Supporting Information

$B(C_6F_5)_3$-catalyzed three-component tandem reaction to construct novel polycyclic quinone derivatives: synthesis of a carbonate salts chromogenic chemosensor.

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Table of contents

1 General information

Unless specifically noted, all regeats were purchased commercially without further purification. Analytical thin–layer chromatography (TLC) was performed on Silica Gel GF-254 plates and detected by UV light (254 nm). Column chromatography was carried out using silica gel (particle size 200-300 mesh). ^{1}H-NMR and ^{13}C-NMR ^{19}F-NMR were recorded by 400 MHz, 101 MHz and 376 MHz Brüker spectrometer in $CDCl_3$ or DMSO-d_6. NMR data are reported according to the following order: (1) chemical shifts were quoted in parts per million (ppm) referenced to deuterated solvent; (2) peak splitting patterns were discribed using s (singlet), d (doublet), t (triplet), dd (doublet of doublet), td (triplet of doublet), ddd (doublet of doublet of doublet), m (multiplet); (3) coupling constants (J) were reported in Hertz (Hz). 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 970CRT/XP Fluorescence spectrophotometer.

2 Experiment section

2.1 Condition optimizations

Table S1 Screening of catalysts [a, b]

Entry	Catalyst (mol %)	Yield (%)
1	$B(C_6F_5)_3$ (5)	65
2	$C_6H_5B(OH)_2$ (5)	46
3	$BF_3.OEt_2$ (5)	trace

4	$Fe(acac)_3$ (5)	ND [c]
5	$Ni(OTf)_2$ (5)	57
6	$CoCl_2$ (5)	54
7	$Cu(OTf)_2$ (5)	41
8	TsOH. H_2O	32
9	HCl	50
10	$B(C_6F_5)_3$ (3)	53
11	$B(C_6F_5)_3$ (10)	68

Reaction conditions: [a] 1,4-naphthoquinone **1** (0.3 mmol, 1 equiv), 1-methylindole **2** (0.3 mmol, 1 equiv), N-phenylmaleimide **3** (0.3 mmol, 1 equiv), catalyst (5 mol %), and CH_3CN (3 mL) were stirred under sealed tube at 80 °C for 24 h. [b] Isolated yield. [c] ND: not detected.

Table S2 Screening of Bases [a, b]

Entry	**Catalyst (mol %)**	**Base (mol %)**	**Yield (%)**
1	$B(C_6F_5)_3$ (5)	Me_3P (5)	28
2	$B(C_6F_5)_3$ (5)	Ph_3P (5)	39
3	$B(C_6F_5)_3$ (5)	Ph_2PH (5)	51
4	$B(C_6F_5)_3$ (5)	$P(Cy)_3$ (5)	trace
5	$B(C_6F_5)_3$ (5)	DBU (5)	trace
6	$B(C_6F_5)_3$ (5)	DABCO (5)	trace
7	$B(C_6F_5)_3$ (5)	TEMP (5)	35

Reaction conditions: [a] 1,4-naphthoquinone **1** (0.3 mmol, 1 equiv), 1-methylindole **2** (0.3 mmol, 1 equiv), N-phenylmaleimide **3** (0.3 mmol, 1 equiv), $B(C_6F_5)_3$ (5 mol %), base (5 mol %) and CH_3CN (3 mL) were stirred under sealed tube at 80 °C for 24 h. [b] Isolated yield.

Table S3 Screening of temperature and time [a, b]

Entry	Catalyst (mol %)	T (°C)	t (h)	Yield (%)
1	$B(C_6F_5)_3$ (5)	rt	24	trace
2	$B(C_6F_5)_3$ (5)	30	24	19
3	$B(C_6F_5)_3$ (5)	50	24	47
4	$B(C_6F_5)_3$ (5)	100	24	78
5	$B(C_6F_5)_3$ (5)	120	24	77
6	$B(C_6F_5)_3$ (5)	100	20	68
7	$B(C_6F_5)_3$ (5)	100	16	63

Reaction conditions: [a] 1,4-naphthoquinone **1** (0.3 mmol, 1 equiv), 1-methylindole **2** (0.3 mmol, 1 equiv), N-phenylmaleimide **3** (0.3 mmol, 1 equiv), $B(C_6F_5)_3$ (5 mol %), and CH_3CN (3 mL) were stirred under sealed tube. [b] Isolated yield.

Table S4 Screening of solvents [a, b]

Entry	Catalyst (mol %)	Solvent (0.1M)	T (°C)	t (h)	Yield (%)
1	$B(C_6F_5)_3$ (5)	CH_3CN	100	24	78
2	$B(C_6F_5)_3$ (5)	H_2O	100	24	37
3	$B(C_6F_5)_3$ (5)	EtOH	100	24	53
4	$B(C_6F_5)_3$ (5)	THF	100	24	34
5	$B(C_6F_5)_3$ (5)	DCE	100	24	22
6	$B(C_6F_5)_3$ (5)	DMF	100	24	60
7	$B(C_6F_5)_3$ (5)	$(CH_2OH)_2$	100	24	65
8	$B(C_6F_5)_3$ (5)	toluene	100	24	43

Reaction conditions: [a] 1,4-naphthoquinone **1** (0.3 mmol, 1 equiv), 1-methylindole **2** (0.3 mmol, 1 equiv), N-phenylmaleimide **3** (0.3 mmol, 1 equiv), $B(C_6F_5)_3$ (5 mol %), and solvent (3 mL) were stirred under sealed tube at 100 °C for 24 h. [b] Isolated yield.

2.2 Experimental procedures

2.2.1 The synthesis of compounds 4a-4r, 5a-5m

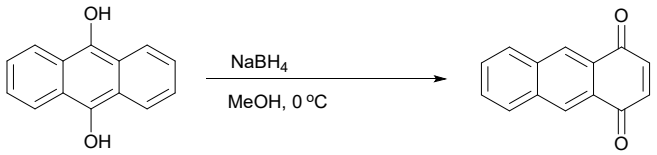
$B(C_6F_5)_3$ (5 mol % or 10 mol %) and CH_3CN (3 mL) were added to a sealed tube with quinones (0.3 mmol, 1 equiv), indoles **2** (0.3 mmol, 1 equiv), maleimides **3** (0.3 mmol, 1 equiv). Then, the sealed tube was stirred at 100-120 ^oC oil bath for 24 hours. After completing the reaction, the sealed tube was cooled to room temperature. Next, the mixture was washed with 5 mL of saturated brine, and extracted with 5 mL x 3 of dichloromethane (DCM). The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Target compounds were separated successfully by column chromatography using PE/EA.

2.2.2 The synthesis of compounds 5n, 5o

$B(C_6F_5)_3$ (10 mol %) and CH_3CN (3 mL) were added to a sealed tube with 1,4-naphthoquinone **1a** (0.6 mmol, 2 equiv), 1-methylindole **2a** (0.6 mmol, 2 equiv), maleimides **3** (0.3 mmol, 1 equiv) and maleimides **3'** (0.3 mmol, 1 equiv). Then, the sealed tube was stirred at 100 ^oC oil bath for 24 hours. After completing the reaction, the sealed tube was cooled to room temperature. Next, the mixture was washed with 5 mL of saturated brine, and extracted with 5 mL x 3 of dichloromethane (DCM). The organic layer was collected, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Target compounds were separated successfully by column chromatography using PE/EA.

2.2.3 The synthesis of substrates

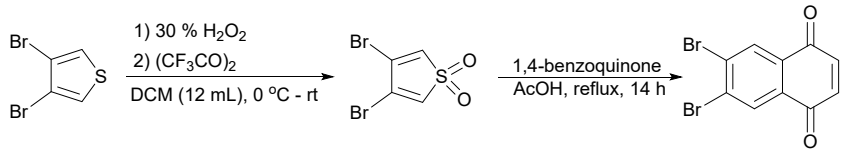
2.2.3.1 The synthesis of anthracene-1,4-dione (1b)



6 1b

Compound **1b** was prepared according to literature report.[1] $NaBH_4$ (0.64g, 16.8 mmol) was added to a 0 °C methanol (20 mL) solution of quinizarin **6** (1g, 4.2 mmol) under Ar atmosphere and stirred for 1 h. Then, 12 mL 6 M HCl was slowly added to the solution at 0 °C. The solid was filtered and washed with water three times, Next, recrystallized from acetone/PE after drying to give anthracene-1,4-dione.

2.2.3.2 The synthesis of 6,7-dibromonaphthalene-1,4-dione (1d)

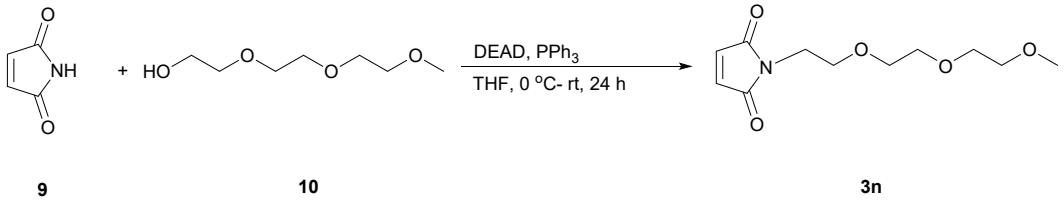


7 8 1d

Compound **1d** was prepared according to literature report.[2] 30% H_2O_2 (8 mL) was added to in a 100 mL flask and the mixture was stirred in ice bath. Then, $(CF_3CO)_2$ (120 mmol, 12 equiv) was added dropwise to the mixture. 0.5 hours later, 3,4-dibromothiophene **7** (2.42 g, 10 mmol) in DCM (12 mL) was added all at once. The mixture was moved to room temperature and stirred for 2.5 hours. Saturated $NaHCO_3$ was slowly add to adjust the pH to around 9, extracted with 10 mL x 3 of dichloromethane (DCM), and dried over anhydrous $MgSO_4$. The crude product **8** was obtained after removing solvent under reduced pressure, and proceeded to the next step without further purification. **8** (7.5 g, 6 mmol) and 1,4-benzoquinone (5.3 g, 10.8 mmol) were dissolved in 20 mL AcOH and refluxed for 14 hours. The solution was poured into water. The mixture was extracted with dichloromethane (3×15 mL). Then, the organic layer was washed with water three times, dried over anhydrous $MgSO_4$, filtered, and then the solvent was completely removed. **1d** was purified by column

chromatography.

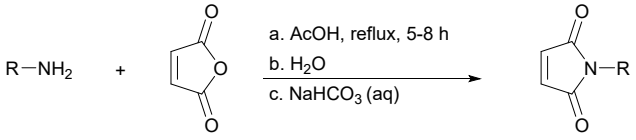
2.2.3.3 The synthesis of 1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1H-pyrrole- 2,5-dione (3n)



9 **10** **3n**

Compound **3n** was prepared according to Mitsnobu reaction and literature report.[3] PPh_3 (2.2 mmol) and DEAD (2.2 mmol) were added in a 50 mL flask with 10 mL THF and stirred for 20 min at 0 °C to give a yellow mixture. Next, Compound 10 (3 mmol) in 5 mL THF was added to the falsk, and the mixture was stirred for 20 min. Finally, the maleimide (2 mmol) dissolved in 5 mL of THF was added. The mixture was moved to room temperature and stirred for 24 hours. After completion of the reaction, the mixture was washed with 10 mL of saturated brine, and extracted with ethyl acetate (3x10 mL), and dried over anhydrous $MgSO_4$. Then the solvent was completely removed, and **3n** was purified by column chromatography.

2.2.3.4 The synthesis of N-aryl/N-alkyl maleimide derivatives

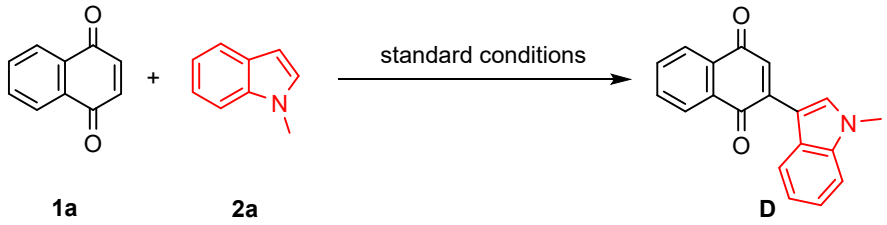


3

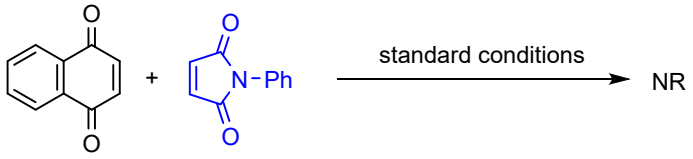
Compound **3** was prepared according to literature report.[4] Maleic anhydride (2.0 equiv.) and primary amine (5mmol.) were added in a 50 mL flask with 7.5 mL AcOH. The reaction mixture was refluxed for 6-8 h at 125 °C. Progress of the reaction was monitored by TLC, the mixture was moved to room temperature after completion of the reaction. Saturated $NaHCO_3$ was slowly add to adjust the pH to around 9, extracted with ethyl acetate (3x20 mL), and dried over anhydrous $MgSO_4$. Then the solvent was

completely removed, and **3** was purified by column chromatography.

2.3 Control experiments



(a)



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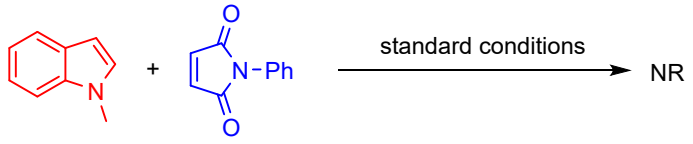
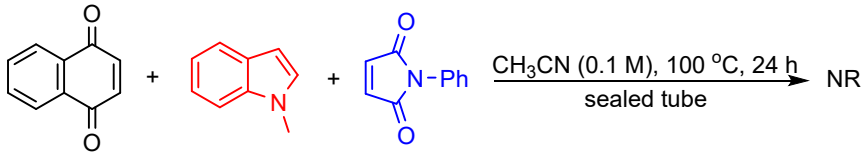
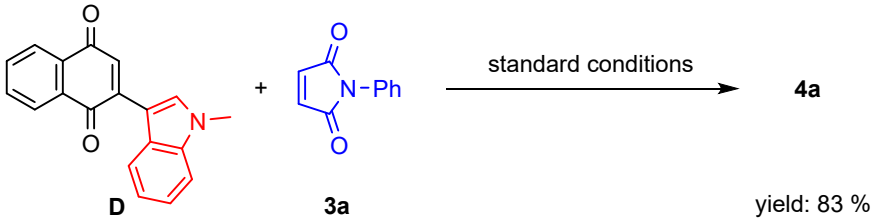


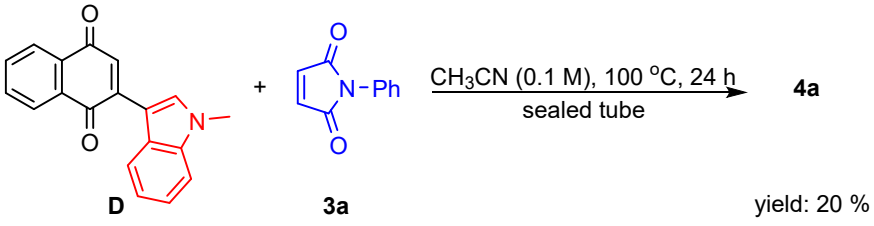
(c)



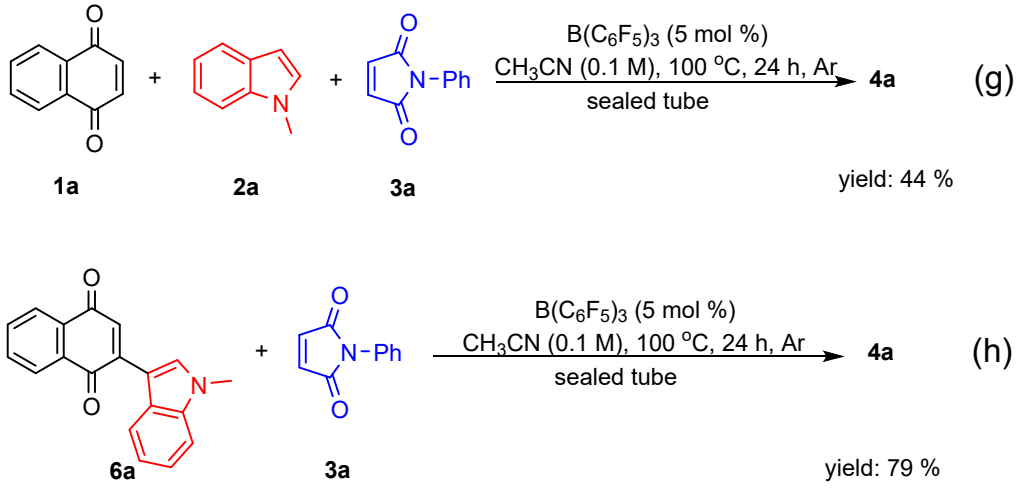
(d)



(e)



(f)



Scheme S1 Control experiments

3 Characterization data of products

3.1 Photophysical characterization data

Measurement method: Rhodamine 6G (R_{6G}) was selected as the standard to determine the relative quantum yield of the compound (Φ=0.95 in EtOH).[5] Prepare the ethyl acetate solution of compound **4** and **5** with a concentration of 2.5 x 10^{-6} mol/L, and prepare the ethanol solution of Rhodamine 6G with a concentration of 2.5 x 10^{-6} mol/L, measure the UV spectrum and fluorescence emission spectrum (Excitation wavelength at 530 nm) of the solution. The Photophysical characterization datas of compound **4** and **5** were shown in Table S5.

Formula:[6] $$\Phi_F = \Phi_R \frac{A_R D_F \eta_F^2}{A_F D_R \eta_R^2}$$

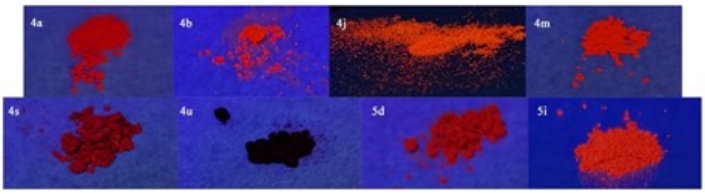
Φ_F: the quantum yield of the compounds **4** and **5**; Φ_R: the quantum yield of R_{6G};

A_F: UV absorbance of the compounds **4** and **5**; A_R: UV absorbance of R_{6G};

D_F: the integrated area of the fluorescence emission intensity of the compounds **4** and **5** under the excitation wavelength; D_R: the integrated area of the fluorescence emission intensity of R_{6G} under the excitation wavelength;

η_F: the refractive index of the solvent to be tested; η_R: the refractive index of the standard solvent.

The parameters setting for fluorescence emission spectrum: the scanning range of emission wavelength was from 350 nm to 750 nm, excitation wavelength at 530 nm, emission slit width was 10 nm, excitation slit width was 5 nm, the sensitivity was 1, the scanning speed was medium speed.



FigureS1 Some compounds under 365nm UV

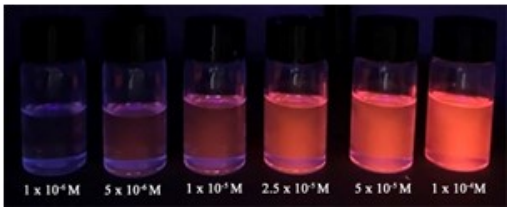


Figure S2 Gradient concentration of **4a** under 365 nm UV (EA as solvent)

Table S5 Photophysical characterization data of compound **4**

compound	**λ_{max} (nm)**	**λ_{em} (nm)**	**Φ_F**
4a	530	584	0.56
4b	490	563	0.26
4c	510	572	0.83
4d	530	584	0.61
4f	530	565	0.72

4g	580	-	-
4h	540	592	0.47
4i	540	589	0.28
4j	495	530	0.98
4k	510	542	0.95
4l	530	577	0.63
4m	525	545	0.81
4n	515	564	0.85
4o	510	551	0.85
4p	540	596	0.29
4s	530	579	0.67
4t	560	614	0.05
4u	545	604	0.17
5a	530	586	0.6
5b	525	580	0.54
5c	530	581	0.61
5d	530	580	0.54
5e	530	583	0.58
5f	530	578	0.61
5g	530	583	0.54
5h	530	584	0.54
5i	530	582	0.57
5j	530	581	0.58
5k	520	587	0.49
5l	525	581	0.57
5m	530	578	0.65
5n	530	575	0.61
5o	530	576	0.61

3.2 UV spectrum of compound 4 and 5

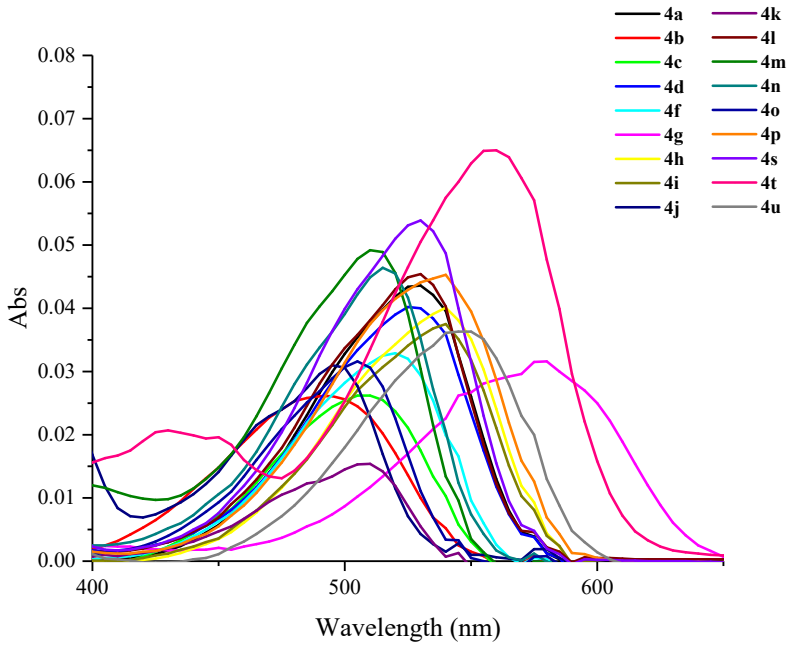


Figure S3 UV/VIS spectrum of compound **4**

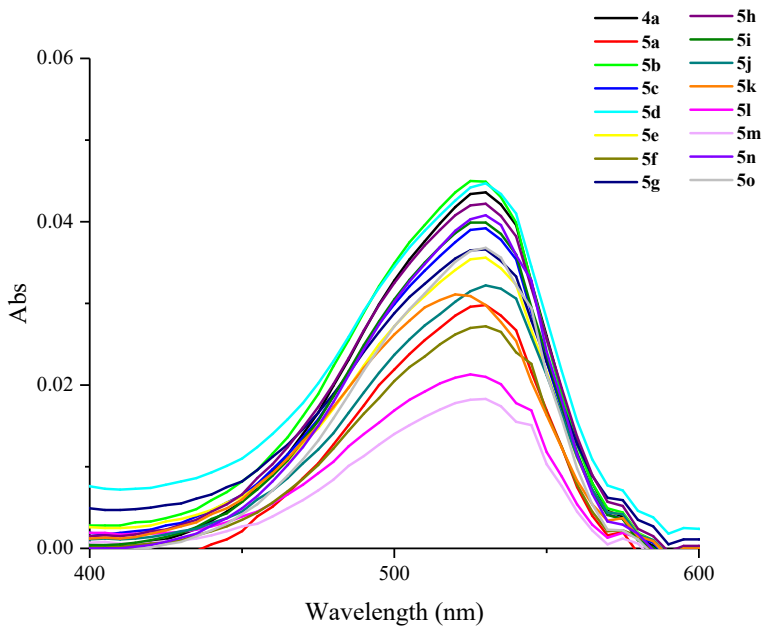


Figure S4 UV/VIS spectrum of compound **5**

3.3 Fluorescence emission spectrum

The parameters setting for fluorescence emission spectrum: the scanning range of emission wavelength was from 350 nm to 750 nm, excitation wavelength was determined according to the fluorescence excitation spectrum of different compounds, emission slit width was 10 nm, excitation slit width was 5 nm, the sensitivity was 1, the scanning speed was medium speed.

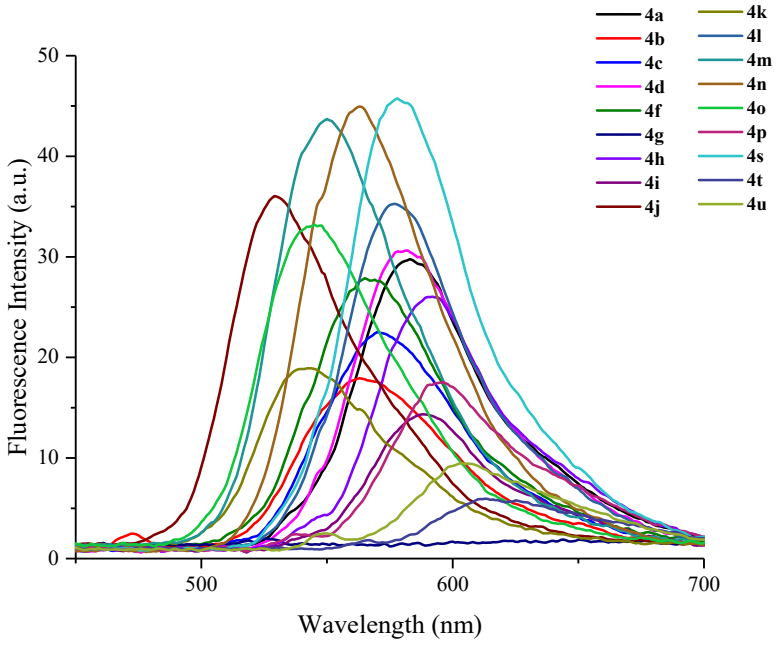


Figure S5 Fluorescence emission spectrum of compound **4**

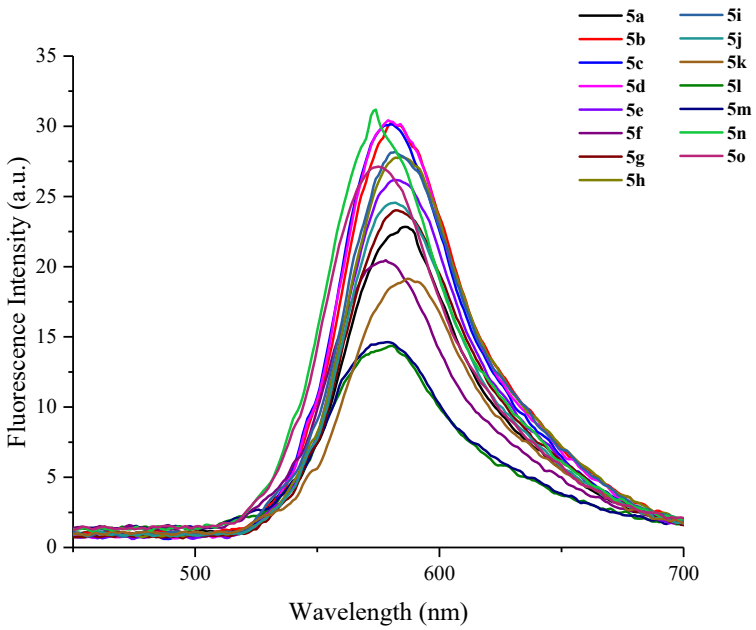


Figure S6 Fluorescence emission spectrum of compound **5**

3.4 The UV/VIS and fluorescence emission spectrum of the interaction of metal salts with 4j

The parameters setting for fluorescence emission spectrum: the scanning range of emission wavelength was from 350 nm to 750 nm, excitation wavelength at 516 nm, emission slit width was 10 nm, excitation slit width was 5 nm, the sensitivity was 1, the scanning speed was medium speed.

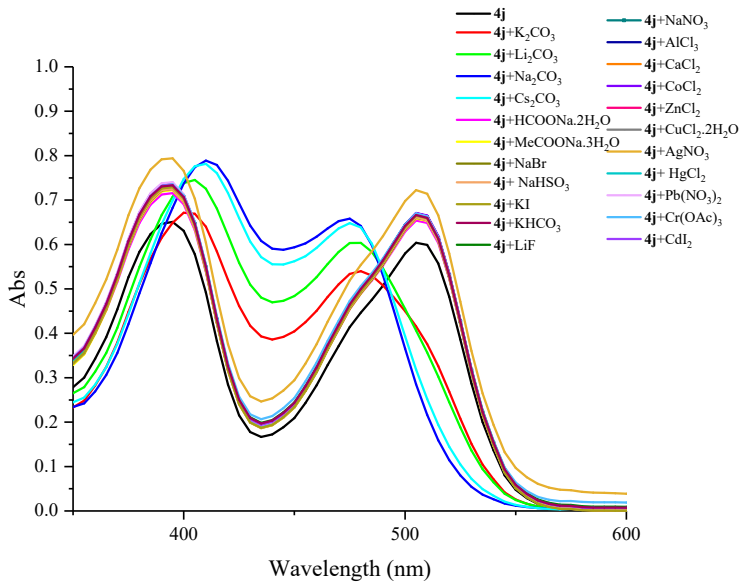


Figure S7 The UV/VIS spectrum of the interaction of different metal salts with **4j** (C_{4j} =5 x 10^{-5} mol/L, DMF:H_2O=5:1, n(**4j**) : n (salts) = 1:7)

Figure S8 The interaction of different metal salts with **4j**

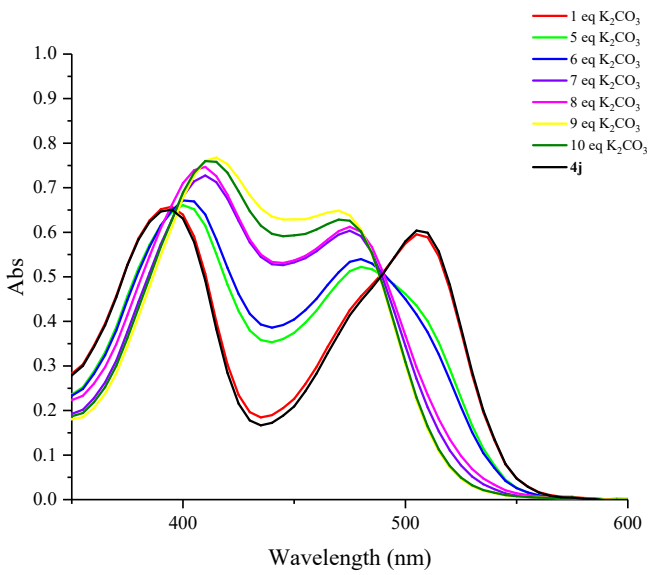


Figure S9 The UV/VIS spectrum with different ratios of **4j** to K_2CO_3 ($C_{\mathbf{4j}}$=5 x 10^{-5} mol/L)

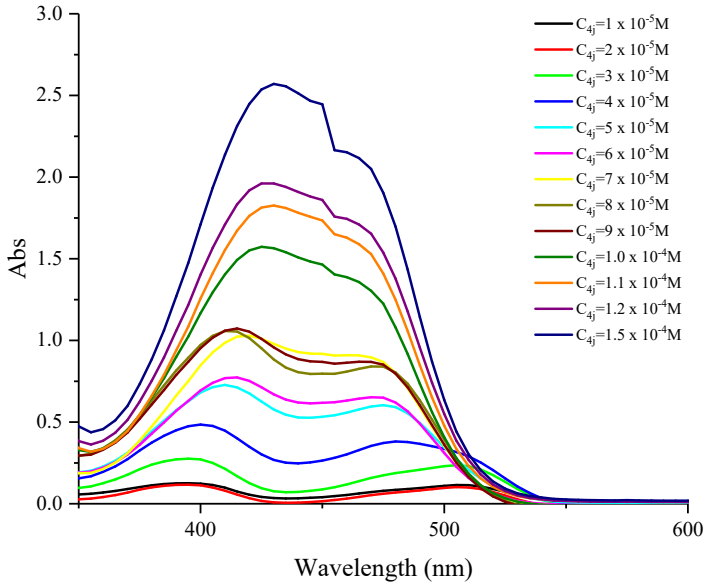


Figure S10 The UV/VIS spectrum of gradient concentration of **4j** and K_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n (K_2CO_3) = 1:7)

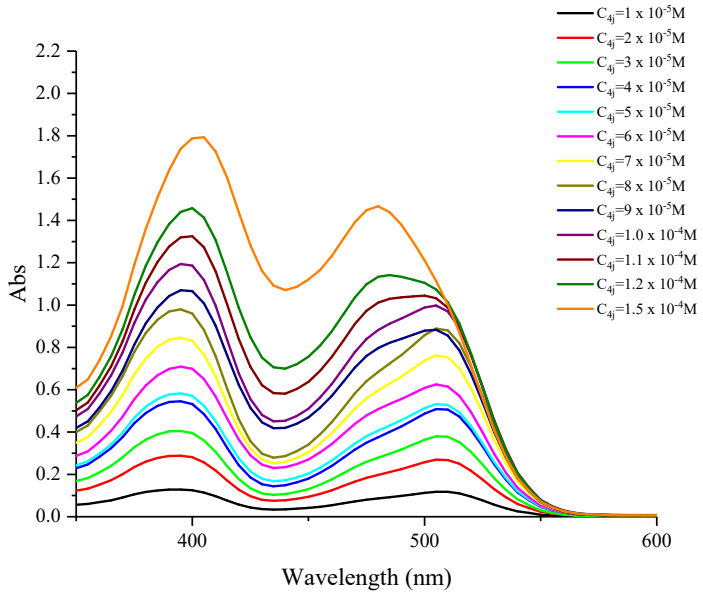


Figure S11 The UV/VIS spectrum of gradient concentration of **4j** and Li_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n(Li_2CO_3) = 1:7)

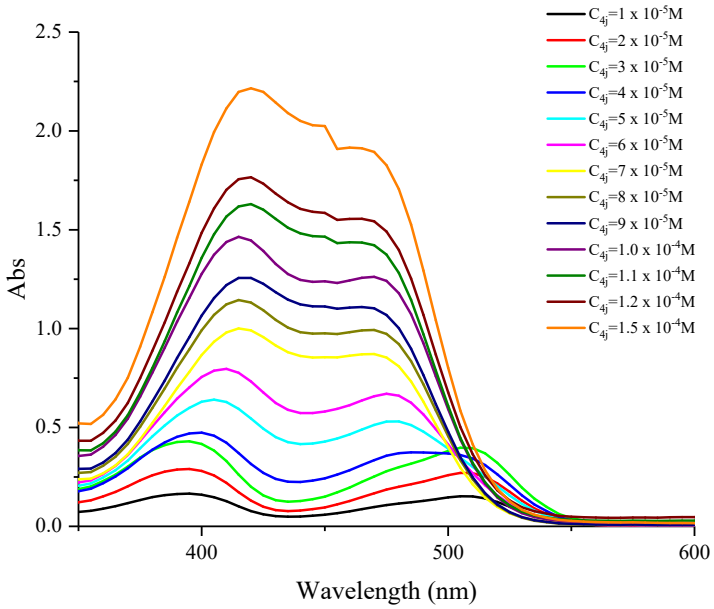


Figure S12 The UV/VIS spectrum of gradient concentration of **4j** and Na_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n(Na_2CO_3) = 1:7)

