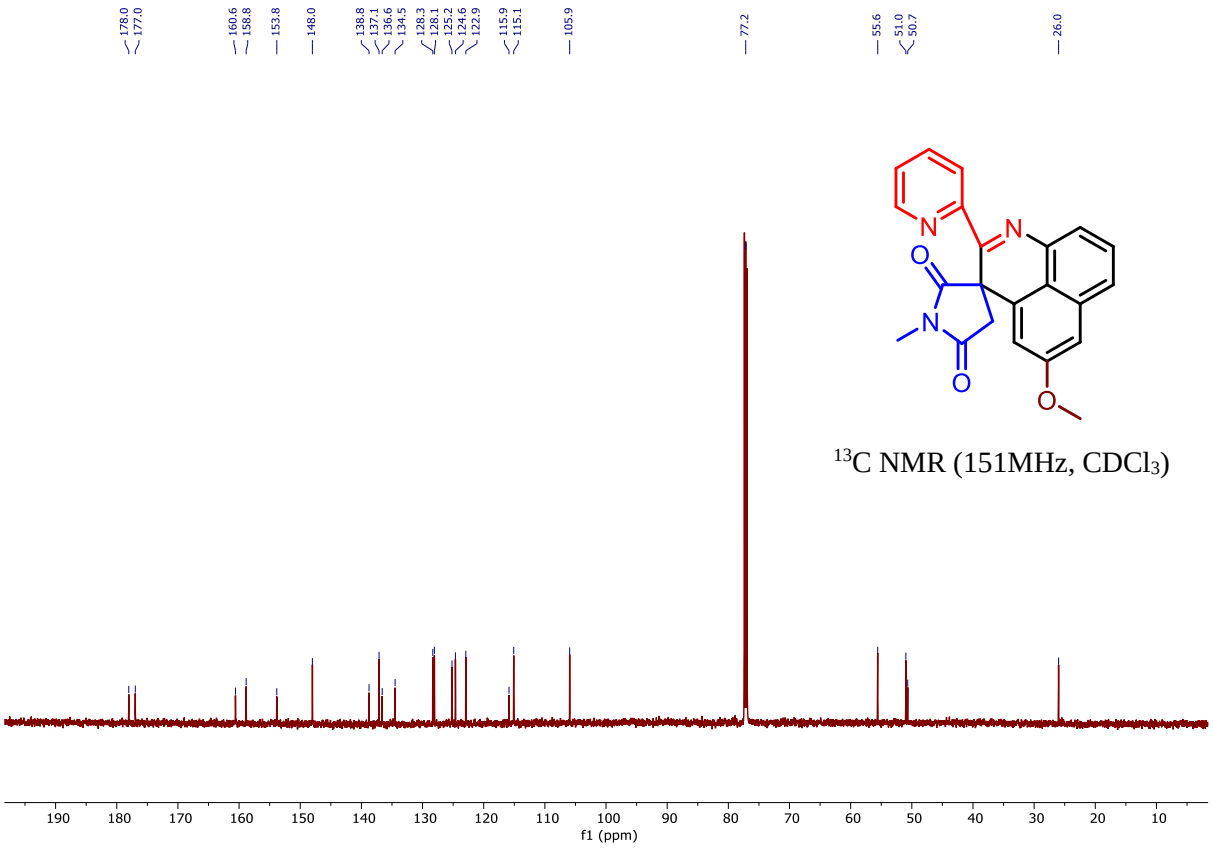
^{13}C NMR (151MHz, $CDCl_3$)

5-methoxy-1'-methyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3h)



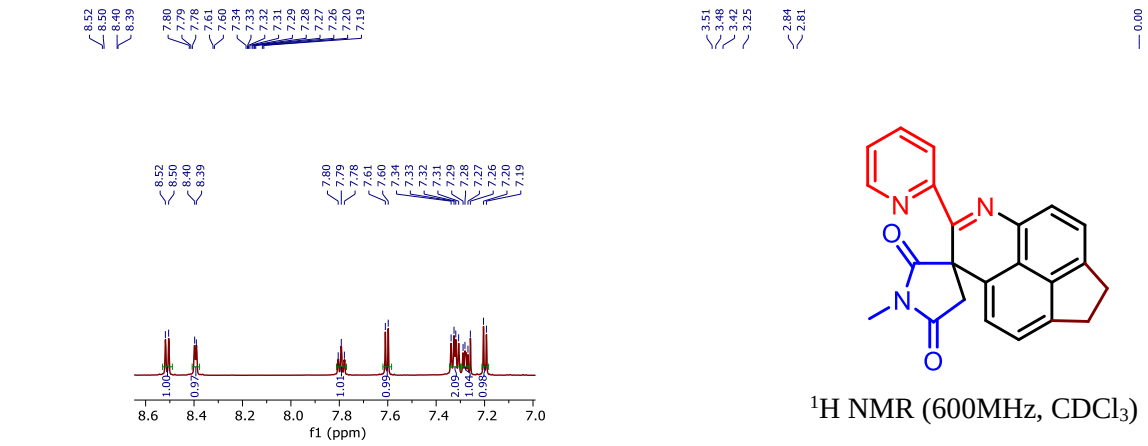
^{1}H NMR (600MHz, $CDCl_3$)



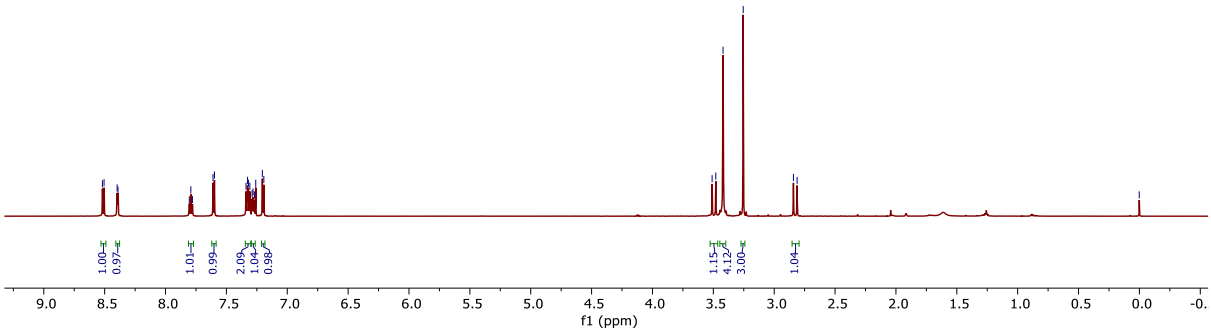


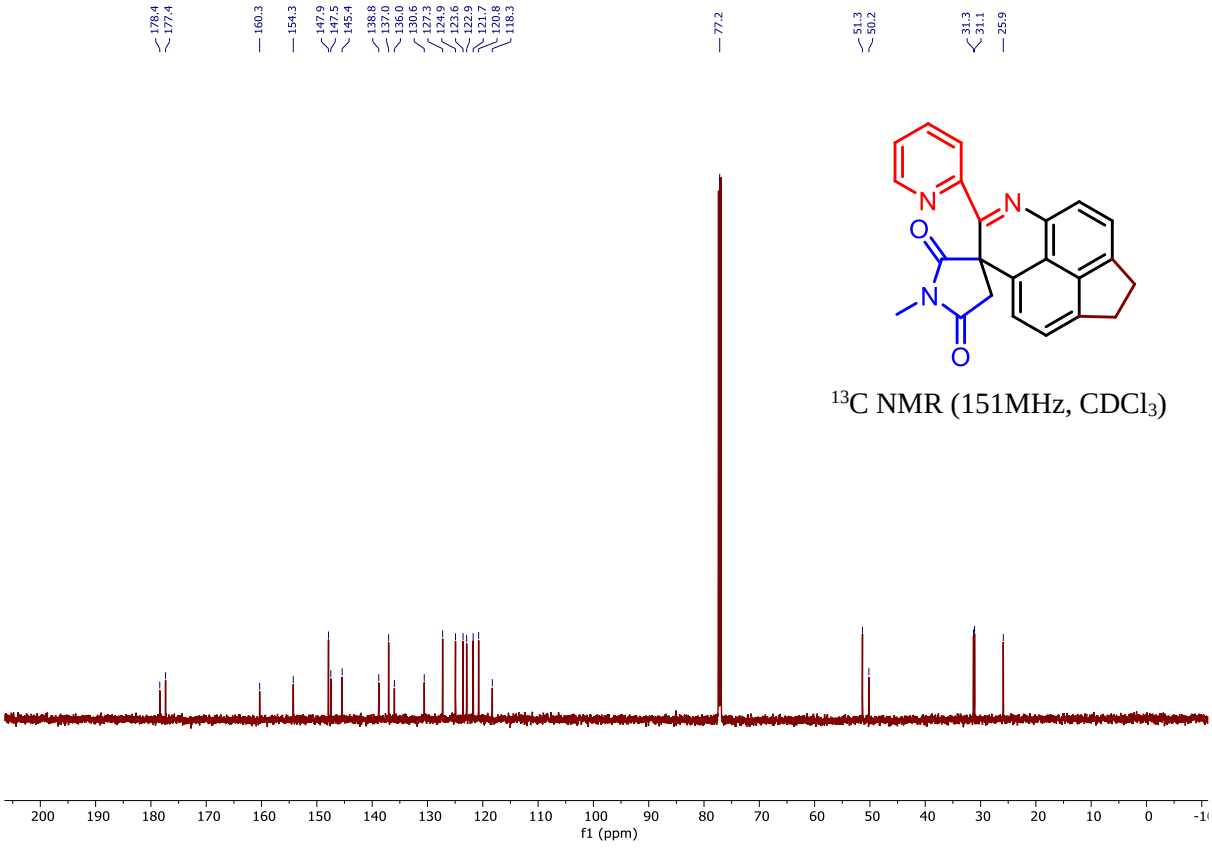
^{13}C NMR (151MHz, $CDCl_3$)

1'-methyl-2-(pyridin-2-yl)-6,7-dihydrospiro[indeno[6,7,1-def]quinoline-3,3'-pyrrolidine]-2',5'-dione (3i)



