Electronic supplementary materials *Mendeleev Commun.*, 2024, **34**, 238–241

Transition metal-free visible light induced intramolecular C–Hal/C–H bond activation leading to cyclization into pyrimido[5′,4′:3,4]pyrrolo[1,2-*f*]phenanthridines

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S1. General information and materials

General Information.

Solvents were purified and dried according to standard methods and stored over activated 3 Å molecular sieves prior to use. Column chromatography was conducted on silica gel 60 (230−400 mesh, Merck). Glassware was dried at 120 °C in an oven for at least 3 h before use. ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance NEO 300 spectrometer at 300 MHz for ^{1}H, 75 MHz for ^{13}C and 280 MHz for ^{19}F. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent residual signals as internal standards: δ 7.26 ($CDCl_3$) for ^{1}H, δ 77.16 ($CDCl_3$) for ^{13}C. ^{19}F NMR chemical shifts were obtained using C_6F_6 as an internal standard (164.9 ppm).

High-resolution mass spectra (HRMS) were obtained on a Bruker maXis QTOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. HRMS measurements were conducted in positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was performed with the use of a low-concentration tuning mix solution, Agilent. Direct syringe injection was implemented for the analyzed solutions at a 3 μL min^{-1} flow rate. In HRMS measurements, nitrogen was applied as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was 250 °C. All the spectra were recorded with 1 Hz frequency and processed using Bruker Data Analysis 4.0 software.

GC-MS experiments were performed using an Agilent 7890A GC instrument equipped with an Agilent 5975C mass-selective detector (electron ionization, 70 eV) and an HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as the carrier gas at a flow rate of 1.0 ml min^{-1}.

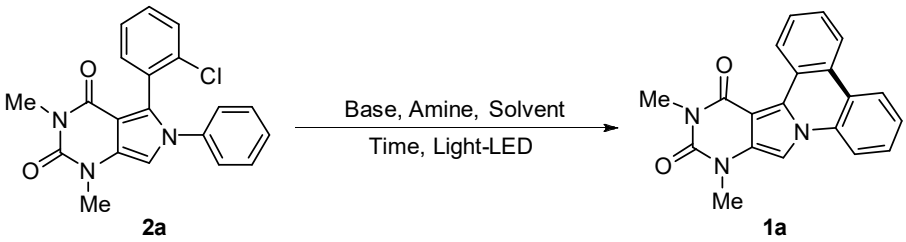
Irradiation Sources: Light emitting diodes (LEDs) were used for irradiation of the reaction mixtures: violet LED, λ_{max} = 395 nm, 30 W, blue LED λ_{max} = 460 nm, 30 W and UVA LED, λ_{max} = 365 nm, 10 W. For the 1 sun (100 mW/cm^2 illumination) measurement, a solar simulator was utilized from Toption Group Co., Model TOP-X500, which was equipped with a 500 W xenon lamp as the light source.

Starting compounds 5-(2-chlorobenzoyl)-1,3,6-trimethylpyrimidine-2,4(1*H*,3*H*)-dione (**7a**)[S1], 5-(2-bromobenzoyl)-1,3,6-trimethylpyrimidine-2,4(1*H*,3*H*)-dione **7b**)[S1,2], 5-benzoyl-1,3,6-trimethylpyrimidine-2,4(1*H*,3*H*)-dione (**7c**)[S2], 1,3,6-trimethyl-5-(4-methylbenzoyl)pyrimidine-2,4(1*H*,3*H*)-dione (**7d**)[S1], 5-(4-fluorobenzoyl)-1,3,6-trimethylpyrimidine-2,4(1*H*,3*H*)-dione (**7e**)[S1], 5-(4-methoxybenzoyl)-1,3,6-trimethylpyrimidine-2,4(1*H*,3*H*)-dione (**7f**)[S1], 5-(2-bromobenzoyl)-6-(bromomethyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**8b**)[S3], 5-benzoyl-6-(bromomethyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (**8c**)[S2], 5-(2-bromophenyl)-1,3-dimethyl-6-

phenyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2'a**)[S3], 5-(2-bromophenyl)-1,3-dimethyl-6-(2-methylphenyl)-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2g**)[S3], 5-(2-bromophenyl)-1,3-dimethyl-6-(4-methylphenyl)-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2'b**)[S3], 5-(2-bromophenyl)-6-(4-ethylphenyl)-1,3-dimethyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2h**)[S3], 5-(2-bromophenyl)-6-(4-methoxyphenyl)-1,3-dimethyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2k**)[S3], 5-(2-bromophenyl)-6-[4-(diethylamino)phenyl]-1,3-dimethyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2i**)[S3], 5-(2-bromophenyl)-6-(2,5-dimethylphenyl)-1,3-dimethyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2j**)[S3], 5-(2-bromophenyl)-6-(3,5-dimethylphenyl)-1,3-dimethyl-1,6-dihydro-2*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*)-dione (**2k**)[S3] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

S2. Extended experimental data

Table S1. Optimization of the reaction conditions.[a]



2a **1a**

Entry	Light source (λ, nm/W)	Base	Additive	Solvent	Time, h	Yield, %[b]
1.	365/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	5	89
2.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	5	91
3.	460/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	5	1
4.	460/2×40	Cs_2CO_3	DIPEA (1.6 eq)	DMF	5	3
5.	460/2×40	Cs_2CO_3	DIPEA (1.6 eq)	DMF	12	46
6.	Sunlight[c]	Cs_2CO_3	DIPEA (1.6 eq)	DMF	5	20
7.	Sunlight[d]	none	DIPEA (3.2 eq)	DMF	44	91
8.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	1	64
9.	395/30	Cs_2CO_3	DIPEA (1.6 eq), TEMPO (3 eq)	DMF	5	trace
10.	395/30	Cs_2CO_3	DIPEA (1.6 eq), $Pd(PPh_3)_4$ (1 mol%)	DMF	1	65
11.	395/30	Cs_2CO_3	DIPEA (1.6 eq), $Pd(OAc)_2$ (1 mol%)	DMF	1	62
12.	395/30	Cs_2CO_3	DIPEA (1.6 eq), $[RuCl_2(cymene)]_2$ (1 mol%)	DMF	1	64
13.	395/30	Cs_2CO_3	DIPEA (1.6 eq), $Ni(OAc)_2$ (1 mol%)	DMF	1	0
14.	395/30	Cs_2CO_3	DIPEA (1.6 eq), CuCl (1 mol%)	DMF	1	0
15.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	2	81
16.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	8	96
17.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	12	97[e]
18.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMF	20	97[e]
19.	395/30	none	DIPEA (1.6 eq)	DMF	12	75
20.	395/30	none	DIPEA (3.2 eq)	DMF	12	95
21.	395/30	Cs_2CO_3	none	DMF	12	28
22.	395/30	none	none	DMF	12	trace
23.	None	Cs_2CO_3	DIPEA (1.6 eq)	DMF	72	0
24.	395/30	Cs_2CO_3	TEA (1.6 eq)	DMF	12	48
25.	395/30	Cs_2CO_3	DBU (1.6 eq)	DMF	12	89
26.	395/30	Cs_2CO_3	DABCO (1.6 eq)	DMF	12	58
27.	395/30	K_2CO_3	DIPEA (1.6 eq)	DMF	12	93
28.	395/30	K_3PO_4	DIPEA (1.6 eq)	DMF	12	92
29.	395/30	KOAc	DIPEA (1.6 eq)	DMF	12	91
30.	395/30	*t*-BuOK	DIPEA (1.6 eq)	DMF	12	93
31.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMSO	12	13
32.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	DMA	12	95
33.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	PhMe	12	26
34.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	MeCN	12	20
35.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	THF	12	21
36.	395/30	Cs_2CO_3	DIPEA (1.6 eq)	$CHCl_3$	12	trace

[a] *Reagent and conditions*: **2a** (0.1 mmol), base (0.16 mmol), additive, solvent (2.5 mL), light source, 30±5 °C; [b] GC-MS yield. [c] For the 1 sun (100 mW/cm^2 illumination) measurement, we used a solar simulator (Toption Group Co., Model TOP-X500) equipped with a 500 W xenon lamp as a light source. [d] The reaction was carried out in a glass vial exposed to sunlight (August 25-28, at Novocherkassk, 3th floor roof top, clear sky at maximum outside temperature 38 °C), for 3 days (solar light irradiation within ~44 h), without stirring. [e] Conversion of **2a** was 100%, a dehalogenation side-product (~ 3% yield) was detected.

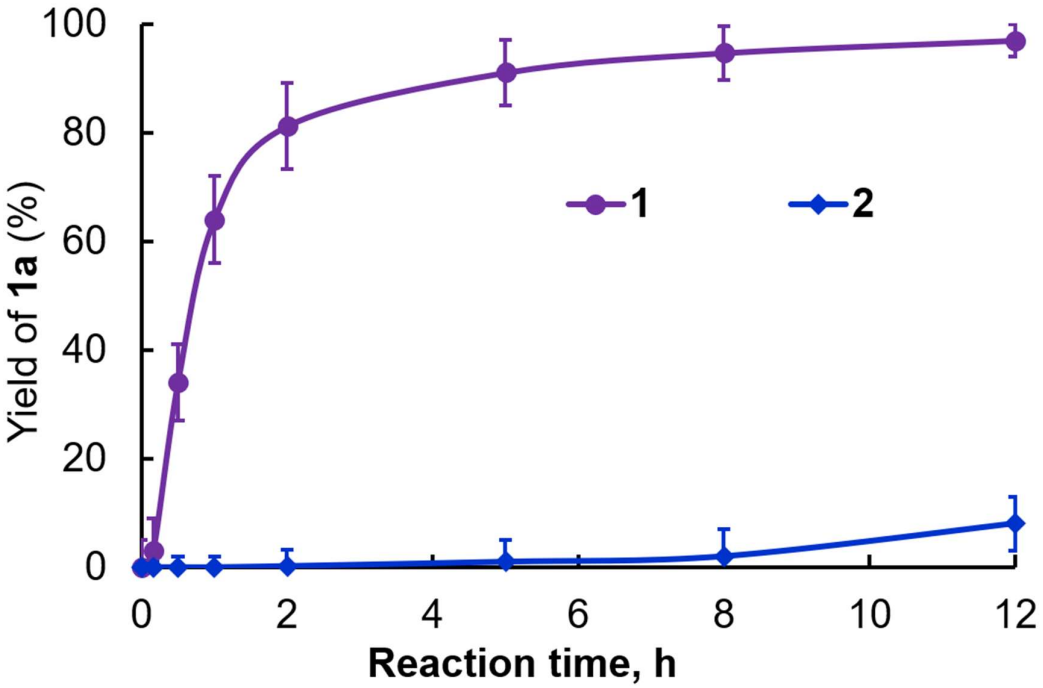


Figure S1. Kinetic curves for the formation of compound **1a** from **2a**. *Reaction conditions:* compound **2a** (0.1 mmol), Cs_2CO_3 (0.16 mmol, 1.6 eq), DIPEA (0.16 mmol, 1.6 eq), DMF (2.5 ml), irradiation under violet LED light (395 nm, 30 W, *curve 1*) or under blue LED light (460 nm, 30 W, *curve 2*).

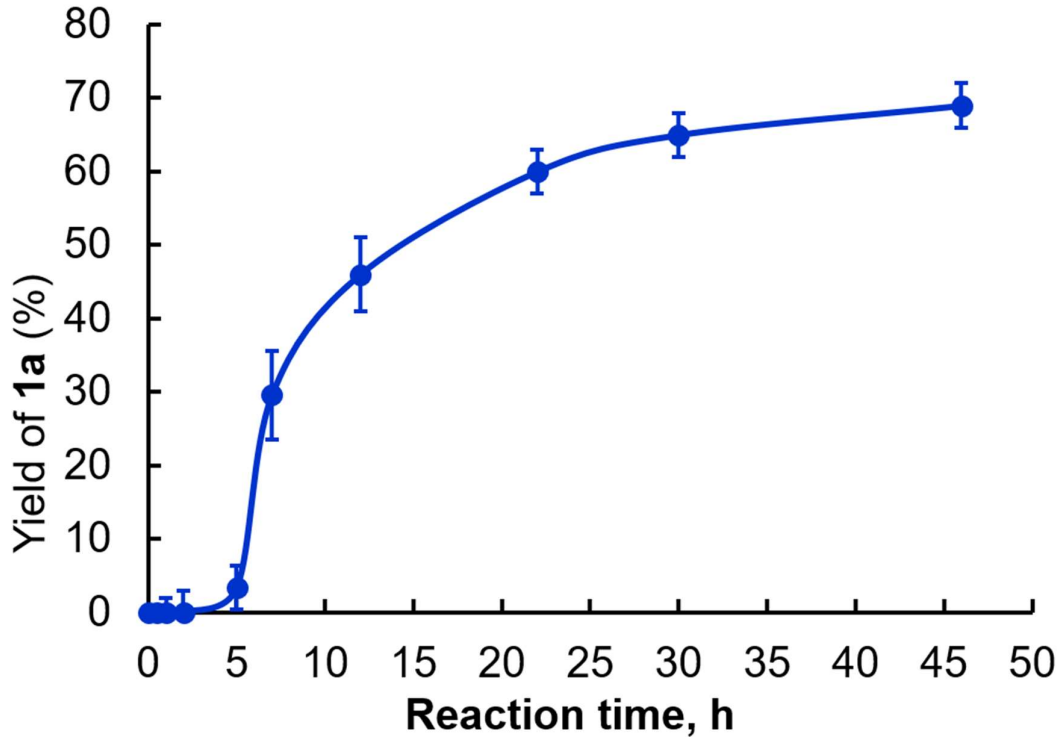


Figure S2. Kinetic curve for the formation of compound **1a** from **2a**. *Reaction conditions:* compound **2a** (0.1 mmol), Cs_2CO_3 (0.16 mmol, 1.6 eq), DIPEA (0.16 mmol, 1.6 eq), DMF (2.5 ml, 0.04 M), blue LED light (460 nm, 2×40 W).

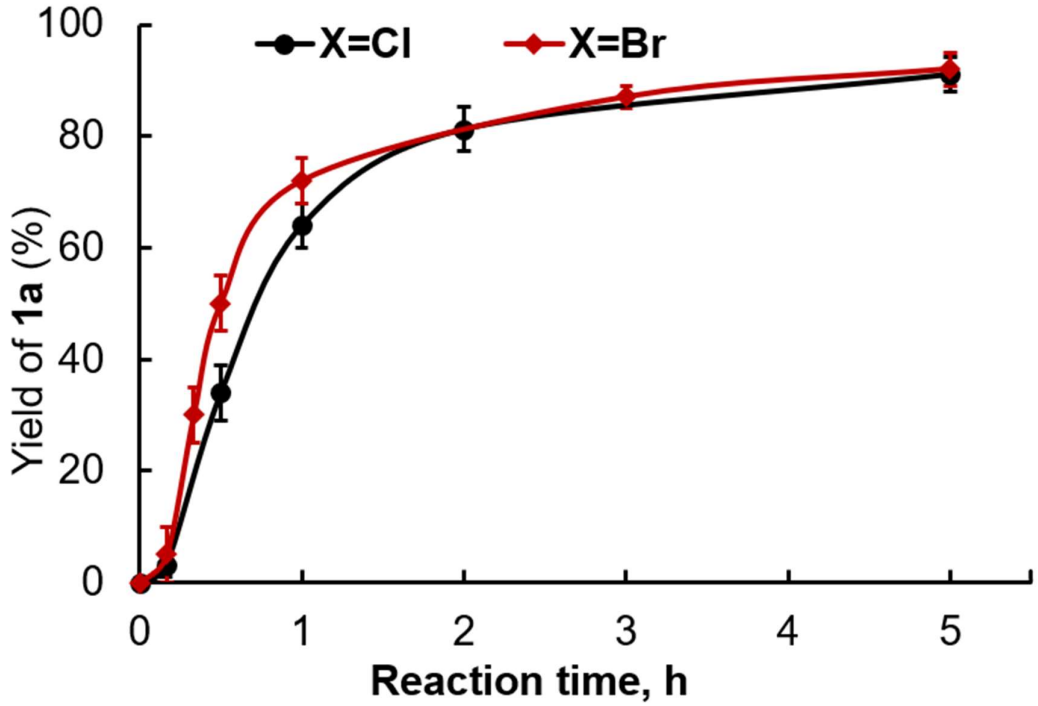


Figure S3. Kinetic curves for the formation of compound **1a** from **2a** (X = Cl, *black line*) and **2'a** (X=Br, *red line*). *Reaction conditions:* compound **2a** or **2'a** (0.1 mmol), Cs_2CO_3 (0.16 mmol, 1.6 eq), DIPEA (0.16 mmol, 1.6 eq), DMF (2.5 ml, 0.04 M), violet LED light (395 nm, 30 W).

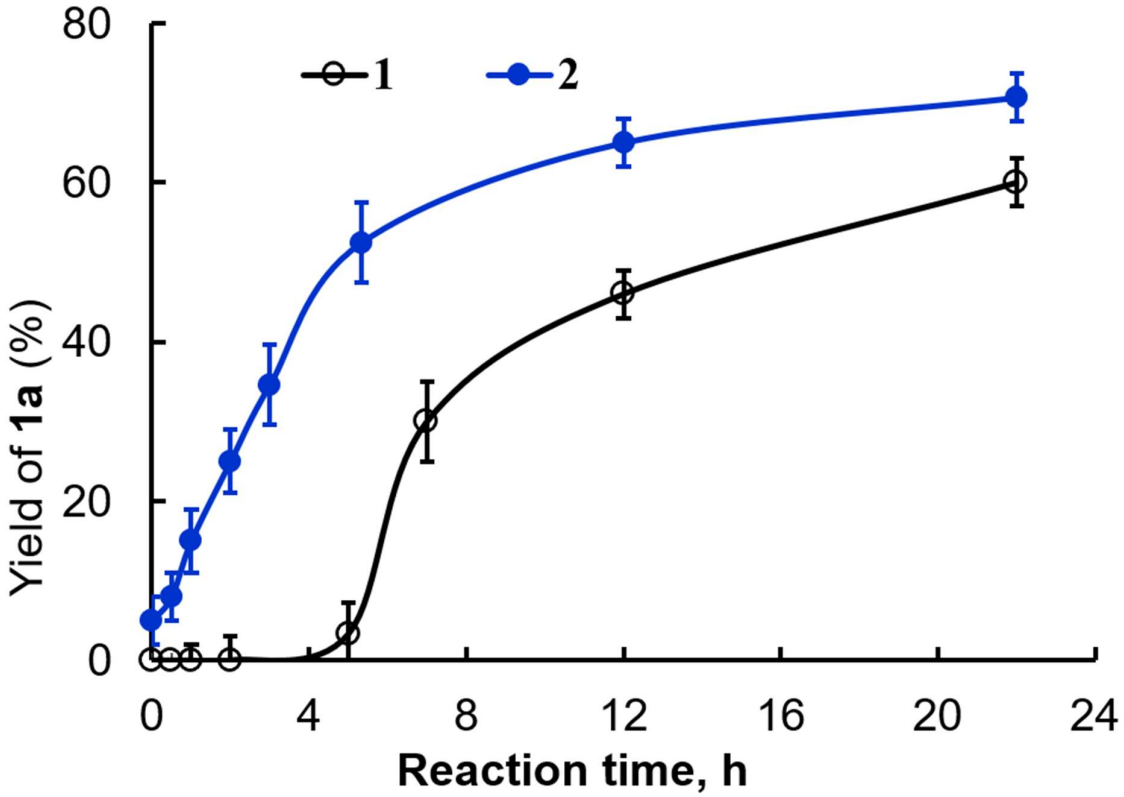
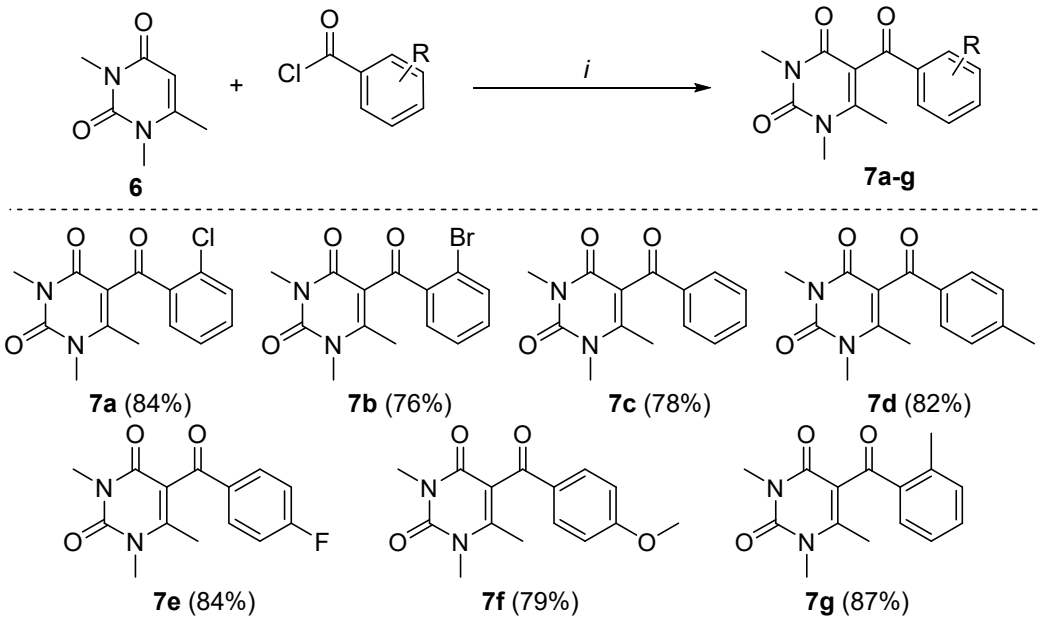
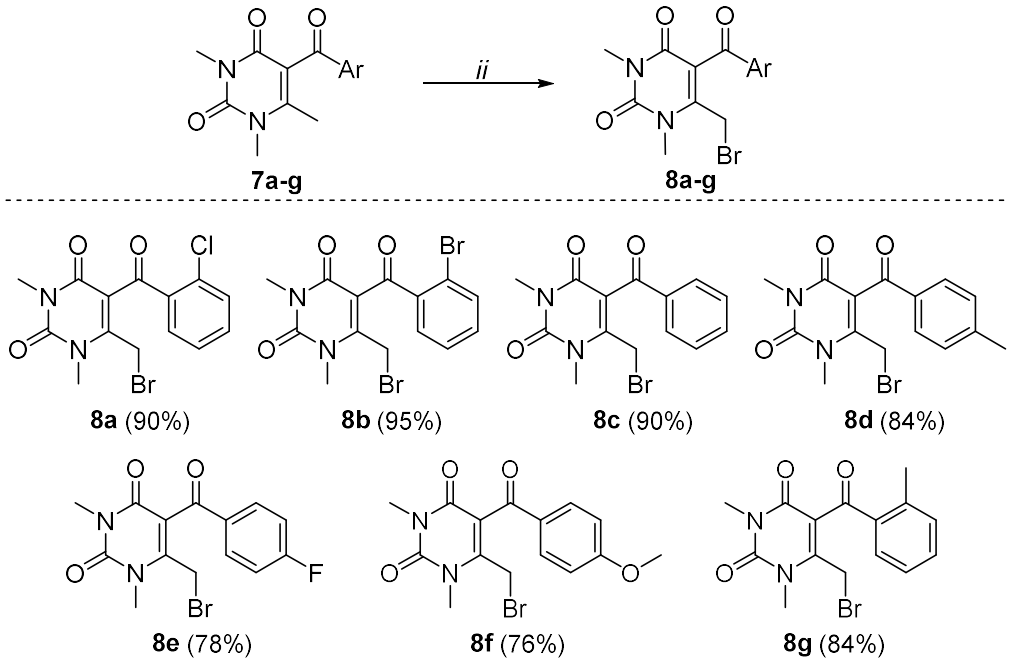


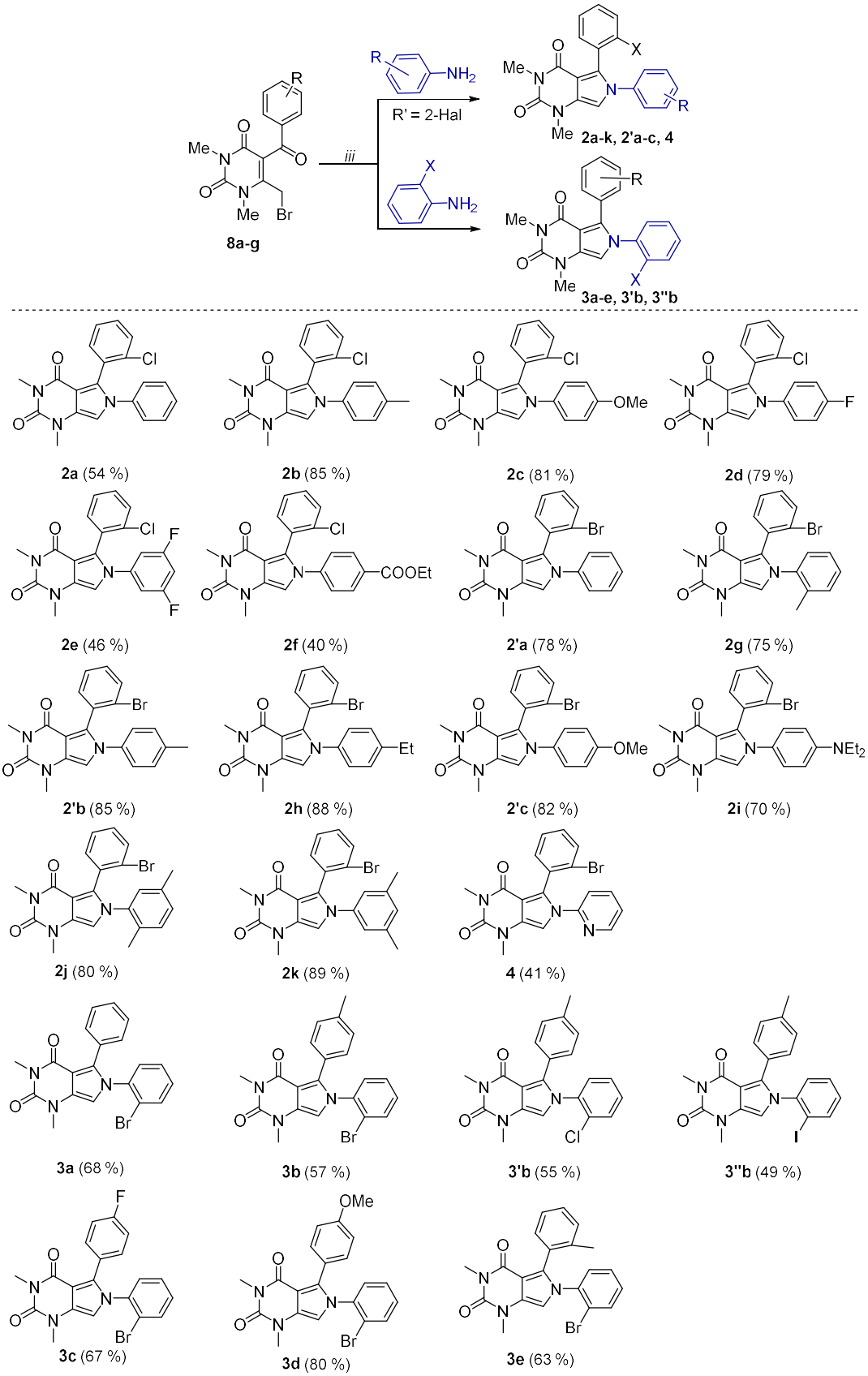
Figure S4. Kinetic curves for the formation of compound **1a**. Curve *1* – the reaction in the absence of **1a**, curve *2* – the reaction in the presence of **1a** (5 mol.%). *Reaction conditions*: **2a** (0.1 mmol), Cs_2CO_3 (0.16 mmol, 1.6 eq), DIPEA (0.16 mmol, 1.6 eq), DMF (2.5 mL, 0.04 M), 30 °C, blue LED (460 nm, 2×40 W).



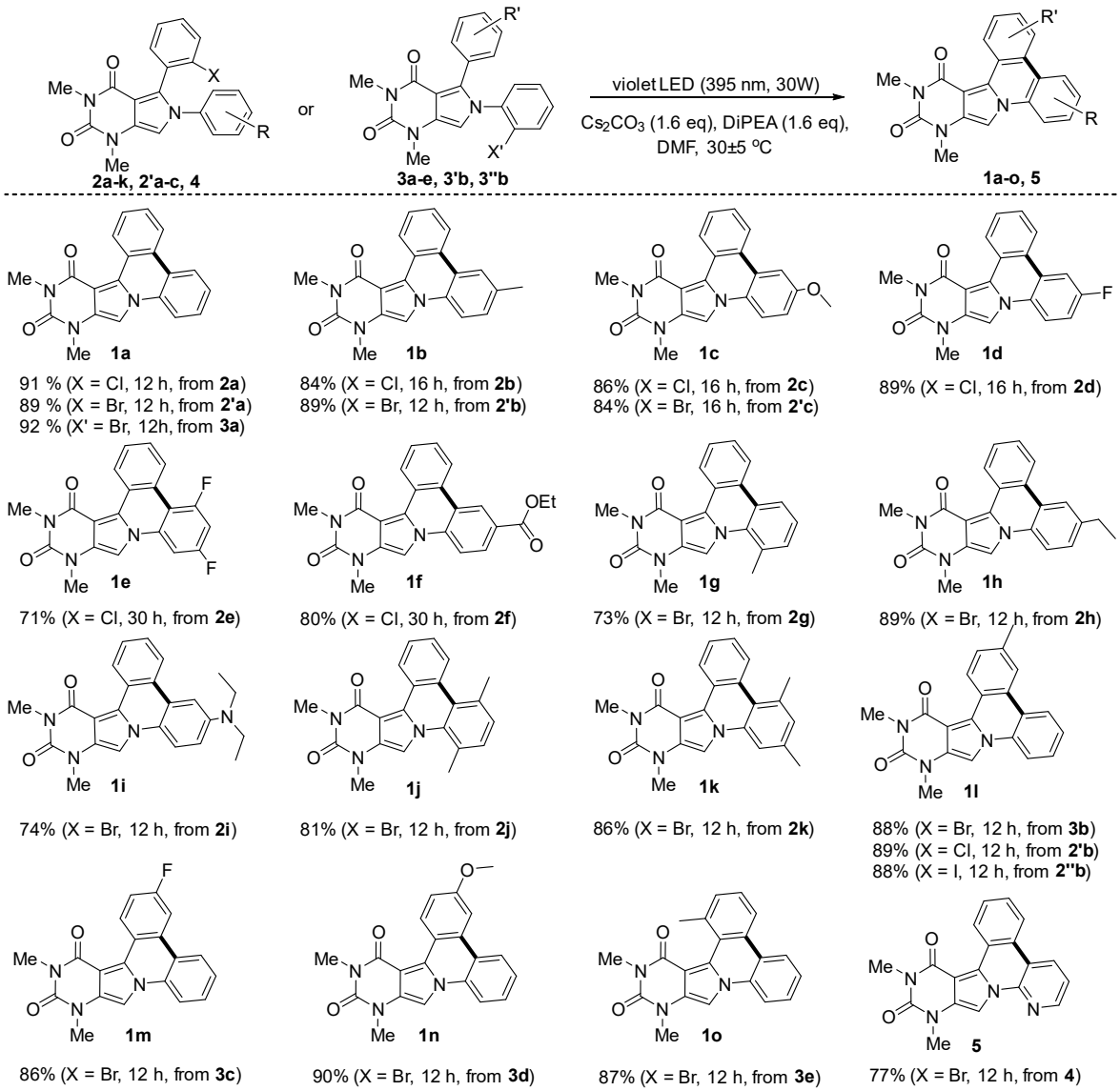
Scheme S1. Synthesis of starting compounds **7.** *Reaction conditions*: *i* ArCOCl (0.015 mmol), $ZnCl_2$ (0.015 mmol), benzene, reflux, 24 h.



Scheme S2 Synthesis of starting compounds **8.** *Reaction conditions*: *ii* compounds **7a-g** (5 mmol), Br_2 (0.8 g, 5 mmol), $CHCl_3$ (5 ml), 1 h, 60 °C.



Scheme S3 Synthesis of starting compounds **2a-k, 2'a-c, 3a-e, 3'b, 3''b, 4.** *Reaction conditions*: *iii* compound **8a-g** (1 mmol), (hetero)aromatic amine (1.05 mmol), Et_3N (1.05 mmol), EtOH (5 ml), reflux.



Scheme S4 Synthesis of compounds **1a-o, 5.** *Reaction conditions*: **2a-k, 2'a-c, 3a-e, 3'b, 3''b, 4** (0.5 mmol), Cs_2CO_3 (0.8 mmol), DIPEA (0.8 mmol), DMF (12.5 ml), 30±5 °C, violet LED (395 nm, 30W).