Figure S13 The gradient concentration of **4j** and Na_2CO_3

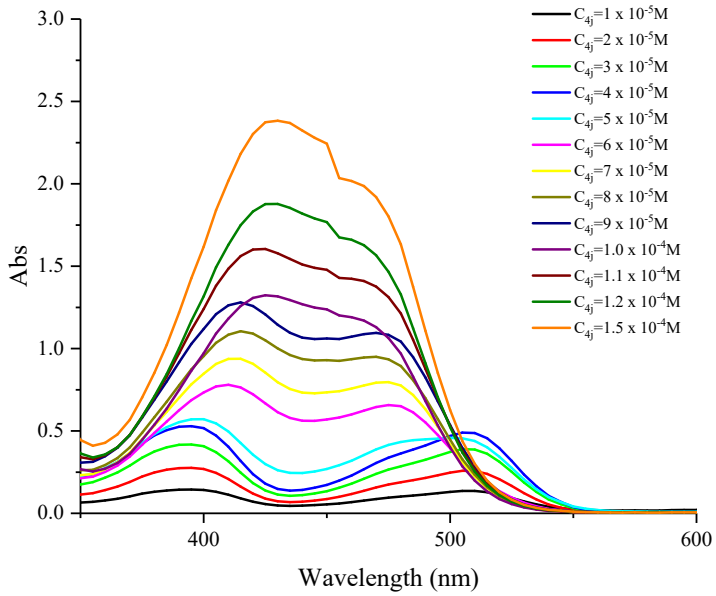


Figure S14 the UV/VIS spectrum of gradient concentration of **4j** and Cs_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n(Cs_2CO_3) = 1:7)

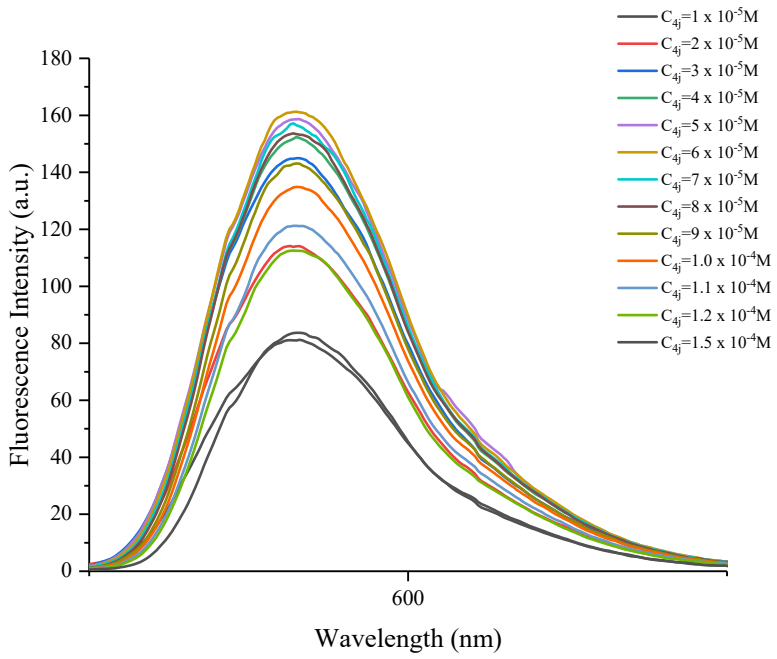


Figure S15 The fluorescence emission spectrum of gradient concentration of **4j** (DMF:H_2O=5:1)

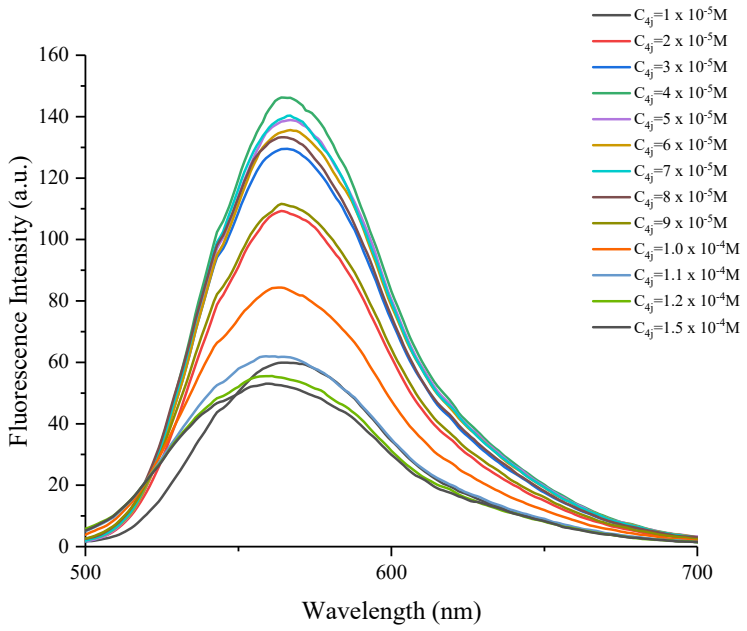


Figure S16 The fluorescence emission spectrum of gradient concentration of **4j** and Li_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n(Li_2CO_3) = 1:7)

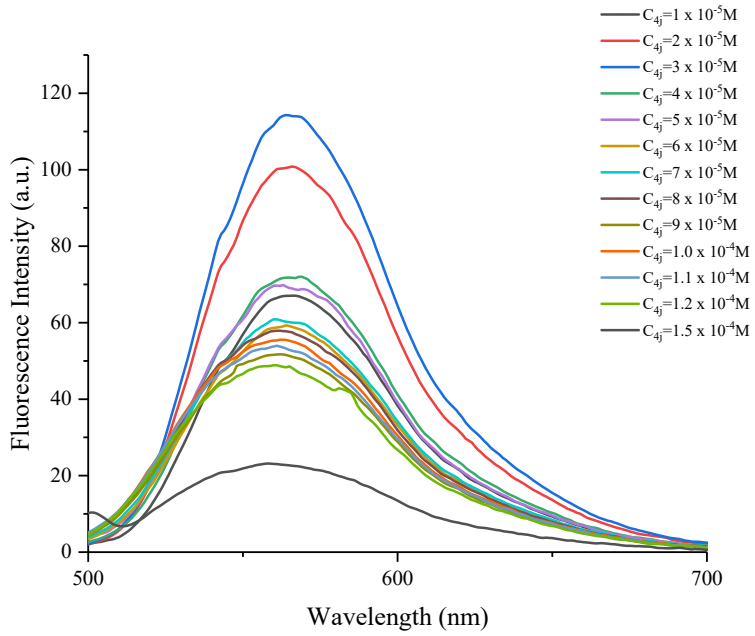


Figure S17 The fluorescence emission spectrum of gradient concentration of **4j** and Na_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n (Na_2CO_3) = 1:7)

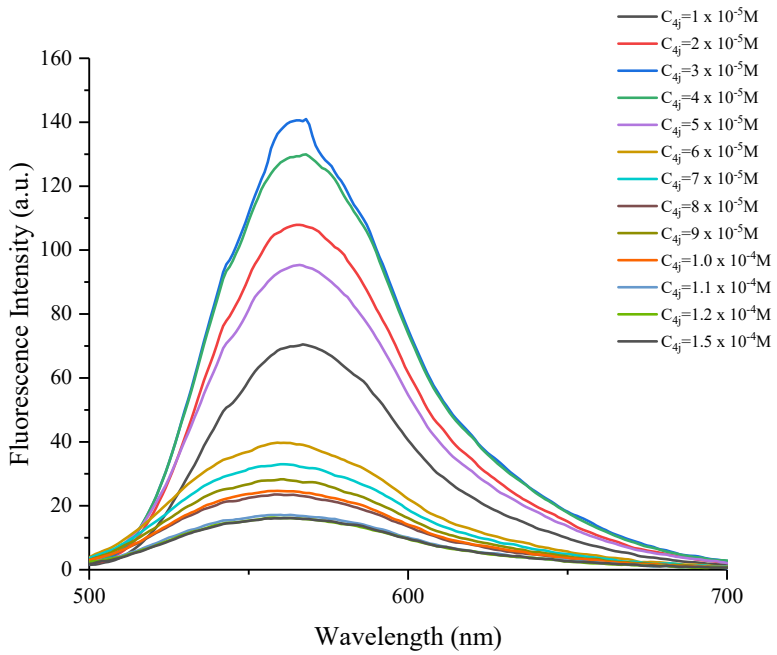


Figure S18 The fluorescence emission spectrum of gradient concentration of **4j** and K_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n (K_2CO_3) = 1:7)

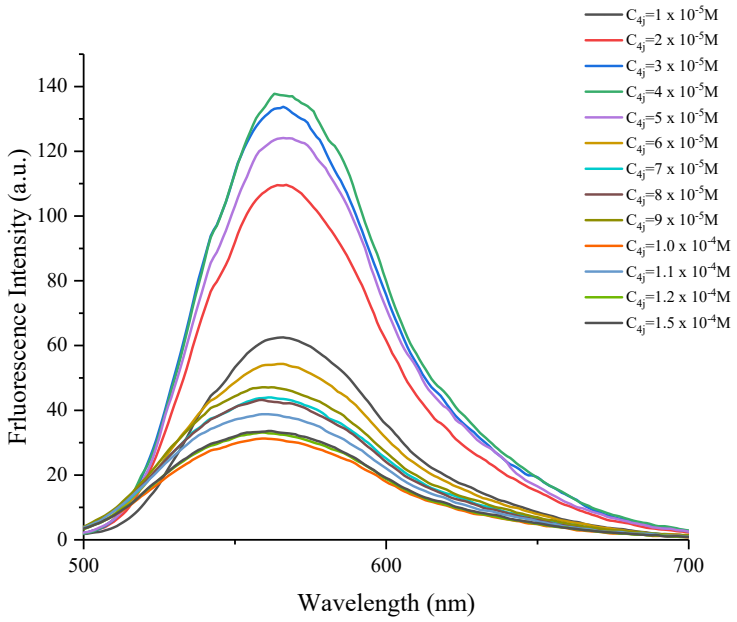
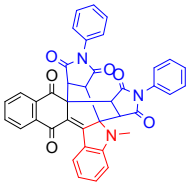


Figure S19 The fluorescence emission spectrum of gradient concentration of **4j** and Cs_2CO_3 (DMF:H_2O=5:1, n(**4j**) : n (Cs_2CO_3) = 1:7)

3.5 Physical datas of products

5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (4a)



Yield: 78 %, 74 mg; red soild; m.p. 282-283 °C; Rf = 0.26 (PE:EA=1:1).

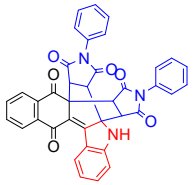
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (d, *J* = 8.0 Hz, 1H), 8.21 – 8.15 (m, 2H), 7.88 – 7.81 (m, 2H), 7.47 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.33 – 7.22 (m, 6H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.65 – 6.57 (m, 4H), 4.28 (d, *J* = 8.5 Hz, 2H), 4.05 (d, *J* = 8.5 Hz, 2H), 3.42 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.1, 178.5, 174.7, 172.0, 159.0, 153.5, 137.3,

136.0, 135.4, 135.2, 134.1, 131.7, 129.7, 129.5, 129.1, 127.8, 126.7, 126.6, 119.5, 117.2, 116.4, 107.8, 72.7, 51.9, 46.0, 41.8, 28.6.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{25}N_3NaO_6^+$: 654.1635; Found: 654.1633.

7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4b)



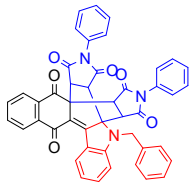
Yield: 54 %, 50 mg; orange soild; m.p. 208-210 °C; Rf =0.15 (PE:EA=1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, *J* = 8.2 Hz, 1H), 8.37 – 8.32 (m, 1H), 8.29 – 8.24 (m, 1H), 7.77 – 7.71 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 6.8, 4.4 Hz, 6H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 6.70 (dd, *J* = 6.7, 2.9 Hz, 4H), 5.93 (s, 1H), 4.14 (d, *J* = 8.7 Hz, 2H), 3.58 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.9, 179.0, 173.3, 171.1, 158.6, 153.3, 136.9, 135.8, 135.0, 134.9, 133.8, 130.6, 130.1, 129.2, 129.1, 128.3, 126.7, 126.1, 120.7, 120.2, 118.1, 111.6, 69.7, 51.8, 45.8, 45.2.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{38}H_{23}N_3NaO_6^+$: 640.1479; Found: 640.1509.

5-benzyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4c)



Yield: 70 %, 74 mg; red soild; m.p. 284-287 °C; Rf = 0.36 (PE:EA=1:1).

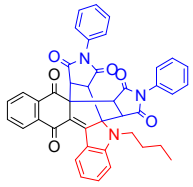
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 – 9.16 (d, 1H), 8.21 – 8.15 (m, 2H), 7.87 – 7.80 (m, 4H), 7.39 – 7.25 (m, 10H), 6.82 – 6.78 (m, 1H), 6.66 – 6.58 (m, 4H), 6.50 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 2H), 4.39 (d, *J* = 8.5 Hz, 2H), 4.06 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.8, 178.8, 174.5, 172.4, 160.0, 154.3, 137.4,

136.8, 135.8, 135.3, 135.2, 134.2, 131.8, 129.6, 129.5, 129.2, 129.0, 128.7, 127.8, 127.7, 126.8, 126.7, 120.8, 118.2, 116.7, 110.0, 74.1, 52.0, 49.3, 46.2, 42.2.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{45}H_{30}N_3O_6^+$: 708.2135; Found: 708.2132.

5-butyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4d)



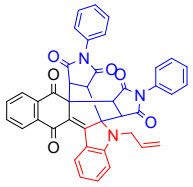
Yield: 71 %, 72 mg; red soild; m.p. 260-263 °C; Rf = 0.66 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.15 (d, *J* = 7.4 Hz, 1H), 8.24 – 8.11 (m, 2H), 7.88 – 7.79 (m, 2H), 7.47 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 7.32 – 7.24(m, 5H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.62 – 6.59 (m, 3H), 4.33 (d, *J* = 8.5 Hz, 2H), 4.01 (d, *J* = 8.5 Hz, 2H), 3.86 – 3.75 (m, 2H), 1.98 (dt, *J* = 15.9, 8.0 Hz, 2H), 1.50 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.1, 178.5, 174.5, 172.0, 159.4, 154.1, 137.2, 136.0, 135.3, 135.1, 134.0, 131.8, 129.8, 129.5, 129.1, 127.8, 126.7, 126.6, 119.8, 117.3, 116.0, 108.4, 73.2, 51.9, 46.0, 44.3, 42.1, 30.5, 20.8, 14.5.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{42}H_{32}N_3O_6^+$: 674.2291; Found: 674.2291.

5-allyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4f)



Yield: 76 %, 75 mg; red soild; m.p. 246-248 °C;Rf = 0.4 (PE:EA=1:1).

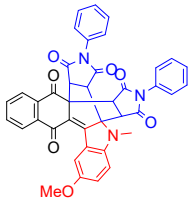
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.15 (d, *J* = 7.5 Hz, 1H), 8.21 – 8.15 (m, 2H), 7.87 – 7.82 (m, 2H), 7.45 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.33 – 7.23 (m, 6H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.66 – 6.58 (m, 4H), 6.48-6.40 (m, 1H), 5.61 (dd, *J*

= 17.4, 1.4 Hz, 1H), 5.31 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.57 (d, *J* = 6.4 Hz, 2H), 4.31 (d, *J* = 8.5 Hz, 2H), 4.04 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 194.0, 178.7, 174.6, 172.1, 159.2, 153.6, 137.0, 136.1, 135.9, 135.3, 135.2, 134.2, 131.7, 129.7, 129.5, 129.1, 127.8, 126.7, 126.6, 120.0, 118.2, 117.6, 116.5, 108.9, 73.2, 51.9, 47.2, 45.9, 42.1.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{41}H_{28}N_3O_6^+$: 658.1978; Found: 658.1981.

2-methoxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4g)



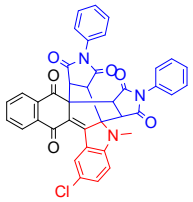
Yield: 92 %, 91 mg; purple soild; m.p. 271-271 °C; Rf = 0.29 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.76 (d, *J* = 2.7 Hz, 1H), 8.21 – 8.15 (m, 2H), 7.83 (m, 2H), 7.33 – 7.20 (m, 7H), 6.88 (d, *J* = 9.1 Hz, 1H), 6.68 – 6.60 (m, 4H), 4.26 (d, *J* = 8.6 Hz, 2H), 4.02 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 3.40 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 194.2, 178.2, 174.7, 172.0, 155.2, 153.7, 150.9, 136.1, 135.3, 135.1, 133.9, 131.7, 129.5, 129.1, 127.9, 127.4, 126.7, 126.6, 119.6, 115.7, 111.4, 108.6, 73.1, 56.2, 51.9, 45.8, 41.8, 28.7.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{40}H_{28}N_3O_7^+$: 662.1927; Found: 662.1926.

2-chloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4h)



Yield: 87 %, 87 mg; red soild; m.p. 298-302 °C; Rf = 0.23 (PE:EA= 1:1).

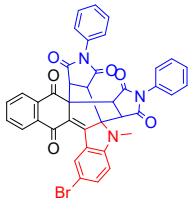
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.22 (d, *J* = 1.8 Hz, 1H), 8.31 – 8.25 (m, 2H), 7.98 – 7.92 (m, 2H), 7.57 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.37 (dq, *J* = 14.4, 7.2 Hz, 6H), 7.04 (d,

J = 8.9 Hz, 1H), 6.70 (d, *J* = 7.4 Hz, 4H), 4.38 (d, *J* = 8.5 Hz, 2H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.7, 178.9, 174.6, 171.9, 157.5, 152.0, 136.8, 135.6, 135.4, 135.3, 134.5, 131.6, 129.6, 129.2, 128.1, 127.9, 126.7, 126.6, 120.4, 120.1, 117.8, 109.4, 73.2, 52.0, 45.7, 41.7, 28.8.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{24}ClN_3NaO_6^+$: 688.1246; Found: 688.1284.

2-bromo-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4i)



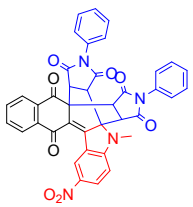
Yield: 83 %, 88 mg; red soild; m.p. 288-291 °C; Rf = 0.2 (PE:EA= 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.30 (d, *J* = 2.1 Hz, 1H), 8.25 – 8.17 (m, 2H), 7.90 – 7.85 (m, 2H), 7.59 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.36 – 7.25 (m, 6H), 6.92 (d, *J* = 8.9 Hz, 1H), 6.68 – 6.60 (m, 4H), 4.31 (d, *J* = 8.6 Hz, 2H), 4.06 (d, *J* = 8.5 Hz, 2H), 3.42 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.7, 179.0, 174.6, 171.9, 157.8, 151.9, 139.3, 135.6, 135.4, 135.3, 134.5, 131.6, 131.1, 129.6, 129.2, 128.0, 126.7, 126.6, 120.9, 117.8, 109.9, 107.9, 73.1, 52.0, 45.8, 41.8, 28.8.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{25}BrN_3O_6^+$: 710.0927; Found: 710.0923.

5-methyl-2-nitro-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4j)



Yield: 46 %, 47 mg; orange soild; m.p. 297-300 °C; Rf = 0.14 (PE:EA=1:1).

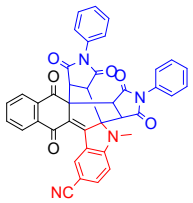
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.07 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 9.3, 2.5 Hz,

1H), 8.29 – 8.21 (m, 2H), 7.94 – 7.88 (m, 2H), 7.33 – 7.24 (m, 6H), 7.12 (d, *J* = 9.4 Hz, 1H), 6.68 – 6.61 (m, 4H), 4.42 (d, *J* = 8.5 Hz, 2H), 4.13 (d, *J* = 8.5 Hz, 2H), 3.55 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.1, 179.5, 174.5, 171.9, 161.3, 150.7, 137.8, 135.5, 135.5, 135.2, 135.0, 132.3, 131.4, 129.6, 129.2, 128.2, 126.9, 126.6, 126.2, 120.4, 118.6, 107.9, 74.2, 52.1, 46.0, 41.8, 29.5.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{25}N_4O_8^+$: 677.1672; Found: 677.1667.

5-methyl-6,8,9,14,16,18-hexaoxo-7,17-diphenyl-5b,7,8,8a,9,14-hexahydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-2-carbonitrile (4k)



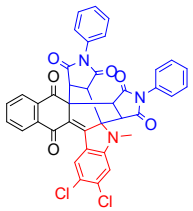
Yield: 53 %, 52 mg; orange soild; m.p. 278-281 °C; Rf = 0.16 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.47 (d, *J* = 1.5 Hz, 1H), 8.26 – 8.19 (m, 2H), 7.90 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.83 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.34 – 7.25 (m, 6H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.66 – 6.60 (m, 4H), 4.37 (d, *J* = 8.5 Hz, 2H), 4.10 (d, *J* = 8.5 Hz, 2H), 3.49 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.3, 179.4, 174.5, 171.9, 160.0, 150.8, 139.4, 135.5, 135.3, 134.8, 134.0, 131.5, 129.6, 129.3, 128.1, 126.9, 126.6, 120.1, 119.6, 119.2, 109.1, 98.5, 73.4, 52.0, 45.9, 41.7, 29.1.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{40}H_{25}N_4O_6^+$: 657.1774; Found: 657.1774.

2,3-dichloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4l)



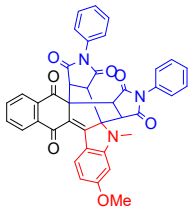
Yield: 74 %, 78 mg; red soild; m.p. 306-308 °C; Rf = 0.2 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.31 (s, 1H), 8.24 – 8.19 (m, 2H), 7.91 – 7.86 (m, 2H), 7.36 – 7.26 (m, 7H), 6.67 – 6.63 (m, 4H), 4.32 (d, *J* = 8.5 Hz, 2H), 4.07 (d, *J* = 8.5 Hz, 2H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.4, 179.2, 174.5, 172.0, 157.5, 150.9, 139.7, 135.4, 135.4, 134.7, 131.5, 129.7, 129.6, 129.2, 128.0, 126.8, 126.6, 119.1, 118.7, 118.5, 109.3, 73.5, 52.0, 45.8, 41.8, 29.0.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{23}Cl_2N_3NaO_6^+$: 722.0856; Found: 722.0883.

3-methoxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4m)



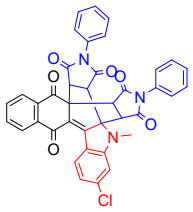
Yield: 76 %, 75 mg; orange soild; m.p. 289-293 °C; Rf = 0.14 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (d, *J* = 9.0 Hz, 1H), 8.19 – 8.13 (m, 2H), 7.85 – 7.77 (m, 2H), 7.34 – 7.24 (m, 6H), 6.64 (d, *J* = 7.2 Hz, 4H), 6.40 – 6.33 (m, 2H), 4.24 (d, *J* = 8.6 Hz, 2H), 4.01 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.6, 177.7, 174.7, 172.2, 167.7, 161.7, 152.6, 136.4, 135.2, 135.0, 133.5, 131.8, 131.4, 129.5, 129.1, 127.6, 126.7, 126.5, 113.7, 112.5, 107.5, 90.4, 73.6, 56.2, 51.5, 46.5, 41.9, 28.7.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{40}H_{28}N_3O_7^+$: 662.1927; Found: 662.1926.

3-chloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4n)



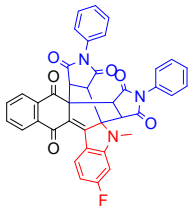
Yield: 66 %, 66 mg; orange soild; m.p. 313-316 °C; Rf = 0.34 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.13 (d, *J* = 8.7 Hz, 1H), 8.21 – 8.16 (m, 2H), 7.88 – 7.84 (m, 2H), 7.34 – 7.25 (m, 6H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.78 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.64 – 6.59 (m, 4H), 4.30 (d, *J* = 8.5 Hz, 2H), 4.06 (d, *J* = 8.5 Hz, 2H), 3.42 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 193.8, 178.8, 174.6, 172.0, 159.4, 152.0, 142.3, 135.7, 135.4, 135.3, 134.3, 131.6, 131.0, 129.6, 129.2, 127.8, 126.7, 126.6, 118.3, 117.5, 117.3, 110.0, 107.5, 73.3, 51.9, 46.0, 41.8, 28.8.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{25}ClN_3O_6^+$: 666.1432; Found: 666.1428.

3-fluoro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4o)



Yield: 69 %, 67 mg; orange soild; m.p. 285-287 °C; Rf = 0.28 (PE:EA=1:1).

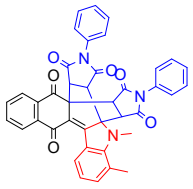
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.22 (dd, *J* = 9.0, 6.2 Hz, 1H), 8.20 – 8.15 (m, 2H), 7.88 – 7.83 (m, 2H), 7.33 – 7.24 (m, 6H), 6.81 (dd, *J* = 10.6, 2.3 Hz, 1H), 6.64 – 6.60 (m, 4H), 6.57 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.28 (d, *J* = 8.6 Hz, 2H), 4.05 (d, *J* = 8.5 Hz, 2H), 3.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 193.9, 178.6, 174.6, 172.0, δ 168.9 (d, *J* = 253.3

Hz), 160.9 (d, *J* = 14.7 Hz), 152.2, 135.8, 135.4, 135.2, 134.2, 132.3 (d, *J* = 12.1 Hz), 131.7, 129.5, 129.2, 127.8, 126.6, 116.4, 116.1 (d, *J* = 2.3 Hz), 110.0, 105.4 (d, *J* = 23.9 Hz), 94.4 (d, *J* = 26.3 Hz), 73.7, 51.8, 46.1, 41.8, 28.9; ^{19}F NMR (376 MHz, dmso) δ -100.17.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{25}FN_3O_6^+$: 650.1727; Found: 650.1730.

4,5-dimethyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (4p)



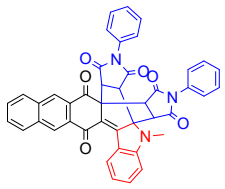
Yield: 90 %, 74 mg; red soild; m.p. 276-278 °C; Rf = 0.4 (PE:EA=1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (d, *J* = 8.2 Hz, 1H), 8.29 (t, *J* = 8.6 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.25 – 7.21 (m, 6H), 7.17 (d, *J* = 7.1 Hz, 1H), 6.75 – 6.67 (m, 5H), 4.07 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.63 (d, *J* = 8.8 Hz, 2H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 178.4, 173.4, 170.6, 157.5, 152.8, 140.5, 136.4, 134.9, 134.8, 133.4, 130.7, 129.3, 129.0, 128.3, 126.4, 126.2, 120.4, 118.8, 118.1, 115.3, 72.5, 51.8, 45.3, 42.0, 31.8, 20.4.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{40}H_{28}N_3O_6^+$: 646.1973; Found: 646.2003.

5-methyl-7,19-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrroloanthra[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,16,18,20(7*H*)-hexaone (4s)



Yield: 70 %, 71 mg; red soild; m.p. 289-292 °C; Rf = 0.23 (PE:EA=1:1).

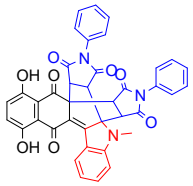
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (d, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 9.2 Hz, 2H), 8.30 (dd, *J* = 6.1, 3.4 Hz, 1H), 8.21 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.74 (dq, *J* = 6.8, 3.5 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.29 – 7.19 (m, 6H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.6

Hz, 1H), 6.63 – 6.58 (m, 4H), 4.29 (d, *J* = 8.5 Hz, 2H), 4.10 (d, *J* = 8.5 Hz, 2H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 194.1, 178.4, 174.8, 172.0, 159.0, 153.8, 137.2, 135.3, 134.7, 132.0, 131.7, 131.6, 130.4, 130.1, 130.1, 129.9, 129.9, 129.8, 129.4, 129.1, 128.5, 126.6, 119.7, 117.2, 116.8, 107.8, 72.8, 52.3, 45.9, 41.8, 28.6.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{43}H_{28}N_3O_6^+$: 682.1973; Found: 682.2005.

10,13-dihydroxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (4r)



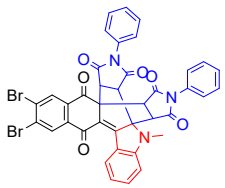
Yield: 77 %, 77 mg; purple soild; m.p. 211-213 ºC; Rf = 0.22 (PE:EA=1:2).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 13.48 (s, 1H), 12.36 (s, 1H), 9.06 (d, *J* = 8.2 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.27 (m, 8H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.70 – 6.62 (m, 4H), 4.37 (d, *J* = 8.6 Hz, 2H), 4.09 (d, *J* = 8.6 Hz, 2H), 3.47 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 200.2, 183.0, 174.3, 171.8, 159.8, 156.9, 155.4, 155.2, 138.3, 131.6, 130.4, 129.6, 129.4, 129.2, 127.6, 126.6, 119.3, 117.9, 116.2, 115.2, 114.3, 108.4, 73.2, 51.7, 45.8, 41.5, 28.7.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{26}N_3O_8^+$: 664.1714; Found: 664.1744.

11,12-dibromo-5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (4u)



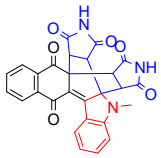
Yield: 58 %, 69 mg; red soild; m.p. 316-320 °C; Rf = 0.34 (PE:EA=1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (d, *J* = 8.2 Hz, 1H), 8.52 (s, 1H), 8.51 (s, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 4H), 6.88 – 6.79 (m, 2H), 6.74 – 6.67 (m, 4H), 4.08 (d, *J* = 8.8 Hz, 2H), 3.67 (d, *J* = 8.8 Hz, 2H), 3.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.6, 176.5, 173.4, 170.3, 159.1, 153.2, 138.0, 135.4, 134.1, 133.7, 133.1, 131.6, 131.6, 130.5, 130.3, 129.3, 129.1, 126.0, 119.3, 118.3, 115.2, 107.5, 72.3, 51.9, 45.4, 42.1, 28.3.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{24}Br_2N_3O_6^+$: 788.0032; Found: 788.0029.

5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5a)



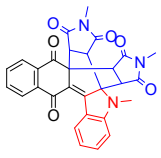
Yield: 60 %, 43 mg; red soild; m.p. 278-281 °C; Rf = 0.15(PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.10 (s, 2H), 9.07 (d, *J* = 8.1 Hz, 1H), 8.23 – 8.12 (m, 2H), 7.88 (dd, *J* = 9.1, 5.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.69 (t, *J* = 7.6 Hz, 1H), 3.89 (d, *J* = 8.6 Hz, 2H), 3.75 (d, *J* = 8.6 Hz, 2H), 3.33 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.3, 178.6, 176.9, 174.3, 158.9, 153.6, 136.8, 136.2, 135.4, 134.9, 134.0, 130.1, 127.7, 126.6, 119.5, 116.6, 107.7, 72.2, 51.2, 47.1, 42.9, 28.5.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{27}H_{18}N_3O_6^+$: 480.1190; Found: 480.1212.

5,7,17-trimethyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5b)



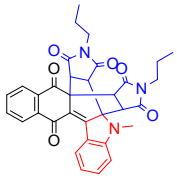
Yield: 75 %, 57 mg; red soild; m.p. 273-275 °C; Rf = 0.17 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (d, *J* = 8.1 Hz, 1H), 8.22 – 8.14 (m, 2H), 7.91 – 7.85 (m, 2H), 7.48 – 7.43 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 4.02 (d, *J* = 8.6 Hz, 2H), 3.80 (d, *J* = 8.6 Hz, 2H), 3.38 (s, 3H), 2.38 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.1, 178.3, 175.4, 172.9, 158.8, 153.3, 137.0, 136.1, 135.2, 135.1, 134.0, 130.0, 127.8, 126.7, 119.3, 116.8, 116.2, 107.6, 72.2, 51.3, 45.8, 41.7, 28.5, 24.8.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{21}N_3NaO_6^+$: 530.1323; Found: 530.1350.

5-methyl-7,17-dipropyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5c)



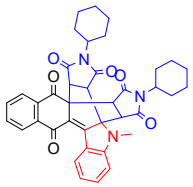
Yield: 67 %, 57 mg; red soild; m.p. 291-293 °C; Rf = 0.43 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.00 (d, *J* = 7.9 Hz, 1H), 8.23 – 8.15 (m, 2H), 7.91 – 7.86 (m, 2H), 7.48 – 7.43 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 4.00 (d, *J* = 8.5 Hz, 2H), 3.81 (d, *J* = 8.5 Hz, 2H), 3.39 (s, 3H), 2.91 (t, *J* = 6.9 Hz, 4H), 0.89 – 0.81 (m, 4H), 0.32 (t, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.2, 178.2, 175.4, 172.8, 158.8, 153.3, 136.9, 136.2, 135.3, 135.1, 133.9, 130.0, 127.6, 126.6, 119.7, 116.7, 116.3, 107.5, 72.3, 51.5, 45.6, 41.6, 39.8, 28.5, 20.4, 10.9.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{33}H_{30}N_3O_6^+$: 564.2135; Found: 564.2132.

7,17-dicyclohexyl-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5d)



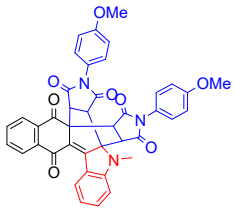
Yield: 72 %, 70 mg; red soild; m.p. 296-300 °C; Rf = 0.63 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.97 (d, *J* = 8.0 Hz, 1H), 8.17 (td, *J* = 4.4, 2.4 Hz, 2H), 7.90 – 7.84 (m, 2H), 7.47 – 7.42 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.66 (t, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 8.5 Hz, 2H), 3.75 (d, *J* = 8.5 Hz, 2H), 3.35 (s, 3H), 1.53 – 1.26 (m, 11H), 1.02 – 0.73 (m, 11H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.4, 178.3, 175.4, 172.6, 158.8, 153.0, 136.9, 136.0, 135.5, 135.0, 133.9, 129.7, 127.7, 126.5, 119.7, 116.7, 116.2, 107.5, 72.4, 51.7, 50.9, 45.3, 41.1, 28.4, 28.1, 27.9, 25.4, 24.9.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{38}N_3O_6^+$: 644.2761; Found: 644.2758.

7,17-bis(4-methoxyphenyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5e)



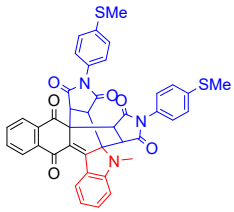
Yield: 57 %, 59 mg; red soild; m.p. 220-222 °C; Rf = 0.14 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.13 (d, *J* = 7.9 Hz, 1H), 8.18 (ddd, *J* = 4.9, 2.3, 0.9 Hz, 2H), 7.87 – 7.82 (m, 2H), 7.47 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.86 – 6.80 (m, 4H), 6.76 – 6.72 (m, 1H), 6.54 – 6.47 (m, 4H), 4.23 (d, *J* = 8.5 Hz, 2H), 4.01 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 6H), 3.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.2, 178.5, 174.9, 172.2, 159.5, 159.0, 153.5, 137.2, 136.0, 135.4, 135.1, 134.0, 129.7, 127.8, 127.8, 126.6, 124.2, 119.5, 117.1, 116.4, 114.8, 107.8, 72.7, 55.8, 51.9, 45.8, 41.7, 28.6.

HRMS (ESI): m/z: $[M+Na]^+$ Calcd. for $C_{41}H_{29}N_3NaO_8^+$: 714.1847; Found: 714.1881.