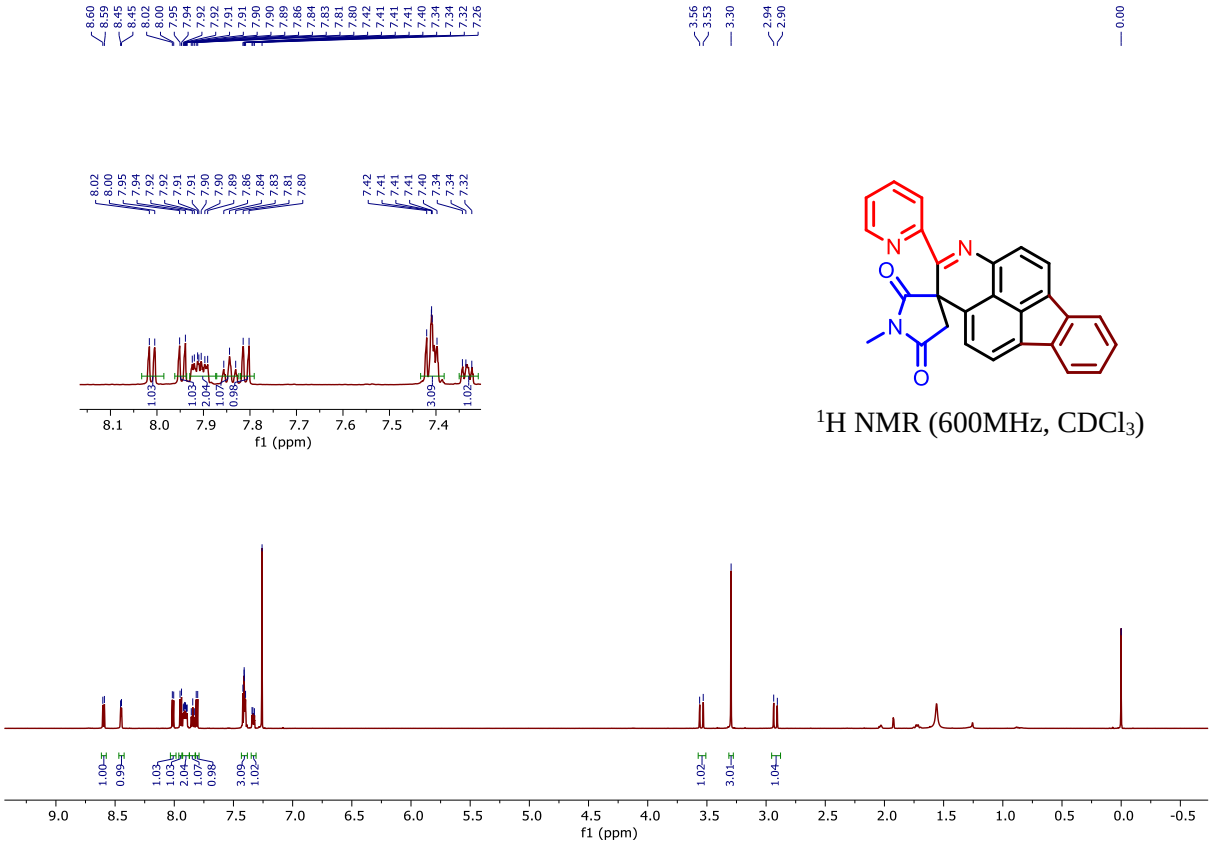
^{1}H NMR (600MHz, $CDCl_3$)



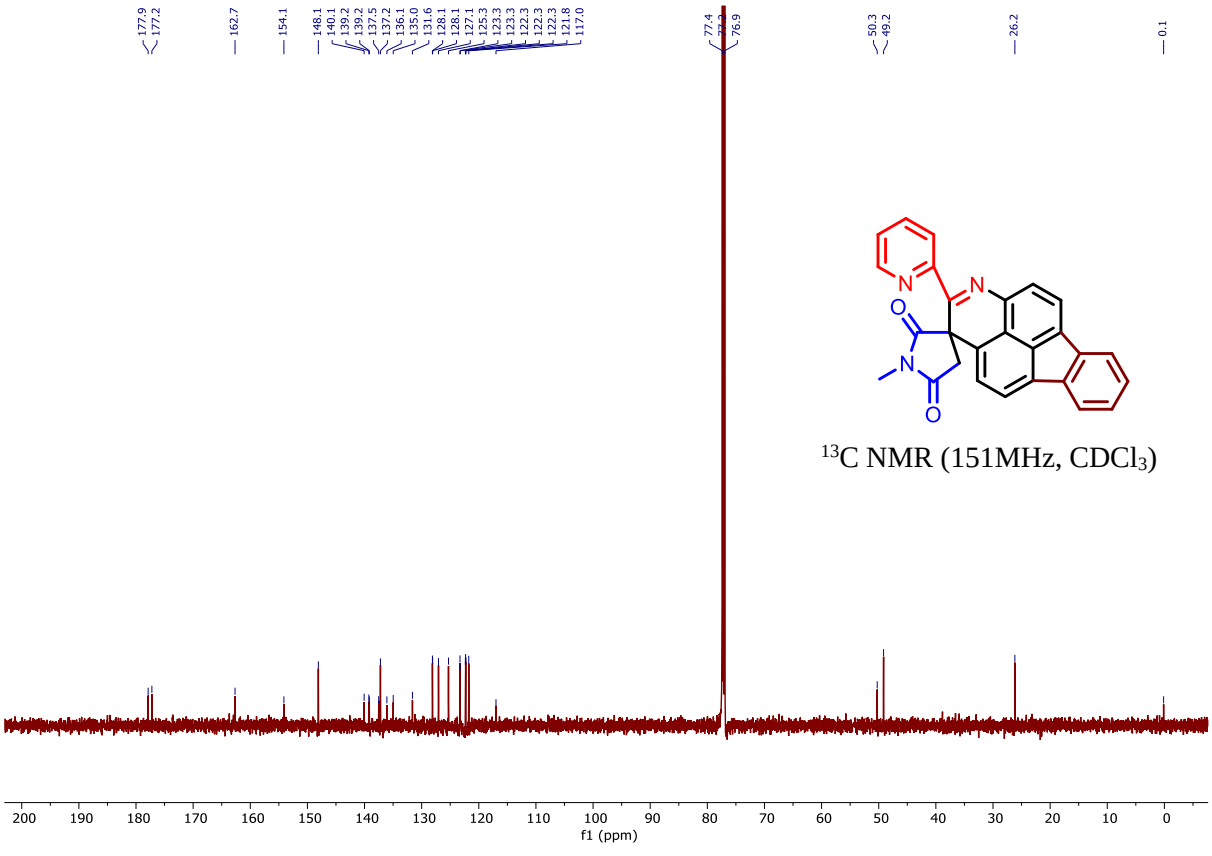


^{13}C NMR (151MHz, $CDCl_3$)

1'-methyl-2-(pyridin-2-yl)spiro[fluoreno[2,1,9-def]quinoline-3,3'-pyrrolidine]-2',5'-dione (3j)

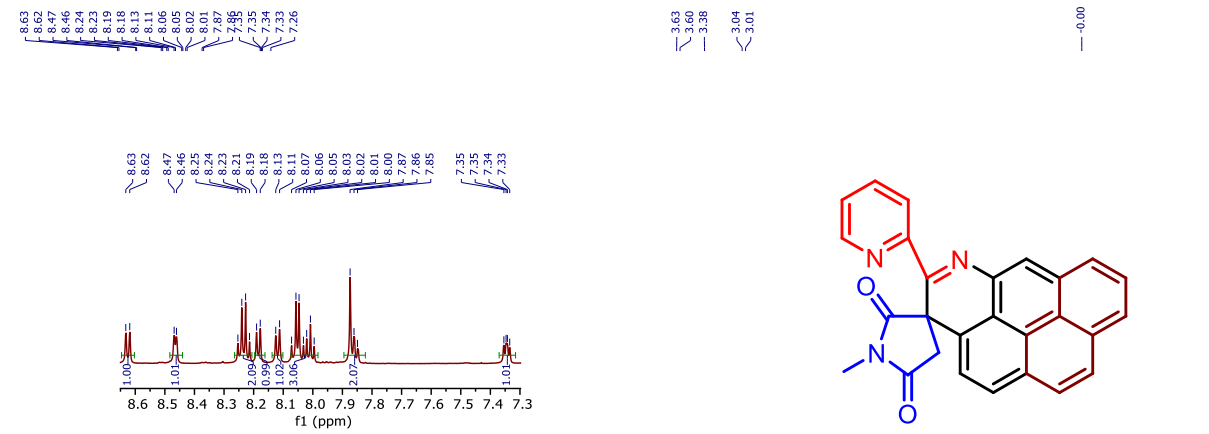


^{1}H NMR (600MHz, $CDCl_3$)

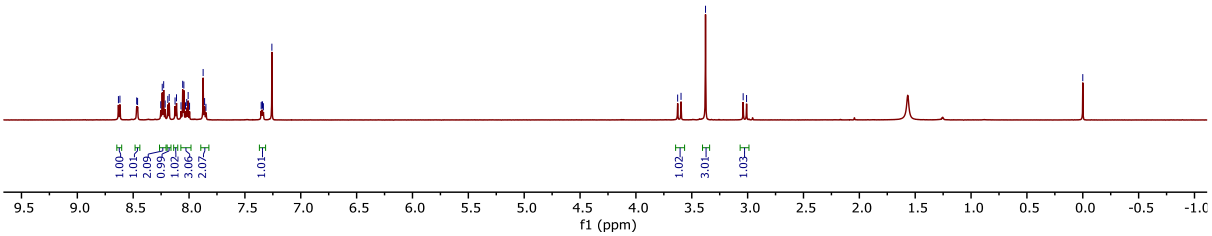


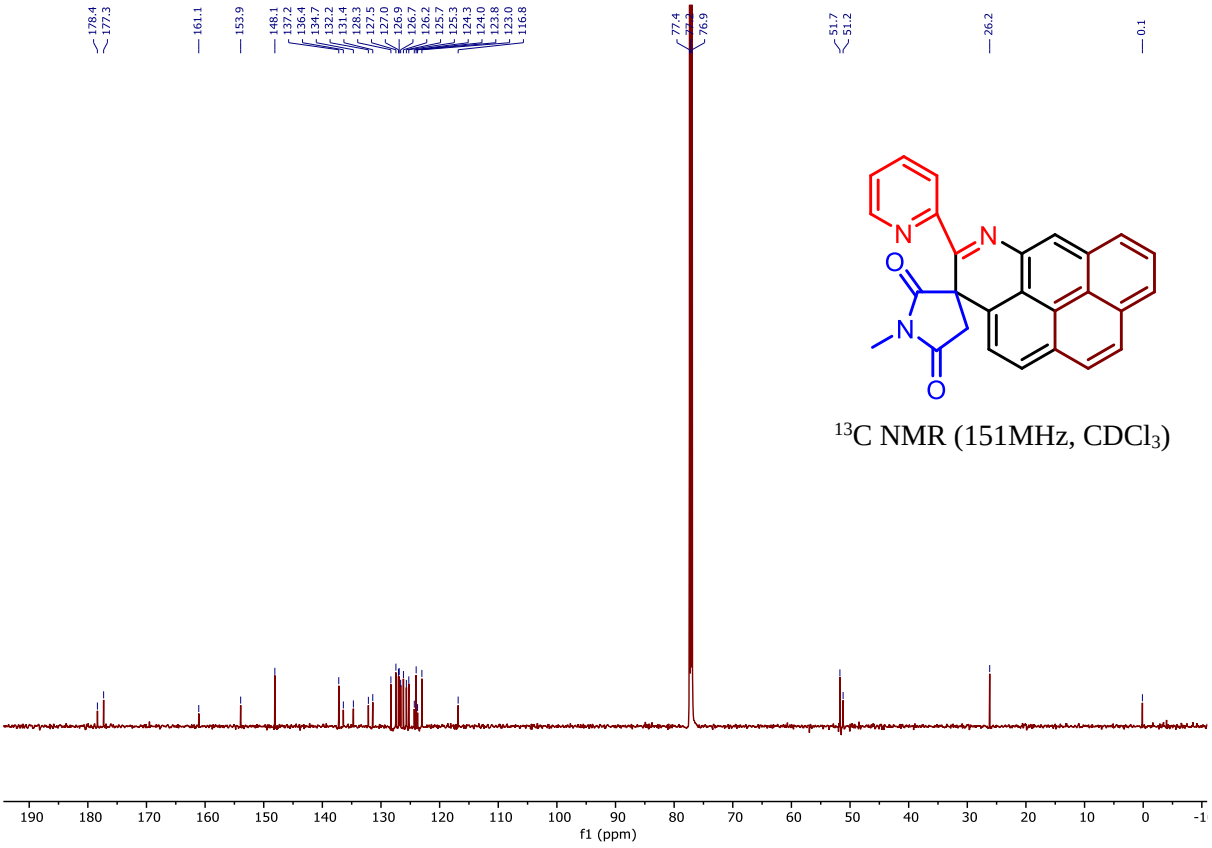
^{13}C NMR (151MHz, $CDCl_3$)

