Supporting Information

Iron(II)-catalyzed annulation to construct novel quinone-fused cyclopenta[2,1-*b*]indoles: A promising Type I photosensitizer

Hong Xu[a, b, c†], Xiao-Chun Liu [a†], Bei Wang[a], Fuyu Li [a, b, c], Yao Xiao [c], Dongwei Huang [c], Ning Ma [a], Ya-Hui Zhang[a]*, Jiyu Wang[a, b, c]*

Ji-Yu Wang: Jiyuwang@cioc.ac.cn.; Ya-Hui Zhang: yahuizhang@mail.xhu.edu.cn.

[†]These authors contributed equally to this work.

*Corresponding author:
Ya-Hui Zhang: yahuizhang@mail.xhu.edu.cn.; Ji-Yu Wang: Jiyuwang@cioc.ac.cn.
[†]Hong Xu and Xiao-Chun Liu contributed equally to this work.

Contents

1.General Information

Unless otherwise noted, all reagents were from commercial sources and used as received without further purification. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (GF-254 silica gel plate) using UV light (254 nm) to visualize the course of the reactions. ^{1}H, ^{13}C NMR spectra were recorded spectra were recorded at 400 MHz on an Agilent spectrometer. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (J) are in Hertz (Hz). NMR spectra were taken using TMS (1H, δ = 0), $CDCl_3$ (^{1}H, δ = 7.26), and $CDCl_3$ (^{13}C, CPD δ = 77.16) as the internal standards, respectively. HRMS were undertaken on a Thermo Scientific LTQ Orbitrap XL instrument. Melting points were tested with Hanon MP430. UV spectrums were tested with UNICO 4802 UV-VIS double beam spectrophotometer. The fluorescence emission spectrums were tested with FluroMax-4 Fluorescence spectrophotometer. Dulbecco's modifies eagle medium (DMEM) and FBS were purchased from Gibco (USA). Penicillin−streptomycin was purchased from Macgene (China). The 2',7'-Dichlorofluorescein diacetate (DCFH-DA) and 9,10-Anthracenediyl-bis(methylene) dimalonic acid (ABDA) required for the active oxygen test were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Thiazolyl Blue(MTT) were purchased from Bide Pharmatech Co., Ltd. Calcein-AM/PI Live-Dead Cell Staining Kit were purchased from Beijing Solarbio Science and Technology Co., Lta. DCFH-DA was purchased from Beyotime. The absorbance intensity of the ABDA indicator collected on the Thermo Fisher UV-2700 spectrophotometer. Record cell imaging using a confocal laser PL microscope (Zeiss LSM 780). Electron paramagnetic resonance (EPR) spectra were measured on Bruker Paramagnetic Resonance Spectrometer EMXplus. Redox potential was measured on Chi660e electrochemical workstation. TD-DFT calculations were performed on Gaussian 09 program. The ground-state (S_0) geometries were optimized with B3LYP

by using 6-311G(d) basis sets. The other Chemicals and analytical grade solvents were purchased from Adamas-Beta and used without further purification unless otherwise stated.

The indolylquinones (**1a-1u**) were prepared according to the reported literature procedure.[1]

2. Methods and Experimental Procedures

2.1Tables for the optimization of reaction conditions

Table S1 Screening of the necessity of each substance [a, b]

Entry	Catalyst (20 mol%)	Oxidant (2 eq)	Base (0.5 eq)	Yield/ %
1	$FeSO_4.7H_2O$	$K_2S_2O_8$	Cs_2CO_3	78
2	$FeSO_4.7H_2O$	$K_2S_2O_8$	-	N.D
3	-	$K_2S_2O_8$	Cs_2CO_3	37
4	$FeSO_4.7H_2O$	-	Cs_2CO_3	N.D

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.5 equiv), $FeSO_4.7H_2O$ (20 mol%), $K_2S_2O_8$ (2 equiv), CH_3CN (1 mL), T_1= T_2=65 °C, t_1= t_2=3 h. [b] Isolated yield. [c] N.D means not detected.

Table S2 Screening of the necessity of base [a, b]

Entry	Base (0.5 eq)	t/h	Yield/ %
1	K_3PO_4	24+8	10
2	Et_3N	24+8	24
3	DMAP	24+6	11
4	DBU	12	15
5	Cs_2CO_3	3	78
6	$NaHCO_3$	24+12	9
7	Na_2CO_3	24+12	20
8	NaOH	24+12	17
9	PPh_3	5	N.D
10	NaH	24+12	13
11	t-BuOK	24+12	18
12	Morpholine	24+12	8

13	Py	36	N.D

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), base (0.5 equiv), $FeSO_4.7H_2O$ (20 mol%), $K_2S_2O_8$ (2 equiv), CH_3CN (1 mL), $T_1= T_2=65$ °C, $t=t_1+t_2$. [b] Isolated yield. [c] N.D means not detected.

Table S3 Screening of catalyst [a, b]

Entry	Catalyst (20 mol%)	t_2/h	Yield/%
1	$FeBr_3$	3	56
2	$FeCl_3.6H_2O$	3	N.D
3	$Fe(NO_3)_3.9H_2O$	1.5	59
4	$Fe(OTs)_3.6H_2O$	3	N.D
5	$Fe(OTf)_3$	3	30
6	$Fe(C_2O_4)_3$	3	28
7	FeS	3	N.D
8	FeC_2O_4	3	N.D
9	$FeCl_2.4H_2O$	3	59
10	$CuSO_4.5H_2O$	1.5	59
11	$Cu(acac)_2$	3	N.D
12	CuBr	3	N.D
13	$CoCl_2$	3	57
14	$NiCl_2$	3	45
15	$Ni(OTf)_2$	3	39
16	$Zn(NO_3)_2$	3	53
17	$Co(NO_3)_2$	3	56
18	$BiCl_3$	1.5	63
19	---	3	37

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.5 equiv), catalyst (20 mol%), $K_2S_2O_8$ (2 equiv), CH_3CN (1 mL), $T_1= T_2=65$ °C, $t_1= 3$ h. [b] Isolated yield. [c] N.D means not detected.

Table S4 Screening of oxidant [a, b]

Entry	Oxidant (2 eq)	Yield/%
1	H_2O_2	N.D
2	DTBP	N.D
3	TBHP	N.D
4	BPO	10%
5	PCC	N.D
6	TEMPO	N.D
7	DMSO	N.D

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.5 equiv), $FeSO_4.7H_2O$ (20 mol%), oxidant (2 equiv), CH_3CN (1 mL), T_1= T_2=65 °C, t_1= t_2=3 h. [b] Isolated yield. [c] N.D means not detected.

Table S5 Screening of the amount of catalyst and oxidant [a, b]

Entry	Catlyst(x mol%)	Oxdiant(y equiv)	Yield/%
1	$FeSO_4.7H_2O$ (5)	$K_2S_2O_8$ (2)	28
2	$FeSO_4.7H_2O$ (10)	$K_2S_2O_8$ (2)	43
3	$FeSO_4.7H_2O$ (15)	$K_2S_2O_8$ (2)	66
4	$FeSO_4.7H_2O$ (20)	$K_2S_2O_8$ (2)	75
5	$FeSO_4.7H_2O$ (20)	$K_2S_2O_8$ (1.5)	48
6	$FeSO_4.7H_2O$ (20)	$K_2S_2O_8$ (1)	25

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.5 equiv), $FeSO_4.7H_2O$ (x mol%), $K_2S_2O_8$ (y equiv), CH_3CN (1 mL), T_1= T_2=65 °C, t_1= t_2=3 h. [b] Isolated yield. [c] N.D means not detected.

Table S6 Screening of solvent and temperature [a, b]

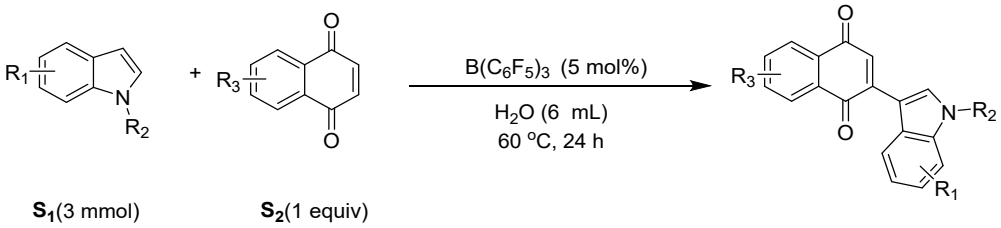
Entry	Solvent	T/°C	Yield/%
1	1,4-Dioxane	65	trace
2	EA	65	trace
3	THF	65	trace

4	toluene	65	trace
5	DMF	65	N.D
6	DMSO	65	N.D
7	CH_3CN	85	68
8	CH_3CN	75	65
9	CH_3CN	65	71
10	CH_3CN	55	25

Reaction conditions: [a] **1a** (0.1 mmol), **2a** (0.2 mmol), Cs_2CO_3 (0.5 equiv), $FeSO_4.7H_2O$ (x equiv), $K_2S_2O_8$ (y equiv), solvent (1 mL), T_1 =65 °C, t_1= 3 h, T_2, t_2. [b] Isolated yield. [c] N.D means not detected.

2.2 General procedures for the Synthesis of Substrates and Products

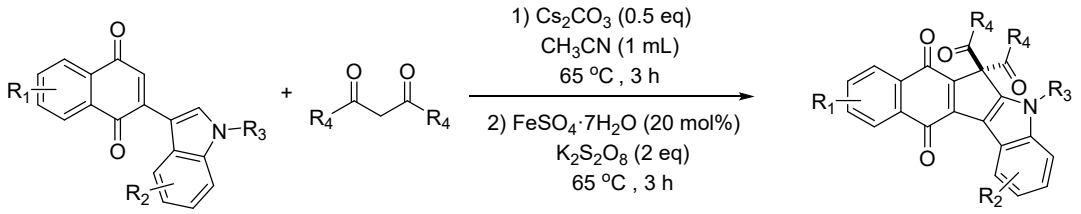
A) General procedures for the synthesis of indolylquinones



S_1(3 mmol) **S_2**(1 equiv)

Indol-3-ylquinones **(1a-1u).**[1] Indole (3 mmol), naphthoquinone (3 mmol), $(C_6F_5)_3B$ (77 mg, 5 mol%) were sequentially weighed into the reaction flask, then 6ml of water was added, and the reaction was heated to 60 °C for 24 h in the oil bath. After the reaction was completed, the aqueous phase was extracted three times with ethyl acetate. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain **1a-1u**. If the product is not pure, it can be recrystallized with ethyl acetate.

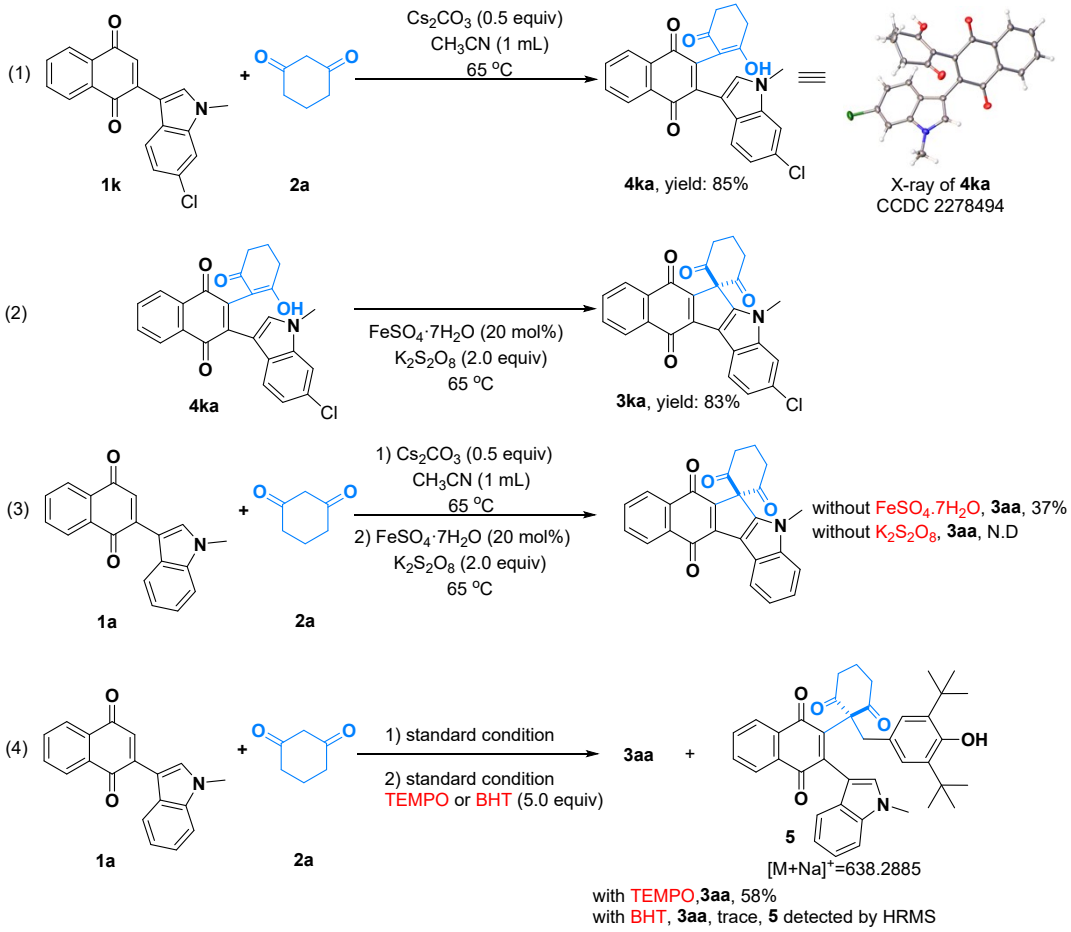
B) General procedures for the synthesis of benzo[5,6]indeno[2,1-b]indole-7,12-dione derivatives.



1 2 3

Indolylquinone (0.1 mmol, 1.0 equiv), 1,3-dicarbonyl compound (0.2 mmol, 2.0 equiv), Cs_2CO_3 (17mg, 0.05 mmol, 0.5 equiv) were sequentially weighed into the reaction flask and immediately dissolve them with 0.5 ml CH_3CN, and the mixture was heated to 65 °C and stirred for 3 h in the oil bath. Then sequentially add $FeSO_4.7H_2O$ (5.6 mg, 0.02 mmol, 0.2 equiv), $K_2S_2O_8$ (54.0 mg, 0.2 mmol, 2 equiv) and stirred for 3 h in the 65 °C oil bath. After the reaction was completed, the solution was diluted with water and extracted three times with EtOAc. The organic phase was dried with anhydrous magnesium sulfate. The solvent was evaporated to dryness under reduced pressure, and the product was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to obtain benzo[5,6]indeno[2,1-*b*]indole-7,12-dione derivatives . If the product is not pure, it can be recrystallized with ethyl acetate and petroleum ether.

2.3 Mechanistic experiments



Scheme S1 Mechanistic experiments.

2.4 Photophysical properties

The parameters setting for fluorescence emission spectrum: the scanning range of emission wavelength was from 375 nm to 800 nm, excitation wavelength was the λmax of the UV/VIS spectrum of every compound, emission slit width was 5 nm, excitation slit width was 5 nm, the sensitivity was 1, the scanning speed was medium speed.

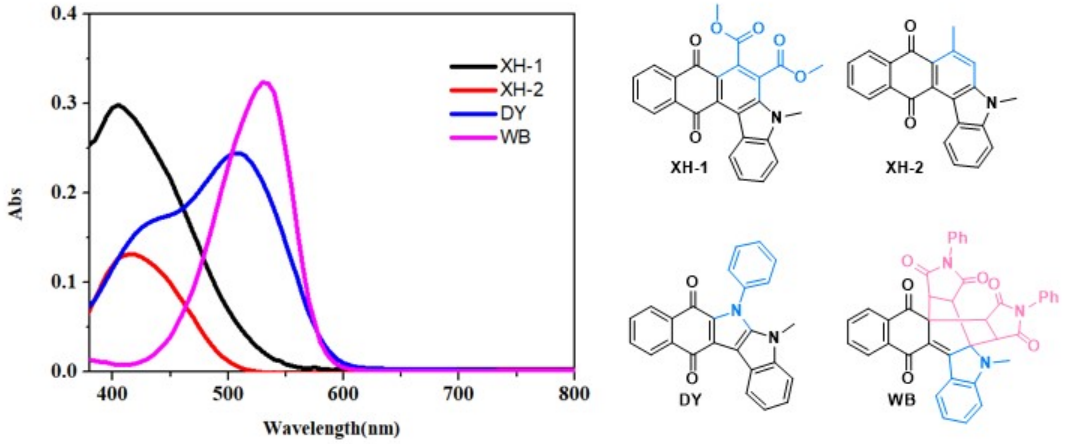


Figure S1 The UV-VIS spectrum of compound **XH-1, XH-2, DY, WB** (C=2.5X10^{-5} M) in DCM

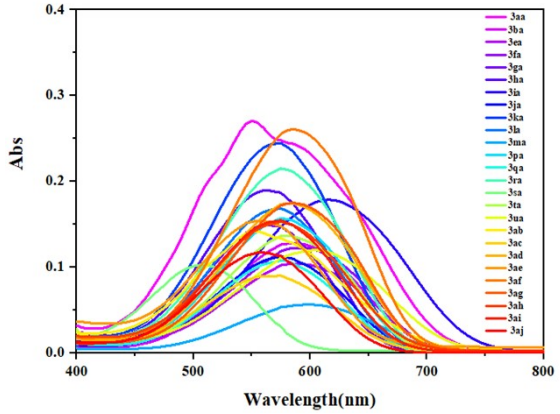
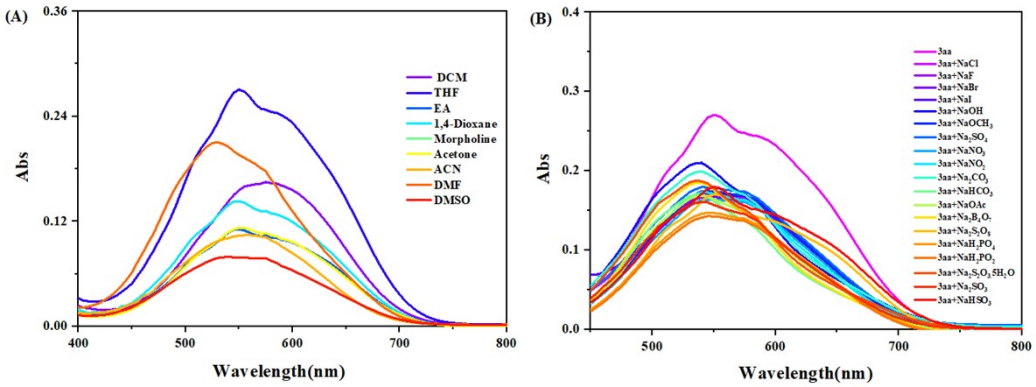


Figure S2 The UV-VIS spectrum of compound **3aa-3aj** (C=2.5X10^{-5} M) in THF



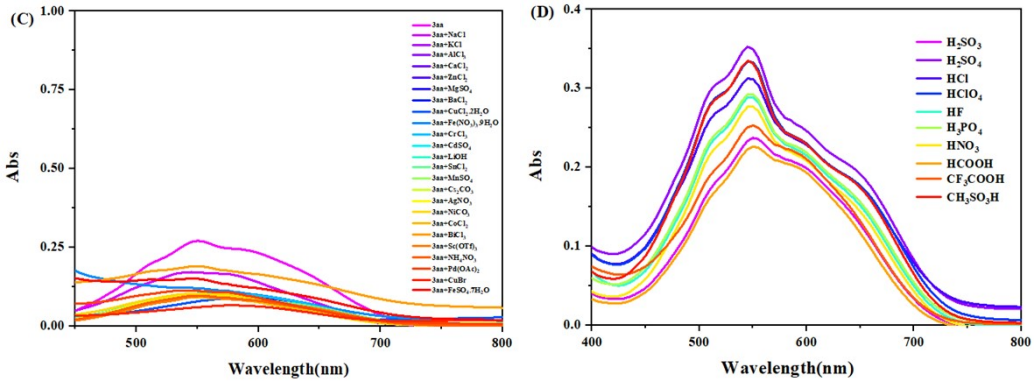


Figure S3 （A) The UV-VIS spectrum of compound **3aa** (C=2.5X10^{-5} M) in different solvents. (B) The UV-VIS spectrum of compound **3aa** (C=2.5X10^{-5} M) with different anionic salts (C=5X10^{-4} M) in THF. (C) The UV-VIS spectrum of compound **3aa** (C=2.5X10^{-5}M) with different metal salts (C=5X10^{-4} M) in THF. (D) The UV-VIS spectrum of compound **3aa** (C=2.5X10^{-5} M) with different acids (C=0.5 M) in THF.

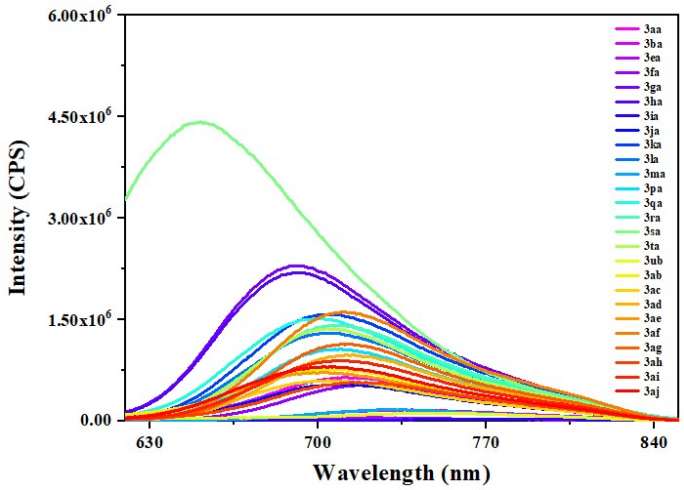


Figure S4 The fluorescence emission spectrum of compound **3aa-3aj** (C=2.5X10^{-5} M) in THF

Table S6 Photophysical characterization data of all compounds

Entry	compound	λ_{max} (nm)	λ_{em} (nm)
1	**3aa**	550	712
2	**3ba**	585	739
3	**3ea**	585	717
4	**3fa**	595	723
5	**3ga**	595	692
6	**3ha**	565	691
7	**3ia**	615	773

8	**3ja**	575	710
9	**3ka**	575	704
10	**3la**	575	706
11	**3ma**	600	730
12	**3pa**	575	709
13	**3qa**	575	700
14	**3ra**	575	705
15	**3sa**	505	653
16	**3ta**	580	704
17	**3ua**	605	752
18	**3ab**	555	707
19	**3ac**	575	704
20	**3ad**	585	715
21	**3ae**	555	704
22	**3af**	585	710
23	**3ag**	585	714
24	**3ah**	575	717
25	**3ai**	575	712
26	**3aj**	560	702

2.5 Preparation of photosensitizers

10 μmol photosensitizer was dissolved in 10 mL dimethyl sulfoxide (DMSO) to prepare a 10^{-3} mol/L solution.

2.6 Total ROS detection by indicator DCFH

25 μL 2',7'-Dichlorodihydrofluorescein (DCFH, 4×10^{-5} mol/L) as an indicator was added into 10 μL photosensitizers (1×10^{-3} mol/L) and 965 μL PBS. Control group were prepared by adding 25 μL DCFH into 975 μL PBS. After that, the obtained solutions were exposed to 660 nm laser irradiation (500 mW/cm^2) for different times, the PL intensities at 521 nm were recorded under excitation at 480 nm.

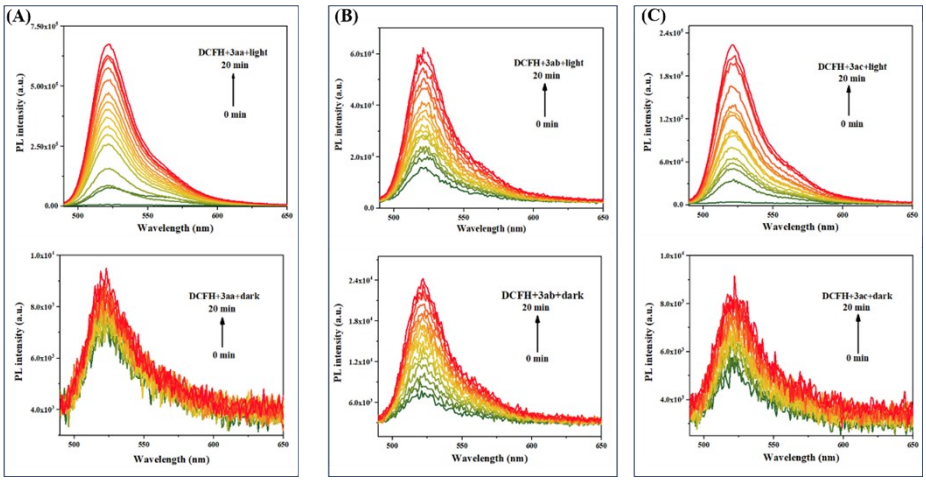


Figure S5 Fluorescent spectra of **3aa**/**3ab**/**3ac**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

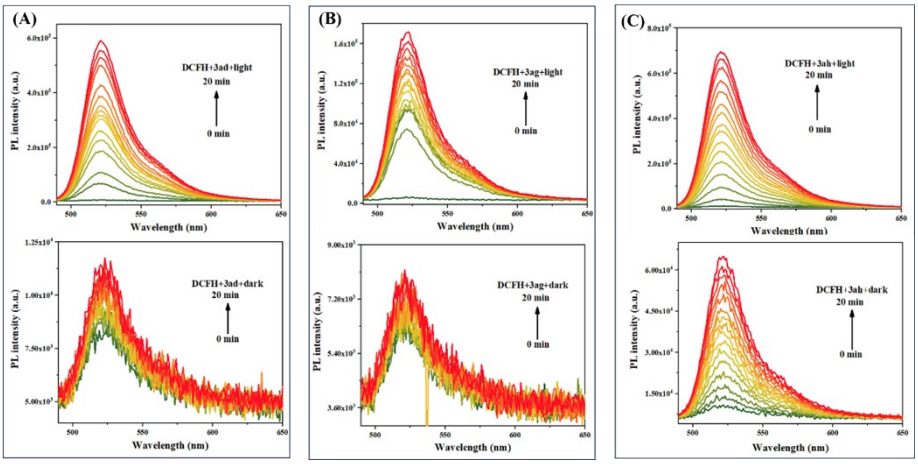


Figure S6 Fluorescent spectra of **3ad**/**3ag**/**3ah**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

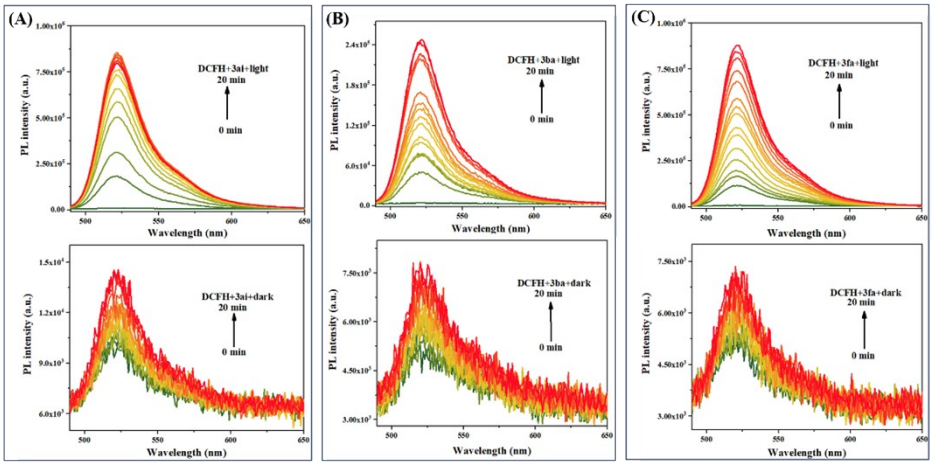


Figure S7 Fluorescent spectra of **3ai**/**3ba**/**3fa**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

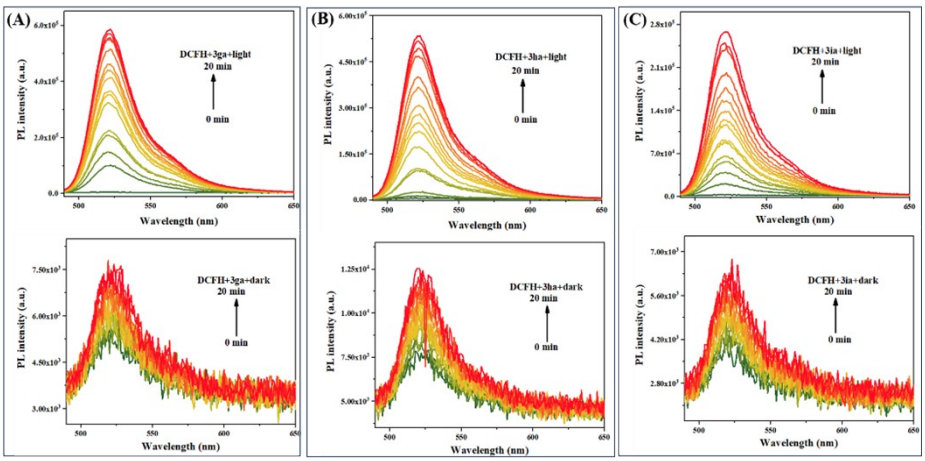


Figure S8 Fluorescent spectra of **3ga**/**3ha**/**3ia**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

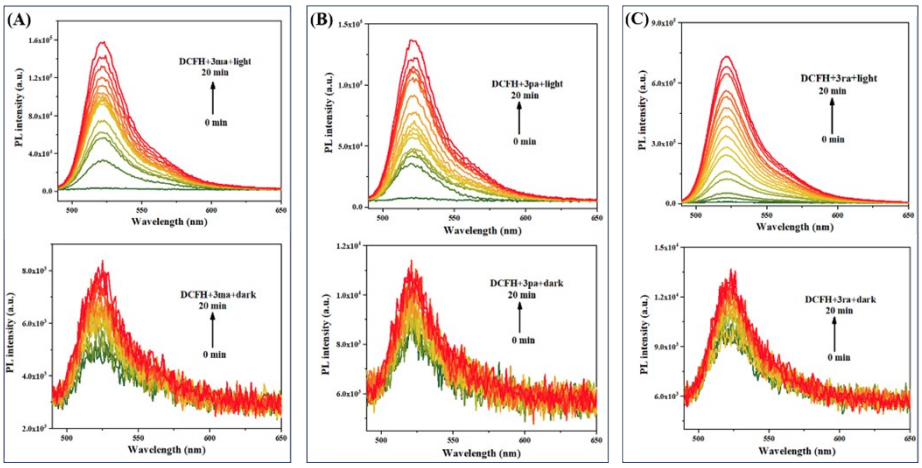


Figure S9 Fluorescent spectra of **3ma**/**3pa**/**3ra**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

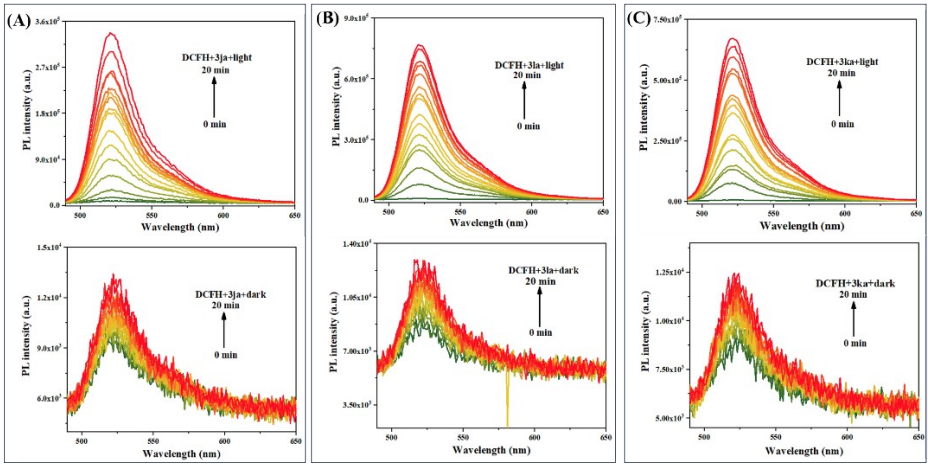


Figure S10 Fluorescent spectra of **3ja**/**3la**/**3ka**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min.

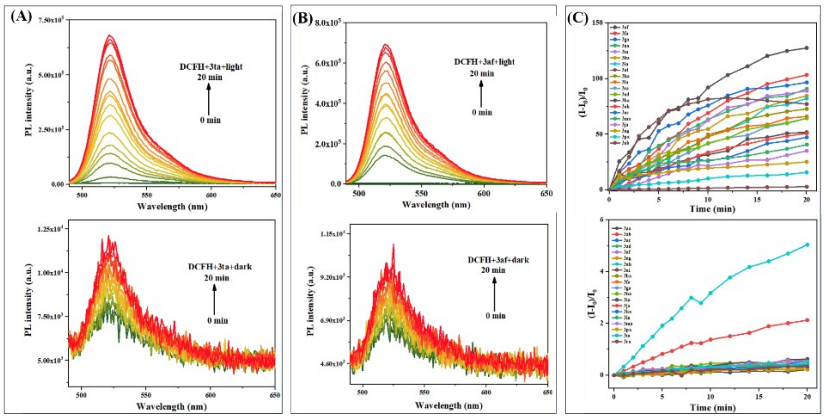


Figure S11 (A)Fluorescent spectra of **3ta/3af**+ DCFH under 660 nm laser irradiation (500 mW/cm^2) or at dark for 20 min. (B)Fluorescence intensity net change $(I-I_0)/I_0$ at 521 nm for the DCFH indicator with **3af** and its series of compounds upon 660 nm irradiation (500 mW/cm^2) or at dark, [DCFH] = 1.0×10^{-6} mol/L, [**3af**] = 1.0×10^{-5} mol/L.

2.7 Detection of $^1O_2$ Generation by indicator ABDA

10 μL 9,10-anthracenediyl-bis(methylene)-dimalonic acid (ABDA, 1×10^{-2} mol/L) as an indicator was added into 10 μL photosensitizers (1×10^{-3} mol/L) and 1980 μL PBS. Control group were prepared by adding 10 μL ABDA (1×10^{-2} mol/L) into 10 μL DMSO and 1980 μL PBS. After that, the obtained solutions were exposed to 660 nm laser irradiation (500 mW/cm^2) for different times, the absorption spectra of ABDA were measured.