5-methyl-7,17-bis(4-(methylthio)phenyl)-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5f)



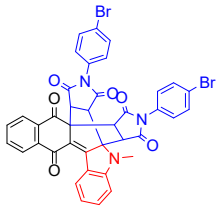
Yield: 51 %, 55 mg; red soild; m.p. 241-244 °C; Rf = 0.16 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.12 (d, *J* = 8.1 Hz, 1H), 8.18 (dd, *J* = 5.5, 2.6 Hz, 2H), 7.85 (p, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 4H), 4.26 (d, *J* = 8.5 Hz, 2H), 4.02 (d, *J* = 8.5 Hz, 2H), 3.41 (s, 3H), 2.36 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 194.1, 178.5, 174.7, 172.0, 159.0, 153.5, 139.8, 137.3, 136.0, 135.3, 135.1, 134.1, 129.7, 128.2, 127.8, 127.0, 126.6, 126.5, 119.4, 117.2, 116.3, 107.8, 72.7, 51.9, 45.9, 41.7, 28.6, 14.9.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{41}H_{30}N_3O_6S_2^+$: 724.1576; Found: 724.1575.

7,17-bis(4-bromophenyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5g)



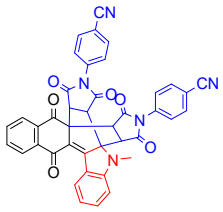
Yield: 80 %, 95 mg; red soild; m.p. 233-237 °C; Rf = 0.34 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.10 (d, *J* = 8.1 Hz, 1H), 8.22 – 8.14 (m, 2H), 7.89 – 7.83 (m, 2H), 7.59 – 7.50 (m, 4H), 7.50 – 7.45 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.62 – 6.52 (m, 4H), 4.29 (d, *J* = 8.6 Hz, 2H), 4.03 (d, *J* = 8.6 Hz, 2H), 3.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d$_6$): δ 194.0, 178.5, 174.4, 171.7, 159.0, 153.4, 137.4, 135.9, 135.3, 135.2, 134.1, 132.6, 130.9, 129.7, 128.6, 127.8, 126.6, 122.2, 119.3, 117.3, 116.3, 107.8, 72.6, 51.8, 46.0, 41.8, 28.6.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{24}Br_2N_3O_6^+$: 790.0006; Found: 790.0038.

4,4'-(5-methyl-6,8,9,14,16,18-hexaoxo-5b,6,8,8a,9,14-hexahydro-5H,7H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-7,17-diyl)dibenzonitrile (5h)



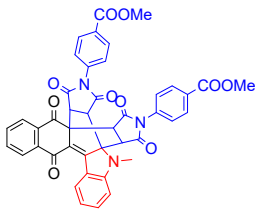
Yield: 72 %, 74 mg; red soild; m.p. 260-263 °C; Rf = 0.11 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.10 (d, *J* = 8.1 Hz, 1H), 8.20 (ddd, *J* = 6.7, 3.6, 1.5 Hz, 2H), 7.89 (m, 7.92-7.87 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 4H), 7.51 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 4H), 6.76 (t, *J* = 7.6 Hz, 1H), 4.36 (d, *J* = 8.6 Hz, 2H), 4.08 (d, *J* = 8.6 Hz, 2H), 3.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.9, 178.4, 174.2, 171.5, 159.0, 153.4, 137.5, 135.9, 135.5, 135.3, 135.2, 134.2, 133.8, 129.7, 127.9, 127.3, 126.7, 119.2, 118.4, 117.4, 116.2, 111.8, 107.9, 72.6, 51.8, 46.0, 41.8, 28.6.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{41}H_{24}N_5O_6^+$: 682.1727; Found: 682.1726.

dimethyl 4,4'-(5-methyl-6,8,9,14,16,18-hexaoxo-5b,6,8,8a,9,14-hexahydro-5H,7H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-7,17-diyl)dibenzoate (5i)



Yield: 69 %, 77 mg; red soild; m.p. 252-256 °C; Rf = 0.18 (PE:EA=1:1).

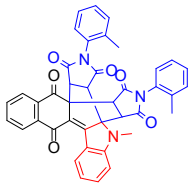
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (d, *J* = 8.1 Hz, 1H), 8.22 – 8.18 (m, 2H), 7.93 – 7.85 (m, 6H), 7.50 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.85 –

6.79 (m, 4H), 6.76 (dd, *J* = 11.3, 4.0 Hz, 1H), 4.35 (d, *J* = 8.6 Hz, 2H), 4.08 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 6H), 3.45 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.0, 178.4, 174.3, 171.7, 165.7, 159.0, 153.5, 137.4, 135.9, 135.7, 135.3, 134.2, 130.4, 130.0, 129.8, 127.9, 126.8, 126.6, 119.3, 117.3, 116.3, 107.9, 72.7, 52.8, 51.8, 46.1, 41.9, 28.6.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{43}H_{30}N_3O_{10}^+$: 748.1931; Found: 748.1929.

5-methyl-7,17-di-o-tolyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5j)



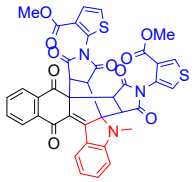
Yield: 68 %, 68 mg; red soild; m.p. 287-289 °C; Rf = 0.26 (PE:EA=1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 – 9.16 (m, 1H), 8.33 (dd, *J* = 14.1, 7.7 Hz, 2H), 7.85 – 7.76 (m, 1H), 7.75 – 7.67 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.22 – 6.98 (m, 6H), 6.94 – 6.24 (m, 4H), 4.20 – 4.06 (m, 2H), 3.69 – 3.57 (m, 2H), 3.34 – 3.20 (m, 3H), 2.09 – 1.43 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.6, 194.6, 178.6, 178.6, 174.1, 173.8, 170.7, 170.6, 158.7, 153.2, 137.4, 137.3, 136.4, 136.3, 136.1, 136.0, 135.1, 135.1, 135.0, 133.6, 131.2, 131.0, 130.8, 130.6, 130.1, 130.1, 129.9, 129.7, 128.3, 127.5, 127.4, 127.3, 126.8, 126.8, 126.3, 120.0, 119.7, 117.9, 117.8, 116.5, 116.3, 107.2, 107.2, 77.4, 77.0, 76.7, 72.1, 71.9, 51.8, 51.7, 45.8, 45.6, 45.5, 42.6, 42.5, 42.5, 28.2, 28.1, 28.1, 17.4, 17.2, 17.2.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{41}H_{30}N_3O_6^+$: 660.2135; Found: 660.2134.

methyl 4-(7-(3-(methoxycarbonyl)thiophen-2-yl)-5-methyl-6,8,9,14,16,18-hexaoxo-5b,7,8,8a,9,14-hexahydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazol-17-yl)thiophene-3-carboxylate (5k)



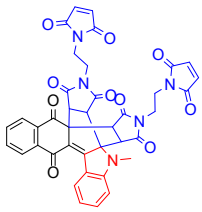
Yield: 54 %, 62 mg; red soild; m.p. 208-219 °C; Rf = 0.2 (PE:EA=1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (d, *J* = 8.1 Hz, 1H), 8.36 – 8.31 (m, 1H), 8.31 – 8.26 (m, 1H), 7.76 – 7.69 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 5.3 Hz, 2H), 6.84 – 6.75 (m, 2H), 6.35 (d, *J* = 5.0 Hz, 2H), 4.16 (d, *J* = 8.9 Hz, 2H), 3.76 (d, *J* = 8.9 Hz, 2H), 3.68 (s, 6H), 3.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.5, 178.9, 172.2, 169.7, 160.0, 158.6, 152.2, 137.1, 136.3, 134.9, 134.6, 133.4, 132.5, 130.5, 130.5, 128.0, 127.0, 126.8, 126.7, 117.8, 116.8, 107.1, 72.0, 52.2, 51.6, 45.7, 42.6, 28.3.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{26}N_3O_{10}S_2^+$: 760.1060; Found: 760.1063.

7,17-bis(2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5l)



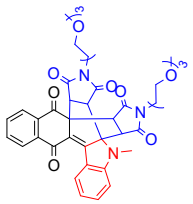
Yield: 51 %, 55 mg; red soild; m.p. 283-287 °C; Rf = 0.13 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.96 (d, *J* = 7.9 Hz, 1H), 8.20 – 8.14 (m, 2H), 7.91 – 7.86 (m, 2H), 7.47 – 7.42 (m, 1H), 6.87 (d, *J* = 10.5 Hz, 5H), 6.67 (t, *J* = 7.4 Hz, 1H), 4.03 (d, *J* = 8.7 Hz, 2H), 3.73 (d, *J* = 8.7 Hz, 2H), 3.35 (s, 3H), 3.15 – 3.05 (m, 8H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 193.8, 178.1, 175.0, 172.5, 171.0, 158.7, 152.9, 137.0, 136.2, 135.2, 135.0, 134.9, 134.0, 130.3, 127.9, 126.6, 119.3, 117.0, 115.9, 107.6, 71.9, 51.1, 45.5, 41.4, 36.9, 34.5, 28.5.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{28}N_5O_{10}^+$: 726.1836; Found: 726.1830.

7,17-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5m)



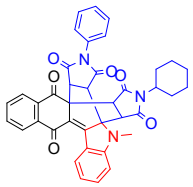
Yield: 44 %, 51 mg; red soild; m.p. 200-202 °C; Rf = 0.14 (PE:EA=1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (d, *J* = 8.1 Hz, 1H), 8.39 – 8.34 (m, 1H), 8.30 – 8.26 (m, 1H), 7.79 (p, *J* = 5.7 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.76 (dd, *J* = 14.5, 7.7 Hz, 2H), 3.87 (d, *J* = 8.7 Hz, 2H), 3.53 – 3.45 (m, 10H), 3.43 (s, 3H), 3.40 – 3.32 (m, 10H), 3.32 – 3.23 (m, 8H), 3.12 (t, *J* = 5.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.8, 178.4, 173.8, 171.3, 158.5, 152.1, 136.9, 136.1, 135.0, 134.6, 133.5, 130.5, 127.9, 126.7, 119.6, 117.4, 116.2, 106.8, 71.8, 71.7, 70.3, 69.9, 66.5, 59.0, 51.3, 45.2, 42.1, 38.3, 28.2.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{41}H_{46}N_3O_{12}^+$: 772.3081; Found: 772.3080.

7-cyclohexyl-5-methyl-17-phenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolo-naphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5n)



Yield: 30 %, 57 mg; red soild; m.p. 294-296 °C; Rf = 0.4 (PE:EA=1:1).

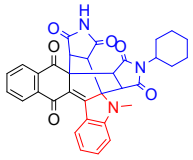
^{1}H NMR (400 MHz, DMSO-d_6): δ 9.07 (d, *J* = 8.1 Hz, 1H), 8.23 – 8.16 (m, 2H), 7.91 – 7.84 (m, 2H), 7.48 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.32 – 7.22 (m, 3H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 11.3, 4.0 Hz, 1H), 6.62 – 6.55 (m, 2H), 4.18 (d, *J* = 8.5 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.97 (d, *J* = 8.5 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 3.40 (s, 3H), 1.53 – 1.36 (m, 5H), 1.08 – 0.71 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.2, 178.4, 175.4, 174.7, 172.7, 172.0, 158.9,

153.3, 137.1, 136.0, 135.4, 135.1, 134.0, 131.7, 129.7, 129.4, 129.1, 127.8, 126.6, 126.5, 119.6, 117.0, 116.3, 107.7, 72.6, 51.8, 50.9, 45.9, 45.3, 41.8, 41.1, 28.5, 28.1, 27.9, 25.4, 24.9.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{39}H_{32}N_3O_6^+$: 638.2291; Found: 638.2291.

7-cyclohexyl-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (5o)



Yield: 37 %, 62 mg; red soild; m.p. 212-217 °C; Rf = 0.34 (PE:EA=1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.14 (s, 1H), 9.07 (d, *J* = 7.9 Hz, 1H), 8.25 – 8.18 (m, 2H), 7.95 – 7.89 (m, 2H), 7.52 – 7.47 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 3.94 (dd, *J* = 15.9, 8.5 Hz, 2H), 3.79 (dd, *J* = 8.5, 3.7 Hz, 2H), 3.38 (s, 3H), 1.55 – 1.37 (m, 5H), 1.11 – 0.75 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 194.3, 178.5, 176.8, 175.4, 174.3, 172.7, 158.9, 153.3, 136.9, 136.1, 135.4, 134.9, 133.9, 129.8, 127.7, 126.5, 119.6, 116.7, 116.4, 107.6, 72.3, 51.4, 50.9, 46.8, 45.6, 42.7, 41.3, 28.5, 28.0, 27.9, 25.4, 24.9.

HRMS (ESI): m/z: $[M+H]^+$ Calcd. for $C_{33}H_{28}N_3O_6^+$: 562.1978; Found: 562.1976.

3.6 X-Ray Diffraction Analysis

Copound **4a** X-Ray crystal diffraction data: Single crystals of 4a were grown in slowly diffusion with acetone as red needle-shaped crystals. A suitable crystal was collected on a Xcalibur, Eos diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. 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 2091590 for compounds **4a**.

Crystal structure determination of **4a**:

Crystal Data for **4a** ($C_{42}H_{31}N_3O_7$, M =689.70 g/mol): triclinic, space group P-1 (no. 2), a = 10.0108(6) Å, b = 12.3924(11) Å, c = 15.3068(16) Å, α = 70.467(9)°, β = 88.314(7)°, γ = 74.969(6)°, V = 1725.0(3) Å^3, Z = 2, T = 293.15 K, μ(MoKα) = 0.091 mm^{-1}, Dcalc = 1.328 g/cm^3, 14135 reflections measured (6.022° ≤ 2Θ ≤ 52.734°), 7039 unique (R_{int} = 0.0474, R_{sigma} = 0.1227) which were used in all calculations. The final R_1 was 0.0620 (I > 2σ(I)) and wR_2 was 0.1572.

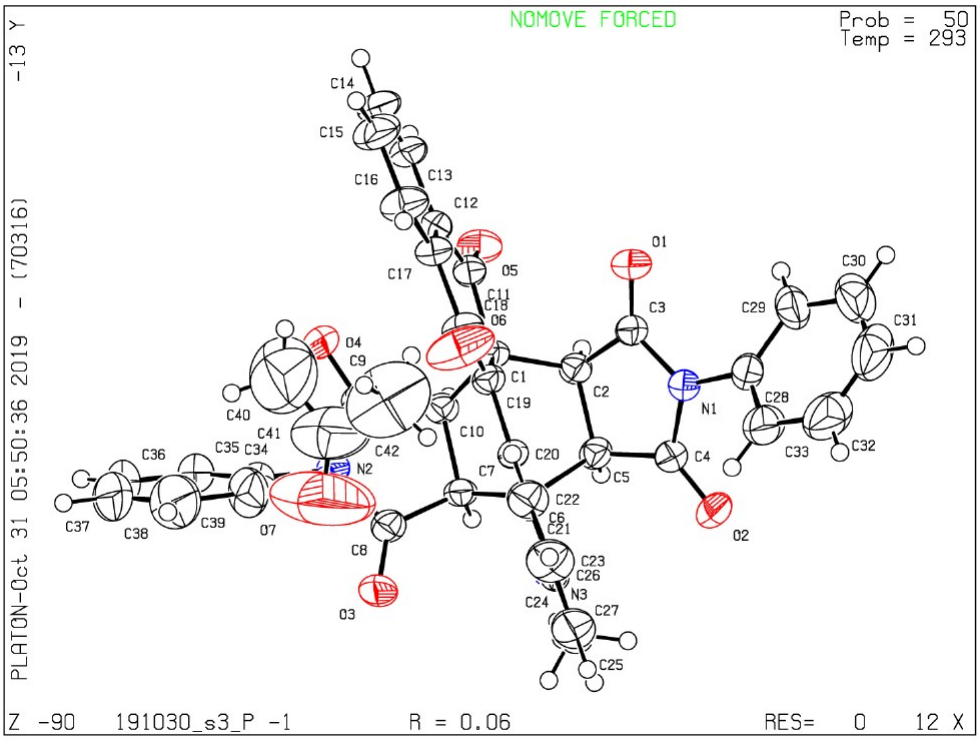


Table S6 Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{42}H_{31}N_3O_7$
Formula weight	689.70
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1

a/Å	10.0108(6)
b/Å	12.3924(11)
c/Å	15.3068(16)
α/°	70.467(9)
β/°	88.314(7)
γ/°	74.969(6)
Volume/Å^3	1725.0(3)
Z	2
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	0.091
F(000)	720.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.022 to 52.734
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	14135
Independent reflections	7039 [R_{int} = 0.0474, R_{sigma} = 0.1227]
Data/restraints/parameters	7039/0/472
Goodness-of-fit on F^2	0.949
Final R indexes [I>=2σ (I)]	R_1 = 0.0620, wR_2 = 0.1212
Final R indexes [all data]	R_1 = 0.1408, wR_2 = 0.1572
Largest diff. peak/hole / e Å^{-3}	0.24/-0.26

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4a**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	7163.0(19)	5464.6(19)	1752.8(16)	58.5(6)
O2	3291(2)	5024.0(19)	573.7(15)	55.1(6)

O3	402.7(19)	9606.5(19)	1197.3(15)	55.0(6)
O4	4591.3(19)	10344.5(19)	1386.2(15)	51.9(6)
O5	7065.7(18)	8439.2(19)	710.8(14)	49.5(6)
O6	4618(2)	6588(3)	3839.0(15)	84.0(9)
N1	5280(2)	4954(2)	1340.3(16)	39.0(6)
N2	2375(2)	10126(2)	1423.7(16)	37.2(6)
N3	1448(2)	7091(2)	1077.6(16)	37.4(6)
C1	5073(2)	7824(2)	1315.5(18)	31.4(6)
C2	5252(2)	6980(2)	743.7(18)	34.0(7)
C3	6056(3)	5747(3)	1330(2)	38.0(7)
C4	4051(3)	5522(3)	788(2)	39.3(7)
C5	3854(2)	6845(2)	498.4(19)	35.3(7)
C6	2727(2)	7432(2)	1048.5(19)	32.3(7)
C7	2589(2)	8774(2)	620.6(19)	33.3(7)
C8	1622(3)	9516(3)	1105.2(19)	36.9(7)
C9	3744(3)	9896(3)	1200(2)	38.2(7)
C10	4009(2)	8997(2)	713.2(18)	32.8(7)
C11	6459(3)	8115(3)	1408(2)	36.1(7)
C12	6993(3)	7973(2)	2331(2)	35.9(7)
C13	8178(3)	8355(3)	2398(2)	48.4(8)
C14	8723(3)	8209(3)	3256(3)	61.5(10)
C15	8119(3)	7703(3)	4050(3)	64.2(10)
C16	6946(3)	7323(3)	3993(2)	58.1(9)
C17	6371(3)	7469(3)	3135(2)	40.0(7)
C18	5097(3)	7048(3)	3112(2)	43.7(8)
C19	4450(3)	7276(2)	2207.9(18)	32.7(6)

C20	3237(2)	7009(2)	2063.9(18)	31.8(6)
C21	2278(3)	6397(2)	2599(2)	35.2(7)
C22	2226(3)	5776(3)	3540(2)	48.6(8)
C23	1161(3)	5250(3)	3823(3)	62.2(10)
C24	156(3)	5334(3)	3183(3)	61.8(10)
C25	178(3)	5911(3)	2257(3)	49.2(8)
C26	1246(3)	6456(2)	1967(2)	36.9(7)
C27	570(3)	7326(3)	267(2)	52.9(9)
C28	5691(3)	3696(3)	1802(2)	47.1(8)
C29	7031(3)	3053(3)	1761(2)	61.0(10)
C30	7372(5)	1836(4)	2175(3)	84.8(14)
C31	6398(6)	1284(4)	2599(3)	103.9(18)
C32	5067(5)	1918(4)	2651(3)	92.2(15)
C33	4721(4)	3143(3)	2250(3)	66.3(10)
C34	1807(3)	10907(3)	1927(2)	43.2(8)
C35	1728(3)	12100(3)	1529(3)	57.4(9)
C36	1185(4)	12848(4)	2021(3)	80.2(13)
C37	736(4)	12422(5)	2878(4)	98.5(17)
C38	823(4)	11220(5)	3270(3)	92.4(14)
C39	1366(3)	10455(4)	2797(2)	65.5(10)
O7	1169(5)	7859(7)	4977(4)	267(4)
C40	3202(8)	8353(7)	5118(5)	190(3)
C41	2323(7)	7543(10)	5267(5)	147(3)
C42	3052(8)	6300(7)	5827(4)	164(3)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4a**. 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	33.1(12)	58.1(16)	88.6(17)	-33.2(14)	-13.3(11)	-6.5(11)
O2	49.1(13)	49.4(14)	75.3(16)	-31.5(13)	-16.1(11)	-11.7(11)
O3	27.5(11)	54.1(15)	92.7(18)	-33.7(13)	13.2(11)	-16.0(10)
O4	38.3(12)	55.4(15)	78.1(16)	-36.8(13)	5.9(11)	-20.6(11)
O5	33.5(11)	62.2(15)	54.9(14)	-16.6(12)	12.1(10)	-21.2(11)
O6	82.5(17)	145(3)	43.0(14)	-21.0(16)	11.2(12)	-76.0(18)
N1	32.4(13)	35.9(15)	50.2(15)	-19.4(13)	-6.4(11)	-4.3(12)
N2	28.1(13)	36.8(14)	49.9(15)	-17.2(12)	2.8(11)	-11.0(11)
N3	27.9(12)	39.5(15)	50.8(15)	-16.1(13)	-1.1(11)	-17.4(11)
C1	24.9(14)	35.4(16)	35.8(16)	-11.5(13)	3.7(11)	-12.3(13)
C2	28.8(15)	40.8(18)	38.1(16)	-18.7(14)	8.5(12)	-12.5(13)
C3	29.3(16)	44.6(19)	48.1(18)	-26.0(16)	3.8(14)	-9.9(14)
C4	32.8(16)	42.7(19)	47.8(19)	-22.8(16)	-0.6(14)	-8.5(15)
C5	34.2(16)	42.5(18)	35.7(16)	-19.7(14)	3.3(12)	-12.7(14)
C6	21.1(14)	33.1(16)	44.2(17)	-12.8(14)	-1.6(12)	-9.5(12)
C7	25.1(14)	32.3(16)	41.4(16)	-9.8(14)	-1.0(12)	-9.2(12)
C8	34.1(17)	33.3(17)	43.1(17)	-9.6(14)	4.0(13)	-13.3(14)
C9	32.0(16)	35.2(17)	47.7(18)	-11.0(15)	-0.4(13)	-12.9(14)
C10	29.0(15)	33.4(17)	36.5(16)	-9.1(14)	6.5(12)	-13.2(13)
C11	29.3(15)	36.1(17)	47.0(18)	-16.8(15)	8.1(14)	-12.6(13)
C12	24.2(14)	29.9(16)	53.8(19)	-16.6(15)	-0.7(13)	-3.9(12)
C13	33.8(17)	44(2)	73(2)	-21.8(18)	-2.7(16)	-16.2(15)
C14	41.1(19)	60(2)	91(3)	-28(2)	-13.2(19)	-20.5(18)
C15	55(2)	73(3)	70(3)	-26(2)	-20.6(19)	-21(2)
C16	49(2)	77(3)	53(2)	-22(2)	-7.9(16)	-22.8(19)
C17	30.9(16)	45.3(19)	45.6(18)	-17.2(15)	-5.9(13)	-10.0(14)
C18	36.5(17)	61(2)	40.0(18)	-18.9(16)	4.4(14)	-21.3(16)

C19	29.7(15)	36.0(17)	35.8(16)	-13.6(14)	4.6(12)	-12.9(13)
C20	25.9(14)	32.7(16)	41.3(17)	-15.8(13)	3.7(12)	-10.9(12)
C21	28.0(15)	30.6(17)	48.2(18)	-11.4(14)	5.6(13)	-12.6(13)
C22	43.8(18)	43(2)	55(2)	-7.8(16)	8.3(15)	-17.2(16)
C23	55(2)	61(2)	69(2)	-12(2)	19.4(18)	-26.7(19)
C24	45(2)	52(2)	94(3)	-21(2)	26(2)	-28.2(18)
C25	32.6(17)	40.6(19)	86(3)	-29.4(19)	12.1(16)	-19.3(15)
C26	29.8(15)	28.3(16)	54.0(19)	-15.7(15)	5.0(14)	-8.1(13)
C27	39.7(18)	60(2)	63(2)	-23.4(19)	-10.1(16)	-16.5(16)
C28	47.3(19)	36.9(19)	60(2)	-23.1(17)	-12.0(16)	-4.4(17)
C29	59(2)	58(2)	67(2)	-39(2)	-14.1(18)	8.6(19)
C30	80(3)	68(3)	98(3)	-44(3)	-36(3)	21(3)
C31	125(4)	47(3)	130(4)	-31(3)	-67(4)	4(3)
C32	93(3)	53(3)	121(4)	-12(3)	-41(3)	-21(3)
C33	58(2)	41(2)	95(3)	-15(2)	-19(2)	-11.1(19)
C34	32.1(16)	45(2)	60(2)	-27.0(18)	5.5(14)	-10.5(15)
C35	47.4(19)	49(2)	82(3)	-32(2)	-0.4(17)	-9.5(17)
C36	62(3)	62(3)	134(4)	-62(3)	1(3)	-8(2)
C37	72(3)	112(4)	153(5)	-102(4)	20(3)	-20(3)
C38	88(3)	129(5)	90(3)	-72(3)	33(2)	-34(3)
C39	73(2)	73(3)	64(2)	-41(2)	26.3(19)	-22(2)
O7	96(3)	511(11)	242(6)	-233(7)	-22(3)	-19(5)
C40	207(8)	187(8)	182(7)	-97(6)	-49(6)	-13(6)
C41	95(5)	284(11)	100(5)	-118(6)	12(4)	-47(6)
C42	201(7)	227(9)	81(4)	-39(5)	35(4)	-105(7)

Table S8 Bond Lengths for **4a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C3	1.208(3)	C12	C17	1.391(4)
O2	C4	1.209(3)	C13	C14	1.374(4)
O3	C8	1.205(3)	C14	C15	1.371(4)
O4	C9	1.214(3)	C15	C16	1.389(4)
O5	C11	1.213(3)	C16	C17	1.385(4)
O6	C18	1.217(3)	C17	C18	1.503(4)
N1	C3	1.398(3)	C18	C19	1.453(4)
N1	C4	1.392(3)	C19	C20	1.380(3)
N1	C28	1.430(4)	C20	C21	1.443(3)
N2	C8	1.394(3)	C21	C22	1.394(4)
N2	C9	1.382(3)	C21	C26	1.407(4)
N2	C34	1.429(3)	C22	C23	1.377(4)
N3	C6	1.444(3)	C23	C24	1.386(4)
N3	C26	1.365(3)	C24	C25	1.360(4)
N3	C27	1.445(3)	C25	C26	1.395(4)
C1	C2	1.549(4)	C28	C29	1.384(4)
C1	C10	1.567(3)	C28	C33	1.369(4)
C1	C11	1.543(3)	C29	C30	1.378(5)
C1	C19	1.506(3)	C30	C31	1.361(6)
C2	C3	1.508(4)	C31	C32	1.376(6)
C2	C5	1.524(3)	C32	C33	1.385(5)
C4	C5	1.508(4)	C34	C35	1.380(4)
C5	C6	1.562(4)	C34	C39	1.369(4)
C6	C7	1.540(4)	C35	C36	1.379(5)
C6	C20	1.521(4)	C36	C37	1.352(6)
C7	C8	1.512(4)	C37	C38	1.387(6)

C7	C10	1.536(3)	C38	C39	1.374(5)
C9	C10	1.504(4)	O7	C41	1.168(6)
C11	C12	1.464(4)	C40	C41	1.458(9)
C12	C13	1.405(3)	C41	C42	1.486(9)

Table S9 Bond Angles for **4a**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C3	N1	C28	126.1(2)	C13	C12	C11	118.3(3)
C4	N1	C3	111.7(2)	C17	C12	C11	122.2(2)
C4	N1	C28	122.1(2)	C17	C12	C13	119.5(3)
C8	N2	C34	124.2(2)	C14	C13	C12	119.7(3)
C9	N2	C8	112.7(2)	C15	C14	C13	120.9(3)
C9	N2	C34	123.1(2)	C14	C15	C16	119.9(3)
C6	N3	C27	124.2(2)	C17	C16	C15	120.3(3)
C26	N3	C6	110.1(2)	C12	C17	C18	122.2(2)
C26	N3	C27	125.6(2)	C16	C17	C12	119.7(3)
C2	C1	C10	105.0(2)	C16	C17	C18	118.1(3)
C11	C1	C2	109.6(2)	O6	C18	C17	119.3(3)
C11	C1	C10	108.0(2)	O6	C18	C19	123.0(2)
C19	C1	C2	107.8(2)	C19	C18	C17	117.7(3)
C19	C1	C10	109.4(2)	C18	C19	C1	122.2(2)
C19	C1	C11	116.5(2)	C20	C19	C1	112.7(2)
C3	C2	C1	109.7(2)	C20	C19	C18	125.0(2)
C3	C2	C5	104.9(2)	C19	C20	C6	114.2(2)
C5	C2	C1	110.8(2)	C19	C20	C21	138.8(2)
O1	C3	N1	124.1(3)	C21	C20	C6	107.0(2)
O1	C3	C2	127.3(3)	C22	C21	C20	134.0(2)
N1	C3	C2	108.6(2)	C22	C21	C26	118.9(2)

O2	C4	N1	125.0(3)	C26	C21	C20	107.1(2)
O2	C4	C5	126.5(3)	C23	C22	C21	119.0(3)
N1	C4	C5	108.5(2)	C22	C23	C24	120.5(3)
C2	C5	C6	108.8(2)	C25	C24	C23	122.5(3)
C4	C5	C2	104.5(2)	C24	C25	C26	117.2(3)
C4	C5	C6	112.2(2)	N3	C26	C21	111.6(2)
N3	C6	C5	114.0(2)	N3	C26	C25	126.6(3)
N3	C6	C7	115.3(2)	C25	C26	C21	121.8(3)
N3	C6	C20	104.0(2)	C29	C28	N1	120.1(3)
C7	C6	C5	105.2(2)	C33	C28	N1	118.8(3)
C20	C6	C5	109.5(2)	C33	C28	C29	121.0(3)
C20	C6	C7	108.9(2)	C30	C29	C28	118.6(4)
C8	C7	C6	114.2(2)	C31	C30	C29	120.4(4)
C8	C7	C10	105.2(2)	C30	C31	C32	121.4(4)
C10	C7	C6	108.8(2)	C31	C32	C33	118.6(4)
O3	C8	N2	124.2(3)	C28	C33	C32	119.9(4)
O3	C8	C7	127.6(3)	C35	C34	N2	119.2(3)
N2	C8	C7	108.2(2)	C39	C34	N2	119.4(3)
O4	C9	N2	124.7(3)	C39	C34	C35	121.5(3)
O4	C9	C10	126.0(3)	C36	C35	C34	118.9(4)
N2	C9	C10	109.3(2)	C37	C36	C35	120.7(4)
C7	C10	C1	110.5(2)	C36	C37	C38	119.8(4)
C9	C10	C1	110.1(2)	C39	C38	C37	120.7(4)
C9	C10	C7	104.5(2)	C34	C39	C38	118.5(4)
O5	C11	C1	118.3(2)	O7	C41	C40	122.5(10)
O5	C11	C12	123.0(2)	O7	C41	C42	124.7(9)
C12	C11	C1	118.7(2)	C40	C41	C42	112.8(6)

Table S10 Torsion Angles for **4a**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C4	C5	C2	-166.0(3)	C10	C1	C11	C12	116.6(3)
O2	C4	C5	C6	76.4(4)	C10	C1	C19	C18	-121.6(3)
O4	C9	C10	C1	63.6(4)	C10	C1	C19	C20	59.3(3)
O4	C9	C10	C7	-177.7(3)	C10	C7	C8	O3	179.9(3)
O5	C11	C12	C13	7.4(4)	C10	C7	C8	N2	1.4(3)
O5	C11	C12	C17	-172.2(3)	C11	C1	C2	C3	74.3(3)
O6	C18	C19	C1	-178.8(3)	C11	C1	C2	C5	-170.3(2)
O6	C18	C19	C20	0.3(5)	C11	C1	C10	C7	-178.2(2)
N1	C4	C5	C2	13.1(3)	C11	C1	C10	C9	-63.2(3)
N1	C4	C5	C6	-104.6(2)	C11	C1	C19	C18	1.1(4)
N1	C28	C29	C30	-176.8(3)	C11	C1	C19	C20	-178.1(2)
N1	C28	C33	C32	175.8(3)	C11	C12	C13	C14	-178.5(3)
N2	C9	C10	C1	-115.3(2)	C11	C12	C17	C16	178.0(3)
N2	C9	C10	C7	3.4(3)	C11	C12	C17	C18	-0.8(4)
N2	C34	C35	C36	-179.6(3)	C12	C13	C14	C15	-0.5(5)
N2	C34	C39	C38	180.0(3)	C12	C17	C18	O6	178.2(3)
N3	C6	C7	C8	58.3(3)	C12	C17	C18	C19	-5.1(4)
N3	C6	C7	C10	175.4(2)	C13	C12	C17	C16	-1.6(4)
N3	C6	C20	C19	-178.2(2)	C13	C12	C17	C18	179.6(3)
N3	C6	C20	C21	3.4(3)	C13	C14	C15	C16	0.4(5)
C1	C2	C3	O1	-52.7(4)	C14	C15	C16	C17	-0.9(5)
C1	C2	C3	N1	125.1(2)	C15	C16	C17	C12	1.5(5)
C1	C2	C5	C4	-129.6(2)	C15	C16	C17	C18	-179.7(3)
C1	C2	C5	C6	-9.6(3)	C16	C17	C18	O6	-0.6(5)
C1	C11	C12	C13	-173.5(2)	C16	C17	C18	C19	176.1(3)

C1	C11	C12	C17	6.8(4)	C17	C12	C13	C14	1.1(4)
C1	C19	C20	C6	-5.6(3)	C17	C18	C19	C1	4.7(4)
C1	C19	C20	C21	172.0(3)	C17	C18	C19	C20	-176.2(3)
C2	C1	C10	C7	64.9(3)	C18	C19	C20	C6	175.3(3)
C2	C1	C10	C9	179.9(2)	C18	C19	C20	C21	-7.1(5)
C2	C1	C11	O5	49.6(3)	C19	C1	C2	C3	-53.4(3)
C2	C1	C11	C12	-129.6(3)	C19	C1	C2	C5	62.0(3)
C2	C1	C19	C18	124.7(3)	C19	C1	C10	C7	-50.6(3)
C2	C1	C19	C20	-54.4(3)	C19	C1	C10	C9	64.4(3)
C2	C5	C6	N3	-164.0(2)	C19	C1	C11	O5	172.3(3)
C2	C5	C6	C7	68.8(2)	C19	C1	C11	C12	-6.8(4)
C2	C5	C6	C20	-48.1(3)	C19	C20	C21	C22	-1.4(6)
C3	N1	C4	O2	169.1(3)	C19	C20	C21	C26	-178.7(3)
C3	N1	C4	C5	-9.9(3)	C20	C6	C7	C8	-58.1(3)
C3	N1	C28	C29	-42.7(4)	C20	C6	C7	C10	59.1(3)
C3	N1	C28	C33	139.9(3)	C20	C21	C22	C23	-177.6(3)
C3	C2	C5	C4	-11.3(3)	C20	C21	C26	N3	-2.1(3)
C3	C2	C5	C6	108.7(2)	C20	C21	C26	C25	177.7(2)
C4	N1	C3	O1	-179.8(3)	C21	C22	C23	C24	0.0(5)
C4	N1	C3	C2	2.3(3)	C22	C21	C26	N3	-179.9(3)
C4	N1	C28	C29	133.3(3)	C22	C21	C26	C25	-0.1(4)
C4	N1	C28	C33	-44.2(4)	C22	C23	C24	C25	1.2(6)
C4	C5	C6	N3	-48.9(3)	C23	C24	C25	C26	-1.8(5)
C4	C5	C6	C7	-176.1(2)	C24	C25	C26	N3	-179.0(3)
C4	C5	C6	C20	67.0(3)	C24	C25	C26	C21	1.2(4)
C5	C2	C3	O1	-171.8(3)	C26	N3	C6	C5	114.4(3)
C5	C2	C3	N1	6.0(3)	C26	N3	C6	C7	-123.9(3)

C5	C6	C7	C8	-175.3(2)	C26	N3	C6	C20	-4.8(3)
C5	C6	C7	C10	-58.2(3)	C26	C21	C22	C23	-0.5(4)
C5	C6	C20	C19	59.7(3)	C27	N3	C6	C5	-61.7(3)
C5	C6	C20	C21	-118.7(2)	C27	N3	C6	C7	60.0(4)
C6	N3	C26	C21	4.5(3)	C27	N3	C6	C20	179.2(3)
C6	N3	C26	C25	-175.3(3)	C27	N3	C26	C21	-179.5(3)
C6	C7	C8	O3	-60.8(4)	C27	N3	C26	C25	0.7(5)
C6	C7	C8	N2	120.6(2)	C28	N1	C3	O1	-3.5(5)
C6	C7	C10	C1	-7.1(3)	C28	N1	C3	C2	178.7(3)
C6	C7	C10	C9	-125.5(2)	C28	N1	C4	O2	-7.3(4)
C6	C20	C21	C22	176.4(3)	C28	N1	C4	C5	173.6(2)
C6	C20	C21	C26	-1.0(3)	C28	C29	C30	C31	1.1(6)
C7	C6	C20	C19	-54.8(3)	C29	C28	C33	C32	-1.7(5)
C7	C6	C20	C21	126.8(2)	C29	C30	C31	C32	-1.8(7)
C8	N2	C9	O4	178.3(3)	C30	C31	C32	C33	0.7(7)
C8	N2	C9	C10	-2.7(3)	C31	C32	C33	C28	1.0(6)
C8	N2	C34	C35	-114.7(3)	C33	C28	C29	C30	0.6(5)
C8	N2	C34	C39	65.9(4)	C34	N2	C8	O3	2.2(4)
C8	C7	C10	C1	115.7(2)	C34	N2	C8	C7	-179.2(2)
C8	C7	C10	C9	-2.8(3)	C34	N2	C9	O4	-1.7(5)
C9	N2	C8	O3	-177.8(3)	C34	N2	C9	C10	177.3(2)
C9	N2	C8	C7	0.8(3)	C34	C35	C36	C37	-0.1(5)
C9	N2	C34	C35	65.3(4)	C35	C34	C39	C38	0.7(5)
C9	N2	C34	C39	-114.1(3)	C35	C36	C37	C38	0.1(6)
C10	C1	C2	C3	-169.9(2)	C36	C37	C38	C39	0.3(7)
C10	C1	C2	C5	-54.5(3)	C37	C38	C39	C34	-0.7(6)
C10	C1	C11	O5	-64.3(3)	C39	C34	C35	C36	-0.3(5)

Table S11 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å2×10^3) for **4a**

Atom	*x*	*y*	*z*	U(eq)
H2	5727	7272	179	41
H5	3620	7218	-171	42
H7	2280	9051	-38	40
H10	4351	9316	99	39
H13	8592	8705	1864	58
H14	9511	8458	3299	74
H15	8495	7613	4627	77
H16	6545	6969	4532	70
H22	2901	5719	3970	58
H23	1116	4834	4449	75
H24	-562	4982	3395	74
H25	-492	5940	1835	59
H27A	819	7916	-252	79
H27B	-381	7610	386	79
H27C	689	6608	128	79
H29	7689	3433	1461	73
H30	8272	1390	2164	102
H31	6638	460	2860	125
H32	4413	1532	2949	111
H33	3831	3590	2286	80
H35	2035	12395	939	69
H36	1127	13654	1760	96
H37	371	12934	3204	118
H38	509	10930	3858	111
H39	1433	9648	3061	79

H40A	3563	8479	4515	284
H40B	3955	8015	5585	284
H40C	2666	9098	5158	284
H42A	3105	6225	6470	247
H42B	3971	6102	5622	247
H42C	2551	5772	5748	247

4 Reference

[1] Y. Hong, J. Chen, Z. Zhang, Y. Liu, W. Zhang, *Org. Lett.*, 2016, **18**, 2640.