1'-methyl-4-(pyridin-2-yl)spiro[phenanthro[3,4,5-defg]quinoline-3,3'-pyrrolidine]-2',5'-dione (3k)



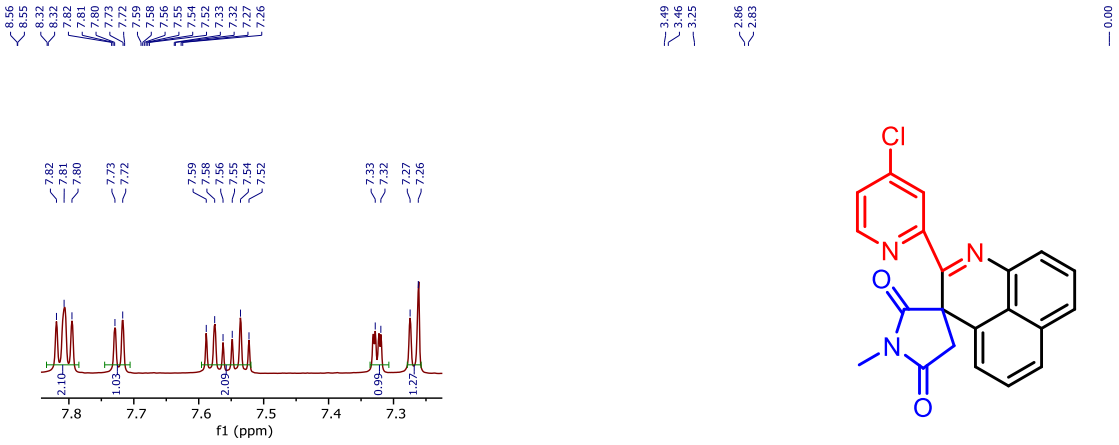
^{1}H NMR (600MHz, $CDCl_3$)



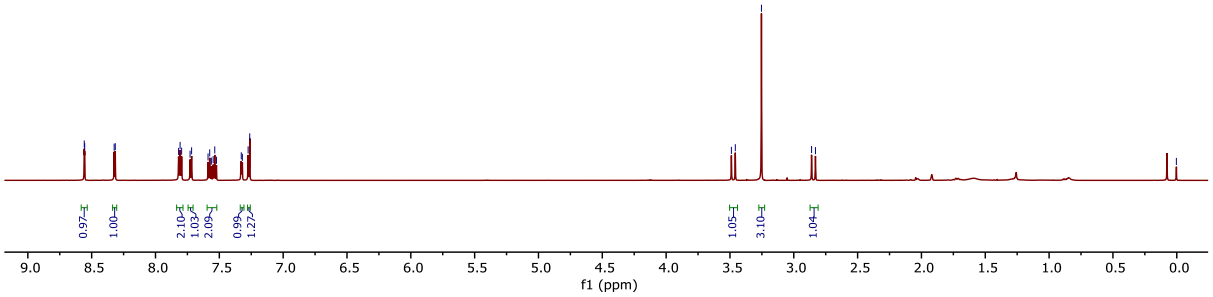


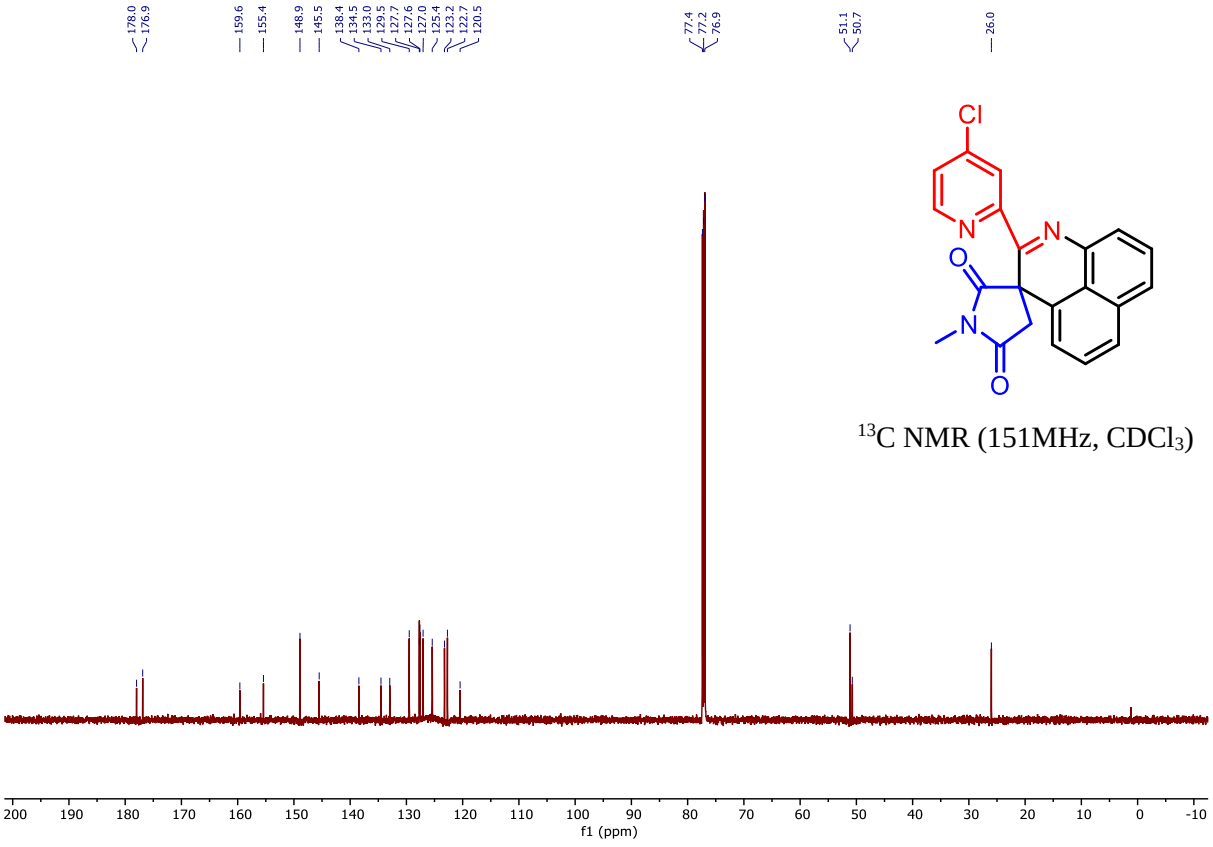
^{13}C NMR (151MHz, $CDCl_3$)

2-(4-chloropyridin-2-yl)-1'-methylspiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3l)



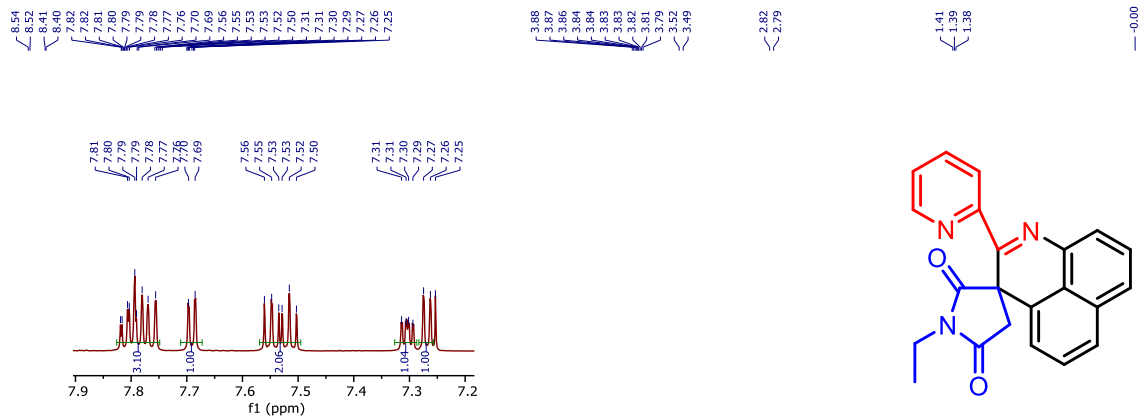
^{1}H NMR (600MHz, $CDCl_3$)



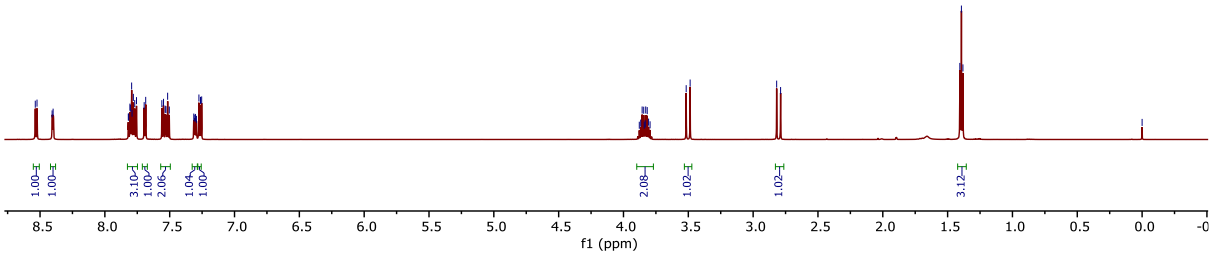


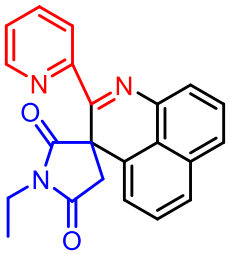
^{13}C NMR (151MHz, $CDCl_3$)