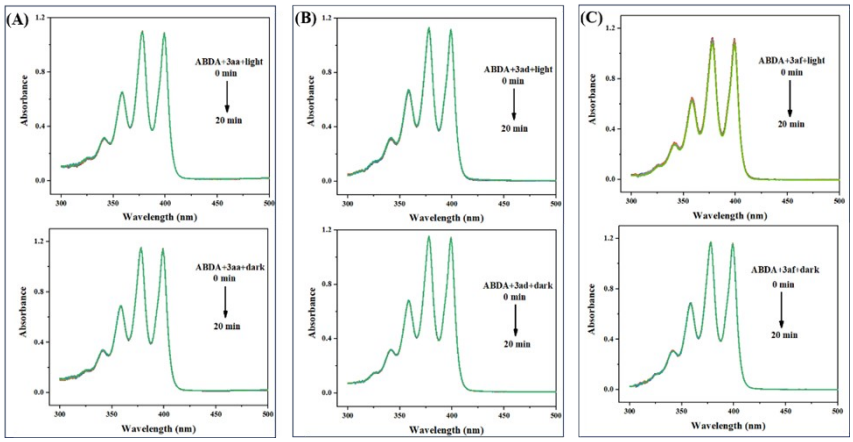


Figure S12 Absorbance intensity of the ABDA indicator with **3aa**/**3ad**/**3af** upon 660 nm laser irradiation (500 mW/cm^2) or at dark, [ABDA] = 1.0×10^{-4} mol/L, [**3af**] = 1.0×10^{-5} mol/L.

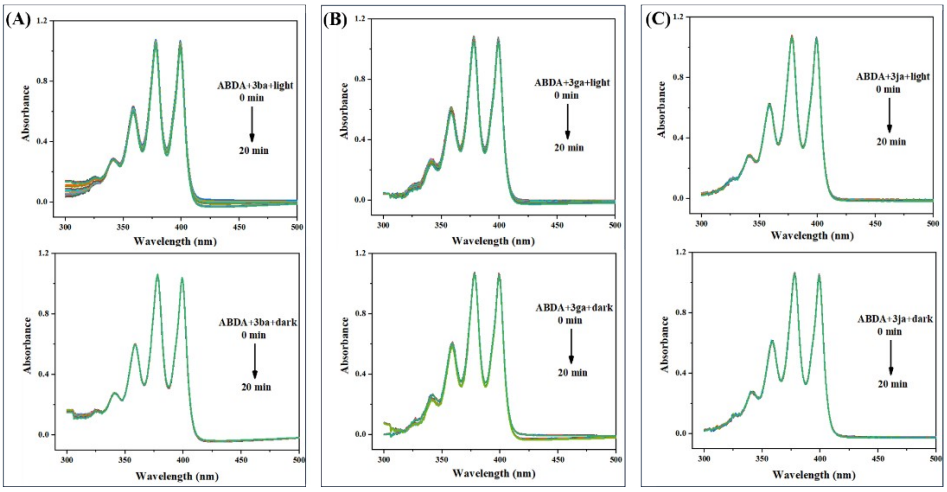


Figure S13 Absorbance intensity of the ABDA indicator with **3ba**/**3ga**/**3ja** upon 660 nm laser irradiation (500 mW/cm^2) or at dark, [ABDA] = 1.0×10^{-4} mol/L, [3af] = 1.0×10^{-5} mol/L.

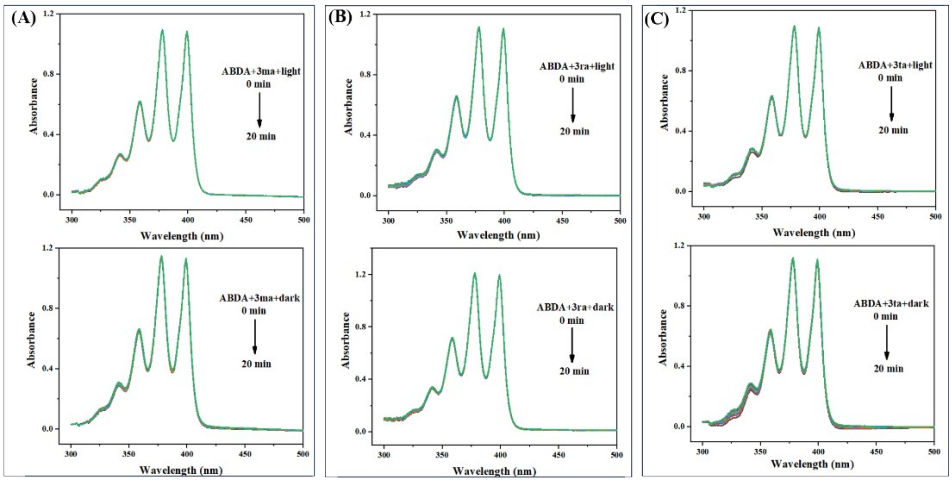


Figure S14 Absorbance intensity of the ABDA indicator with **3ma**/**3ra**/**3ta** upon 660 nm laser irradiation (500 mW/cm^2) or at dark, [ABDA] = 1.0×10^{-4} mol/L, [**3af**] = 1.0×10^{-5} mol/L.

2.8 EPR Analysis

EPR analysis was carried out to confirm the generation of •OH using DMPO as spin-trap agent. The working samples containing 70.8 × 10^{-3} mol/L DMPO and 1 × 10^{-3} mol/L of 3af was injected quantitatively into quartz capillaries, and the spectra of spin was monitored before and after the solution was irradiated by 650 nm laser irradiation.

2.9 TD-DFT calculation

Use Gaussian 09 program for TD-DFT calculation. Optimize the ground state molecular configuration using the B3LYP (6-311G (d)) group.

Table S7 Calculated energy of the singlet (S) and triplet (T) excited states (Gaussian/B3LYP/6-311G(d)).

		1	2	3	4	5
3af	S (eV)	1.7999	2.4876	2.6655	2.7685	3.1369
	T (eV)	0.9986	2.0903	2.1948	2.6442	2.7079

2.10 Electrochemical Experiments

Cyclic voltammogram of *p*-BQ and **3af** in DCM by argon bubbling with 0.1 M $(n\text{-}Bu)_4N^+PF_6^-$ as the supporting electrolyte, Ag/Ag^+ as the reference electrode, a glassy-carbon electrode as the working electrode and a Pt wire as the counter electrode; scan rate, 50 mV s^{-1}.

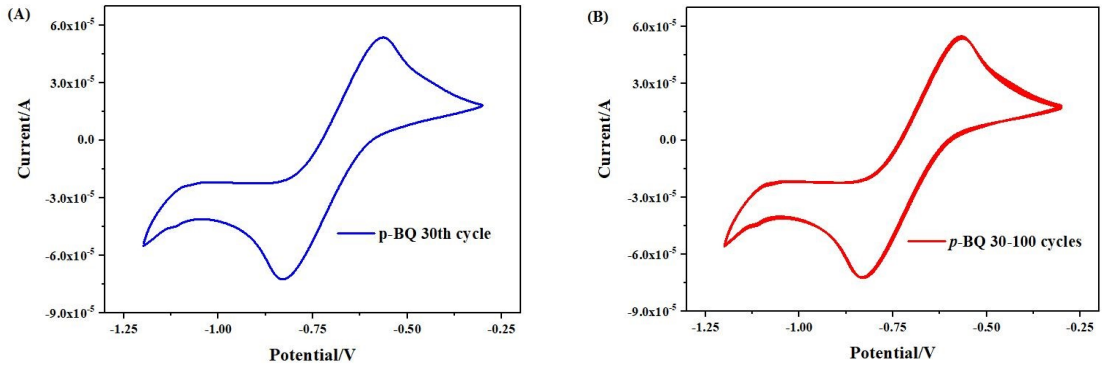


Figure S15 (A) The 30th cycle and (B) the 30-100 cycles of cyclic voltammograms of *p*-benzoquinone(*p*-BQ).

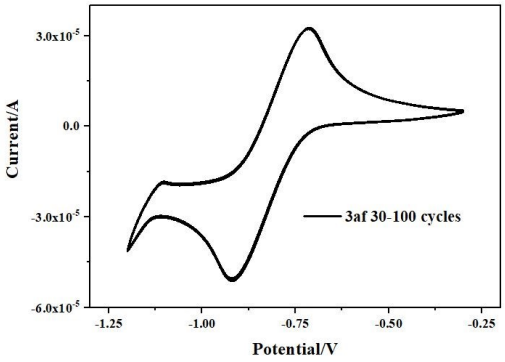


Figure S16 The 30-100 cycles of cyclic voltammograms of **3af**.

2.11 Cell Culture

4T1 cell line was purchased from Chinese Academy of Science Cell Bank for Type Culture Collection, and grown in 1640 culture medium containing 10% FBS and 1% antibiotics (penicillin-streptomycin) at 37 °C in a humidified environment of 5% CO_2.

2.12 In Vitro Cytotoxicity

4T1 cells were seeded in 96-well plates at a density of 5×10^3 cells/well and incubated for 24 h. Then the cells were incubated with different concentrations of 3af in fresh medium. The cells were exposed to 660 nm laser irradiation (500 mW/cm^2) for 10 min after 12 h incubation. At the same time, the 3af incubated cells without laser irradiation were also conducted for the dark cytotoxicity study. After further incubation for 24 h, the medium was removed and washed with PBS for three times. Cells were then incubated with fresh serum-free medium containing 10% MTT for 4 h in the dark. Then, all the media were removed and 150 μL dimethyl sulfoxide (DMSO) was added. Finally, the absorbance of the products was measured at a wavelength of 570 nm by a microplate reader. The results were expressed as the viable percentage of cells after different treatments relative to the control cells without any treatment. The following steps of MTT test were the same as the above procedures.

2.13 Live/Dead Cell Staining

First, 4T1 cells were seeded and cultured in glass bottom dish for 24 h, then exposed to different following treatments: 1) Blank; 2) irradiated 660 nm laser irradiation (500 mW/cm^2) for 10 min; 3) incubated with **3af** for 24 h; 4) incubated with **3af** for 24 h and irradiated with 660 nm laser irradiation (500 mW/cm^2) for 10 min. After different treatments, the cells were incubated at 37 °C for another 24 h, then successively stained with PI and FDA in PBS for 10 min. Subsequently, the cells were gently washed and

then imaged by CLSM. Conditions: excitation wavelength: 488 nm for FDA and 543 nm for PI; emission filter: 500-550 nm for FDA and 550–650 nm for PI.

2.14 Intracellular ROS Generation

4T1 cells were primarily seeded and cultured in glass bottom dish for 24 h. The original culture medium was then replaced with 1 mL of fresh one with or without **3af**, followed by incubation of 12 h. Then the cells were washed with PBS for three times, and incubated with 1 mL fresh FBS-free medium containing 10 mM DCFH-DA for another 20 min. The **3af** loaded cells were subsequently irradiated using a 660 nm laser (500 mW/cm^2) for 10 min. After further incubation at 37 °C, the cells were imaged by CLSM with the excitation at 488 nm and emission was collected from 500-550 nm.

3. X-Ray Crystallographic Data

3.1 X-Ray Crystallographic Data of 3aa

Single crystals of $C_{25}H_{17}NO_4$ **3aa** were grown from ethyl acetate and PE. The ellipsoids are shown at 50% probability levels. A suitable crystal was selected and collected at 170.00 (10) K on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2277737 for compound **3aa**.

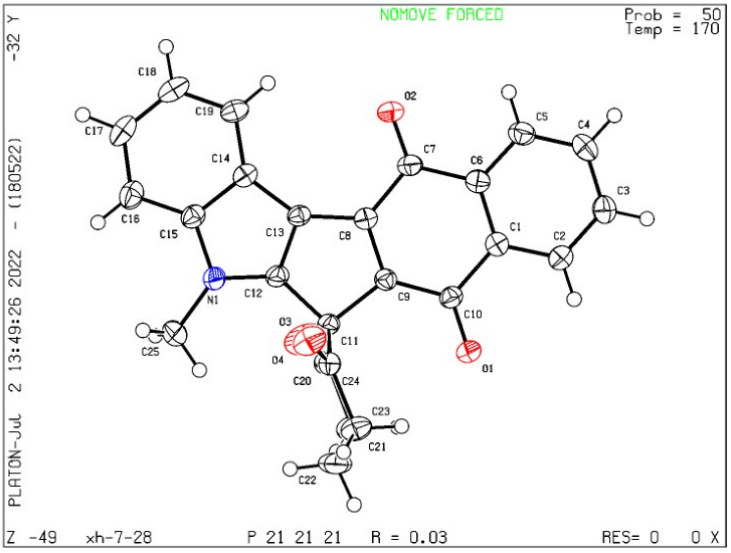


Figure S17 ORTEP Drawing of **3aa** (The ellipsoids are shown at 50% probability levels)

Table S8 Crystal data and structure refinement for 3aa.

Identification code	3aa
Empirical formula	$C_{25}H_{17}NO_4$
Formula weight	395.39
Temperature/K	170.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.62350(10)
b/Å	11.7760(2)
c/Å	16.9508(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1920.97(5)
Z	4
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.760
F(000)	824.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.144 to 143.204
Index ranges	-11 ≤ h ≤ 8, -14 ≤ k ≤ 9, -20 ≤ l ≤ 18
Reflections collected	6335
Independent reflections	3418 [R_{int} = 0.0115, R_{sigma} = 0.0143]
Data/restraints/parameters	3418/0/272
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0828
Final R indexes [all data]	R_1 = 0.0324, wR_2 = 0.0837
Largest diff. peak/hole / e Å^{-3}	0.12/-0.21
Flack parameter	-0.04(12)

Crystal structure determination of 3aa

Crystal Data for $C_{25}H_{17}NO_4$ (M =395.39 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.62350(10) Å, b = 11.7760(2) Å, c = 16.9508(3) Å, V = 1920.97(5) Å^3, Z = 4, T = 170.00(10) K, μ(Cu Kα) = 0.760 mm^{-1}, *Dcalc* = 1.367 g/cm^3, 6335 reflections measured (9.144° ≤ 2Θ ≤ 143.204°), 3418 unique (R_{int} = 0.0115, R_{sigma} = 0.0143) which were used in all calculations. The final R_1 was 0.0314 (I > 2σ(I)) and wR_2 was 0.0837 (all data).

Table S9 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5363.4(15)	2781.3(11)	6373.6(9)	36.7(3)
O2	7740.7(15)	6717.6(12)	7264.3(10)	40.8(4)
O3	2181.2(15)	5078.6(13)	6958.5(9)	40.3(4)
O4	4701(2)	5135.8(16)	4632.5(9)	58.2(5)
N1	3143.7(17)	7123.0(13)	5696.5(9)	27.6(3)
C1	7196.4(18)	3682.0(16)	7069.0(10)	24.5(4)
C2	7792(2)	2652.2(16)	7286.8(11)	27.9(4)
C3	9016(2)	2634.6(17)	7722.9(11)	31.7(4)
C4	9642.3(19)	3641.4(18)	7952.8(12)	33.5(4)
C5	9051(2)	4669.2(17)	7749.9(11)	31.0(4)
C6	7834.9(19)	4698.7(16)	7308.7(10)	25.6(4)
C7	7211.2(19)	5812.7(16)	7097.1(11)	26.7(4)
C8	5880.4(18)	5776.5(15)	6657.8(10)	22.1(3)
C9	5282.2(17)	4776.0(15)	6424.8(10)	22.8(3)
C10	5879.8(19)	3673.0(15)	6598.4(10)	24.6(4)
C11	3924.7(18)	5017.4(14)	5963.0(10)	23.5(4)
C12	3950.3(19)	6293.8(15)	5992.5(10)	24.6(4)
C13	5068.0(18)	6723.1(15)	6397.9(10)	23.0(3)
C14	4973.7(19)	7938.6(15)	6357.2(10)	24.2(4)
C15	3763(2)	8157.0(15)	5907.5(10)	26.7(4)
C16	3327(2)	9252.4(17)	5719.2(11)	33.3(4)
C17	4139(2)	10137.0(16)	5994.2(12)	36.2(5)
C18	5331(2)	9942.6(16)	6441.2(12)	34.0(4)
C19	5759(2)	8854.4(15)	6628.3(11)	28.1(4)
C20	4080(2)	4569.2(16)	5104.8(11)	29.9(4)
C21	3449(2)	3443.7(18)	4905.9(12)	38.5(5)
C22	2040(2)	3263(2)	5293.2(13)	43.0(5)
C23	2116(2)	3389.3(17)	6182.4(13)	36.9(5)
C24	2664.7(19)	4530.1(15)	6423.6(11)	25.7(4)
C25	1906(3)	7008.8(18)	5216.9(14)	44.8(6)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	41.5(8)	22.1(6)	46.5(8)	-3.5(6)	-16.1(7)	-1.2(6)
O2	33.9(7)	25.5(6)	63.1(10)	-5.2(7)	-15.2(7)	-5.6(6)
O3	42.2(8)	37.1(8)	41.7(8)	-7.3(7)	13.2(7)	-4.0(7)

Table S10 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	85.4(13)	58.9(11)	30.4(7)	-3.6(7)	15.7(8)	-28.4(11)
N1	33.4(8)	22.8(7)	26.5(7)	2.1(6)	-7.0(6)	-0.7(6)
C1	24.3(8)	26.7(8)	22.6(8)	-0.2(7)	2.3(7)	0.5(7)
C2	30.5(9)	25.6(8)	27.8(9)	-0.5(7)	1.8(8)	-0.1(8)
C3	28.7(9)	32.7(9)	33.6(10)	2.0(8)	1.4(8)	5.6(8)
C4	24.2(9)	41.9(10)	34.4(10)	0.2(9)	-4.1(8)	3.1(8)
C5	25.7(9)	32.7(9)	34.5(9)	-2.4(8)	-1.9(8)	-4.0(8)
C6	24.0(8)	27.7(9)	25.0(8)	-0.6(7)	1.9(7)	-1.6(7)
C7	25.5(8)	25.1(8)	29.5(9)	-2.8(7)	-0.3(8)	-4.0(8)
C8	23.9(8)	23.2(8)	19.3(7)	0.2(6)	2.7(7)	-2.3(7)
C9	24.1(8)	23.5(8)	20.8(7)	0.4(7)	-1.6(7)	-1.1(7)
C10	28.2(8)	21.8(8)	23.8(8)	-1.5(7)	-0.6(7)	-1.2(7)
C11	26.9(8)	21.4(8)	22.1(8)	0.7(6)	-3.9(7)	-2.1(7)
C12	29.9(8)	21.7(8)	22.2(8)	2.3(6)	-2.6(7)	-3.9(7)
C13	26.2(8)	22.2(8)	20.6(7)	0.0(7)	0.6(7)	-3.4(7)
C14	29.6(8)	22.8(8)	20.3(8)	-0.1(6)	4.4(7)	-2.2(7)
C15	33.9(9)	23.3(9)	22.9(8)	0.7(7)	0.7(7)	-1.8(7)
C16	41.7(11)	26.8(9)	31.5(9)	4.4(8)	-0.3(9)	2.9(9)
C17	49.9(12)	20.3(9)	38.5(10)	2.3(8)	8.8(9)	2.0(9)
C18	43.7(11)	22.6(9)	35.6(9)	-4.9(8)	10.5(9)	-8.1(8)
C19	32.4(9)	26.5(9)	25.5(8)	-4.2(7)	5.7(7)	-5.8(8)
C20	34.6(10)	31.6(9)	23.5(8)	-0.5(7)	-2.1(8)	-3.2(8)
C21	51.3(12)	37.0(11)	27.3(9)	-9.5(8)	-3.4(9)	-7.0(10)
C22	42.5(11)	41.0(11)	45.4(12)	-8.1(10)	-11.3(9)	-13.9(10)
C23	36.4(10)	31.7(10)	42.7(11)	-1.5(8)	4.2(9)	-10.9(9)
C24	26.7(8)	23.6(8)	26.8(8)	2.6(7)	-3.2(7)	0.1(7)
C25	51.7(13)	33.1(11)	49.6(12)	-1.9(9)	-28.5(11)	3.1(10)

Table S11 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.223(2)	C9	C10	1.451(2)
O2	C7	1.215(2)	C9	C11	1.549(2)
O3	C24	1.207(2)	C11	C12	1.504(2)
O4	C20	1.201(3)	C11	C20	1.555(2)
N1	C12	1.345(2)	C11	C24	1.552(2)

Table S11 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C15	1.402(2)	C12	C13	1.373(2)
N1	C25	1.448(3)	C13	C14	1.436(2)
C1	C2	1.391(3)	C14	C15	1.416(3)
C1	C6	1.406(3)	C14	C19	1.395(2)
C1	C10	1.497(2)	C15	C16	1.393(3)
C2	C3	1.391(3)	C16	C17	1.383(3)
C3	C4	1.386(3)	C17	C18	1.394(3)
C4	C5	1.381(3)	C18	C19	1.383(3)
C5	C6	1.389(3)	C20	C21	1.497(3)
C6	C7	1.486(3)	C21	C22	1.521(3)
C7	C8	1.482(2)	C22	C23	1.517(3)
C8	C9	1.369(2)	C23	C24	1.500(2)
C8	C13	1.431(2)			

Table S12 Bond Angles for 3aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C15	106.87(15)	C12	C11	C20	111.64(14)
C12	N1	C25	128.08(16)	C12	C11	C24	111.44(15)
C15	N1	C25	124.99(16)	C24	C11	C20	114.86(14)
C2	C1	C6	119.05(16)	N1	C12	C11	134.74(17)
C2	C1	C10	118.94(16)	N1	C12	C13	111.82(16)
C6	C1	C10	122.00(16)	C13	C12	C11	113.42(16)
C3	C2	C1	120.20(17)	C8	C13	C14	145.68(17)
C4	C3	C2	120.34(18)	C12	C13	C8	107.17(15)
C5	C4	C3	120.02(17)	C12	C13	C14	107.07(16)
C4	C5	C6	120.21(18)	C15	C14	C13	105.01(15)
C1	C6	C7	120.35(15)	C19	C14	C13	136.11(18)
C5	C6	C1	120.17(17)	C19	C14	C15	118.87(17)
C5	C6	C7	119.48(16)	N1	C15	C14	109.23(15)
O2	C7	C6	123.26(16)	C16	C15	N1	128.16(17)
O2	C7	C8	120.33(17)	C16	C15	C14	122.61(17)
C8	C7	C6	116.41(15)	C17	C16	C15	116.77(19)
C9	C8	C7	122.20(16)	C16	C17	C18	121.63(18)
C9	C8	C13	110.59(15)	C19	C18	C17	121.45(18)
C13	C8	C7	127.18(16)	C18	C19	C14	118.68(18)
C8	C9	C10	123.03(15)	O4	C20	C11	118.88(17)
C8	C9	C11	110.02(14)	O4	C20	C21	122.94(18)

Table S12 Bond Angles for 3aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C9	C11	126.95(15)	C21	C20	C11	118.18(16)
O1	C10	C1	121.07(16)	C20	C21	C22	112.90(18)
O1	C10	C9	122.99(16)	C23	C22	C21	111.83(18)
C9	C10	C1	115.93(15)	C24	C23	C22	112.09(17)
C9	C11	C20	109.22(14)	O3	C24	C11	118.77(16)
C9	C11	C24	109.68(13)	O3	C24	C23	123.27(18)
C12	C11	C9	98.79(13)	C23	C24	C11	117.96(16)

Table S13 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C7	C8	C9	176.82(18)	C10	C9	C11	C12	-179.03(16)
O2	C7	C8	C13	-1.2(3)	C10	C9	C11	C20	-62.3(2)
O4	C20	C21	C22	-140.5(2)	C10	C9	C11	C24	64.3(2)
N1	C12	C13	C8	-177.70(14)	C11	C9	C10	O1	1.6(3)
N1	C12	C13	C14	-0.2(2)	C11	C9	C10	C1	-179.05(15)
N1	C15	C16	C17	-179.23(18)	C11	C12	C13	C8	0.9(2)
C1	C2	C3	C4	0.8(3)	C11	C12	C13	C14	178.42(15)
C1	C6	C7	O2	-177.40(19)	C11	C20	C21	C22	39.6(3)
C1	C6	C7	C8	2.4(2)	C12	N1	C15	C14	-0.94(19)
C2	C1	C6	C5	0.6(3)	C12	N1	C15	C16	178.33(19)
C2	C1	C6	C7	-178.96(17)	C12	C11	C20	O4	27.9(3)
C2	C1	C10	O1	-3.5(3)	C12	C11	C20	C21	-152.22(17)
C2	C1	C10	C9	177.15(16)	C12	C11	C24	O3	-26.6(2)
C2	C3	C4	C5	0.1(3)	C12	C11	C24	C23	153.90(16)
C3	C4	C5	C6	-0.6(3)	C12	C13	C14	C15	-0.42(19)
C4	C5	C6	C1	0.3(3)	C12	C13	C14	C19	-179.10(19)
C4	C5	C6	C7	179.87(17)	C13	C8	C9	C10	179.48(16)
C5	C6	C7	O2	3.0(3)	C13	C8	C9	C11	-0.31(19)
C5	C6	C7	C8	-177.25(15)	C13	C14	C15	N1	0.83(19)
C6	C1	C2	C3	-1.2(3)	C13	C14	C15	C16	-178.49(18)
C6	C1	C10	O1	177.63(17)	C13	C14	C19	C18	178.0(2)
C6	C1	C10	C9	-1.7(2)	C14	C15	C16	C17	0.0(3)
C6	C7	C8	C9	-2.9(2)	C15	N1	C12	C11	-177.48(19)
C6	C7	C8	C13	179.03(16)	C15	N1	C12	C13	0.7(2)
C7	C8	C9	C10	1.2(3)	C15	C14	C19	C18	-0.6(2)
C7	C8	C9	C11	-178.63(15)	C15	C16	C17	C18	-0.3(3)
C7	C8	C13	C12	177.88(16)	C16	C17	C18	C19	0.2(3)

Table S13 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	C8	C13	C14	2.1(4)	C17	C18	C19	C14	0.3(3)
C8	C9	C10	O1	-178.15(18)	C19	C14	C15	N1	179.79(15)
C8	C9	C10	C1	1.2(2)	C19	C14	C15	C16	0.5(3)
C8	C9	C11	C12	0.75(17)	C20	C11	C12	N1	62.3(3)
C8	C9	C11	C20	117.44(16)	C20	C11	C12	C13	-115.81(17)
C8	C9	C11	C24	-115.87(15)	C20	C11	C24	O3	-154.81(17)
C8	C13	C14	C15	175.4(2)	C20	C11	C24	C23	25.7(2)
C8	C13	C14	C19	-3.3(4)	C20	C21	C22	C23	-56.2(3)
C9	C8	C13	C12	-0.33(19)	C21	C22	C23	C24	57.6(3)
C9	C8	C13	C14	-176.2(2)	C22	C23	C24	O3	137.9(2)
C9	C11	C12	N1	177.15(19)	C22	C23	C24	C11	-42.6(2)
C9	C11	C12	C13	-0.99(19)	C24	C11	C12	N1	-67.6(3)
C9	C11	C20	O4	-80.3(2)	C24	C11	C12	C13	114.27(17)
C9	C11	C20	C21	99.6(2)	C24	C11	C20	O4	156.03(19)
C9	C11	C24	O3	81.8(2)	C24	C11	C20	C21	-24.1(2)
C9	C11	C24	C23	-97.75(18)	C25	N1	C12	C11	-0.3(3)
C10	C1	C2	C3	179.91(16)	C25	N1	C12	C13	177.88(19)
C10	C1	C6	C5	179.52(16)	C25	N1	C15	C14	-178.25(18)
C10	C1	C6	C7	-0.1(3)	C25	N1	C15	C16	1.0(3)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H2	7370.51	1973.58	7140.23	34
H3	9415.56	1943.68	7861.12	38
H4	10461.36	3624.77	8243.81	40
H5	9468.03	5343.76	7909.15	37
H16	2529.78	9382.29	5422.96	40
H17	3882.52	10879.88	5878.16	43
H18	5850.82	10558.41	6617.42	41
H19	6554.15	8735.57	6928.89	34
H21A	4074.76	2844.76	5073.06	46
H21B	3343.37	3388.06	4338.11	46
H22A	1382.91	3809.98	5083.92	52
H22B	1702.22	2508.78	5164.58	52
H23A	1195.81	3285.25	6404.34	44
H23B	2714.22	2801.49	6395.55	44

Table S14 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H25A	2106.93	7242.78	4686.52	67
H25B	1181.01	7477.47	5429.76	67
H25C	1609.67	6230.35	5216.55	67

3.2 X-Ray Crystallographic Data of 3af

Single crystals of $C_{55}H_{44}Cl_2N_2O_8$ **3af** were grown from ethyl acetate and PE. The ellipsoids are shown at 50% probability levels. A suitable crystal was selected and collected at 295.25 (10) K on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2277739 for compound **3af**.

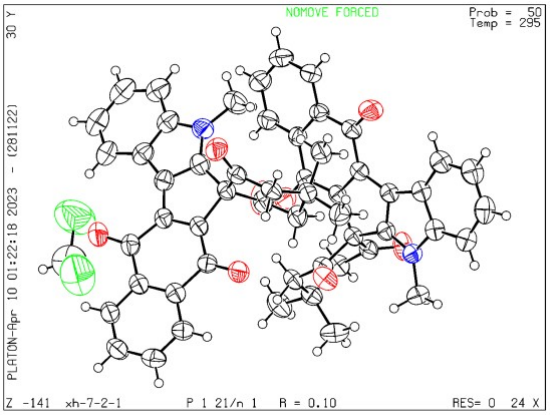


Figure S18 ORTEP Drawing of **3af** (The ellipsoids are shown at 50% probability levels)

Table S15 Crystal data and structure refinement for 3af.

Identification code	**3af**
Empirical formula	$C_{55}H_{44}Cl_2N_2O_8$
Formula weight	931.82
Temperature/K	295.25(10)
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	12.9040(3)
b/Å	19.5240(5)
c/Å	18.0622(6)
α/°	90
β/°	98.725(3)
γ/°	90
Volume/Å^3	4497.9(2)
Z	4
ρ_{calc}g/cm^3	1.376
μ/mm^{-1}	1.799
F(000)	1944.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.708 to 133.2
Index ranges	-14 ≤ h ≤ 15, -16 ≤ k ≤ 23, -21 ≤ l ≤ 21
Reflections collected	31882
Independent reflections	7932 [R_{int} = 0.0640, R_{sigma} = 0.0434]
Data/restraints/parameters	7932/0/611
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0990, wR_2 = 0.2847
Final R indexes [all data]	R_1 = 0.1180, wR_2 = 0.2981
Largest diff. peak/hole / e Å^{-3}	1.50/-1.14

Crystal structure determination of 3af

Crystal Data for $C_{55}H_{44}Cl_2N_2O_8$ (*M* =931.82 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 12.9040(3) Å, *b* = 19.5240(5) Å, *c* = 18.0622(6) Å, *β* = 98.725(3)°, *V* = 4497.9(2) Å^3, *Z* = 4, *T* = 295.25(10) K, μ(Cu Kα) = 1.799 mm^{-1}, *Dcalc* = 1.376 g/cm^3, 31882 reflections measured (6.708° ≤ 2Θ ≤ 133.2°), 7932 unique (R_{int} = 0.0640, R_{sigma} = 0.0434) which were used in all calculations. The final R_1 was 0.0990 (I > 2σ(I)) and wR_2 was 0.2981 (all data).