[2] D. Xia, X. Guo, L. Chen, M. Baumgarten, A. Keerthi, K. Müllen, *Angew. Chem. Int. Ed.*, 2016, **55**, 941.

[3] M. Delor, J. Dai, T. D. Roberts, J. R. Rogers, S. M. Hamed, J. B. Neaton, P. L. Geissler, M. B. Francis, N. S. Ginsberg, *J. Am. Chem. Soc.*, 2018, **140**, 6278.

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

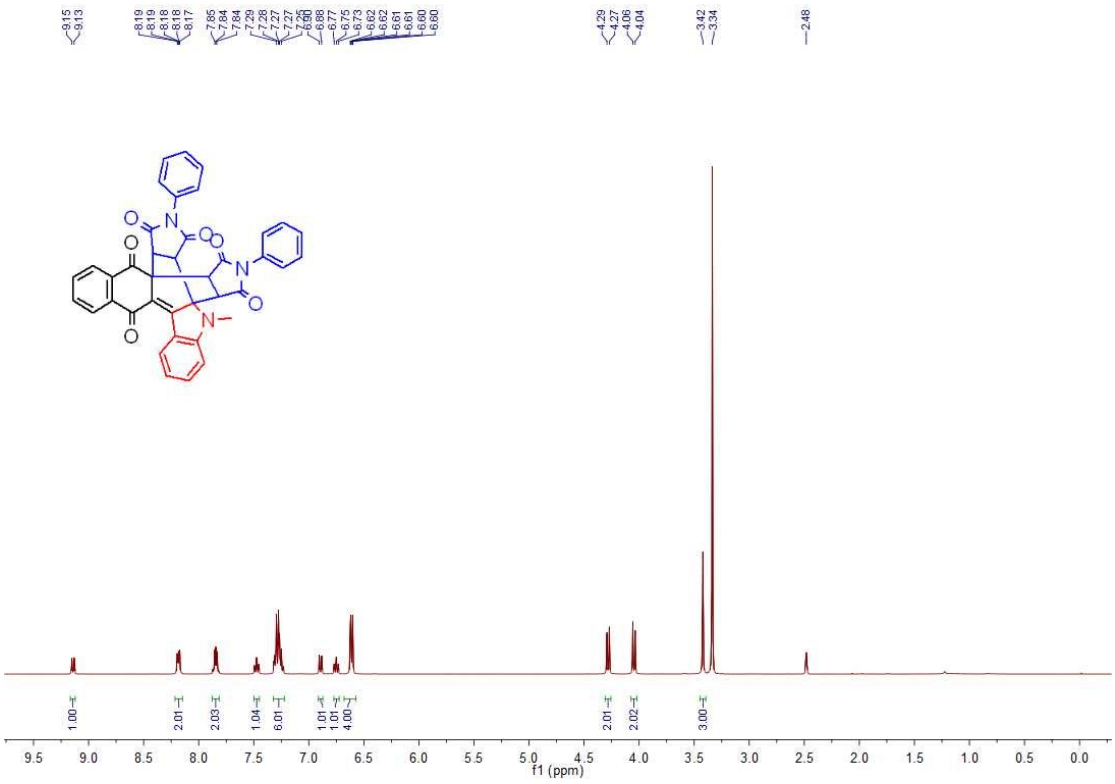
[5] M. Fischer, J. Georges, *Chem. Phys. Lett.*, 1996, **260**,115.

[6] J. N. Demas, G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

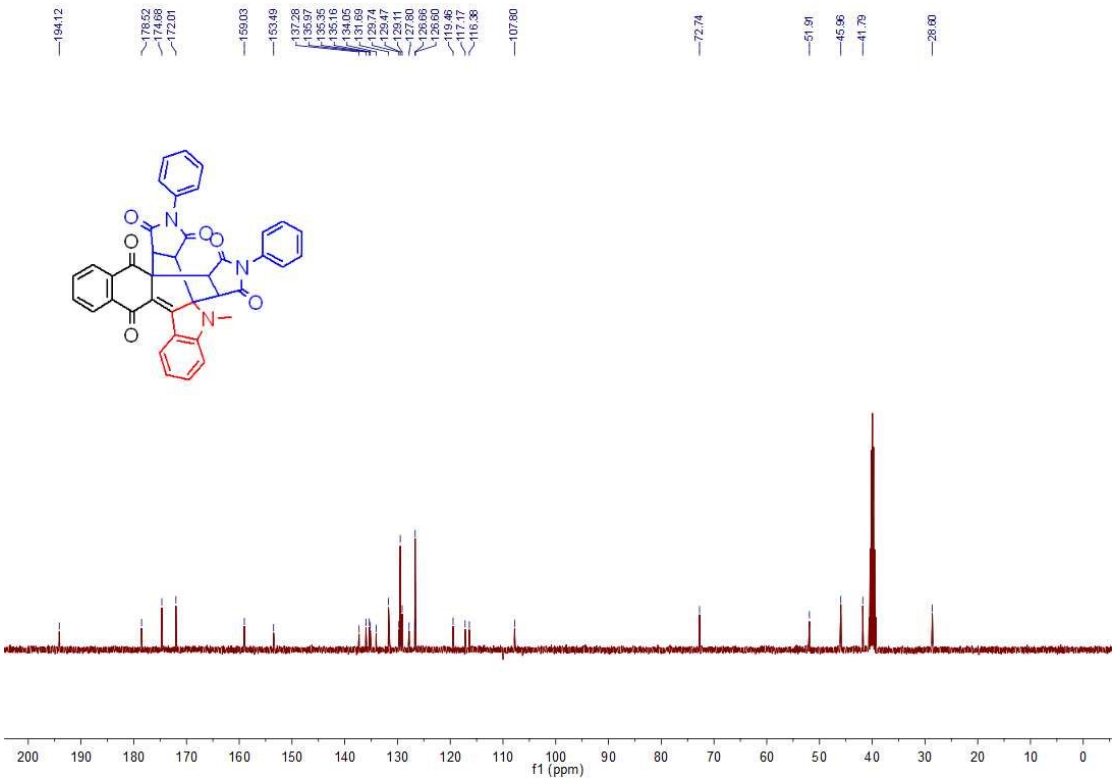
5 NMR spectra of products

5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (**4a**)

^{1}H NMR (400 MHz)

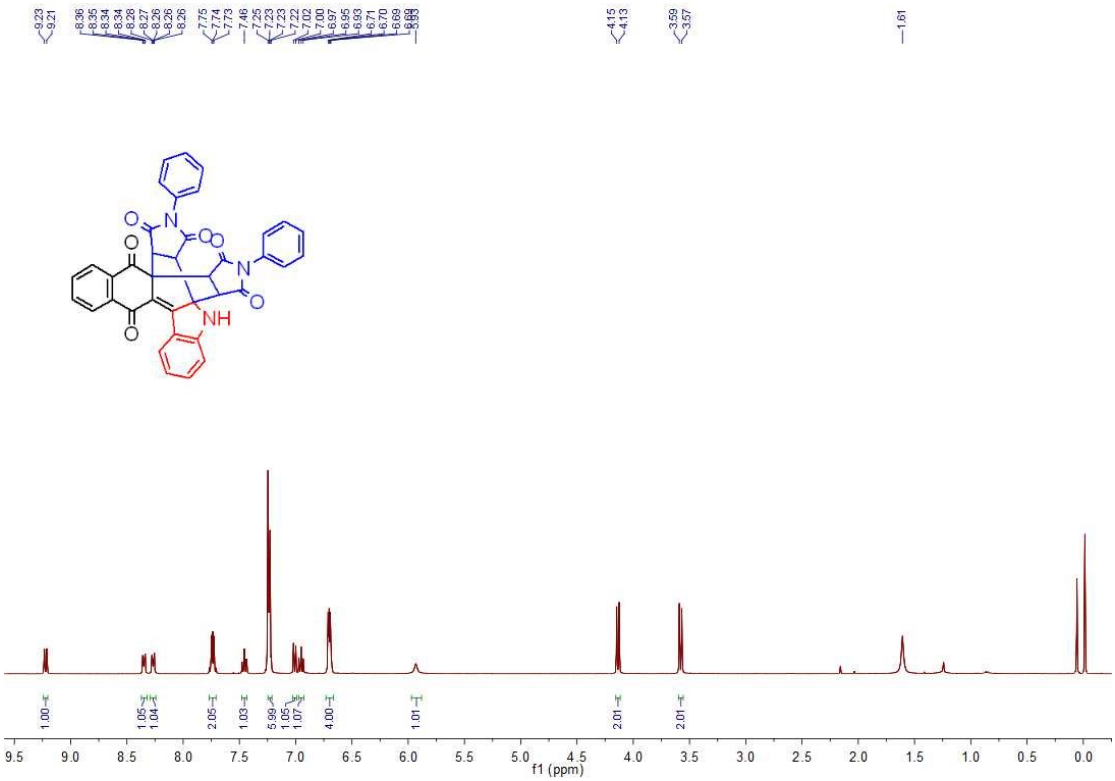


^{13}C NMR (101 MHz)

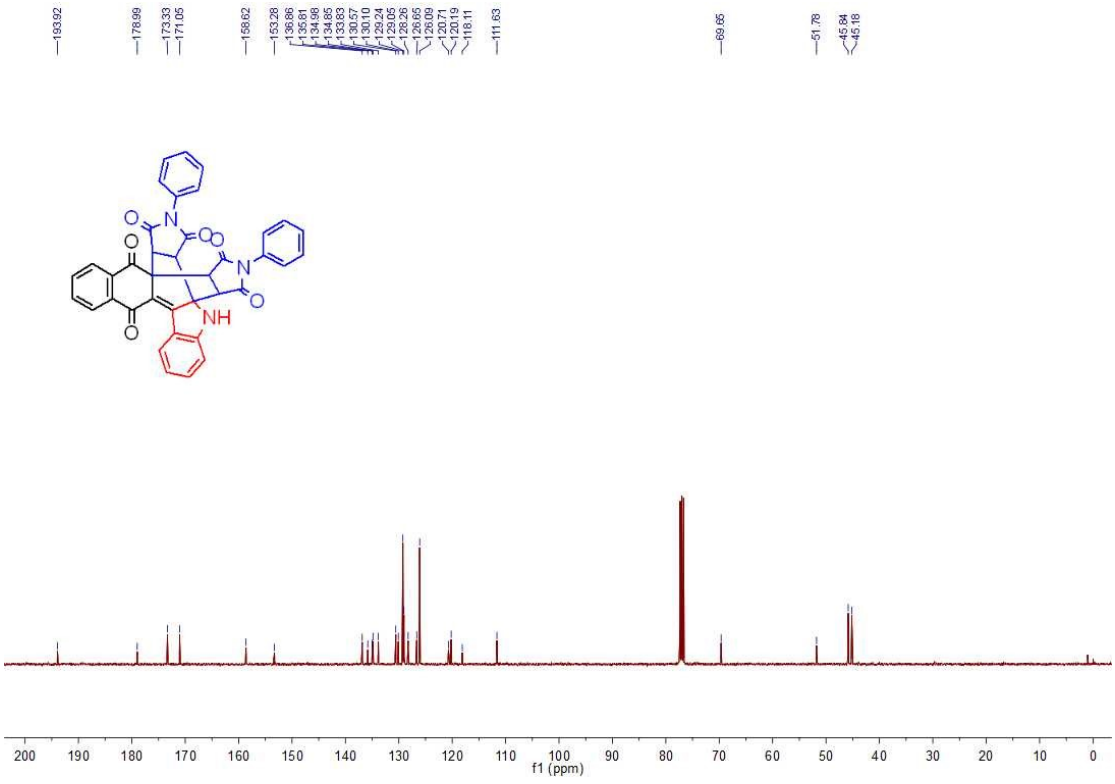


7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4b**)

^{1}H NMR (400 MHz)



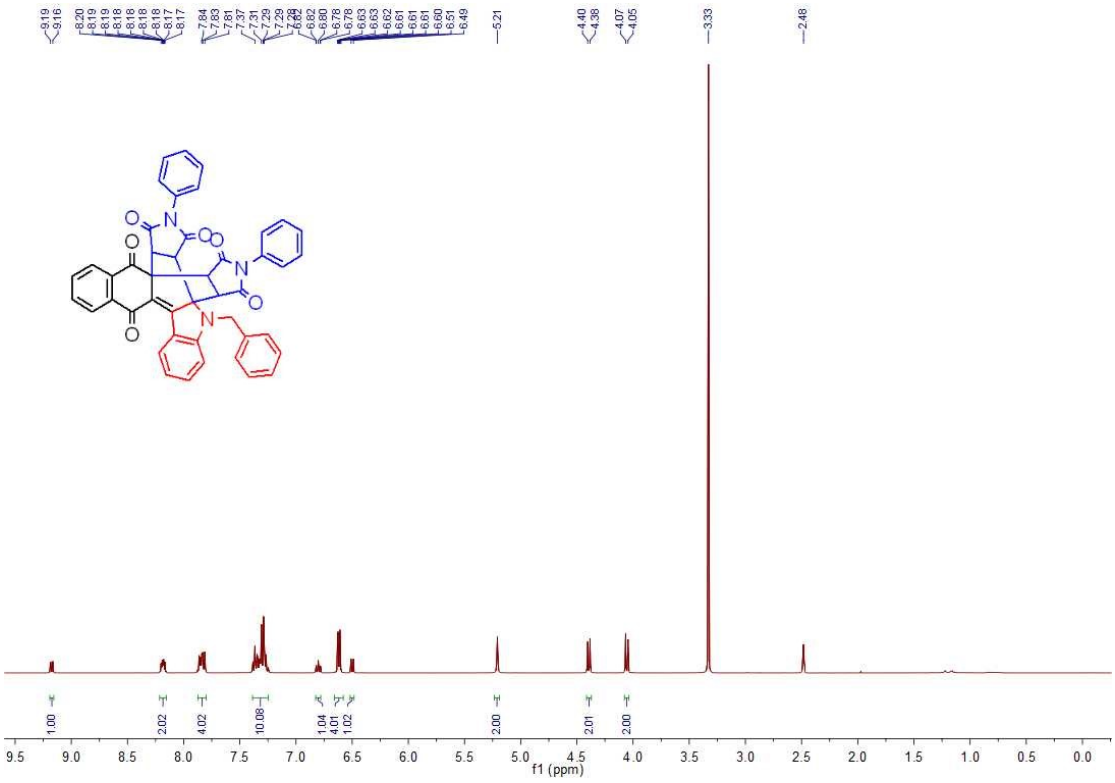
^{13}C NMR (101 MHz)



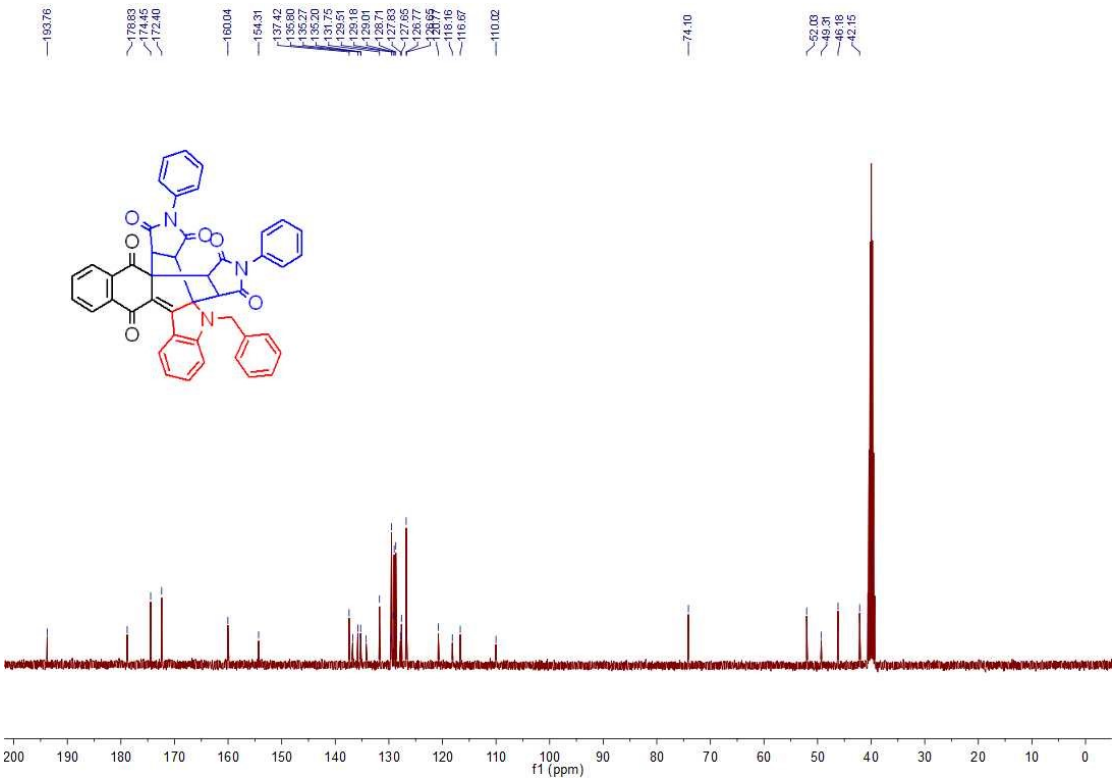
5-benzyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-

c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4c**)

^{1}H NMR (400 MHz)

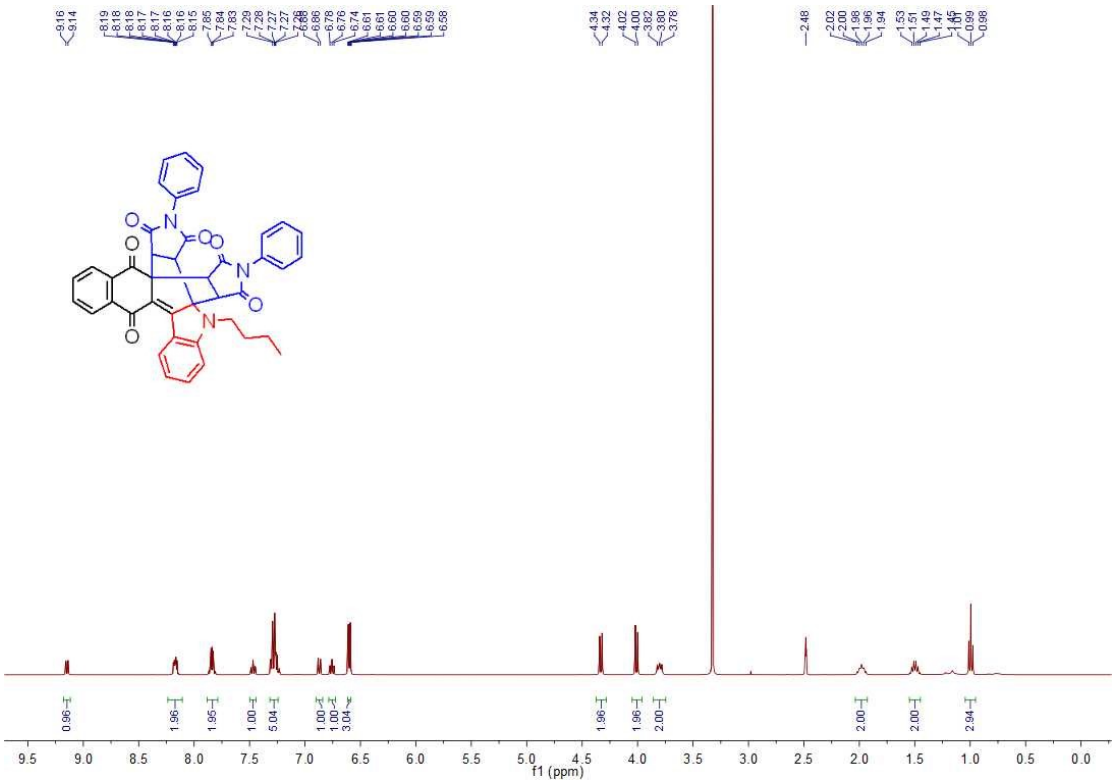


^{13}C NMR (101 MHz)

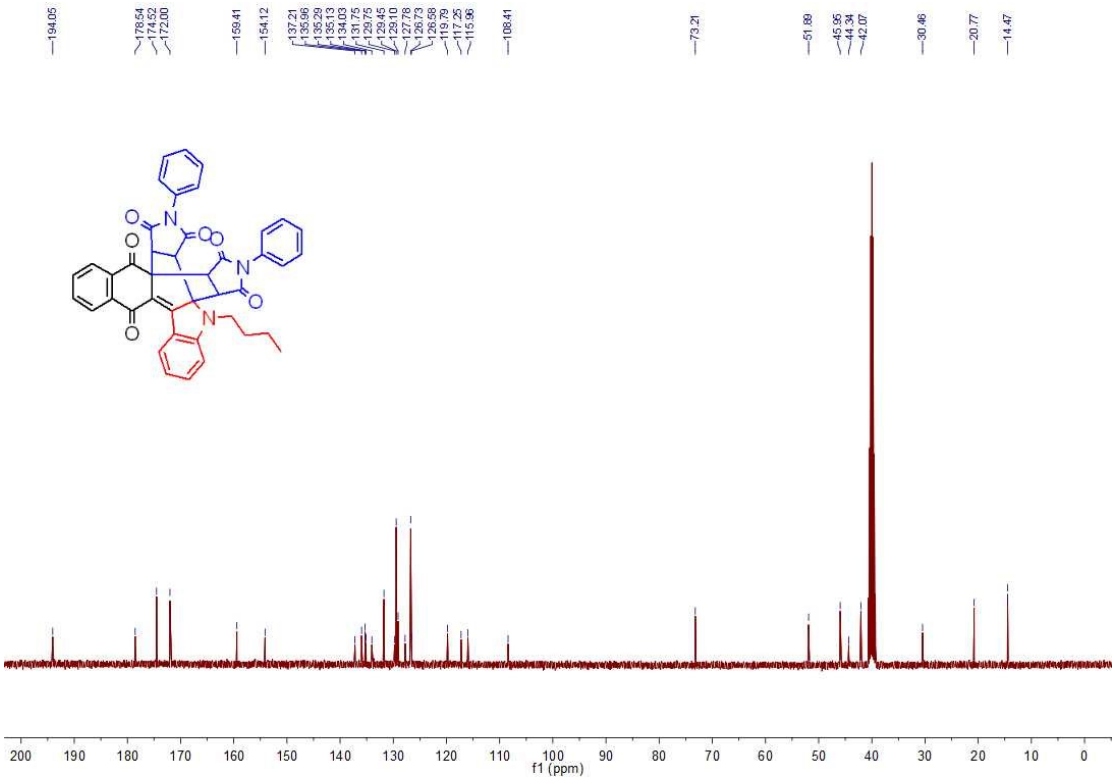


5-butyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4d**)

^{1}H NMR (400 MHz)



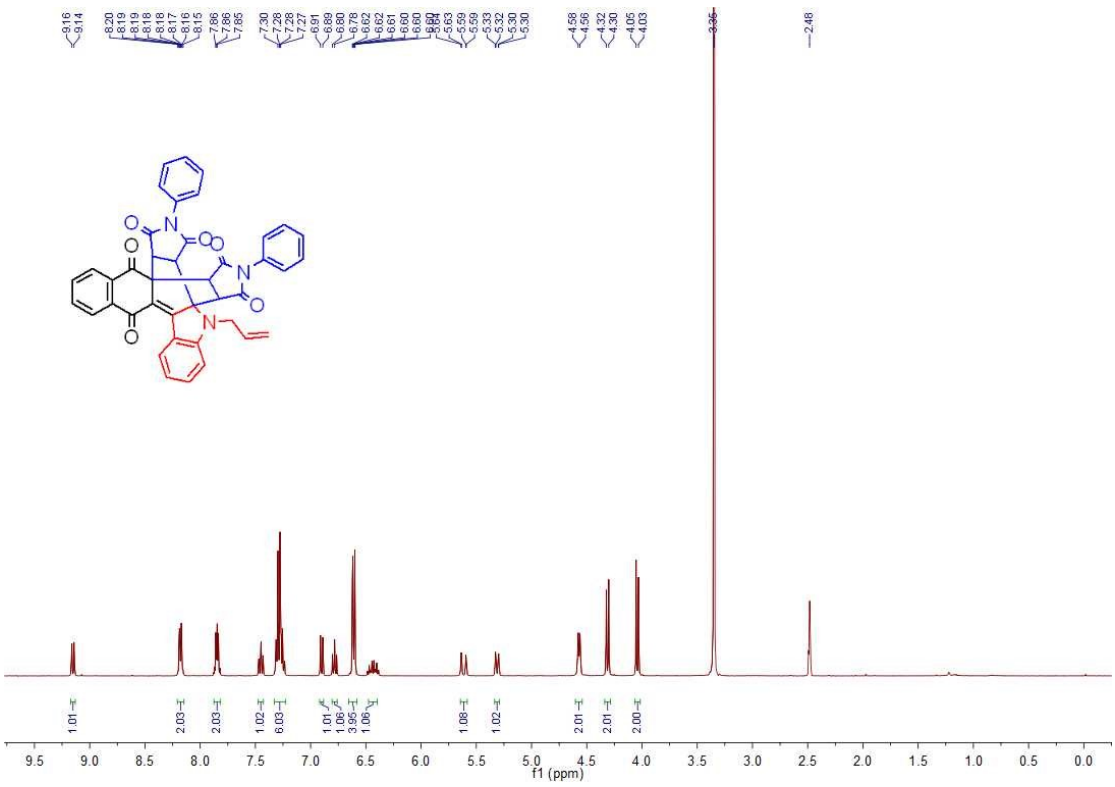
^{13}C NMR (101 MHz)



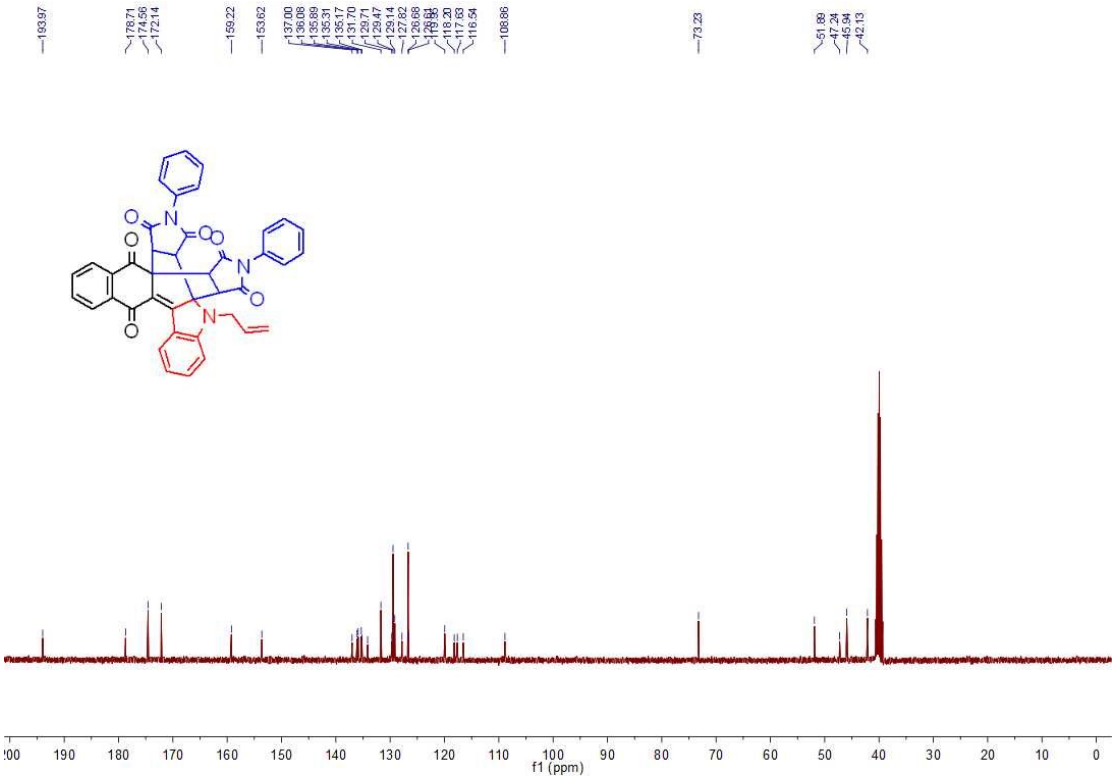
5-allyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-

c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4f**)

^{1}H NMR (101 MHz)

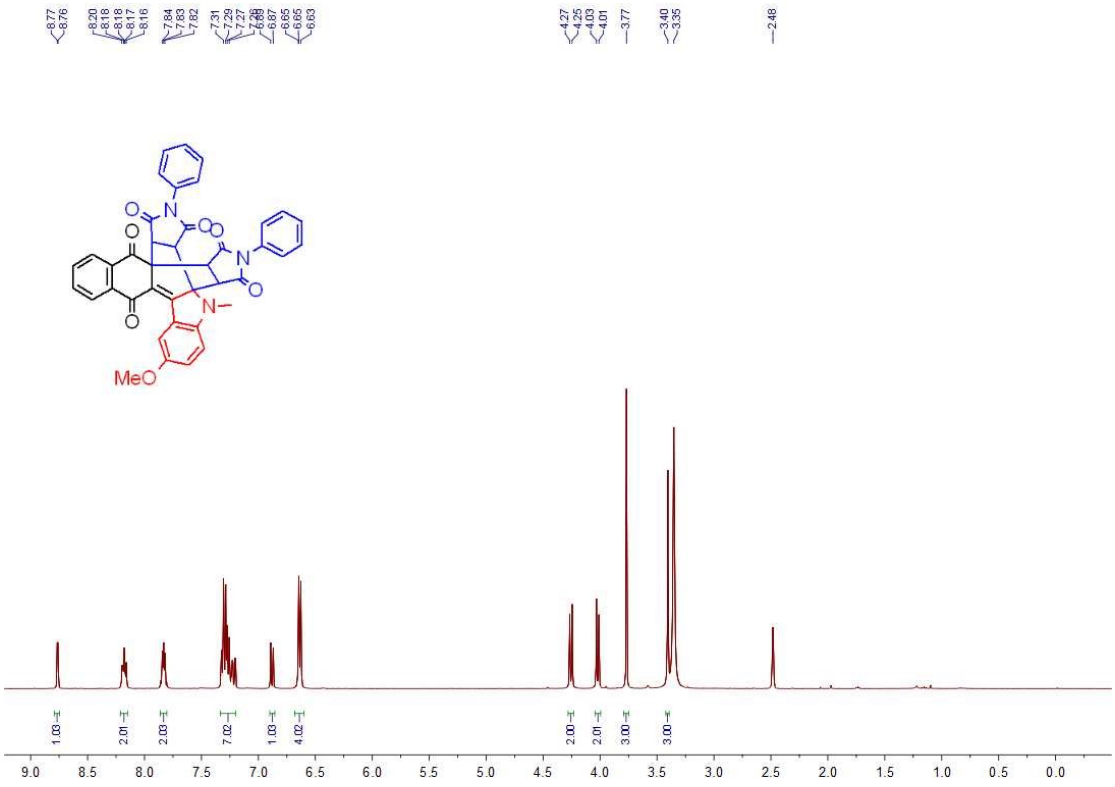


^{13}C NMR (400 MHz)