1'-ethyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3m)

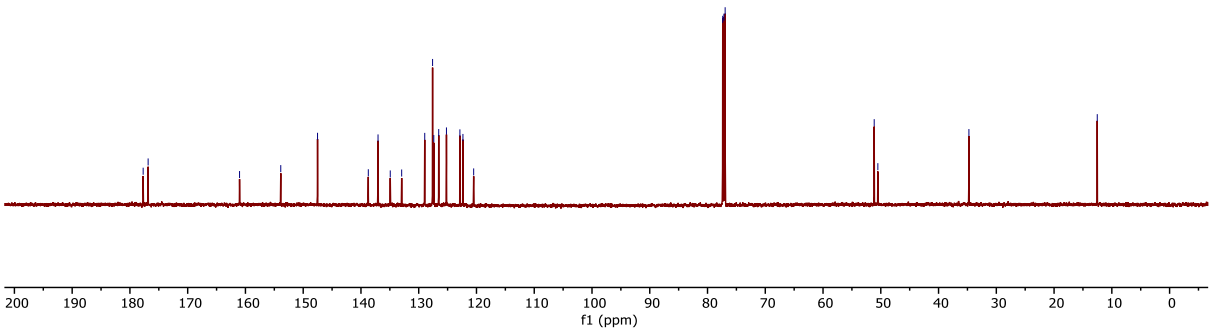


^{1}H NMR (600MHz, $CDCl_3$)

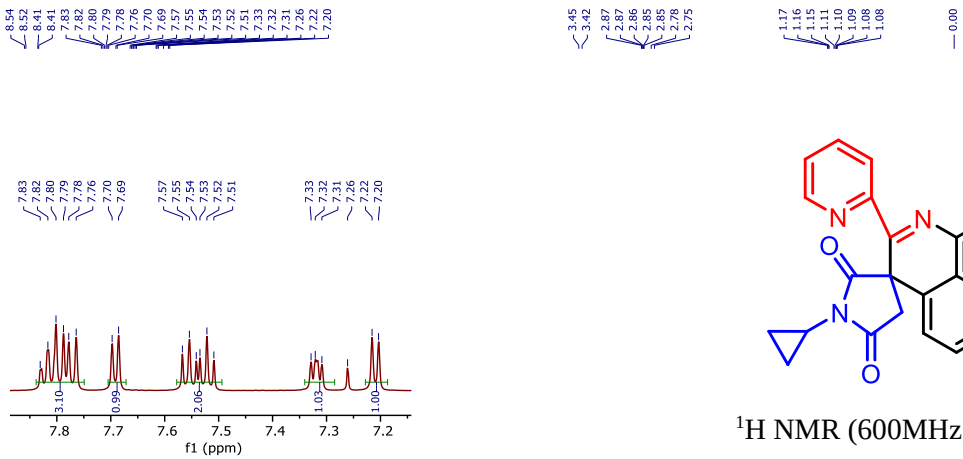




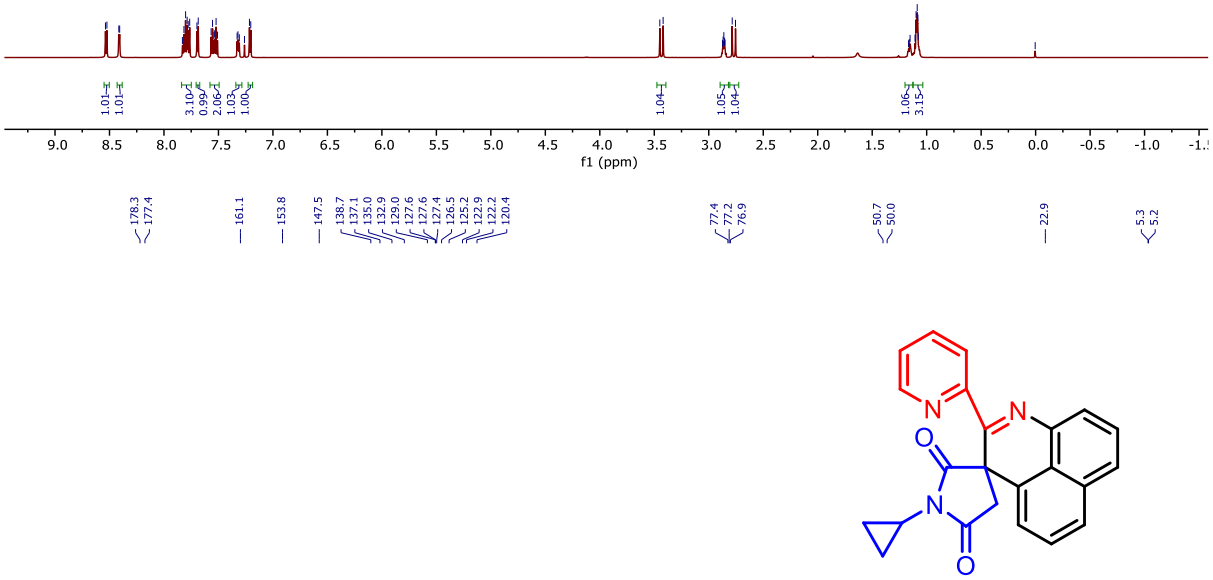
^{13}C NMR (151MHz, $CDCl_3$)



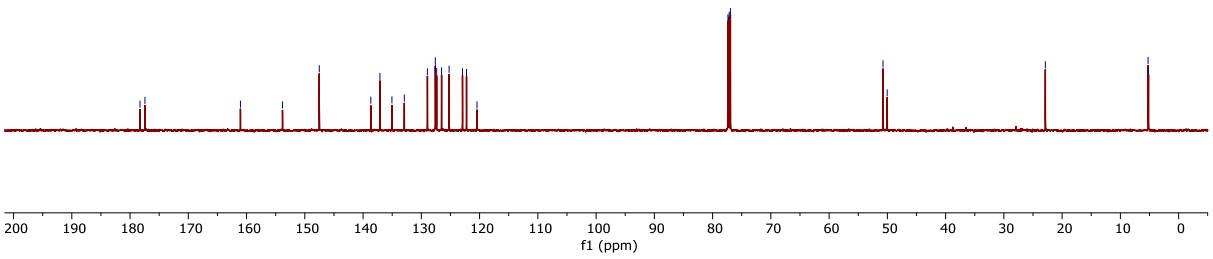
1'-cyclopropyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3n)



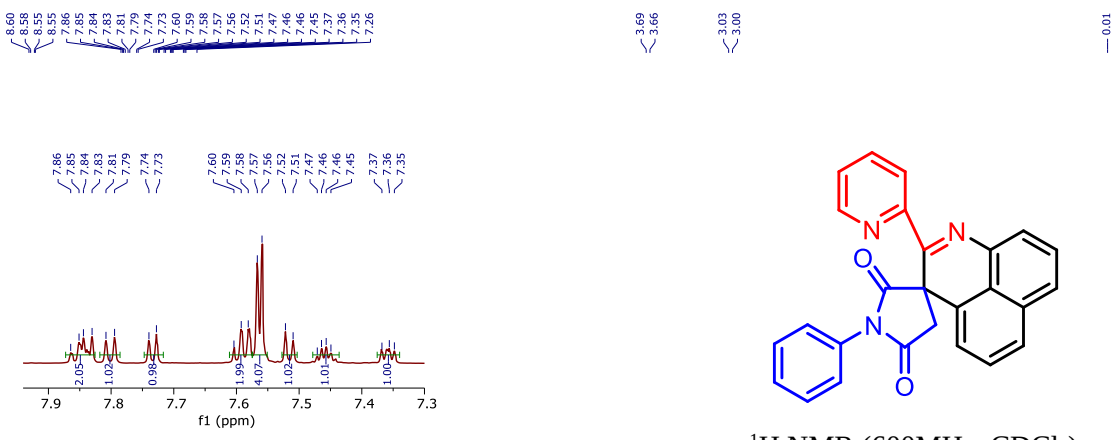
^{1}H NMR (600MHz, $CDCl_3$)



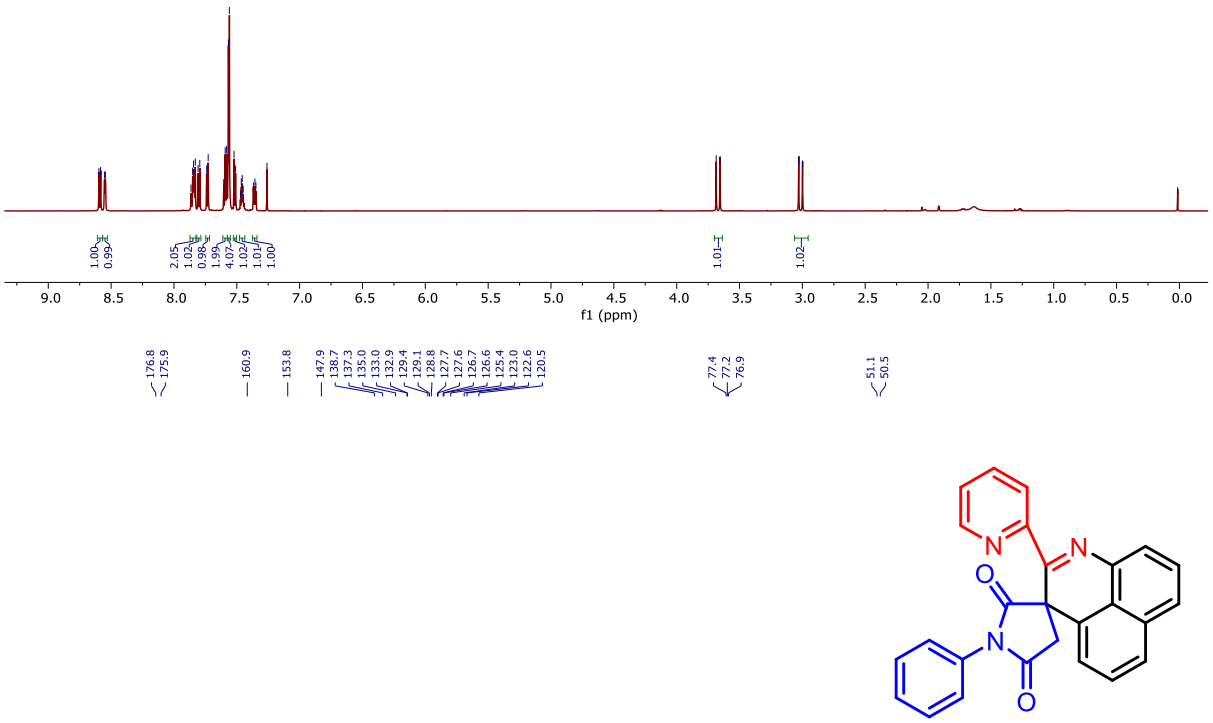
^{13}C NMR (151MHz, $CDCl_3$)