Table S16 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3af. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6027(3)	5871.5(18)	6024.1(16)	166.1(13)
Cl2	5773(4)	5681(2)	4441(2)	198.4(18)
C1S	5546(8)	6134(6)	5149(5)	132(3)

Table S16 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3af. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2237(3)	2483.2(17)	7094.3(19)	59.3(9)
O2	-329(3)	1739.8(18)	5424(2)	68.4(10)
O3	2331(3)	2761.5(16)	4648.1(19)	58.6(9)
O4	3508(3)	148.0(17)	5250(2)	63.4(9)
N1	988(3)	1107.4(18)	6955(2)	45.0(8)
C1	1931(3)	221(2)	6559(2)	44.7(10)
C2	2286(4)	-461(2)	6565(3)	55.7(11)
C3	1994(4)	-905(3)	7081(3)	63.7(13)
C4	1367(4)	-693(3)	7601(3)	64.8(14)
C5	1006(4)	-27(2)	7620(3)	53.7(11)
C6	1283(3)	422(2)	7083(2)	46.6(10)
C7	1434(3)	1323(2)	6369(2)	43.1(9)
C8	2026(3)	816(2)	6112(2)	41.8(9)
C9	2497(3)	1095(2)	5509(2)	40.8(9)
C10	2204(3)	1767(2)	5378(2)	39.3(9)
C11	1455(3)	1980(2)	5937(2)	41.4(9)
C12	1878(3)	2589(2)	6448(2)	43.5(9)
C13	1760(3)	3290(2)	6113(3)	48.4(10)
C14	618(3)	3446(2)	5772(3)	48.2(10)
C15	198(3)	2888(2)	5203(3)	48.2(10)
C16	351(3)	2167(2)	5502(2)	43.5(9)
C17	2569(3)	2161(2)	4791(2)	43.2(9)
C18	3290(3)	1800(2)	4340(2)	44.1(9)
C19	3231(3)	735(2)	5093(2)	44.9(10)
C20	3614(3)	1122(2)	4477(2)	44.3(9)
C21	4283(4)	810(2)	4049(3)	54.8(11)
C22	4614(5)	1170(3)	3471(3)	67.7(14)
C23	4299(5)	1834(3)	3333(3)	71.5(15)
C24	3635(4)	2151(3)	3754(3)	57.9(12)
C25	-61(5)	3470(3)	6401(3)	70.9(15)
C26	590(5)	4136(3)	5377(3)	71.5(15)
C27	302(4)	1496(3)	7368(3)	55.3(11)
O54	4429(3)	2425(2)	6124(2)	84.0(13)
O55	7702(2)	1820.0(18)	7181(2)	63.8(9)
O66	7517(3)	4685.6(19)	6824(2)	75.7(11)
O67	5562(3)	2898.7(17)	8405(2)	63.2(9)

Table S16 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3af. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N64	6623(3)	2366(2)	5493(2)	55.5(10)
C36	6123(3)	2454(2)	6856(2)	44.4(9)
C37	6251(3)	3150(2)	7292(2)	44.2(9)
C38	5958(3)	3313(2)	8016(2)	44.9(10)
C39	6132(3)	4040(2)	8277(3)	46.5(10)
C40	5777(4)	4248(2)	8927(3)	51.7(11)
C41	5925(4)	4916(3)	9175(3)	60.0(12)
C42	6426(4)	5382(3)	8773(3)	61.0(13)
C43	6776(4)	5185(2)	8136(3)	55.0(11)
C44	6634(3)	4511(2)	7873(3)	47.2(10)
C45	6988(4)	4315(2)	7162(3)	51.0(11)
C46	6686(3)	3624(2)	6877(2)	44.6(9)
C47	6843(3)	3339(2)	6167(3)	49.9(10)
C48	6532(4)	2666(2)	6158(3)	51.2(11)
C49	4943(3)	2238(2)	6701(3)	52.3(11)
C50	4528(3)	1812(2)	7268(3)	53.5(11)
C51	5251(3)	1212(2)	7573(3)	49.7(10)
C52	6346(3)	1495(2)	7869(3)	47.5(10)
C53	6816(3)	1902(2)	7311(2)	45.4(10)
C56	4806(5)	865(3)	8217(3)	68.2(14)
C57	5317(4)	688(3)	6959(3)	62.1(13)
C58	6990(4)	2865(3)	5042(3)	55.8(12)
C59	7168(4)	2805(3)	4313(3)	68.5(14)
C60	7462(4)	3394(4)	3970(3)	76.7(17)
C61	7606(4)	4011(4)	4347(3)	73.5(16)
C62	7450(4)	4068(3)	5081(3)	62.3(13)
C63	7127(3)	3488(3)	5445(3)	54.4(11)
C65	6391(5)	1661(3)	5273(3)	77.1(16)

Table S17 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	211(3)	167(3)	111.2(19)	10.3(17)	-5(2)	-39(2)
Cl2	310(5)	165(3)	130(2)	-33(2)	66(3)	-20(3)

Table S17 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1S	116(7)	151(8)	123(7)	-3(6)	-6(6)	11(6)
O1	64(2)	55.0(19)	52(2)	-2.1(14)	-13.1(16)	6.5(15)
O2	50.8(19)	62(2)	86(3)	10.1(18)	-8.7(17)	-13.0(16)
O3	66(2)	44.7(18)	67(2)	13.5(15)	18.0(17)	9.6(15)
O4	71(2)	49.1(19)	73(2)	9.5(16)	20.8(18)	20.6(16)
N1	45.8(19)	43.8(19)	45(2)	3.3(15)	7.1(15)	3.3(15)
C1	43(2)	42(2)	46(2)	5.1(17)	-1.7(18)	2.8(17)
C2	56(3)	49(3)	60(3)	7(2)	0(2)	9(2)
C3	68(3)	49(3)	71(3)	17(2)	-3(3)	8(2)
C4	62(3)	61(3)	67(3)	25(3)	-4(3)	-5(2)
C5	49(2)	58(3)	52(3)	12(2)	2(2)	1(2)
C6	42(2)	47(2)	48(2)	6.0(18)	-2.5(18)	1.0(18)
C7	43(2)	39(2)	46(2)	1.4(17)	2.3(18)	1.1(17)
C8	40(2)	38(2)	46(2)	1.9(17)	-0.3(17)	2.8(16)
C9	40(2)	39(2)	41(2)	-1.5(16)	-1.0(16)	1.6(16)
C10	39(2)	37(2)	40(2)	-2.0(16)	0.3(16)	-1.3(15)
C11	40(2)	37(2)	45(2)	0.8(16)	-0.5(17)	4.0(16)
C12	37(2)	44(2)	47(2)	-5.1(18)	-0.8(18)	5.6(17)
C13	51(2)	39(2)	53(3)	-7.6(18)	-1(2)	-3.9(18)
C14	51(2)	41(2)	51(3)	-0.9(18)	0.6(19)	8.3(18)
C15	39(2)	47(2)	55(3)	0.2(19)	-5.9(18)	4.5(17)
C16	38(2)	45(2)	45(2)	-4.8(17)	-1.2(17)	-1.2(17)
C17	42(2)	39(2)	46(2)	0.6(17)	-1.1(17)	-0.5(16)
C18	44(2)	45(2)	42(2)	-2.6(17)	3.7(18)	-4.1(17)
C19	43(2)	40(2)	49(2)	-3.0(18)	-2.2(18)	5.3(17)
C20	42(2)	48(2)	42(2)	-6.8(18)	3.4(17)	0.2(17)
C21	59(3)	51(3)	56(3)	-11(2)	13(2)	1(2)
C22	80(4)	68(3)	61(3)	-11(3)	31(3)	5(3)
C23	96(4)	66(3)	61(3)	-2(3)	38(3)	-8(3)
C24	72(3)	51(3)	53(3)	-3(2)	16(2)	-2(2)
C25	71(3)	80(4)	63(3)	-5(3)	14(3)	26(3)
C26	83(4)	49(3)	77(4)	5(2)	-6(3)	8(3)
C27	52(2)	61(3)	56(3)	-2(2)	16(2)	6(2)
O54	56(2)	107(3)	79(3)	31(2)	-23(2)	-17(2)
O55	43.0(18)	63(2)	87(3)	4.4(18)	12.7(16)	7.6(15)
O66	92(3)	60(2)	81(3)	-5.5(18)	31(2)	-23(2)

Table S17 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3af. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O67	87(2)	46.7(18)	61(2)	4.6(15)	27.9(18)	-3.8(16)
N64	57(2)	61(2)	48(2)	-9.3(18)	6.1(18)	-4.3(18)
C36	42(2)	41(2)	48(2)	-2.7(17)	1.6(18)	-1.4(17)
C37	38(2)	39(2)	53(2)	-0.9(18)	-0.2(18)	1.0(16)
C38	42(2)	43(2)	49(2)	1.8(18)	6.3(18)	5.2(17)
C39	41(2)	43(2)	53(3)	2.3(18)	-0.9(18)	5.8(17)
C40	52(2)	52(3)	51(3)	0(2)	7(2)	8(2)
C41	58(3)	61(3)	60(3)	-11(2)	6(2)	13(2)
C42	58(3)	47(3)	76(3)	-13(2)	4(2)	1(2)
C43	51(2)	43(2)	71(3)	-2(2)	8(2)	-4.2(19)
C44	39(2)	41(2)	59(3)	-0.3(19)	-0.6(19)	3.4(17)
C45	49(2)	46(2)	58(3)	6(2)	7(2)	-2.9(19)
C46	34.9(19)	46(2)	50(2)	0.5(18)	-0.8(17)	-0.8(17)
C47	44(2)	54(3)	51(3)	1(2)	4.3(19)	-3.2(19)
C48	49(2)	53(3)	50(3)	-3(2)	0(2)	-4(2)
C49	41(2)	50(2)	62(3)	0(2)	-5(2)	-0.3(19)
C50	38(2)	52(3)	69(3)	0(2)	1(2)	-0.3(18)
C51	48(2)	42(2)	59(3)	-1.1(19)	6(2)	-3.2(18)
C52	47(2)	41(2)	50(2)	-3.9(18)	-3.3(19)	8.0(18)
C53	40(2)	42(2)	51(2)	-6.8(18)	-1.9(18)	2.8(17)
C56	68(3)	63(3)	76(4)	9(3)	19(3)	-1(2)
C57	60(3)	54(3)	71(3)	-8(2)	8(2)	-7(2)
C58	43(2)	76(3)	47(3)	-1(2)	2.8(19)	-3(2)
C59	52(3)	96(4)	56(3)	-9(3)	4(2)	-4(3)
C60	53(3)	123(5)	54(3)	4(3)	9(2)	-6(3)
C61	56(3)	100(4)	64(3)	19(3)	10(3)	-7(3)
C62	48(3)	75(3)	64(3)	10(3)	10(2)	-5(2)
C63	41(2)	71(3)	50(3)	1(2)	2.8(19)	-2(2)
C65	97(4)	72(4)	62(3)	-22(3)	12(3)	-16(3)

Table S18 Bond Lengths for 3af.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1S	1.688(10)	C23	C24	1.376(7)
Cl2	C1S	1.618(10)	O54	C49	1.203(6)
O1	C12	1.207(5)	O55	C53	1.211(5)

Table S18 Bond Lengths for 3af.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C16	1.204(5)	O66	C45	1.220(6)
O3	C17	1.230(5)	O67	C38	1.232(5)
O4	C19	1.222(5)	N64	C48	1.356(6)
N1	C6	1.401(5)	N64	C58	1.399(6)
N1	C7	1.346(6)	N64	C65	1.452(7)
N1	C27	1.455(6)	C36	C37	1.568(6)
C1	C2	1.408(6)	C36	C48	1.498(7)
C1	C6	1.411(6)	C36	C49	1.563(6)
C1	C8	1.431(6)	C36	C53	1.554(6)
C2	C3	1.368(7)	C37	C38	1.449(6)
C3	C4	1.392(8)	C37	C46	1.364(6)
C4	C5	1.385(7)	C38	C39	1.502(6)
C5	C6	1.393(6)	C39	C40	1.385(6)
C7	C8	1.374(6)	C39	C44	1.393(6)
C7	C11	1.504(6)	C40	C41	1.383(7)
C8	C9	1.432(6)	C41	C42	1.384(8)
C9	C10	1.377(6)	C42	C43	1.354(7)
C9	C19	1.473(6)	C43	C44	1.402(6)
C10	C11	1.556(6)	C44	C45	1.476(7)
C10	C17	1.446(6)	C45	C46	1.477(6)
C11	C12	1.552(6)	C46	C47	1.440(6)
C11	C16	1.562(5)	C47	C48	1.373(6)
C12	C13	1.494(6)	C47	C63	1.437(7)
C13	C14	1.540(6)	C49	C50	1.482(7)
C14	C15	1.538(6)	C50	C51	1.546(6)
C14	C25	1.537(7)	C51	C52	1.535(6)
C14	C26	1.523(7)	C51	C56	1.532(7)
C15	C16	1.510(6)	C51	C57	1.522(7)
C17	C18	1.503(6)	C52	C53	1.483(6)
C18	C20	1.398(6)	C58	C59	1.376(7)
C18	C24	1.390(6)	C58	C63	1.414(7)
C19	C20	1.490(6)	C59	C60	1.386(9)
C20	C21	1.385(6)	C60	C61	1.381(9)
C21	C22	1.380(7)	C61	C62	1.376(8)
C22	C23	1.370(8)	C62	C63	1.405(7)

Table S19 Bond Angles for 3af.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl2	C1S	Cl1	119.3(7)	C48	N64	C58	107.2(4)
C6	N1	C27	125.7(4)	C48	N64	C65	127.6(4)
C7	N1	C6	106.9(3)	C58	N64	C65	125.1(4)
C7	N1	C27	127.3(4)	C48	C36	C37	99.2(3)
C2	C1	C6	118.9(4)	C48	C36	C49	112.5(4)
C2	C1	C8	135.8(4)	C48	C36	C53	112.9(4)
C6	C1	C8	105.3(4)	C49	C36	C37	110.4(3)
C3	C2	C1	118.8(5)	C53	C36	C37	109.1(3)
C2	C3	C4	121.3(5)	C53	C36	C49	112.0(3)
C5	C4	C3	121.9(5)	C38	C37	C36	128.4(4)
C4	C5	C6	116.8(5)	C46	C37	C36	109.4(4)
N1	C6	C1	109.1(4)	C46	C37	C38	122.2(4)
C5	C6	N1	128.6(4)	O67	C38	C37	123.9(4)
C5	C6	C1	122.3(4)	O67	C38	C39	119.8(4)
N1	C7	C8	111.5(4)	C37	C38	C39	116.3(4)
N1	C7	C11	135.9(4)	C40	C39	C38	119.3(4)
C8	C7	C11	112.6(4)	C40	C39	C44	119.4(4)
C1	C8	C9	145.1(4)	C44	C39	C38	121.2(4)
C7	C8	C1	107.1(4)	C41	C40	C39	120.2(5)
C7	C8	C9	107.8(4)	C40	C41	C42	120.2(5)
C8	C9	C19	125.9(4)	C43	C42	C41	120.1(5)
C10	C9	C8	110.8(4)	C42	C43	C44	120.8(5)
C10	C9	C19	123.2(4)	C39	C44	C43	119.3(4)
C9	C10	C11	109.0(3)	C39	C44	C45	121.0(4)
C9	C10	C17	121.4(4)	C43	C44	C45	119.7(4)
C17	C10	C11	129.6(3)	O66	C45	C44	123.6(4)
C7	C11	C10	99.8(3)	O66	C45	C46	120.3(4)
C7	C11	C12	112.2(3)	C44	C45	C46	116.1(4)
C7	C11	C16	112.0(3)	C37	C46	C45	122.5(4)
C10	C11	C16	110.1(3)	C37	C46	C47	110.7(4)
C12	C11	C10	113.2(3)	C47	C46	C45	126.8(4)
C12	C11	C16	109.4(3)	C48	C47	C46	107.4(4)
O1	C12	C11	119.5(4)	C48	C47	C63	107.3(4)
O1	C12	C13	123.3(4)	C63	C47	C46	145.1(4)
C13	C12	C11	117.1(4)	N64	C48	C36	135.6(4)
C12	C13	C14	112.0(4)	N64	C48	C47	111.1(4)
C15	C14	C13	110.2(3)	C47	C48	C36	113.2(4)
C25	C14	C13	109.2(4)	O54	C49	C36	117.9(4)
C25	C14	C15	109.4(4)	O54	C49	C50	124.0(4)

Table S19 Bond Angles for 3af.

C26	C14	C13	108.4(4)	C50	C49	C36	118.1(4)
C26	C14	C15	109.5(4)	C49	C50	C51	114.2(4)
C26	C14	C25	110.1(4)	C52	C51	C50	109.0(3)
C16	C15	C14	114.0(4)	C56	C51	C50	109.3(4)
O2	C16	C11	119.4(4)	C56	C51	C52	109.0(4)
O2	C16	C15	123.4(4)	C57	C51	C50	110.3(4)
C15	C16	C11	117.3(3)	C57	C51	C52	110.2(4)
O3	C17	C10	124.2(4)	C57	C51	C56	109.0(4)
O3	C17	C18	119.3(4)	C53	C52	C51	113.9(4)
C10	C17	C18	116.5(3)	O55	C53	C36	118.3(4)
C20	C18	C17	122.7(4)	O55	C53	C52	123.8(4)
C24	C18	C17	118.5(4)	C52	C53	C36	117.9(4)
C24	C18	C20	118.7(4)	N64	C58	C63	109.1(4)
O4	C19	C9	121.1(4)	C59	C58	N64	128.2(5)
O4	C19	C20	122.1(4)	C59	C58	C63	122.7(5)
C9	C19	C20	116.8(3)	C58	C59	C60	117.0(6)
C18	C20	C19	119.2(4)	C61	C60	C59	121.9(6)
C21	C20	C18	120.8(4)	C62	C61	C60	121.1(6)
C21	C20	C19	119.9(4)	C61	C62	C63	118.9(6)
C22	C21	C20	119.3(5)	C58	C63	C47	105.3(4)
C23	C22	C21	120.1(5)	C62	C63	C47	136.3(5)
C22	C23	C24	121.3(5)	C62	C63	C58	118.4(5)
C23	C24	C18	119.7(5)				

Table S20 Torsion Angles for 3af.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C12	C13	C14	-122.7(5)	O54	C49	C50	C51	134.8(5)
O3	C17	C18	C20	178.7(4)	O66	C45	C46	C37	168.7(5)
O3	C17	C18	C24	-2.4(6)	O66	C45	C46	C47	-8.1(7)
O4	C19	C20	C18	-178.2(4)	O67	C38	C39	C40	-4.6(6)
O4	C19	C20	C21	1.7(6)	O67	C38	C39	C44	176.1(4)
N1	C7	C8	C1	1.4(5)	N64	C58	C59	C60	175.5(5)
N1	C7	C8	C9	-178.1(3)	N64	C58	C63	C47	1.0(5)
N1	C7	C11	C10	177.8(5)	N64	C58	C63	C62	-177.3(4)
N1	C7	C11	C12	57.7(6)	C36	C37	C38	O67	1.1(7)
N1	C7	C11	C16	-65.7(6)	C36	C37	C38	C39	-177.2(4)
C1	C2	C3	C4	-0.7(8)	C36	C37	C46	C45	-174.8(4)

C1	C8	C9	C10	-179.7(6)	C36	C37	C46	C47	2.4(5)
C1	C8	C9	C19	-1.9(9)	C36	C49	C50	C51	-44.7(6)
C2	C1	C6	N1	-177.4(4)	C37	C36	C48	N64	-175.5(5)
C2	C1	C6	C5	1.9(7)	C37	C36	C48	C47	0.1(5)
C2	C1	C8	C7	176.3(5)	C37	C36	C49	O54	90.8(5)
C2	C1	C8	C9	-4.7(10)	C37	C36	C49	C50	-89.7(5)
C2	C3	C4	C5	0.3(8)	C37	C36	C53	O55	-91.7(5)
C3	C4	C5	C6	1.2(7)	C37	C36	C53	C52	89.4(4)
C4	C5	C6	N1	176.8(4)	C37	C38	C39	C40	173.8(4)
C4	C5	C6	C1	-2.3(7)	C37	C38	C39	C44	-5.5(6)
C6	N1	C7	C8	-1.0(5)	C37	C46	C47	C48	-2.3(5)
C6	N1	C7	C11	179.9(5)	C37	C46	C47	C63	171.4(6)
C6	C1	C2	C3	-0.3(7)	C38	C37	C46	C45	6.2(6)
C6	C1	C8	C7	-1.1(5)	C38	C37	C46	C47	-176.6(4)
C6	C1	C8	C9	178.0(6)	C38	C39	C40	C41	-179.7(4)
C7	N1	C6	C1	0.3(5)	C38	C39	C44	C43	179.7(4)
C7	N1	C6	C5	-178.9(4)	C38	C39	C44	C45	1.7(6)
C7	C8	C9	C10	-0.6(5)	C39	C40	C41	C42	0.3(7)
C7	C8	C9	C19	177.2(4)	C39	C44	C45	O66	-172.8(5)
C7	C11	C12	O1	7.3(6)	C39	C44	C45	C46	5.7(6)
C7	C11	C12	C13	-169.5(4)	C40	C39	C44	C43	0.4(6)
C7	C11	C16	O2	-14.2(6)	C40	C39	C44	C45	-177.6(4)
C7	C11	C16	C15	165.4(4)	C40	C41	C42	C43	-0.2(8)
C8	C1	C2	C3	-177.5(5)	C41	C42	C43	C44	0.2(7)
C8	C1	C6	N1	0.5(5)	C42	C43	C44	C39	-0.3(7)
C8	C1	C6	C5	179.8(4)	C42	C43	C44	C45	177.8(4)
C8	C7	C11	C10	-1.3(4)	C43	C44	C45	O66	9.2(7)
C8	C7	C11	C12	-121.4(4)	C43	C44	C45	C46	-172.3(4)
C8	C7	C11	C16	115.3(4)	C44	C39	C40	C41	-0.4(6)
C8	C9	C10	C11	-0.2(4)	C44	C45	C46	C37	-9.8(6)
C8	C9	C10	C17	-179.4(3)	C44	C45	C46	C47	173.4(4)
C8	C9	C19	O4	-0.9(7)	C45	C46	C47	C48	174.8(4)
C8	C9	C19	C20	179.1(4)	C45	C46	C47	C63	-11.5(9)
C9	C10	C11	C7	0.8(4)	C46	C37	C38	O67	179.9(4)
C9	C10	C11	C12	120.2(4)	C46	C37	C38	C39	1.6(6)
C9	C10	C11	C16	-117.0(4)	C46	C47	C48	N64	178.0(4)
C9	C10	C17	O3	179.8(4)	C46	C47	C48	C36	1.2(5)
C9	C10	C17	C18	-0.6(6)	C46	C47	C63	C58	-175.3(6)
C9	C19	C20	C18	1.8(6)	C46	C47	C63	C62	2.5(11)
C9	C19	C20	C21	-178.3(4)	C48	N64	C58	C59	-177.6(5)

C10	C9	C19	O4	176.6(4)	C48	N64	C58	C63	0.1(5)
C10	C9	C19	C20	-3.3(6)	C48	C36	C37	C38	177.4(4)
C10	C11	C12	O1	-104.7(5)	C48	C36	C37	C46	-1.5(4)
C10	C11	C12	C13	78.6(4)	C48	C36	C49	O54	-19.0(6)
C10	C11	C16	O2	95.9(5)	C48	C36	C49	C50	160.5(4)
C10	C11	C16	C15	-84.5(4)	C48	C36	C53	O55	17.5(6)
C10	C17	C18	C20	-0.9(6)	C48	C36	C53	C52	-161.3(4)
C10	C17	C18	C24	178.0(4)	C48	C47	C63	C58	-1.6(5)
C11	C7	C8	C1	-179.3(3)	C48	C47	C63	C62	176.2(5)
C11	C7	C8	C9	1.2(5)	C49	C36	C37	C38	59.1(5)
C11	C10	C17	O3	0.9(7)	C49	C36	C37	C46	-119.8(4)
C11	C10	C17	C18	-179.5(4)	C49	C36	C48	N64	-58.8(7)
C11	C12	C13	C14	53.9(5)	C49	C36	C48	C47	116.9(4)
C12	C11	C16	O2	-139.2(4)	C49	C36	C53	O55	145.7(4)
C12	C11	C16	C15	40.4(5)	C49	C36	C53	C52	-33.2(5)
C12	C13	C14	C15	-54.6(5)	C49	C50	C51	C52	54.2(5)
C12	C13	C14	C25	65.6(5)	C49	C50	C51	C56	173.3(4)
C12	C13	C14	C26	-174.4(4)	C49	C50	C51	C57	-67.0(5)
C13	C14	C15	C16	51.4(5)	C50	C51	C52	C53	-55.3(5)
C14	C15	C16	O2	133.1(5)	C51	C52	C53	O55	-131.7(5)
C14	C15	C16	C11	-46.5(5)	C51	C52	C53	C36	47.1(5)
C16	C11	C12	O1	132.1(4)	C53	C36	C37	C38	-64.4(5)
C16	C11	C12	C13	-44.6(5)	C53	C36	C37	C46	116.7(4)
C17	C10	C11	C7	179.9(4)	C53	C36	C48	N64	69.1(6)
C17	C10	C11	C12	-60.7(5)	C53	C36	C48	C47	-115.2(4)
C17	C10	C11	C16	62.0(5)	C53	C36	C49	O54	-147.3(5)
C17	C18	C20	C19	0.2(6)	C53	C36	C49	C50	32.1(6)
C17	C18	C20	C21	-179.7(4)	C56	C51	C52	C53	-174.5(4)
C17	C18	C24	C23	179.8(5)	C57	C51	C52	C53	65.9(5)
C18	C20	C21	C22	-1.4(7)	C58	N64	C48	C36	174.6(5)
C19	C9	C10	C11	-178.1(4)	C58	N64	C48	C47	-1.1(5)
C19	C9	C10	C17	2.7(6)	C58	C59	C60	C61	2.1(8)
C19	C20	C21	C22	178.7(4)	C59	C58	C63	C47	178.8(4)
C20	C18	C24	C23	-1.2(7)	C59	C58	C63	C62	0.5(7)
C20	C21	C22	C23	1.3(8)	C59	C60	C61	C62	-0.8(9)
C21	C22	C23	C24	-1.2(9)	C60	C61	C62	C63	-0.7(8)
C22	C23	C24	C18	1.2(9)	C61	C62	C63	C47	-176.8(5)
C24	C18	C20	C19	-178.7(4)	C61	C62	C63	C58	0.8(7)
C24	C18	C20	C21	1.4(6)	C63	C47	C48	N64	1.8(5)
C25	C14	C15	C16	-68.7(5)	C63	C47	C48	C36	-175.0(4)

C26	C14	C15	C16	170.5(4)	C63	C58	C59	C60	-2.0(7)
C27	N1	C6	C1	178.6(4)	C65	N64	C48	C36	-5.4(9)
C27	N1	C6	C5	-0.7(7)	C65	N64	C48	C47	178.9(5)
C27	N1	C7	C8	-179.3(4)	C65	N64	C58	C59	2.4(8)
C27	N1	C7	C11	1.6(8)	C65	N64	C58	C63	-179.9(5)

Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3af.

Atom	*x*	*y*	*z*	U(eq)
H1SA	4791.85	6175.2	5118.92	159
H1SB	5815.64	6591.28	5087.06	159
H2	2711.57	-607.36	6223.67	67
H3	2218.82	-1358.13	7085.37	76
H4	1185.92	-1008.53	7945.96	78
H5	597.71	114.79	7974.45	64
H13A	2203.01	3328.71	5726.29	58
H13B	1995.6	3626.04	6497.12	58
H15A	-545.15	2965.17	5042.59	58
H15B	546.42	2932	4765.64	58
H21	4507.1	362.41	4150.8	66
H22	5052.29	961.62	3173.42	81
H23	4537.55	2074.42	2947.88	86
H24	3418.77	2599.62	3647.04	70
H25A	-773.54	3570.14	6190.73	106
H25B	198.05	3819.29	6754.33	106
H25C	-31.93	3034	6649.51	106
H26A	1029.86	4119.57	4993.64	107
H26B	840.65	4485.73	5733.93	107
H26C	-116.21	4239.11	5155.16	107
H27A	-337.5	1603.04	7043.37	83
H27B	644.43	1912.14	7550.87	83
H27C	145.4	1227.83	7783.12	83
H40	5437.07	3936.74	9198.17	62
H41	5688.09	5052.17	9613.43	72
H42	6523.08	5831.19	8940.8	73
H43	7113.64	5500.55	7869.47	66
H50A	3853.12	1627.43	7048.16	64
H50B	4413.91	2102.17	7684.54	64
H52A	6300.23	1780.8	8301.91	57
H52B	6808.11	1114.79	8033.13	57

Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3af.

Atom	*x*	*y*	*z*	U(eq)
H56A	5268.59	503.68	8420.89	102
H56B	4128.15	677.48	8033.73	102
H56C	4743.33	1195.6	8601.34	102
H57A	5605.82	900.2	6555.85	93
H57B	4628.08	517.76	6775.04	93
H57C	5759.27	315.17	7157.01	93
H59	7094.01	2388.16	4061.56	82
H60	7566.12	3373.42	3472.43	92
H61	7812.5	4393.84	4099.4	88
H62	7555.82	4484.4	5331.5	75
H65A	6478.03	1374.12	5710.08	116
H65B	6860.43	1512.63	4940.37	116
H65C	5681.21	1628.51	5022.82	116

3.3 X-Ray Crystallographic Data of 4ka

Single crystals of $C_{25}H_{18}ClNO_4$ **4ka** were grown from CH_3OH and CH_2Cl_2. The ellipsoids are shown at 50% probability levels. A suitable crystal was selected and collected at 100(10) K on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software with the SHELXT structure solution program via intrinsic phasing algorithm, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018 using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2278494 for compound **4ka**.

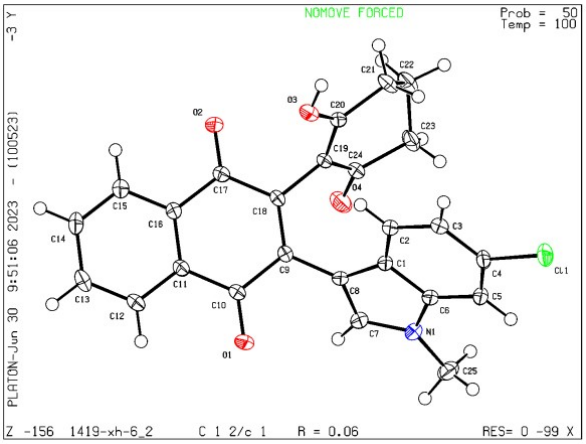


Figure S19 ORTEP Drawing of **4ka** (The ellipsoids are shown at 50% probability levels)

Table S22 Crystal data and structure refinement for 4ka.

Identification code	4ka
Empirical formula	$C_{25}H_{18}ClNO_4$
Formula weight	431.85
Temperature/K	99.98(18)
Crystal system	monoclinic
Space group	C2/c
a/Å	26.1321(6)
b/Å	7.0726(2)
c/Å	21.8672(5)
α/°	90
β/°	98.900(2)
γ/°	90
Volume/Å^3	3992.88(17)
Z	8
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	1.981
F(000)	1792.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.186 to 154.71
Index ranges	-32 ≤ h ≤ 31, -3 ≤ k ≤ 8, -27 ≤ l ≤ 27
Reflections collected	13198
Independent reflections	4049 [R_{int} = 0.0761, R_{sigma} = 0.0433]
Data/restraints/parameters	4049/0/282
Goodness-of-fit on F^2	1.156
Final R indexes [I>=2σ (I)]	R_1 = 0.0603, wR_2 = 0.1914

Final R indexes [all data] $R_1 = 0.0643$, $wR_2 = 0.1953$
Largest diff. peak/hole / e $Å^{-3}$ 0.56/-0.52

Crystal structure determination of 4ka

Crystal Data for $C_{25}H_{18}ClNO_4$ (M =431.85 g/mol): monoclinic, space group C2/c (no. 15), a = 26.1321(6) Å, b = 7.0726(2) Å, c = 21.8672(5) Å, β = 98.900(2)°, V = 3992.88(17) $Å^3$, Z = 8, T = 99.98(18) K, μ(Cu Kα) = 1.981 mm^{-1}, *Dcalc* = 1.437 g/cm^3, 13198 reflections measured (8.186° ≤ 2Θ ≤ 154.71°), 4049 unique (R_{int} = 0.0761, R_{sigma} = 0.0433) which were used in all calculations. The final R_1 was 0.0603 (I > 2σ(I)) and wR_2 was 0.1953 (all data).

Table S23 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å²×10^3) for 4ka. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	4456.2(2)	9277.8(9)	6726.5(2)	32.0(2)
O1	6464.9(5)	4491(2)	4660.0(6)	27.9(4)
O2	7827.8(5)	4967(2)	6744.7(6)	22.7(4)
O3	7085.3(5)	7740(2)	7172.7(6)	23.7(3)
O4	6504.4(6)	1585(2)	6708.2(6)	29.9(4)
N1	5209.5(6)	3699(3)	5600.3(7)	23.2(4)
C1	5740.7(7)	5994(3)	6059.4(8)	20.2(4)
C2	5847.8(7)	7708(3)	6364.8(8)	21.4(4)
C3	5448.2(7)	8708(3)	6562.3(8)	23.9(5)
C4	4943.6(7)	7971(3)	6457.7(8)	23.6(5)
C5	4812.5(7)	6305(3)	6148.5(8)	24.4(5)
C6	5222.1(7)	5313(3)	5949.3(8)	21.8(4)
C7	5702.1(7)	3335(3)	5481.4(8)	22.9(4)
C8	6042.1(7)	4670(3)	5759.3(8)	19.8(4)
C9	6599.9(7)	4749(3)	5752.7(8)	18.7(4)
C10	6777.2(7)	4690(3)	5132.7(8)	20.0(4)
C11	7338.3(7)	4937(3)	5109.0(8)	19.5(4)
C12	7512.9(7)	4943(3)	4540.1(8)	23.0(4)
C13	8036.3(8)	5197(3)	4507.1(9)	25.3(5)
C14	8385.5(8)	5442(3)	5052.3(10)	26.1(5)
C15	8217.2(7)	5399(3)	5623.7(9)	23.6(5)
C16	7692.3(7)	5143(3)	5655.6(8)	19.5(4)
C17	7511.7(7)	5020(3)	6265.1(8)	19.6(4)
C18	6948.7(7)	4880(3)	6284.9(8)	17.9(4)
C19	6780.7(7)	4729(3)	6900.2(8)	19.4(4)

Table S23 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 4ka. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	6854.1(7)	6147(3)	7317.5(8)	20.1(4)
C21	6657.6(8)	6087(3)	7928.9(8)	27.5(5)
C22	6551.4(9)	4087(4)	8129.1(9)	31.2(5)
C23	6245.1(8)	2988(4)	7601.2(9)	29.9(5)
C24	6517.5(7)	2975(3)	7035.3(8)	22.4(4)
C25	4758.8(7)	2512(3)	5416.3(9)	28.4(5)

Table S24 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4ka. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	20.7(3)	50.4(4)	27.1(3)	0.0(2)	10.4(2)	8.1(2)
O1	23.4(7)	46.9(10)	12.6(6)	0.3(6)	0.6(5)	-5.5(6)
O2	18.0(7)	35.1(9)	14.2(6)	2.4(6)	-0.1(5)	0.0(6)
O3	25.7(7)	31.0(8)	14.7(6)	-2.5(6)	3.7(5)	-2.5(6)
O4	37.1(8)	33.4(9)	20.8(7)	-2.7(6)	9.4(6)	-5.4(7)
N1	14.9(7)	33.9(10)	20.2(8)	-1.1(7)	1.1(6)	-2.7(7)
C1	13.5(8)	33.9(12)	13.2(8)	2.2(8)	1.5(6)	-0.4(8)
C2	16.1(8)	33.7(12)	14.1(8)	-1.0(8)	1.5(6)	-0.1(8)
C3	19.8(9)	36.9(13)	15.0(8)	-3.3(8)	2.2(6)	-0.4(8)
C4	15.5(8)	39.3(13)	17.1(8)	2.8(8)	6.0(6)	5.3(8)
C5	14.2(8)	41.4(13)	17.8(8)	2.8(9)	3.7(6)	-1.1(9)
C6	16.1(9)	35.2(12)	13.7(8)	1.5(8)	1.1(6)	-1.6(8)
C7	16.5(8)	34.1(12)	17.5(8)	1.0(8)	0.5(6)	1.2(8)
C8	15.1(9)	31.6(11)	12.1(8)	0.5(7)	-0.1(6)	-0.7(8)
C9	16.6(9)	25.8(11)	14.3(8)	-0.4(7)	4.4(6)	-1.7(7)
C10	19.4(9)	28.3(11)	12.4(8)	0.6(7)	3.0(6)	-0.2(8)
C11	19.0(9)	25.8(11)	14.1(8)	1.2(7)	3.7(7)	1.8(8)
C12	24.9(10)	31.6(12)	13.2(8)	0.0(8)	4.9(7)	0.5(9)
C13	28.3(10)	30.0(12)	20.5(9)	0.2(8)	13.0(8)	1.5(9)
C14	18.0(9)	34.0(12)	28.4(10)	-0.3(9)	10.5(7)	1.9(8)
C15	18.1(9)	32.7(12)	20.6(9)	-1.0(8)	4.7(7)	1.5(8)
C16	16.3(9)	27.1(11)	15.4(9)	0.2(7)	3.6(7)	1.3(8)
C17	18.5(9)	26.2(11)	14.1(8)	0.4(7)	2.2(6)	1.6(8)
C18	17.7(9)	24.4(11)	12.5(8)	-0.3(7)	4.8(6)	0.4(8)

Table S24 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4ka. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	15.8(8)	31.7(11)	10.7(8)	1.2(7)	2.4(6)	0.9(8)
C20	15.1(8)	31.6(11)	13.1(8)	1.0(8)	0.6(6)	2.1(8)
C21	34.2(11)	36.2(13)	13.5(8)	-3.1(8)	8.4(7)	-0.5(9)
C22	36.0(11)	42.5(14)	17.4(9)	-0.2(9)	11.5(8)	-3.1(10)
C23	30.5(10)	42.2(14)	19.9(9)	-2.5(9)	13.0(7)	-9.7(10)
C24	20.1(9)	34.5(12)	12.9(8)	0.2(8)	3.5(6)	-0.6(8)
C25	19.8(9)	36.9(13)	27.0(9)	1.6(9)	-1.7(7)	-7.1(9)