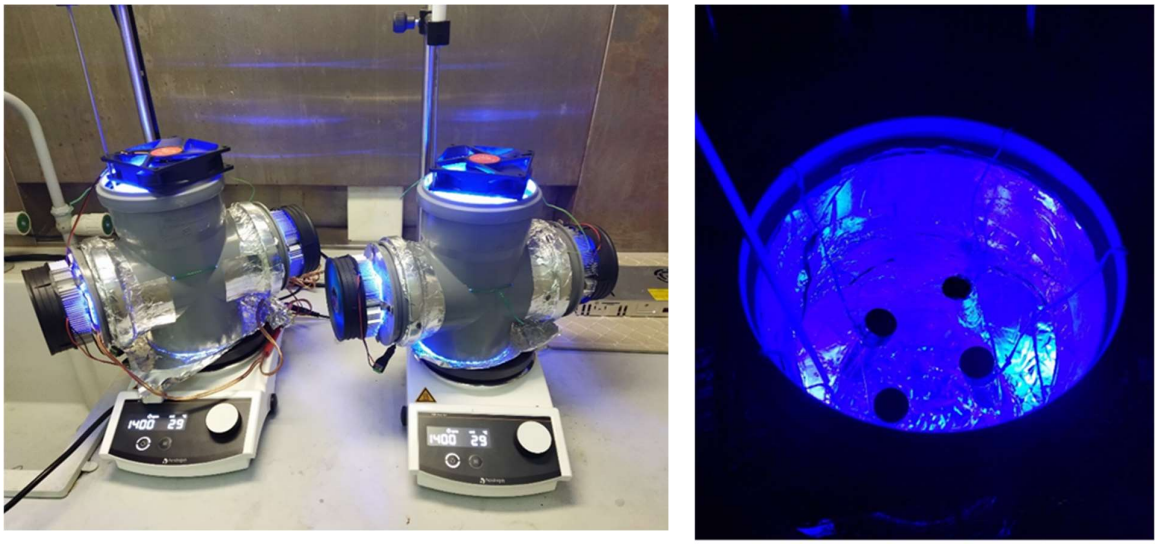


Figure S5. Photoreactors used in the study (left) and the interior view of the reactor (right). The reactors equipped with blue LEDs are shown.

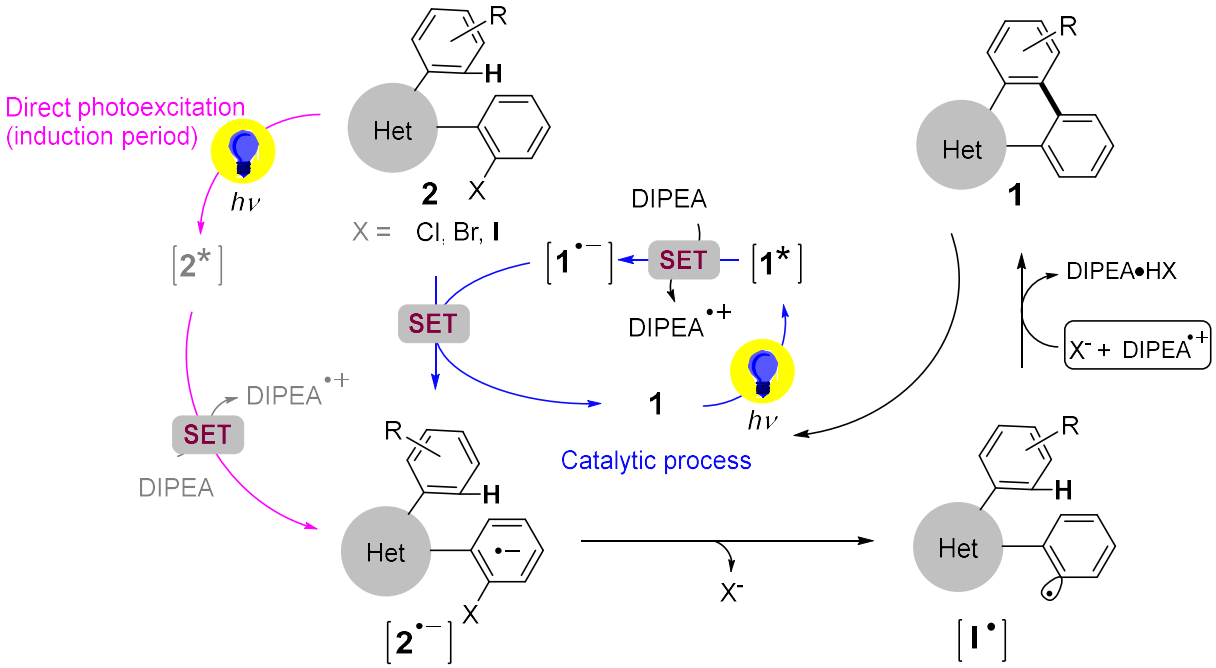
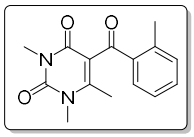


Figure S6. Proposed mechanism for the photoinduced cyclization of compounds **2** including the direct photoexcitation (during induction period) and the catalytic process involving product **1** as photocatalyst.

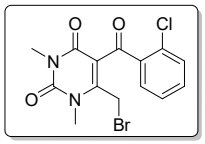
S3. Experimental procedures and characterization of synthesized compounds

General procedure for the synthesis of compounds 7a-g. A mixture of aroyl chloride (0.015 mol), anhydrous $ZnCl_2$ (2.04 g, 0.015 mol) and benzene (10 ml) was refluxed under stirring for 5 min and then cooled to 25 °C. 1,3,6-Trimethyluracil **3** (1.54 g, 0.01 mol) was added. The reaction mixture was then refluxed with stirring for 24 h. The solvent was then rotary evaporated *in vacuo*. The residue obtained was treated with water (25 ml). A precipitate formed was collected by filtration, washed with water (25 ml), then treated with 5% aqueous NaOH solution (30 ml) under stirring for 10 min, filtered off, washed with water, and recrystallized from ethanol. The product obtained was dried at 50 °C *in vacuo* overnight.

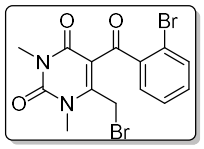


1,3,6-Trimethyl-5-(2-methylbenzoyl)pyrimidine-2,4(1*H*,3*H*)-dione (7g). Yield 2.37 g (87 %), white powder, mp 154—155 °C. HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{17}N_2O_3^+$: *m/z* 273.1253 $[M + H]^+$. Found: 273.1234. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.31 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 3.51 (s, 3H, CH_3), 7.17 – 7.24 (m, 1H, Ar), 7.27 – 7.32 (m, 1H, Ar), 7.38 (dd, 1H, *J* = 7.4, 1.5 Hz, Ar), 7.47 (dd, 1H, *J* = 7.7, 1.4 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 17.6, 21.3, 28.2, 32.2, 114.7, 125.8, 130.0, 132.16, 132.23, 138.1, 139.4, 151.8, 152.4, 160.6, 195.7.

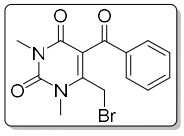
General procedure for the synthesis of compounds 8a-g. A solution of Br_2 (0.8 g, 5 mmol) in $CHCl_3$ (5 ml) was added dropwise under stirring to a solution of compound **7a-g** (5 mmol) in $CHCl_3$ at room temperature. The mixture was then refluxed for 1 h, then chloroform was rotary evaporated to dryness *in vacuo* and the residue was recrystallized from ethanol. The product obtained was dried overnight at 50 °C *in vacuo*.



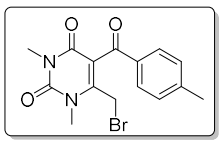
5-(2-Chlorobenzoyl)-6-(bromomethyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (8a). Yield 1.67 g (90 %), white powder, mp 176—177 °C. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{13}BrClN_2O_3^+$: *m/z* 370.9794 $[M + H]^+$. Found: 370.9793. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.33 (s, 3 H, CH_3), 3.70 (s, 3 H, CH_3), 4.58 (s, 2 H, CH_2), 7.36—7.48 (m, 3 H, Ar), 7.63—7.67 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 22.6, 28.5, 31.8, 115.1, 127.3, 130.4, 130.6, 131.9, 132.7, 139.0, 151.5, 152.0, 160.4, 192.2.



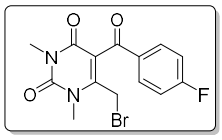
5-(2-Bromobenzoyl)-6-(bromomethyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (8b). Yield 1.976 g (95 %), white powder, mp 177 °C (lit[S3] mp 178-180 °C). The spectral characteristics of the product obtained were described previously. [S3]



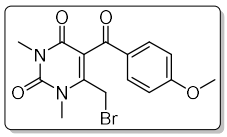
5-Benzoyl-6-(bromomethyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (8c). Yield 1.516 g (90 %), white powder, mp 170 °C (lit[S4] mp 171-172 °C). The spectral characteristics of the product obtained were described previously.[S4]



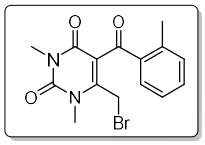
6-(Bromomethyl)-1,3-dimethyl-5-(4-methylbenzoyl)pyrimidine-2,4(1*H*,3*H*)-dione (8d). Yield 1.48 g (84 %), white powder, mp 210—211 °C. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{16}BrN_2O_3^+$: *m/z* 351.0346 $[M + H]^+$. Found: 351.0339. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.41 (s, 3 H, CH_3), 3.36 (s, 3 H, CH_3), 3.62 (s, 3 H, CH_3), 4.24 (s, 2 H, CH_2), 7.27 (dd, 2 H, J = 7.8 Hz, Ar), 7.76 (d, 2 H, J = 8.2 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 22.0, 23.0, 28.5, 31.7, 115.1, 129.6, 129.8, 134.8, 145.4, 148.8, 151.8, 160.5, 192.0.



6-(Bromomethyl)-5-(4-fluorobenzoyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (8e). Yield 1.38 g (78 %), white powder, mp 192—193°C. HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{13}BrFN_2O_3^+$: *m/z* 355.0087 $[M + H]^+$. Found: 355.0088. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.36 (s, 3 H, CH_3), 3.63 (s, 3 H, CH_3), 4.25 (s, 2 H, CH_2), 7.14 (dd, 2 H, J = 8.9, 8.3 Hz, Ar), 7.88 (dd, 2 H, J = 8.9, 5.3 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 22.7, 28.6, 31.7, 114.5, 116.1 (d, $^2J_{C,F}$ = 22.3 Hz), 132.3 (d, $^3J_{CF}$ = 9.7 Hz), 133.7 (d, $^4J_{CF}$ = 3.0 Hz), 149.5, 151.6, 160.5, 166.5 (d, $^1J_{CF}$ = 256.7 Hz), 191.0.



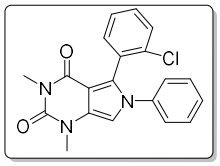
6-(Bromomethyl)-5-(4-methoxybenzoyl)-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione (8f). Yield 1.40 g (76 %), white powder, mp 202—203 °C (dec.). HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{16}BrN_2O_4^+$: *m/z* 367.0288 $[M + H]^+$. Found: 367.0284. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.37 (s, 3 H, CH_3), 3.62 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 4.23 (s, 2 H, CH_2), 6.94 (d, 2 H, J = 8.9 Hz, Ar), 7.85 (d, 2 H, J = 8.9 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 23.2, 28.6, 31.7, 55.7, 114.2, 115.2, 130.1, 132.2, 148.4, 151.8, 160.5, 164.7, 190.6.



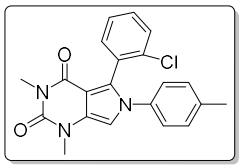
6-(Bromomethyl)-1,3-dimethyl-5-(2-methylbenzoyl)pyrimidine-2,4(1*H*,3*H*)-dione (8g). Yield 1.48 g (84 %), white powder, mp 149—150 °C. HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{16}BrN_2O_3^+$: *m/z* 351.0339 $[M + H]^+$. Found: 351.0339. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.60 (s, 3 H, CH_3), 3.31 (s, 3 H, CH_3), 3.64 (s, 3 H, CH_3), 4.38 (s, 2 H, CH_2), 7.17 – 7.25 (m, 1 H, Ar), 7.27 – 7.34 (m, 1 H, Ar), 7.35 – 7.45 (m, 1 H, Ar), 7.49 (dd, 1 H, J = 7.7, 1.4 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.2, 22.7, 28.5, 31.7, 116.0, 125.8, 130.1, 132.2, 132.5, 137.7, 139.5, 149.6, 151.7, 160.4, 194.8.

General procedure for the synthesis of compounds 2a-k, 2'a-c, 3a-e, 3'b, 3''b, 4. A mixture of compound **8a-g** (1.35 mmol), appropriate arylamine (1.41 mmol), Et_3N (142 mg, 1.4 mmol) and of ethanol (5 ml) was refluxed with stirring for 4 h. The mixture was then cooled to room temperature. A precipitate formed was collected by filtration, washed sequentially with ice-cold ethanol (5 ml) and 1/1 ethanol/water mixture (10 ml),

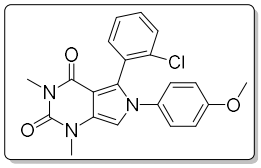
and recrystallized from a suitable solvent. The product obtained was dried overnight at 50 °C *in vacuo*.



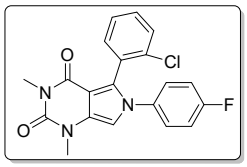
5-(2-Chlorophenyl)-1,3-dimethyl-6-phenyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2a). Yield 265 mg (54 %), white powder, mp 215—216 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}ClN_3O_2^+$: *m*/*z* 366.0999 $[M + H]^+$. Found: 411.0451. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.37 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 6.67 (s, 1 H, Ar), 7.14—7.20 (m, 2 H, Ar), 7.22—7.25 (m, 1 H, Ar), 7.26—7.37 (m, 6 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 27.9, 31.8, 103.7, 105.3, 125.6, 126.5, 128.1, 129.3, 129.5, 129.6, 129.7, 130.4, 130.6, 133.2, 135.2, 138.8, 152.0, 159.8.



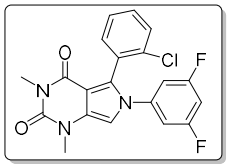
5-(2-Chlorophenyl)-1,3-dimethyl-6-(4-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2b). Yield 437 mg (85 %), white powder, mp 271—272 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}ClN_3O_2^+$: *m*/*z* 380.1160 $[M + H]^+$. Found: 380.1160. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.28 (s, 3 H, CH_3), 3.33 (s, 3 H, CH_3), 3.42 (s, 3 H, CH_3), 6.61 (s, 1 H, Ar), 6.99 —7.07 (m, 4 H, Ar), 7.17—7.34 (m, 4 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.1, 27.8, 31.7, 103.7, 105.1, 125.3, 126.5, 129.5, 129.57, 129.6, 129.8, 130.3, 130.5, 133.1, 135.2, 136.2, 138.1, 152.0, 159.8.



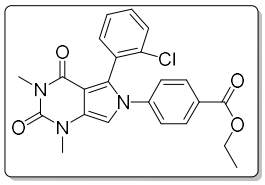
5-(2-Chlorophenyl)-6-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2c). Yield 433 mg (81 %), white powder, mp 200—201 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}ClN_3O_3^+$: *m*/*z* 396.1107 $[M + H]^+$. Found: 396.1109. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.36 (s, 3 H, CH_3), 3.45 (s, 3 H, CH_3), 3.77 (s, 3 H, OCH_3), 6.60 (s, 1 H, Ar), 6.78 (d, 2 H, *J* = 9.0 Hz, Ar), 7.08 (d, 2 H, *J* = 9.0 Hz, Ar), 7.19—7.25 (m, 1 H, Ar), 7.27—7.37 (m, 3 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 27.8, 31.8, 55.6, 103.9, 104.9, 114.3, 126.5, 126.8, 129.53, 129.58, 129.61, 130.5, 131.7, 133.2, 135.2, 152.0, 159.2, 159.8 (some C_{Ar} signals overlap).



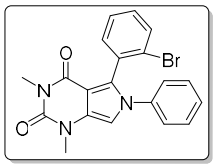
5-(2-Chlorophenyl)-6-(4-fluorophenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2d). Yield 409 mg (79 %), white powder, mp 247—248 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}ClFN_3O_2^+$: *m*/*z* 384.0923 $[M + H]^+$. Found: 384.0910. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.37 (s, 3 H, CH_3), 3.45 (s, 3 H, CH_3), 6.61 (s, 1 H, Ar), 6.95—7.01 (m, 2 H, Ar), 7.13—7.17 (m, 2 H, Ar), 7.21—7.37 (m, 4 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 27.9, 31.8, 103.7, 105.3, 116.3 (d,$^2J_{C,F}$ = 23 Hz), 126.6, 127.5 (d,$^3J_{C,F}$ = 8.7 Hz), 129.3, 129.6, 129.7, 129.8, 130.6, 130.8, 133.2, 134.8 (d,$^4J_{C,F}$ = 3.1 Hz), 152.0, 159.8, 162.0 (d,$^1J_{C,F}$ = 249 Hz).



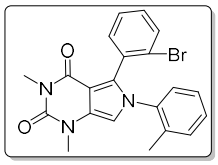
5-(2-Chlorophenyl)-6-(3,5-difluorophenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2e). Yield 248 mg (46 %), white powder, mp 247—248°C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{15}ClF_2N_3O_2^+$: *m/z* 402.0823 $[M + H]^+$. Found: 402.0815. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.36 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 6.64 (s, 1 H, Ar), 6.70—6.78 (m, 3 H, Ar), 7.29—7.41 (m, 4 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 27.9, 31.8, 103.3, 103.8 (t, $^2J_{C,F}$ = 25 Hz), 106.1, 109.1 (dd, $^2J_{C,F}$ = 28.3 Hz, $^3J_{C,F}$ = 9.1 Hz), 126.9, 128.8, 129.9, 130.2, 130.5, 131.2, 133.1, 135.0, 140.8 (t, 6-ArC(1), $^3J_{C,F}$ = 13 Hz), 151.9, 159.6, 162.9 (dd, $^1J_{C,F}$ = 251 Hz, $^3J_{C,F}$ = 14 Hz).



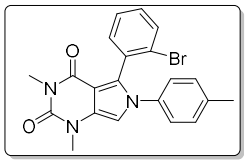
Ethyl 4-[5-(2-chlorophenyl)-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydro-6*H*-pyrrolo[3,4-*d*]pyrimidin-6-yl]benzoate (2f). Yield 234 mg (40 %), white powder, mp 166—167 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{21}ClN_3O_4^+$: *m/z* 438.1228 $[M + H]^+$. Found: 438.1215. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.38 (t, 3 H, *J* = 7.1 Hz, $C\underline{H}_3CH_2$), 3.37 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 4.36 (q, 2 H, *J* = 7.1 Hz, $CH_3C\underline{H}_2$), 6.68 (s, 1 H, Ar), 7.21 (d, 2 H, *J* = 8.7 Hz, Ar), 7.27 — 7.36 (m, 4 H, Ar), 7.97 (d, 2 H, *J* = 8.7 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 14.4, 27.9, 31.8, 61.5, 103.3, 105.9, 125.1, 126.7, 129.1, 129.8, 129.9, 130.1, 130.5, 130.7, 130.9, 133.2, 135.1, 142.5, 151.9, 159.7, 165.7.



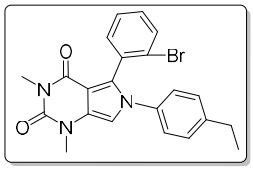
5-(2-Bromophenyl)-1,3-dimethyl-6-phenyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2'a). Yield 432 mg (78 %), white powder, mp 190 °C (lit[S3] mp 190-192 °C). The spectral characteristics of the product obtained were described previously.[S3]



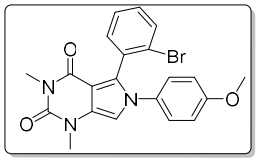
5-(2-Bromophenyl)-1,3-dimethyl-6-(2-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2g). Yield 429 mg (75 %), white powder, mp 260 °C (lit[S3] mp 260-262 °C). The spectral characteristics of the product obtained were described previously.[S3]



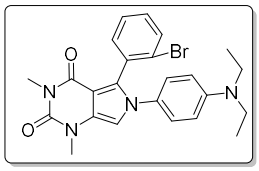
5-(2-Bromophenyl)-1,3-dimethyl-6-(4-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2'b). Yield 486 mg (85 %), white powder, mp 249 °C (lit[S3] mp 249-251 °C). The spectral characteristics of the product obtained were described previously. [S3]



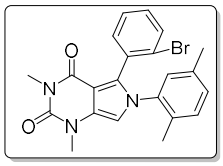
5-(2-Bromophenyl)-6-(4-ethylphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2h). Yield 520 mg (88 %), white powder, mp 187 °C (lit[S3] mp 188-190 °C). The spectral characteristics of the product obtained were described previously.[S3]



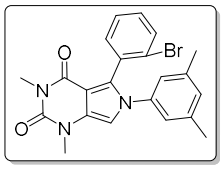
5-(2-Bromophenyl)-6-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2'c). Yield 487 mg (82 %), white powder, mp 225 °C (lit[S3] mp 224-226 °C). The spectral characteristics of the product obtained were described previously.[S3]



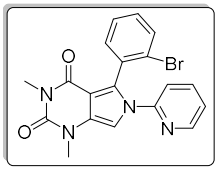
5-(2-Bromophenyl)-6-[4-(diethylamino)phenyl]-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2i). Yield 455 mg (70 %), white powder, mp 215 °C (lit[S3] mp 216-218 °C). The spectral characteristics of the product obtained were described previously.[S3]



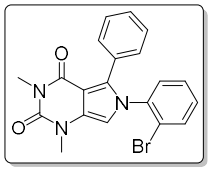
5-(2-Bromophenyl)-6-(2,5-dimethylphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2j). Yield 473 mg (80 %), white powder, mp 221 °C (lit[S3] mp 224-226 °C). The spectral characteristics of the product obtained were described previously. [S3]



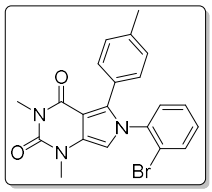
5-(2-Bromophenyl)-6-(3,5-dimethylphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (2k). Yield 526 mg (89 %), white powder, mp 201 °C (lit[S3] mp 200-205 °C). The spectral characteristics of the product obtained were described previously.[S3]



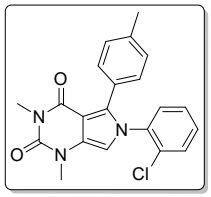
5-(2-Bromophenyl)-1,3-dimethyl-6-(pyridin-2-yl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (4). Yield 228 mg (41 %), white powder, mp 190—191 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{19}H_{16}BrN_4O_2^+$: *m/z* 411.0461 $[M + H]^+$. Found: 411.0451. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.36 (s, 3 H, CH_3), 3.49 (s, 3 H, CH_3), 6.76 (d, 1 H, *J* = 8.2 Hz, Ar), 7.17—7.23 (m, 2 H, Ar), 7.26— 7.43 (m, 3 H, Ar), 7.49—7.55 (m, 1 H, Ar), 7.59—7.62 (m, 1 H, Ar), 8.49—8.51 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 27.9, 31.8, 102.4, 106.4, 117.8, 122.6, 125.3, 127.5, 129.4, 130.9, 131.0, 131.9, 133.0, 133.2, 138.2, 149.3, 150.7, 152.0, 159.8.



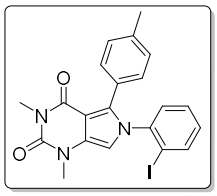
6-(2-Bromophenyl)-1,3-dimethyl-5-phenyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3a). Yield 376 mg (68 %), white powder, mp 210 °C (lit[S3] mp 210-213 °C). The spectral characteristics of the product obtained were described previously.[S3]



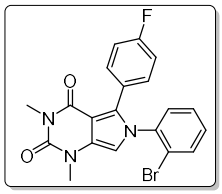
6-(2-Bromophenyl)-1,3-dimethyl-5-(4-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3b). Yield 328 mg (57 %), white powder, mp 204—205 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}BrN_3O_2^+$: *m/z* 424.0654 $[M + H]^+$. Found: 424.0655. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.28 (s, 3 H, CH_3), 3.39 (s, 3 H, CH_3), 3.43 (c, 3 H, CH_3), 6.46 (s, 1 H, Ar), 7.04 (d, 2 H, *J* = 8.0 Hz, Ar), 7.18 — 7.24 (m, 4 H, Ar), 7.27 — 7.32 (m, 1 H, Ar), 7.59 — 7.63 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.5, 28.0, 31.7, 103.2, 104.0, 122.3, 126.0, 128.2, 128.5, 129.8, 130.4, 130.5, 130.7, 133.7, 135.6, 138.5, 138.6, 152.0, 160.2.



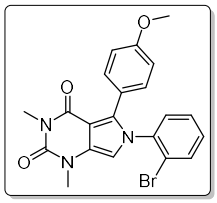
6-(2-Chlorophenyl)-1,3-dimethyl-5-(4-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3'b). Yield 284 mg (55 %), white powder, mp 200—201 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}ClN_3O_2^+$: *m*/*z* 380.1174 $[M + H]^+$. Found: 380.1160. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.28 (s, 3 H, CH_3), 3.39 (s, 3 H, CH_3), 3.43 (s, 3 H, CH_3), 6.47 (s, 1 H, Ar), 7.04 (d, 2 H, *J* = 8.5 Hz, Ar), 7.17—7.25 (m, 4 H, Ar), 7.27—7.35 (m, 1 H, Ar), 7.42—7.45 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.5, 28.0, 31.7, 103.3, 104.0, 126.0, 127.6, 128.6, 129.8, 130.19, 130.22, 130.56, 130.59, 132.3, 135.7, 136.9, 138.7, 152.0, 160.2.



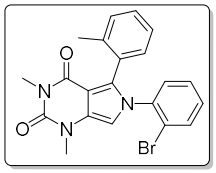
6-(2-Iodophenyl)-1,3-dimethyl-5-(4-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3"b). Yield 310 mg (49 %), white powder, mp 199—200 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}IN_3O_2^+$: *m*/*z* 472.0523 $[M + H]^+$. Found: 472.0516. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.28 (s, 3 H, CH_3), 3.40 (s, 3 H, CH_3), 3.44 (s, 3 H, CH_3), 6.43 (s, 1 H, Ar), 7.02—7.11 (m, 3 H, Ar), 7.19 — 7.23 (m, 3 H, Ar), 7.31 — 7.36 (m, 1 H, Ar), 7.83 — 7.86 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.5, 28.0, 31.8, 97.9, 103.4, 103.8, 125.9, 128.5, 129.1, 129.8, 129.9, 130.5, 131.0, 135.3, 138.6, 140.0, 141.9, 152.0, 160.2.



6-(2-Bromophenyl)-5-(4-fluorophenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3c). Yield 389 mg (67 %), white powder, mp 225—226 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{16}BrFN_3O_2^+$: *m*/*z* 428.0416 $[M + H]^+$. Found: 428.0404. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.40 (s, 3 H, CH_3), 3.44 (s, 3 H, CH_3), 6.48 (s, 1 H, Ar), 6.93 (t, 2 H, *J* = 8.7 Hz, Ar), 7.18 – 7.25 (m, 1 H, Ar), 7.27 – 7.39 (m, 4 H, Ar), 7.56 – 7.67 (m, 1H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 28.0, 31.8, 103.5, 104.3, 115.0 (d, $^2J_{CF}$ = 21.8 Hz), 122.3, 125.0 (d,$^4J_{C,F}$ = 3.7 Hz), 128.4, 129.8, 130.3, 130.7, 132.8 (d, $^3J_{CF}$ = 8.3 Hz), 133.8, 134.2, 138.1, 151.9, 160.2, 162.9 (d, $^1J_{CF}$ = 249.1 Hz). ^{19}F{^{1}H} NMR (280 MHz, DMF-H_6, ppm) δ -114.9.

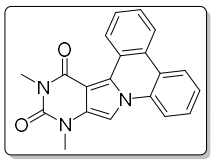


6-(2-Bromophenyl)-5-(4-methoxyphenyl)-1,3-dimethyl-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3d). Yield 475 mg (80 %), white powder, mp 203—204 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}BrN_3O_3^+$: *m*/*z* 440.0588 $[M + H]^+$. Found: 440.0604. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.43 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 6.49 (s, 1 H, Ar), 6.80 (d, 2 H, *J* = 8.8 Hz, Ar), 7.22 – 7.25 (m, 1 H, Ar), 7.27 – 7.40 (m, 4 H, Ar), 7.58 – 7.72 (m, 1H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 28.0, 31.7, 55.3, 103.0, 103.8, 113.3, 121.2, 122.4, 128.3, 129.7, 130.4, 130.5, 132.2, 133.7, 135.4, 138.5, 152.0, 159.8, 160.3.

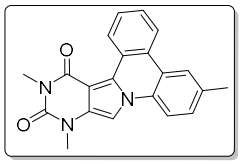


6-(2-Bromophenyl)-1,3-dimethyl-5-(2-methylphenyl)-1*H*-pyrrolo[3,4-*d*]pyrimidine-2,4(3*H*,6*H*)-dione (3e). Yield 360 mg (63 %), white powder, mp 267—268 °C (EtOH). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{19}BrN_3O_2^+$: *m/z* 424.0680 $[M + H]^+$. Found: 424.0655. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 2.24 – 2.28 (m, 3 H, CH_3), 3.37 (s, 3 H, CH_3), 3.45 (s, 3 H, CH_3), 6.54 (s, 1 H, Ar), 6.90 - 7.13 (br.m, 3 H, Ar), 7.13 – 7.23 (m, 4 H, Ar), 7.61 (br.m, 1 H, Ar). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 20.3, 27.9, 31.8, 103.76, 103.79, 104.7, 125.4, 125.5, 128.1, 128.2, 129.2, 129.3, 129.8, 129.9, 130.4, 133.7, 133.8, 152.1, 159.9 (some C_{Ar} signals overlap).

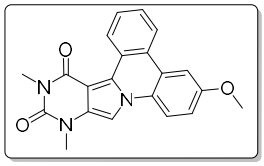
General procedure for the synthesis of compounds 1a-o, 5. The synthesis was carried out under an argon atmosphere. A mixture of compound **2a-k, 2'a-c, 3a-e, 3'b, 3''b, 4** (0.2 mmol), Cs_2CO_3 (104 mg, 0.32 mmol), DIPEA (41 mg, 0.32 mmol) and DMF (2.5 ml) was irradiated by violet LED light (395 nm, 30 W) under stirring at 30±5 °C for 12-30 h (see Schemes 1,2 and S4). Then water (10 ml) was added to the mixture. A precipitate formed was collected by filtration, washed sequentially with water (5 ml) and acetone (5 ml), and dried at 80 °C for 12 h *in vacuo*. Some products containing admixtures were additionally recrystallized from a suitable solvent (see below). It should be noted that due to low solubility of some compounds **1** addition of CF_3COOH was required to obtain NMR spectra (Figures S50, S51, S53, S54).



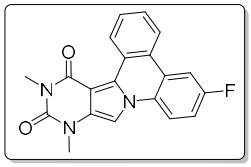
11,13-Dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]phenanthridine-12,14(11*H*,13*H*)-dione (1a). Yield 60 mg (91 %, from **2a**), 58 mg (89 %, from **2'a**), 60 mg (92%, from **3a**), white powder, mp 306—308 °C (lit[S3] mp 304-307 °C). The spectral characteristics of the product obtained were described previously.[S3]



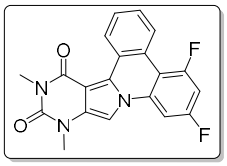
6,11,13-Trimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1b). Yield 57 mg (84 % from **2b**) 61 mg (89 % from **2'b**), white powder, mp >330 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp >330 °C). The spectral characteristics of the product obtained were described previously.[S3]



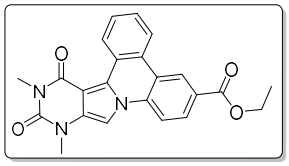
6-Methoxy-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1c). Yield 61 mg (86 % from **2c**), 60 mg (84 % from **2'c**) white powder, mp 287—289 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 286—288 °C). The spectral characteristics of the product obtained were described previously.[S3]



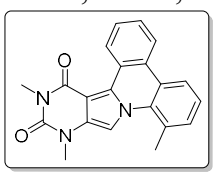
6-Fluoro-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1d). Yield 62 mg (89 %), white powder, mp >330 °C (lit[S3] mp >330 °C). The spectral characteristics of the product obtained were described previously.[S3]



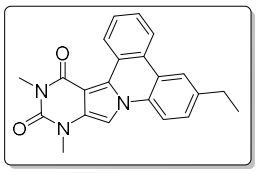
5,7-Difluoro-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1e). Yield 51 mg (71 %) white powder, mp >330 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 314—319 °C). The spectral characteristics of the product obtained were described previously.[S3]



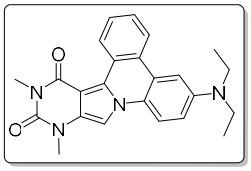
Ethyl 11,13-dimethyl-12,14-dioxo-11,12,13,14-tetrahydropyrimido[5',4':3,4]pyrrolo[1,2-*f*]phenanthridine-6-carboxylate (1f). Yield 64 mg (80 %), white powder, mp 294—295 °C (from DMF-acetone 1:4 mixture). HRMS (ESI-TOF) m/z Calcd for $C_{23}H_{20}N_3O_4^+$: *m*/*z* 402.1439 $[M + H]^+$. Found: 402.1448. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 1.50 (t, 3 H, *J* = 7.1 Hz, $C\underline{H}_3CH_2$), 3.54 (s, 3 H, CH_3), 3.57 (s, 3 H, CH_3), 4.50 (q, 2 H, *J* = 7.1 Hz, $CH_3C\underline{H}_2$), 7.46 (s, 1 H, Ar), 7.67 — 7.76 (m, 2 H, Ar), 7.95 (d, 1 H, *J* = 8.9 Hz, Ar), 8.26 — 8.30 (m, 1 H, Ar), 8.50 — 8.53 (m, 1 H, Ar), 9.20 (d, 1 H, *J* = 1.5 Hz, Ar), 10.32 — 10.35 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 14.6, 28.9, 31.9, 61.7, 95.3, 101.1, 115.9, 122.2, 122.3, 124.8, 126.2, 126.3, 127.5, 128.7, 129.0, 129.2, 129.7, 130.5, 133.5, 134.1, 151.6, 160.2, 165.9.