1'-phenyl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3o)

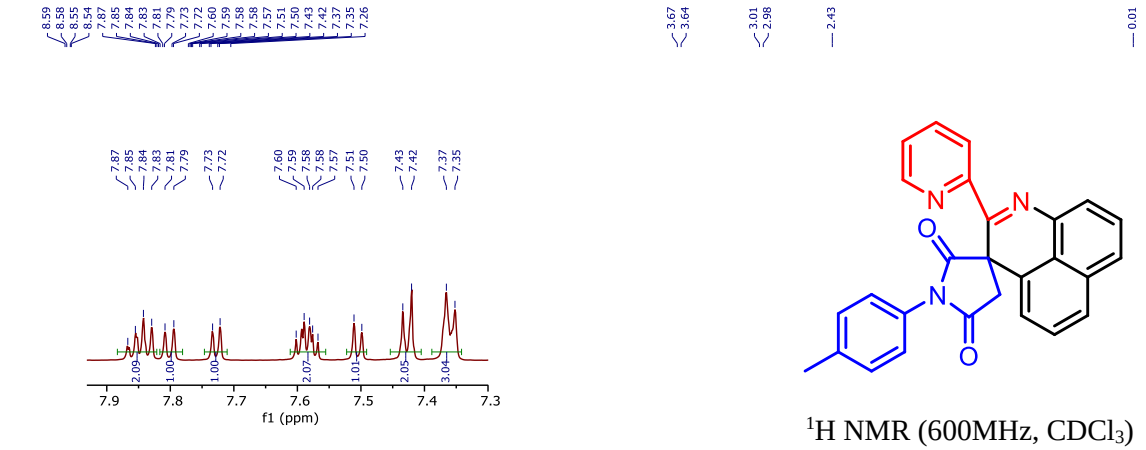


^{1}H NMR (600MHz, $CDCl_3$)

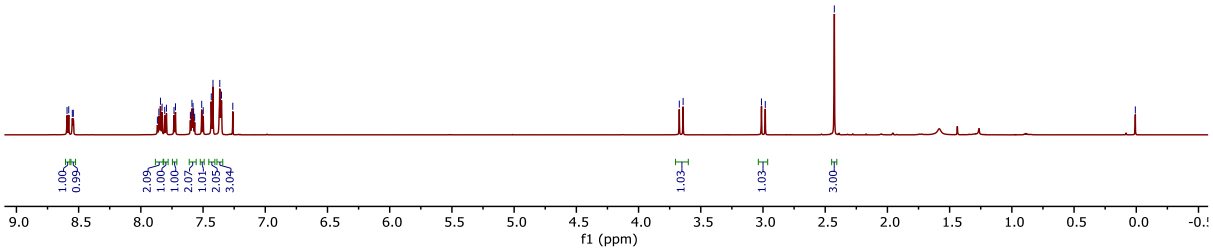


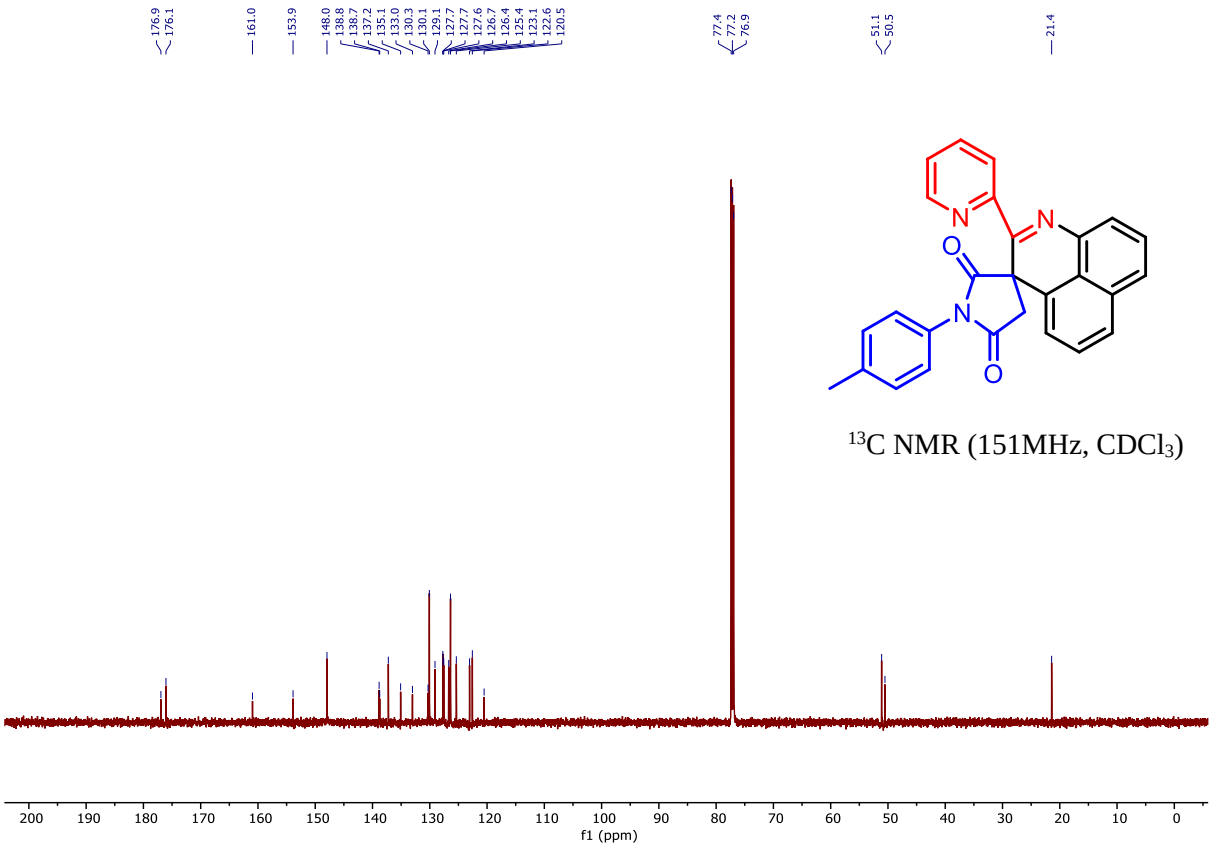
^{13}C NMR (151MHz, $CDCl_3$)

2-(pyridin-2-yl)-1'-(p-tolyl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3p)



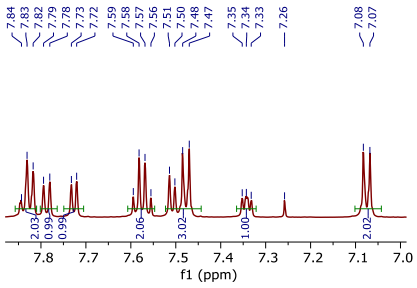
^{1}H NMR (600MHz, $CDCl_3$)

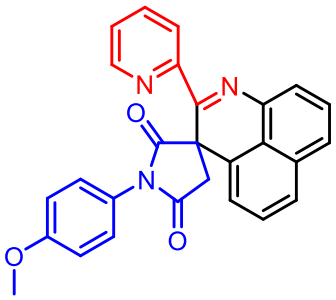




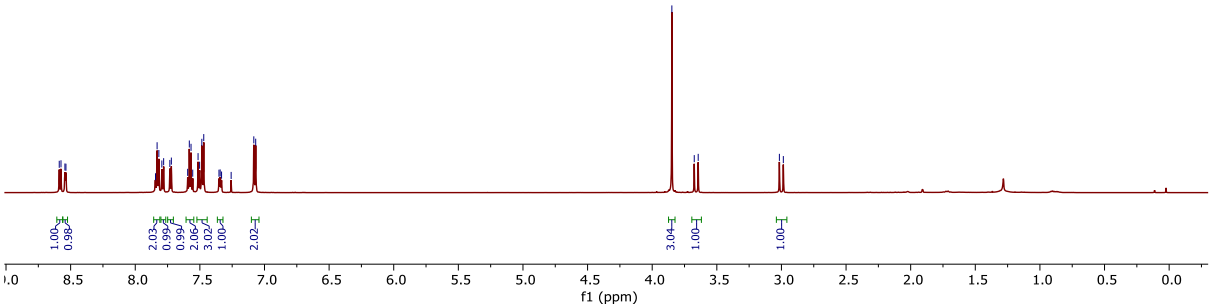
^{13}C NMR (151MHz, $CDCl_3$)

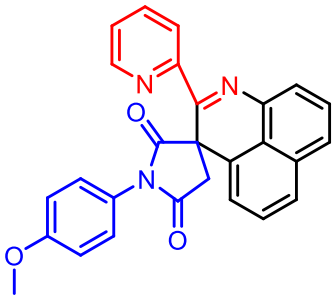
1'-(4-methoxyphenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3q)



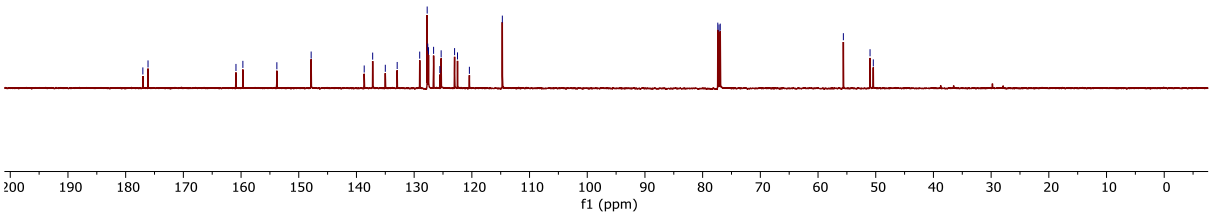


^{1}H NMR (600MHz, $CDCl_3$)