Table S25 Bond Lengths for 4ka.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C4	1.7475(19)	C9	C18	1.366(2)
O1	C10	1.222(2)	C10	C11	1.486(2)
O2	C17	1.231(2)	C11	C12	1.390(2)
O3	C20	1.340(2)	C11	C16	1.401(2)
O4	C24	1.213(3)	C12	C13	1.393(3)
N1	C6	1.371(3)	C13	C14	1.395(3)
N1	C7	1.376(2)	C14	C15	1.388(3)
N1	C25	1.451(2)	C15	C16	1.396(3)
C1	C2	1.391(3)	C16	C17	1.484(2)
C1	C6	1.423(3)	C17	C18	1.482(2)
C1	C8	1.445(3)	C18	C19	1.482(2)
C2	C3	1.385(3)	C19	C20	1.349(3)
C3	C4	1.403(3)	C19	C24	1.470(3)
C4	C5	1.375(3)	C20	C21	1.505(2)
C5	C6	1.404(3)	C21	C22	1.519(3)
C7	C8	1.372(3)	C22	C23	1.514(3)
C8	C9	1.461(3)	C23	C24	1.520(2)
C9	C10	1.500(2)			

Table S26 Bond Angles for 4ka.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N1	C7	108.56(16)	C16	C11	C10	120.49(15)
C6	N1	C25	125.77(16)	C11	C12	C13	120.53(17)

Table S26 Bond Angles for 4ka.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	N1	C25	125.59(19)	C12	C13	C14	119.29(16)
C2	C1	C6	119.45(17)	C15	C14	C13	120.68(17)
C2	C1	C8	134.36(17)	C14	C15	C16	119.90(18)
C6	C1	C8	106.00(17)	C11	C16	C17	120.04(16)
C3	C2	C1	119.29(17)	C15	C16	C11	119.67(16)
C2	C3	C4	119.6(2)	C15	C16	C17	120.26(16)
C3	C4	Cl1	117.66(17)	O2	C17	C16	120.16(16)
C5	C4	Cl1	118.64(14)	O2	C17	C18	120.76(15)
C5	C4	C3	123.69(18)	C18	C17	C16	119.02(15)
C4	C5	C6	115.89(17)	C9	C18	C17	120.96(15)
N1	C6	C1	108.43(16)	C9	C18	C19	121.08(15)
N1	C6	C5	129.42(17)	C17	C18	C19	117.78(15)
C5	C6	C1	122.01(19)	C20	C19	C18	121.95(18)
C8	C7	N1	110.38(19)	C20	C19	C24	120.86(16)
C1	C8	C9	126.47(18)	C24	C19	C18	117.18(17)
C7	C8	C1	106.60(17)	O3	C20	C19	119.17(16)
C7	C8	C9	126.92(19)	O3	C20	C21	117.52(17)
C8	C9	C10	117.14(15)	C19	C20	C21	123.19(19)
C18	C9	C8	121.97(16)	C20	C21	C22	112.64(18)
C18	C9	C10	120.89(16)	C23	C22	C21	110.92(18)
O1	C10	C9	120.57(16)	C22	C23	C24	111.40(16)
O1	C10	C11	121.18(16)	O4	C24	C19	122.45(16)
C11	C10	C9	118.22(15)	O4	C24	C23	120.71(18)
C12	C11	C10	119.61(16)	C19	C24	C23	116.82(17)
C12	C11	C16	119.90(16)				

Table S27 Torsion Angles for 4ka.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C4	C5	C6	-179.44(14)	C10	C9	C18	C17	1.7(3)
O1	C10	C11	C12	0.0(3)	C10	C9	C18	C19	-173.24(19)
O1	C10	C11	C16	-179.3(2)	C10	C11	C12	C13	179.2(2)
O2	C17	C18	C9	-173.4(2)	C10	C11	C16	C15	-179.15(19)
O2	C17	C18	C19	1.6(3)	C10	C11	C16	C17	3.0(3)
O3	C20	C21	C22	-163.04(17)	C11	C12	C13	C14	0.2(3)
N1	C7	C8	C1	-1.7(2)	C11	C16	C17	O2	171.1(2)
N1	C7	C8	C9	178.56(18)	C11	C16	C17	C18	-6.4(3)
C1	C2	C3	C4	0.6(3)	C12	C11	C16	C15	1.5(3)

Table S27 Torsion Angles for 4ka.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C8	C9	C10	-126.3(2)	C12	C11	C16	C17	-176.29(19)
C1	C8	C9	C18	53.4(3)	C12	C13	C14	C15	1.2(3)
C2	C1	C6	N1	175.06(16)	C13	C14	C15	C16	-1.2(3)
C2	C1	C6	C5	-1.0(3)	C14	C15	C16	C11	-0.2(3)
C2	C1	C8	C7	-173.4(2)	C14	C15	C16	C17	177.6(2)
C2	C1	C8	C9	6.4(4)	C15	C16	C17	O2	-6.7(3)
C2	C3	C4	Cl1	179.13(14)	C15	C16	C17	C18	175.84(19)
C2	C3	C4	C5	-2.0(3)	C16	C11	C12	C13	-1.5(3)
C3	C4	C5	C6	1.7(3)	C16	C17	C18	C9	4.0(3)
C4	C5	C6	N1	-175.35(19)	C16	C17	C18	C19	179.05(18)
C4	C5	C6	C1	-0.2(3)	C17	C18	C19	C20	65.2(3)
C6	N1	C7	C8	1.3(2)	C17	C18	C19	C24	-116.1(2)
C6	C1	C2	C3	0.8(3)	C18	C9	C10	O1	176.9(2)
C6	C1	C8	C7	1.4(2)	C18	C9	C10	C11	-5.0(3)
C6	C1	C8	C9	-178.83(18)	C18	C19	C20	O3	0.0(3)
C7	N1	C6	C1	-0.4(2)	C18	C19	C20	C21	175.92(17)
C7	N1	C6	C5	175.4(2)	C18	C19	C24	O4	11.2(3)
C7	C8	C9	C10	53.4(3)	C18	C19	C24	C23	-167.20(16)
C7	C8	C9	C18	-126.9(2)	C19	C20	C21	C22	21.0(3)
C8	C1	C2	C3	175.0(2)	C20	C19	C24	O4	-170.17(18)
C8	C1	C6	N1	-0.6(2)	C20	C19	C24	C23	11.4(3)
C8	C1	C6	C5	-176.73(18)	C20	C21	C22	C23	-47.0(2)
C8	C9	C10	O1	-3.4(3)	C21	C22	C23	C24	55.8(2)
C8	C9	C10	C11	174.75(18)	C22	C23	C24	O4	143.4(2)
C8	C9	C18	C17	-178.0(2)	C22	C23	C24	C19	-38.2(3)
C8	C9	C18	C19	7.0(3)	C24	C19	C20	O3	-178.54(16)
C9	C10	C11	C12	-178.15(19)	C24	C19	C20	C21	-2.7(3)
C9	C10	C11	C16	2.5(3)	C25	N1	C6	C1	176.47(17)
C9	C18	C19	C20	-119.7(2)	C25	N1	C6	C5	-7.8(3)
C9	C18	C19	C24	58.9(3)	C25	N1	C7	C8	-175.55(17)

Table S28 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4ka.

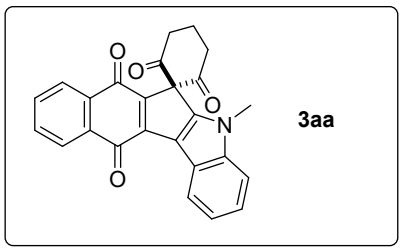
Atom	*x*	*y*	*z*	U(eq)
H3	7116.42	8485.01	7475.4	36
H2	6191.5	8187.12	6436.91	26
H3A	5515.18	9886.24	6767.67	29

Table S28 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4ka.

Atom	*x*	*y*	*z*	U(eq)
H5	4466.09	5852.8	6074.34	29
H7	5793.69	2305.89	5241.04	28
H12	7273.24	4772.51	4170.79	28
H13	8154.49	5204.51	4117.47	30
H14	8742.03	5639.94	5032.09	31
H15	8458.88	5543.13	5992.65	28
H21A	6334.47	6835.8	7896.83	33
H21B	6916.94	6680.92	8249.39	33
H22A	6883.89	3434.63	8270.02	37
H22B	6354.68	4133.74	8481.04	37
H23A	5897.71	3563.45	7490.86	36
H23B	6198.4	1671.02	7735.77	36
H25A	4705.55	1694.03	5762.66	43
H25B	4813.89	1730.33	5062.21	43
H25C	4452.82	3310.6	5299.78	43

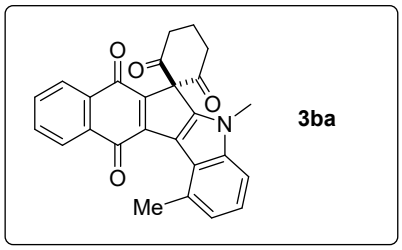
4. Characterization of compounds

5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3aa)



Blue solid, m.p. 233-224 °C, yield: 30.8 mg, 78% yield; Rf: 0.51 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.2 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.72 (dt, *J* = 22.2, 7.4 Hz, 2H), 7.36 (d, *J* = 9.1 Hz, 3H), 3.96 (td, *J* = 14.7, 6.1 Hz, 2H), 3.64 (s, 3H), 2.88 (d, *J* = 15.8 Hz, 2H), 2.61 (d, *J* = 14.0 Hz, 1H), 2.03 (q, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.6, 182.8, 178.7, 156.9, 150.5, 143.0, 136.7, 134.2, 134.1, 132.7, 132.0, 126.4, 126.3, 124.1, 123.1, 122.7, 122.0, 120.1, 110.6, 77.8, 38.9, 32.2, 18.5. HRMS (ESI) Calcd for $C_{25}H_{17}NNaO_4^+$[M+Na]$^+$: 418.1055, Found: 418.1058.

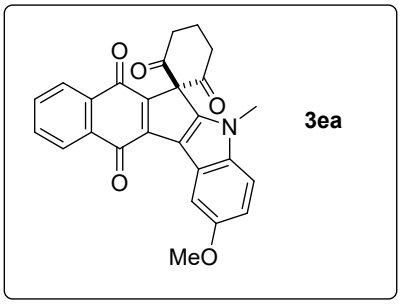
1,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ba)



Blue solid, m.p. 242-243 °C, yield: 26.6 mg, 65% yield; Rf: 0.26 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 6.2 Hz, 2H), 7.23 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 3.89 (dt, *J* = 15.2, 7.4 Hz, 2H), 3.61 (s, 3H), 2.97 (s, 3H), 2.92 (s, 2H), 2.63 (d, *J* = 20.8 Hz, 1H), 2.10 (q, *J* = 14.7, 14.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 203.2, 182.5, 179.0, 157.1,

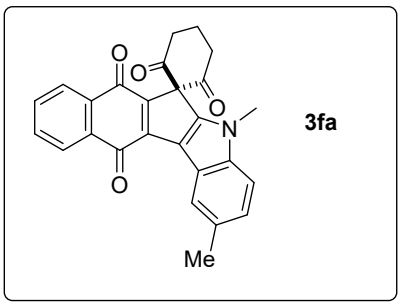
152.1, 142.9, 140.1, 134.0, 133.7, 133.1, 133.0, 132.9, 126.7, 125.6, 124.8, 123.9, 122.3, 118.6, 108.1, 75.3, 38.9, 32.2, 23.1, 18.3. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_4^+$[M+Na]$^+$: 432.1212, Found: 432.1214.

2-methoxy-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ea)



Blue solid, m.p. 242-243 °C, yield: 12.8 mg, 30% yield; Rf: 0.26 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.91 (s, 1H), 7.75 (t, *J* = 6.8 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.27 (s, 1H), 6.99 (dd, *J* = 9.8, 1.9 Hz, 1H), 3.98 (s, 3H), 3.93 (dd, *J* = 14.4, 6.3 Hz, 2H), 3.60 (s, 3H), 2.88 (d, *J* = 15.6 Hz, 2H), 2.65 – 2.55 (m, 1H), 2.01 (q, *J* = 13.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.8, 183.0, 178.5, 156.9, 156.5, 150.5, 137.9, 136.2, 134.2, 132.7, 132.1, 126.3, 122.8, 119.8, 114.1, 111.4, 110.8, 104.9, 77.7, 56.0, 38.9, 32.3, 18.5. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_5^+$[M+Na]$^+$: 448.1161, Found: 448.1154.

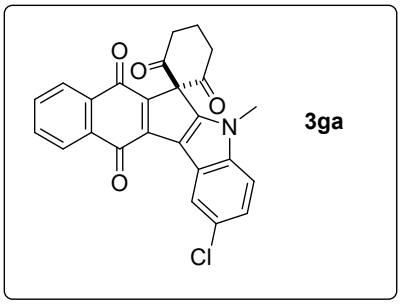
2,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3fa)



Blue solid, m.p. 232-233 °C, yield: 28.7 mg, 70% yield; Rf: 0.29 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.16 (d, *J* = 7.4 Hz, 1H), 8.09 (d, *J* = 7.4 Hz,

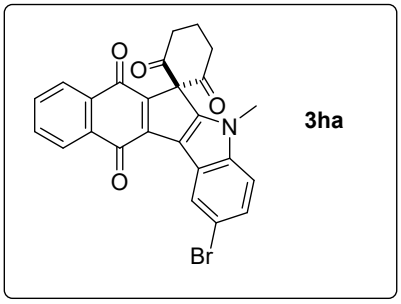
1H), 7.72 (dt, *J* = 21.8, 7.3 Hz, 2H), 7.25 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 3.94 (dt, *J* = 14.5, 7.3 Hz, 2H), 3.59 (s, 3H), 2.87 (d, *J* = 15.7 Hz, 2H), 2.64 – 2.57 (m, 1H), 2.54 (s, 3H), 2.02 (q, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.7, 183.0, 178.5, 157.0, 150.5, 141.4, 136.4, 134.2, 132.6, 132.5, 132.0, 126.3, 126.2, 125.5, 122.9, 122.2, 119.6, 110.2, 77.7, 38.9, 32.2, 21.5, 18.5. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_4^+$[M+Na]$^+$: 432.1212, Found: 432.1219.

2-chloro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ga)



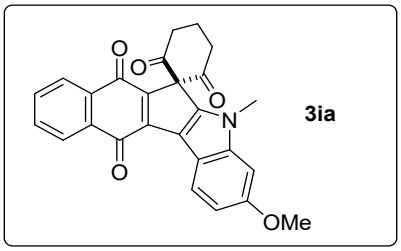
Purple solid, m.p. 250-251 °C, yield: 30.9 mg, 72% yield; Rf: 0.20 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.16 (d, *J* = 6.9 Hz, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.80 – 7.67 (m, 2H), 7.36 – 7.26 (m, 2H), 3.94 (dt, *J* = 14.8, 7.2 Hz, 2H), 3.62 (s, 3H), 2.89 (d, *J* = 15.6 Hz, 2H), 2.67 – 2.55 (m, 1H), 2.10 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.6, 178.9, 157.1, 150.0, 141.2, 137.1, 134.3, 133.9, 132.9, 131.9, 128.6, 126.4, 126.4, 124.2, 122.9, 122.6, 119.3, 111.5, 78.1, 77.3, 77.0, 76.7, 38.8, 32.3, 18.5. HRMS (ESI) Calcd for $C_{25}H_{16}ClNNaO_4^+$ [M+Na]$^+$: 452.0666, Found: 452.0661.

2-bromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ha)



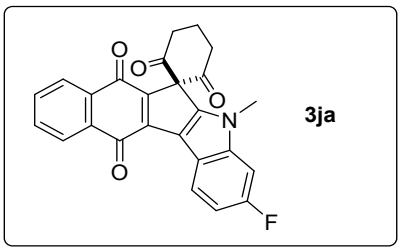
Purple solid, m.p. 254-255 °C, yield: 20.4 mg, 43% yield; Rf: 0.20 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.9 Hz, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.73 (dt, *J* = 18.3, 7.4 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.23 (s, 1H), 3.94 (td, *J* = 14.7, 6.1 Hz, 2H), 3.61 (s, 3H), 2.88 (d, *J* = 15.5 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 1H), 2.10 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.6, 179.0, 157.0, 150.0, 141.6, 137.2, 134.3, 133.9, 133.0, 132.0, 126.9, 126.4, 125.6, 123.4, 119.3, 116.2, 112.0, 78.1, 38.9, 32.3, 18.5. HRMS (ESI) Calcd for $C_{25}H_{16}BrNNaO_4^+$ $[M+Na]^+$: 496.0160, Found: 496.0158.

3-methoxy-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ia)



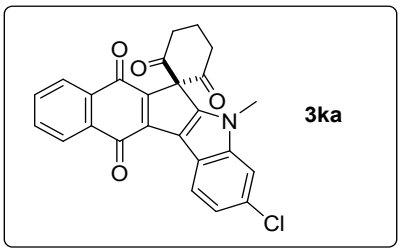
Blue solid, m.p. 229-230 °C, yield: 20.0 mg, 47% yield; Rf: 0.19 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.63 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.84 (s, 1H), 3.97 (dt, *J* = 14.7, 7.2 Hz, 2H), 3.91 (s, 3H), 3.58 (s, 3H), 2.87 (d, *J* = 15.5 Hz, 2H), 2.66 – 2.54 (m, 1H), 2.01 (q, *J* = 13.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.7, 182.9, 178.4, 157.9, 156.5, 150.3, 144.1, 136.2, 134.3, 134.1, 132.6, 132.0, 126.3, 126.2, 123.9, 120.2, 116.1, 111.4, 95.1, 77.9, 55.8, 38.8, 32.2, 18.5. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_5^+$$[M+Na]^+$: 448.1161, Found: 448.1154.

3-fluoro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ja)



Blue solid, m.p. 240-241 °C, yield: 38.0 mg, 92% yield; Rf: 0.60 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.29 (m, 1H), 8.13 (d, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.71 (dt, *J* = 20.5, 7.4 Hz, 2H), 7.09 (q, *J* = 8.0, 7.3 Hz, 2H), 3.94 (dd, *J* = 29.4, 6.0 Hz, 2H), 3.58 (s, 3H), 2.88 (d, *J* = 15.6 Hz, 2H), 2.58 (s, 1H), 2.01 (q, *J* = 15.2, 14.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) 202.4, 182.7, 178.8, 160.8 (d, J = 242.0 Hz), 156.8, 150.1, 143.2, 143.1, 137.1, 134.2, 134.0, 132.8, 131.9, 126.4, 126.3, 124.1 (d, *J* = 10.0 Hz), 120.0, 118.4, 111.0 (d, *J* = 24.0 Hz), 97.8, 97.5, 78.1, 38.8, 32.3, 18.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.59. HRMS (ESI) Calcd for $C_{25}H_{16}FNNaO_4^+$ $[M+Na]^+$: 436.0961, Found: 436.0956.

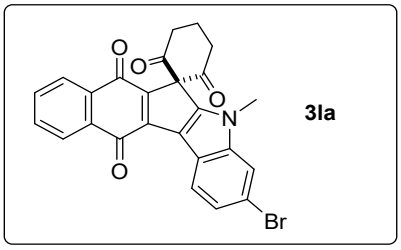
3-chloro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ka)



Purple solid, m.p. 229-230 °C, yield: 30.0 mg, 70% yield; Rf: 0.26 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.5 Hz, 1H), 8.11 (dd, *J* = 21.0, 7.8 Hz, 2H), 7.80 – 7.66 (m, 2H), 7.38 (s, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 3.94 (td, *J* = 14.6, 5.9 Hz, 2H), 3.60 (s, 3H), 2.88 (d, *J* = 16.2 Hz, 2H), 2.61 (d, *J* = 12.0 Hz, 1H), 2.01 (q, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.6, 178.9, 156.9, 150.0, 143.2, 137.3,

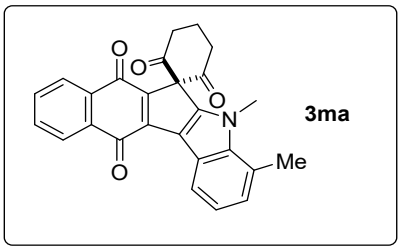
134.2, 133.9, 132.9, 131.9, 130.0, 126.4, 123.8, 123.2, 120.5, 119.9, 110.9, 78.1, 77.3, 77.0, 76.7, 38.8, 32.3, 18.5. HRMS (ESI) Calcd for $C_{25}H_{16}ClNNaO_4^+$ $[M+Na]^+$: 452.0666, Found: 452.0661.

3-bromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3la)



Purple solid, m.p. 239-240 °C, yield: 36.0 mg, 76% yield; Rf: 0.27 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.79 – 7.65 (m, 2H), 7.54 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 3.94 (td, *J* = 14.4, 6.1 Hz, 2H), 3.60 (s, 3H), 2.88 (d, *J* = 15.6 Hz, 2H), 2.64 – 2.54 (m, 1H), 2.09 – 1.92 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.6, 178.9, 156.8, 150.0, 143.5, 137.4, 134.3, 134.0, 132.9, 132.0, 126.4, 125.8, 124.2, 120.8, 119.9, 117.5, 113.8, 78.1, 38.8, 32.3, 18.5. HRMS (ESI) Calcd for $C_{25}H_{16}BrNNaO_4^+$ $[M+Na]^+$: 496.0160, Found: 496.0157.

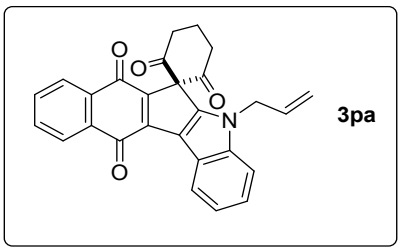
4,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ma)



Blue solid, m.p. 249-250 °C, yield: 25.8 mg, 63% yield; Rf: 0.24 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.3 Hz, 1H), 8.08 (d, *J* = 6.1 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H),

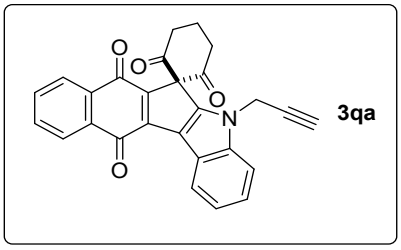
3.96 (td, *J* = 14.9, 6.1 Hz, 2H), 3.85 (s, 3H), 2.88 (d, *J* = 15.7 Hz, 2H), 2.77 (s, 3H), 2.59 (d, *J* = 11.5 Hz, 1H), 2.02 (q, *J* = 14.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.9, 182.8, 178.6, 157.8, 150.5, 141.5, 136.7, 134.1, 134.0, 132.7, 132.0, 127.4, 126.4, 126.2, 123.0, 122.9, 122.5, 121.4, 120.0, 78.5, 38.8, 36.3, 19.7, 18.4. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_4^+$[M+Na]$^+$: 432.1212, Found: 432.1219.

5-allyl-5H-spiro[benzo[5,6]indeno[2,1-b]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3pa)



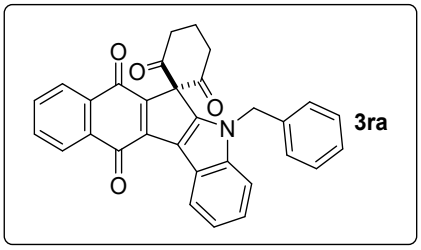
Blue solid, m.p. 211-212^{o}C, yield: 30.8 mg, 73% yield; Rf: 0. 40 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.1 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.4 Hz, 1H), 7.78 – 7.63 (m, 2H), 7.42 – 7.29 (m, 3H), 5.86 (ddt, *J* = 16.0, 10.5, 5.4 Hz, 1H), 4.59 (d, *J* = 5.3 Hz, 2H), 3.95 – 3.74 (m, 2H), 2.85 (d, *J* = 16.0 Hz, 2H), 2.57 (dd, *J* = 10.5, 3.8 Hz, 1H), 2.03 (q, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.8, 182.7, 178.8, 156.1, 150.3, 142.3, 138.8, 134.1, 133.9, 132.8, 132.1, 131.4, 126.4, 126.2, 124.1, 123.2, 122.7, 122.2, 120.7, 119.1, 111.3, 48.9, 38.8, 18.1. HRMS (ESI) Calcd for $C_{27}H_{19}NNaO_4^+$[M+Na]$^+$: 444.1212, Found: 444.1208.

5-(prop-2-yn-1-yl)-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3qa)



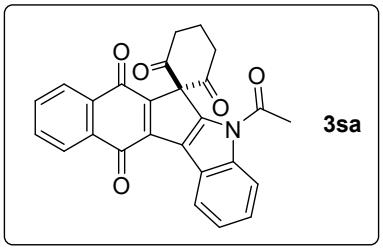
Blue solid, m.p. 206-207°C, yield: 20.5 mg, 49% yield; Rf: 0.58 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.7 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 1H), 7.80 – 7.67 (m, 2H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.44 – 7.35 (m, 2H), 4.75 (d, *J* = 2.3 Hz, 2H), 3.95 – 3.81 (m, 2H), 2.91 (d, *J* = 15.9 Hz, 2H), 2.64 – 2.54 (m, 1H), 2.44 (s, 1H), 2.18 (q, *J* = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.4, 182.6, 179.0, 150.0, 141.9, 139.0, 134.2, 133.8, 132.9, 132.1, 126.4, 126.3, 124.4, 123.3, 122.9, 122.0, 121.6, 110.7, 75.2, 38.8, 35.1, 18.4. HRMS (ESI) Calcd for $C_{27}H_{17}NNaO_4^+$[M+Na]$^+$: 442.1055, Found: 442.1054.

5-benzyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ra)



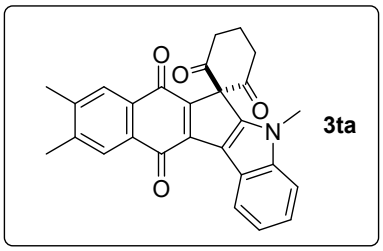
Blue solid, m.p. 195-200°C, yield: 27.3 mg, 58% yield; Rf: 0.50 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 5.5 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.71 (p, *J* = 7.5 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 3H), 5.19 (s, 2H), 3.77 – 3.64 (m, 2H), 2.65 (dt, *J* = 16.1, 4.1 Hz, 2H), 2.53 – 2.40 (m, 1H), 1.83 (qt, *J* = 13.3, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.7, 182.7, 178.8, 156.4, 150.3, 142.6, 139.6, 134.7, 134.1, 133.9, 132.8, 132.1, 129.0, 128.3, 126.8, 126.4, 126.2, 124.2, 123.1, 122.8, 122.3, 121.1, 111.6, 50.2, 38.7, 18.1. HRMS (ESI) Calcd for $C_{31}H_{21}NNaO_4^+$[M+Na]$^+$: 494.1368, Found: 494.1370.

5-acetyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3sa)



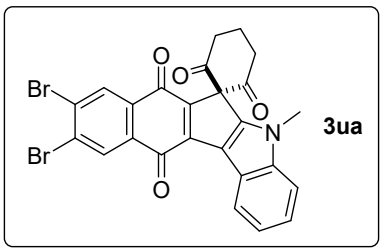
Pink solid, m.p. 252-253°C, yield: 16.1 mg, 38% yield; Rf: 0.50 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 – 8.41 (m, 1H), 8.30 – 8.14 (m, 1H), 8.13 – 8.02 (m, 1H), 7.87 – 7.73 (m, 2H), 7.73 – 7.65 (m, 1H), 7.51 – 7.40 (m, 2H), 3.61 (ddd, *J* = 16.4, 12.8, 6.4 Hz, 2H), 2.89 (dt, *J* = 16.5, 3.9 Hz, 2H), 2.82 (s, 3H), 2.63 (dt, *J* = 13.1, 4.3 Hz, 1H), 2.48 – 2.36 (m, 1H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.1, 182.0, 180.4, 168.0, 152.8, 148.1, 143.9, 139.1, 134.2, 133.5, 133.3, 132.2, 127.8, 126.6, 126.5, 126.0, 124.9, 124.2, 124.0, 114.4, 79.0, 38.5, 25.8, 17.4. HRMS (ESI) Calcd for $C_{26}H_{17}NNaO_5^+$[M+Na]$^+$: 446.1004, Found: 446.1000.

5,9,10-trimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ta)



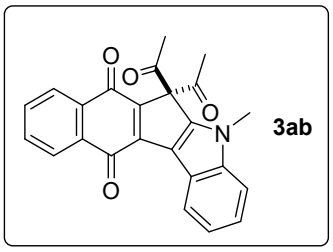
Blue solid, m.p. 232-233°C, yield: 20.7 mg, 49% yield; Rf: 0.25 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.36 (m, 1H), 7.89 (s, 1H), 7.82 (s, 1H), 7.36 (dd, *J* = 8.3, 2.3 Hz, 3H), 4.03 – 3.89 (m, 2H), 3.63 (s, 3H), 2.87 (d, *J* = 15.6 Hz, 2H), 2.59 (d, *J* = 10.9 Hz, 1H), 2.40 (s, 6H), 2.10 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.8, 183.0, 179.2, 156.6, 150.5, 143.9, 142.9, 142.3, 136.7, 132.0, 130.1, 127.6, 127.5, 123.9, 123.2, 122.6, 122.1, 120.1, 110.5, 77.8, 38.9, 32.1, 20.3, 20.0, 18.5. HRMS (ESI) Calcd for $C_{27}H_{21}NNaO_4^+$[M+Na]$^+$: 446.1368, Found: 446.1366.

9,10-dibromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ua)



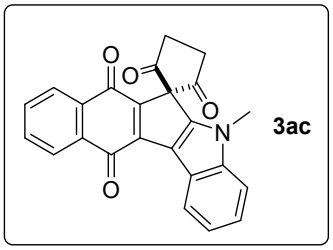
Blue solid, m.p. 228-229°C, yield: 28.8 mg, 52% yield; Rf: 0.31 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 2H), 8.31 (s, 1H), 7.46 – 7.29 (m, 3H), 3.91 (td, J = 14.7, 6.1 Hz, 2H), 3.64 (s, 3H), 2.89 (dt, J = 15.6, 3.7 Hz, 2H), 2.66 – 2.55 (m, 1H), 2.10 – 1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.1, 181.2, 176.5, 158.7, 148.9, 143.2, 135.9, 133.6, 132.1, 131.7, 131.4, 130.2, 124.5, 123.2, 123.1, 121.9, 110.7, 77.2, 38.8, 32.3, 18.5. HRMS (ESI) Calcd for $C_{25}H_{15}Br_2NNaO_4^+$[M+Na]$^+$: 573.9266, Found: 573.9262.

6,6-diacetyl-5-methyl-5,6-dihydrobenzo[5,6]indeno[2,1-*b*]indole-7,12-dione (3ab)



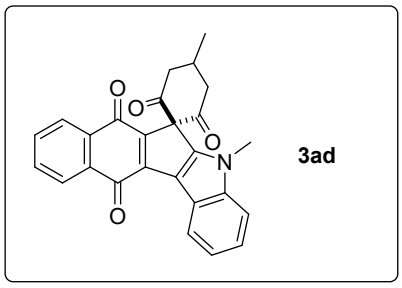
Blue solid, m.p. 192-193°C, yield: 15.3mg, 40% yield; Rf: 0.49 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.41 (m, 1H), 8.20 (dd, *J* = 17.3, 7.5 Hz, 2H), 7.83 – 7.72 (m, 2H), 7.42 (d, *J* = 8.0 Hz, 3H), 3.82 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) 198.8, 182.9, 179.5, 150.9, 150.0, 143.7, 134.5, 134.3, 134.1, 132.9, 132.3, 127.8, 126.5, 124.4, 122.9, 122.8, 121.6, 119.3, 110.9, 79.5, 32.1, 28.4. HRMS (ESI) Calcd for $C_{24}H_{17}NNaO_4^+$[M+Na]$^+$: 406.1055, Found: 406.1052.

5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclopentane]-2',5',7,12-tetraone (3ac)



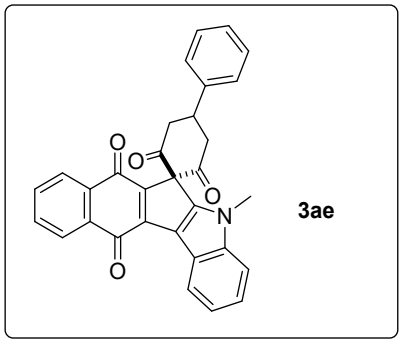
Blue solid, m.p. 241-242°C, yield: 25.9 mg, 68% yield; Rf: 0.20 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 1H), 8.03 (d, *J* = 6.6 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.36 (s, 3H), 3.88 – 3.80 (m, 2H), 3.66 (s, 3H), 3.19 – 3.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) 206.7, 179.1, 153.2, 149.2, 142.5, 136.2, 134.0, 133.2, 133.1, 132.5, 126.7, 126.1, 124.7, 124.2, 122.9, 122.6, 122.0, 121.5, 110.5, 38.3, 32.2. HRMS (ESI) Calcd for $C_{24}H_{15}NNaO_4^+$[M+Na]$^+$: 404.0899, Found: 404.0890.

4',5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ad)



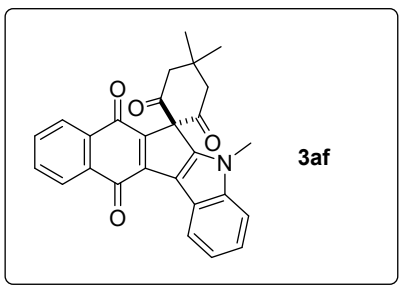
Blue solid, m.p. 241-242°C, yield: 32.3 mg, 79% yield; Rf: 0.49 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 12.2, 5.8 Hz, 1H), 8.12 (dd, *J* = 23.2, 7.4 Hz, 2H), 7.74 – 7.65 (m, 2H), 7.36 (d, *J* = 7.8 Hz, 3H), 4.14 (dd, *J* = 15.4, 5.9 Hz, 1H), 3.82 (t, *J* = 14.3 Hz, 1H), 3.72 (s, 1H), 3.60 (s, 2H), 2.84 (dd, *J* = 15.4, 3.6 Hz, 1H), 2.67 (dd, *J* = 15.4, 4.4 Hz, 1H), 2.29 (s, 1H), 1.42 (d, *J* = 6.3 Hz, 2H), 1.26 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.8, 178.7, 178.5, 157.1, 156.3, 150.4, 143.2, 143.0, 136.0, 135.4, 134.3, 134.2, 134.1, 132.7, 132.7, 132.0, 131.9, 126.8, 126.5, 126.3, 126.3, 124.1, 124.1, 123.2, 123.1, 122.7, 122.7, 122.1, 121.9, 120.1, 110.6, 110.5, 110.3, 79.1, 47.0, 46.1, 32.5, 32.2, 26.7, 25.0, 21.7, 21.5. HRMS (ESI) Calcd for $C_{26}H_{20}NNaO_4^+$[M+Na]$^+$: 410.1392, Found: 410.1395.