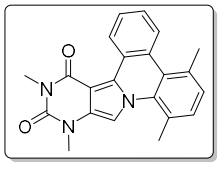
8,11,13-Trimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1g). Yield 50 mg (73 %), white powder, mp 230—231 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 227—230 °C). The spectral characteristics of the product obtained were described previously.[S3]



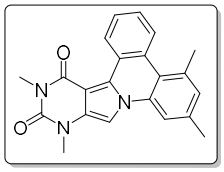
6-Ethyl-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1h). Yield 65 mg (89 %), white powder, mp 316—318 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 315—317 °C). The spectral characteristics of the product obtained were described previously.[S3]



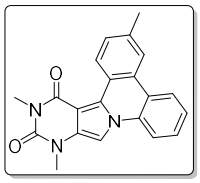
6-(Diethylamino)-11,13-dimethylpyrimido[5',4':3,4]pyrrolo-[1,2-*f*]phenanthridine-12,14(11*H*,13*H*)-dione (1i). Yield 59 mg (74 %), white powder, mp 230—232 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 229—231 °C). The spectral characteristics of the product obtained were described previously.[S3]



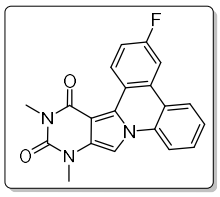
5,8,11,13-Tetramethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1j). Yield 61 mg (81 %), white powder, mp 270—273 °C (from DMF-EtOH 1:4 mixture, lit[S3] mp 272—274 °C). The spectral characteristics of the product obtained were described previously.[S3]



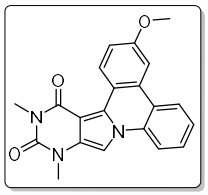
5,7,11,13-Tetramethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1k). Yield 61 mg (86 %), white powder, mp 316—318 °C (lit[S3] mp, 315—317 °C). The spectral characteristics of the product obtained were described previously.[S3]



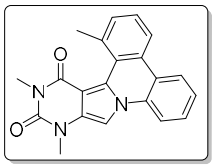
3,11,13-Trimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]phenanthridine-12,14(11*H*,13*H*)-dione (1l). Yield 60 mg (88 % from **3b**), 61 mg (89 %, from **2'b**), 60 mg (88 %, from **2''b**), white-yellow powder, mp 339—340 °C (form DMF). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}N_3O_2^+$: *m/z* 344.1408 $[M + H]^+$. Found: 344.1394. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.59 (s, 3 H, CH_3), 3.53 (s, 6 H, 2 CH_3), 7.39 (s, 1 H, Ar), 7.49 — 7.56 (m, 2 H, Ar), 7.64 (t, 1 H, *J* = 7.5 Hz, Ar), 7.90 (d, 1 H, *J* = 8.3 Hz, Ar), 8.21 (s, 1 H, Ar), 8.50 (d, 1 H, *J* = 8.1 Hz, Ar), 10.19 (d, 1 H, *J* = 8.4 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 22.1, 28.8, 31.8, 94.6, 115.9, 118.0, 122.1, 122.36, 122.45, 124.2, 125.5, 126.7, 128.6, 129.0, 130.0, 131.6, 133.1, 138.7, 142.5, 151.8, 160.4.



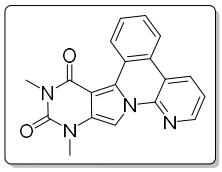
3-Fluoro-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1m). Yield 59 mg (86 %), white powder, mp >320 °C (from DMF). HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{15}FN_3O_2^+$: *m/z* 348.1143 $[M + H]^+$. Found: 348.1143. ^{1}H NMR (300 MHz, $CDCl_3$ + CF_3COOH (3:1), ppm): δ 3.62 (s, 3 H, CH_3), 3.80 (s, 3 H, CH_3), 6.25 (br.s, 2H, protonated pyrrole CH_2), 7.71 – 7.84 (m, 1H, Ar), 7.95 (t, *J* = 7.5 Hz, 1H, Ar), 8.03 (t, *J* = 7.6 Hz, 1H, Ar), 8.10 (d, *J* = 8.4 Hz, 1H, Ar), 8.42 (dd, *J* = 9.7, 2.5 Hz, 1H, Ar), 8.68 (d, *J* = 8.1 Hz, 1H, Ar), 10.66 (dd, *J* = 9.4, 5.5 Hz, 1H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$ + CF_3COOH (3:1), ppm): δ 30.2, 34.9, 56.4 (br.), 109.5 (d, $^2J_{C,F}$ = 23.7 Hz), 117.2, 118.1, 119.79 (d, $^2J_{C,F}$ = 23.7 Hz), 123.1 (d, $^3J_{C,F}$ = 4.1 Hz), 123.16, 124.9, 130.3, 132.3, 134.0, 138.1 (br. d, $^3J_{C,F}$ = 11.2 Hz), 139.5 (br.), 151.1, 157.3, 168.8 (d, $^1J_{C,F}$ = 266 Hz) (some C_{Ar} signals overlap between themselves and with CF_3COOH peaks). ^{19}F{^{1}H} NMR (280 MHz, DMF-H_6, ppm): δ - 75.4.



3-Methoxy-11,13-dimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1n). Yield 64 mg (90 %), white-yellow powder, mp >340 °C (from DMF). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}N_3O_3^+$: *m/z* 360.1344 $[M + H]^+$. Found: 360.1343. ^{1}H NMR (300 MHz, $CDCl_3$ + CF_3COOH (10 μL), ppm): δ 3.56 (s, 3H, CH_3), 3.63 (s, 3H, CH_3), 4.06 (s, 3H, OCH_3), 7.26 (s, 1H, Ar) (overlap with $CHCl_3$), 7.36 (dd, *J* = 9.2, 2.6 Hz, 1H, Ar), 7.56 – 7.74 (m, 3H, Ar), 7.88 (d, *J* = 2.6 Hz, 1H, Ar), 8.47 (d, *J* = 7.6 Hz, 1H, Ar), 10.23 (d, *J* = 9.3 Hz, 1H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$ + CF_3COOH (10 μL), ppm): δ 29.5, 35.4, 55.9, 100.7, 105.8, 116.7, 117.3, 118.9, 123.2, 124.8, 126.7, 128.0, 130.0, 131.2, 132.3, 136.7, 159.5, 161.9 (some C_{Ar} signals are not observed due to low concentration).



1,11,13-Trimethylpyrimido[5',4':3,4]pyrrolo[1,2-*f*]-phenanthridine-12,14(11*H*,13*H*)-dione (1o). Yield 59 mg (87 %), white-yellow powder, mp 242—243 °C (from MeCN). HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}N_3O_2^+$: *m/z* 344.1394 $[M + H]^+$. Found: 344.1394. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 2.70 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 3.56 (s, 3 H, CH_3), 7.42 (s, 1 H, Ar), 7.45 – 7.66 (m, 4 H, Ar), 7.88 (dd, 1 H, *J* = 8.3, 1.2 Hz, Ar), 8.19 (d, 1 H, *J* = 7.5 Hz, Ar), 8.41 (dd, 1 H, *J* = 8.2, 1.4 Hz, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 21.8, 28.5, 31.9, 95.6, 102.9, 115.5, 118.8, 123.2, 123.8, 124.3, 125.6, 128.1, 128.9, 128.9, 129.1, 130.9, 131.4, 132.6, 138.7, 152.2, 159.5.



10,12-Dimethylbenzo[*c*]pyrimido[5',4':3,4]pyrrolo[1,2-*a*][1,8]-naphthyridine-9,11(10*H*,12*H*)-dione (5). Yield 50 mg (77 %), beige powder, mp 335—336 °C (from DMF). HRMS (ESI-TOF) m/z Calcd for $C_{19}H_{15}N_4O_2^+$: *m*/*z* 331.1195 $[M + H]^+$. Found: 331.1190. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 3.53 (s, 3 H, CH_3), 3.55 (s, 3 H, CH_3), 7.51 — 7.55 (m, 1 H, Ar), 7.61 — 7.74 (m, 2 H, Ar), 8.07 (s, 1 H, Ar), 8.32 — 8.35 (m, 1 H, Ar), 8.67 — 8.69 (m, 1 H, Ar), 8.73 — 8.75 (m, 1 H, Ar), 10.24 — 10.27 (m, 1 H, Ar). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm): δ 28.8, 31.9, 96.4, 101.6, 117.2, 121.6, 122.2, 124.9, 125.5, 128.5, 128.7, 129.4, 132.38, 132.5, 142.6, 148.7, 151.7, 160.5 (some C_{Ar} signals overlap).

General procedure of kinetic NMR experiments. The experiment was performed in an argon atmosphere. An aliquot of a 0.6 mL solution containing 24 μmol of compound **3c**, 1.2 μmol (5 mol%) of compound **1a** (if required), 76.8 μmol (3.2 eq.) of DIPEA, and 4 μmol of C_6F_6 in DMF (0.04 M) was placed in an NMR tube. The mixture was irradiated with a 395 nm violet LED at 30 W at 30°C (Figure S6) for different reaction times as shown in Figure 1. For determining the yield of **1m**, ^{19}F NMR utilizing C_6F_6 as an internal standard was applied.

S4. Literature references

S1. A. Ghosh, S. Shee and A. T. Biju, *Org. Lett.*, 2022, **24**, 2772.

S2. C.-H. Lee, W.-C. Wu, P. S. Dangate, L.-C. Shen, W.-S. Chung and C.-M. Sun, *ACS Comb. Sci.*, 2015, **17**, 623.

S3. M. A. Shevchenko, Yu. N. Tkachenko, A. V. Astakhov, O. V. Khazipov, R. V. Tyurin, D. V. Pasyukov, V. A. Tafeenko, O. A. Kravchenko and V. M. Chernyshev, *Russ. Chem. Bull.*, 2018, **67**, 1684.

S4. D. S. Snyder, L. Tradtrantip, C. Yao, M. J. Kurth and A. S. Verkman, *J. Med. Chem.*, 2011, **54**, 5468.

S5. ^{1}H and ^{13}C NMR spectra

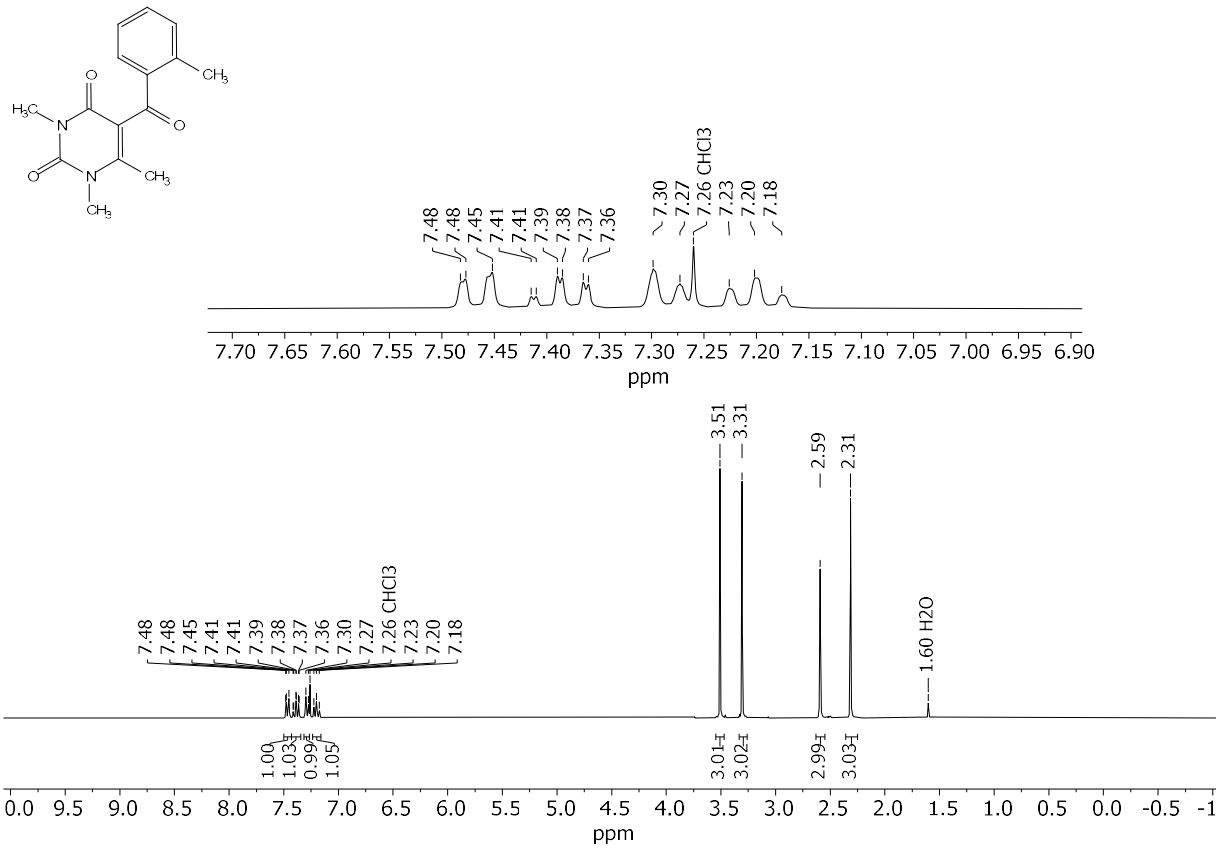


Figure S7. ^{1}H NMR spectrum of **7g** ($CDCl_3$, 300 MHz).

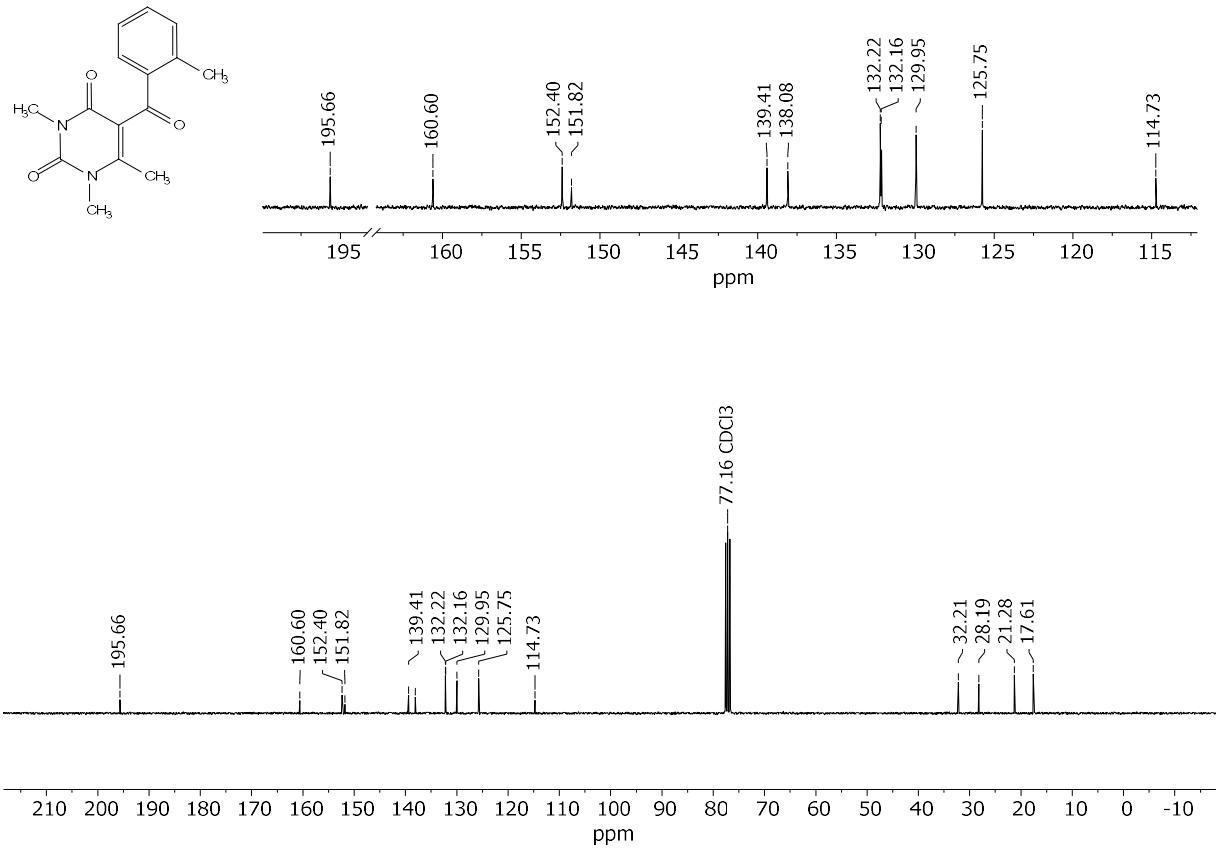


Figure S8. ^{13}C NMR spectrum of **7g** ($CDCl_3$, 75 MHz).

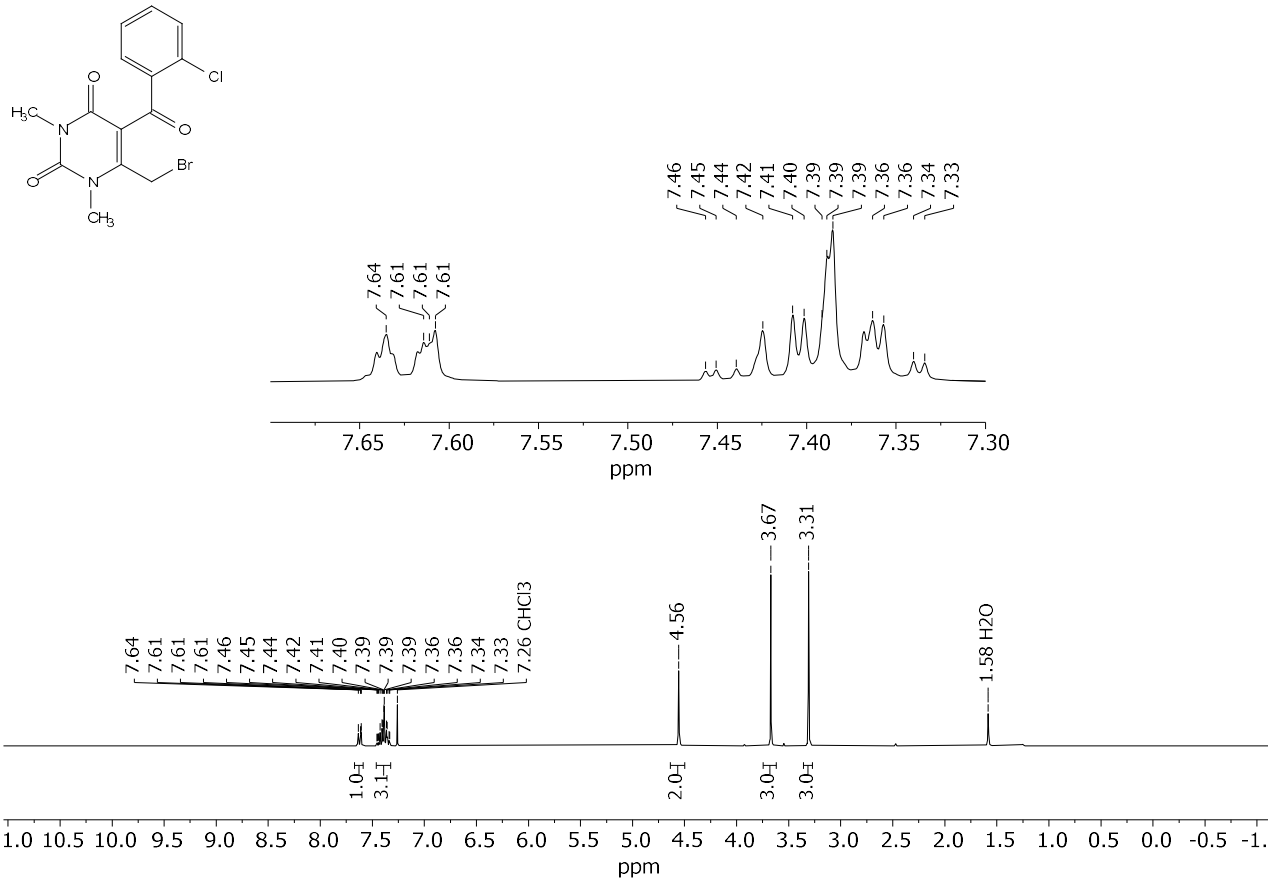


Figure S9. ^{1}H NMR spectrum of **8a** ($CDCl_3$, 300 MHz).

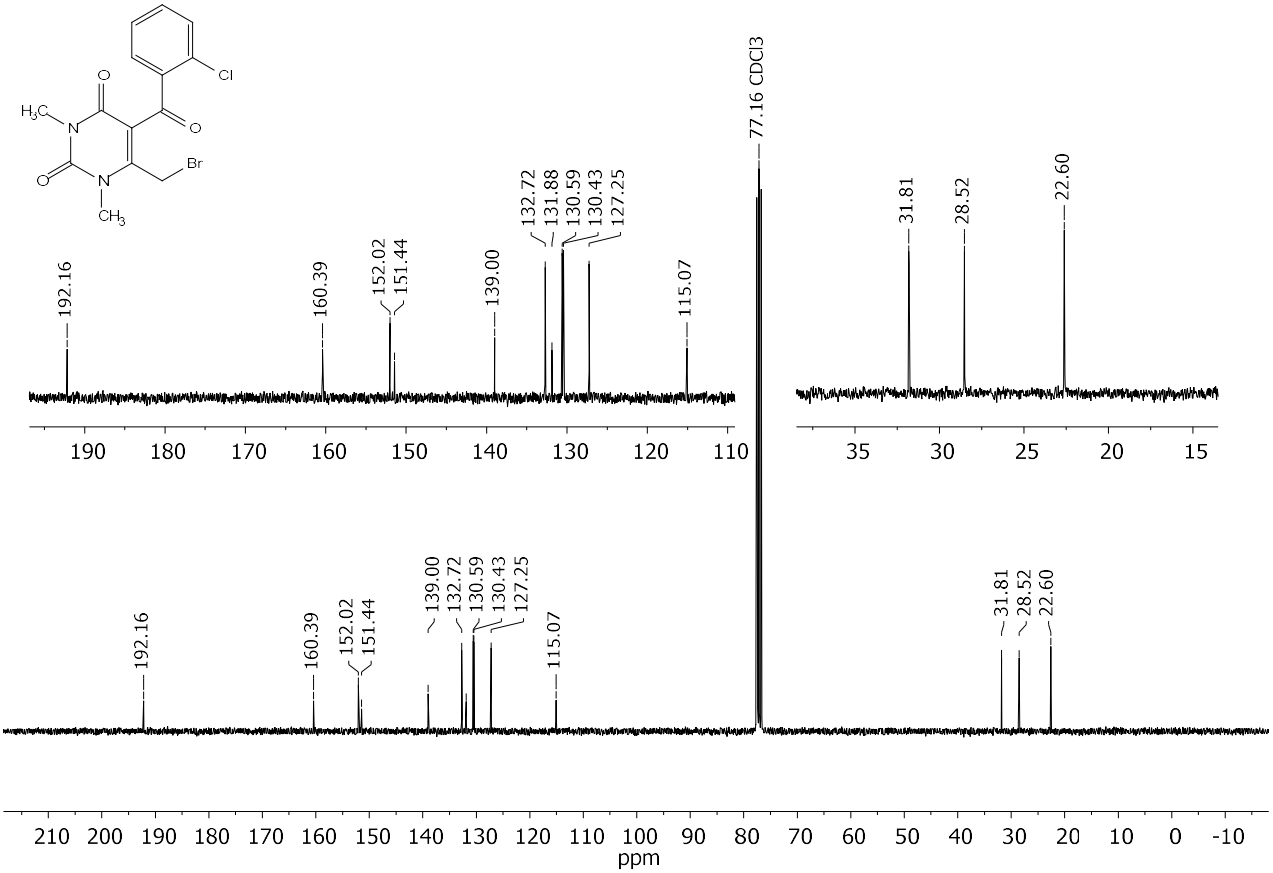


Figure S10. ^{13}C NMR spectrum of **8a** ($CDCl_3$, 75 MHz).

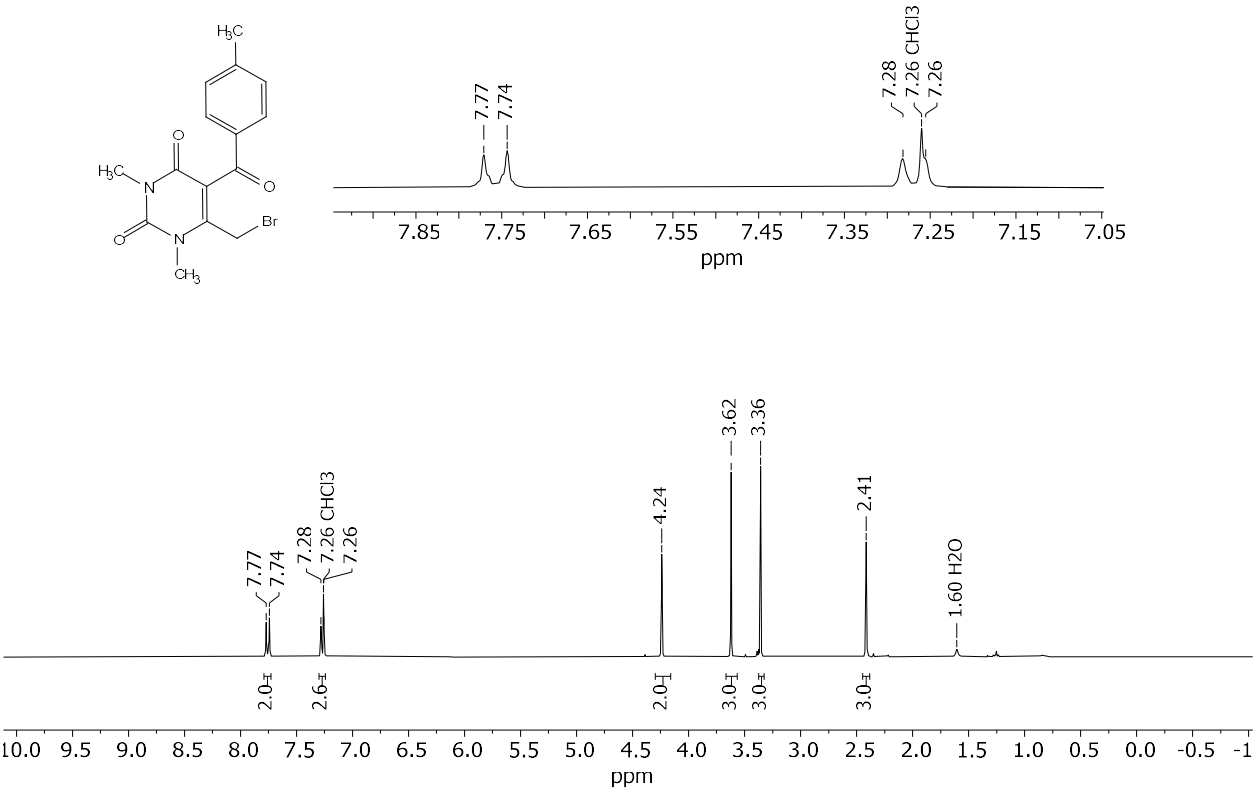


Figure S11. ^{1}H NMR spectrum of **8d** ($CDCl_3$, 300 MHz).

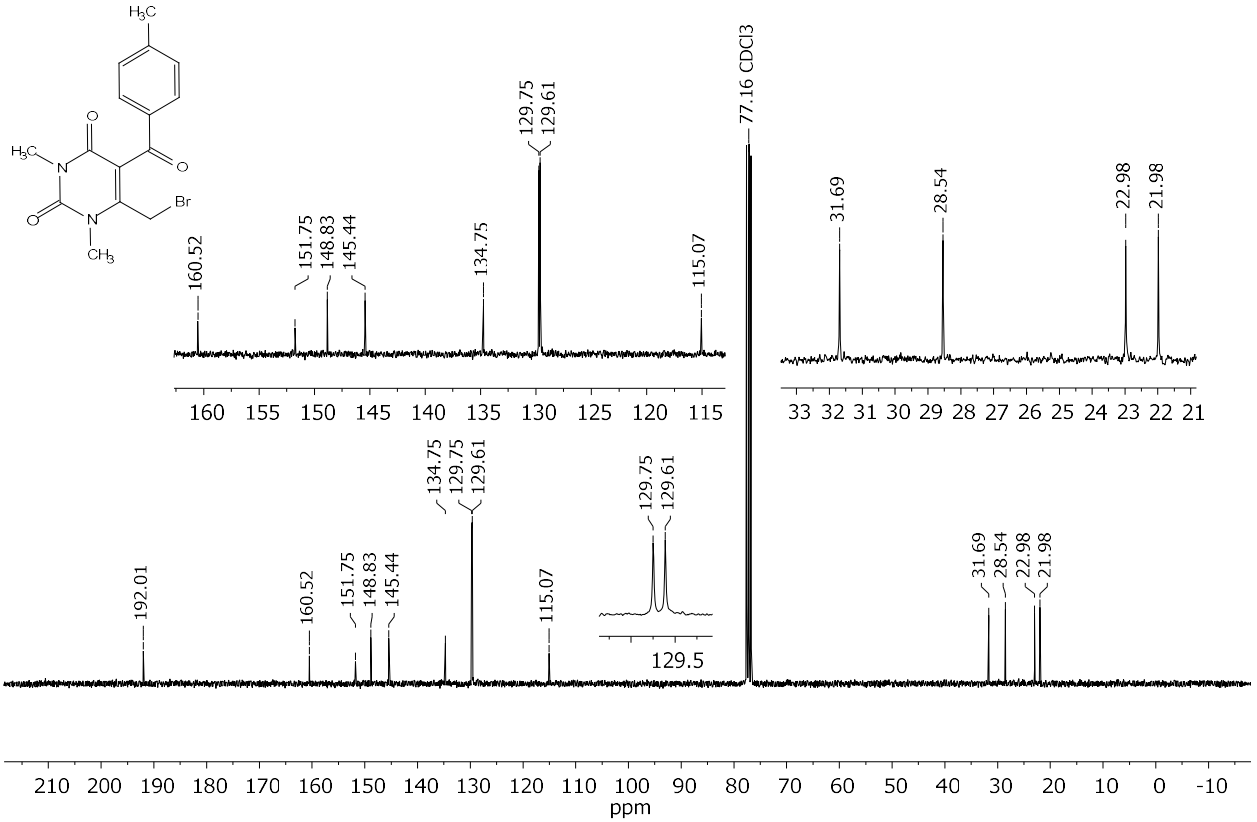


Figure S12. ^{13}C NMR spectrum of **8d** ($CDCl_3$, 75 MHz).