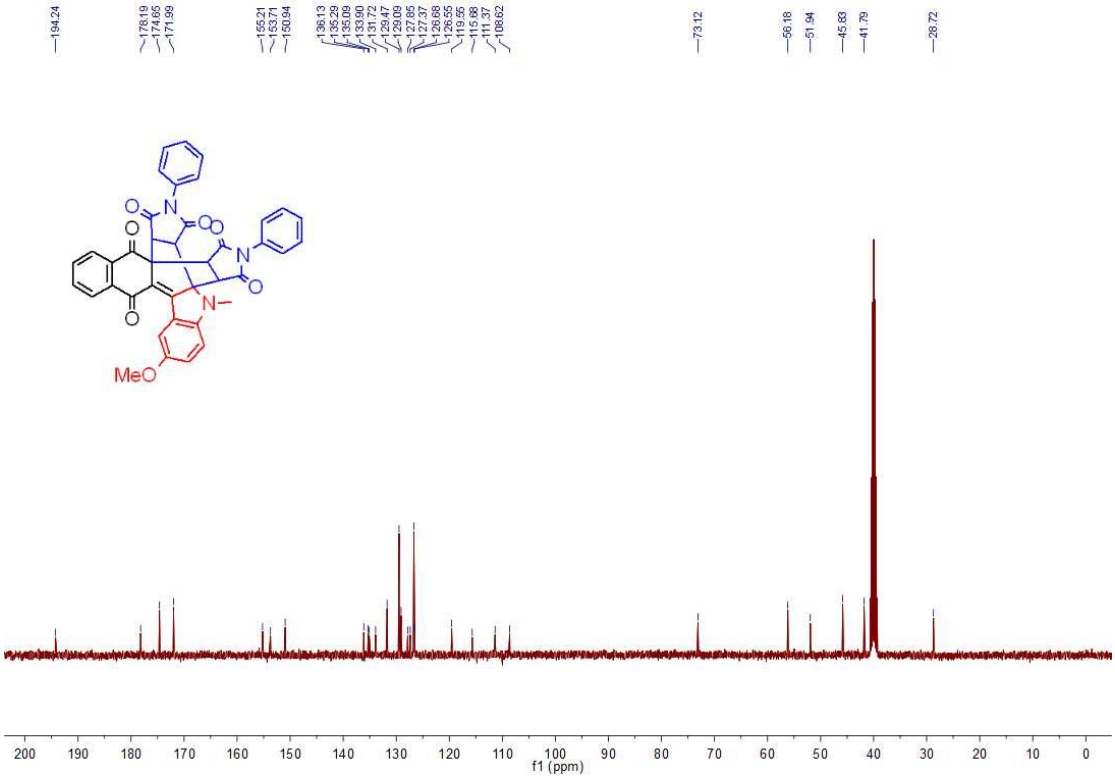


2-methoxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4g**)

^{1}H NMR (400 MHz)



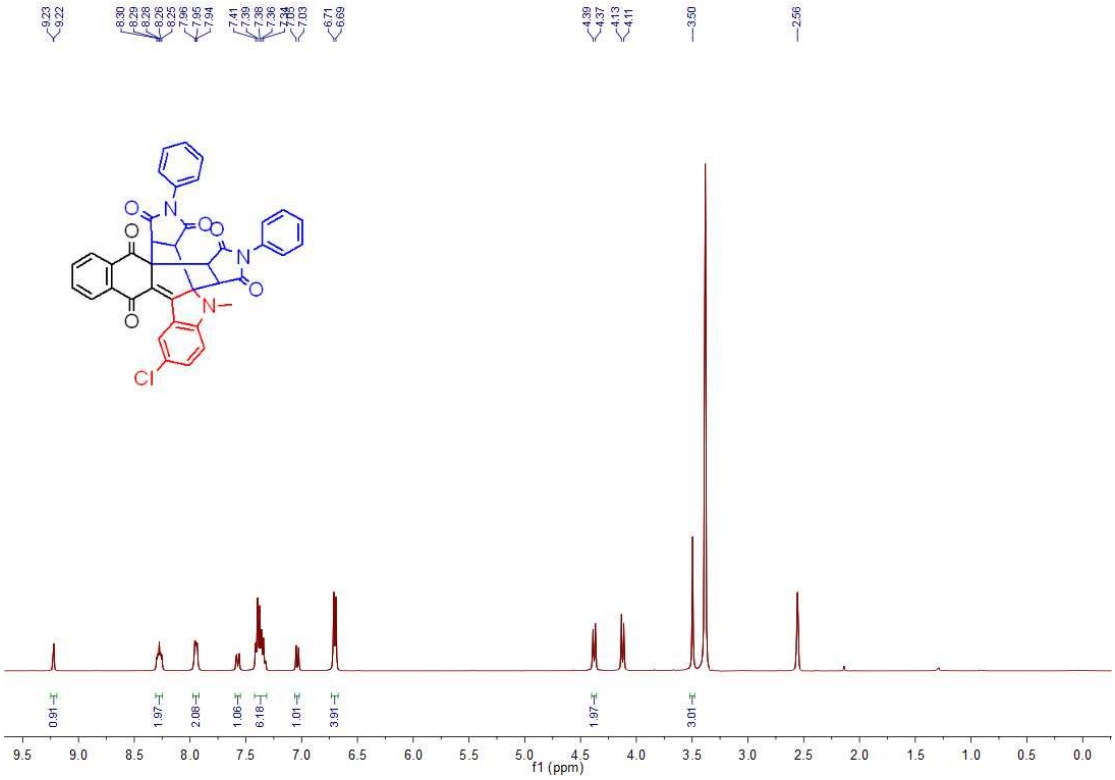
^{13}C NMR (101 MHz)



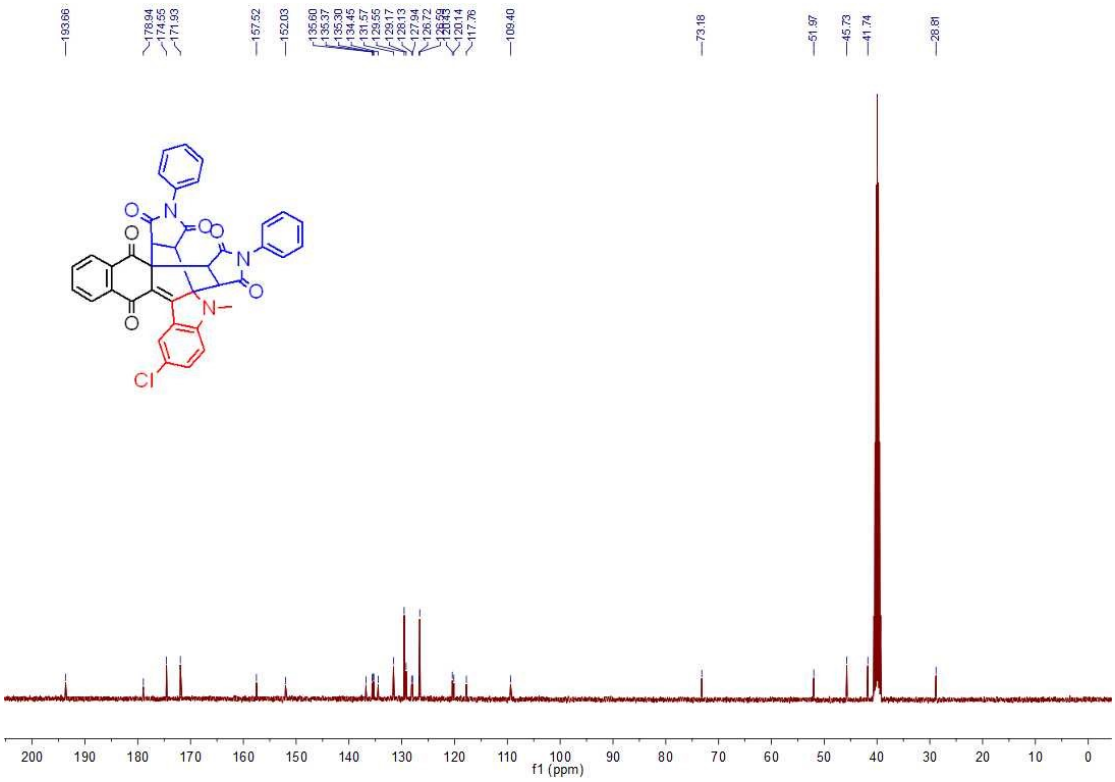
2-chloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4h**)

^{1}H NMR (400 MHz)

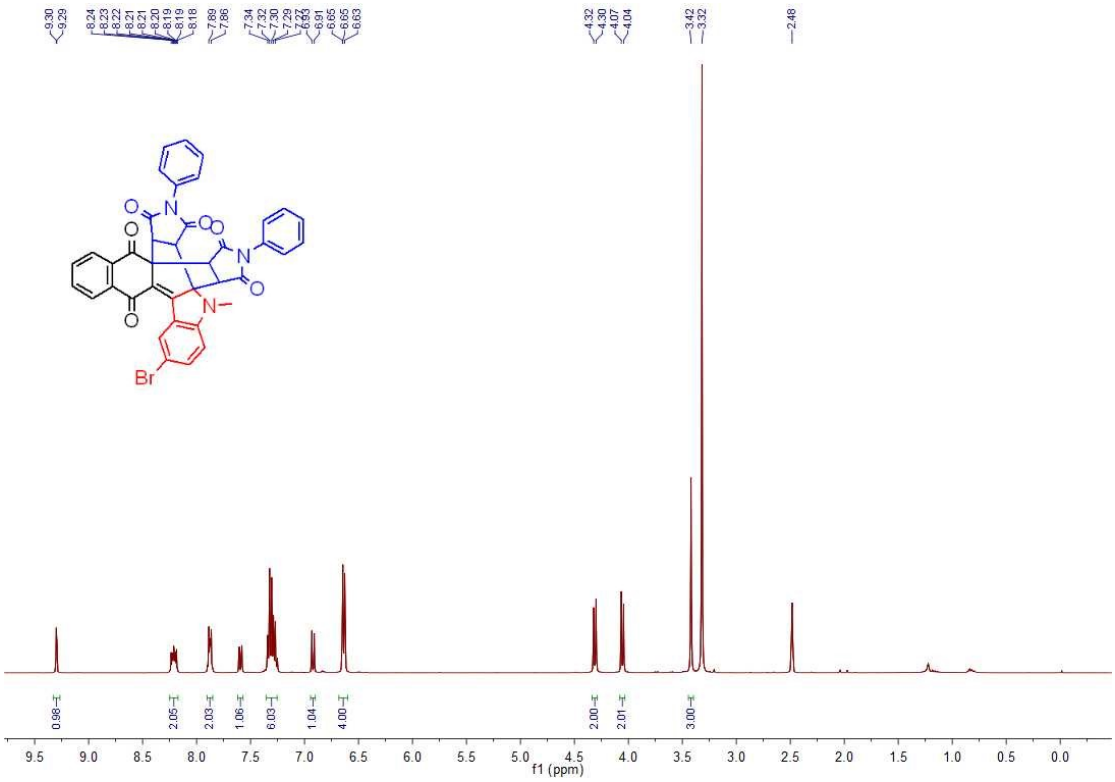


^{13}C NMR (101 MHz)

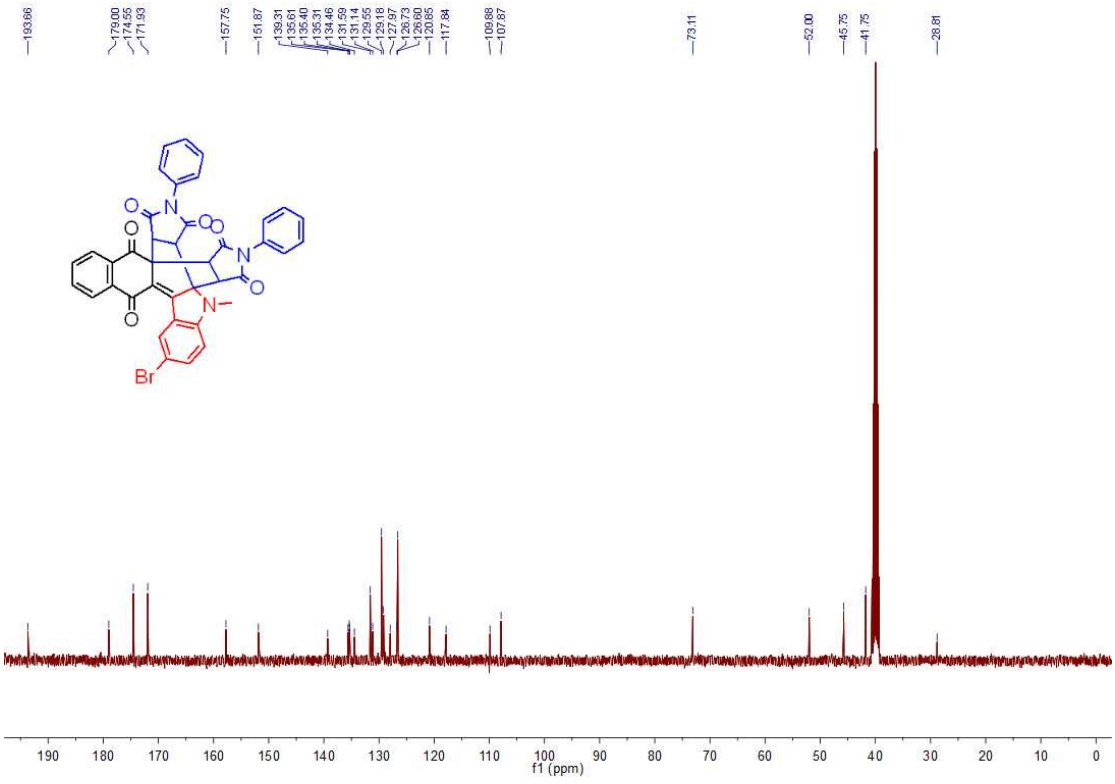


2-bromo-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4i**)

^{1}H NMR (101 MHz)



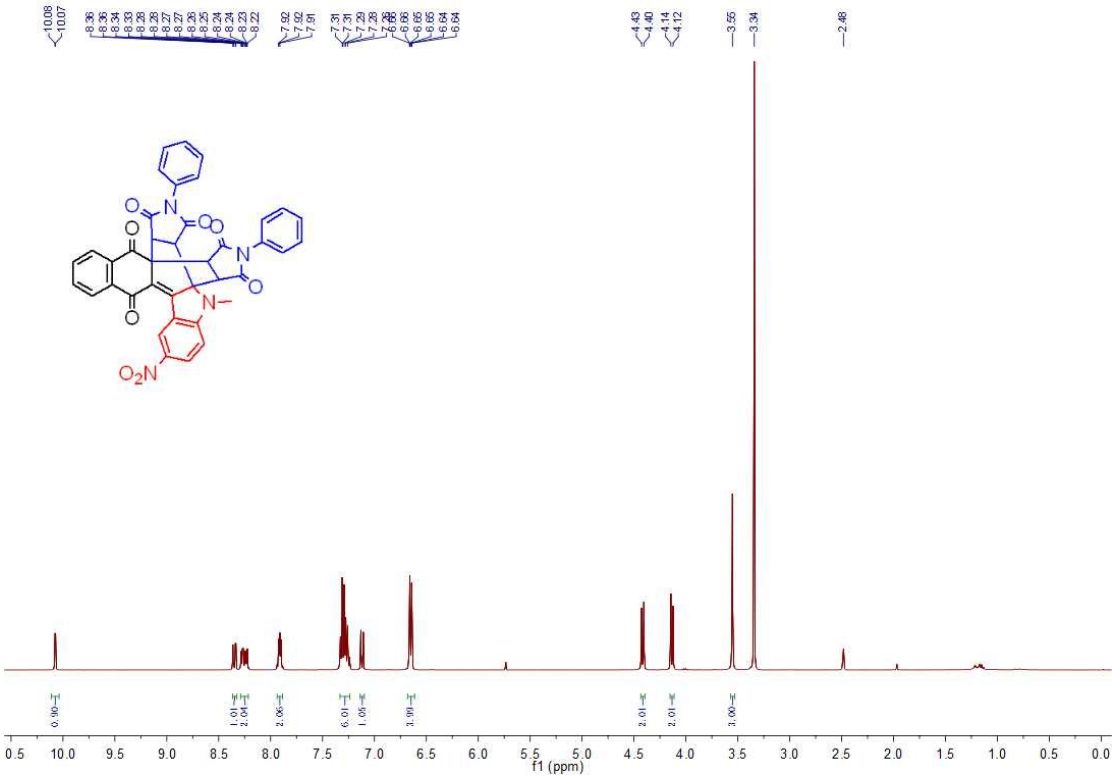
^{13}C NMR (101 MHz)



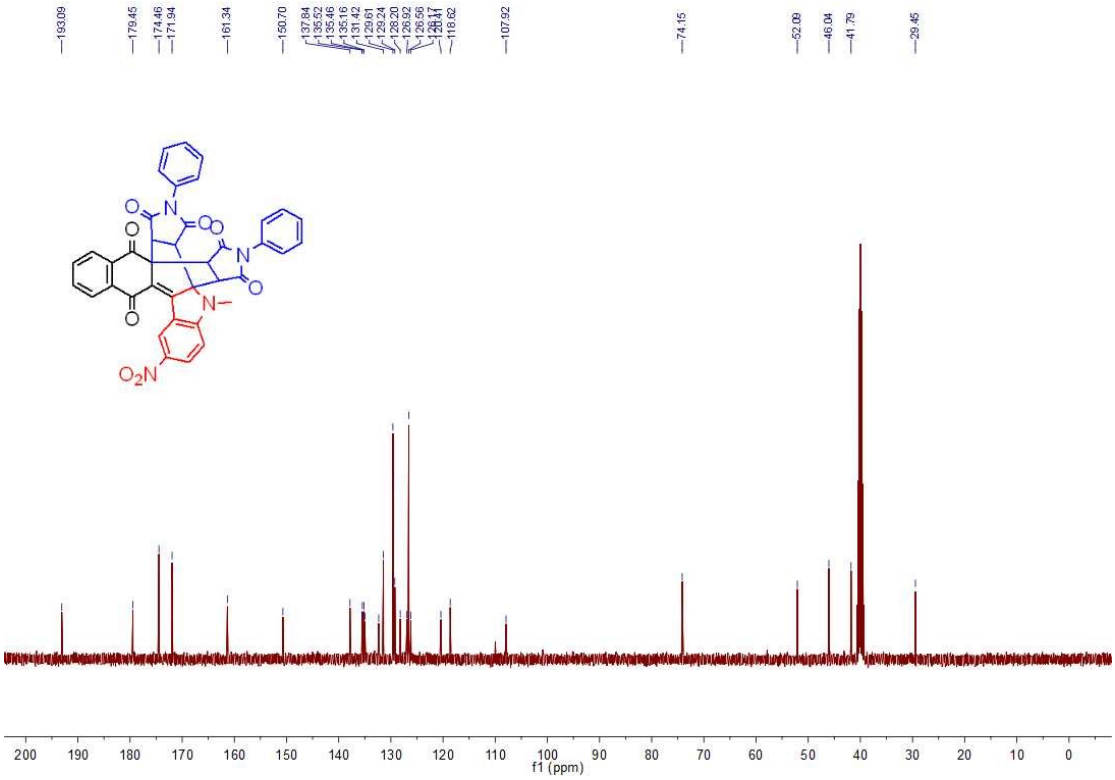
5-methyl-2-nitro-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4j**)

^{1}H NMR (400 MHz)

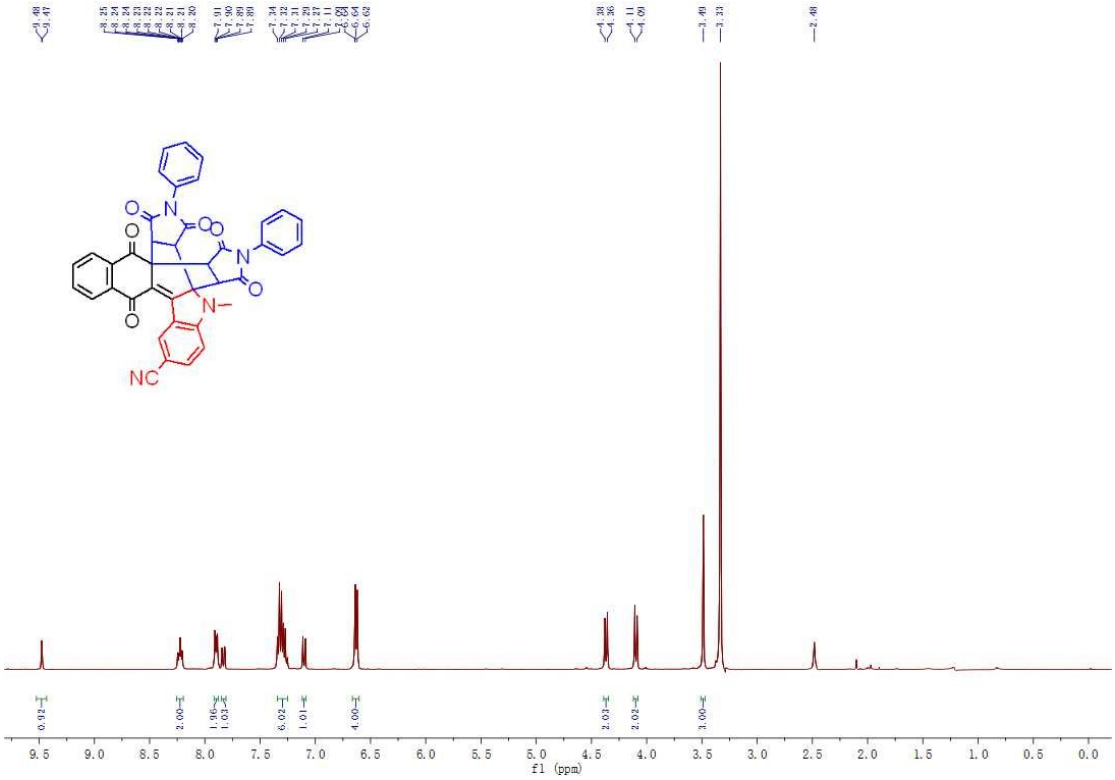


^{13}C NMR (101 MHz)

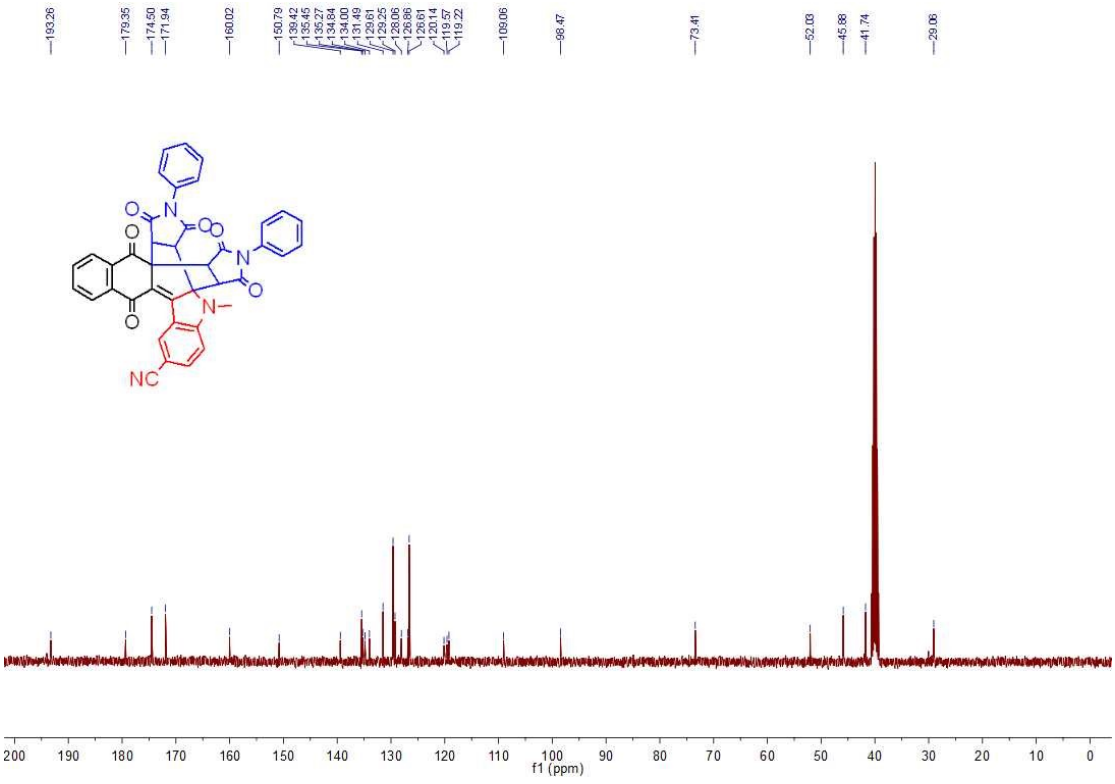


5-methyl-6,8,9,14,16,18-hexaoxo-7,17-diphenyl-5b,7,8,8a,9,14-hexahydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-2-carbonitrile (**4k**)

^{1}H NMR (400 MHz)



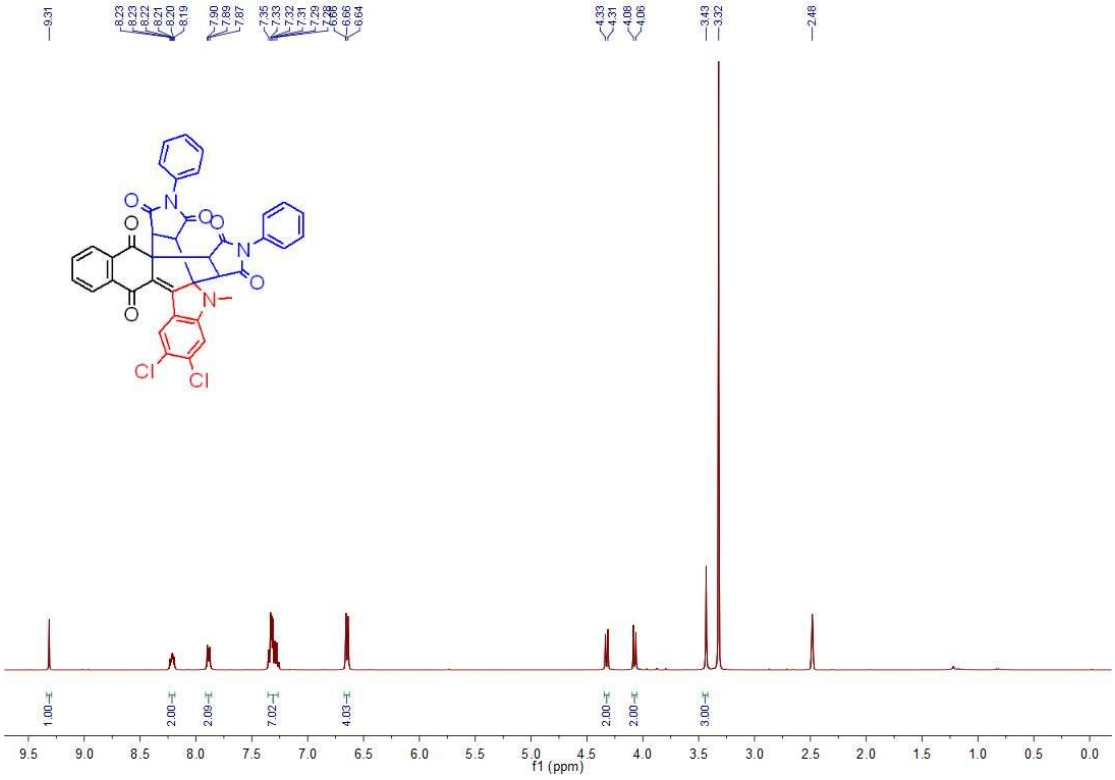
^{13}C NMR (101 MHz)



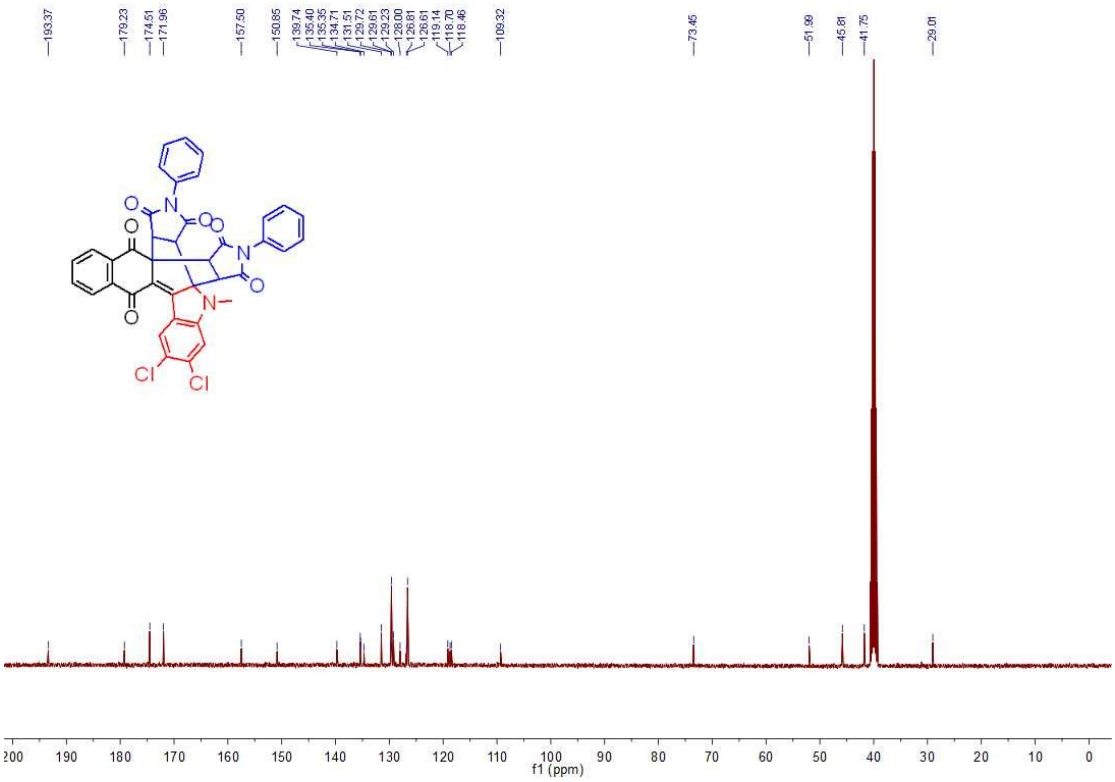
2,3-dichloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4l**)

^{1}H NMR (400 MHz)

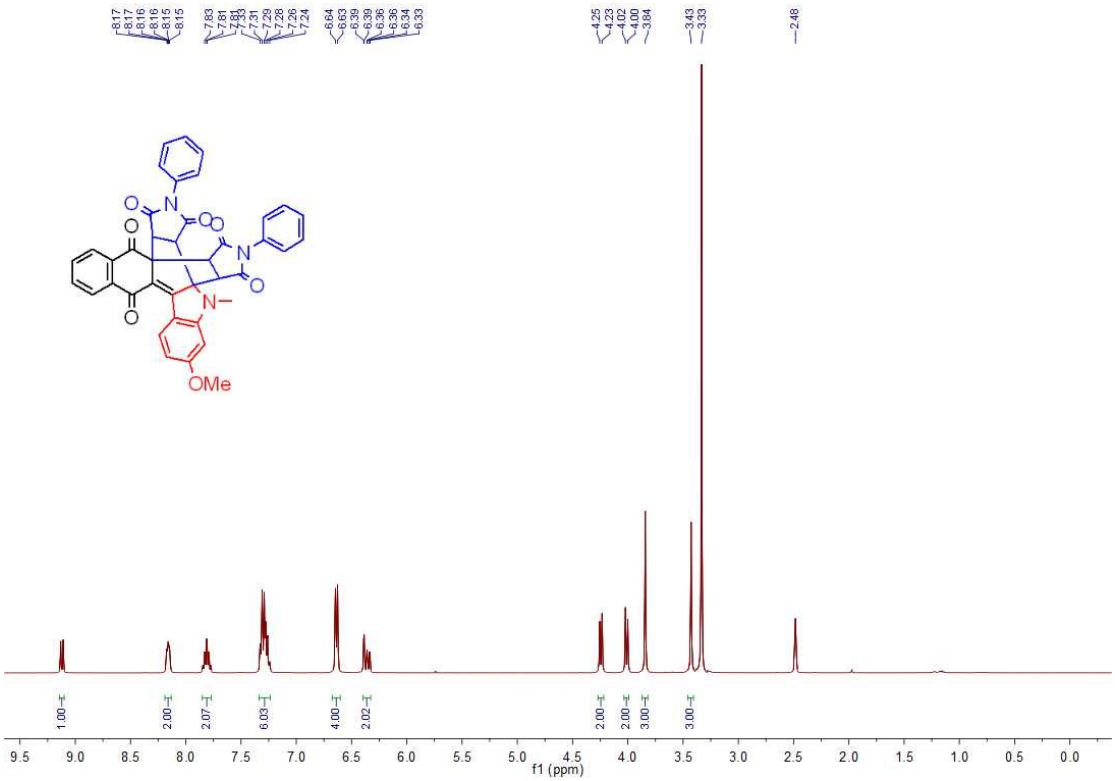


^{13}C NMR (101 MHz)

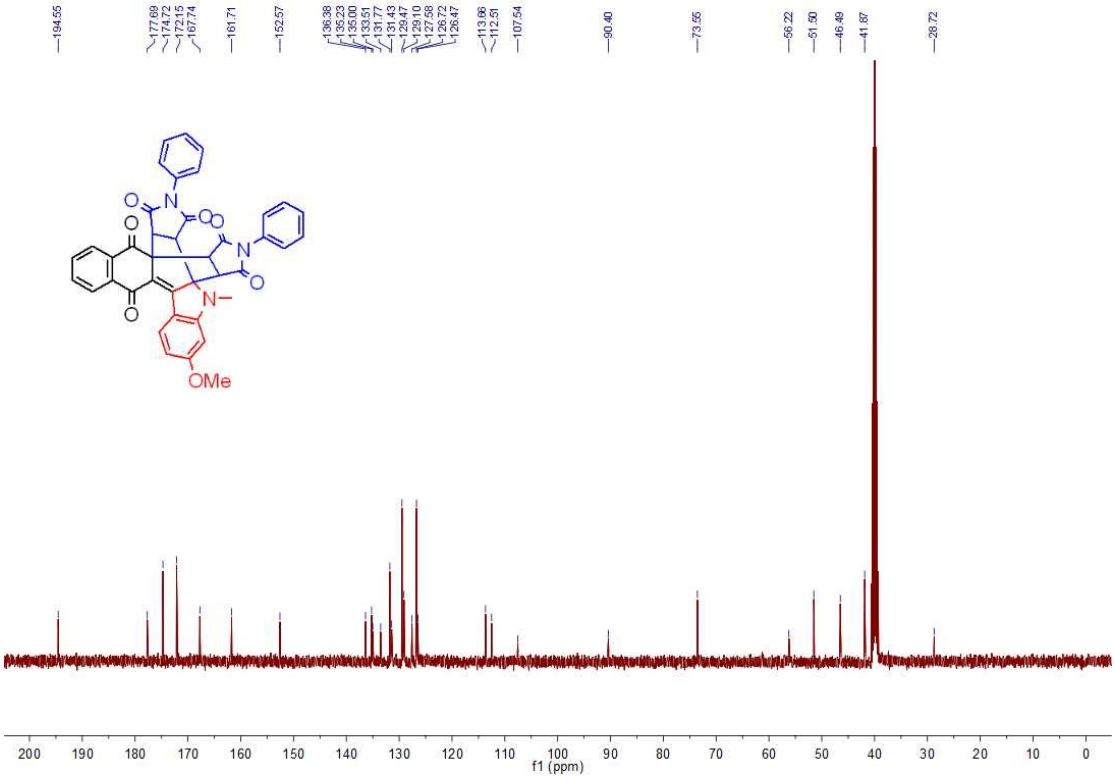


3-methoxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4m**)