5-methyl-4'-phenyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ae)



Blue solid, m.p. 320-321°C, yield: 38.2 mg, 81% yield; Rf: 0.62 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 – 8.29 (m, 1H), 8.17 (dt, *J* = 18.4, 9.0 Hz, 2H), 7.87 – 7.66 (m, 3H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 2H), 7.40 (q, *J* = 6.8 Hz, 3H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 4.53 (dd, *J* = 15.4, 5.7 Hz, 1H), 4.40 (t, *J* = 14.5 Hz, 1H), 4.16 (t, *J* = 5.0 Hz, 1H), 3.70 (s, 1H), 3.50 (dd, *J* = 15.3, 4.1 Hz, 2H), 3.02 (dd, *J* = 15.4, 3.7 Hz, 1H), 2.85 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.2, 201.7, 182.8, 178.8, 178.7, 157.0, 156.6, 150.5, 150.4, 143.1, 141.4, 140.1, 134.3, 134.2, 132.7, 132.7, 131.9, 129.3, 129.2, 127.7, 127.5, 127.5, 127.0, 126.5, 126.3, 126.3, 124.2, 124.1, 123.2, 123.1, 122.8, 122.7, 122.1, 121.9, 120.3, 120.0, 110.7, 110.6, 78.4, 46.5, 44.1, 37.2, 33.1, 32.4, 31.3. HRMS (ESI) Calcd for $C_{31}H_{22}NNaO_4^+$[M+Na]$^+$: 472.1549 , Found: 472.1546.

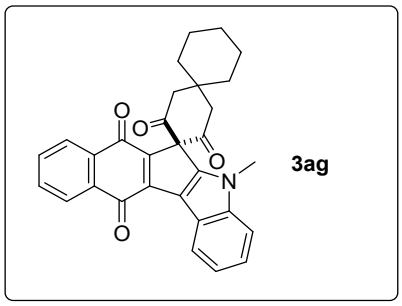
4',4',5-trimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3af)



Blue solid, m.p. 251-252°C, yield: 30.9 mg, 73% yield; Rf: 0.63 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.2 Hz, 1H), 8.15 (dd, *J* = 7.6, 3.7 Hz, 2H), 7.81 – 7.64 (m, 2H), 7.45 – 7.31 (m, 3H), 4.24 (d, *J* = 14.6 Hz, 2H), 3.70 (s, 3H), 2.62 (d, *J*

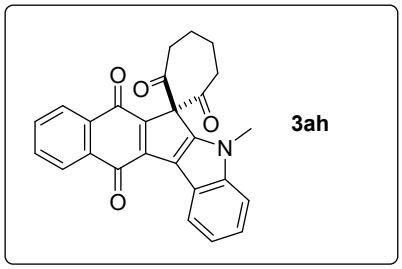
= 14.6 Hz, 2H), 1.47 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.2, 182.9, 178.5, 156.7, 150.1, 143.5, 134.6, 134.2, 132.6, 132.1, 131.7, 126.5, 126.1, 124.2, 123.3, 122.7, 122.0, 120.1, 110.6, 80.1, 51.8, 32.4, 31.3, 30.9, 28.3. HRMS (ESI) Calcd for $C_{27}H_{21}NNaO_4^+$[M+Na]$^+$: 446.1386, Found: 446.1363.

5-methyl-5*H*-dispiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane-4',1''-cyclohexane]-2',6',7,12-tetraone (3ag)



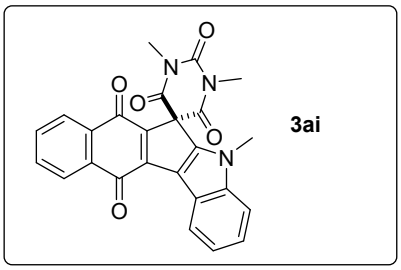
Blue solid, m.p. 350-351°C, yield: 39.9 mg, 86% yield; Rf: 0.65 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.6 Hz, 1H), 8.15 (t, *J* = 7.6 Hz, 2H), 7.78 – 7.67 (m, 2H), 7.43 – 7.34 (m, 3H), 4.30 (d, *J* = 14.4 Hz, 2H), 3.67 (s, 3H), 2.70 (d, *J* = 14.4 Hz, 2H), 1.95 (t, *J* = 7.1 Hz, 2H), 1.83 (dq, *J* = 21.1, 6.7 Hz, 4H), 1.60 (t, *J* = 7.2 Hz, 2H), 1.54 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.2, 183.0, 178.6, 157.0, 150.2, 143.4, 134.6, 134.2, 132.9, 132.6, 131.8, 126.5, 126.2, 124.2, 123.3, 122.7, 122.0, 120.1, 110.6, 79.8, 50.6, 41.2, 40.9, 36.8, 32.4, 26.3, 25.5, 24.1. HRMS (ESI) Calcd for $C_{30}H_{26}NNaO_4^+$[M+Na]$^+$: 464.1862, Found: 464.1851.

5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cycloheptane]-2',7,7',12-tetraone (3ah)



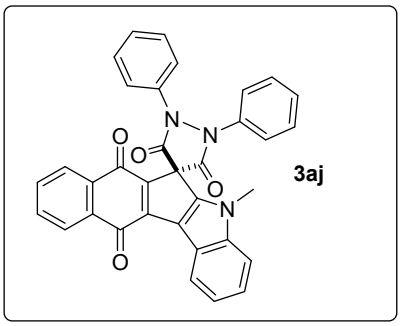
Blue solid, m.p.199-200°C, yield: 26.2 mg, 64% yield; Rf: 0.31 (EA:PE =1:2).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, J = 6.4, 2.8 Hz, 1H), 8.15 (dd, J = 15.2, 8.2 Hz, 2H), 7.85 – 7.65 (m, 2H), 7.43 – 7.30 (m, 3H), 3.88 (s, 3H), 3.67 – 3.55 (m, 2H), 2.79 (t, J = 10.1 Hz, 2H), 2.59 – 2.48 (m, 2H), 2.14 (d, J = 11.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) 202.3, 182.8, 178.6, 155.2, 151.0, 143.1, 137.7, 134.4, 134.1, 132.6, 132.2, 126.4, 126.3, 124.0, 123.1, 122.6, 121.7, 118.9, 110.5, 80.0, 44.9, 33.0, 27.6. HRMS (ESI) Calcd for $C_{26}H_{19}NNaO_4^+$[M+Na]$^+$: 432.1212, Found: 432.1210.

1',3',5-trimethyl-2'H,5H-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,5'-pyrimidine]-2',4',6',7,12(1'*H*,3'*H*)-pentaone (3ai)



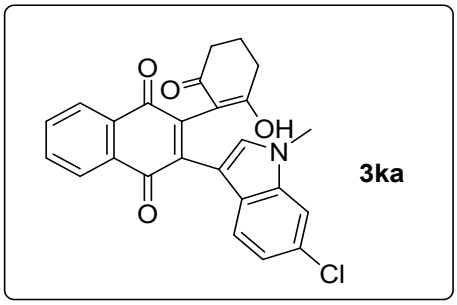
Blue solid, m.p. 345-346°C, yield: 29.4 mg, 67% yield; Rf: 0.46 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.18 (d, *J* = 6.7 Hz, 1H), 8.05 (d, *J* = 6.8 Hz, 1H), 7.72 (s, 2H), 7.39 (s, 3H), 3.73 (s, 3H), 3.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) 182.3, 178.7, 163.4, 152.3, 151.2, 150.7, 142.6, 139.7, 134.2, 133.4, 133.1, 132.3, 126.7, 126.2, 124.4, 123.1, 123.0, 122.1, 120.6, 110.7, 32.0, 29.7. HRMS (ESI) Calcd for $C_{25}H_{17}N_3NaO_5^+$[M+Na]$^+$: 462.1066, Found: 462.1061.

5-methyl-1',2'-diphenyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,4'-pyrazolidine]-3',5',7,12-tetraone (3aj)



Purple solid, m.p. 287-288°C, yield: 33.2 mg, 62% yield; Rf: 0.43 (EA:PE =1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.33 (m, 1H), 8.26 – 8.17 (m, 1H), 8.09 (dt, J = 6.4, 2.1 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.65 – 7.54 (m, 4H), 7.41 (t, J = 7.8 Hz, 4H), 7.37 (d, J = 3.2 Hz, 3H), 7.30 – 7.26 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 182.0, 178.6, 164.3, 150.8, 149.2, 142.4, 140.6, 135.3, 133.9, 133.1, 132.9, 132.5, 129.2, 127.7, 126.6, 126.1, 124.1, 123.6, 122.7, 122.6, 122.0, 120.9, 110.4, 31.7. HRMS (ESI) Calcd for $C_{34}H_{22}N_3NaO_4^+$[M+Na]$^+$: 536.1610, Found: 536.1610.

2-(6-chloro-1-methyl-1H-indol-3-yl)-3-(2-hydroxy-6-oxocyclohex-1-en-1-yl)naphthalene-1,4-dione (3ka)



Red solid, m.p. 197-198°C, yield: 36.7 mg, 85% yield; Rf: 0.2 (EA:PE =1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ10.57 (s, 1H), 8.09 – 8.03 (m, 1H), 8.03 – 7.94 (m, 1H), 7.87 (q, J = 4.5, 3.4 Hz, 2H), 7.56 (d, J = 1.9 Hz, 1H), 7.33 (s, 1H), 7.18 (d, J = 8.6 Hz, 1H), 6.99 (dd, J = 8.6, 1.8 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 2H), 2.07 (s, 2H), 1.78 (dt, J = 11.5, 5.9 Hz, 1H), 1.50 (ddt, J = 13.3, 8.7, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) 184.5, 183.1, 142.1, 140.4, 137.2, 134.5, 134.1, 133.1, 132.7, 132.4, 126.6, 126.5, 126.2, 125.9, 122.3, 119.9, 112.3, 110.4, 108.3, 33.3, 20.6. HRMS (ESI) Calcd for $C_{25}H_{19}NO_4Cl^+$[M+H]$^+$: 432.1003, Found: 432.0995.

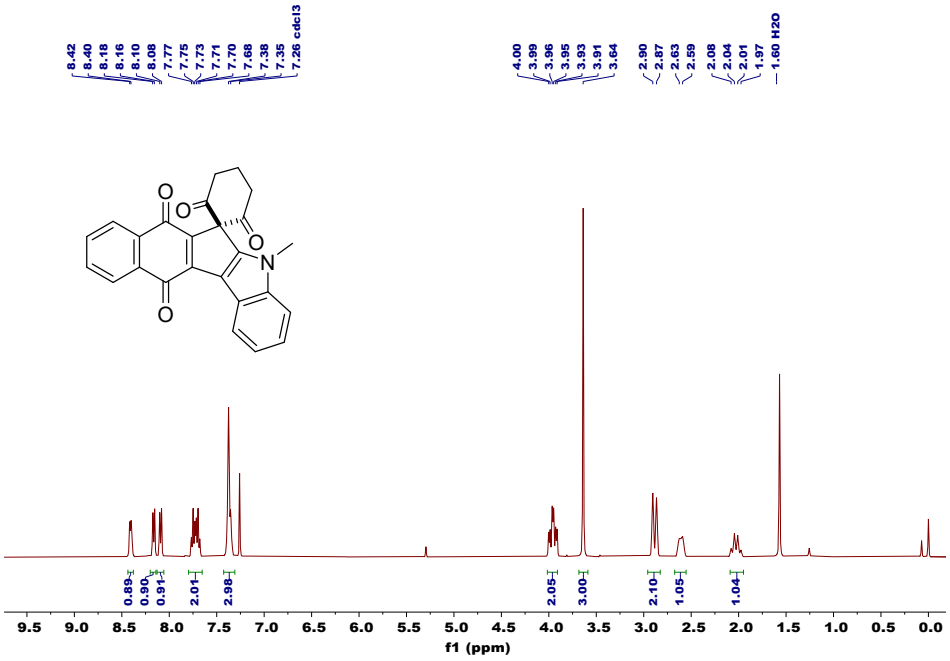
5. References

[1] Y. Dong, H. Zhang, J. Yang, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, B(C6F5)3-Catalyzed C–C Coupling of 1,4-Naphthoquinones with the C-3 Position of Indole Derivatives in Water, *ACS Omega*, 2019, **4**, 21567–21577.

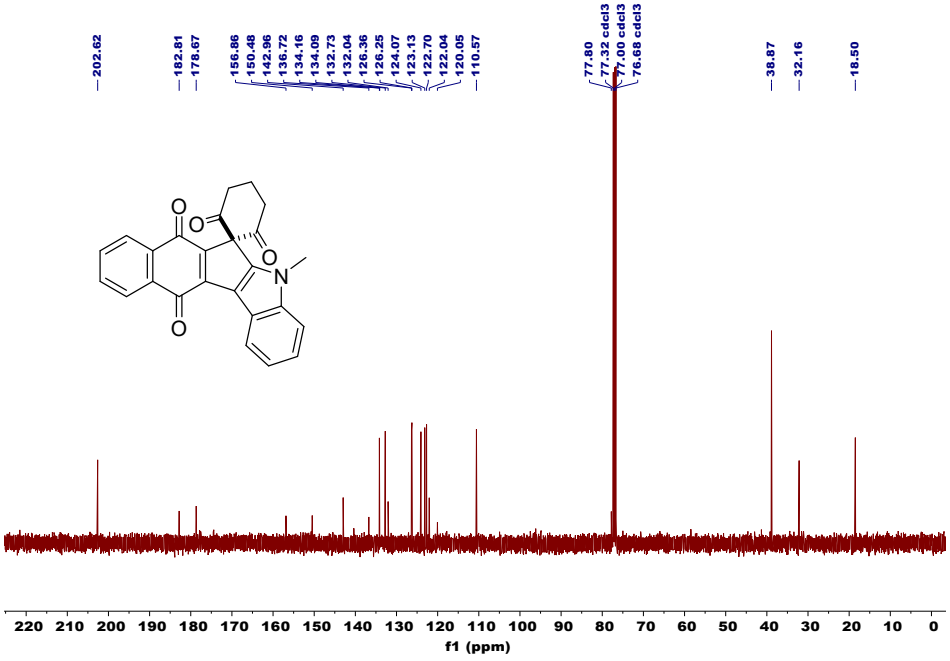
6. NMR Spectra of New Compounds

5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3aa)

^{1}H NMR (400 MHz)

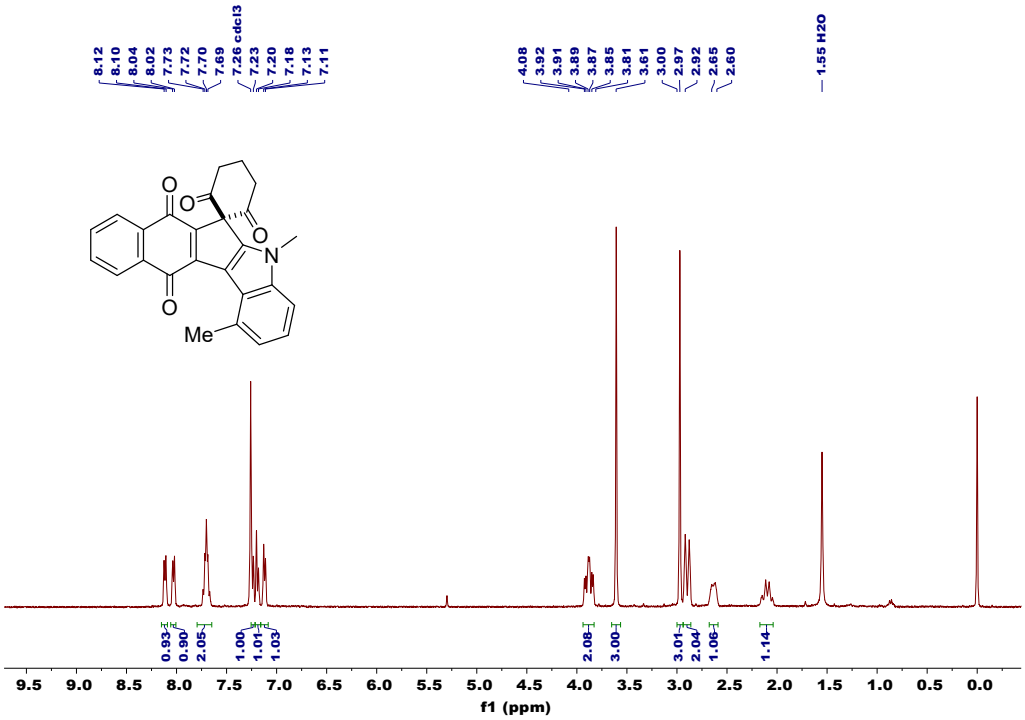


^{13}C NMR (101 MHz)

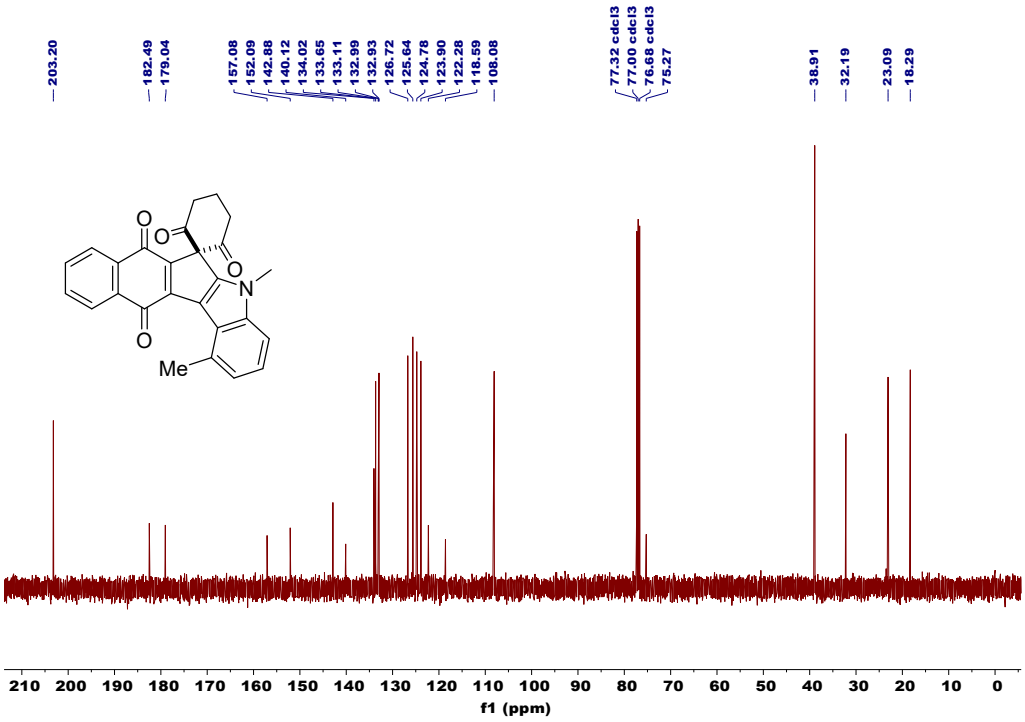


1,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ba)

^{1}H NMR (400 MHz)

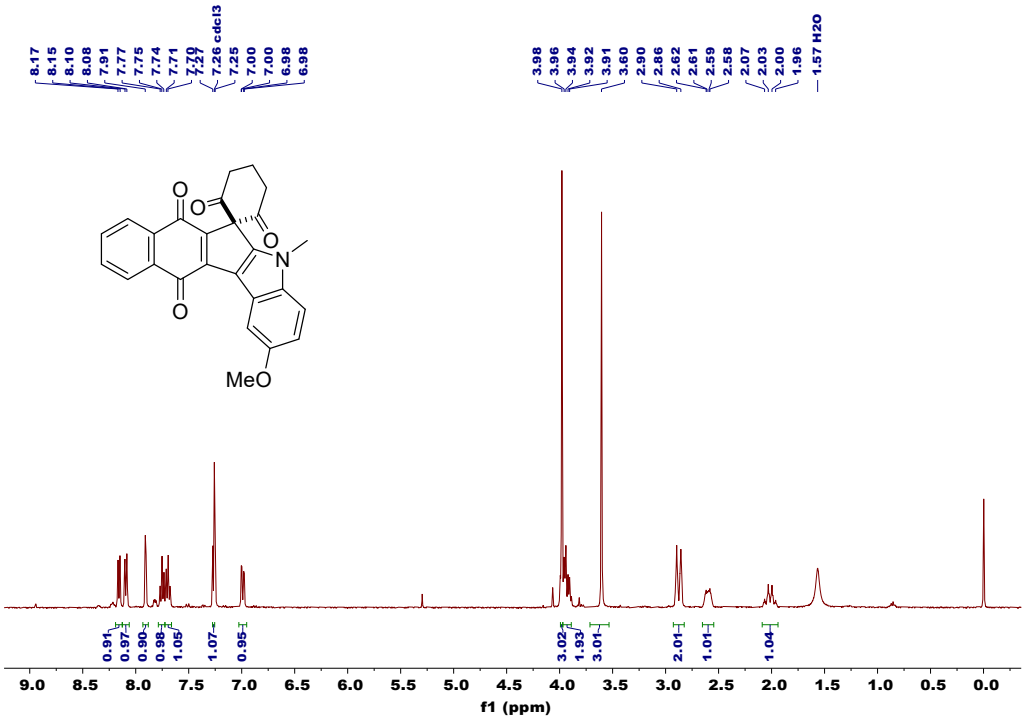


^{13}C NMR (101 MHz)

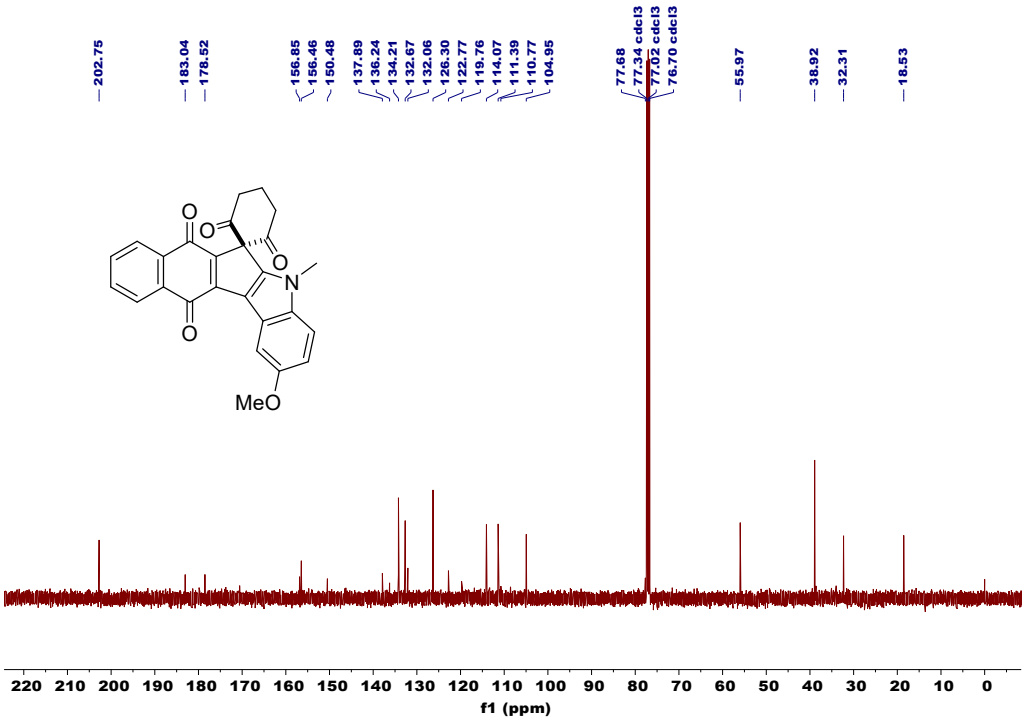


2-methoxy-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ea)

^{1}H NMR (400 MHz)

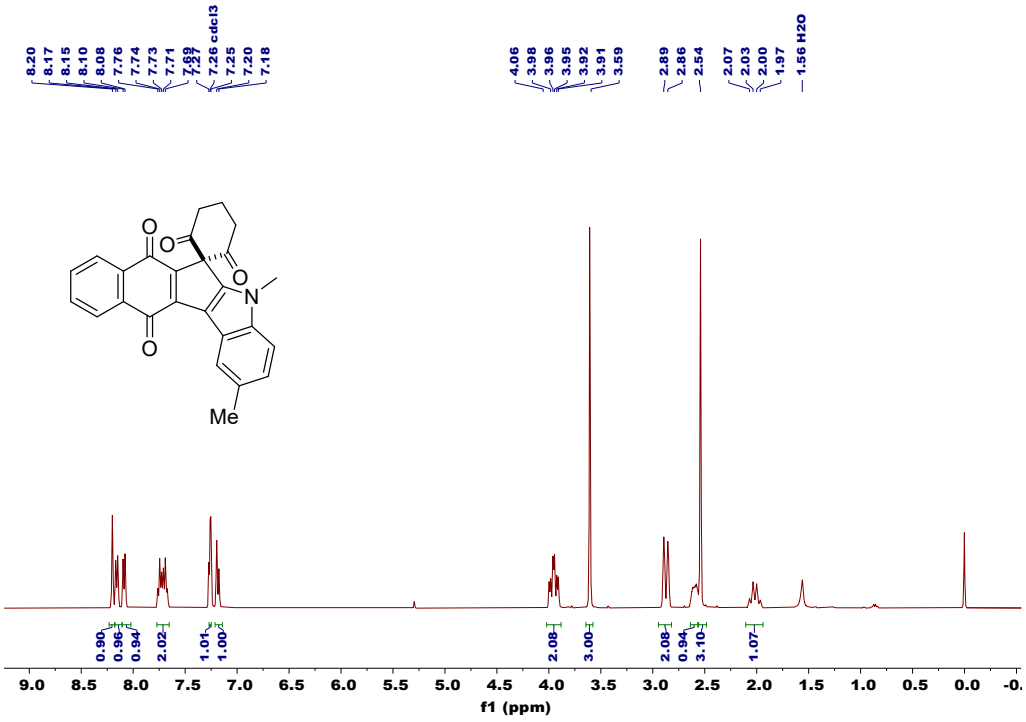


^{13}C NMR (101 MHz)

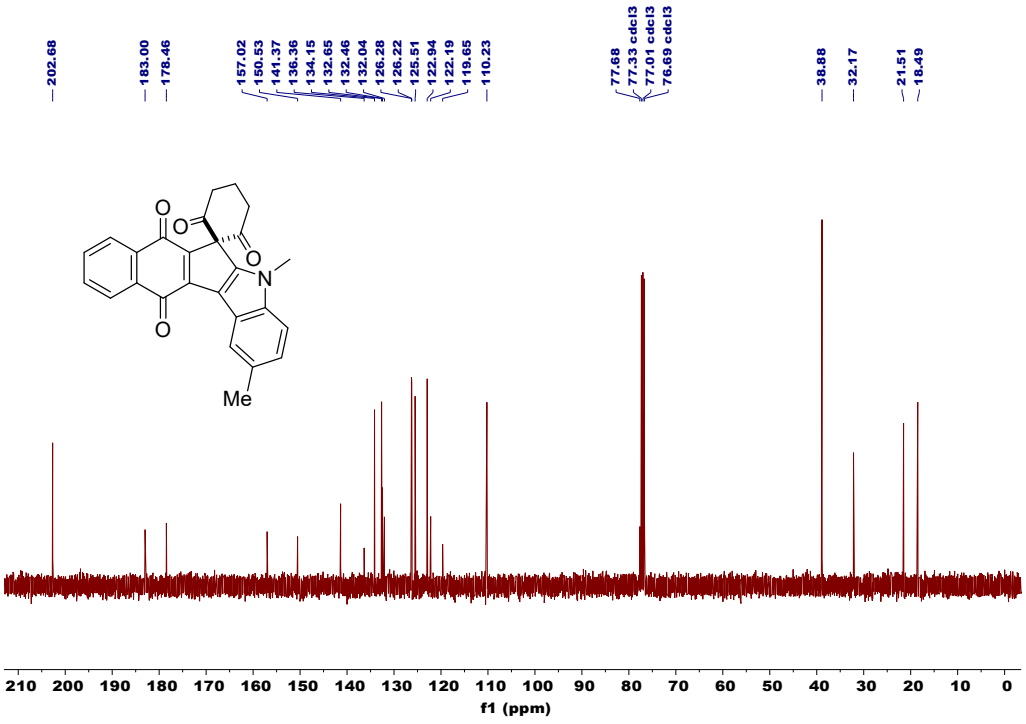


2,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3fa)

^{1}H NMR (400 MHz)

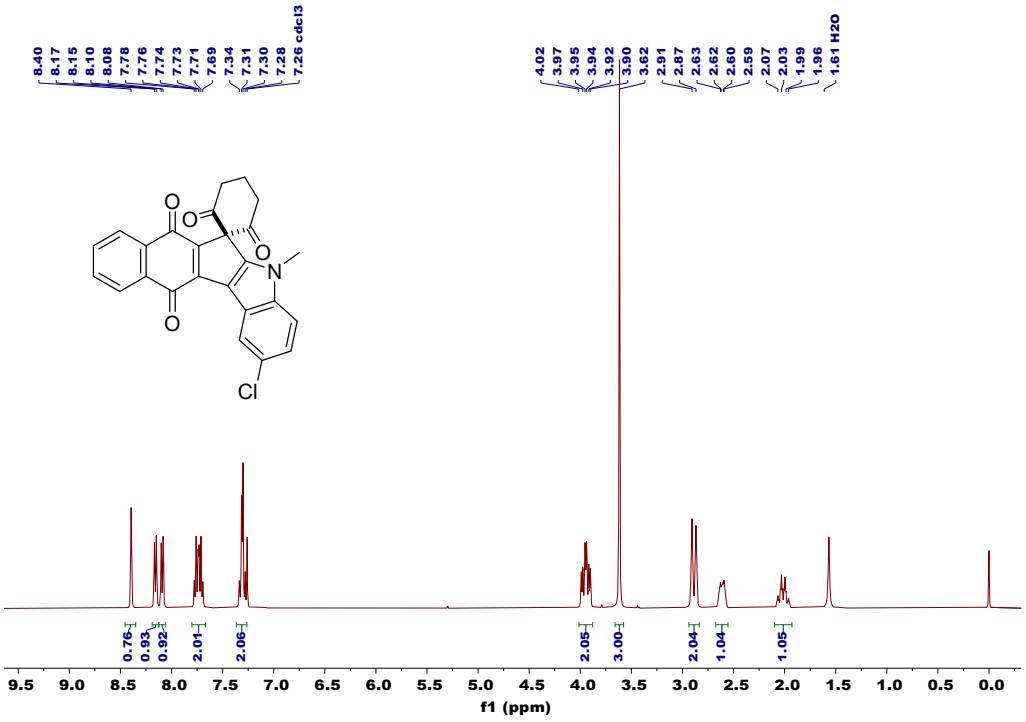


^{13}C NMR (101 MHz)

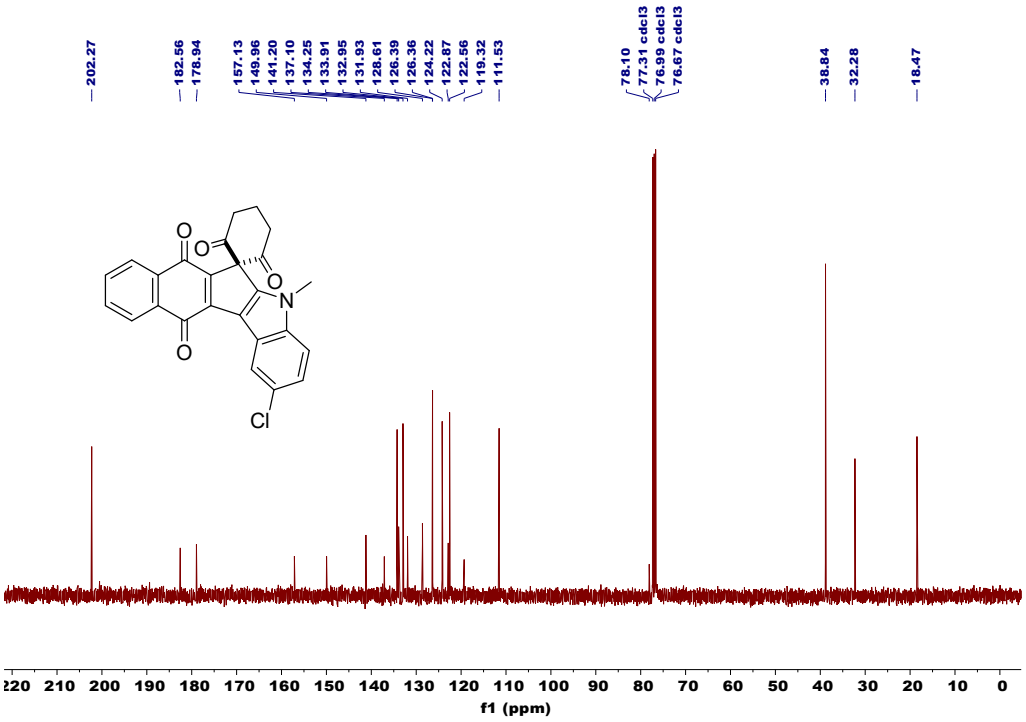


2-chloro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ga)

^{1}H NMR (400 MHz)

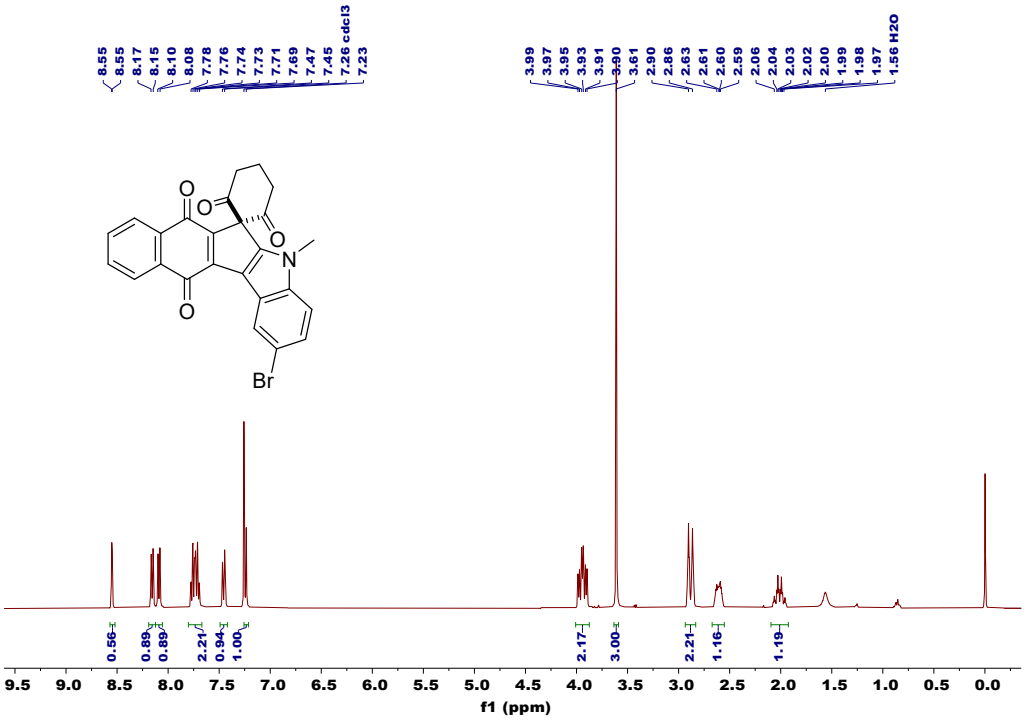


^{13}C NMR (101 MHz)