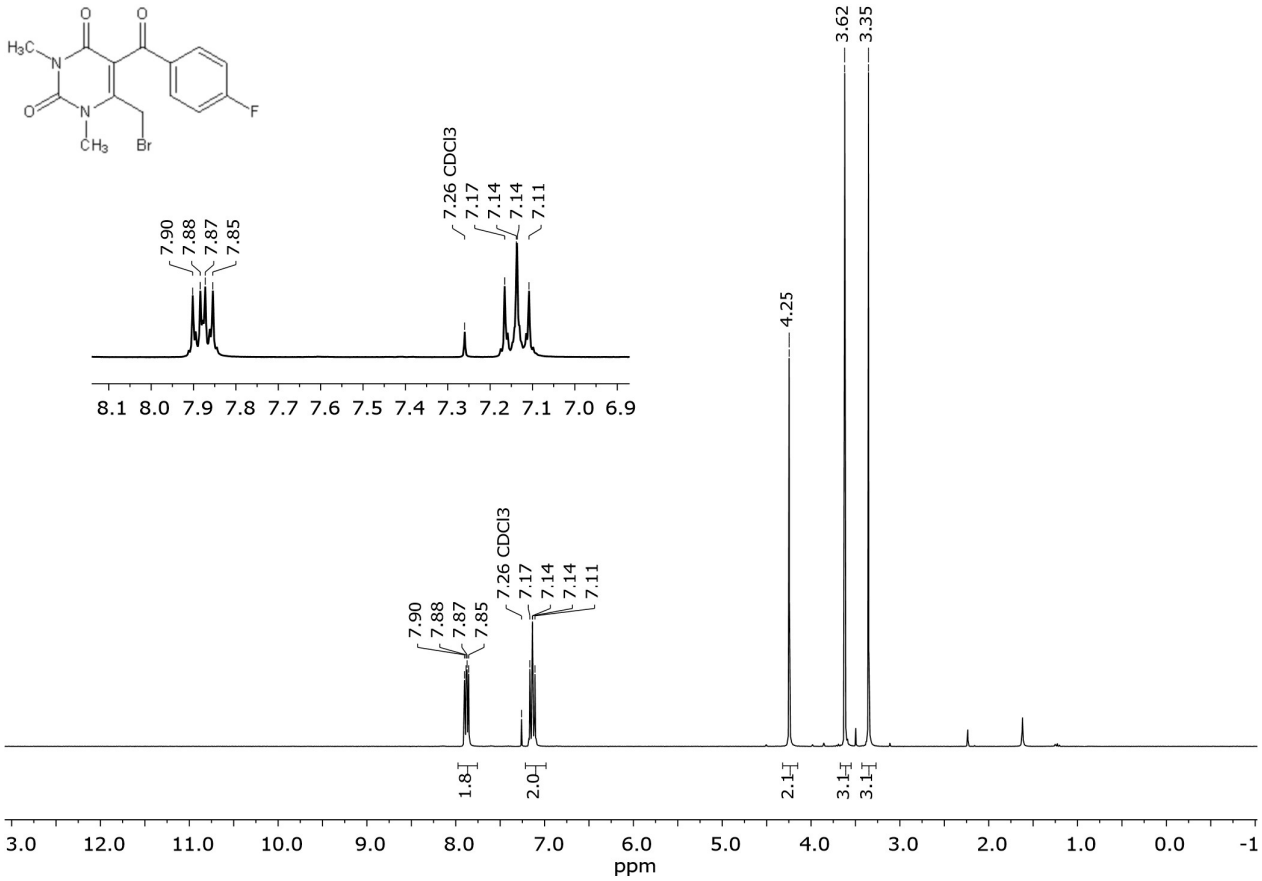


Figure S13. ^{1}H NMR spectrum of **8e** ($CDCl_3$, 300 MHz).

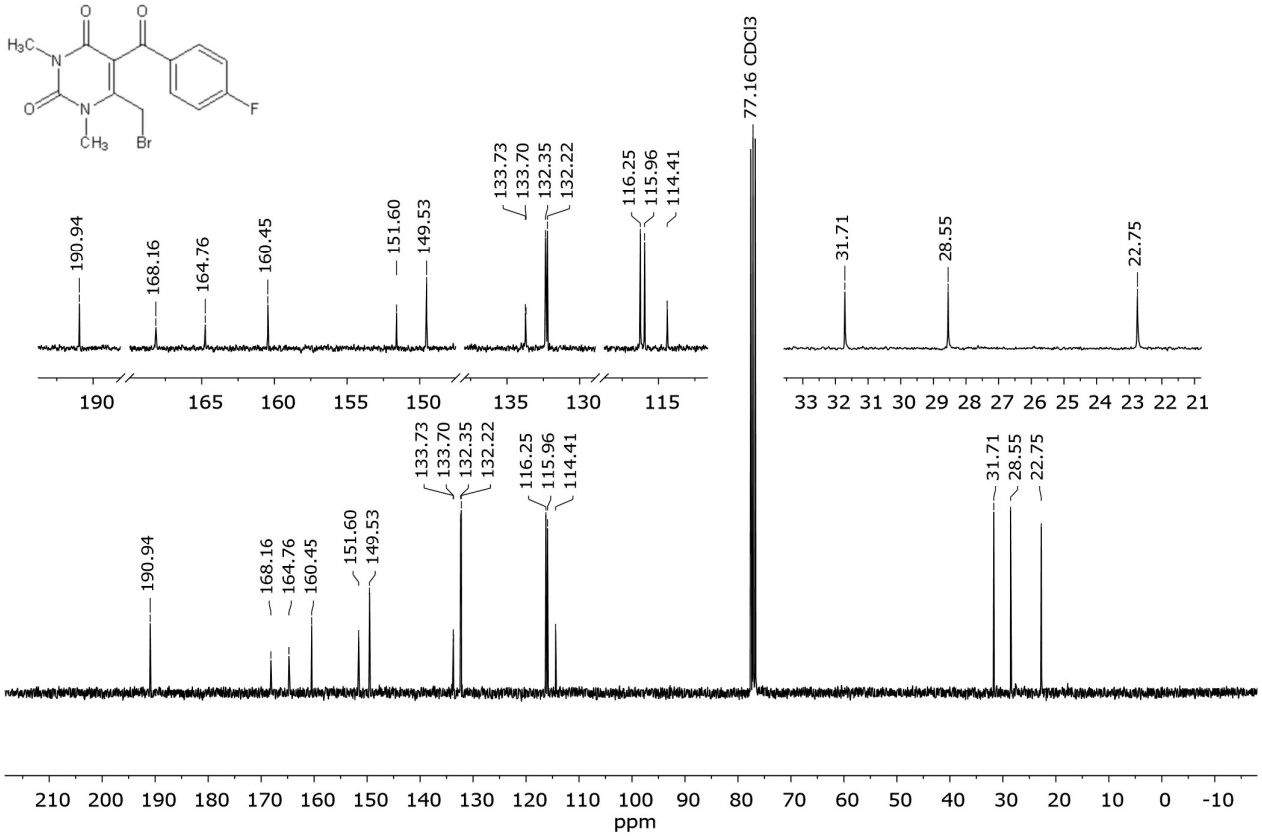


Figure S14. ^{13}C NMR spectrum of **8e** ($CDCl_3$, 75 MHz).

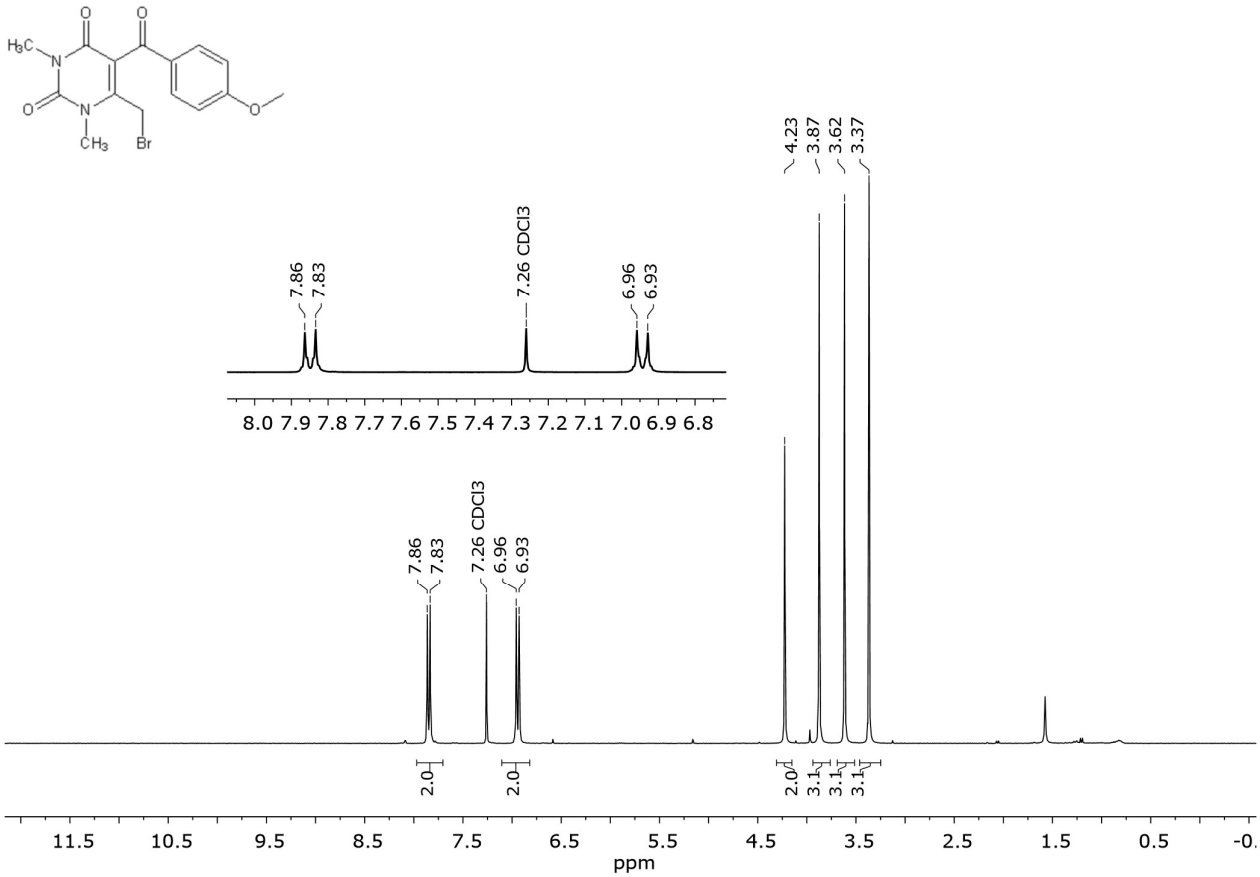


Figure S15. ^{1}H NMR spectrum of **8f** ($CDCl_3$, 300 MHz).

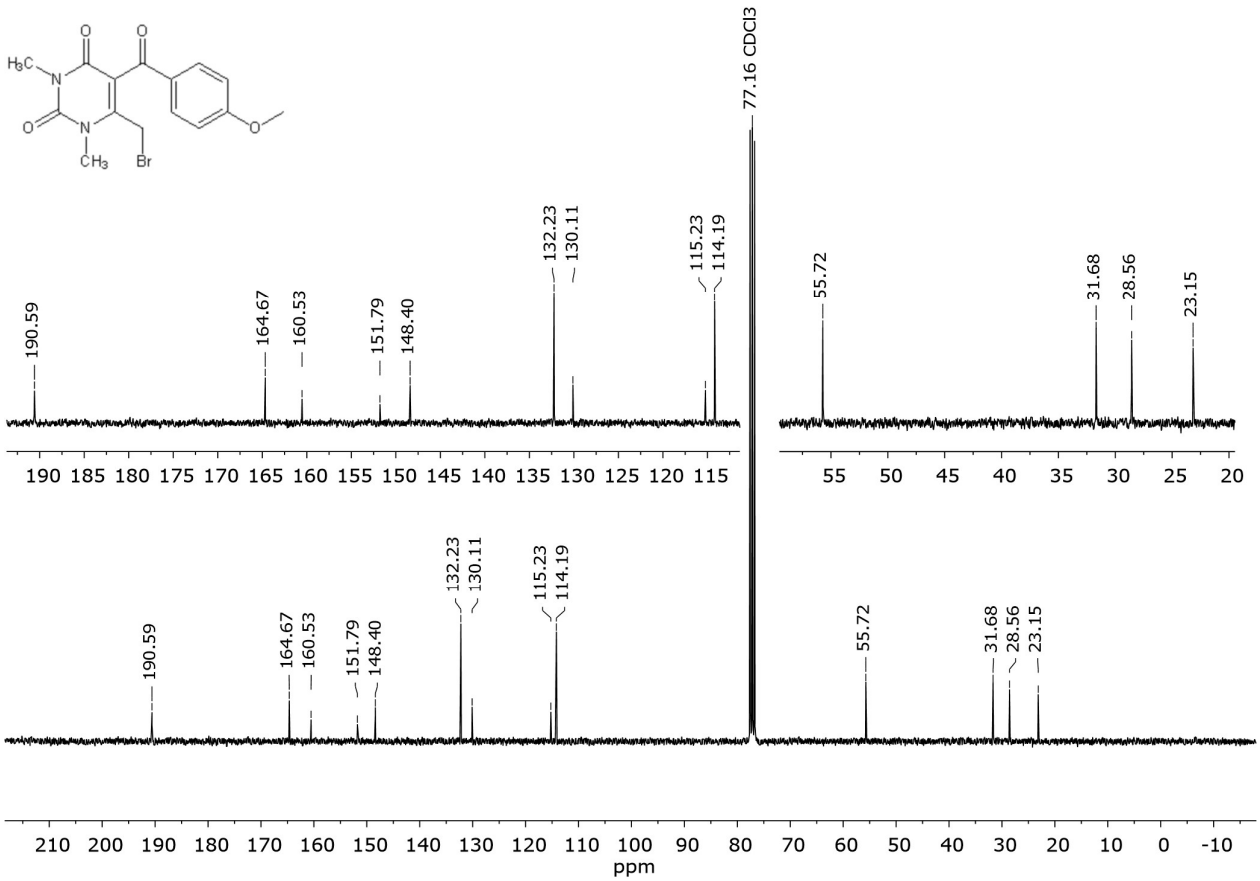


Figure S16. ^{13}C NMR spectrum of **8f** ($CDCl_3$, 75 MHz).

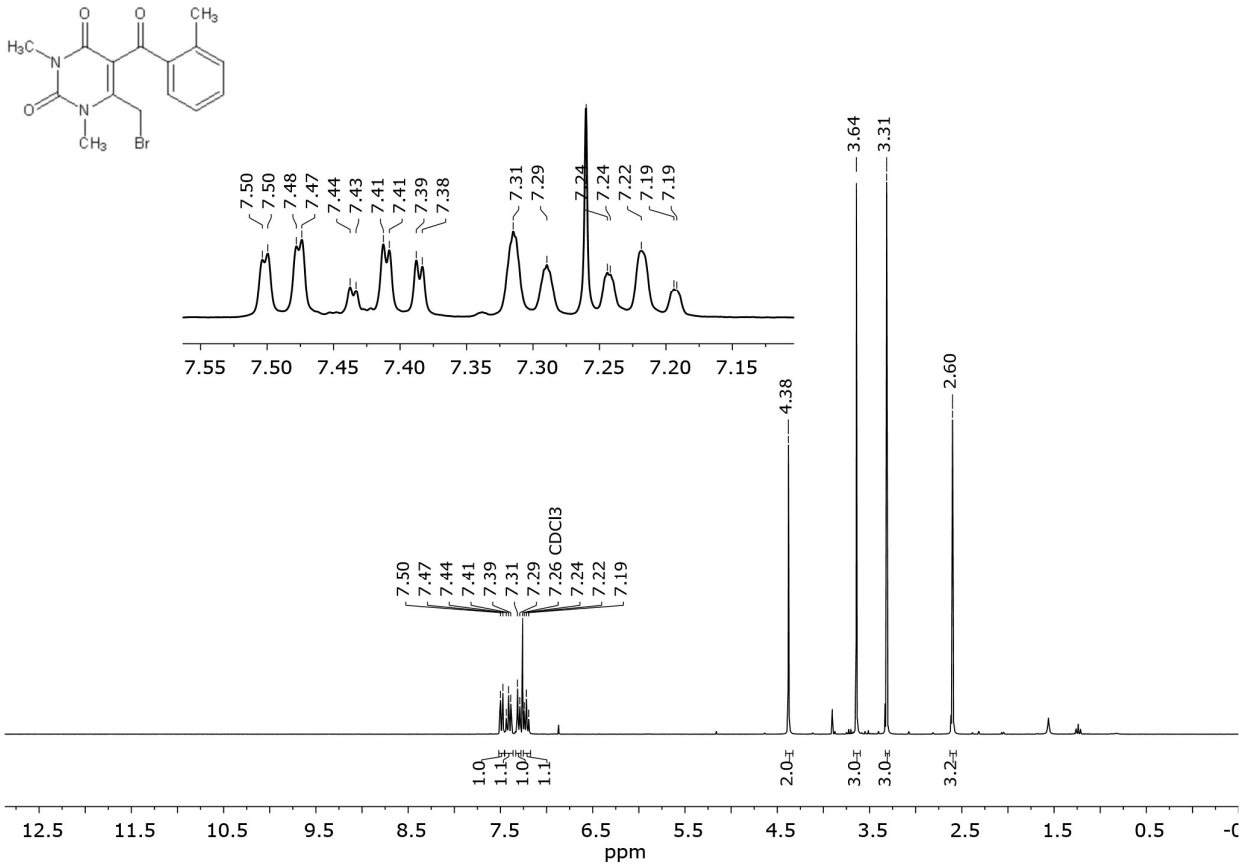


Figure S17. ^{1}H NMR spectrum of **8g** ($CDCl_3$, 300 MHz).

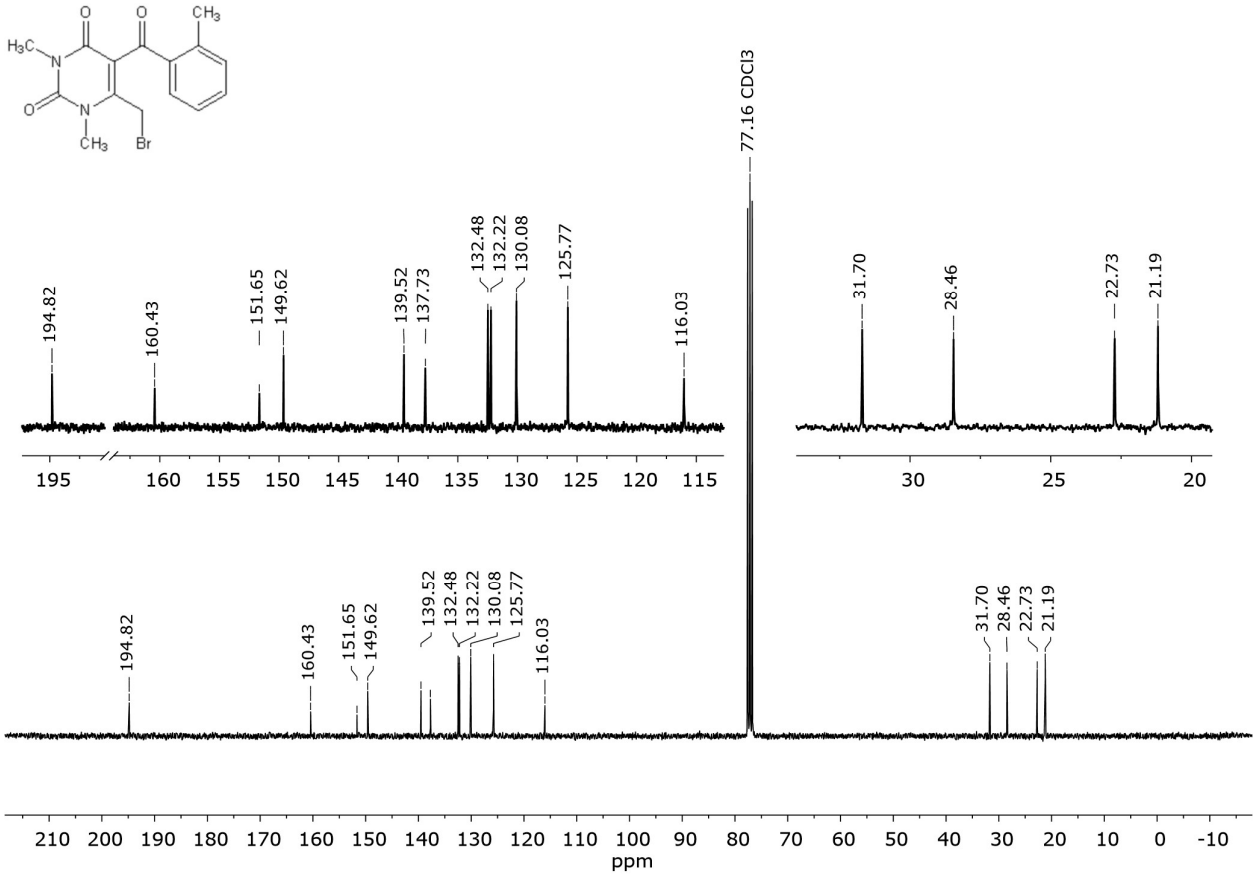


Figure S18. ^{13}C NMR spectrum of **8g** ($CDCl_3$, 75 MHz).

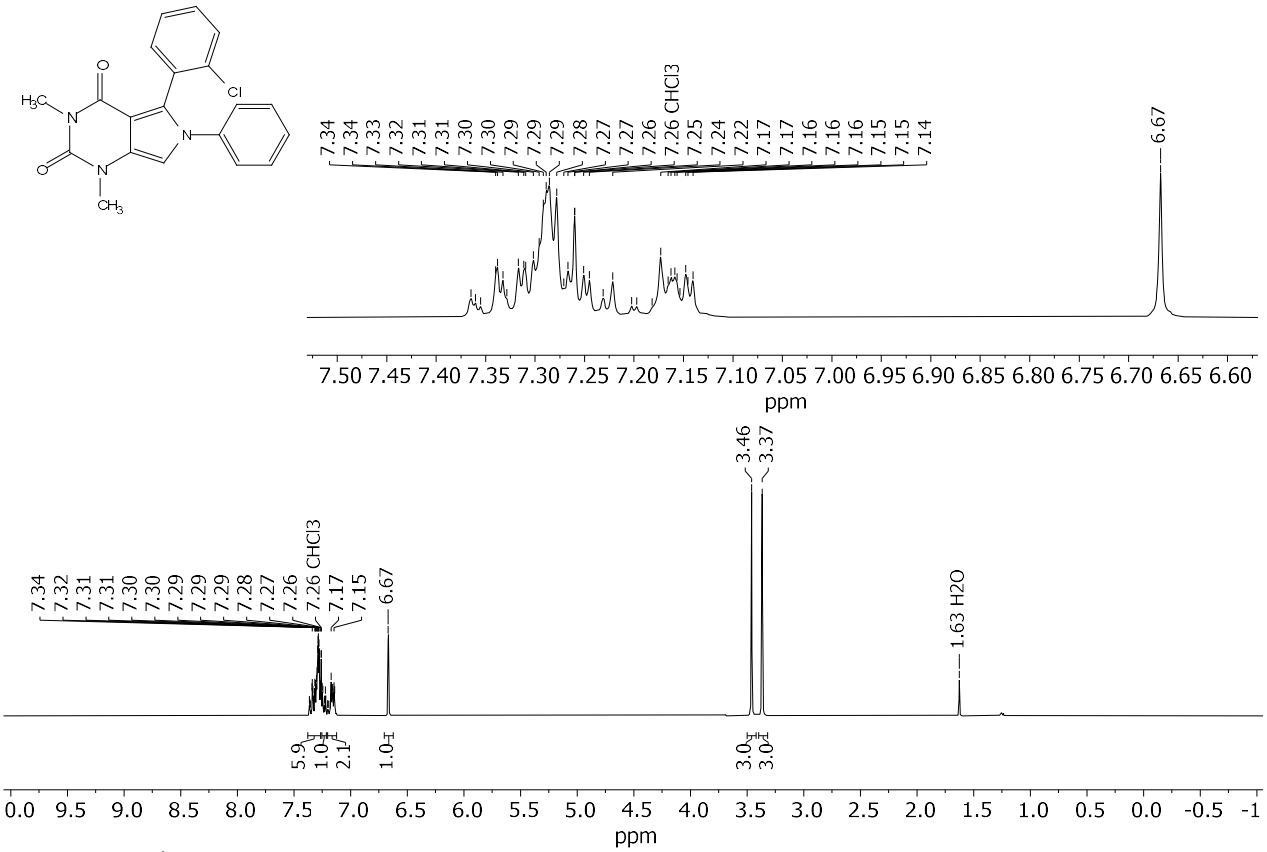


Figure S19. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 300 MHz).

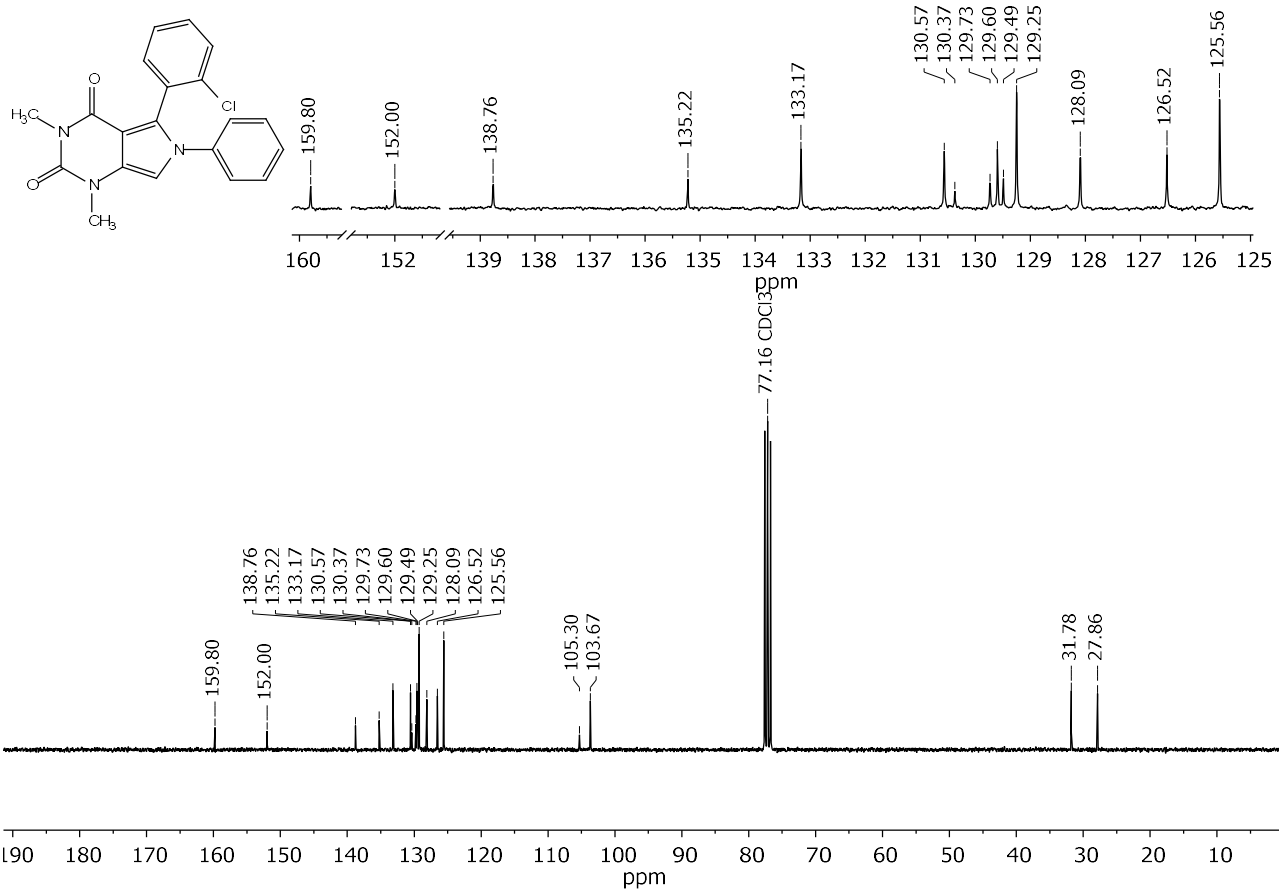


Figure S20. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 75 MHz).

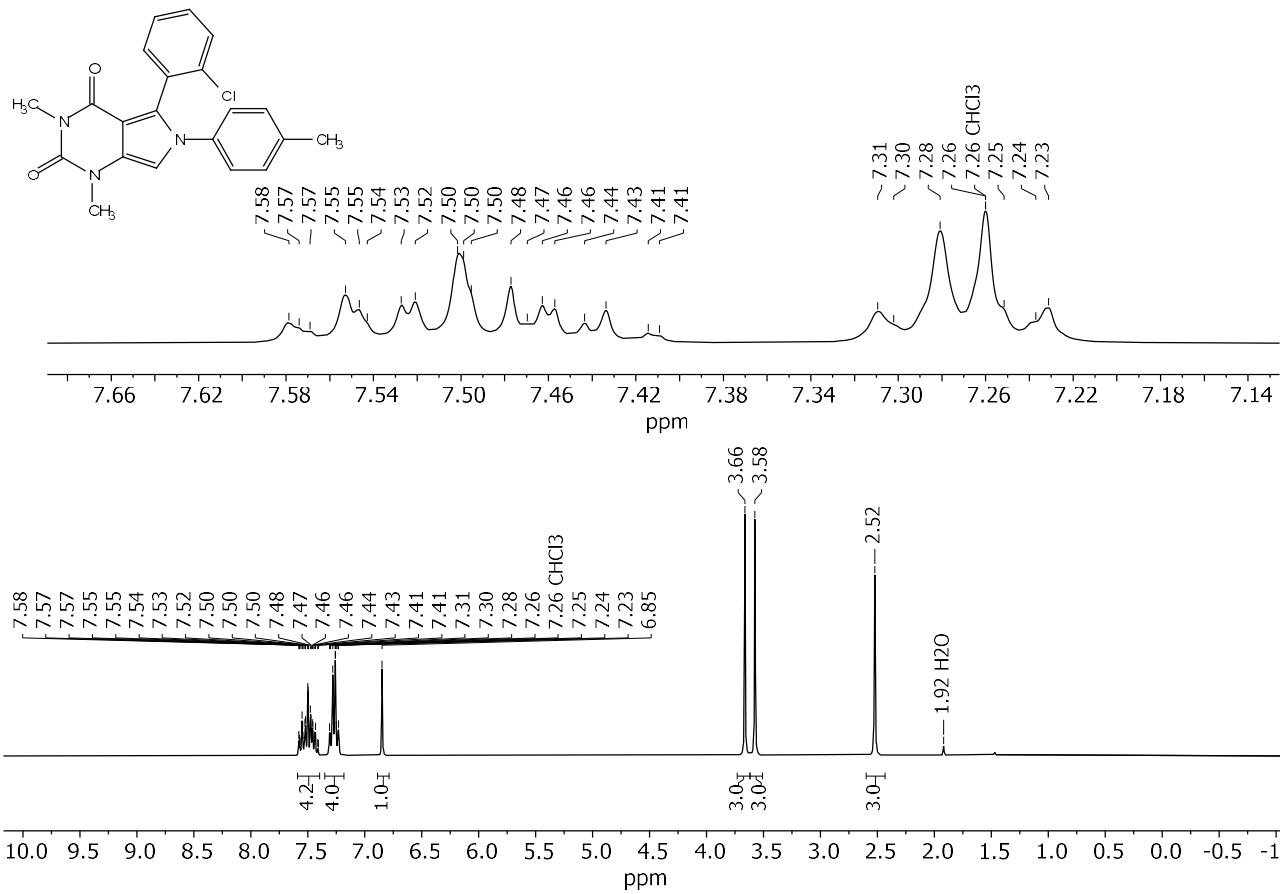


Figure S21. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 300 MHz).