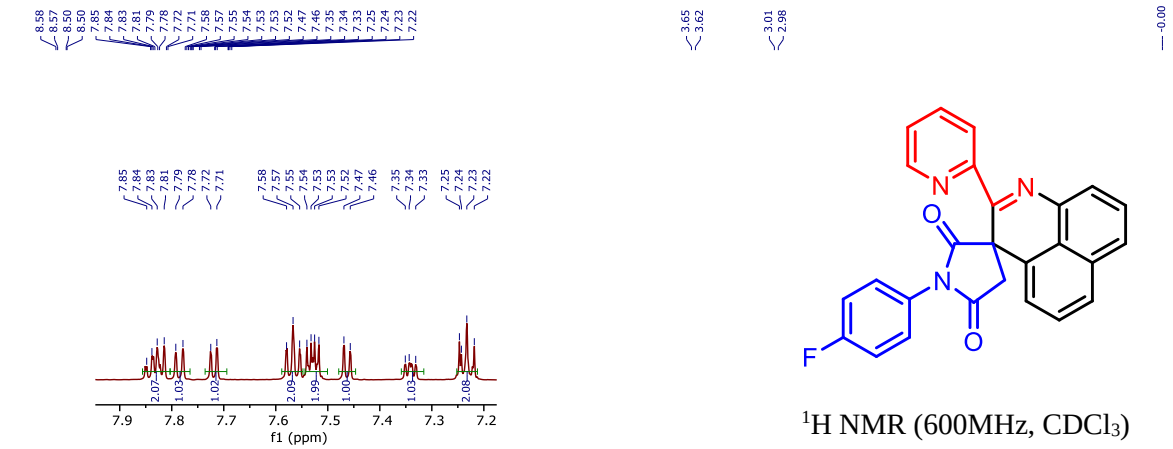




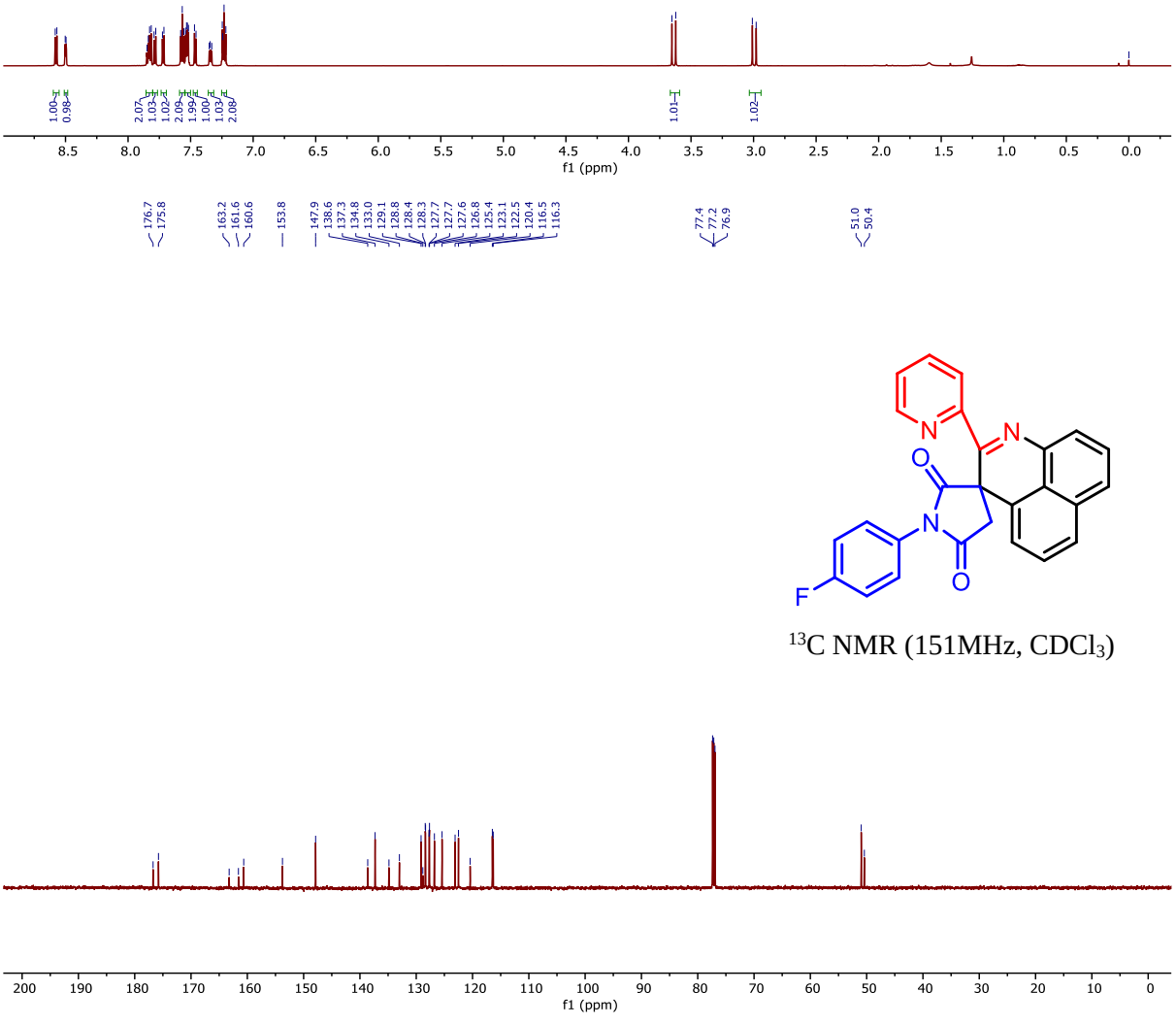
^{13}C NMR (151MHz, $CDCl_3$)



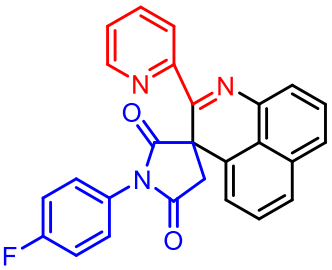
1'-(4-fluorophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3r)



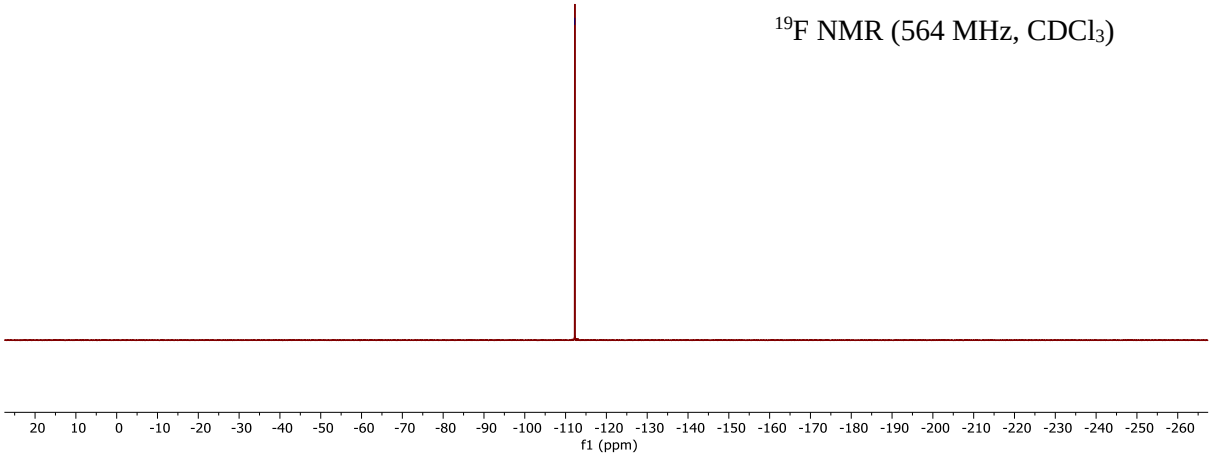
^{1}H NMR (600MHz, $CDCl_3$)



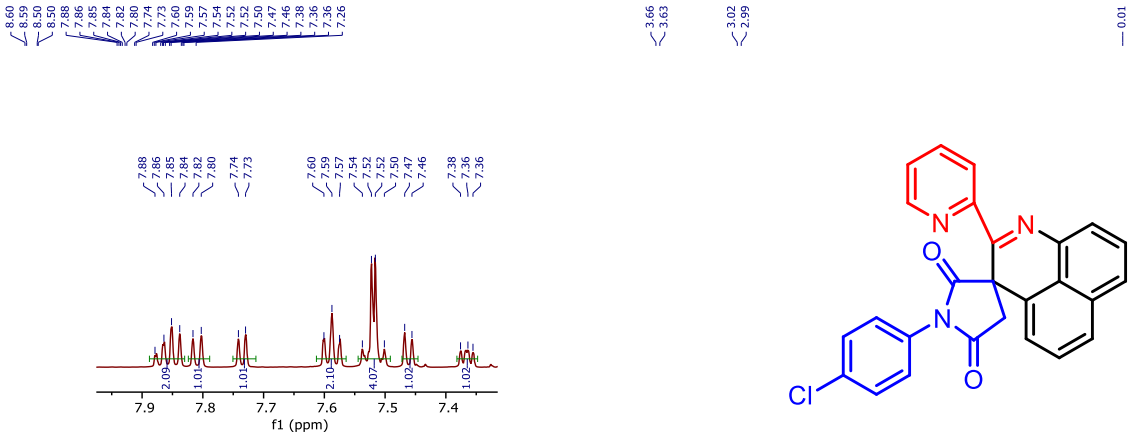
^{13}C NMR (151MHz, $CDCl_3$)



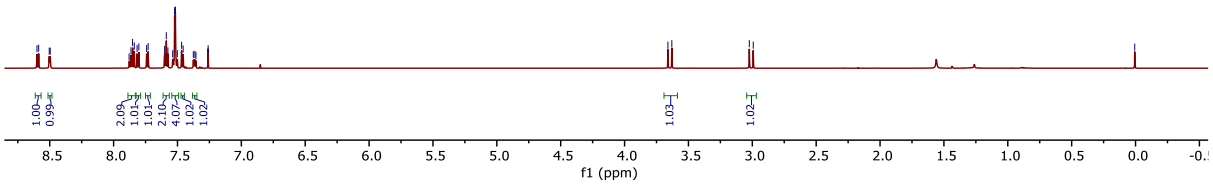
^{19}F NMR (564 MHz, $CDCl_3$)

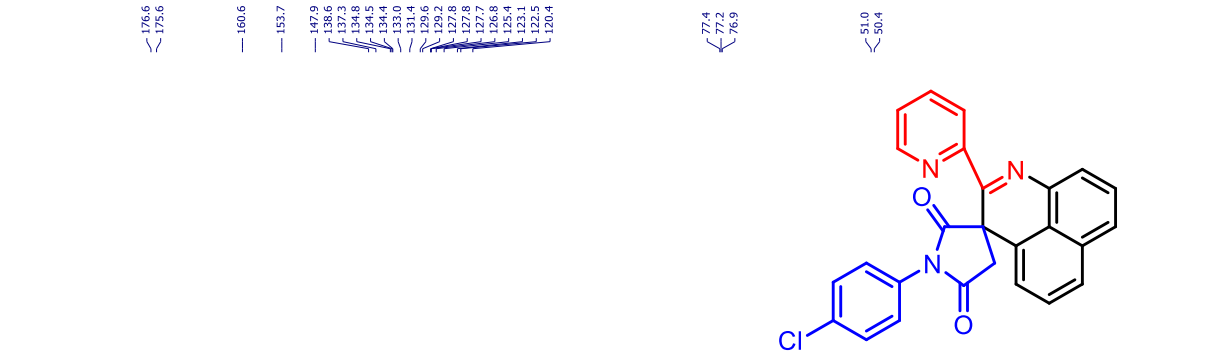


1'-(4-chlorophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3s)