^{1}H NMR (400 MHz)



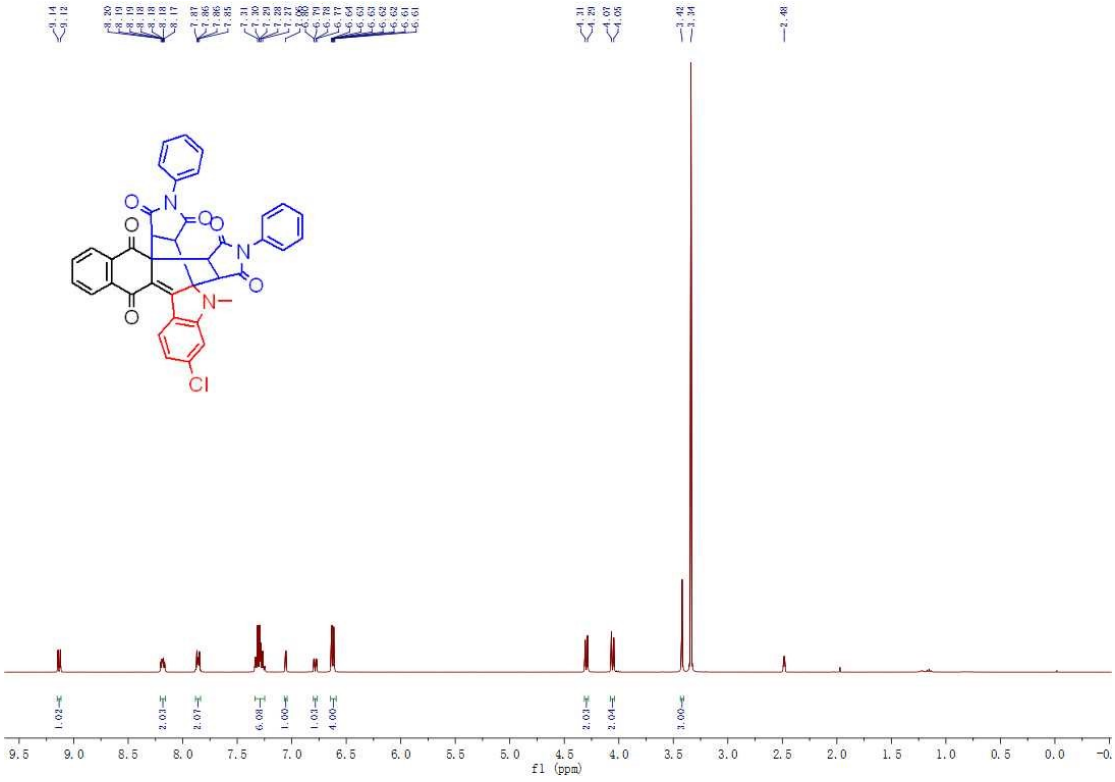
^{13}C NMR (101 MHz)



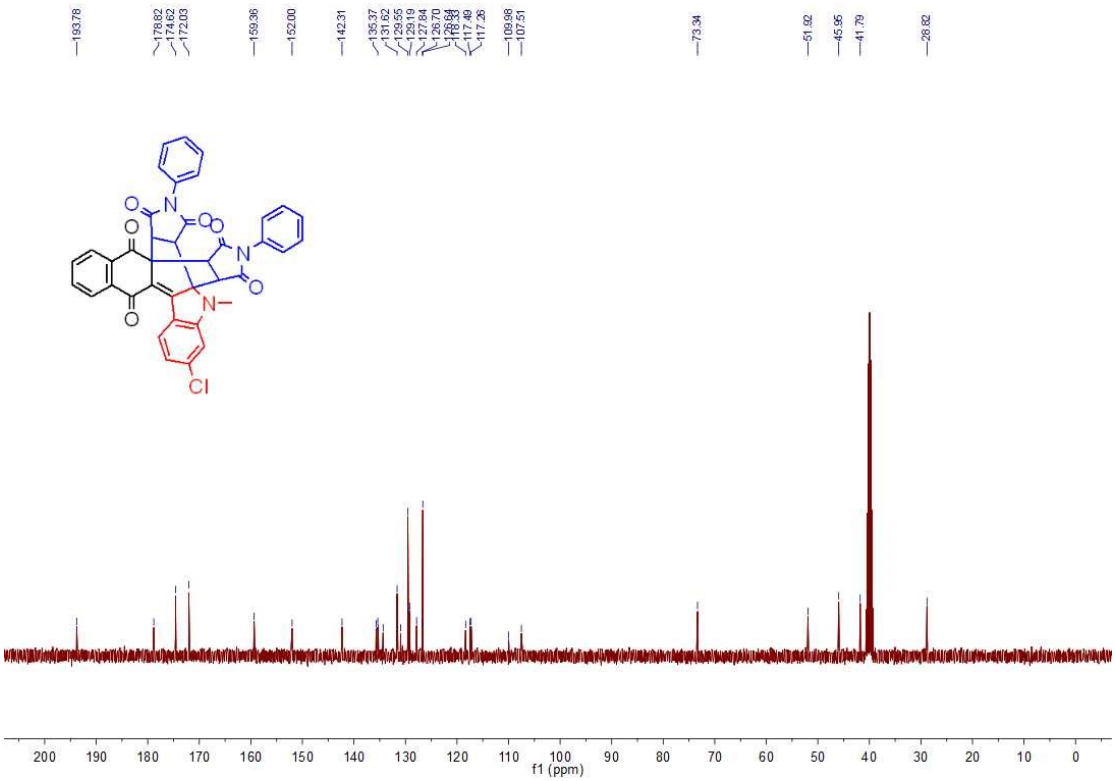
3-chloro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4n**)

^{1}H NMR (400 MHz)

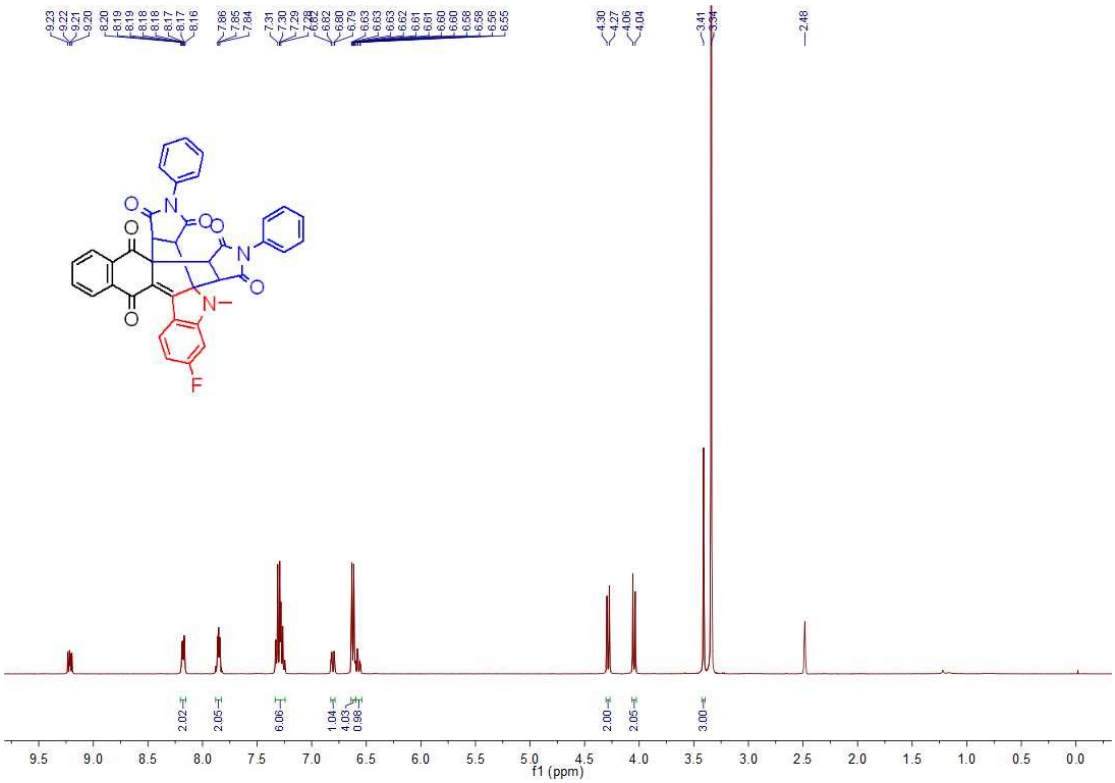


^{13}C NMR (101 MHz)

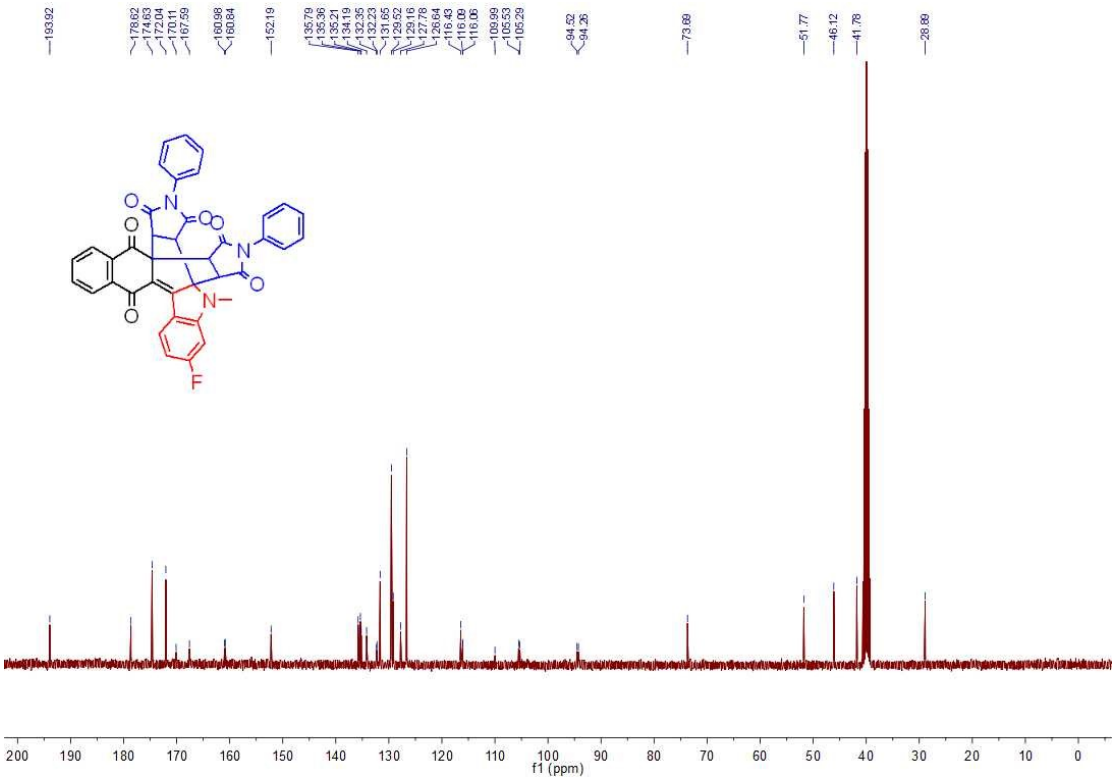


3-fluoro-5-methyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4o**)

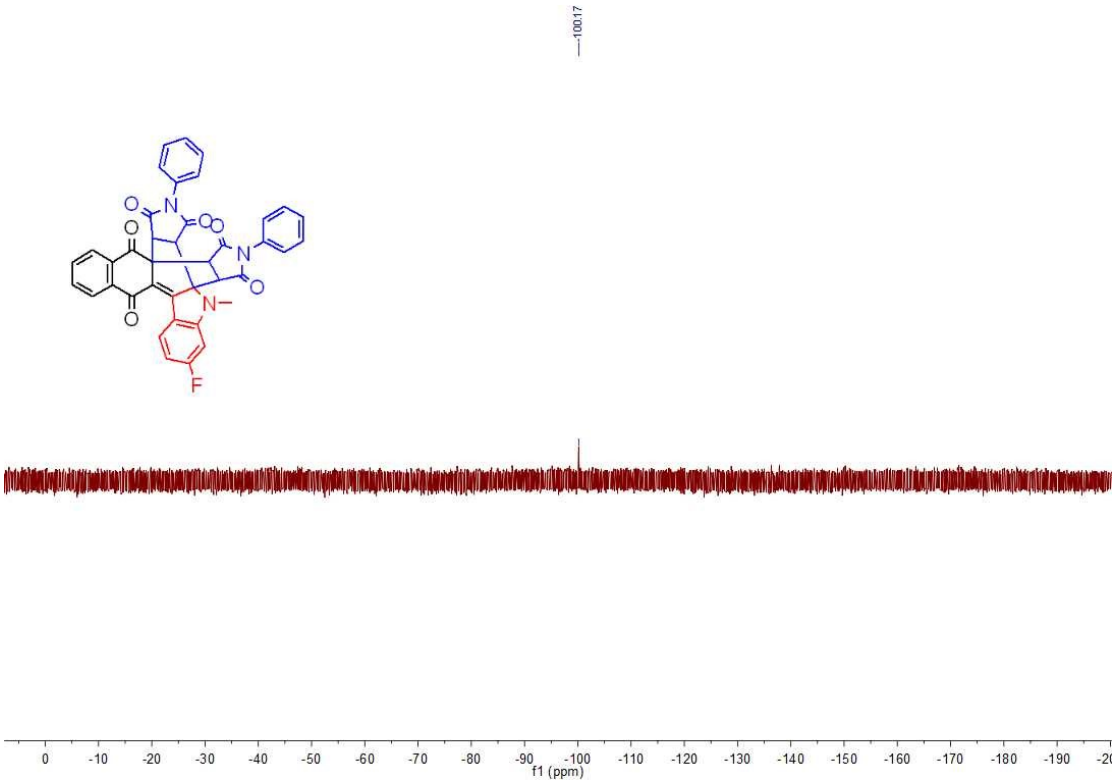
^{1}H NMR (400 MHz)



^{13}C NMR (101 MHz)

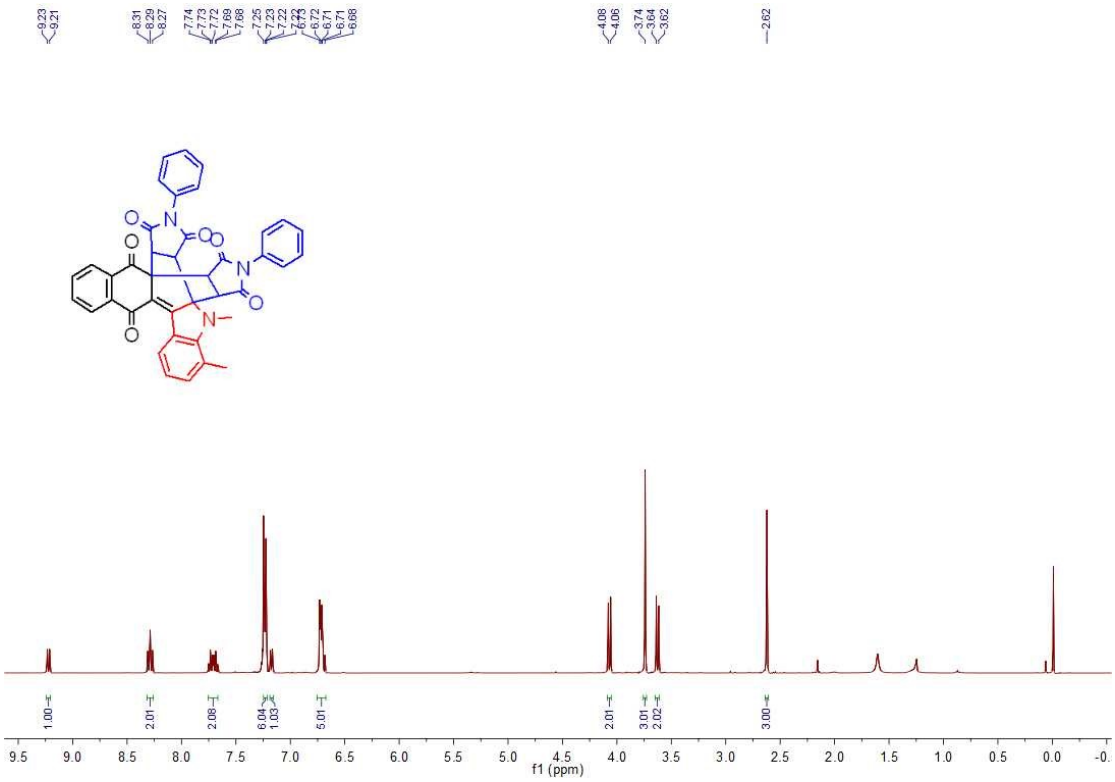


^{19}F NMR (376 MHz)

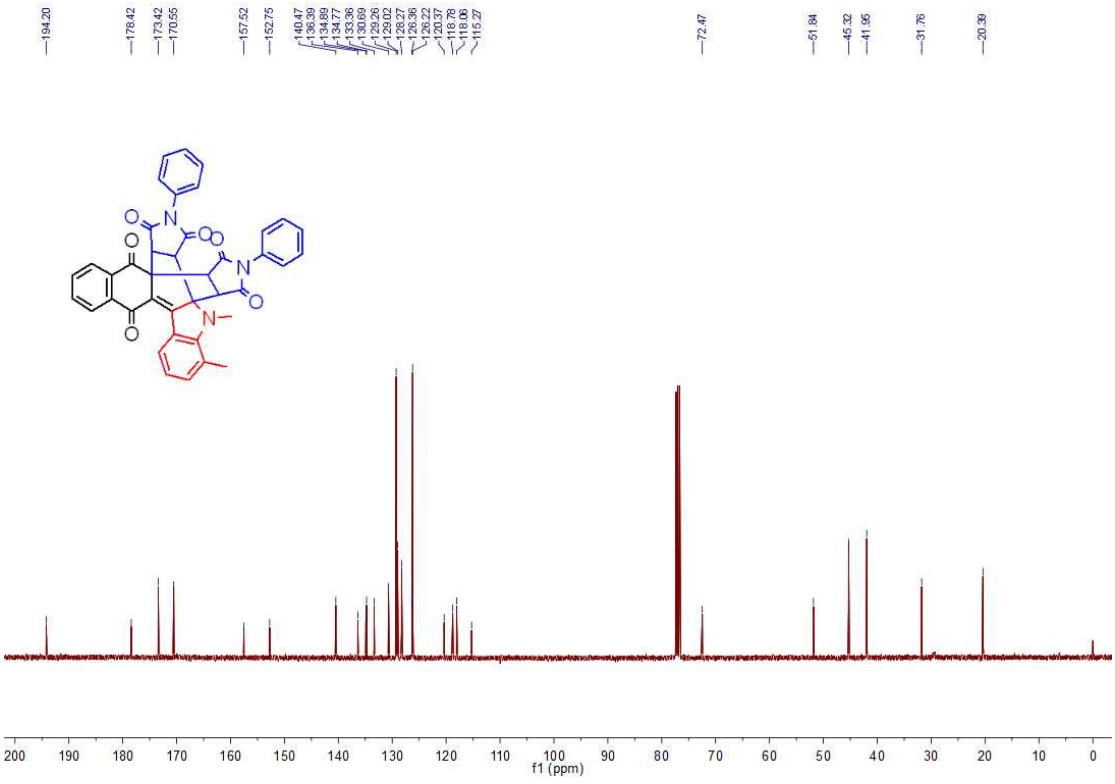


4,5-dimethyl-7,17-diphenyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**4p**)

^{1}H NMR (400 MHz)



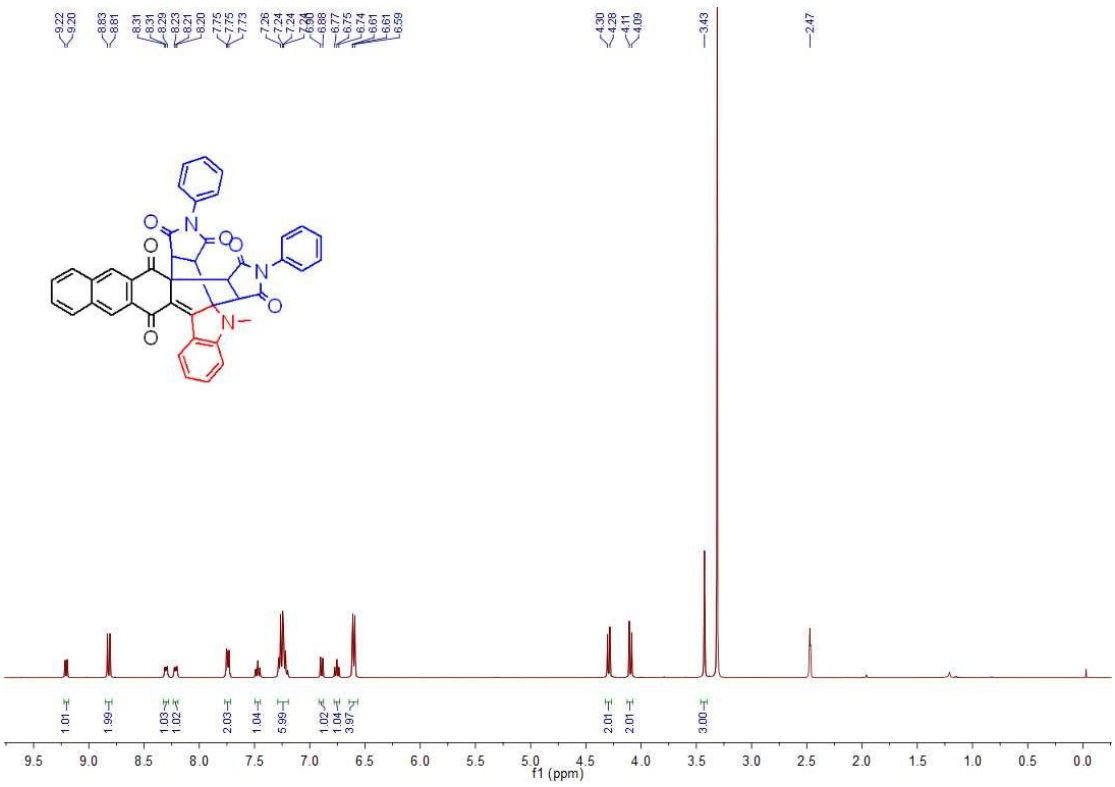
^{13}C NMR (101 MHz)



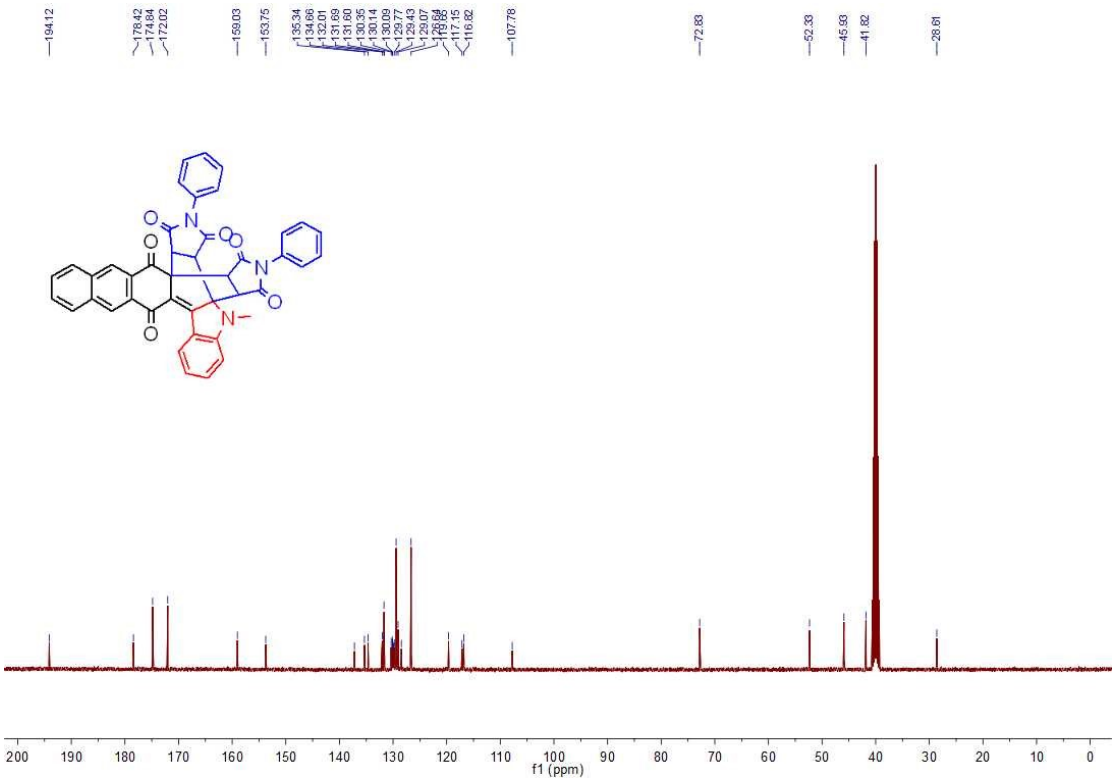
5-methyl-7,19-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrroloanthra[2,3-

c]pyrrolo[3,4-*a*]carbazole-6,8,9,16,18,20(7*H*)-hexaone (**4s**)

^{1}H NMR (400 MHz)

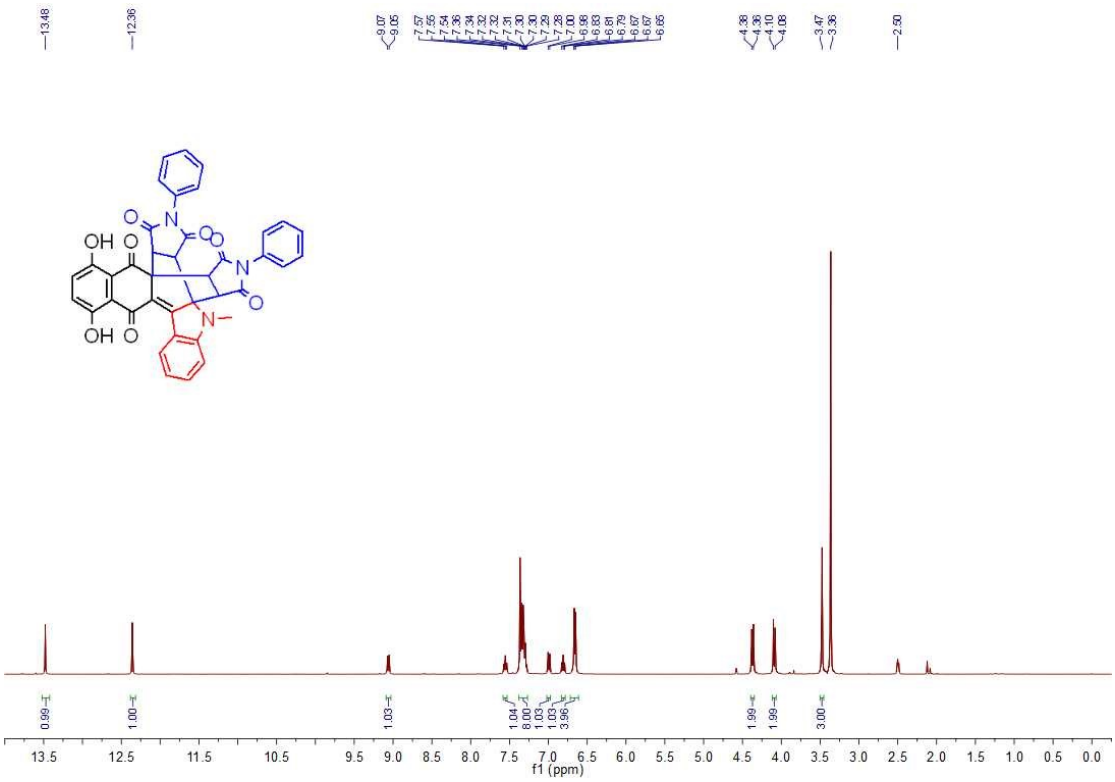


^{13}C NMR (101 MHz)

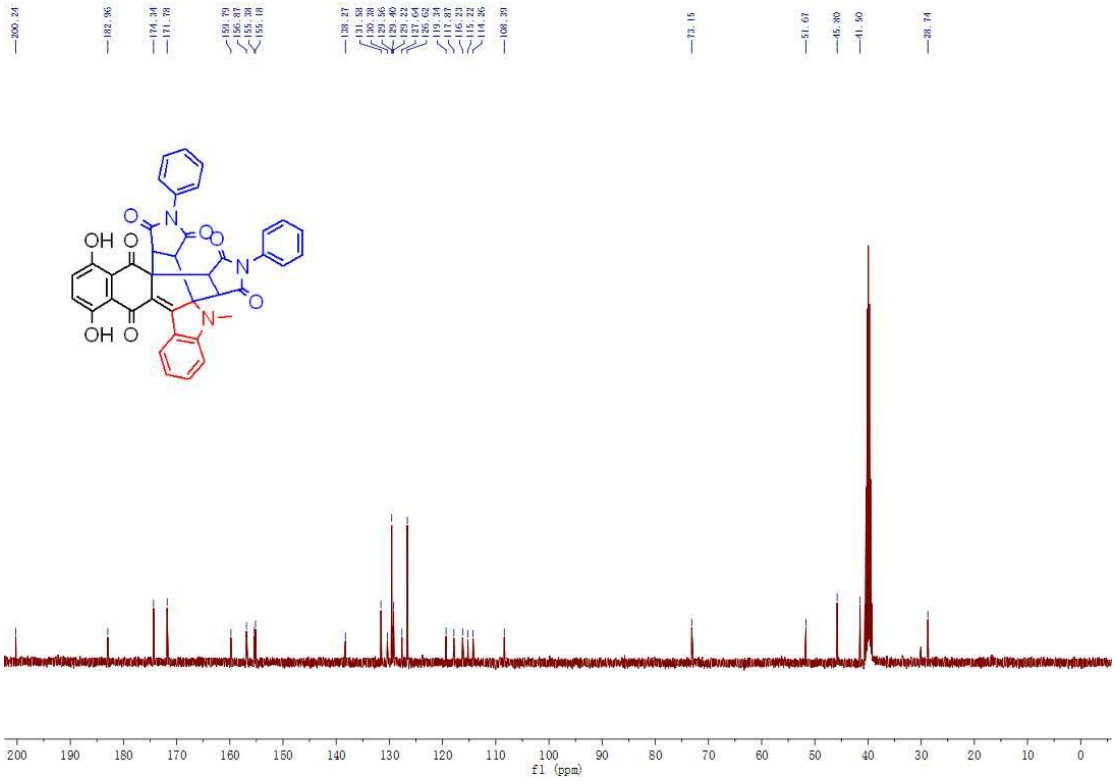


10,13-dihydroxy-5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (**4t**)

^{1}H NMR (400 MHz)



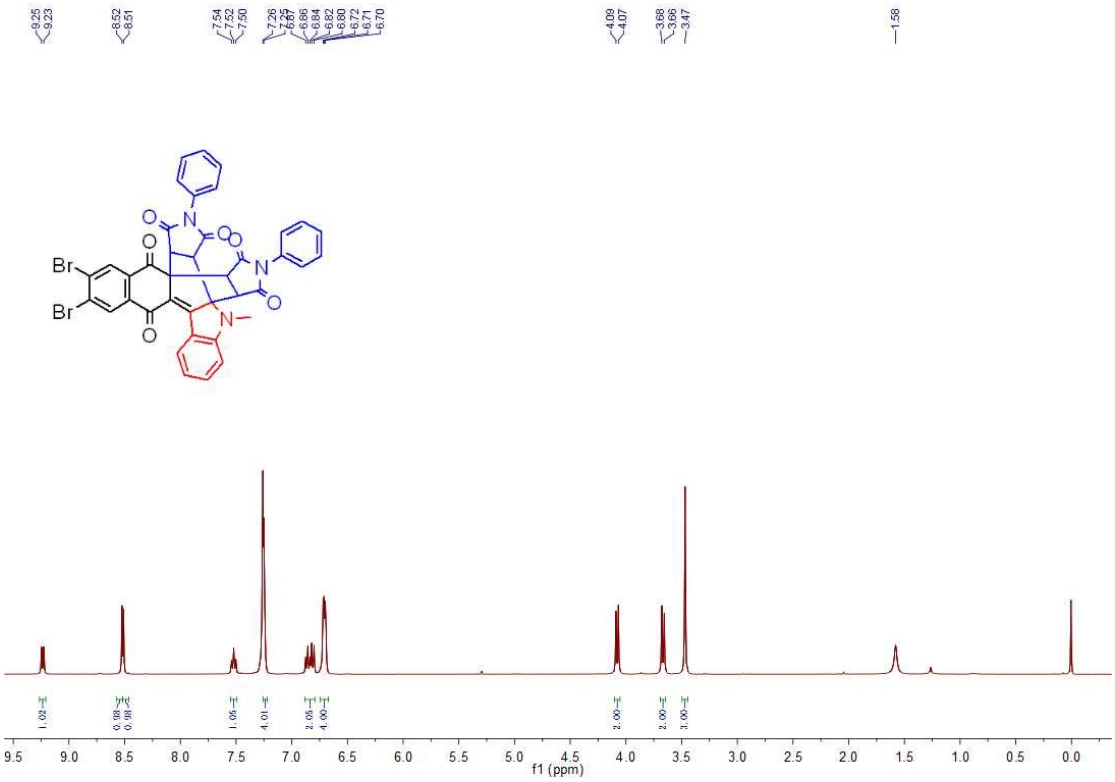
^{13}C NMR (101 MHz)



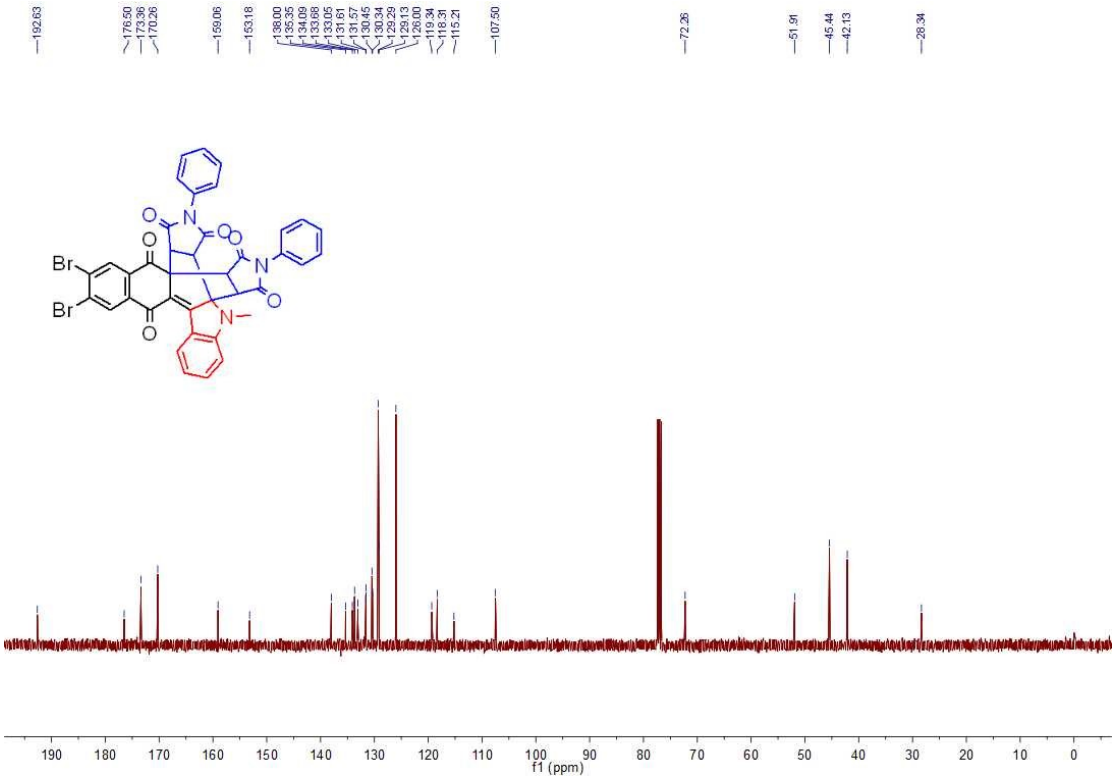
11,12-dibromo-5-methyl-7,17-diphenyl-5b,8a-dihydro-5*H*,6*H*-5a,8b-