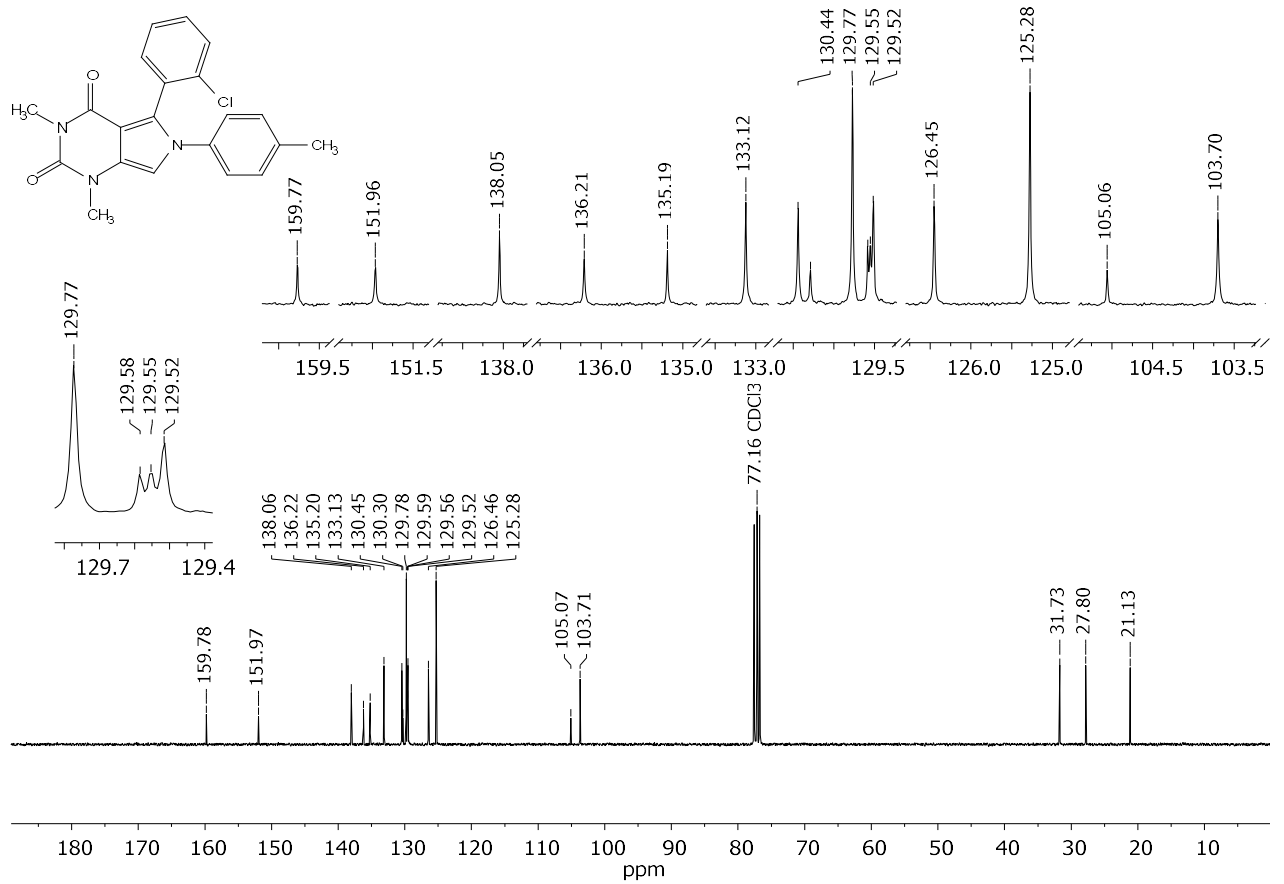


Figure S22. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 75 MHz).

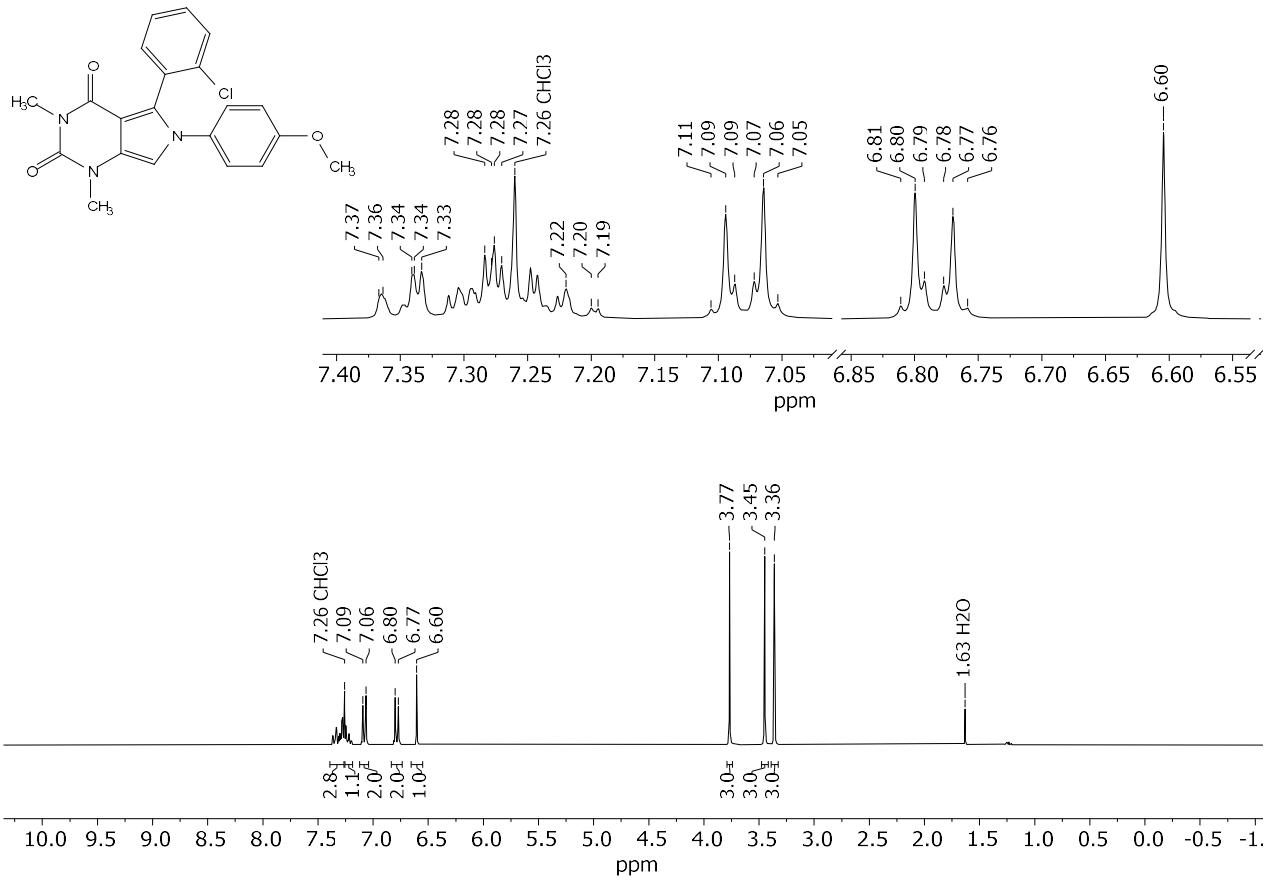


Figure S23. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 300 MHz).

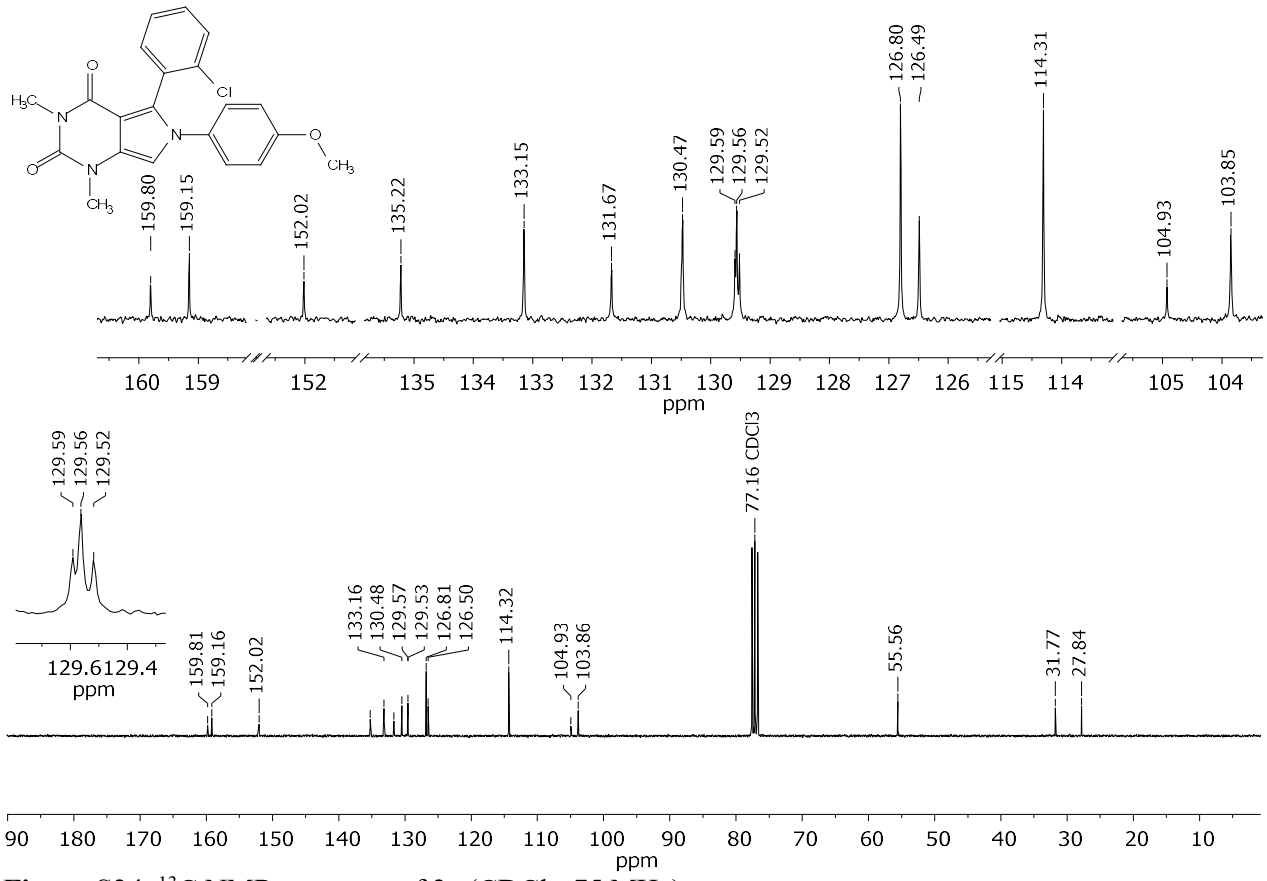


Figure S24. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 75 MHz).

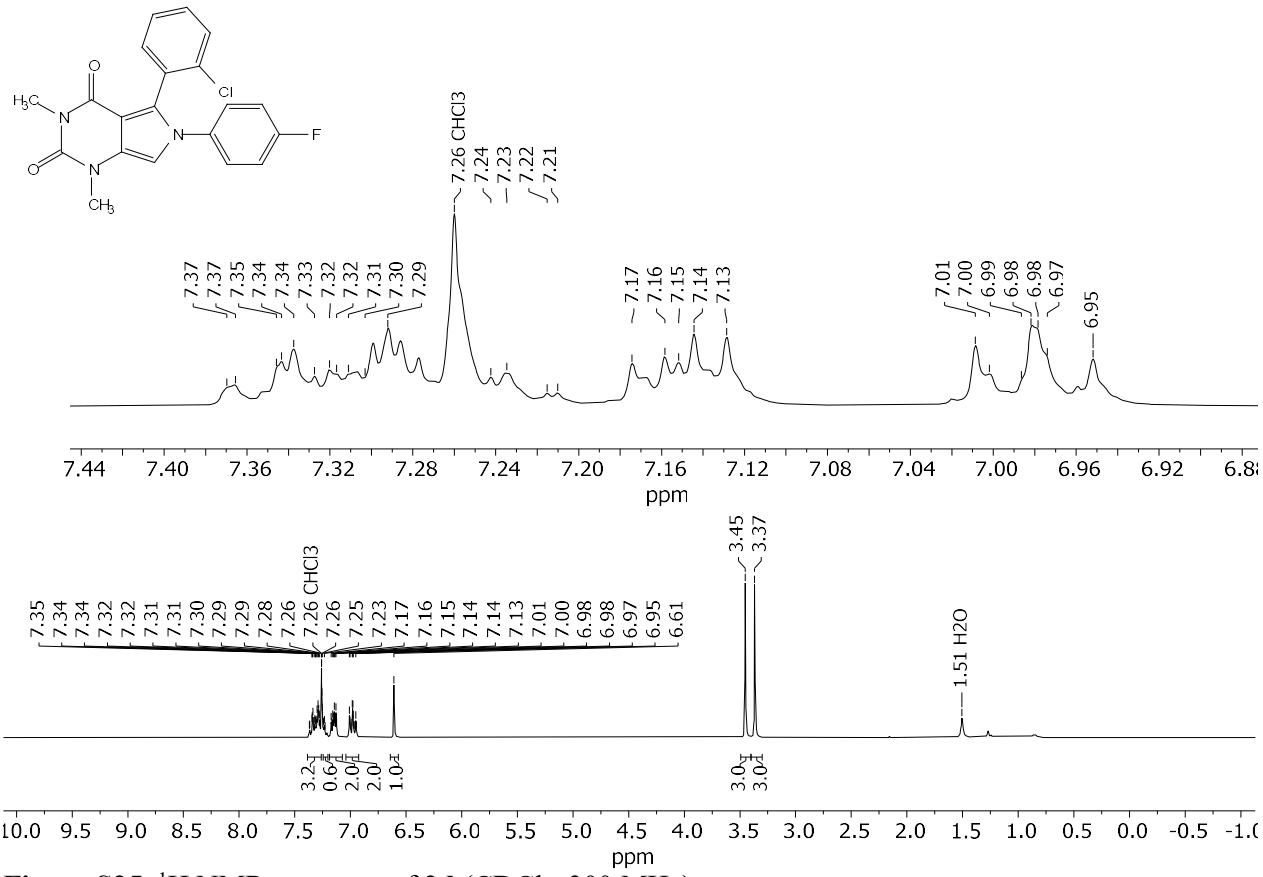


Figure S25. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 300 MHz).

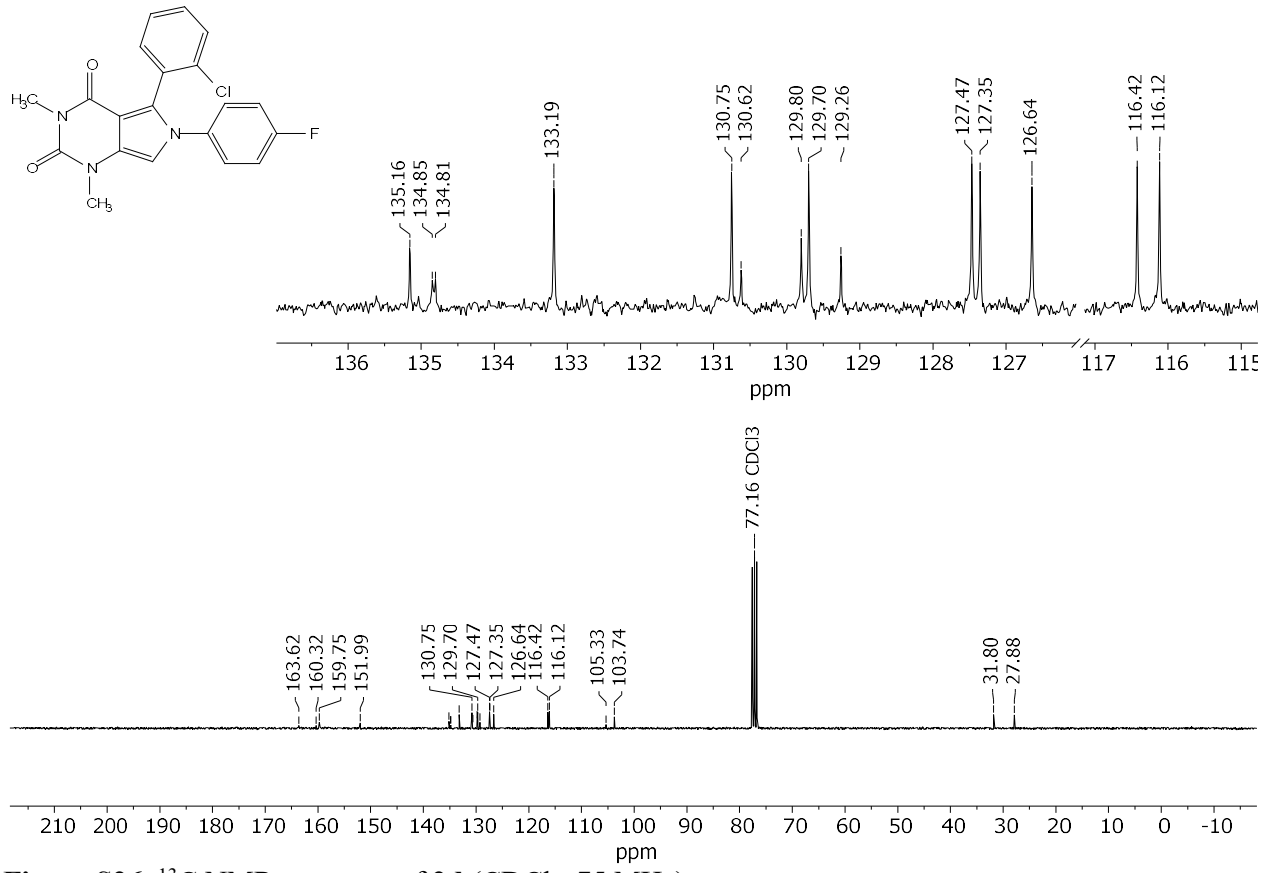


Figure S26. ^{13}C NMR spectrum of **2d** ($CDCl_3$, 75 MHz).

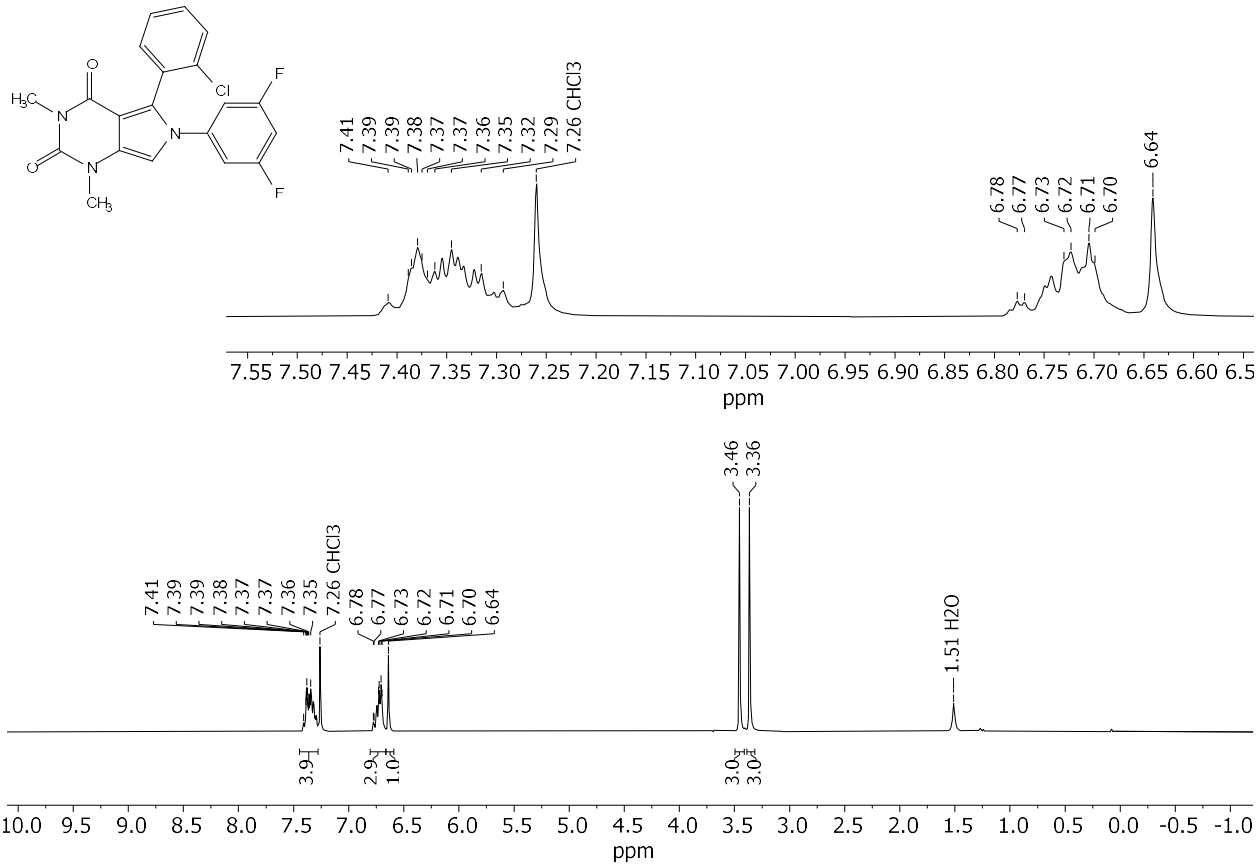


Figure S27. ^{1}H NMR spectrum of **2e** ($CDCl_3$, 300 MHz).

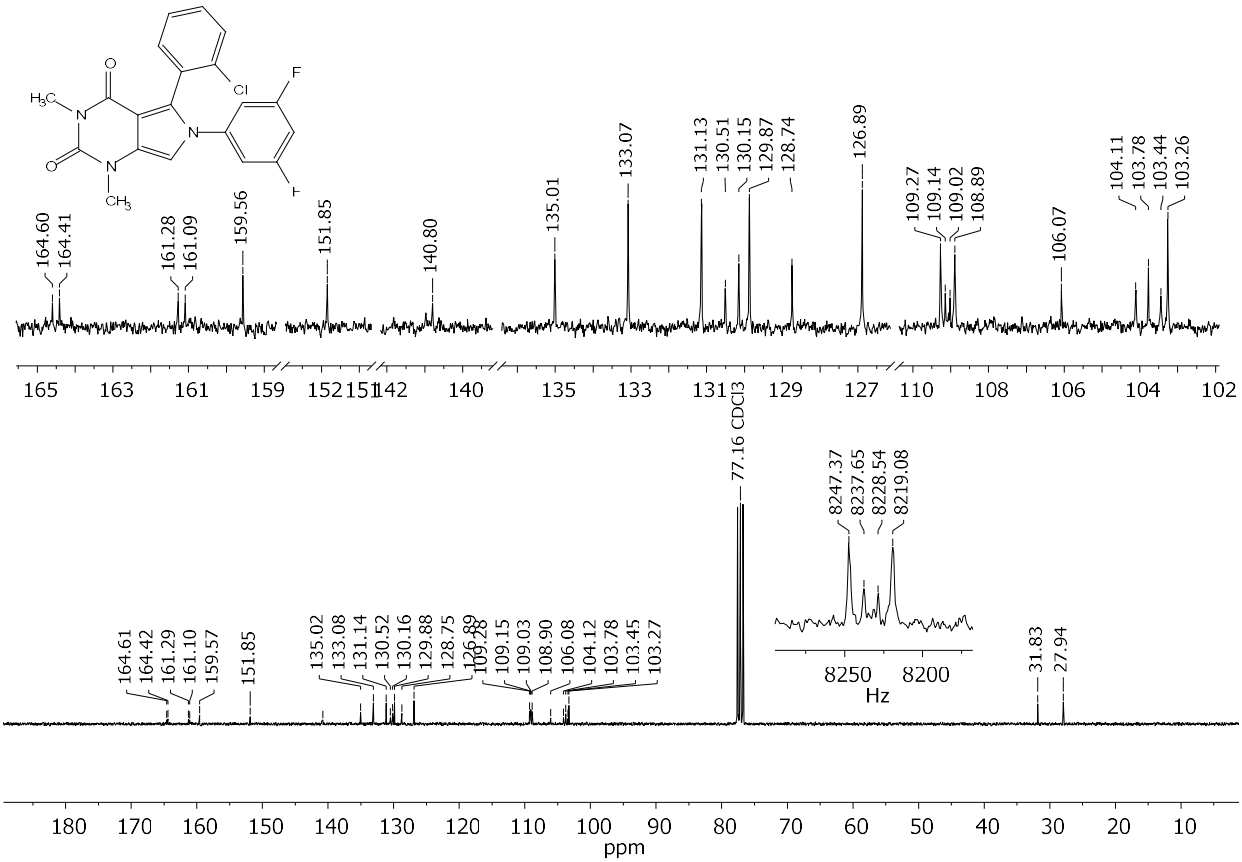


Figure S28. ^{13}C NMR spectrum of **2e** ($CDCl_3$, 75 MHz).

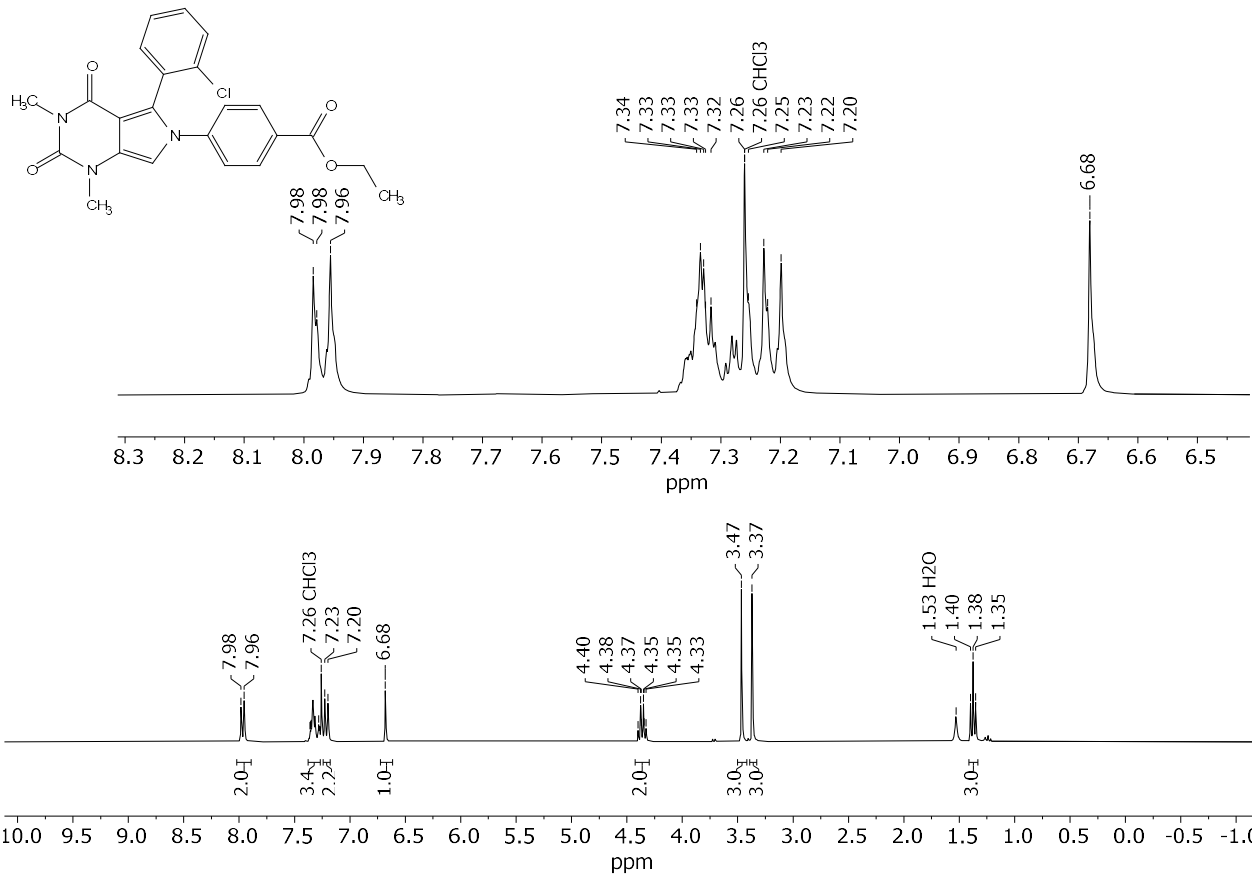


Figure S29. ^{1}H NMR spectrum of **2f** ($CDCl_3$, 300 MHz).

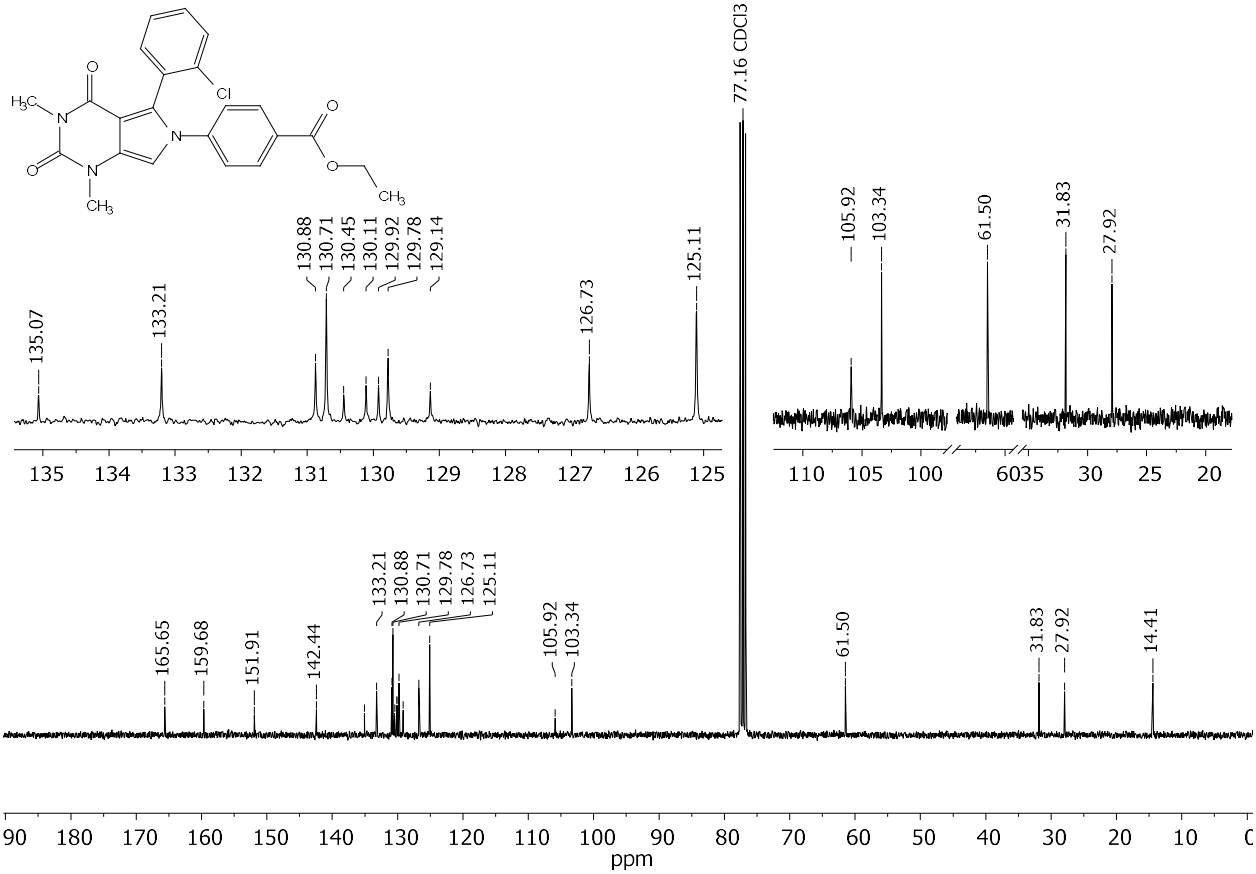


Figure S30. ^{13}C NMR spectrum of **2f** ($CDCl_3$, 75 MHz).

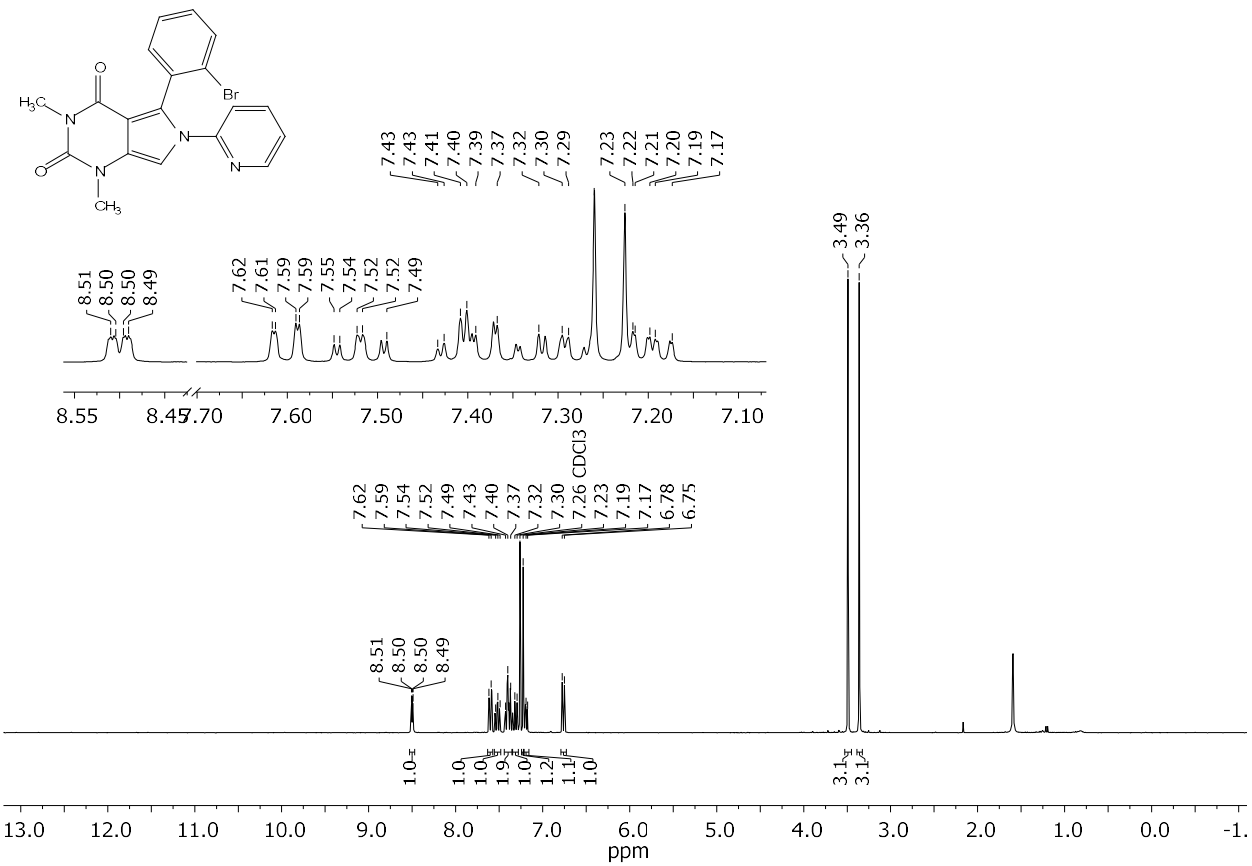


Figure S31. ^{1}H NMR spectrum of **4** ($CDCl_3$, 300 MHz).