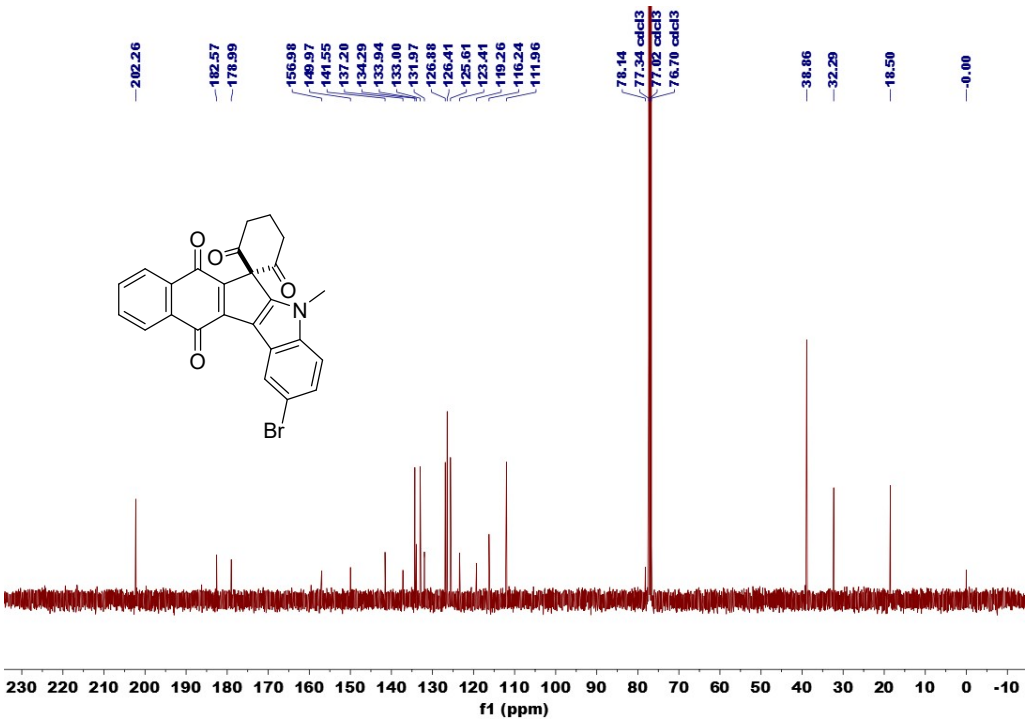


2-bromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ha)

^{1}H NMR (400 MHz)

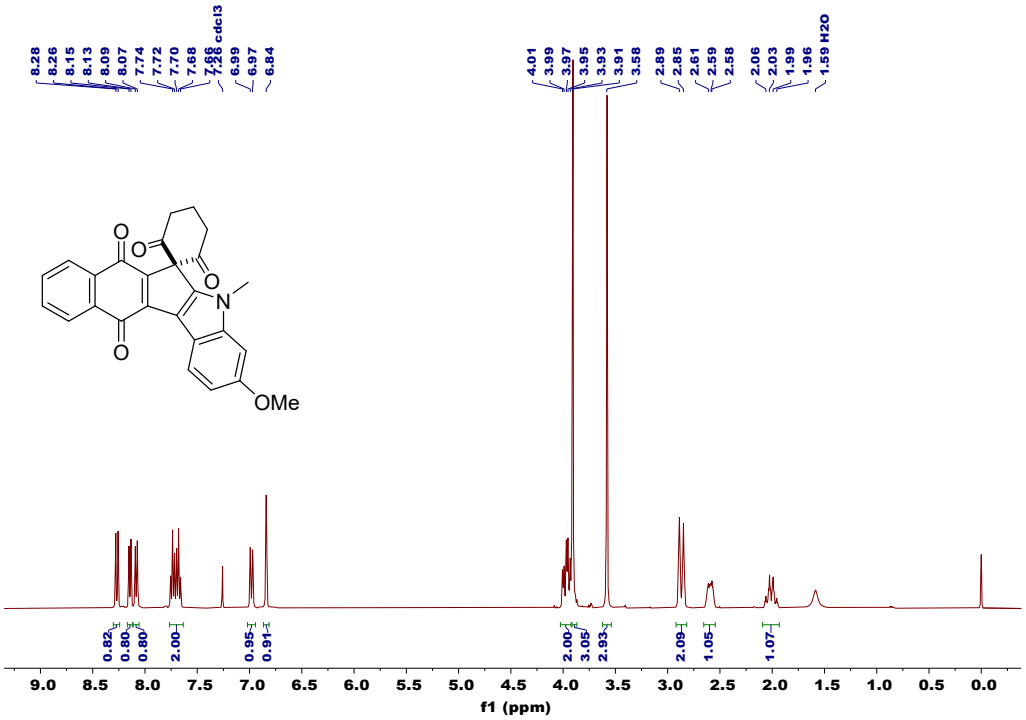


^{13}C NMR (101 MHz)

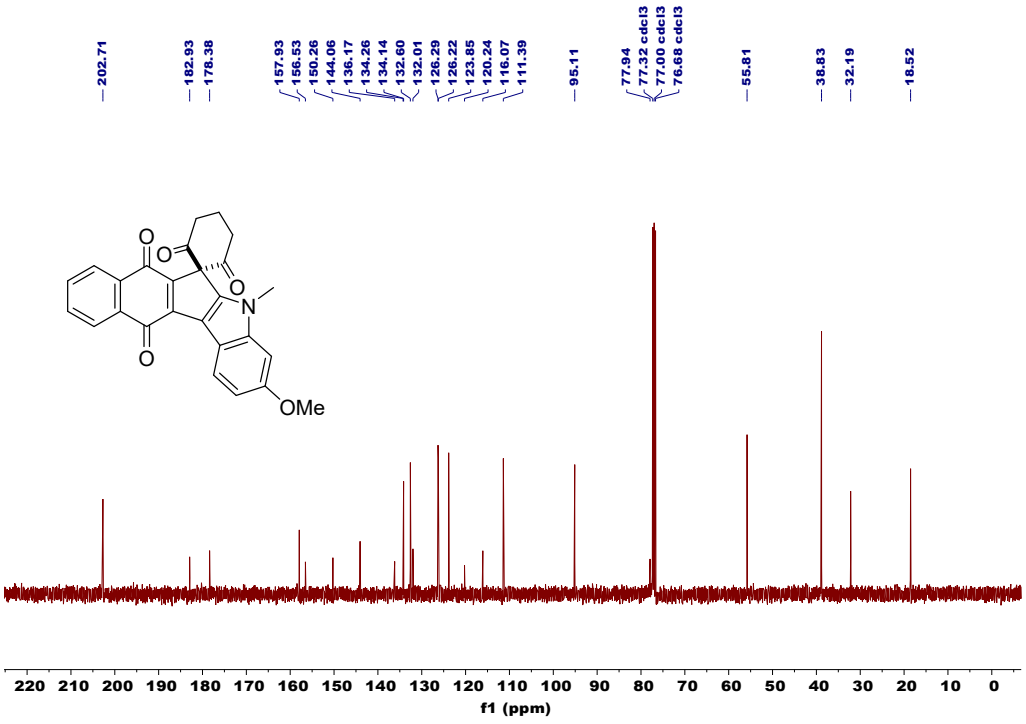


3-methoxy-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ia)

^{1}H NMR (400 MHz)

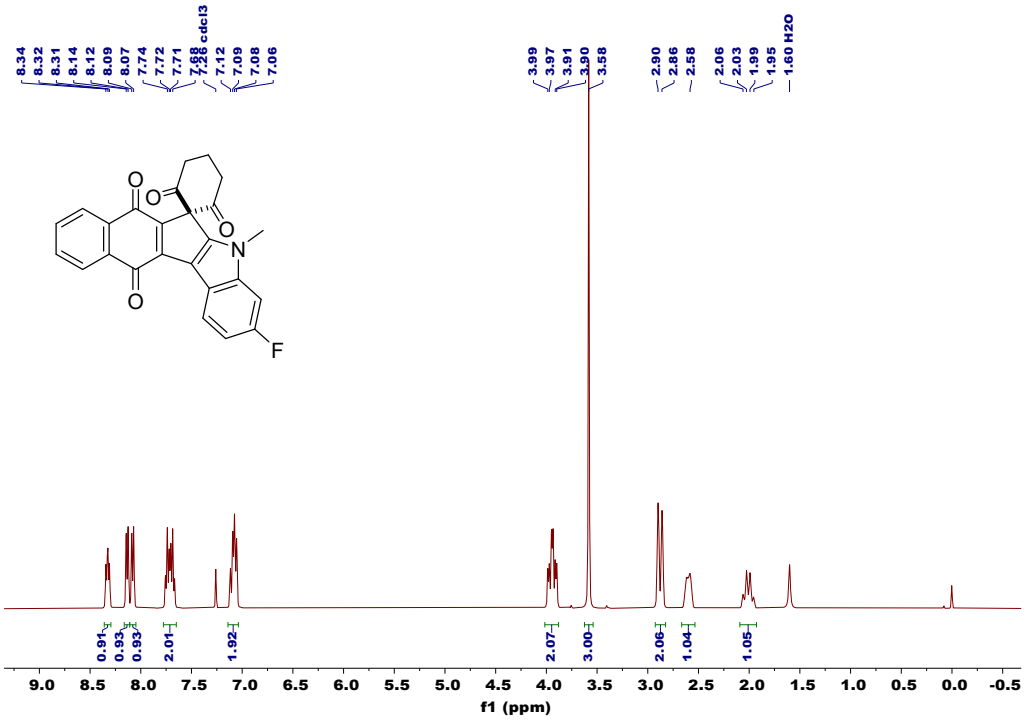


^{13}C NMR (101 MHz)

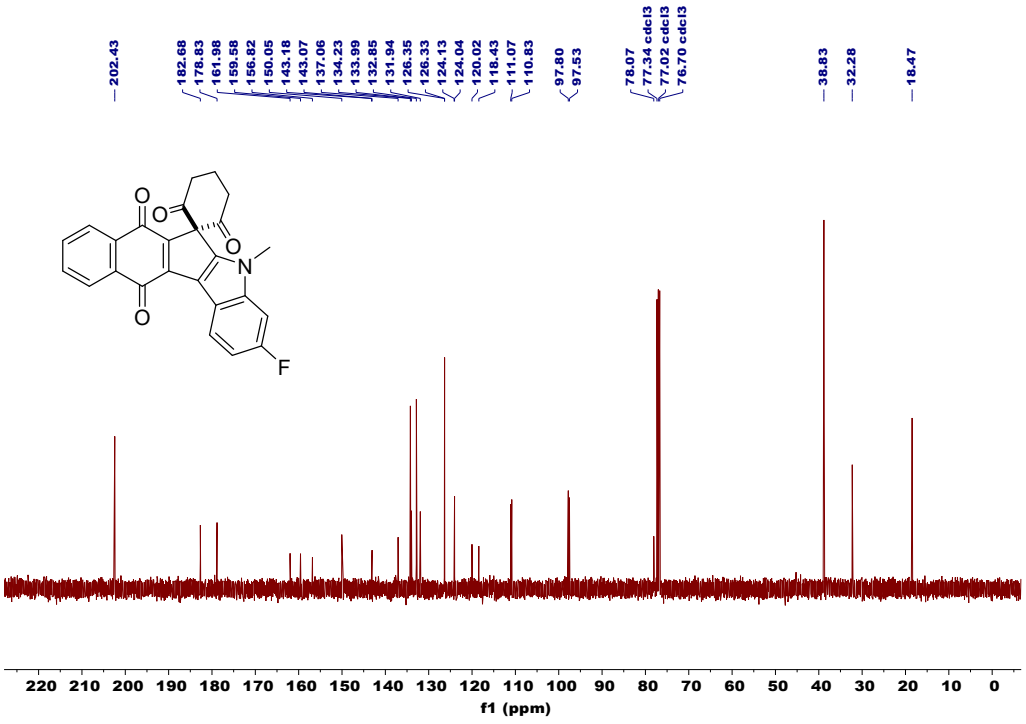


3-fluoro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ja)

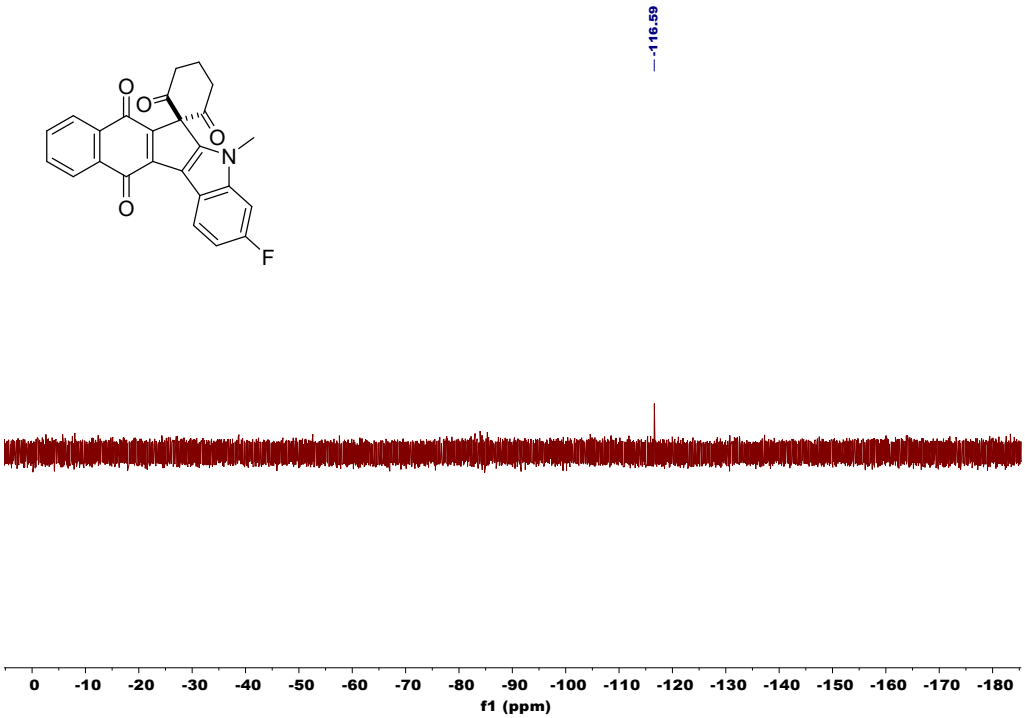
^{1}H NMR (400 MHz)



^{13}C NMR (101 MHz)

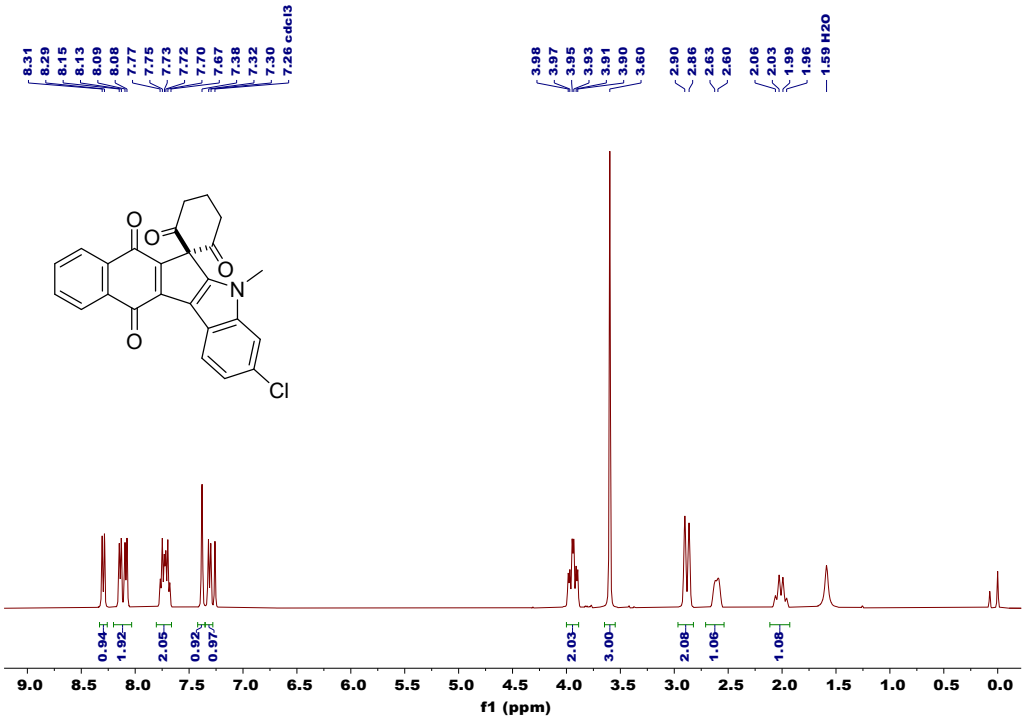


^{19}F NMR (376 MHz)

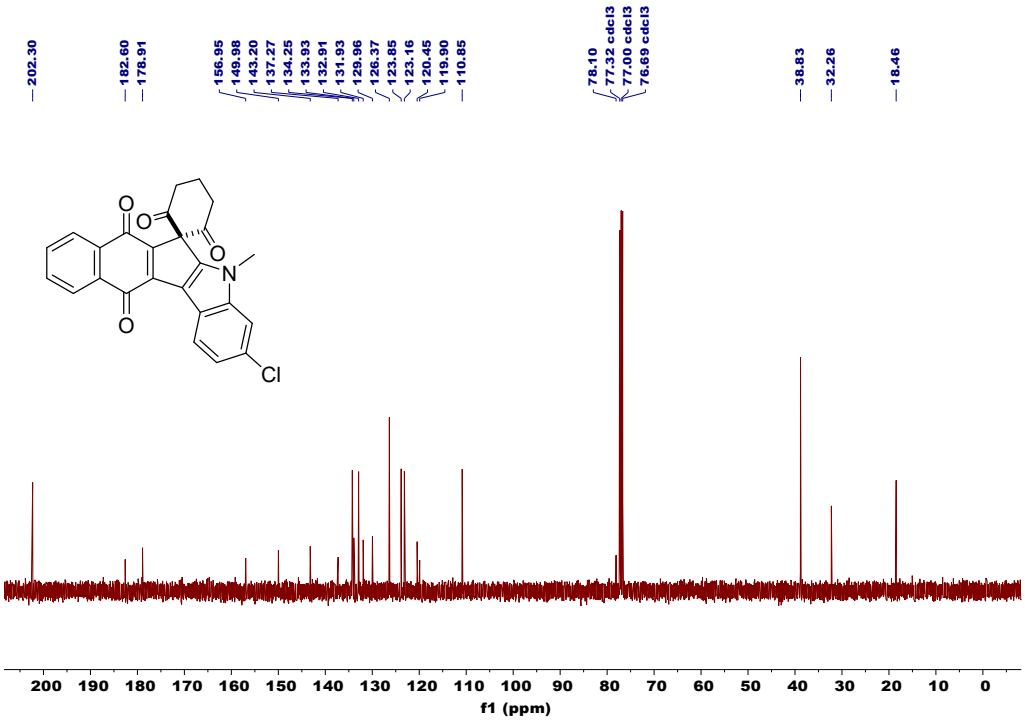


3-chloro-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ka)

^{1}H NMR (400 MHz)

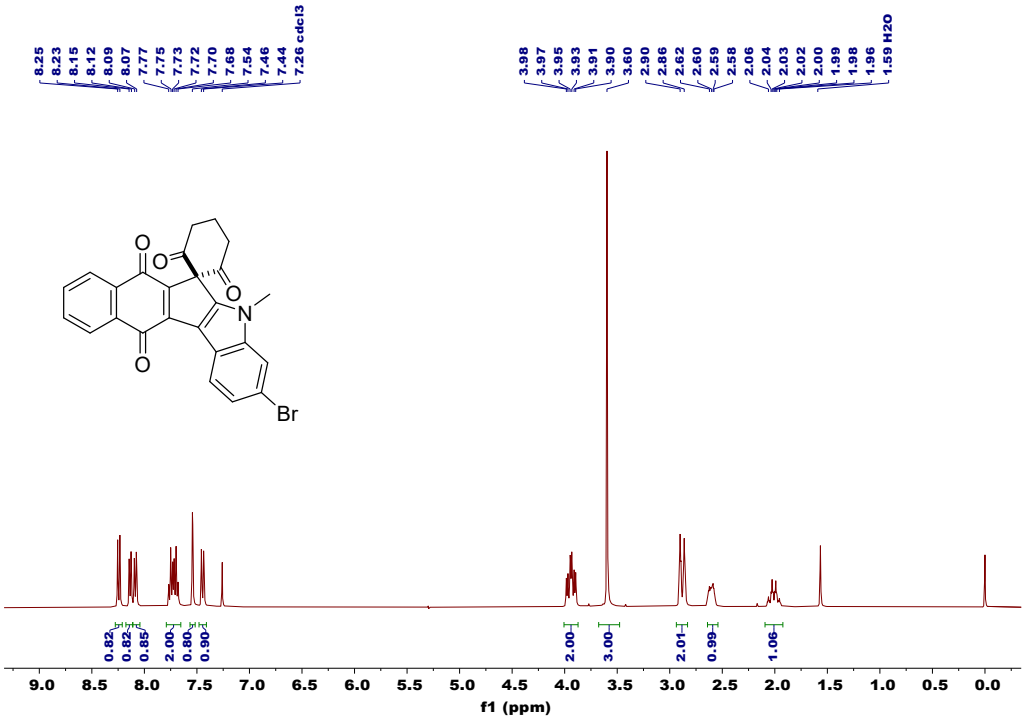


^{13}C NMR (101 MHz)

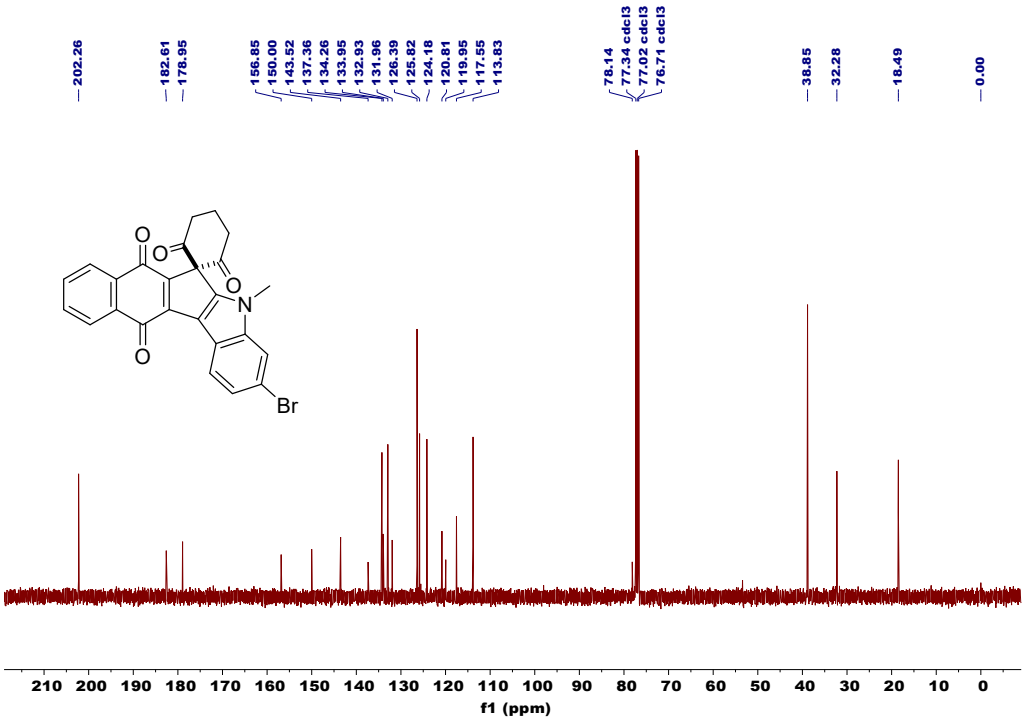


3-bromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3la)

^{1}H NMR (400 MHz)

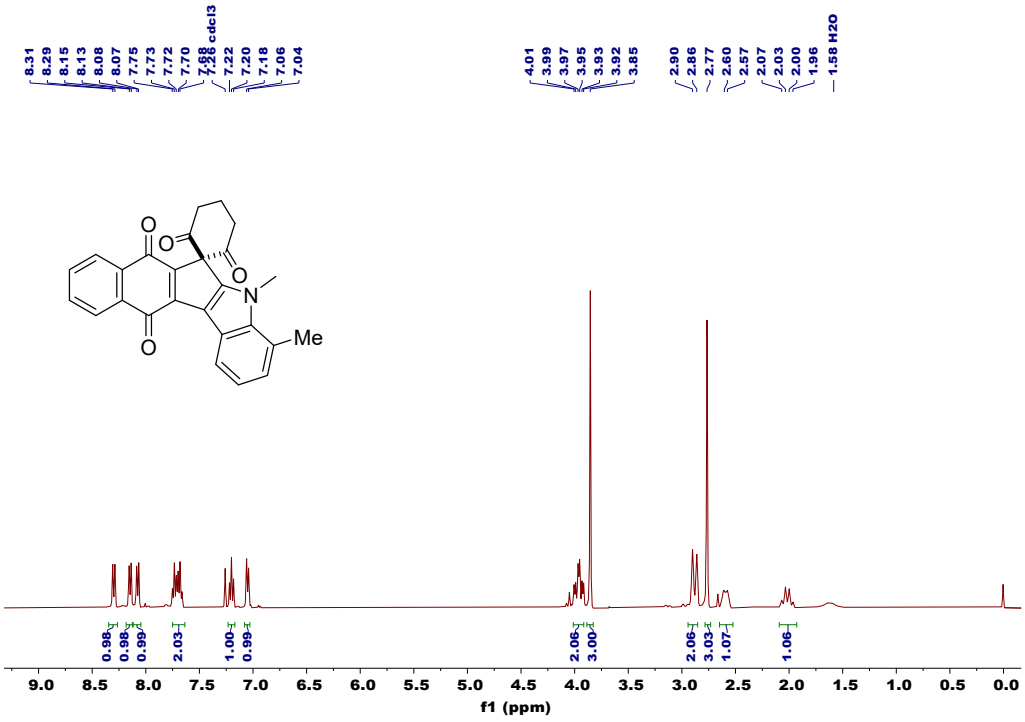


^{13}C NMR (101 MHz)

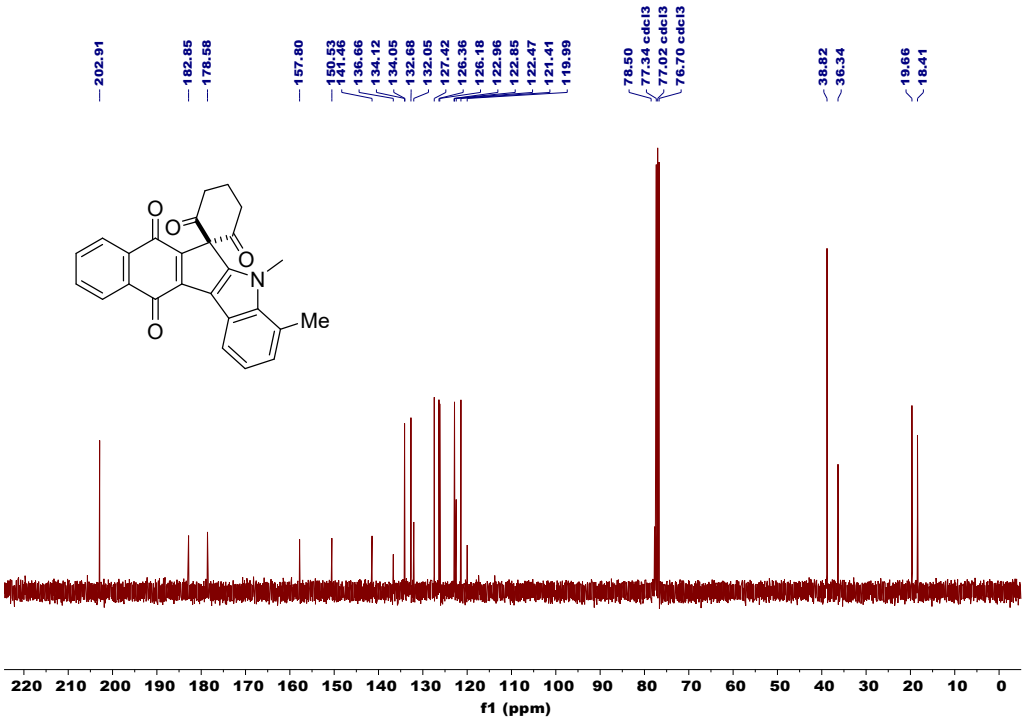


4,5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ma)

^{1}H NMR (400 MHz)

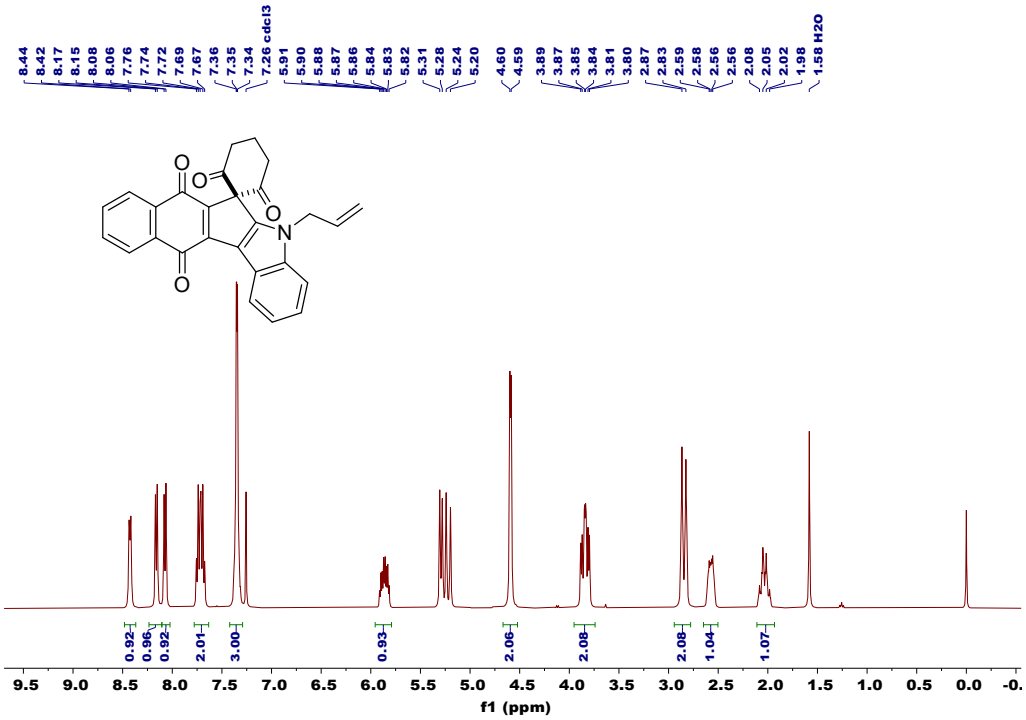


^{13}C NMR (101 MHz)

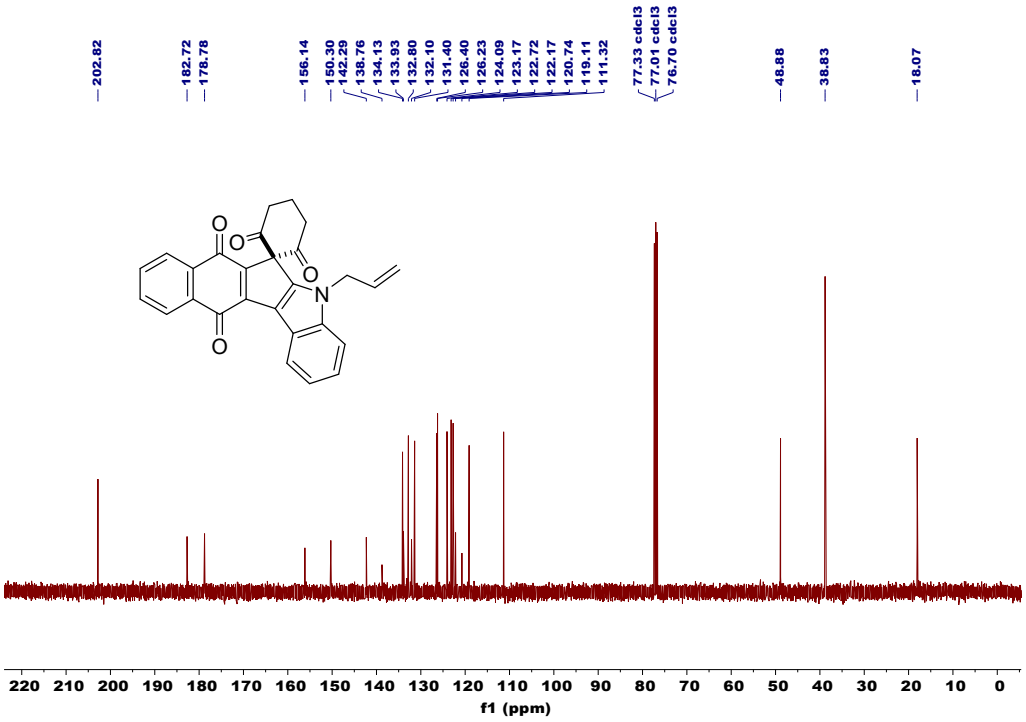


5-allyl-5H-spiro[benzo[5,6]indeno[2,1-b]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3pa)

^{1}H NMR (400 MHz)