[3,4]epipyrrolonaphtho[2,3-*c*]pyrrolo[3,4-*a*]carbazole-6,8,9,14,16,18(7*H*)-hexaone (**4u**)

^{1}H NMR (400 MHz)

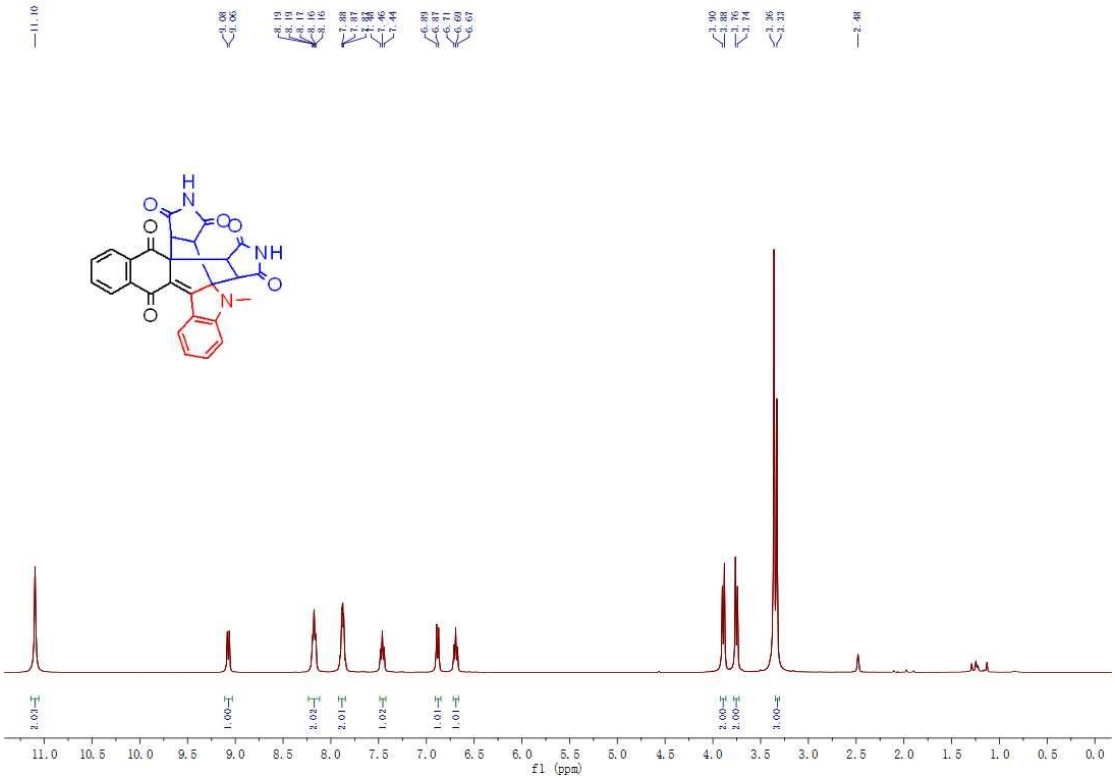


^{13}C NMR (101 MHz)

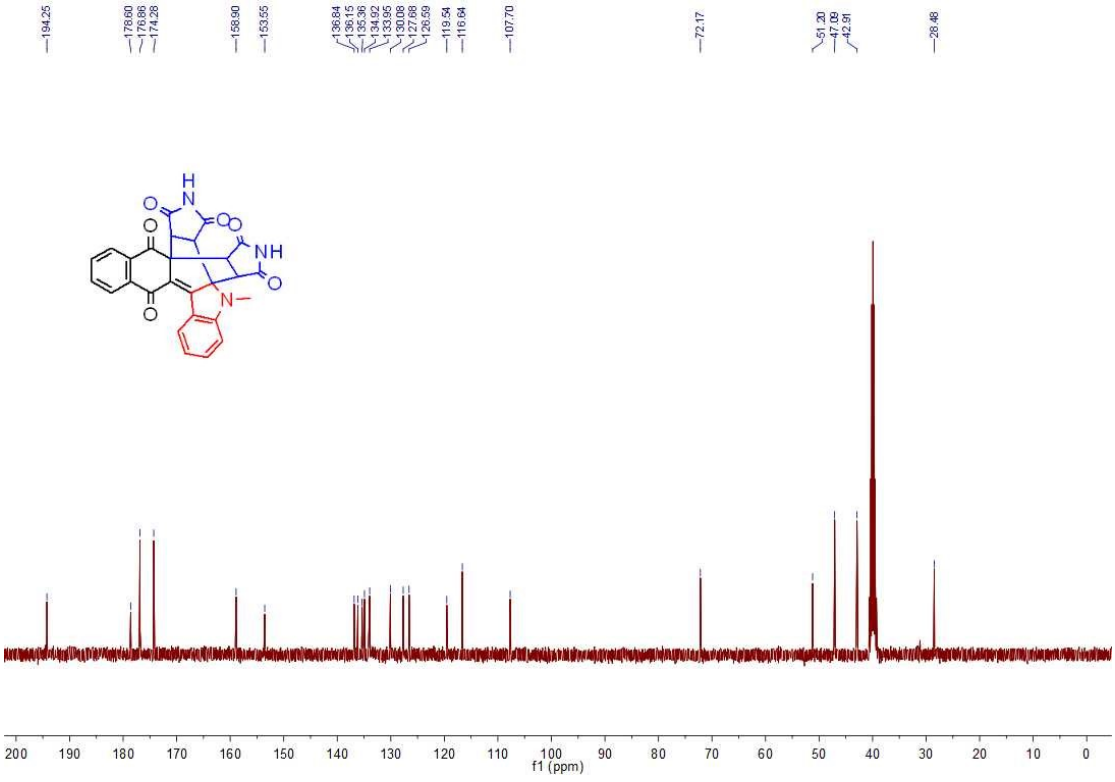


5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5a**)

^{1}H NMR (400 MHz)



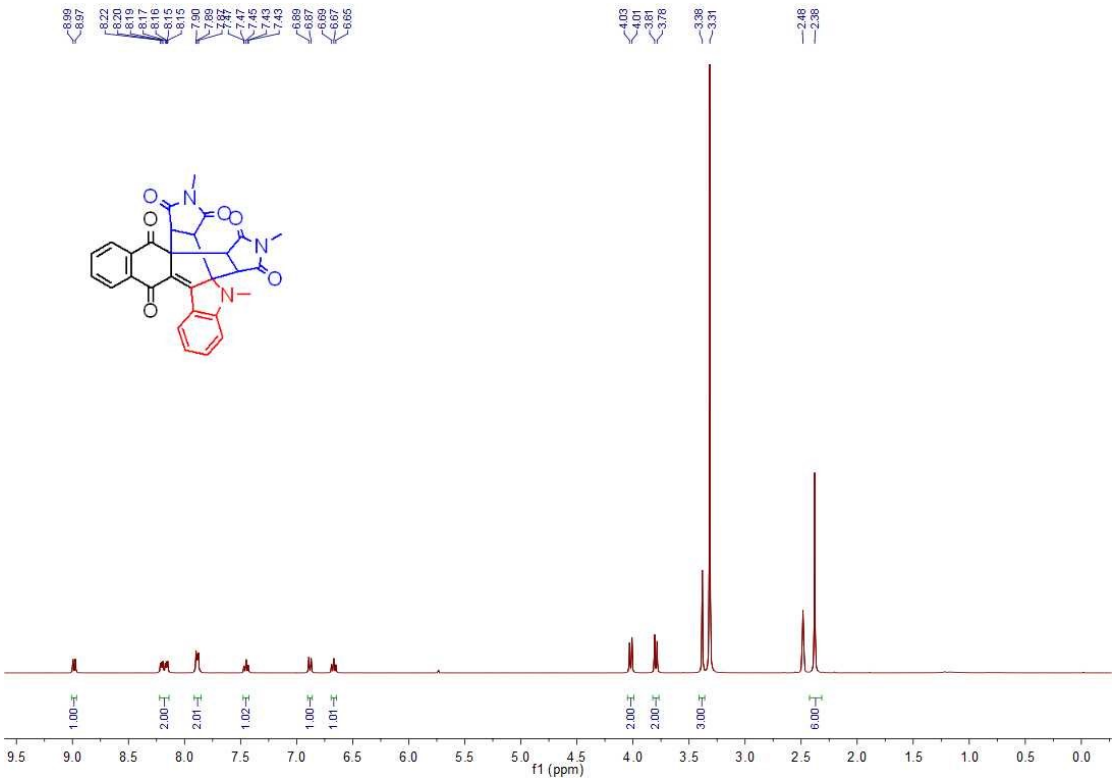
^{13}C NMR (101 MHz)



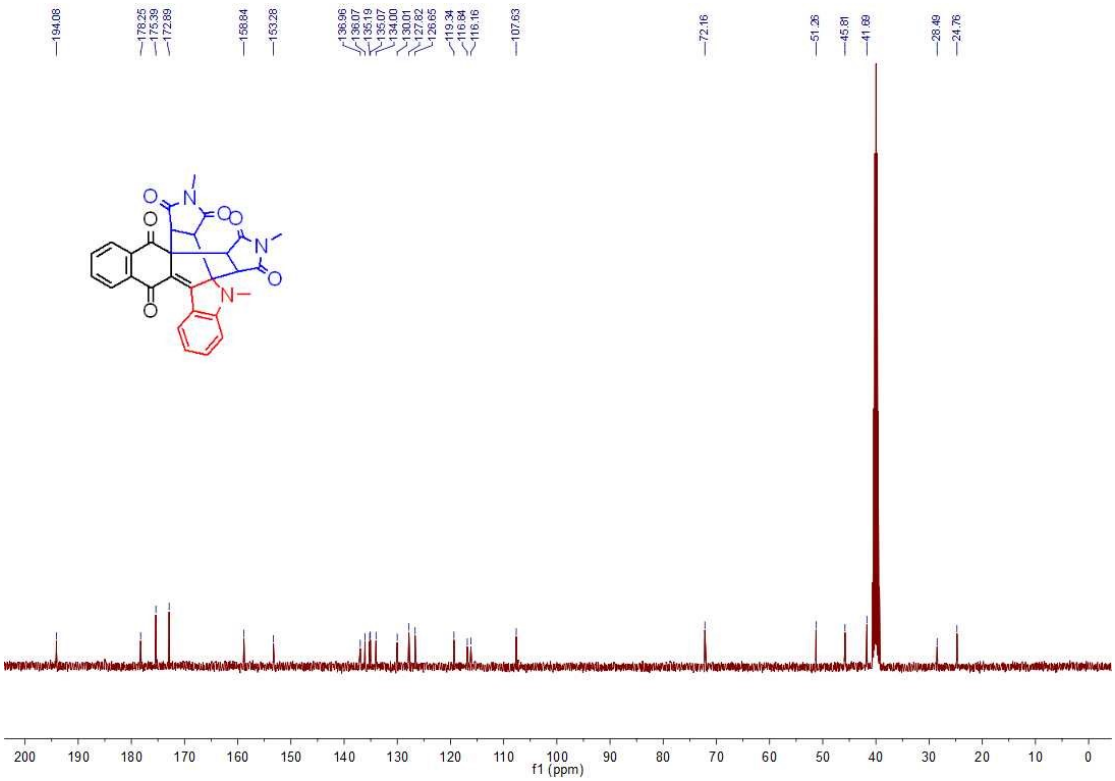
5,7,17-trimethyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-

c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5b**)

^{1}H NMR (400 MHz)

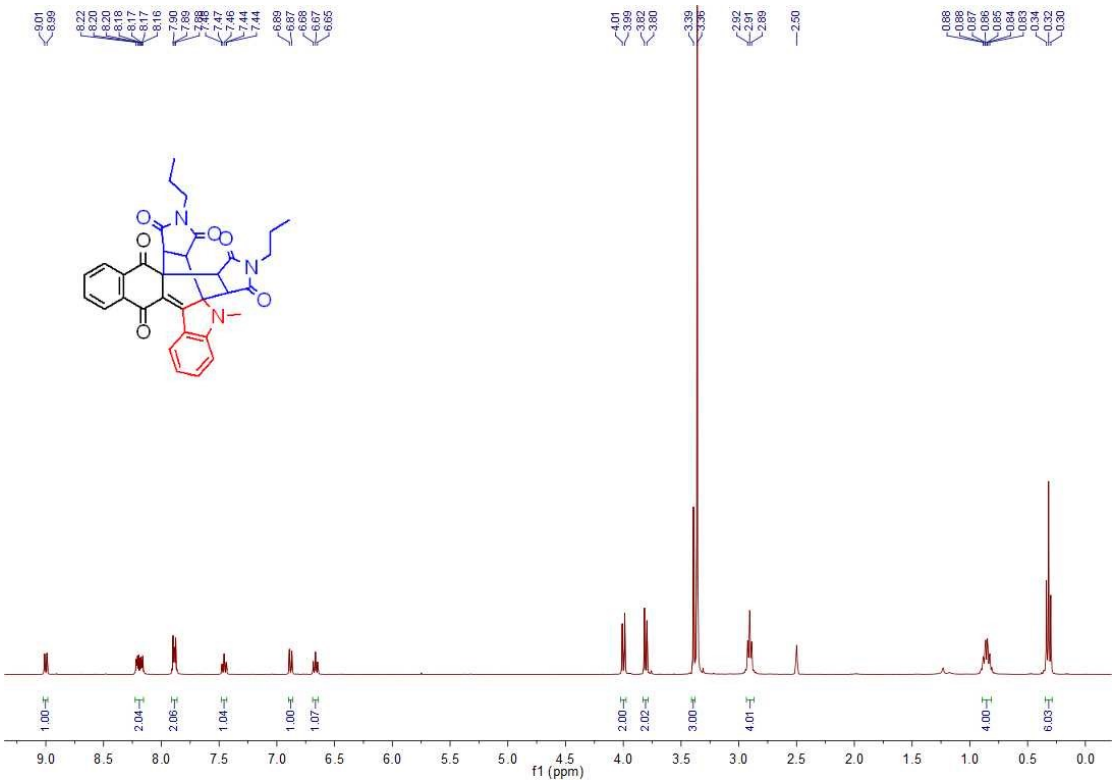


^{13}C NMR (101 MHz)

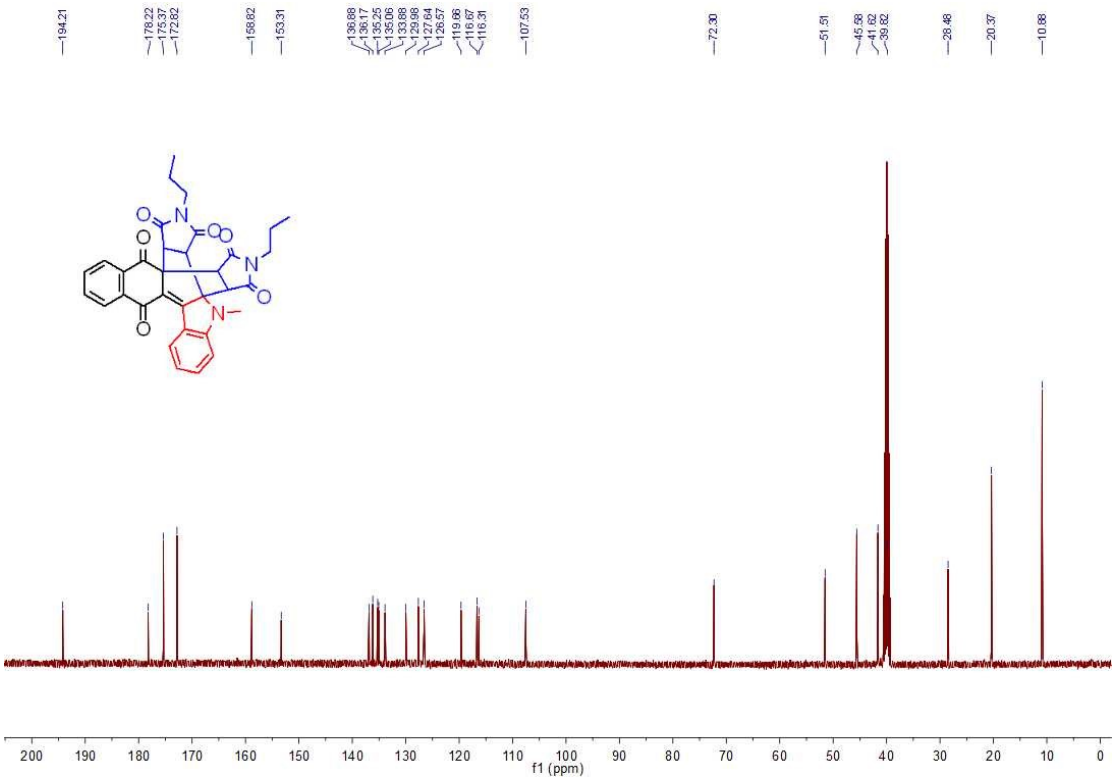


5-methyl-7,17-dipropyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5c**)

^{1}H NMR (400 MHz)



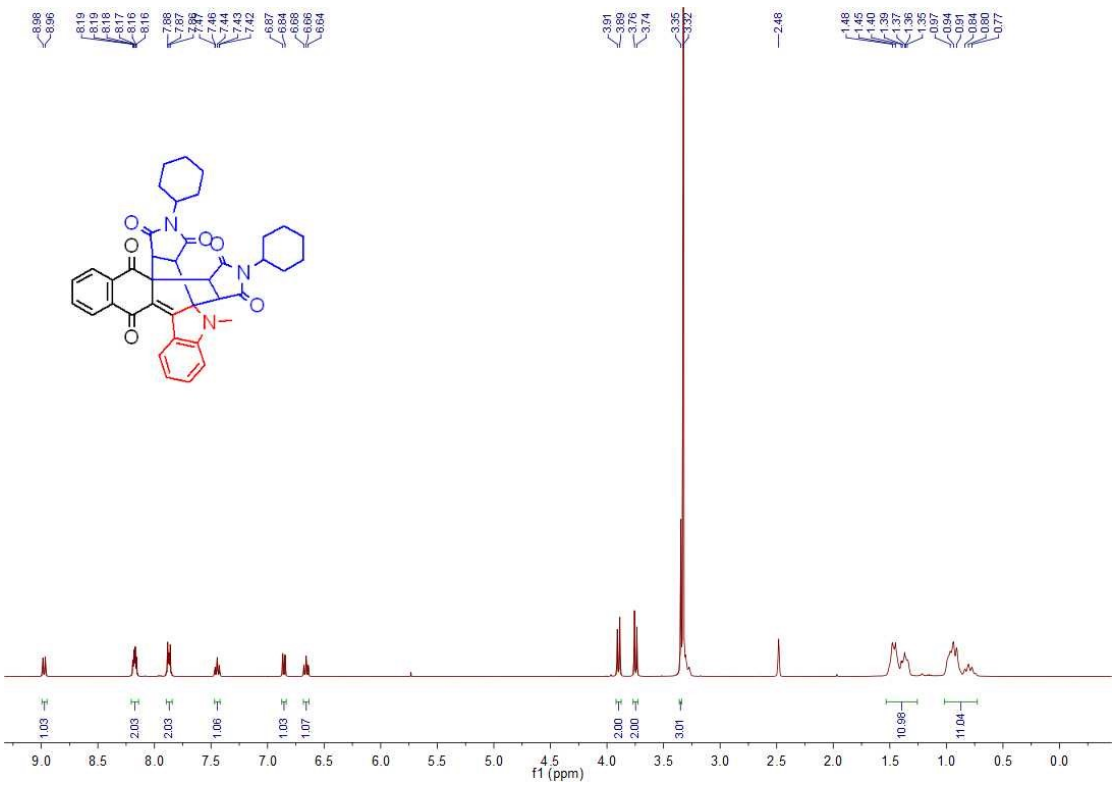
^{13}C NMR (101 MHz)



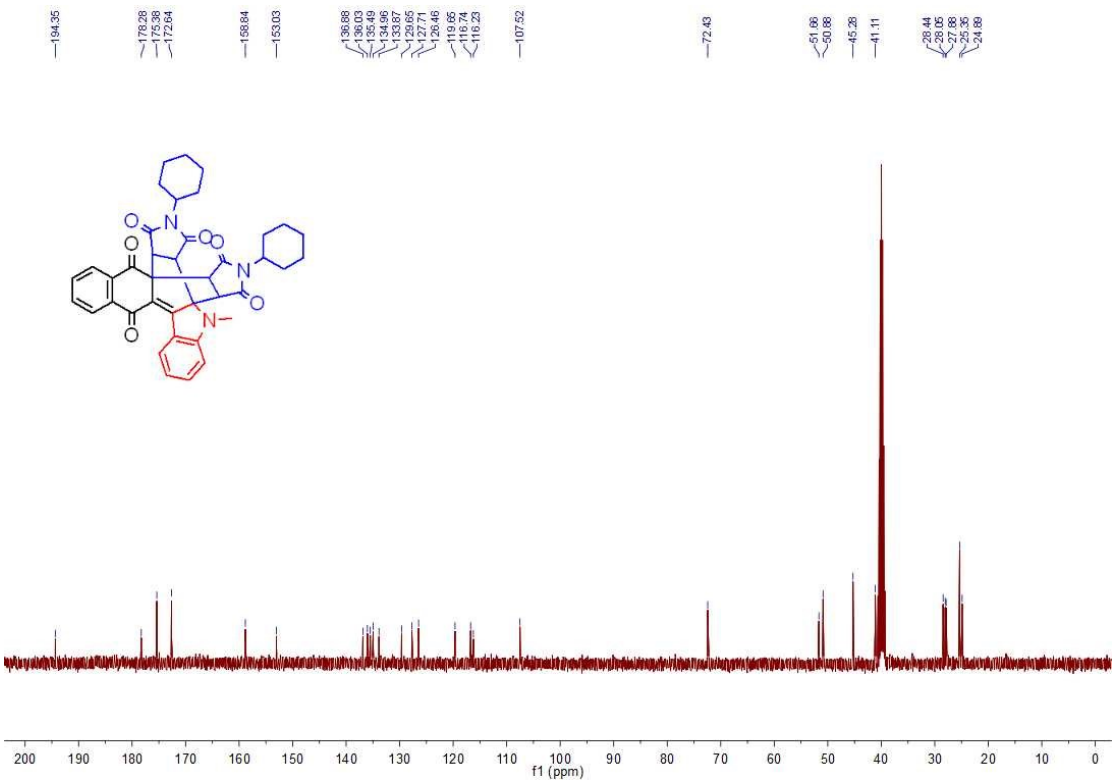
7,17-dicyclohexyl-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-

c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5d**)

^{1}H NMR (400 MHz)

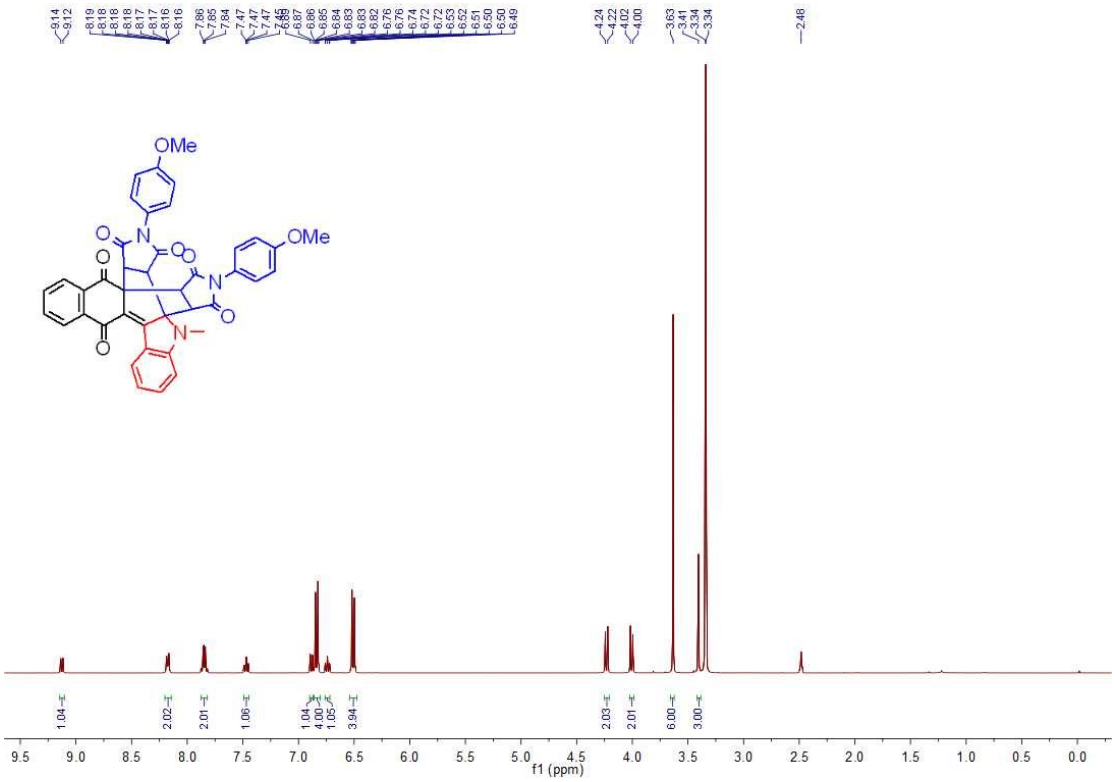


^{13}C NMR (101 MHz)

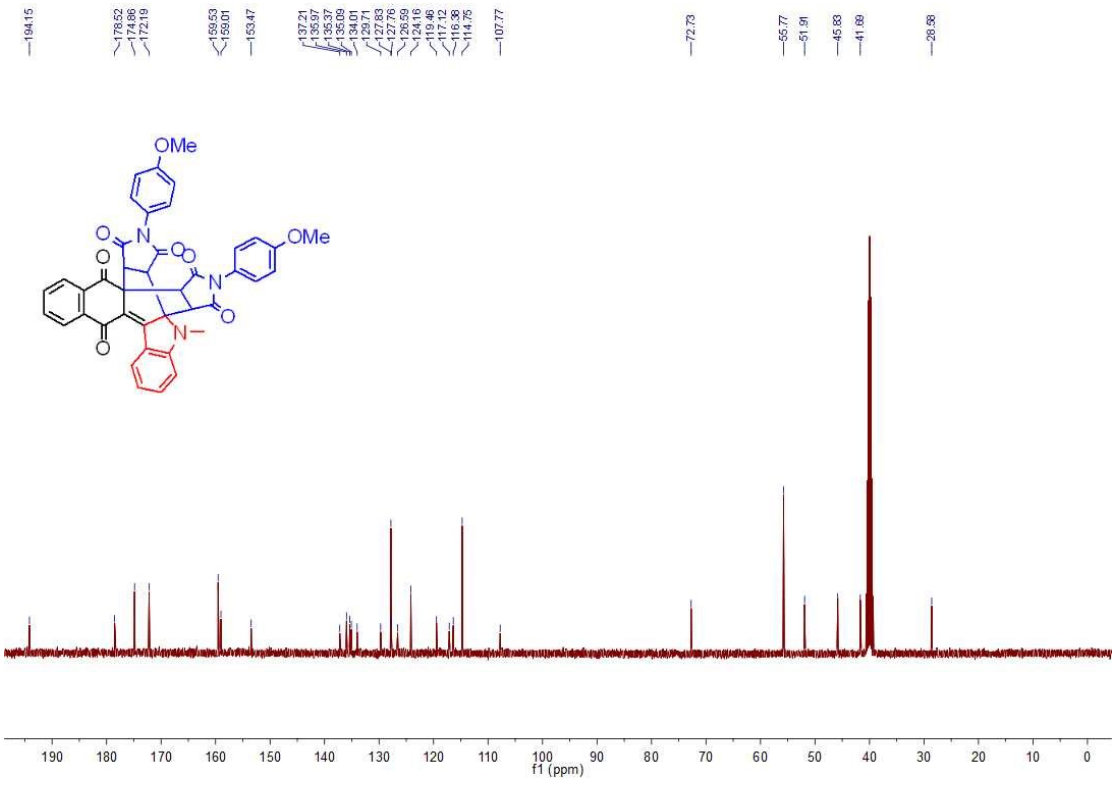


7,17-bis(4-methoxyphenyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5e**)

^{1}H NMR (400 MHz)



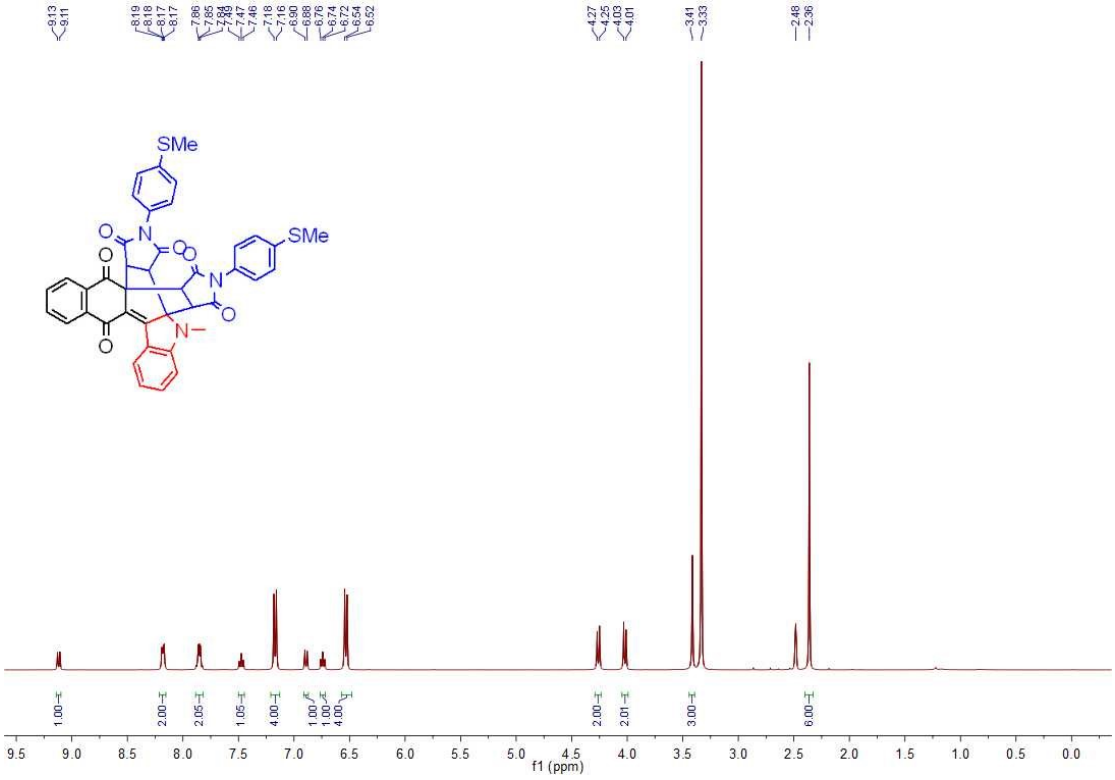
^{13}C NMR (101 MHz)



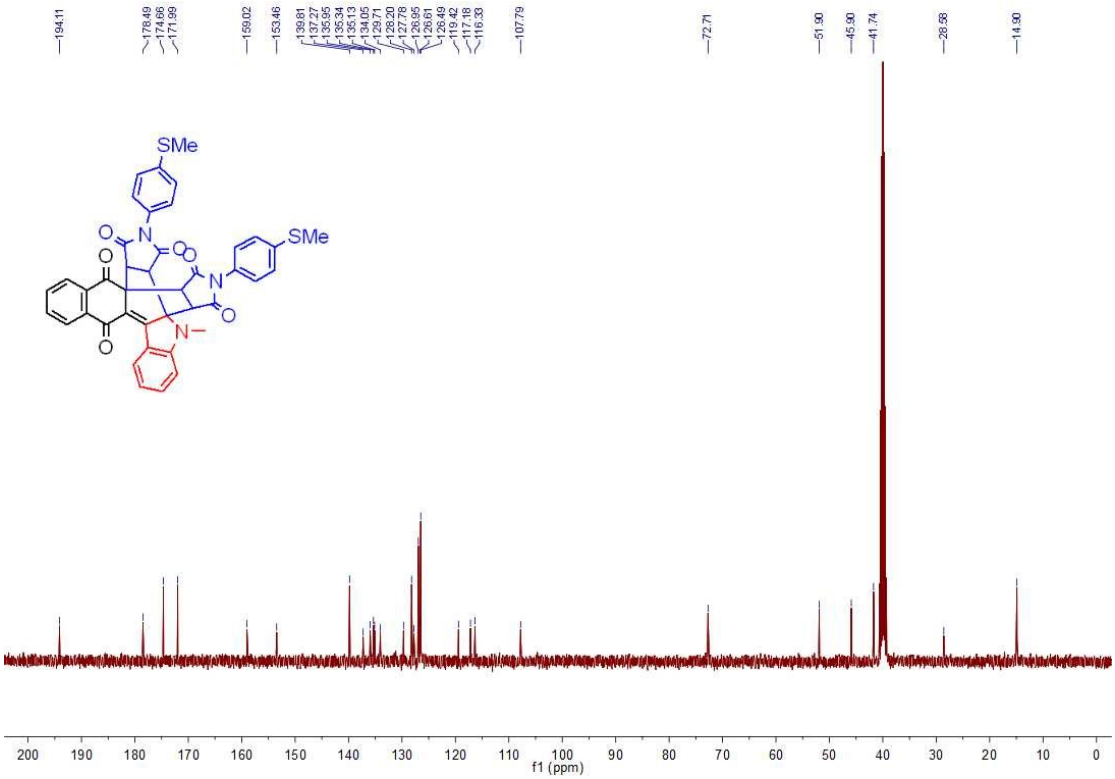
5-methyl-7,17-bis(4-(methylthio)phenyl)-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5f**)

^{1}H NMR (400 MHz)