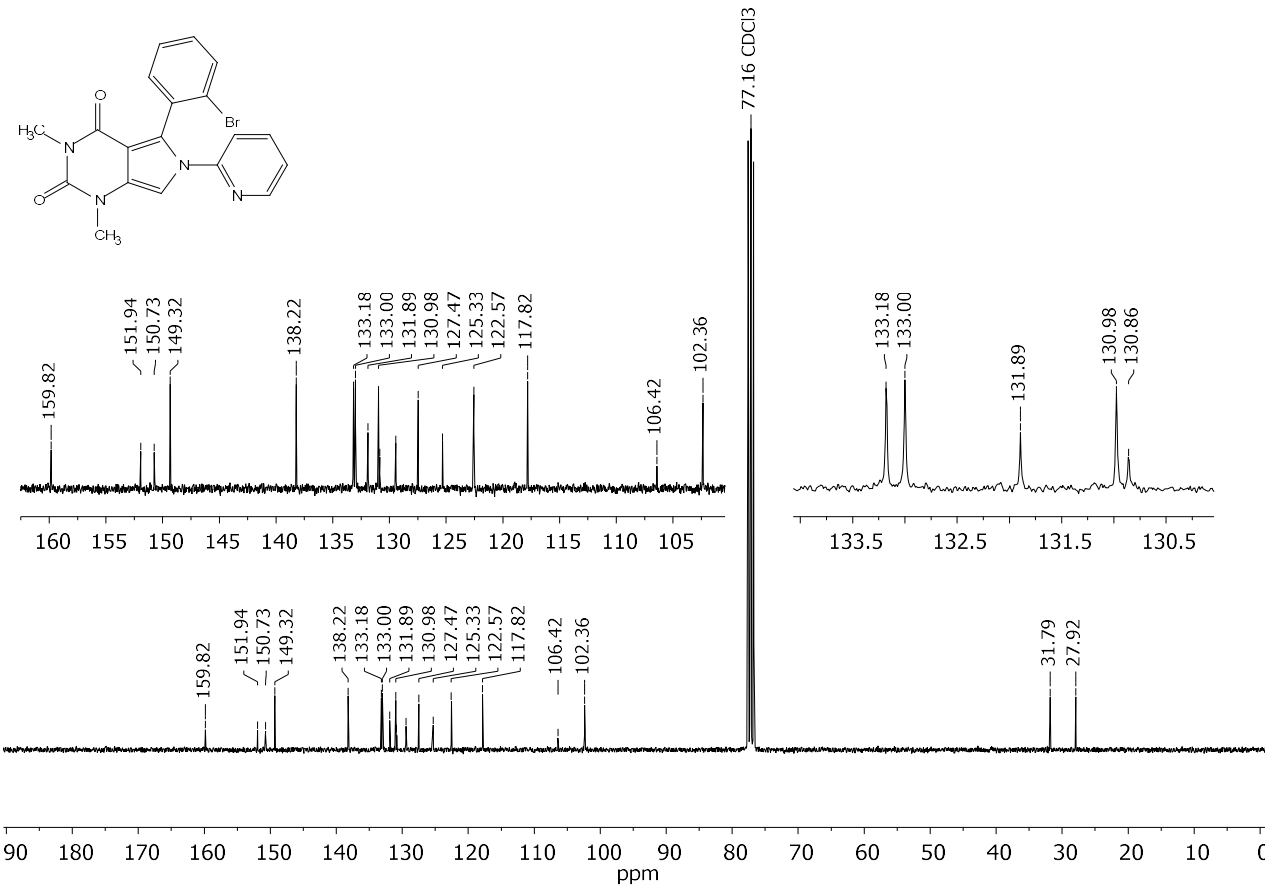


Figure S32. ^{13}C NMR spectrum of **4** ($CDCl_3$, 75 MHz).

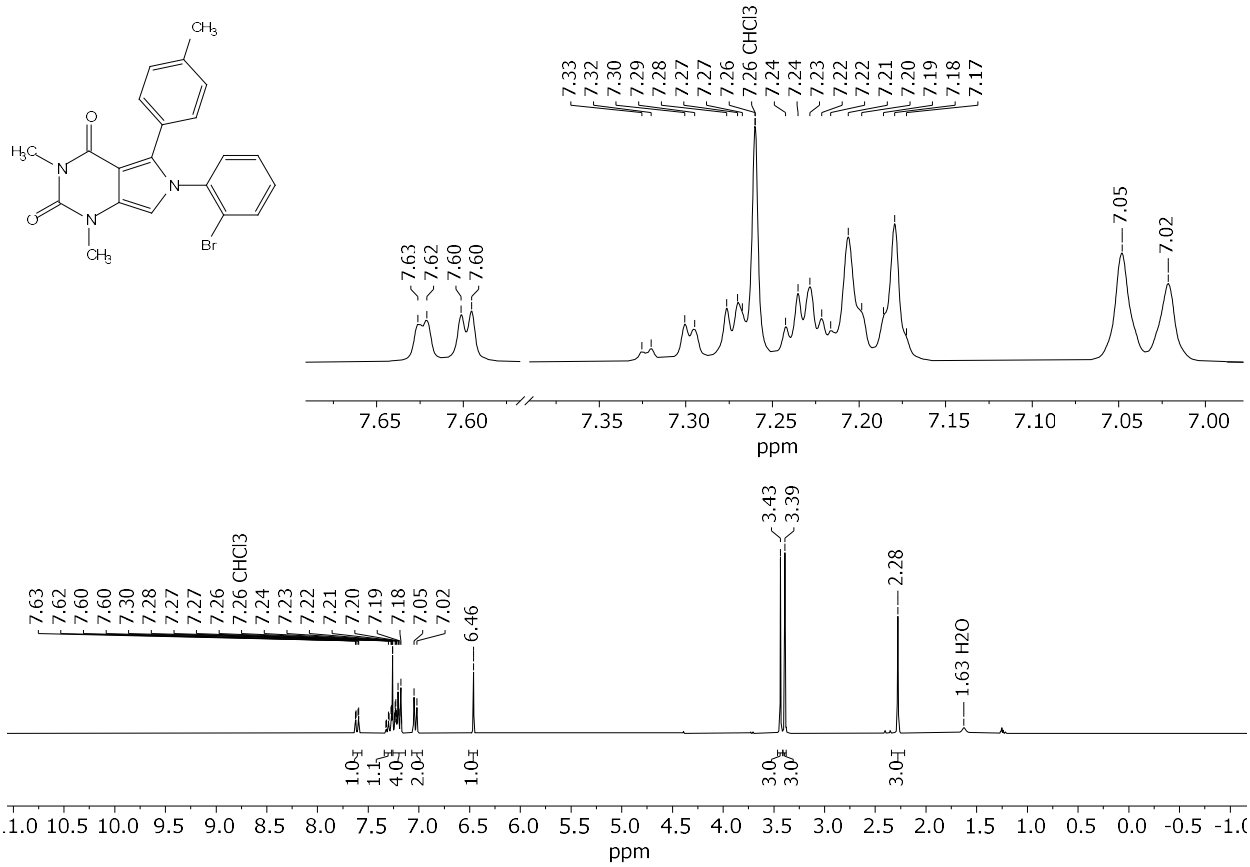


Figure S33. ^{1}H NMR spectrum of **3b** ($CDCl_3$, 300 MHz).

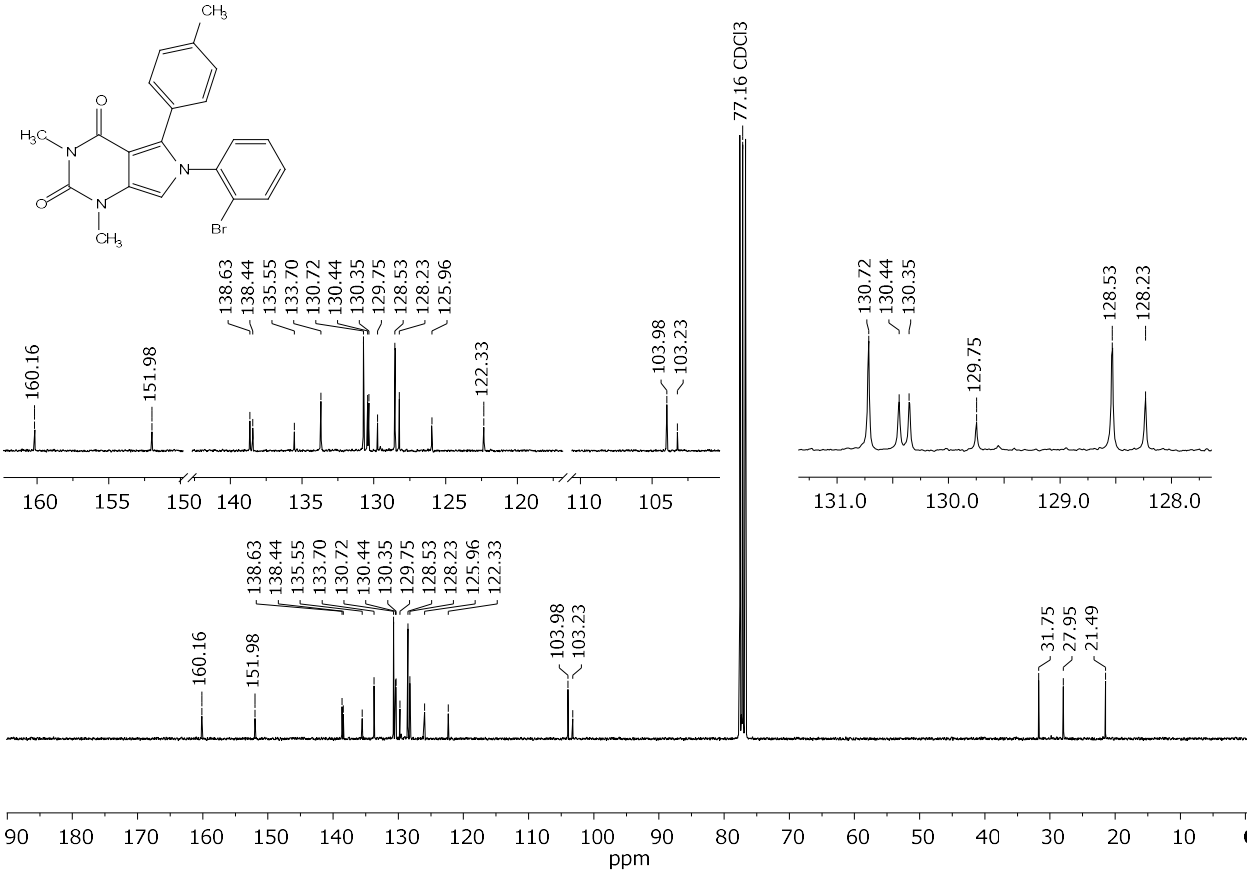


Figure S34. ^{13}C NMR spectrum of **3b** ($CDCl_3$, 75 MHz).

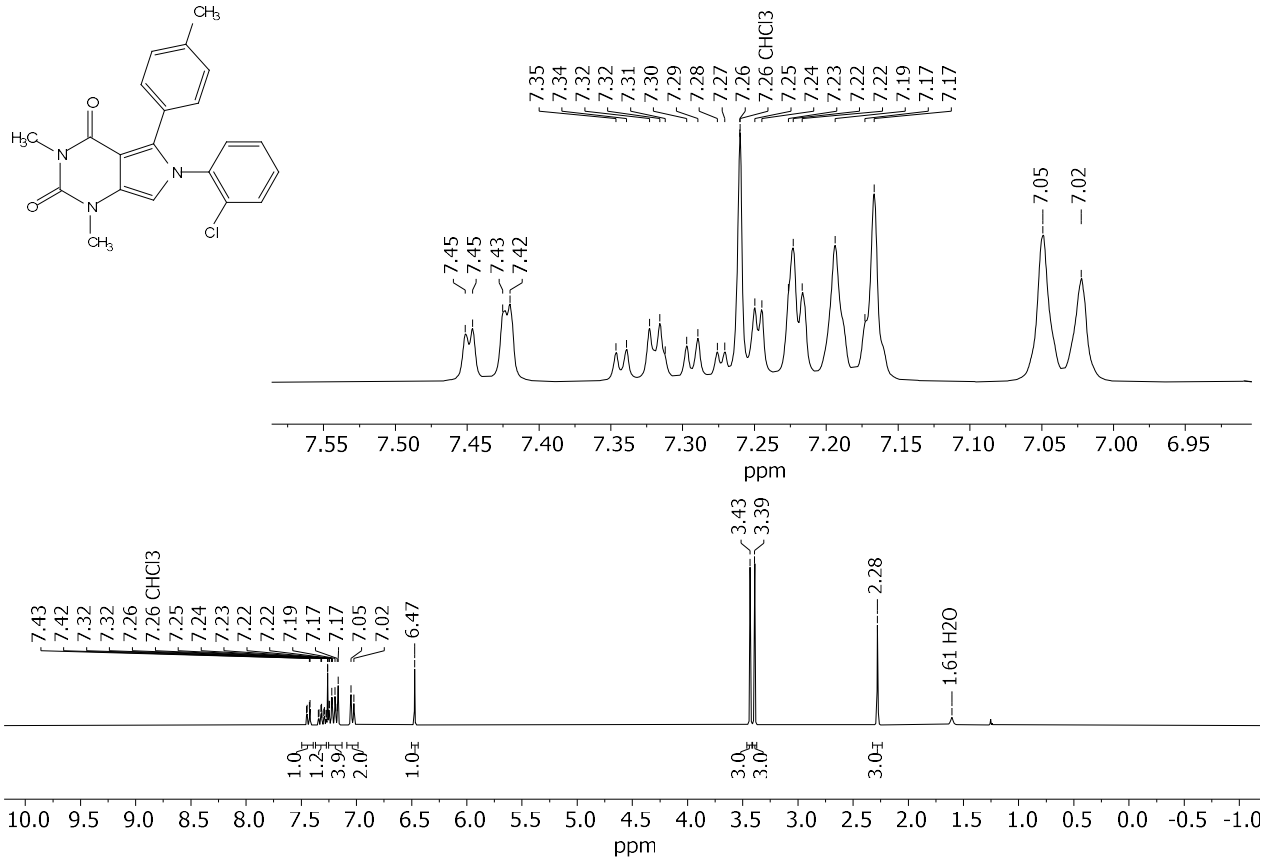


Figure S35. ^{1}H NMR spectrum of **3'b** ($CDCl_3$, 300 MHz).

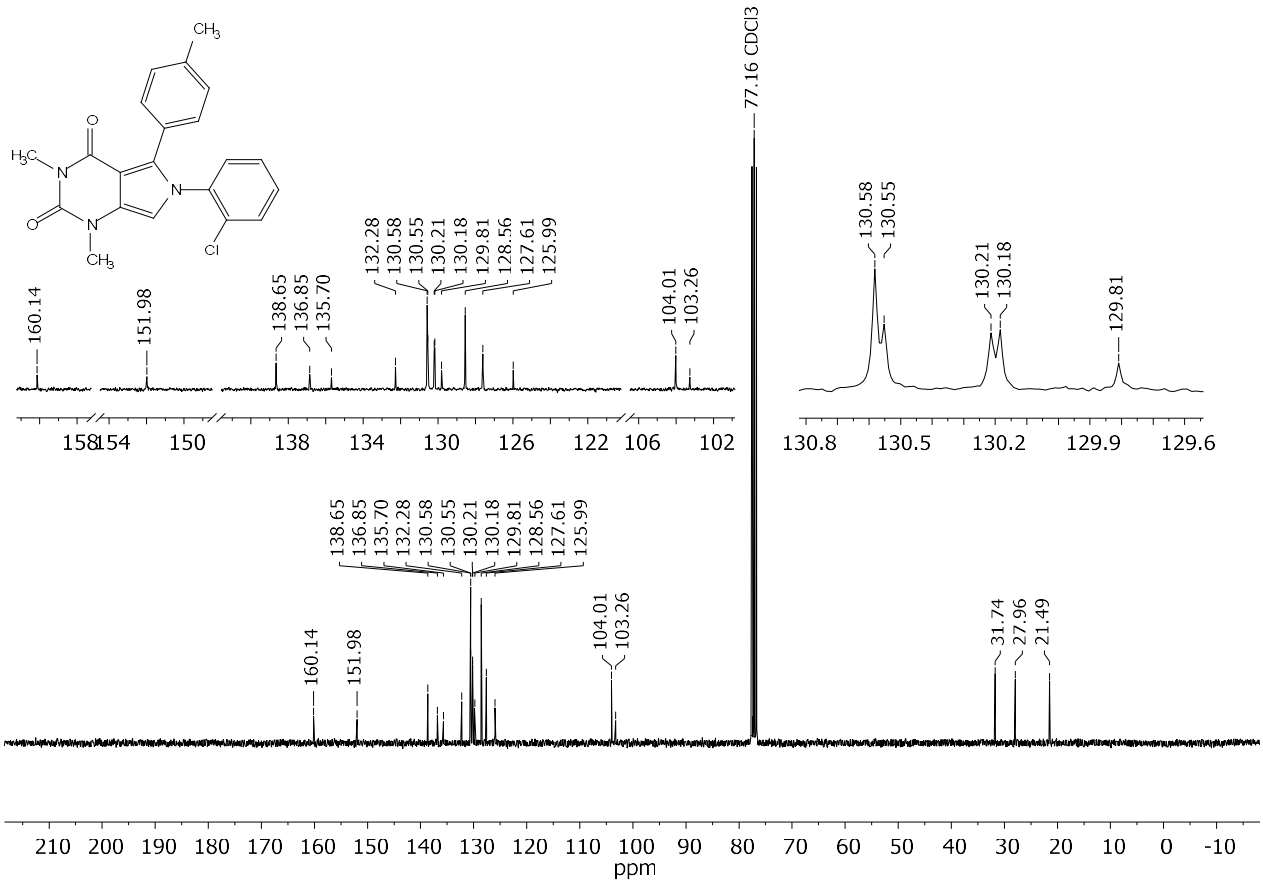


Figure S36. ^{13}C NMR spectrum of **3'b** ($CDCl_3$, 75 MHz).

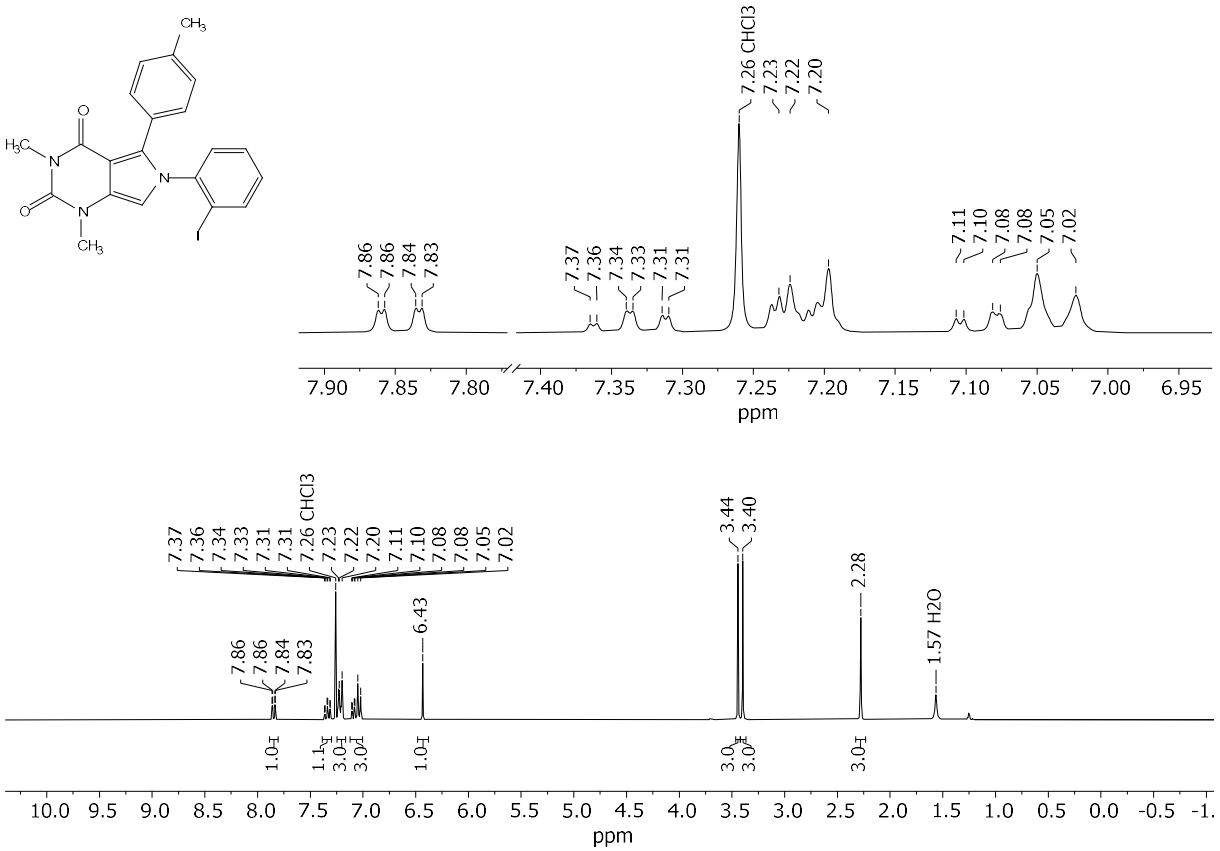


Figure S37. ^{1}H NMR spectrum of **3''b** ($CDCl_3$, 300 MHz).

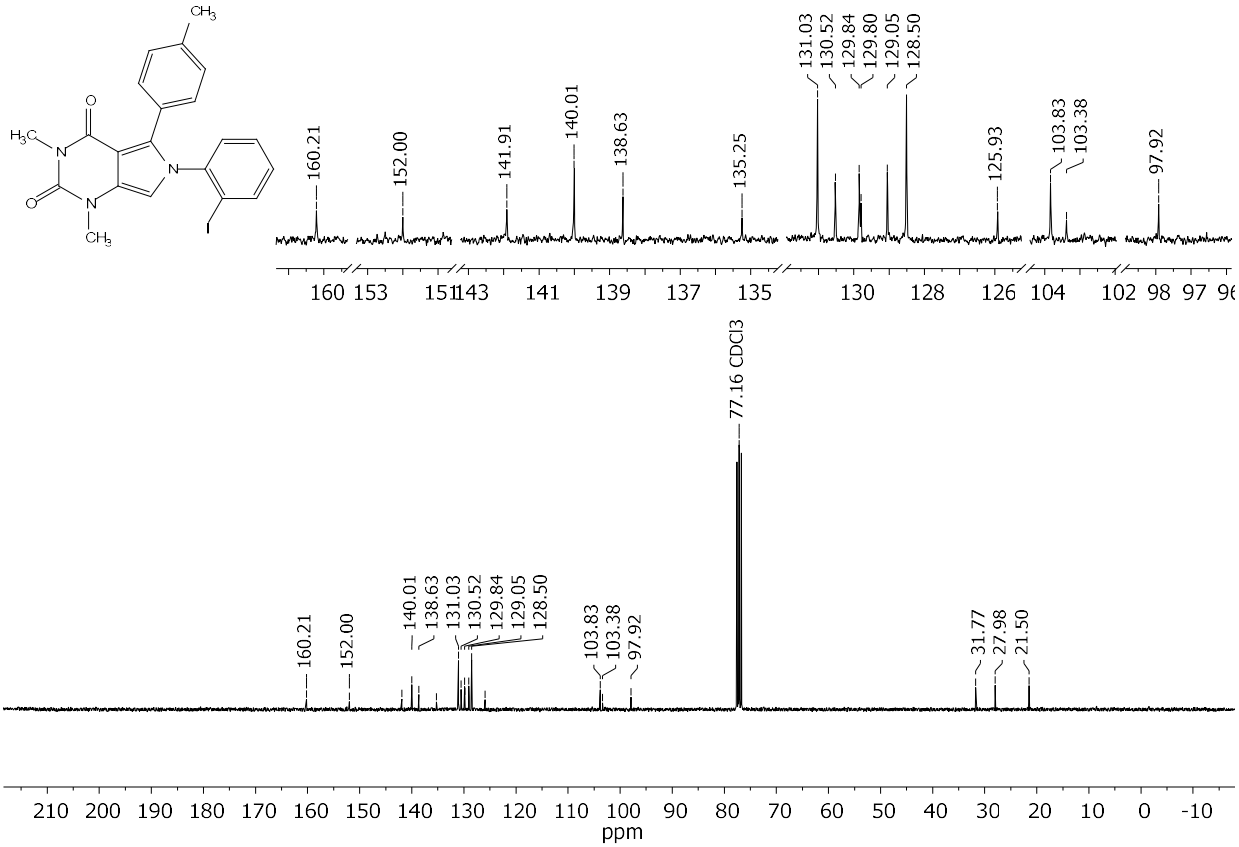


Figure S38. ^{13}C NMR spectrum of **3''b** ($CDCl_3$, 75 MHz).

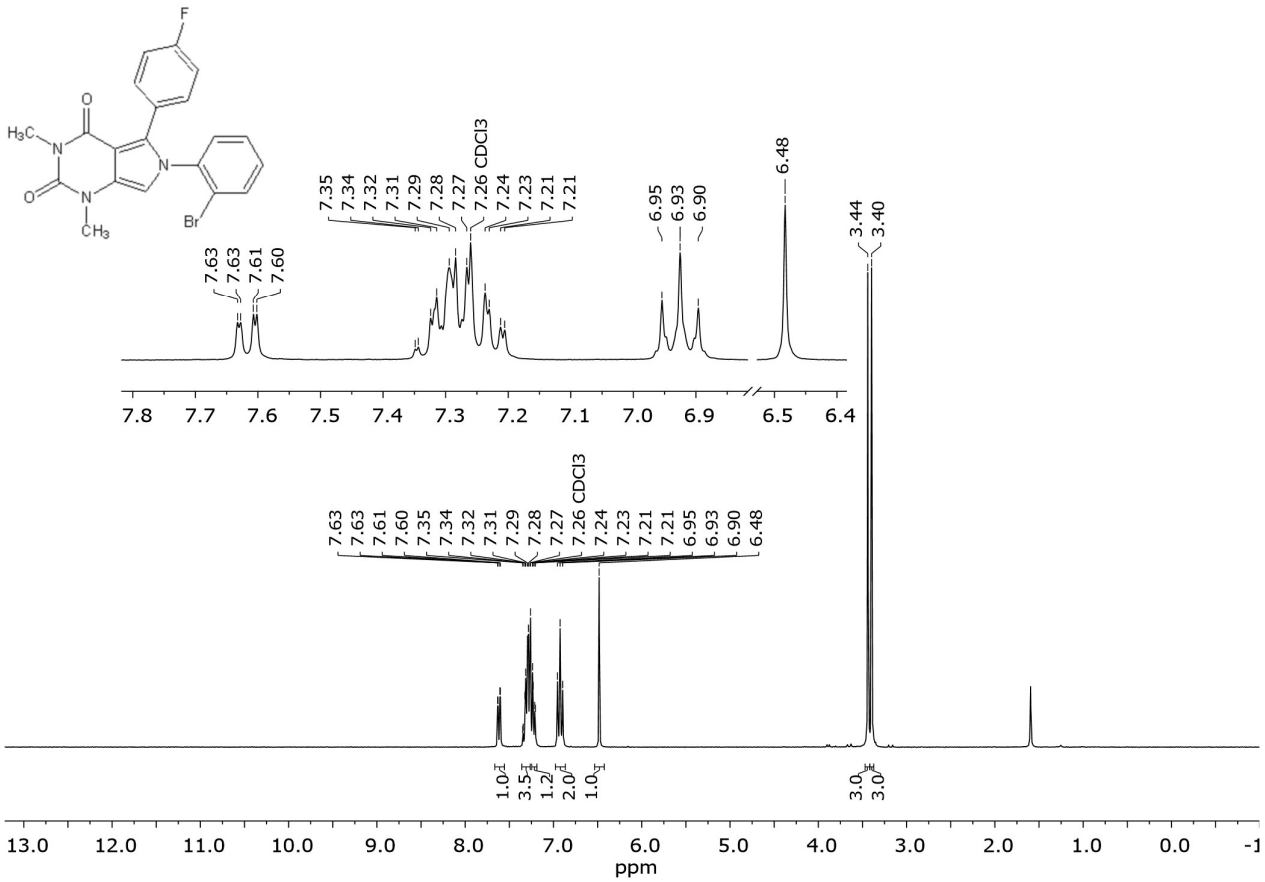


Figure S39. ^{1}H NMR spectrum of **3c** ($CDCl_3$, 300 MHz).

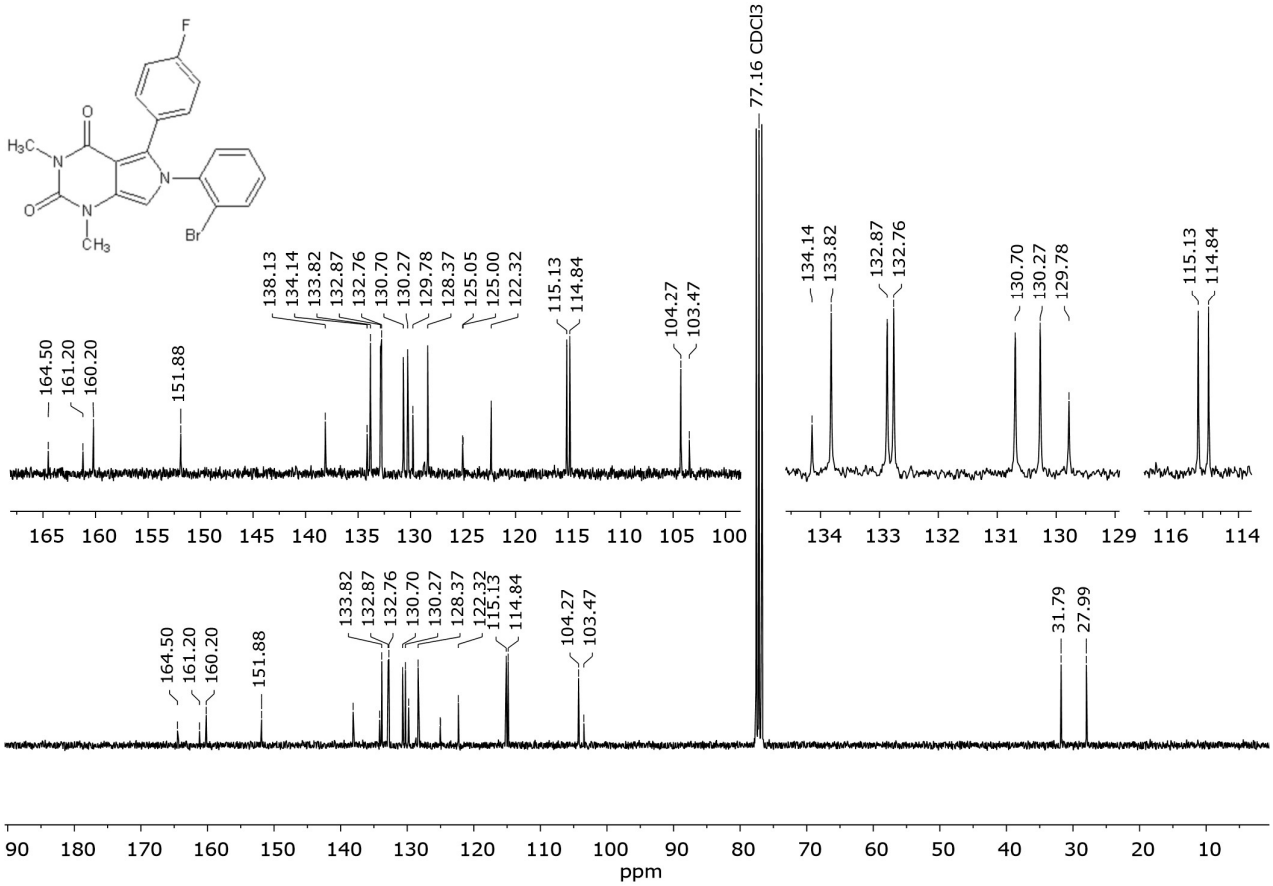


Figure S40. ^{13}C NMR spectrum of **3c** ($CDCl_3$, 75 MHz).