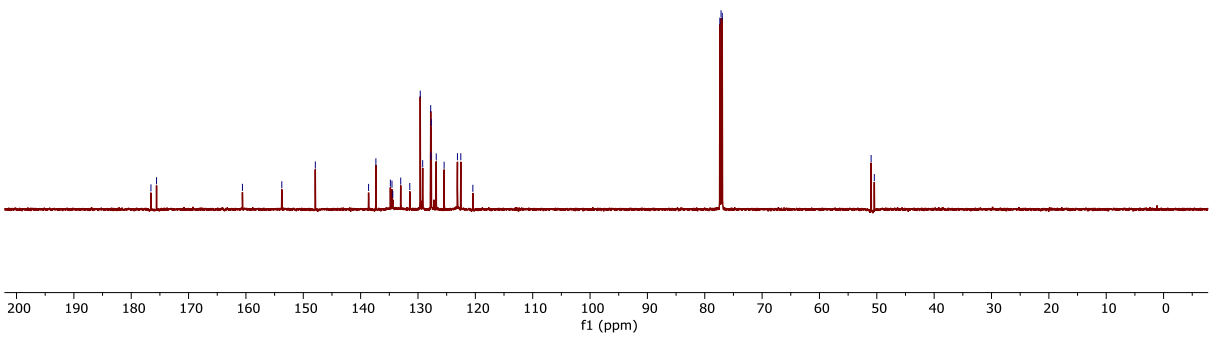


^{1}H NMR (600MHz, $CDCl_3$)

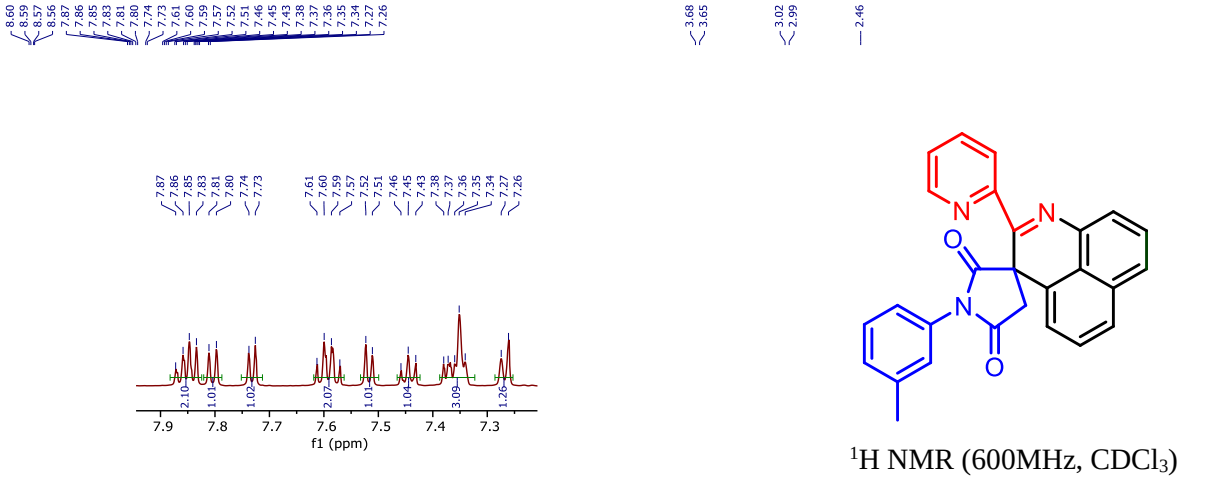




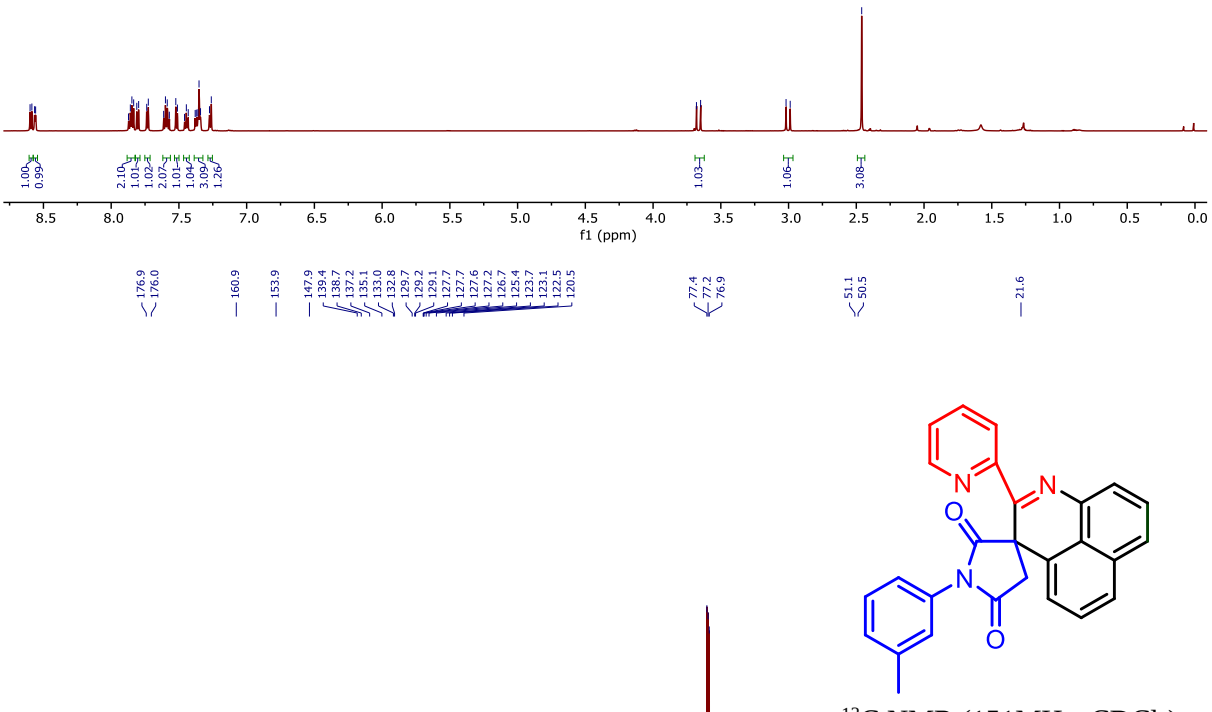
^{13}C NMR (151MHz, $CDCl_3$)



2-(pyridin-2-yl)-1'-(m-tolyl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3t)

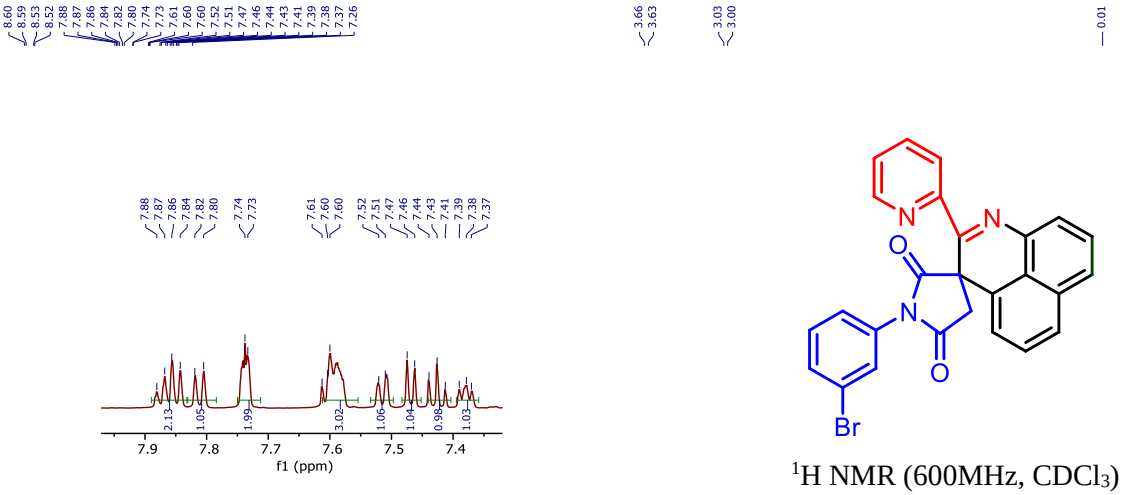


^{1}H NMR (600MHz, $CDCl_3$)

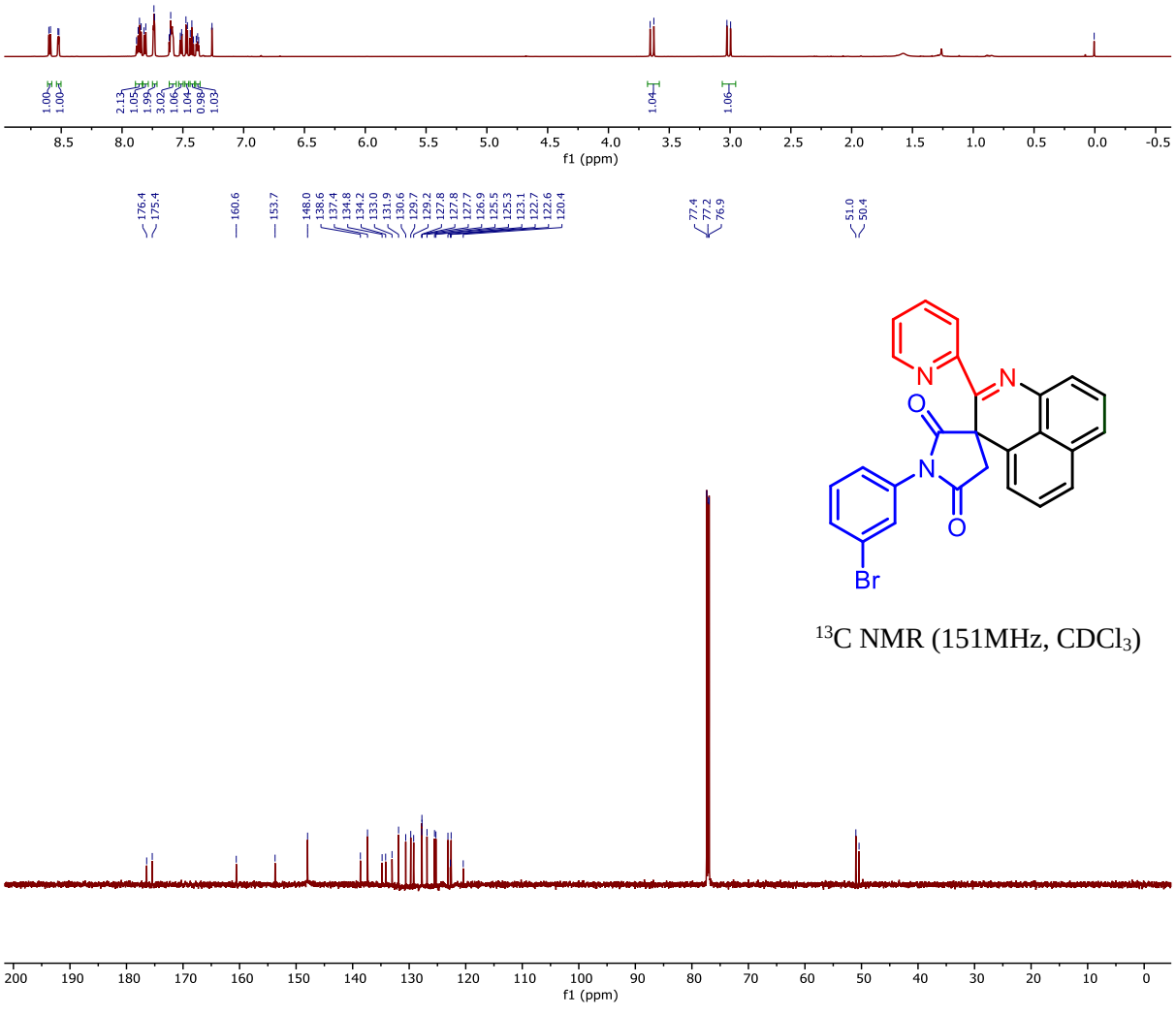


^{13}C NMR (151MHz, $CDCl_3$)