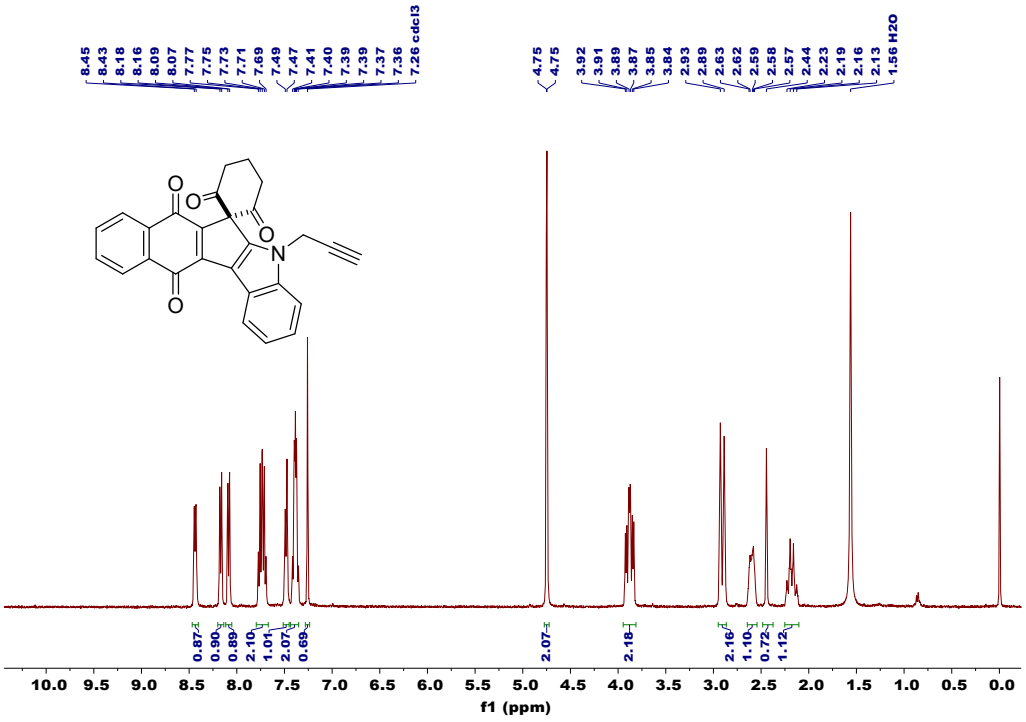


^{13}C NMR (101 MHz)

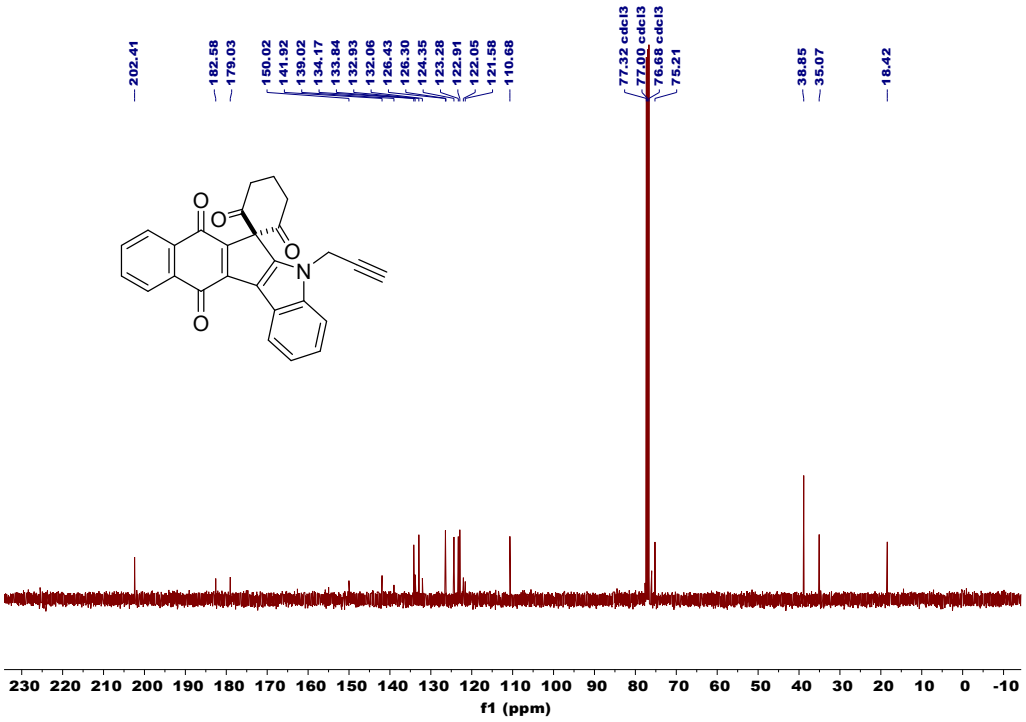


5-(prop-2-yn-1-yl)-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3qa)

^{1}H NMR (400 MHz)

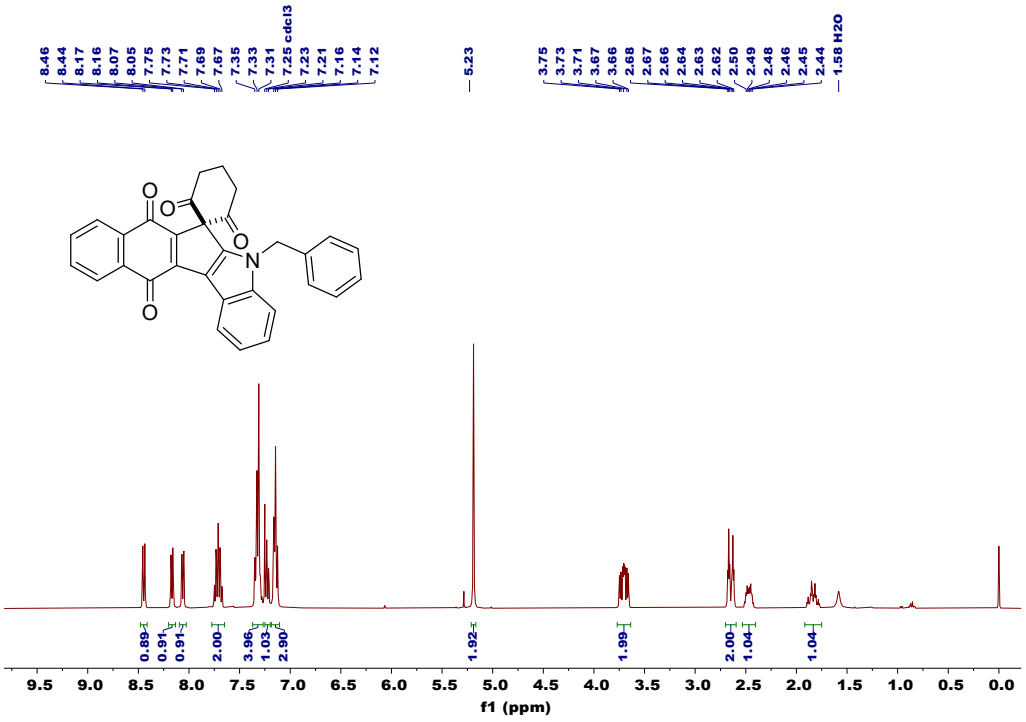


^{13}C NMR (101 MHz)

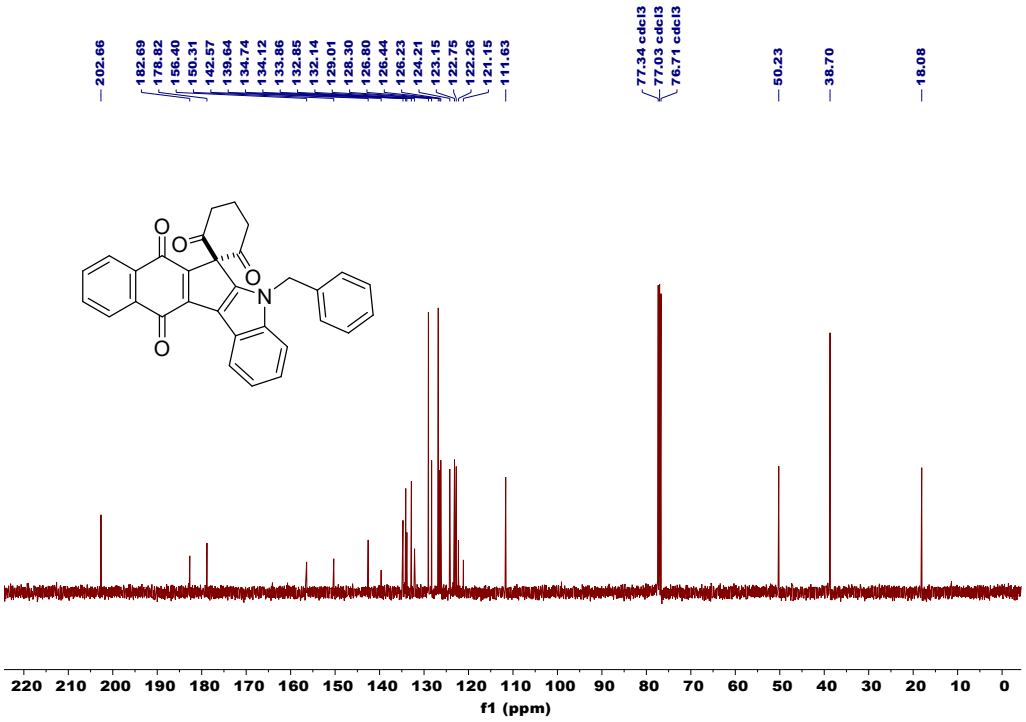


5-benzyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ra)

^{1}H NMR (400 MHz)

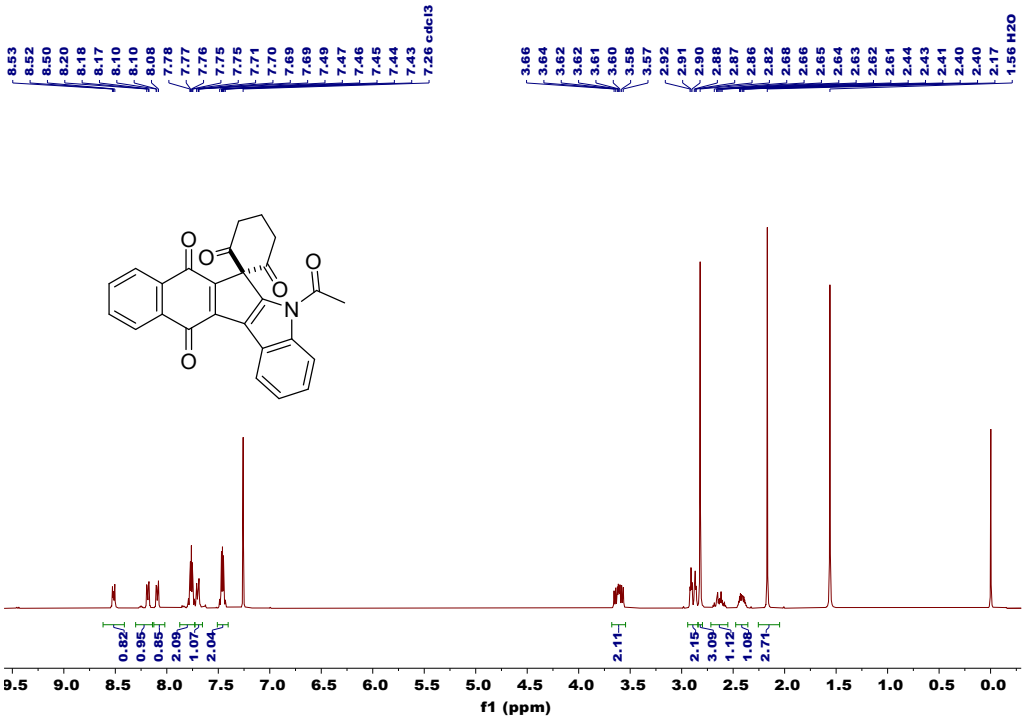


^{13}C NMR (101 MHz)

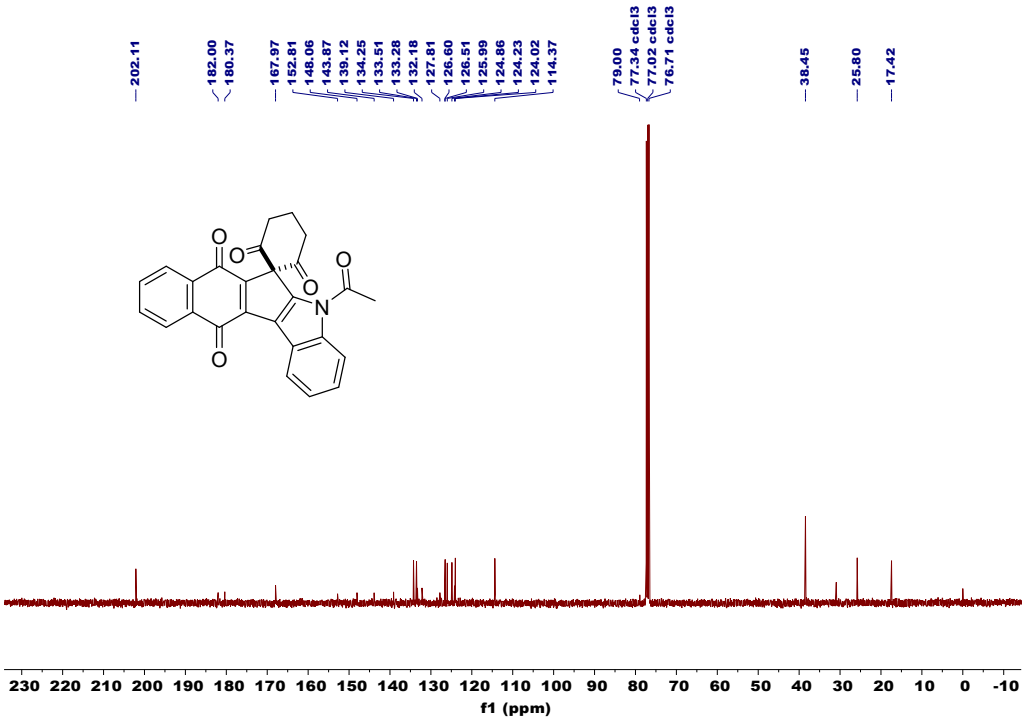


5-acetyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3sa)

^{1}H NMR (400 MHz)

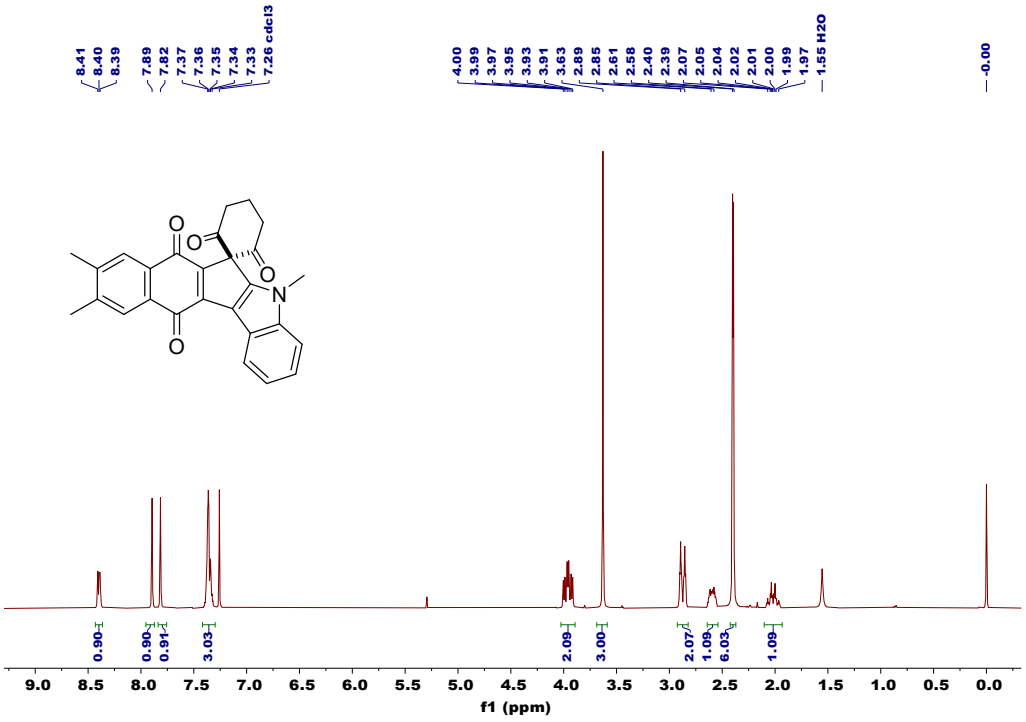


^{13}C NMR (101 MHz)

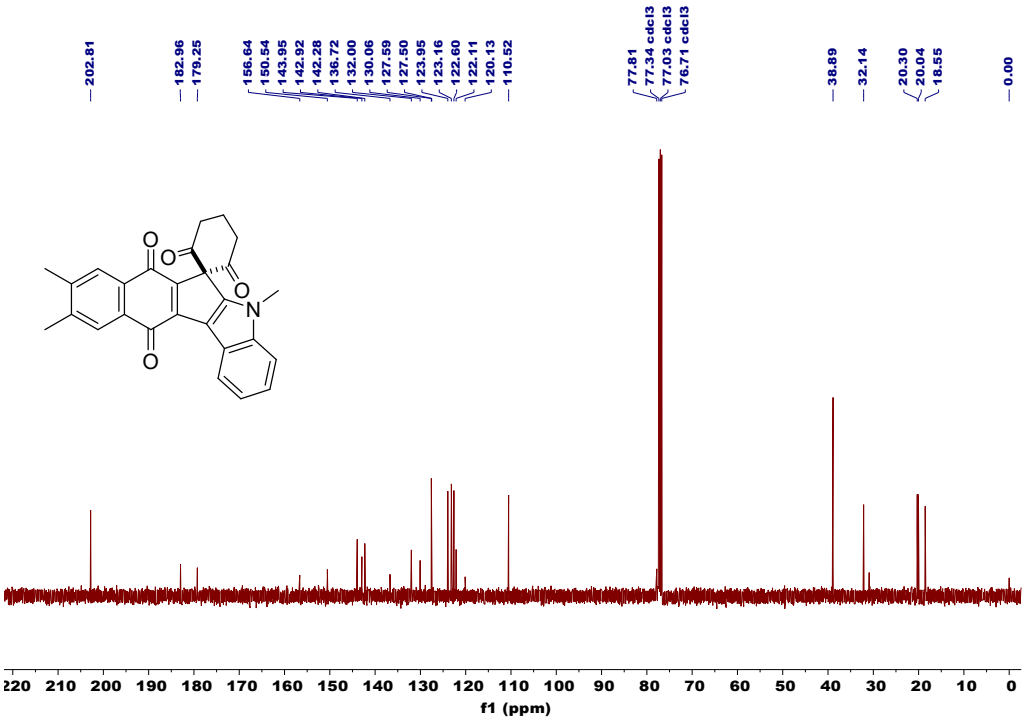


5,9,10-trimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ta)

^{1}H NMR (400 MHz)

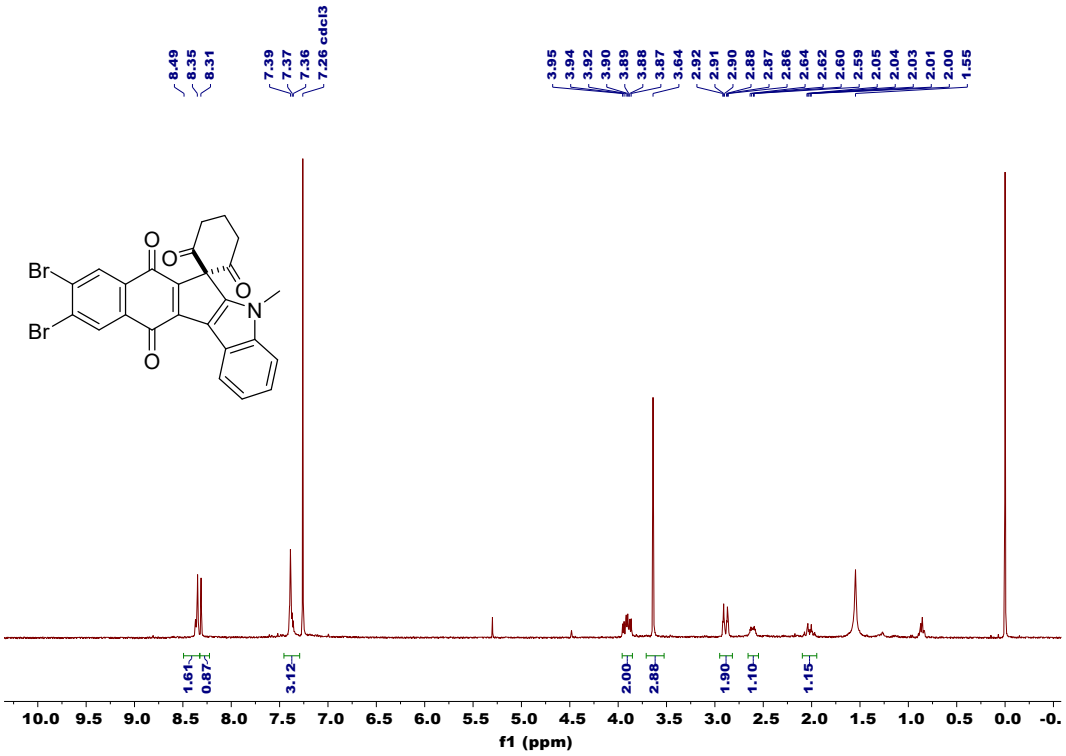


^{13}C NMR (101 MHz)

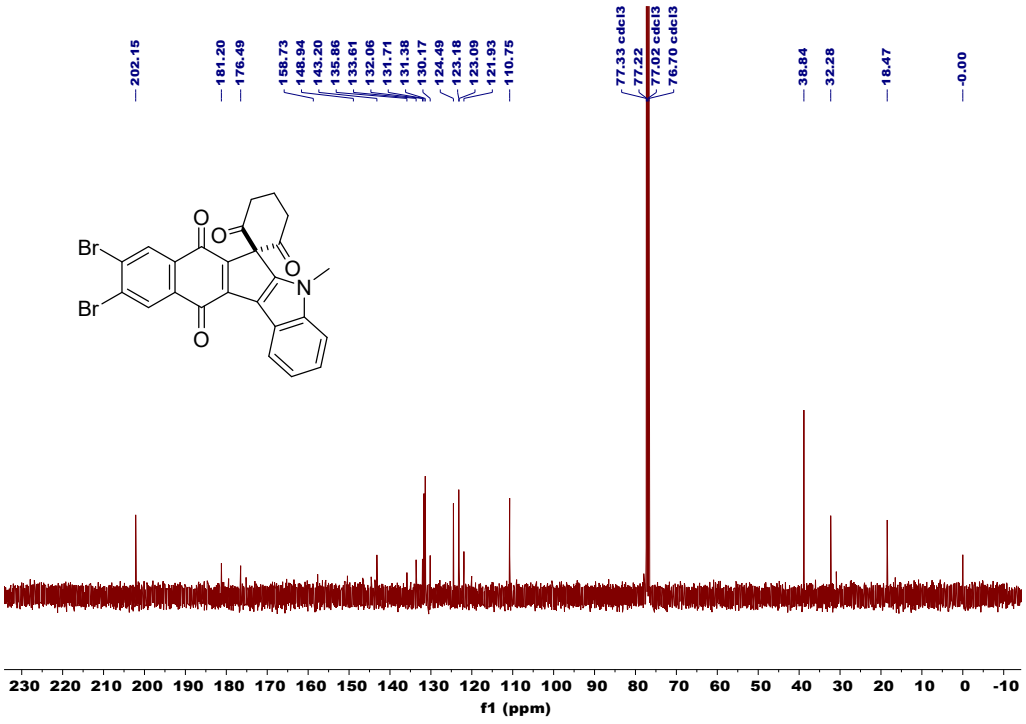


9,10-dibromo-5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ua)

^{1}H NMR (400 MHz)

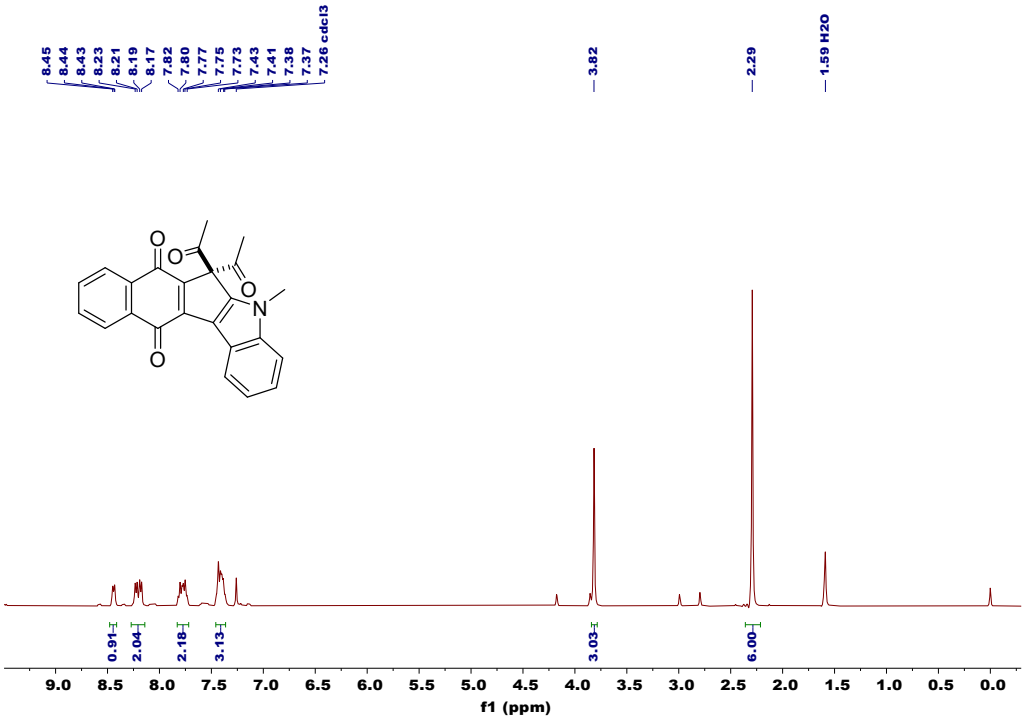


^{13}C NMR (101 MHz)

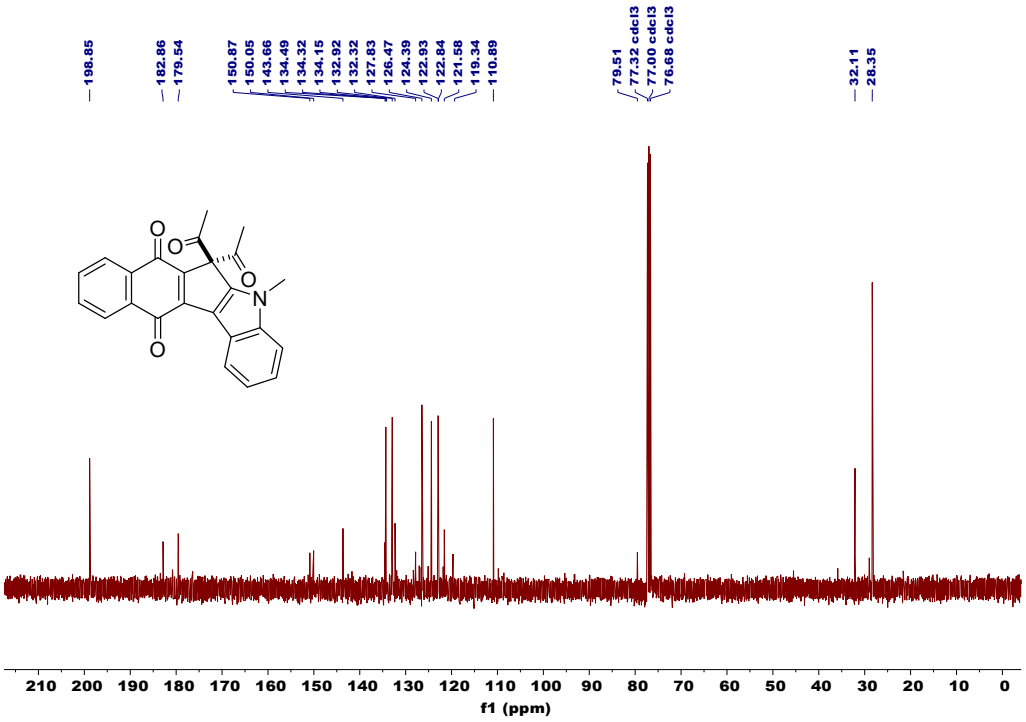


6,6-diacetyl-5-methyl-5,6-dihydrobenzo[5,6]indeno[2,1-*b*]indole-7,12-dione (3ab)

^{1}H NMR (400 MHz)

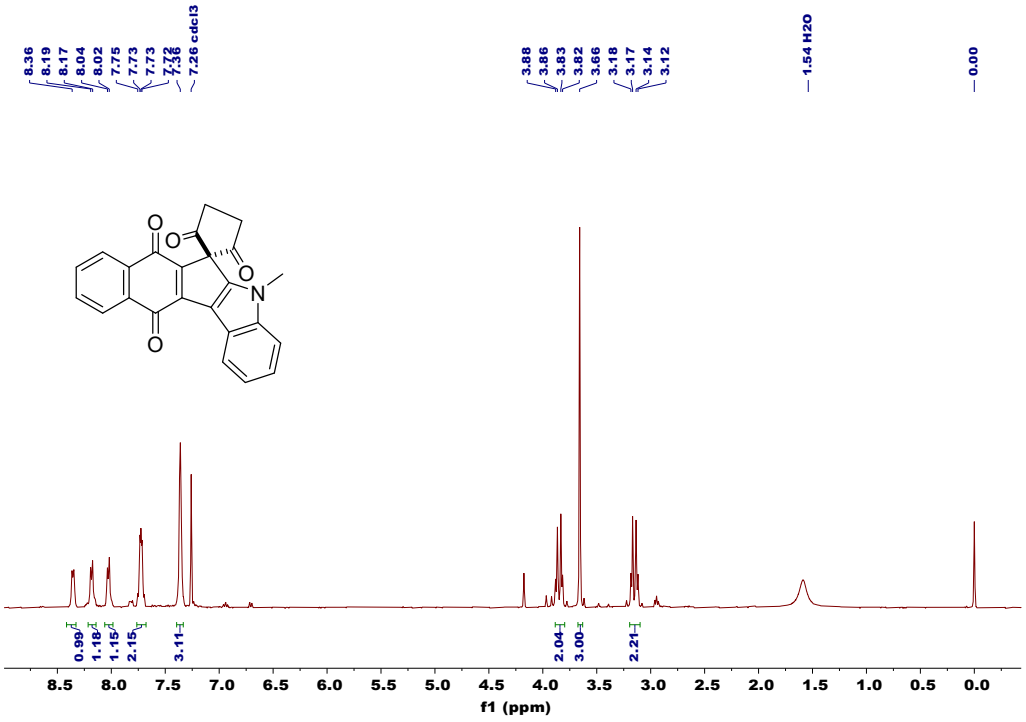


^{13}C NMR (101 MHz)

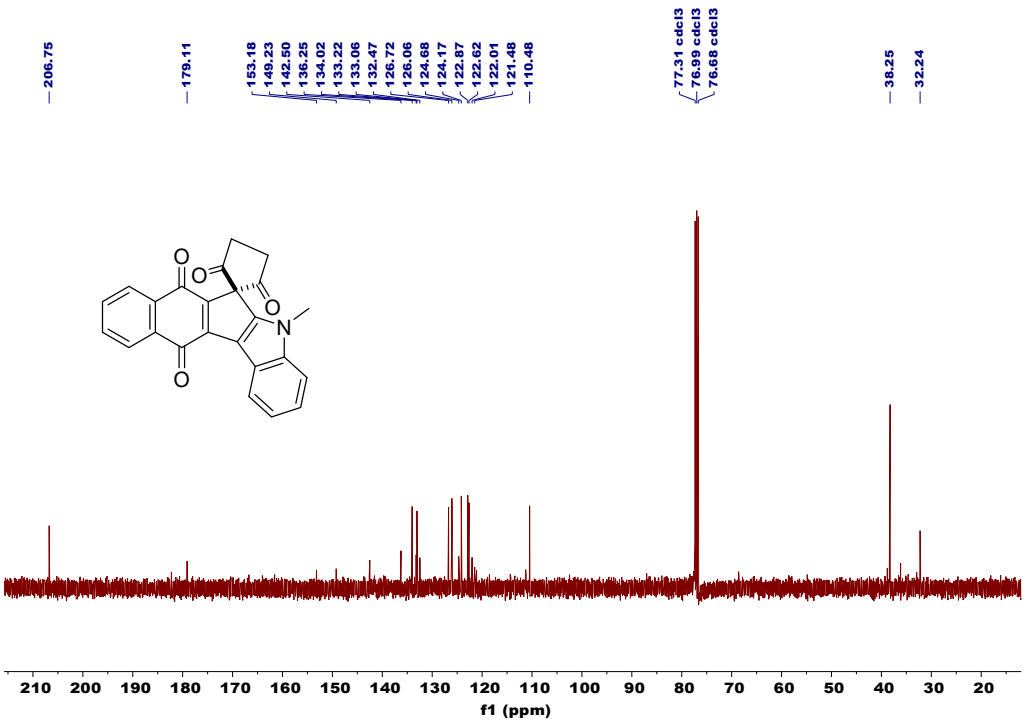


5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclopentane]-2',5',7,12-tetraone (3ac)

^{1}H NMR (400 MHz)

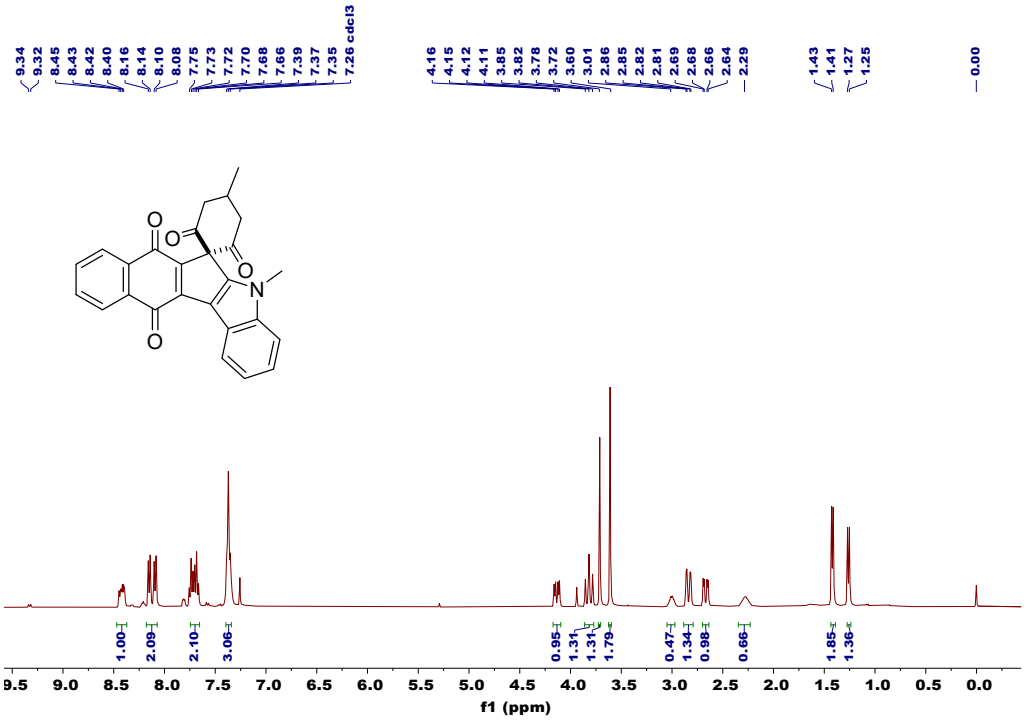


^{13}C NMR (101 MHz)