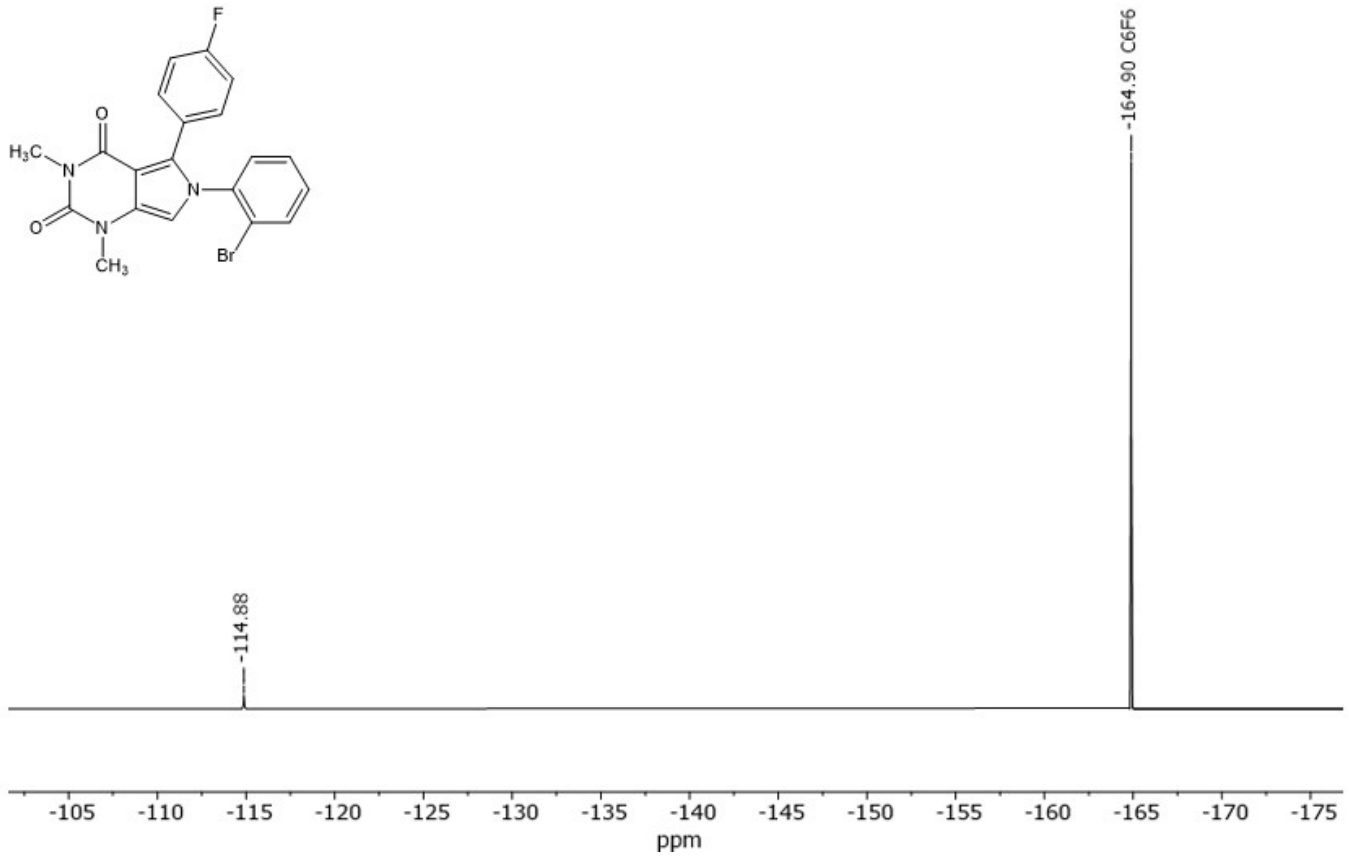


Figure S41. ^{19}F {^{1}H} NMR spectrum of **3c** (DMF-H_6, 280 MHz).

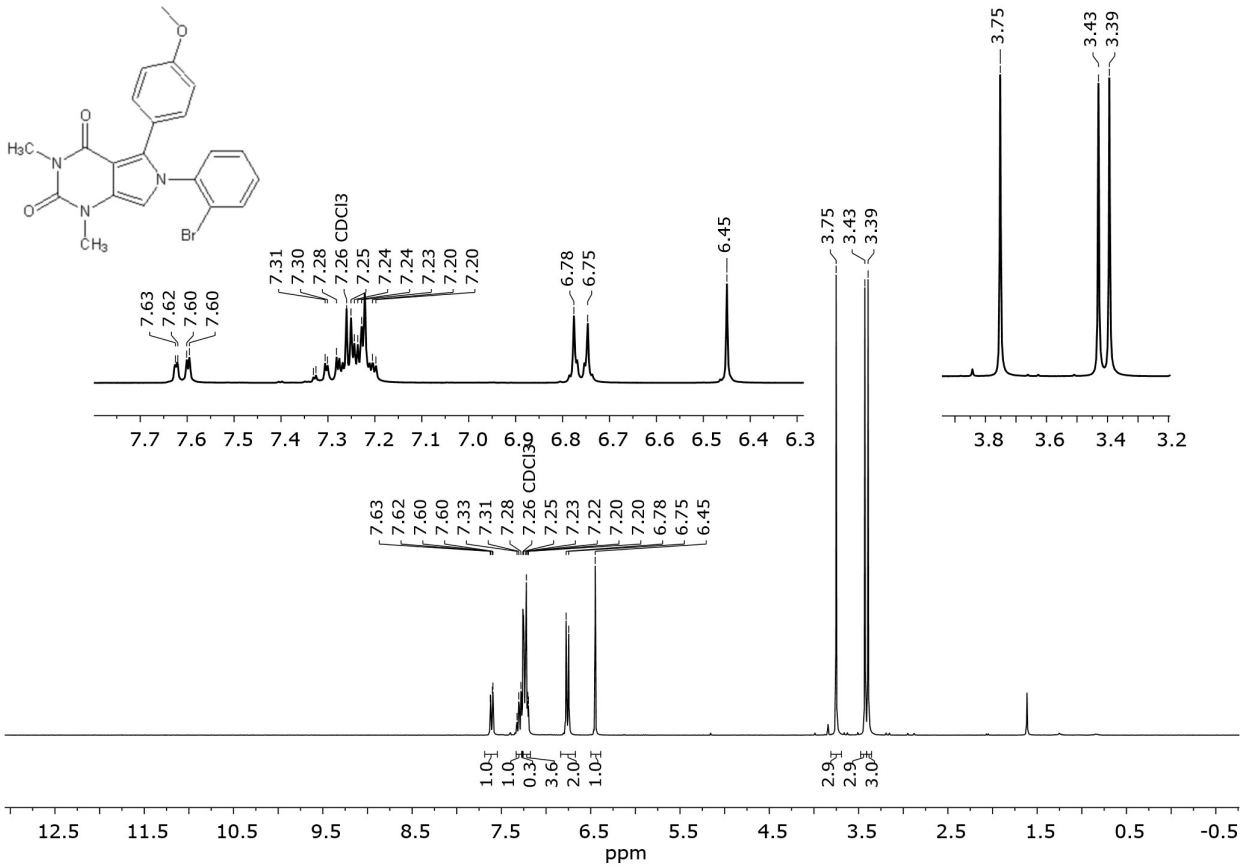


Figure S42. ^{1}H NMR spectrum of **3d** ($CDCl_3$, 300 MHz).

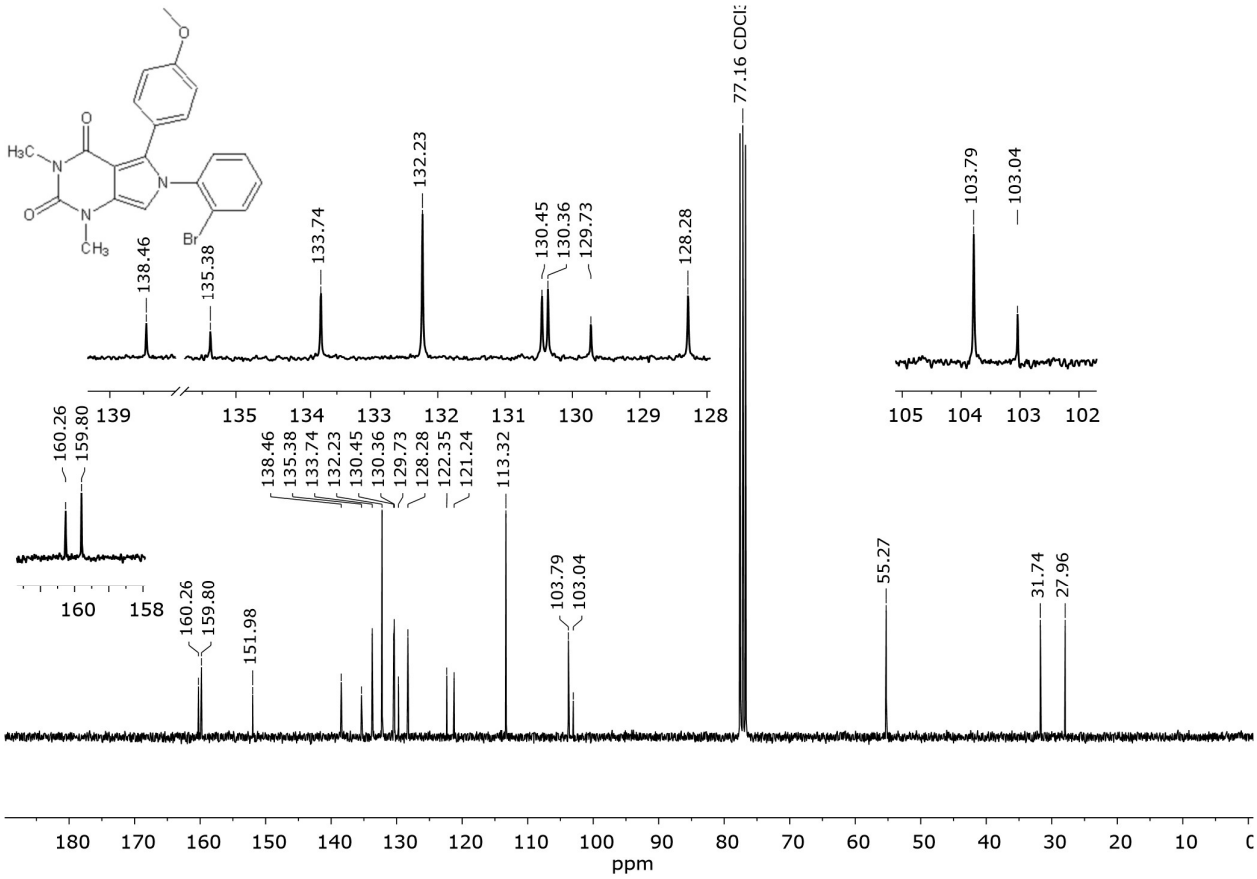


Figure S43. ^{13}C NMR spectrum of **3d** ($CDCl_3$, 75 MHz).

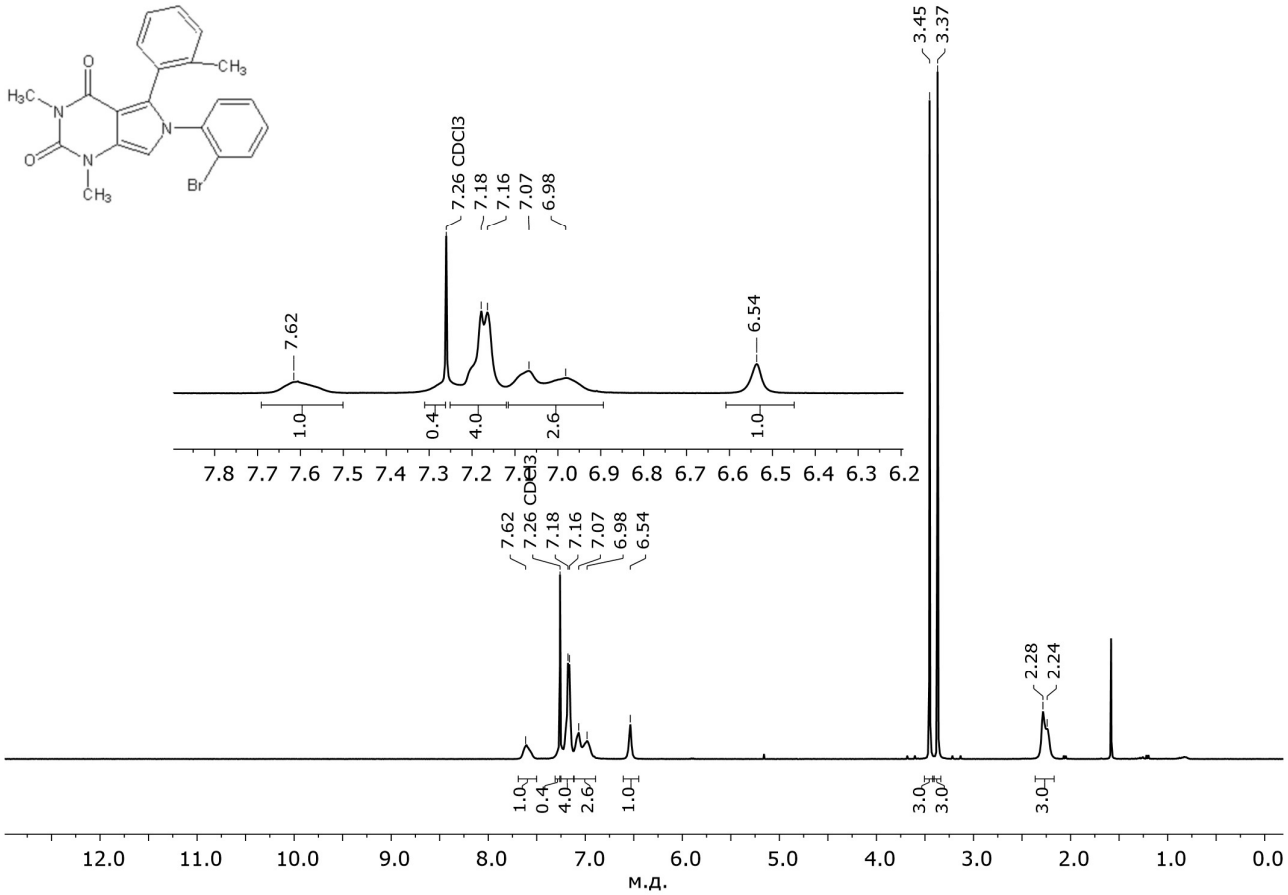


Figure S44. ^{1}H NMR spectrum of **3e** ($CDCl_3$, 300 MHz).

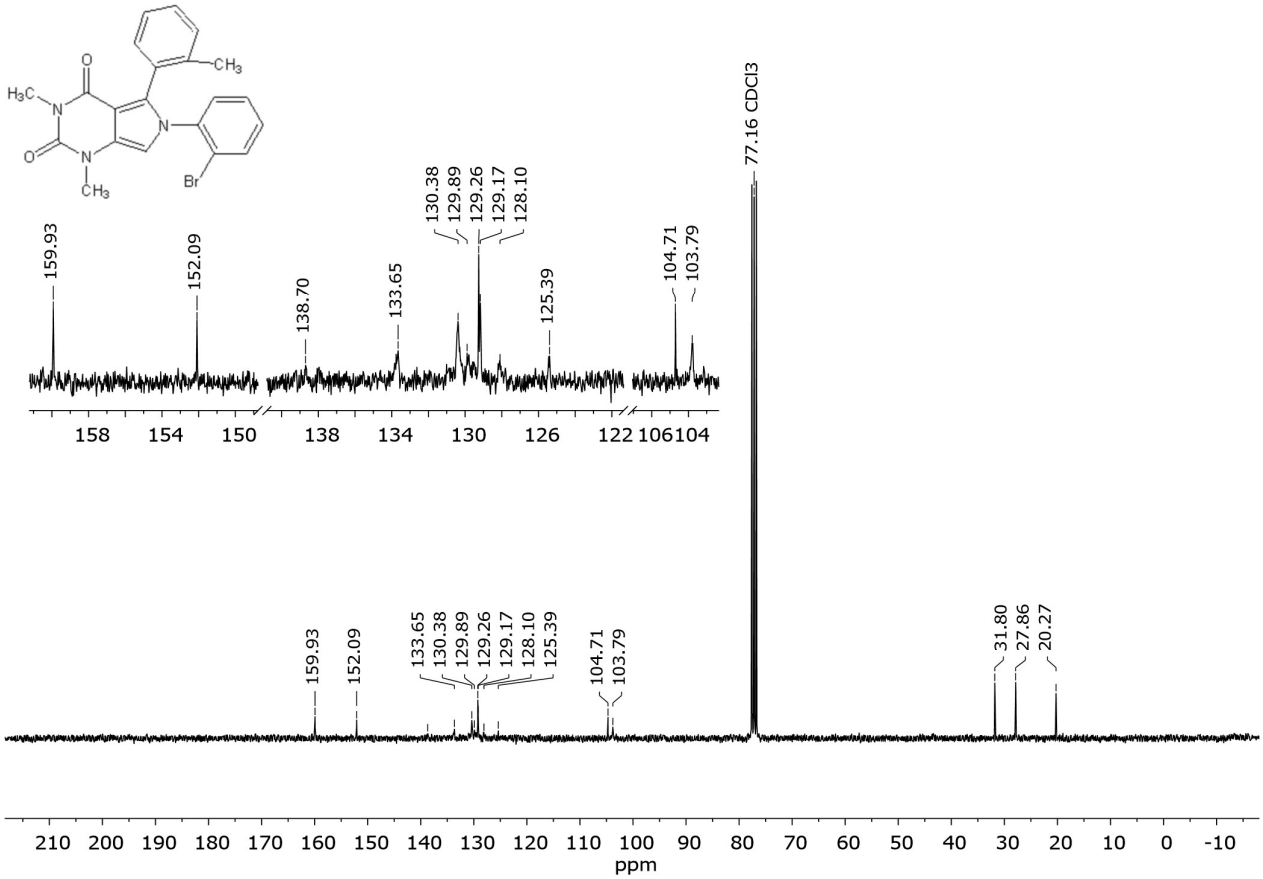


Figure S45. ^{13}C NMR spectrum of **3e** ($CDCl_3$, 75 MHz).

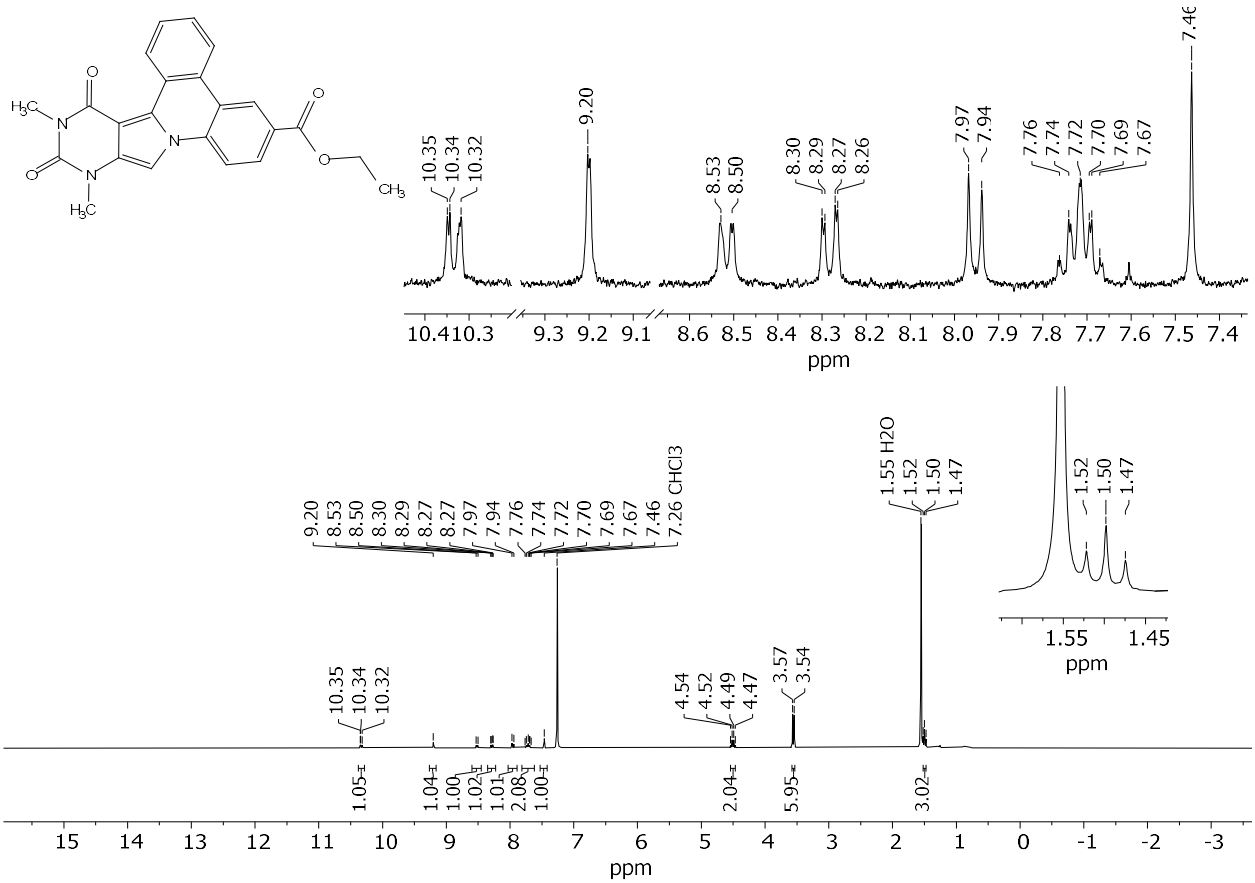


Figure S46. ^{1}H NMR spectrum of **1f** ($CDCl_3$, 300 MHz).

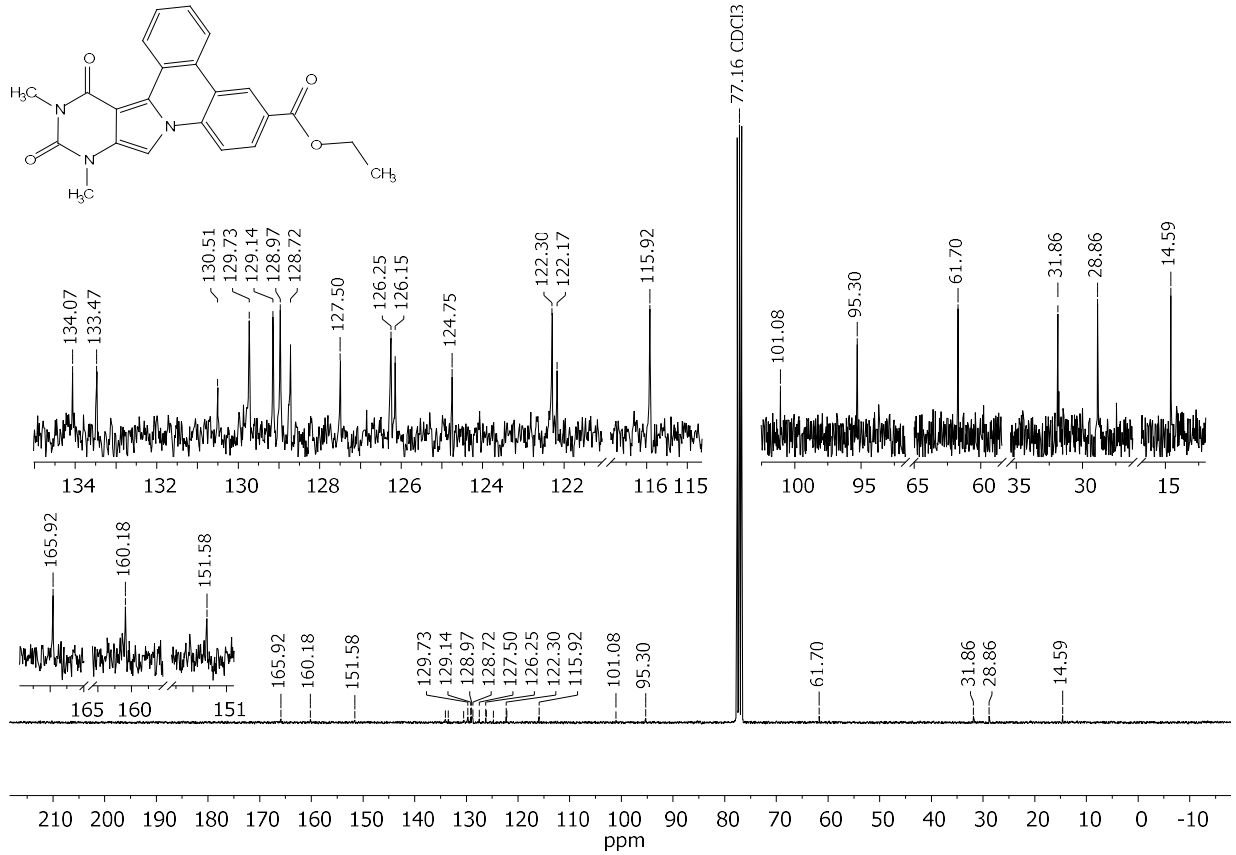


Figure S47. ^{13}C NMR spectrum of **1f** ($CDCl_3$, 75 MHz).

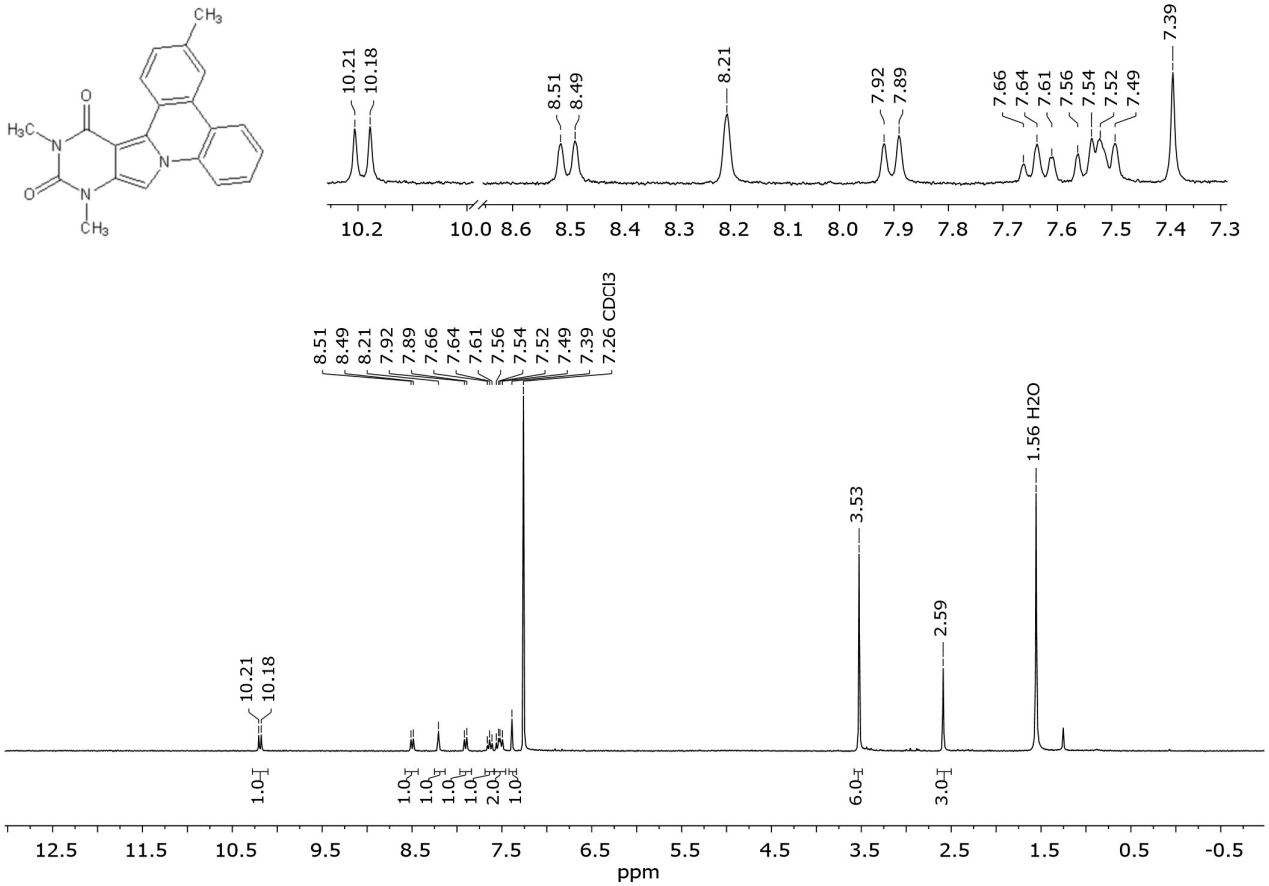


Figure S48. ^{1}H NMR spectrum of **1l** ($CDCl_3$, 300 MHz).

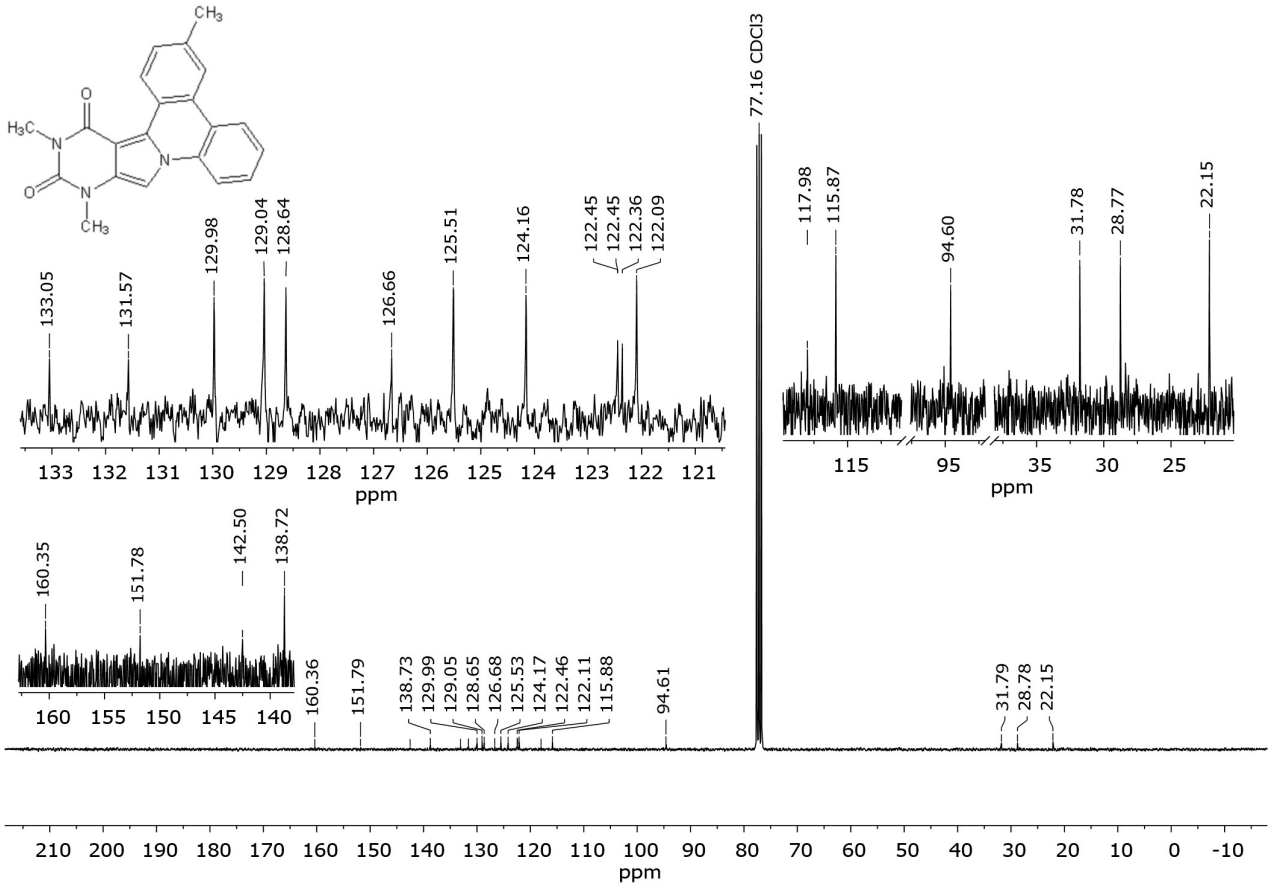


Figure S49. ^{13}C NMR spectrum of **1l** ($CDCl_3$, 75 MHz).