1'-(3-bromophenyl)-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3u)

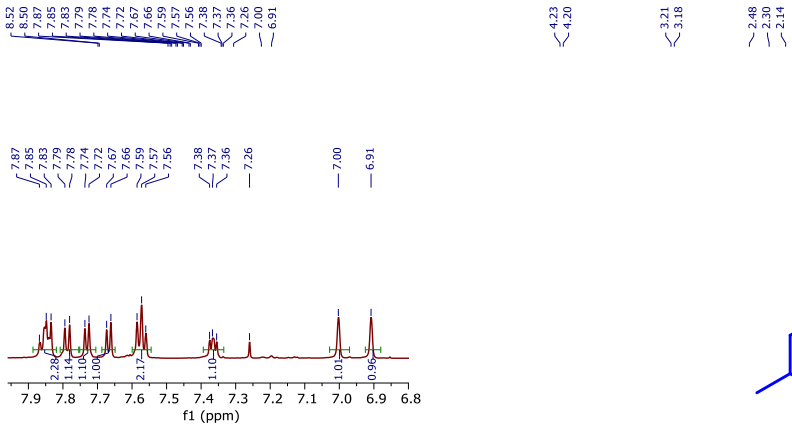


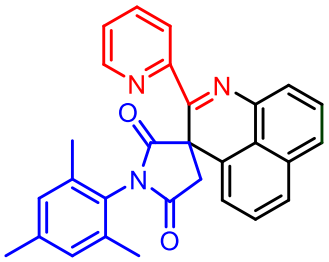
^{1}H NMR (600MHz, $CDCl_3$)



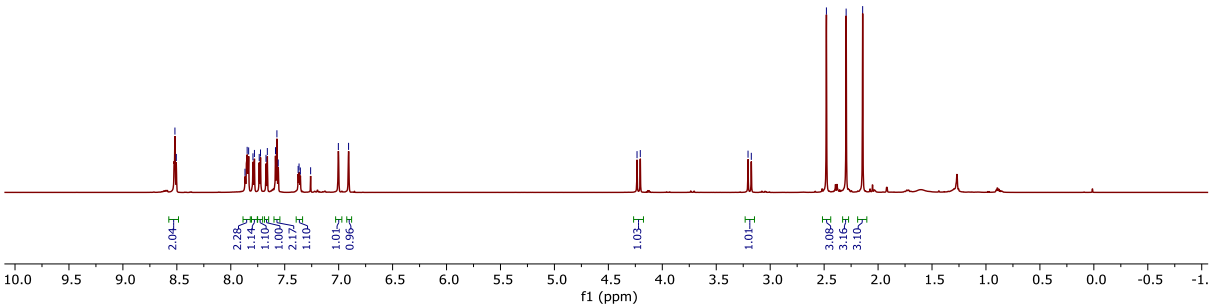
^{13}C NMR (151MHz, $CDCl_3$)

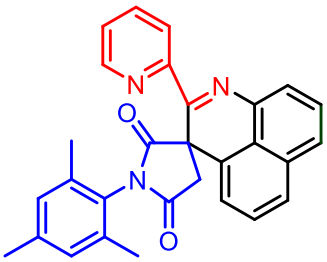
1'-mesityl-2-(pyridin-2-yl)spiro[benzo[de]quinoline-3,3'-pyrrolidine]-2',5'-dione (3v)



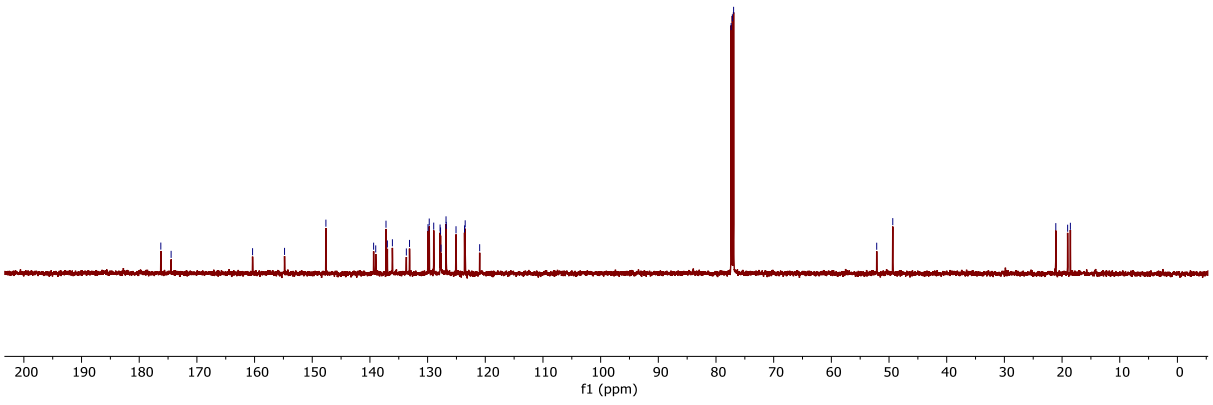


^{1}H NMR (600MHz, $CDCl_3$)



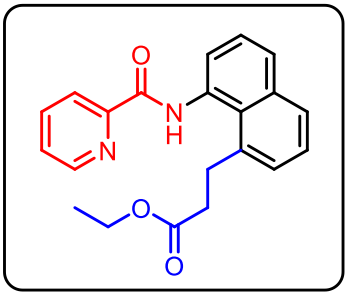


^{13}C NMR (151MHz, $CDCl_3$)



Ethyl 3-(8-(picolinamido)naphthalen-1-yl)propanoate (6a)

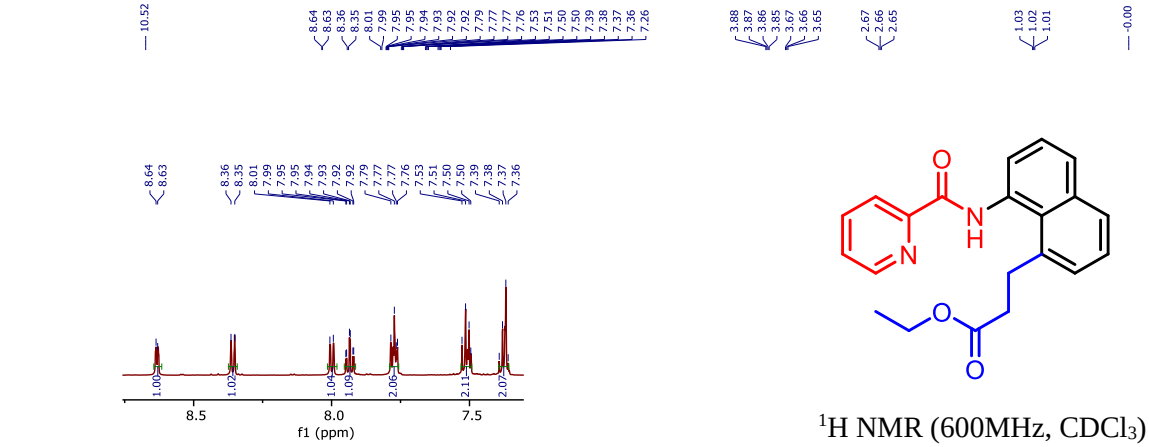
Yellow solid (47 mg, 54%) (n-Hexane: EtOAc = 4:1).



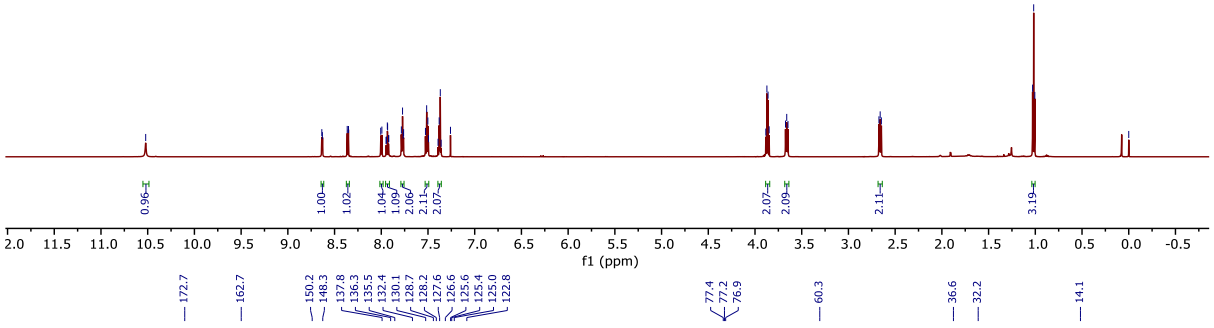
^{1}H NMR (600 MHz, Chloroform-d): δ 10.52 (s, 1H), 8.63 (d, *J* = 3.5 Hz, 1H), 8.36 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.93 (td, *J* = 7.7, 1.7 Hz, 1H), 7.77 (m, 2H), 7.53 – 7.49 (m, 2H), 7.37 (m, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.64 (t, *J* = 7.8 Hz, 2H), 2.68 – 2.64 (t, *J* = 7.8 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H).

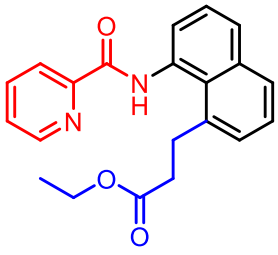
^{13}C NMR (151 MHz, Chloroform-d): δ 172.7, 162.7, 150.2, 148.3, 137.8, 136.3, 135.5, 132.4, 130.1, 128.7, 128.2, 126.6, 125.6, 125.4, 125.0, 122.8, 60.3, 36.6, 32.2, 14.1.

Ethyl 3-(8-(picolinamido)naphthalen-1-yl)propanoate (6a)



^{1}H NMR (600MHz, $CDCl_3$)





^{13}C NMR (151MHz, $CDCl_3$)