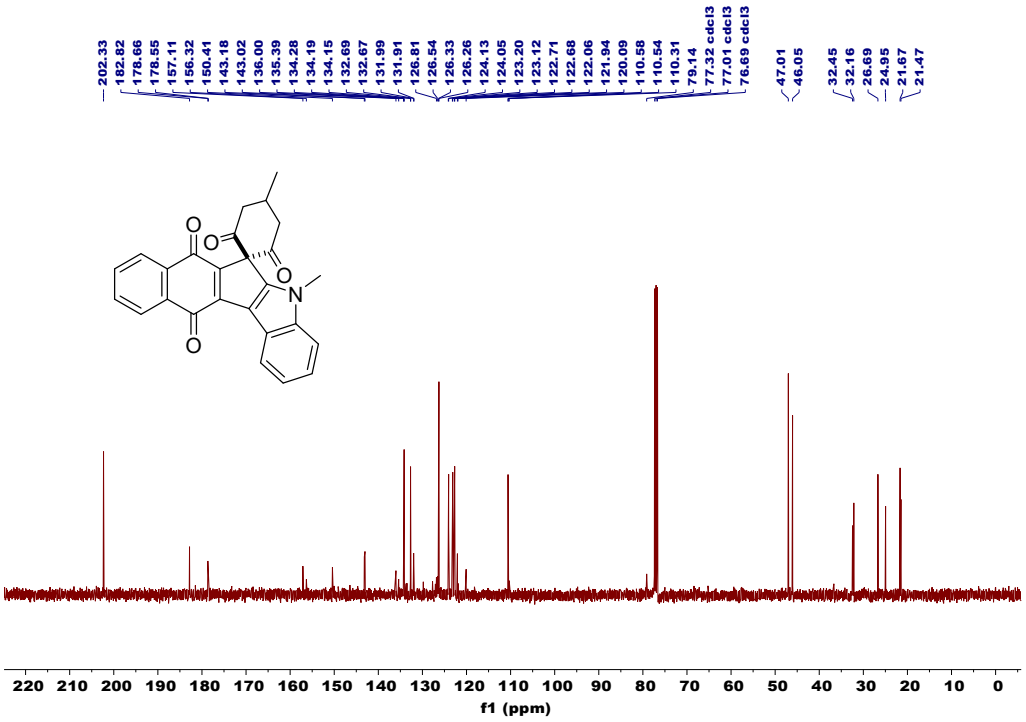


4',5-dimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ad)

^{1}H NMR (400 MHz)

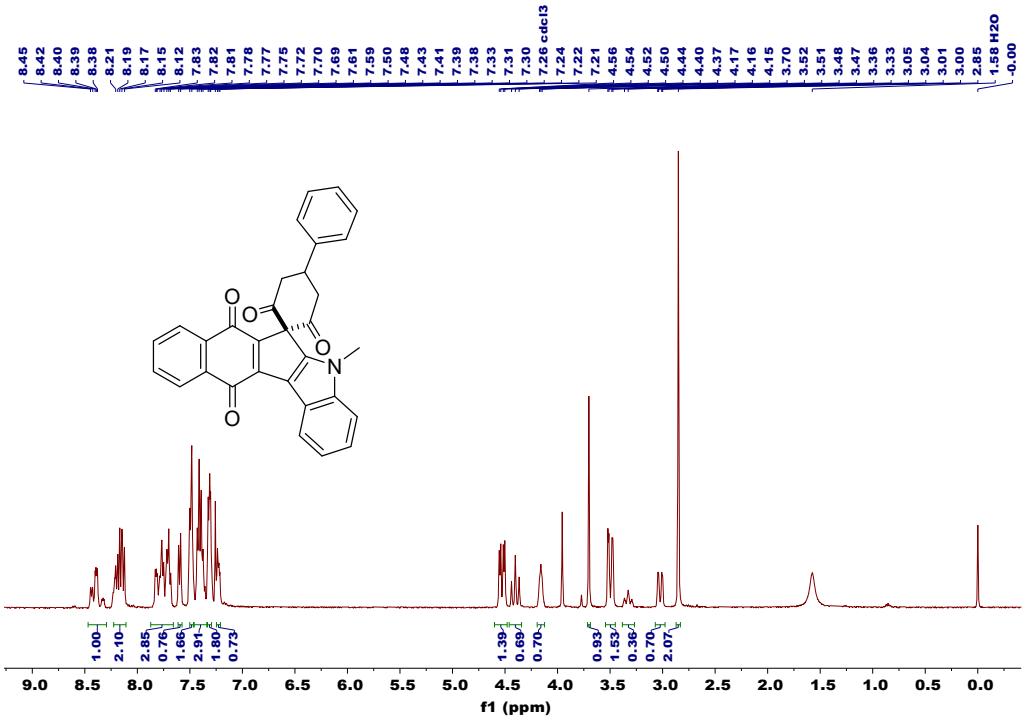


^{13}C NMR (101 MHz)

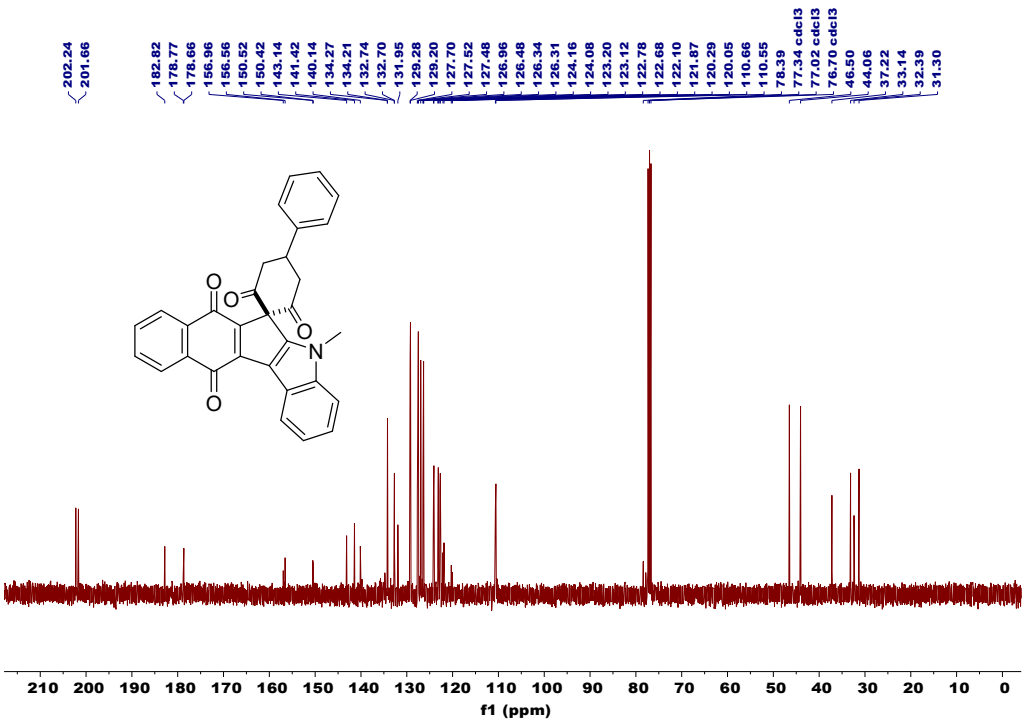


5-methyl-4'-phenyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3ae)

^{1}H NMR (400 MHz)

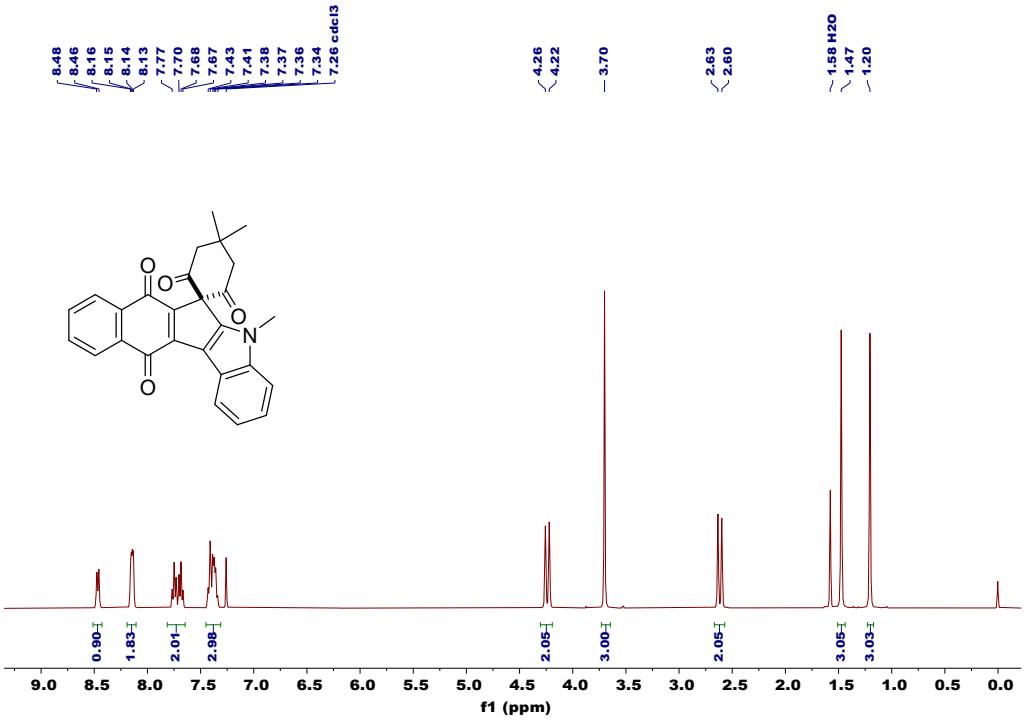


^{13}C NMR (101 MHz)

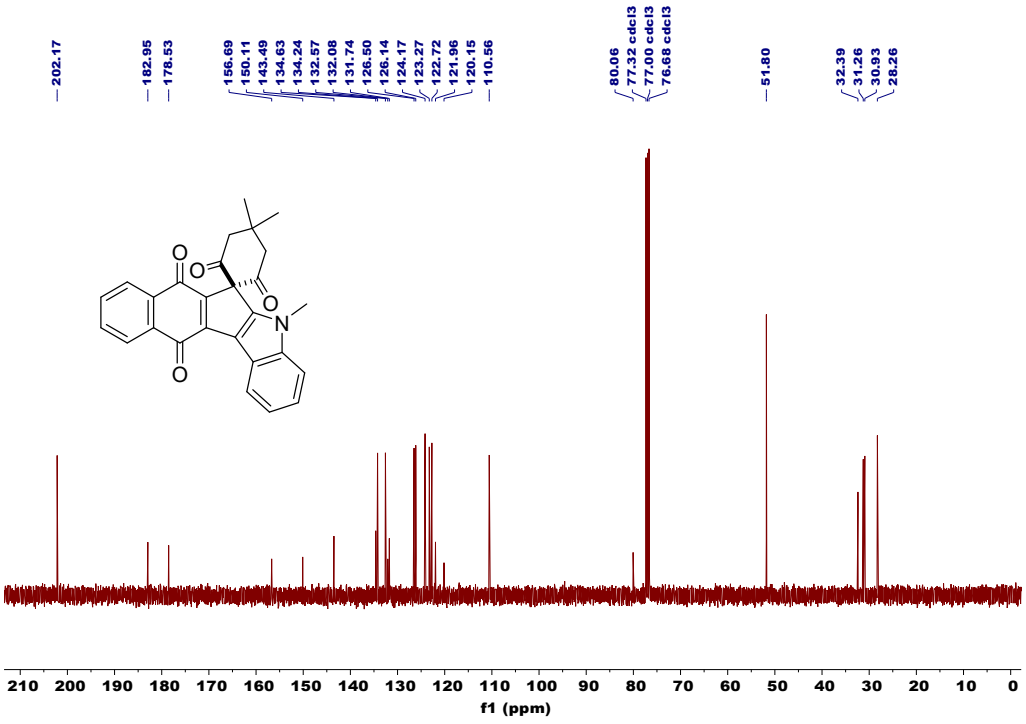


4',4',5-trimethyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane]-2',6',7,12-tetraone (3af)

^{1}H NMR (400 MHz)

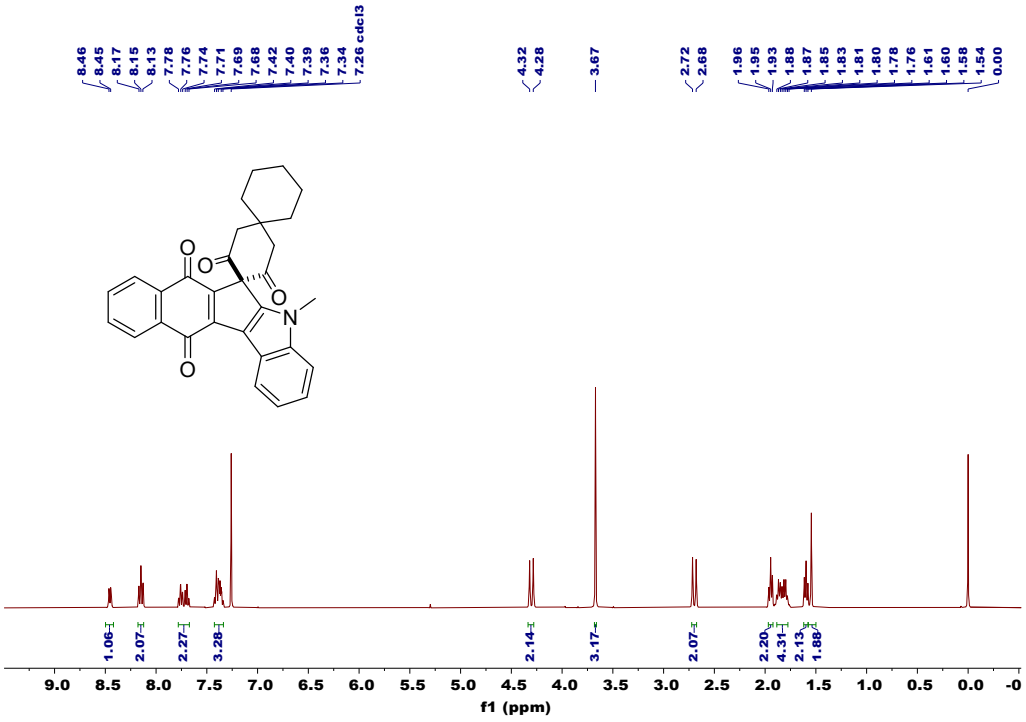


^{13}C NMR (101 MHz)

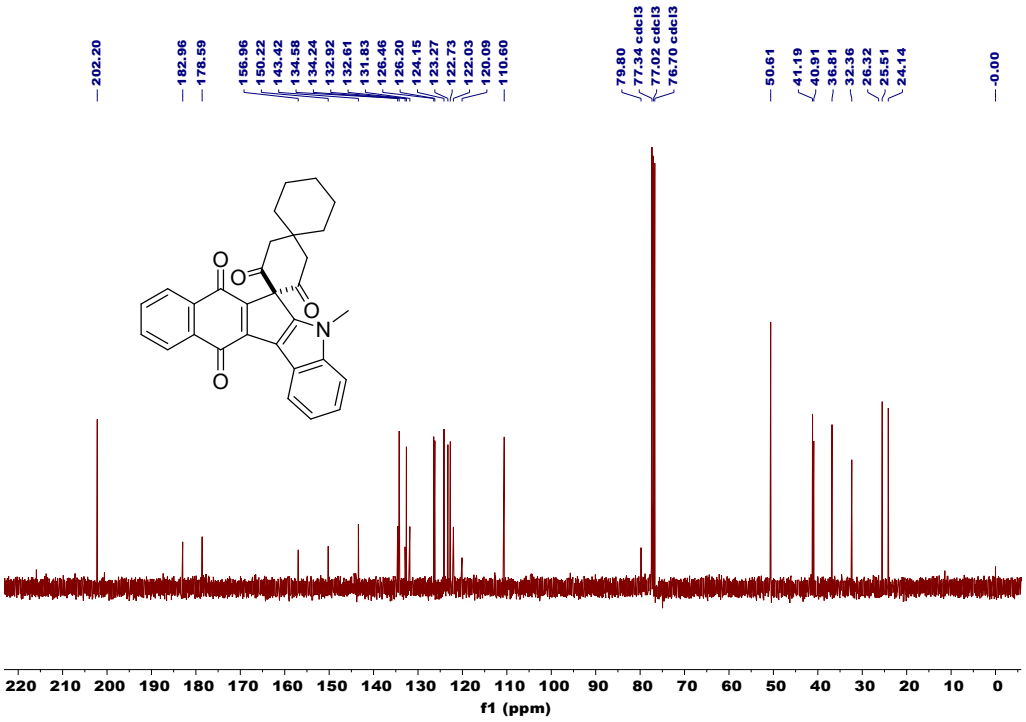


5-methyl-5*H*-dispiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cyclohexane-4',1''-cyclohexane]-2',6',7,12-tetraone (3ag)

^{1}H NMR (400 MHz)

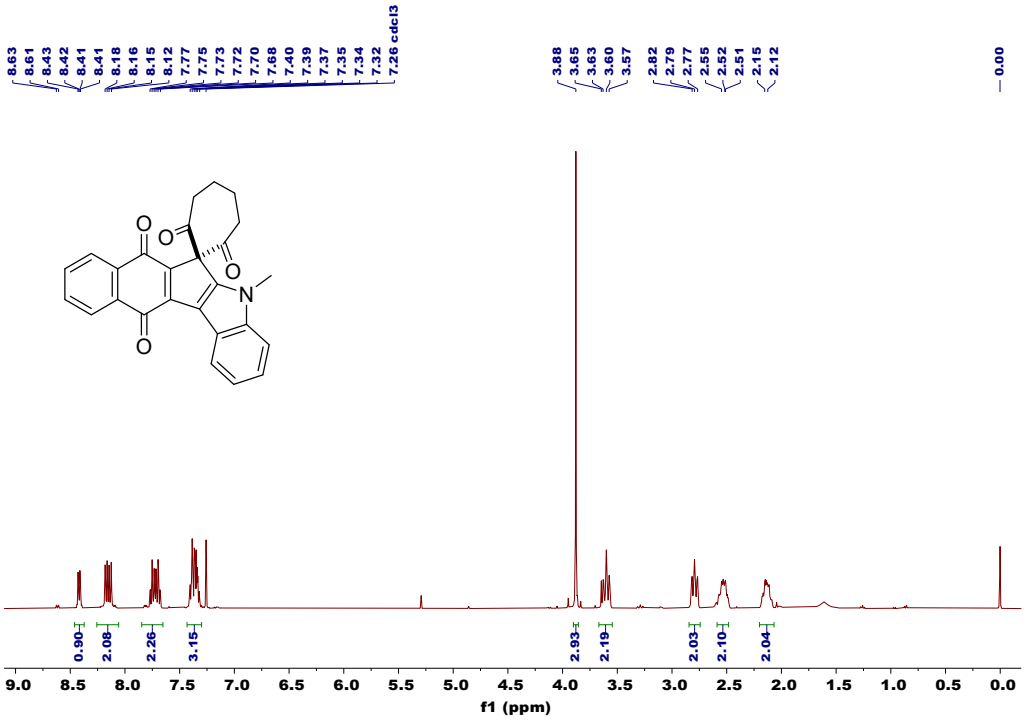


^{13}C NMR (101 MHz)

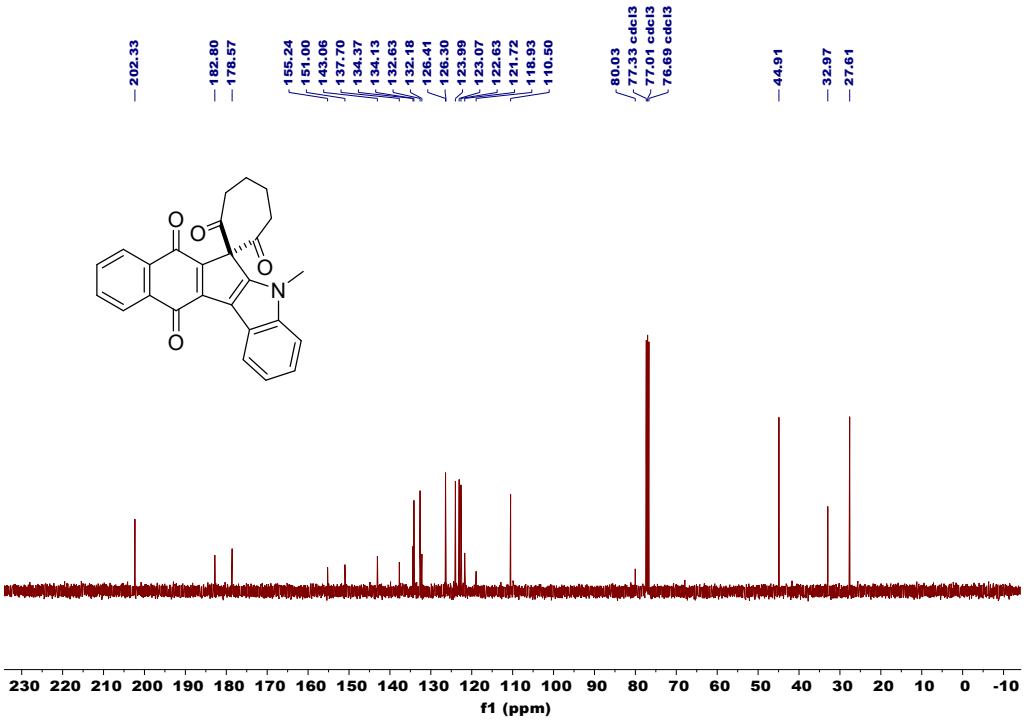


5-methyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,1'-cycloheptane]-2',7,7',12-tetraone (3ah)

^{1}H NMR (400 MHz)

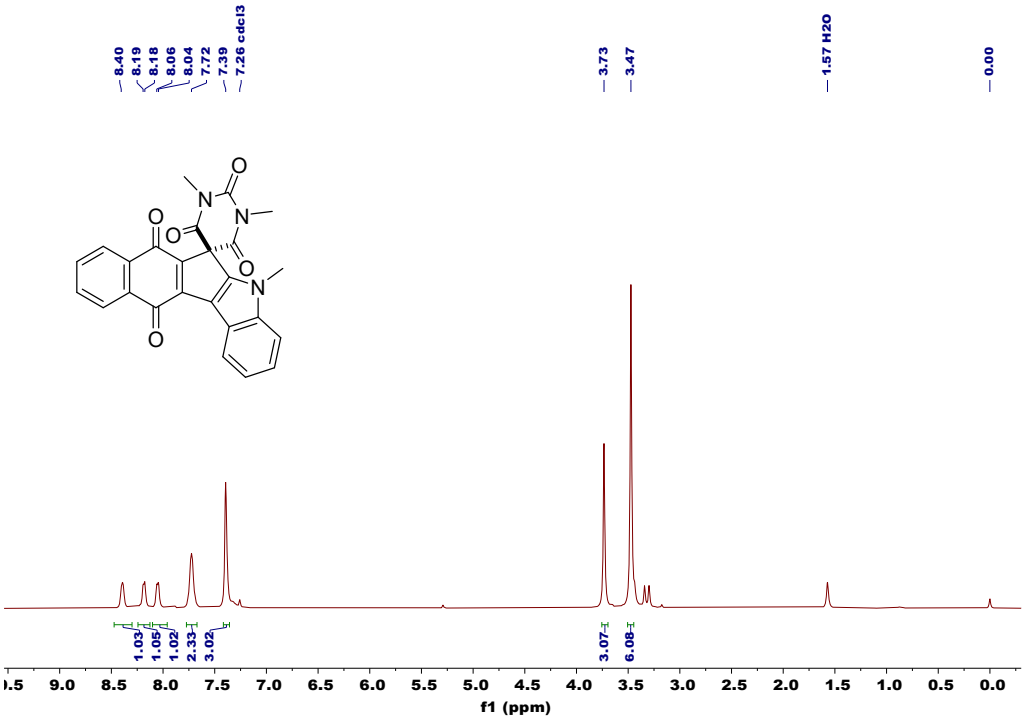


^{13}C NMR (101 MHz)

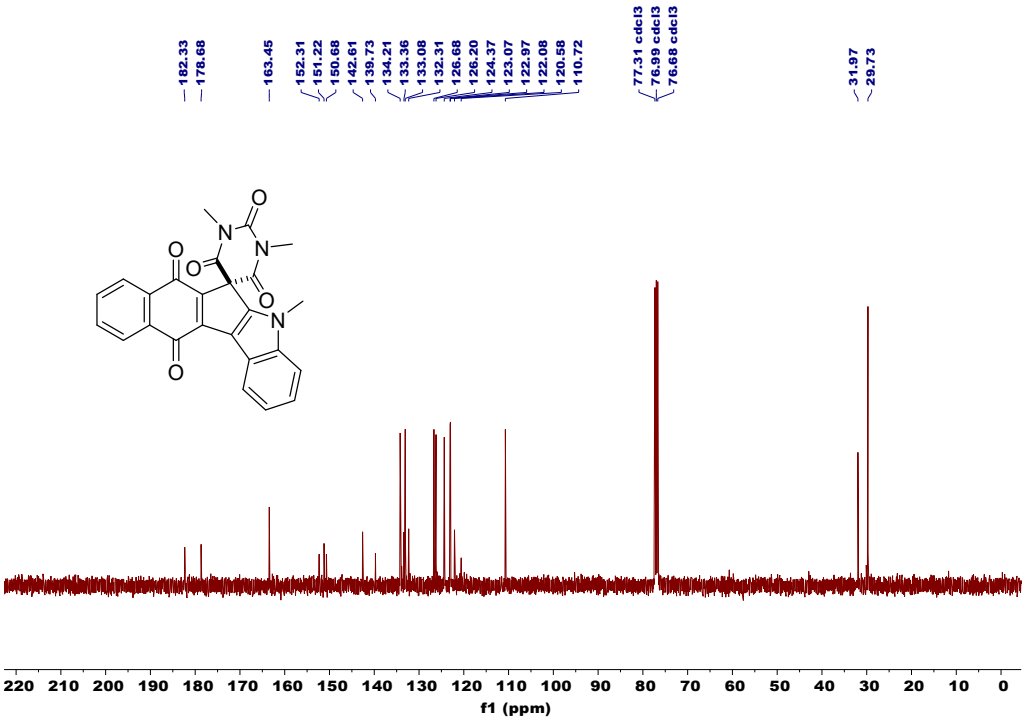


1',3',5-trimethyl-2'H,5H-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,5'-pyrimidine]-2',4',6',7,12(1'*H*,3'*H*)-pentaone (3ai)

^{1}H NMR (400 MHz)

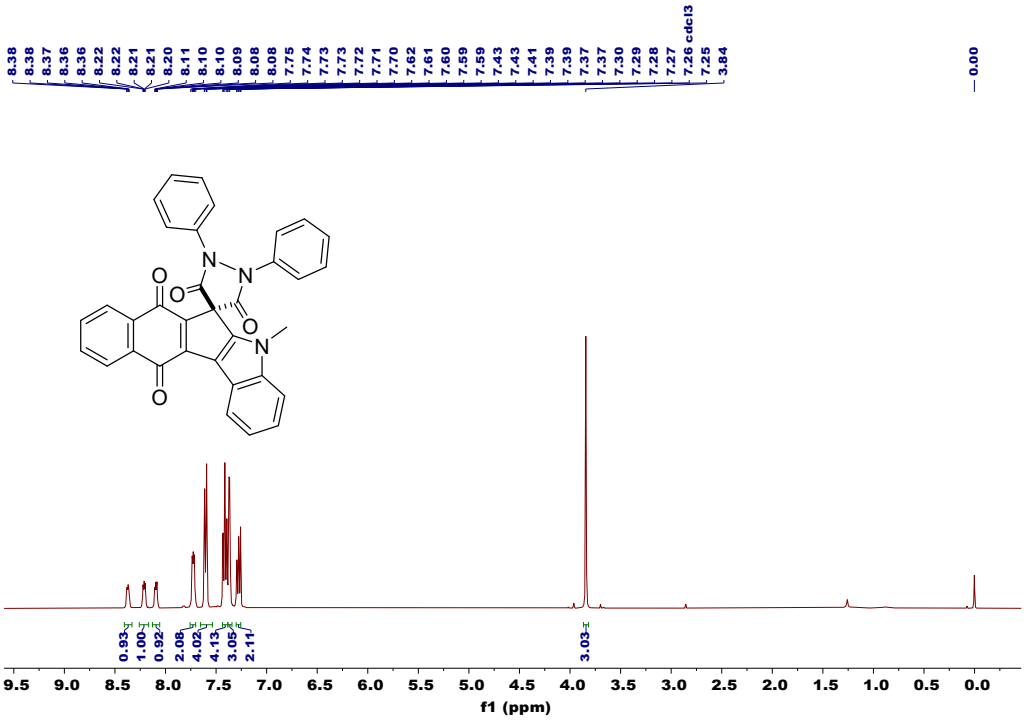


^{13}C NMR (101 MHz)

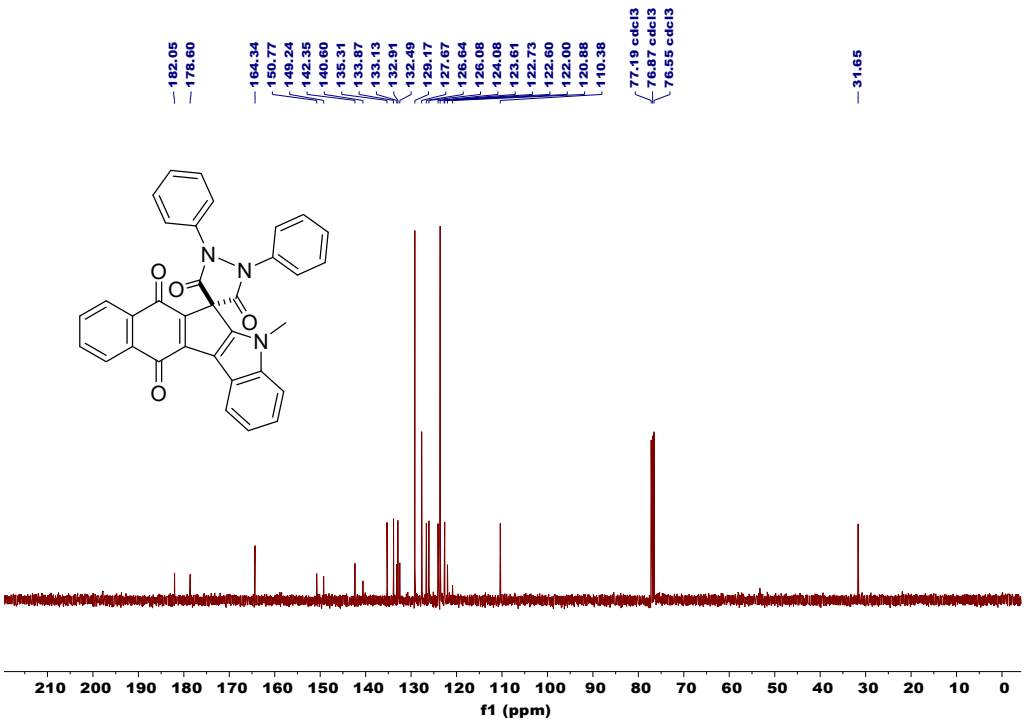


5-methyl-1',2'-diphenyl-5*H*-spiro[benzo[5,6]indeno[2,1-*b*]indole-6,4'-pyrazolidine]-3',5',7,12-tetraone (3aj)

^{1}H NMR (400 MHz)

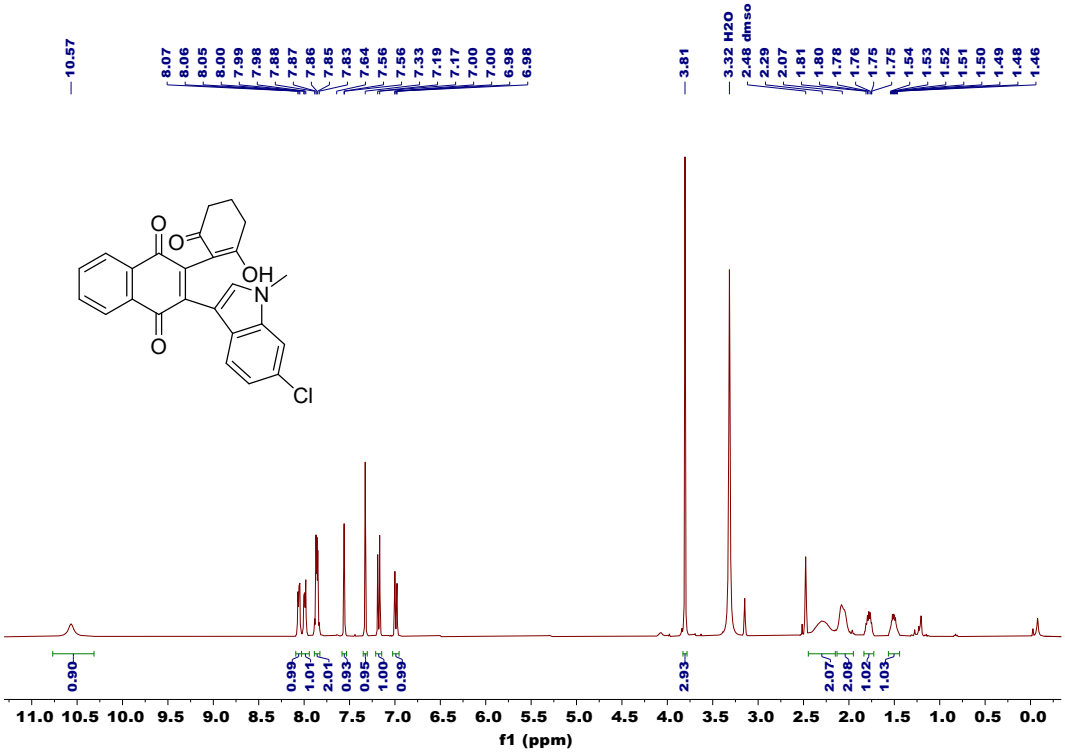


^{13}C NMR (101 MHz)



2-(6-chloro-1-methyl-1H-indol-3-yl)-3-(2-hydroxy-6-oxocyclohex-1-en-1-yl)naphthalene-1,4-dione (4ka)

^{1}H NMR (400 MHz)



^{13}C NMR (101 MHz)