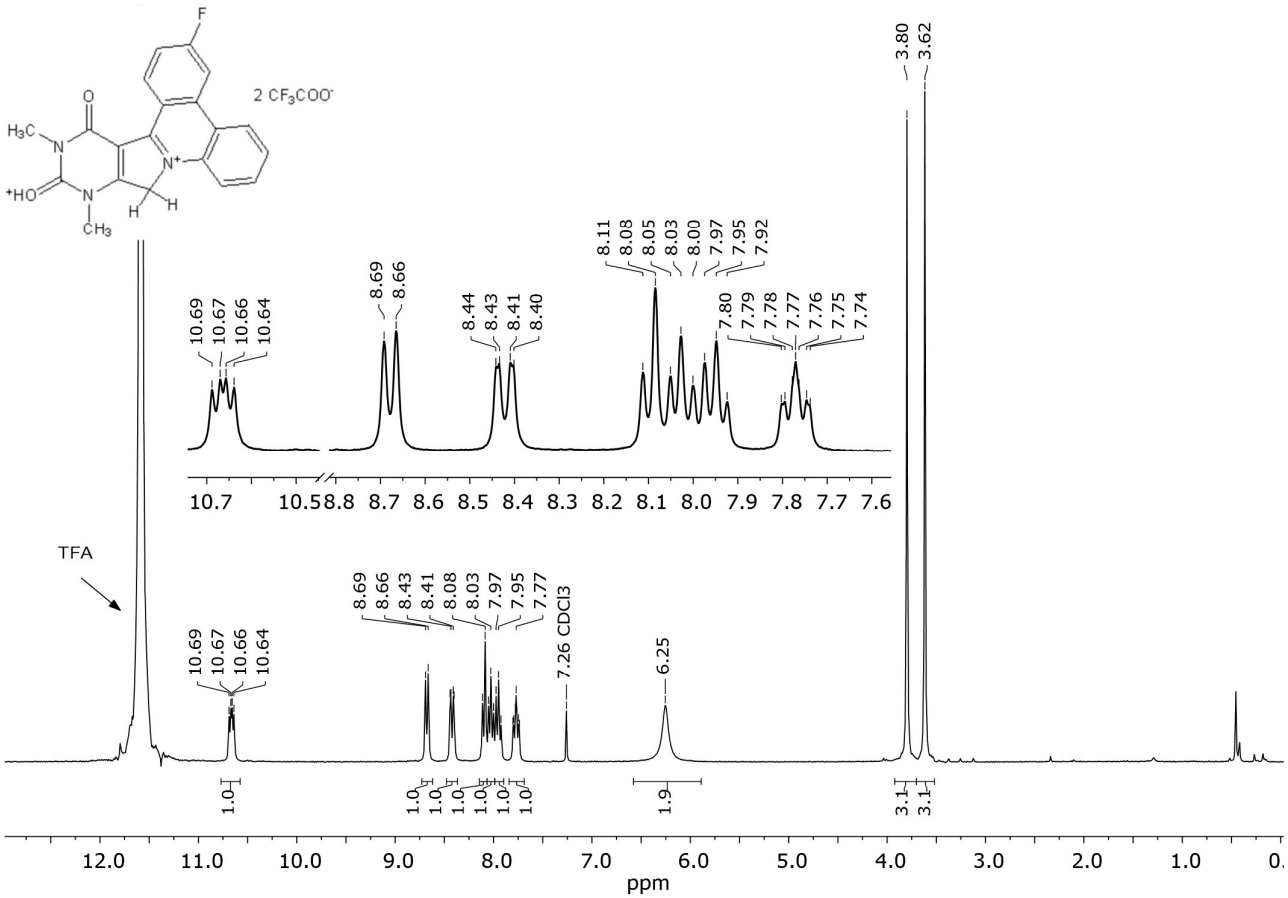


Figure S50. ^{1}H NMR spectrum of **1m** ($CDCl_3$ + CF_3COOH (3:1), 300 MHz).

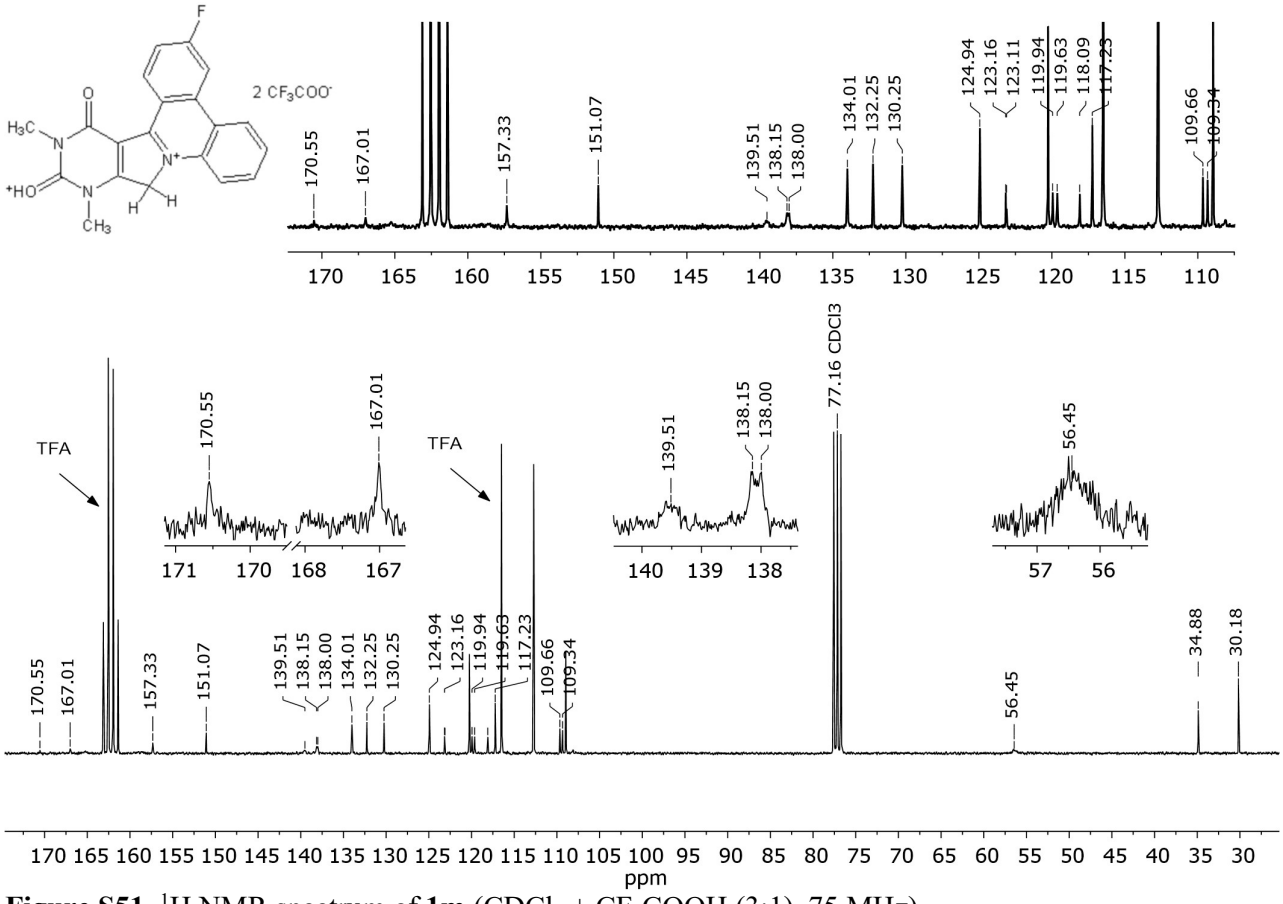


Figure S51. ^{1}H NMR spectrum of **1m** ($CDCl_3$ + CF_3COOH (3:1), 75 MHz).

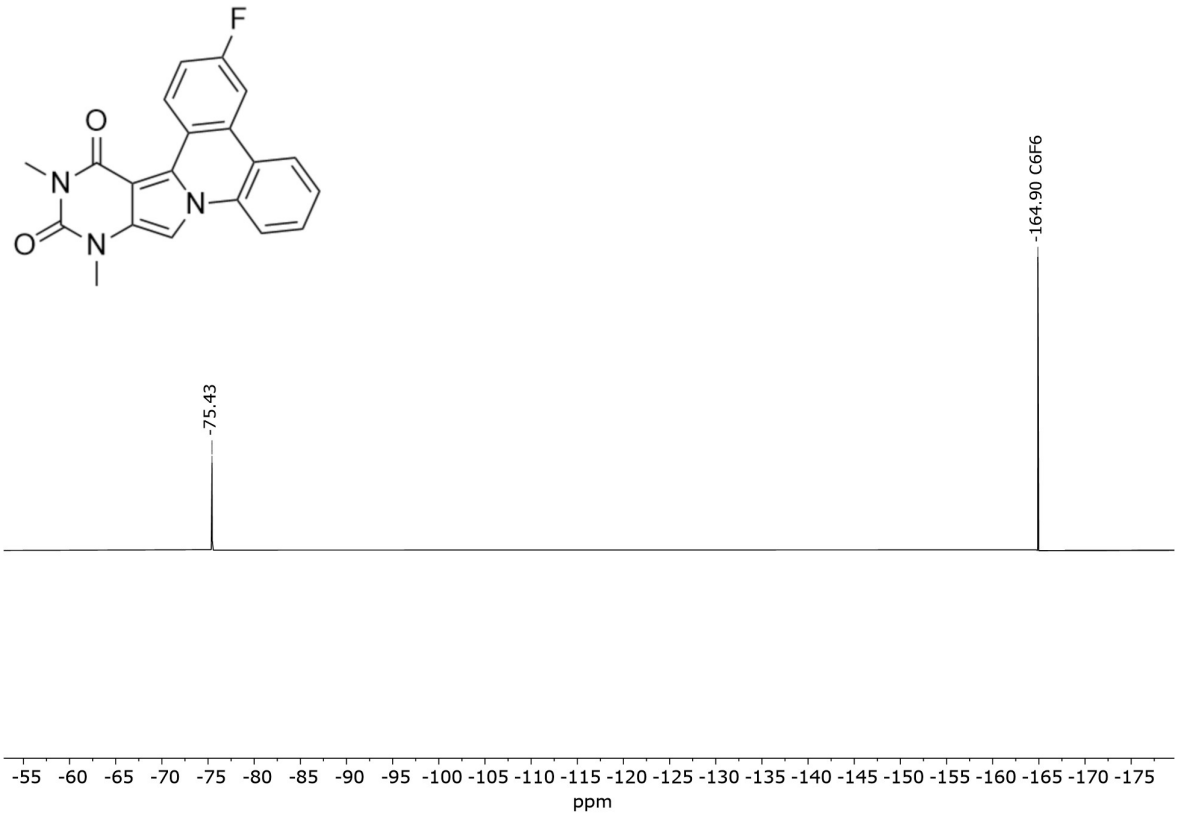


Figure S52. ^{19}F {^{1}H} NMR spectrum of **1m** (DMF-H_6, 280 MHz).

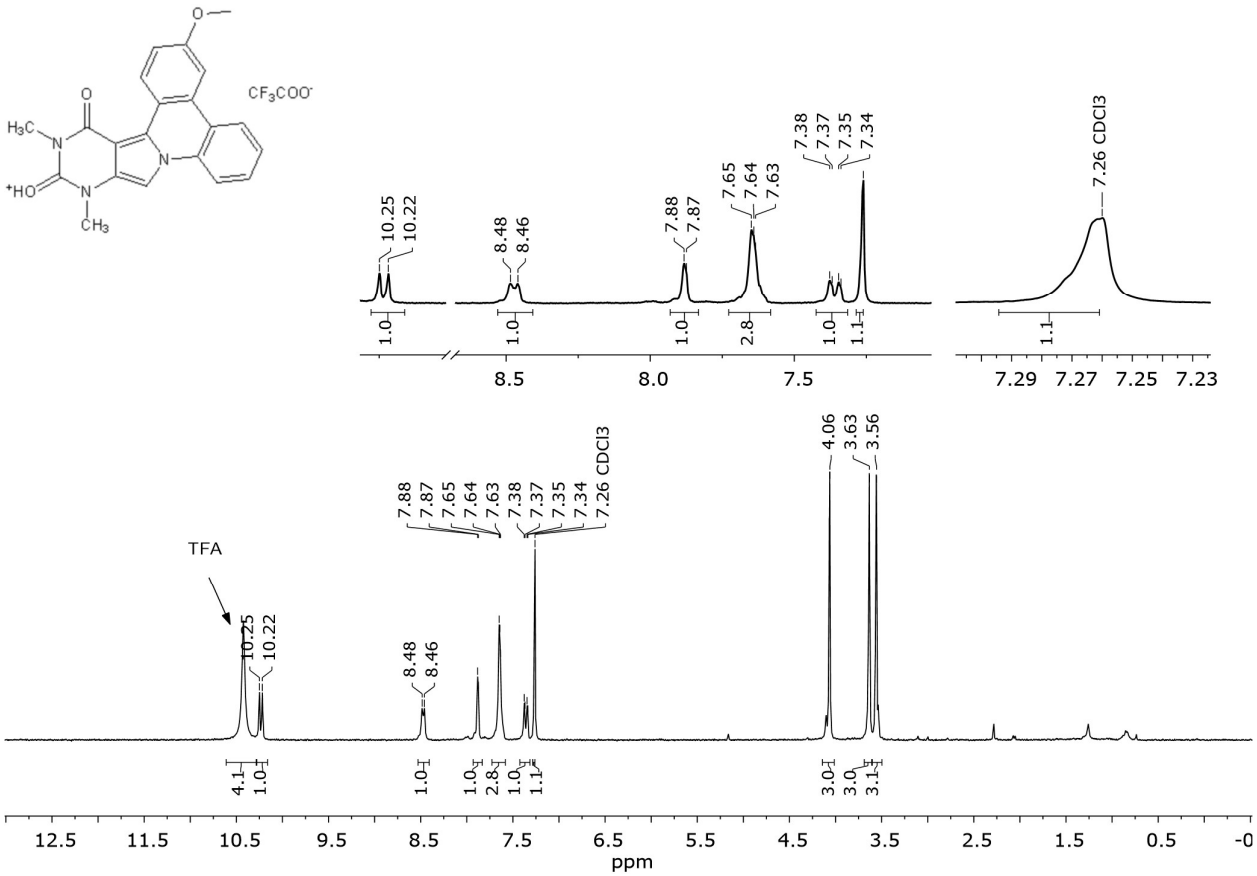


Figure S53. ^{1}H NMR spectrum of **1n** ($CDCl_3$ + TFA (10 μL), 300 MHz).

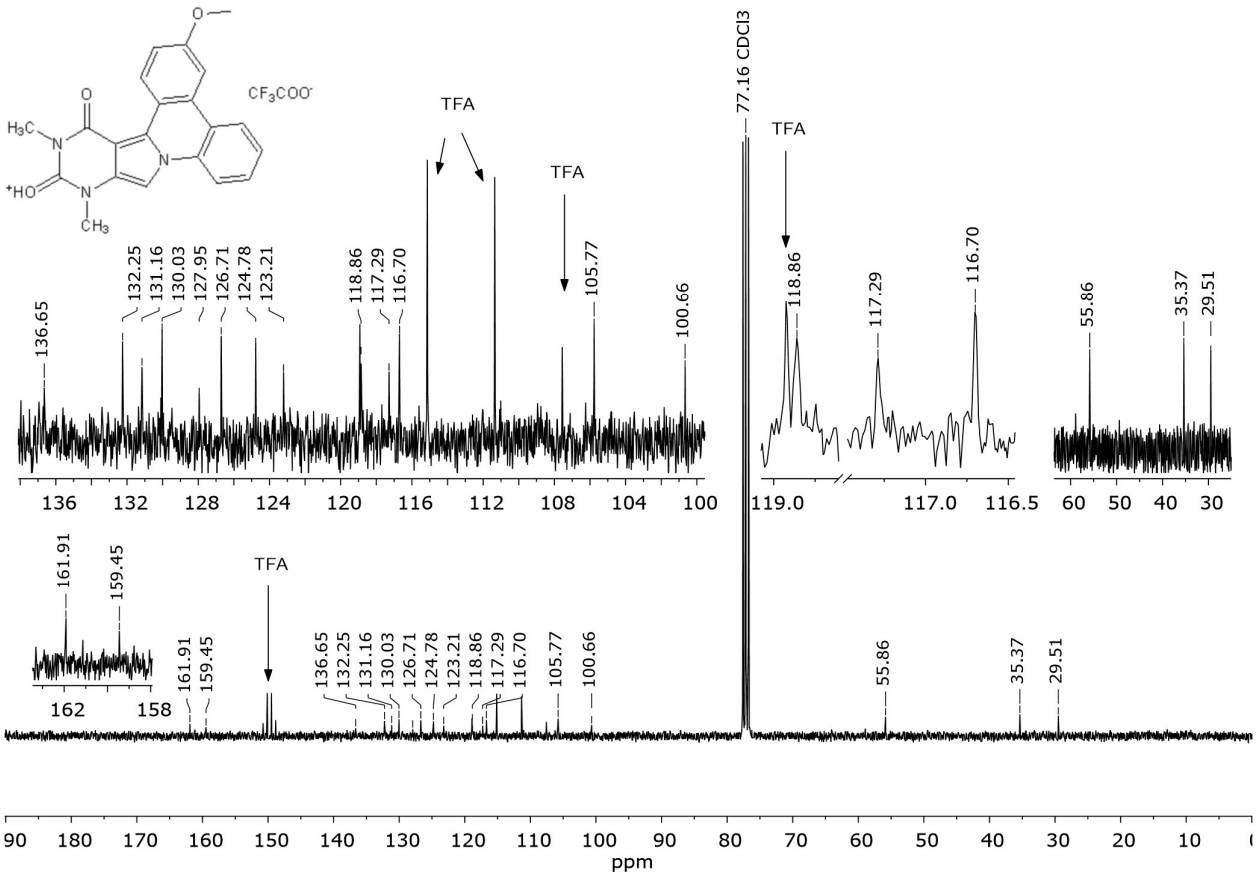


Figure S54. ^{13}C NMR spectrum of **1n** ($CDCl_3$ + TFA (10 μL), 75 MHz).

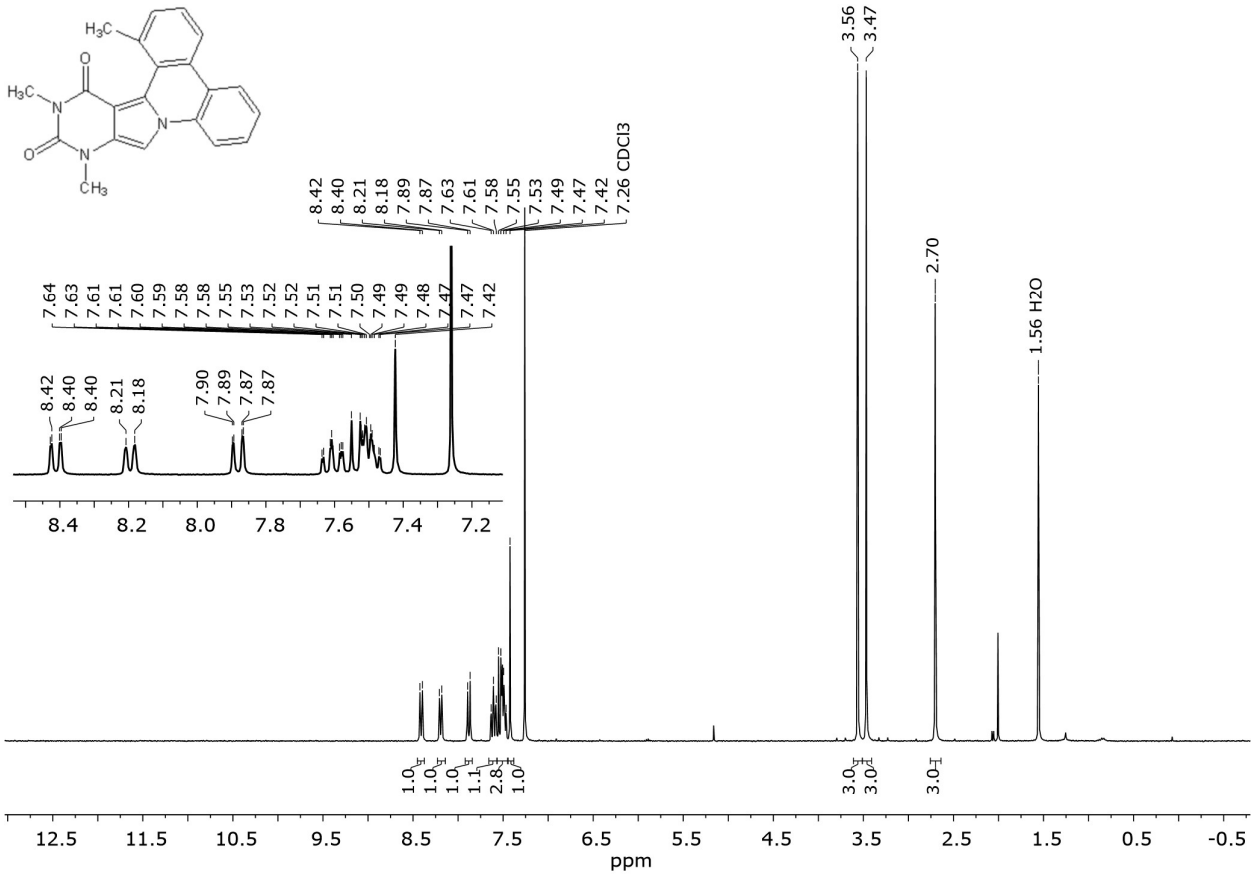


Figure S55. ^{1}H NMR spectrum of **1o** ($CDCl_3$, 300 MHz).

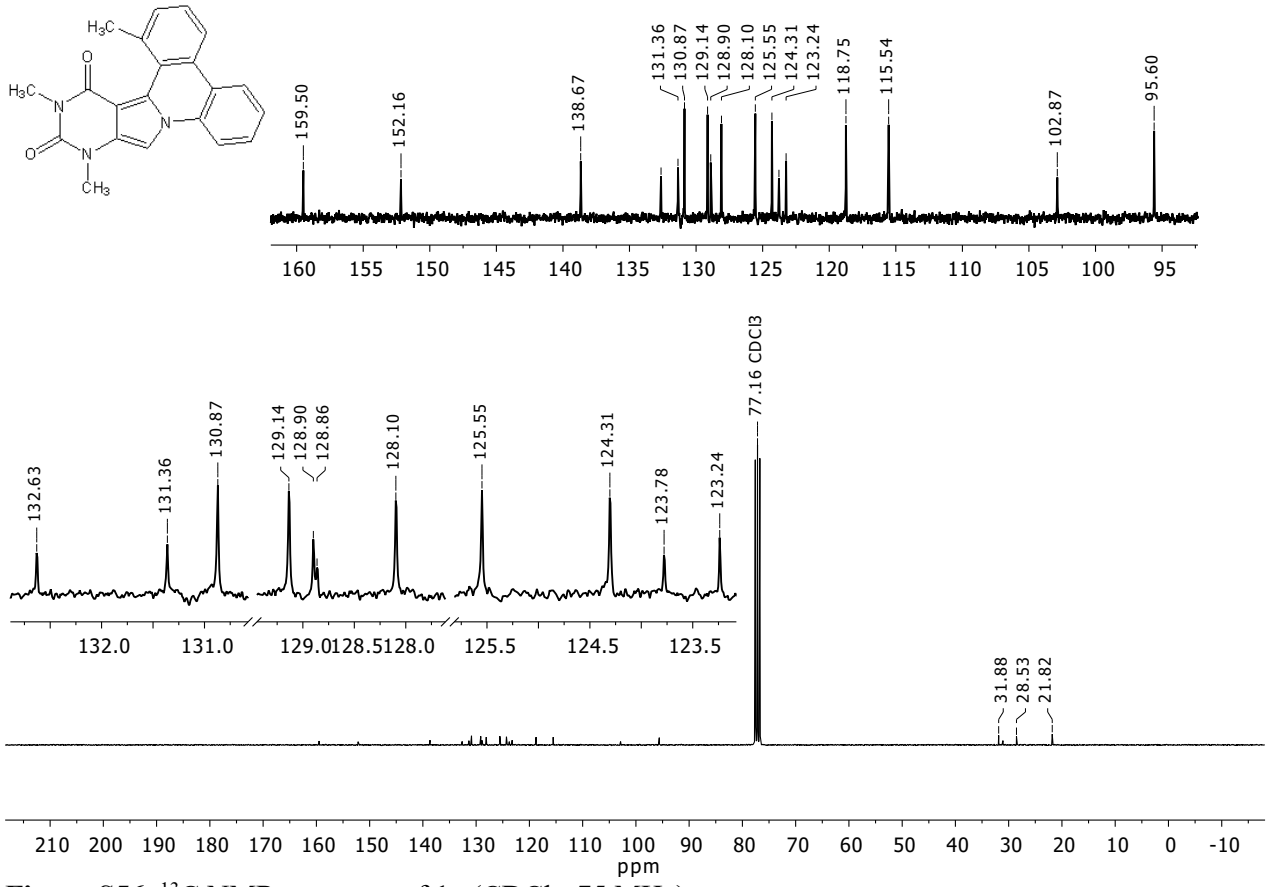


Figure S56. ^{13}C NMR spectrum of **1o** ($CDCl_3$, 75 MHz).

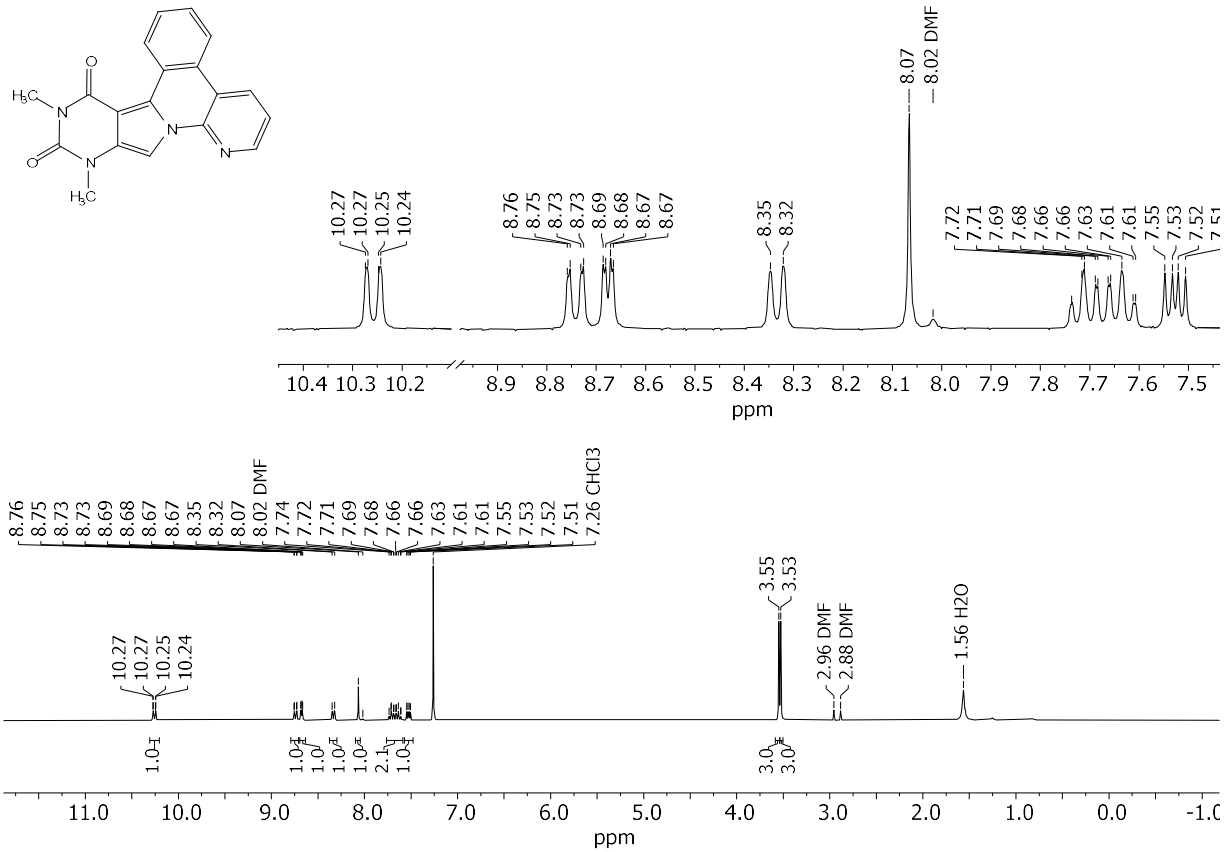


Figure S57. ^{1}H NMR spectrum of **5** ($CDCl_3$, 300 MHz).

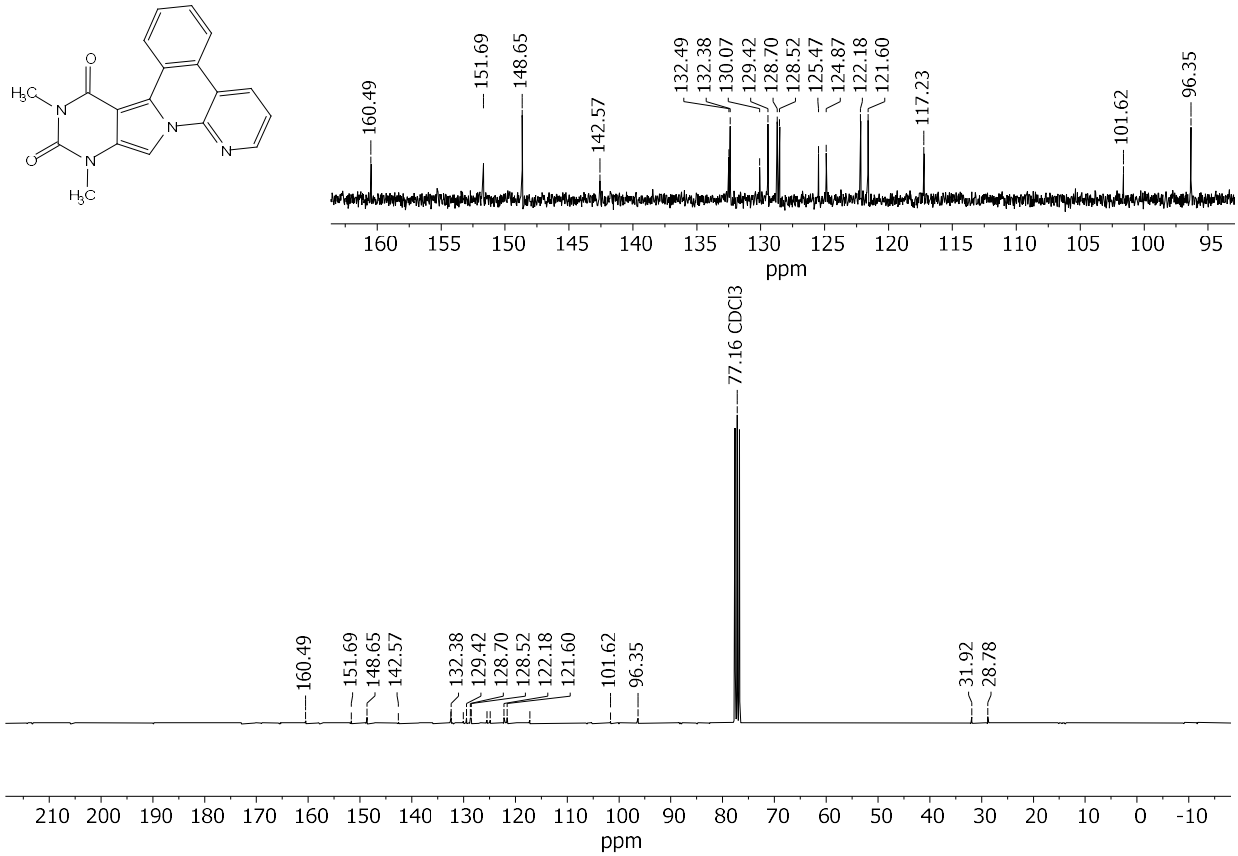


Figure S58. ^{13}C NMR spectrum of **5** ($CDCl_3$, 75 MHz