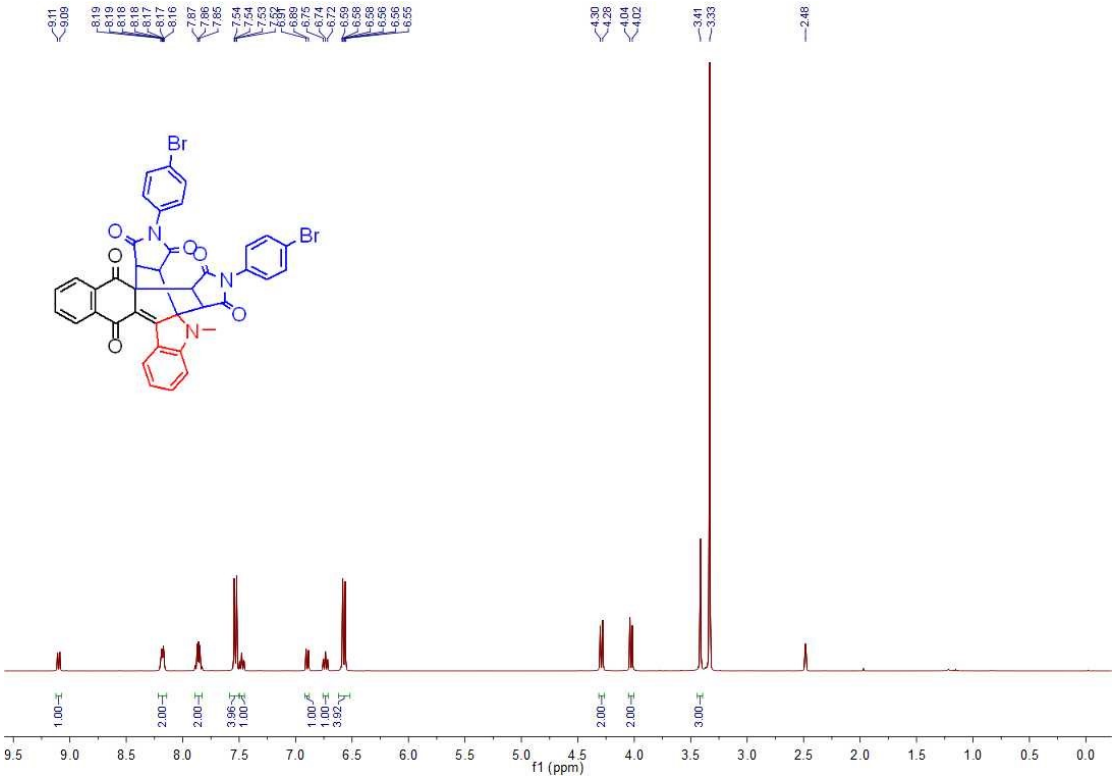


^{13}C NMR (101 MHz)

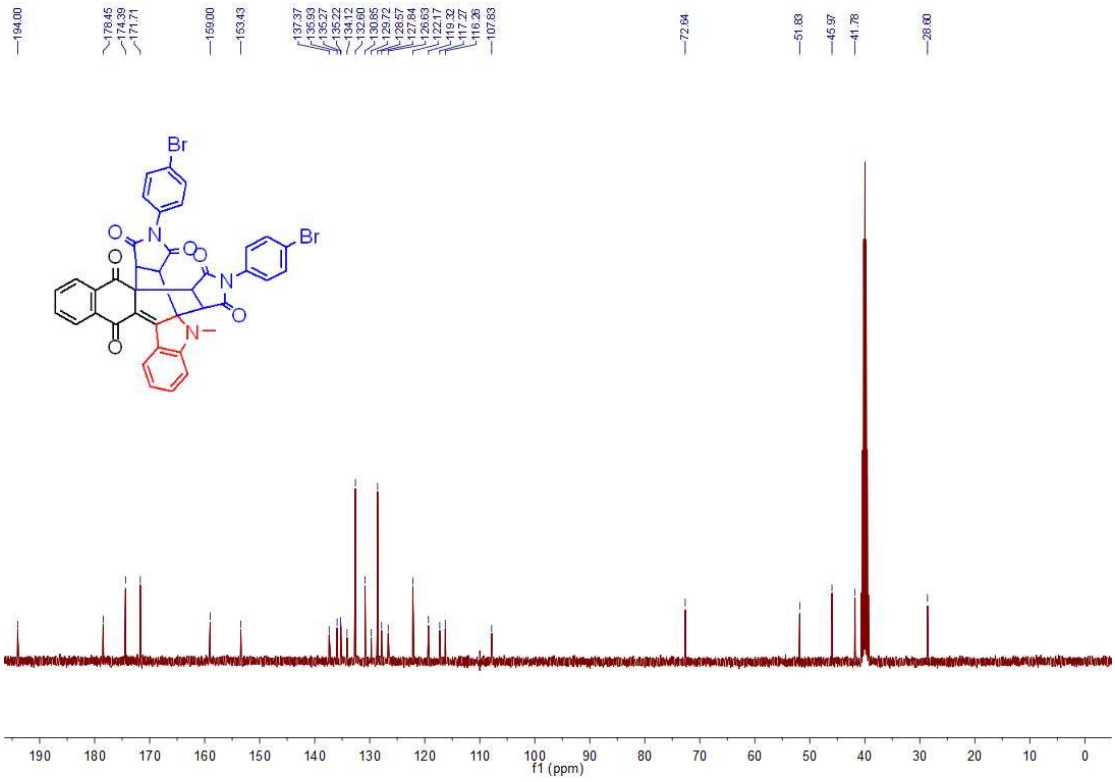


7,17-bis(4-bromophenyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5g**)

^{1}H NMR (400 MHz)



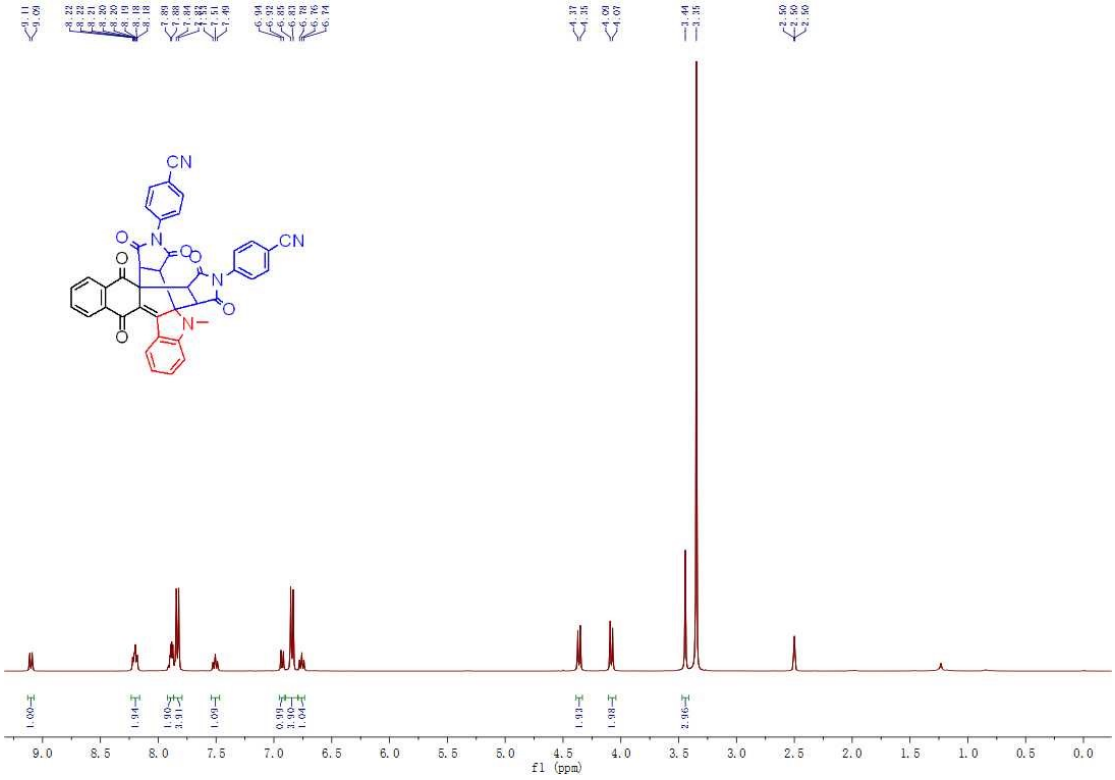
^{13}C NMR (101 MHz)



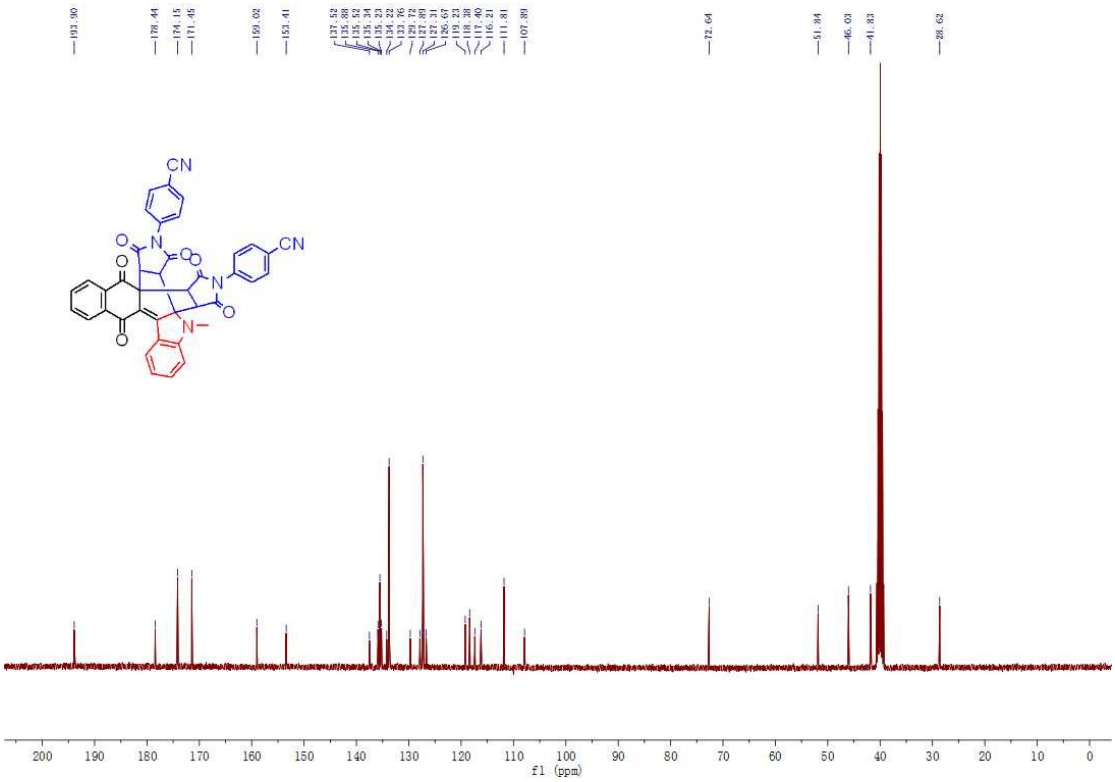
4,4'-(5-methyl-6,8,9,14,16,18-hexaoxo-5b,6,8,8a,9,14-hexahydro-5H,7H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-7,17-diyl)dibenzonitrile (**5h**)

^{1}H NMR (400 MHz)

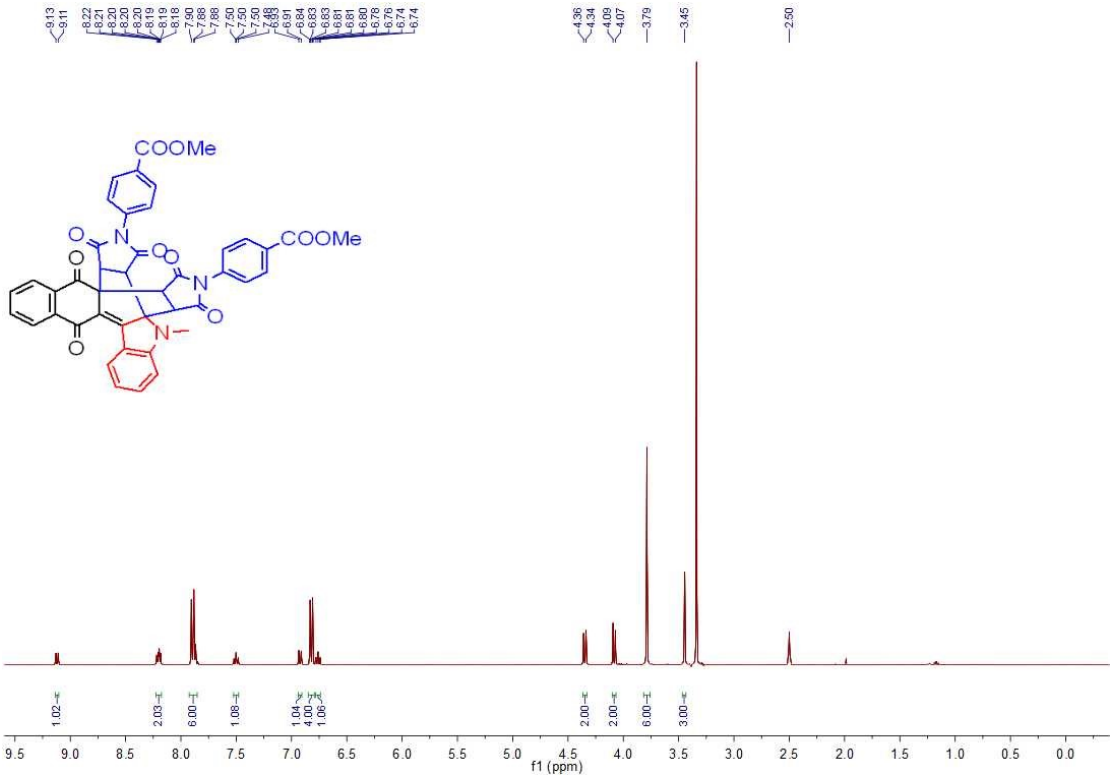


^{13}C NMR (101 MHz)

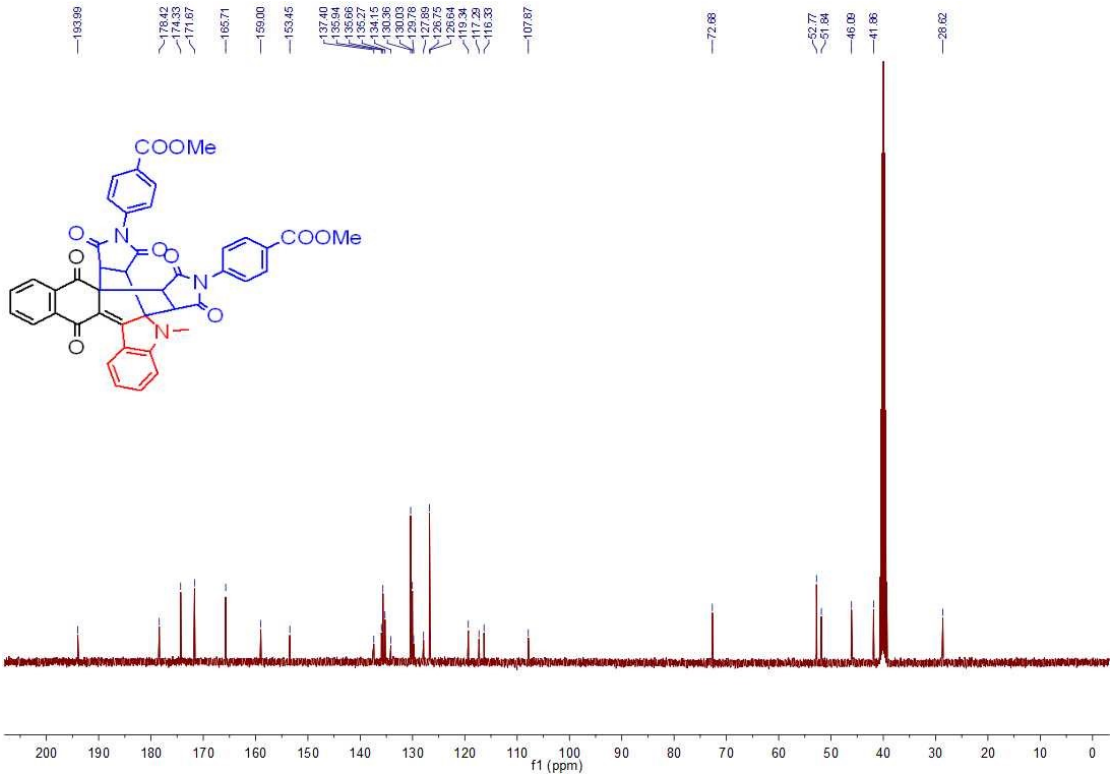


dimethyl 4,4'-(5-methyl-6,8,9,14,16,18-hexaoxo-5b,6,8,8a,9,14-hexahydro-5H,7H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-7,17-diyl)dibenzoate (**5i**)

^{1}H NMR (400 MHz)



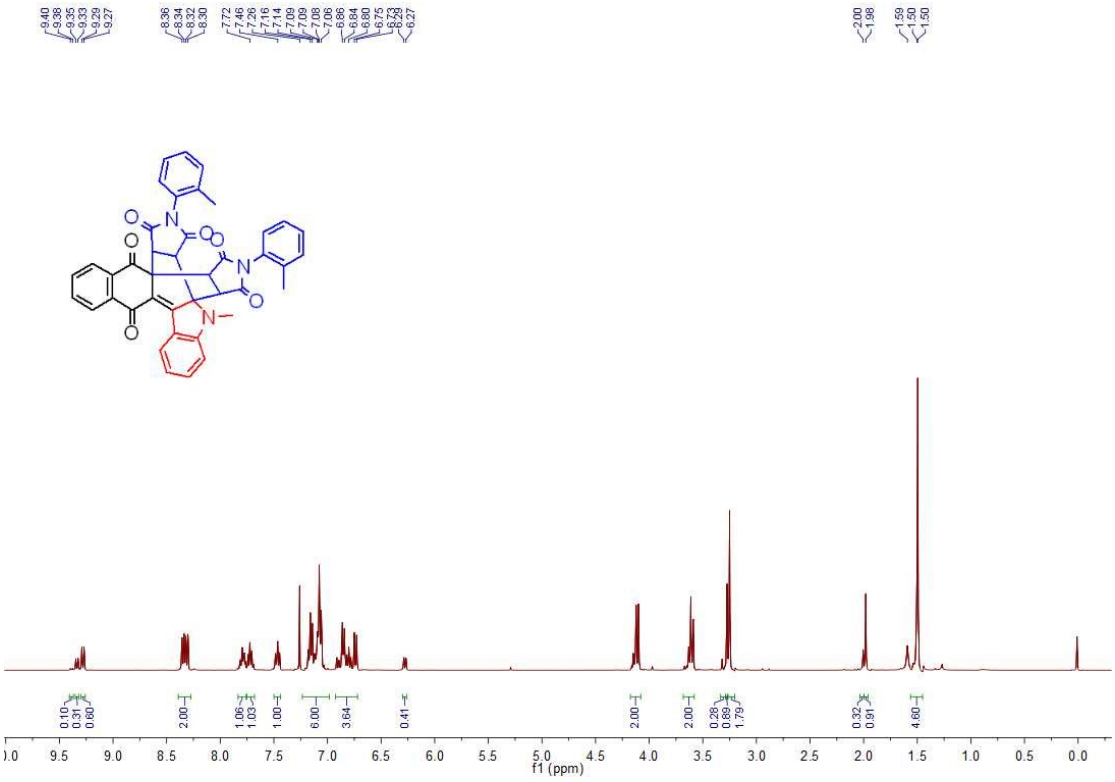
^{13}C NMR (101 MHz)



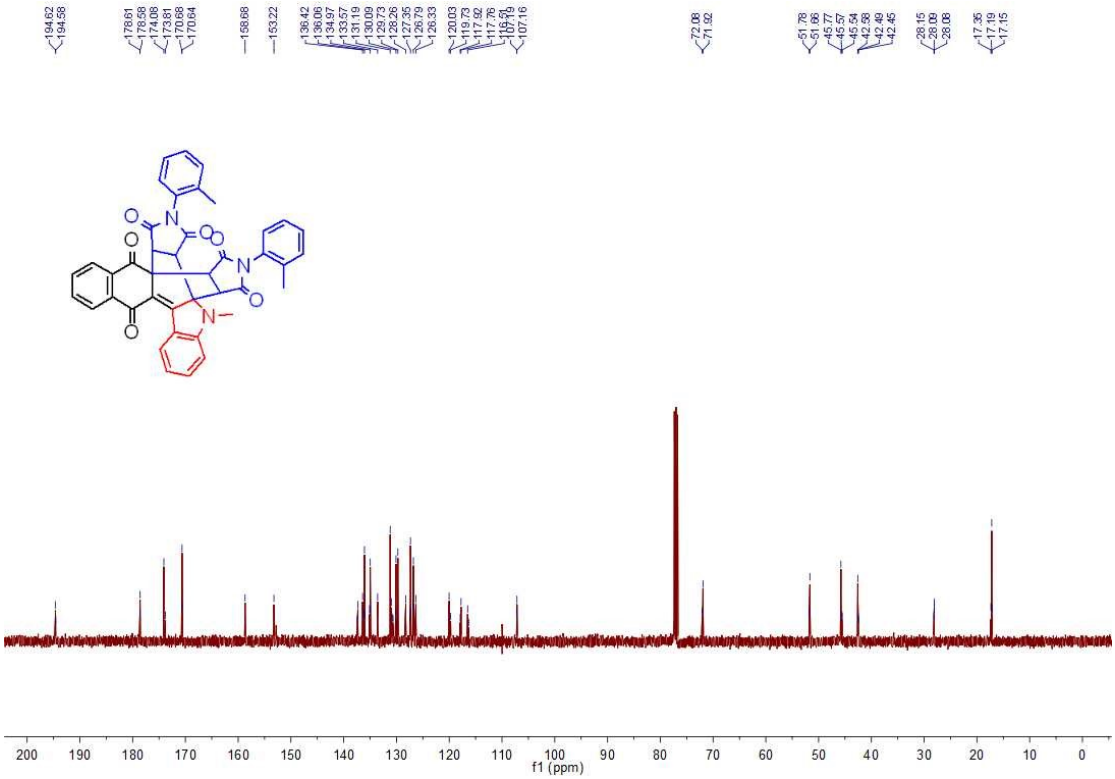
5-methyl-7,17-di-o-tolyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-

c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5j**)

^{1}H NMR (400 MHz)

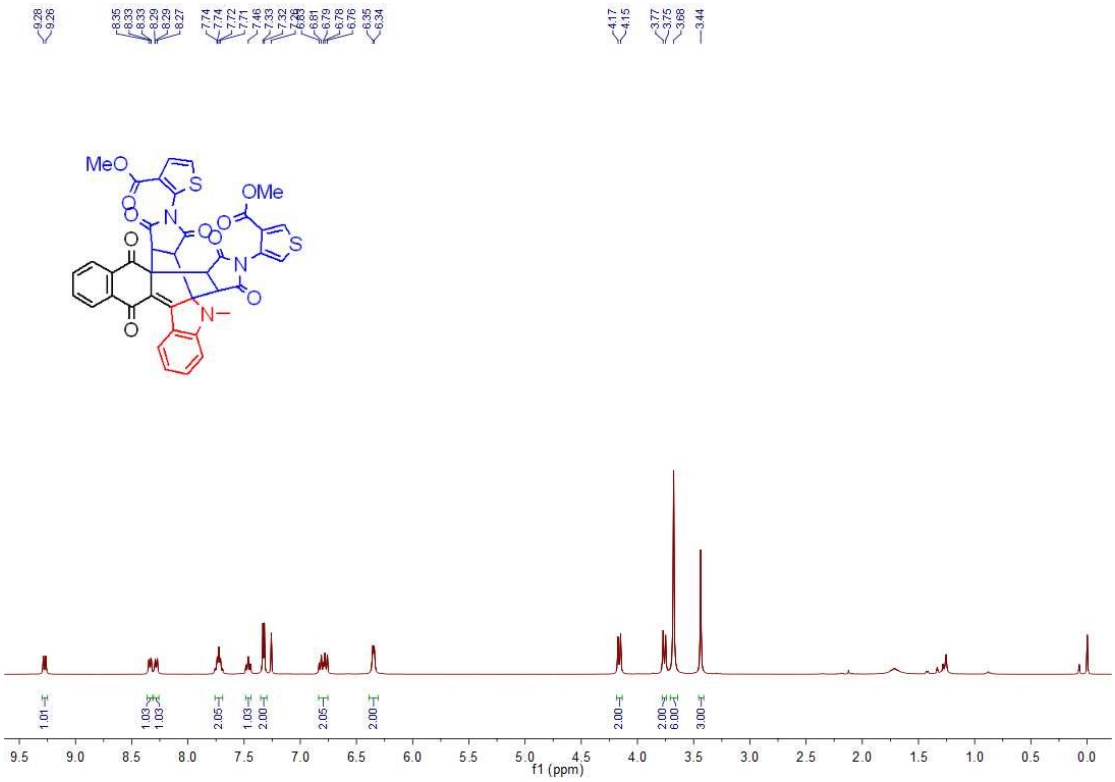


^{13}C NMR (101 MHz)

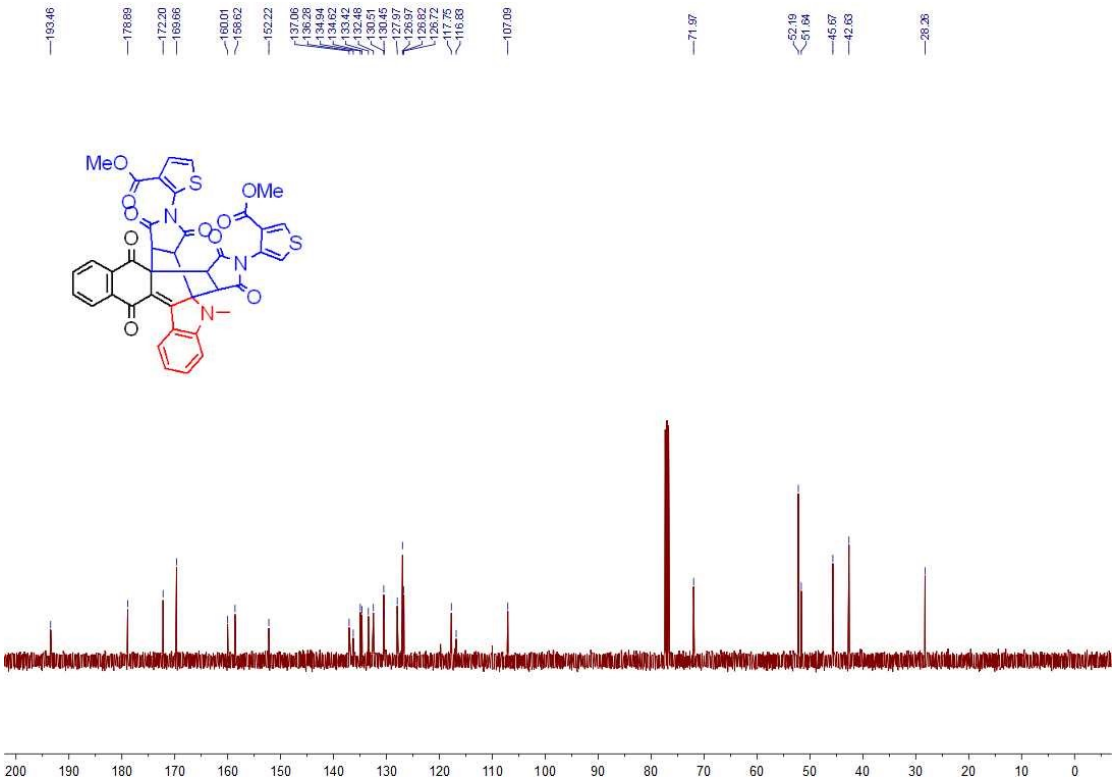


methyl 4-(7-(3-(methoxycarbonyl)thiophen-2-yl)-5-methyl-6,8,9,14,16,18-hexaoxo-5b,7,8,8a,9,14-hexahydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazol-17-yl)thiophene-3-carboxylate (**5k**)

^{1}H NMR (400 MHz)



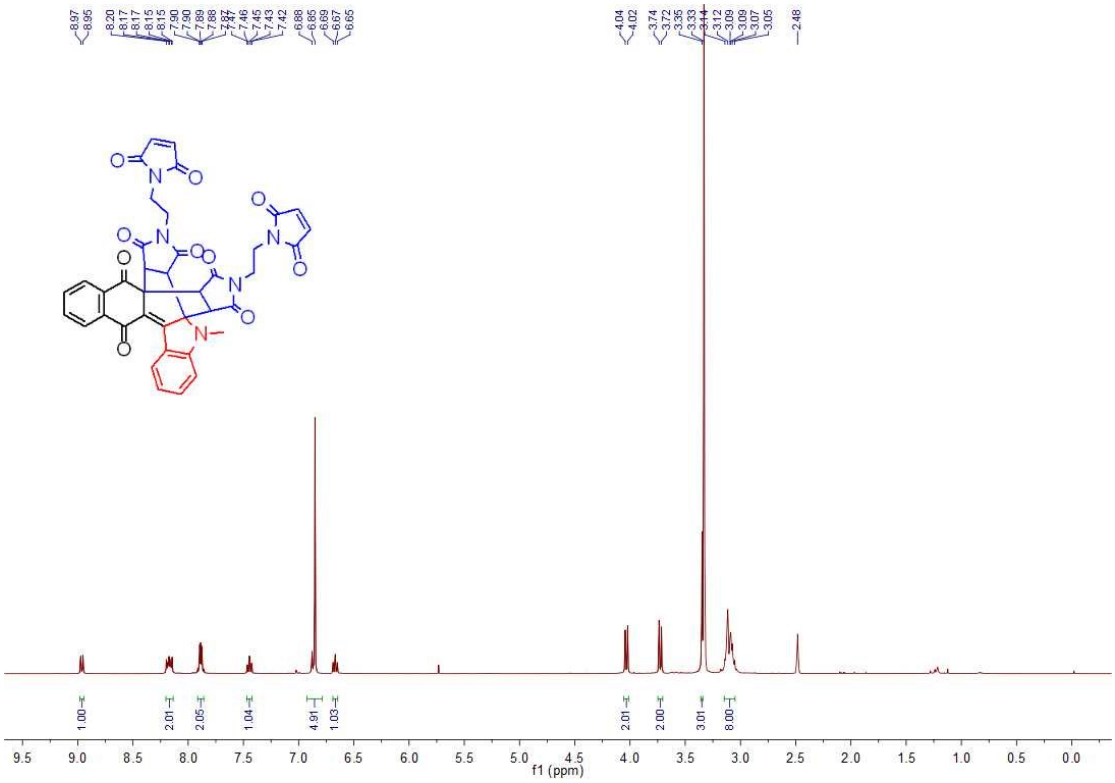
^{13}C NMR (101 MHz)



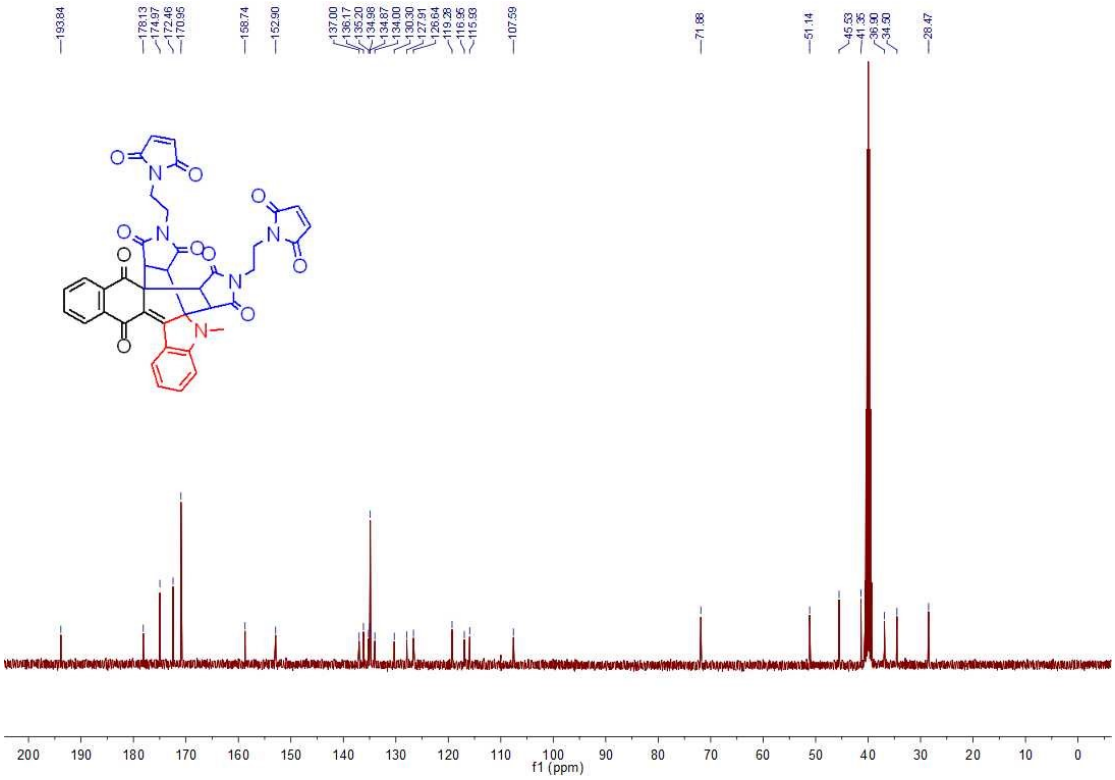
7,17-bis(2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl)-5-methyl-5b,8a-dihydro-

5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5l**)

^{1}H NMR (400 MHz)

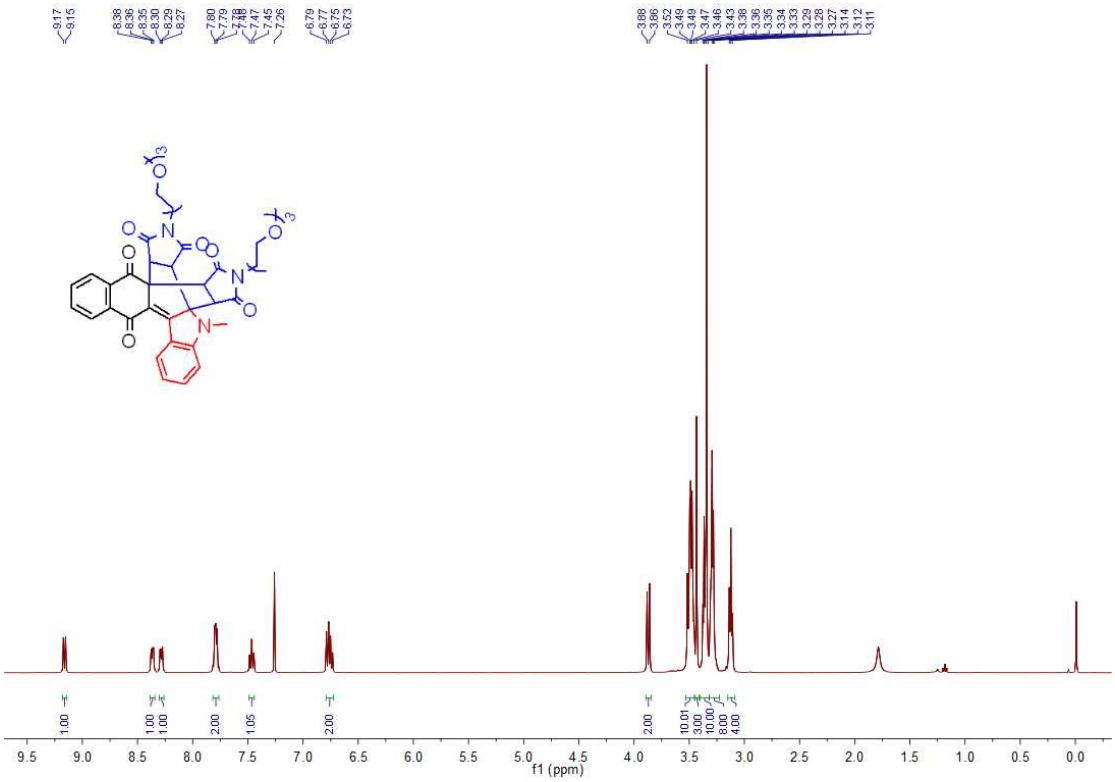


^{13}C NMR (101 MHz)

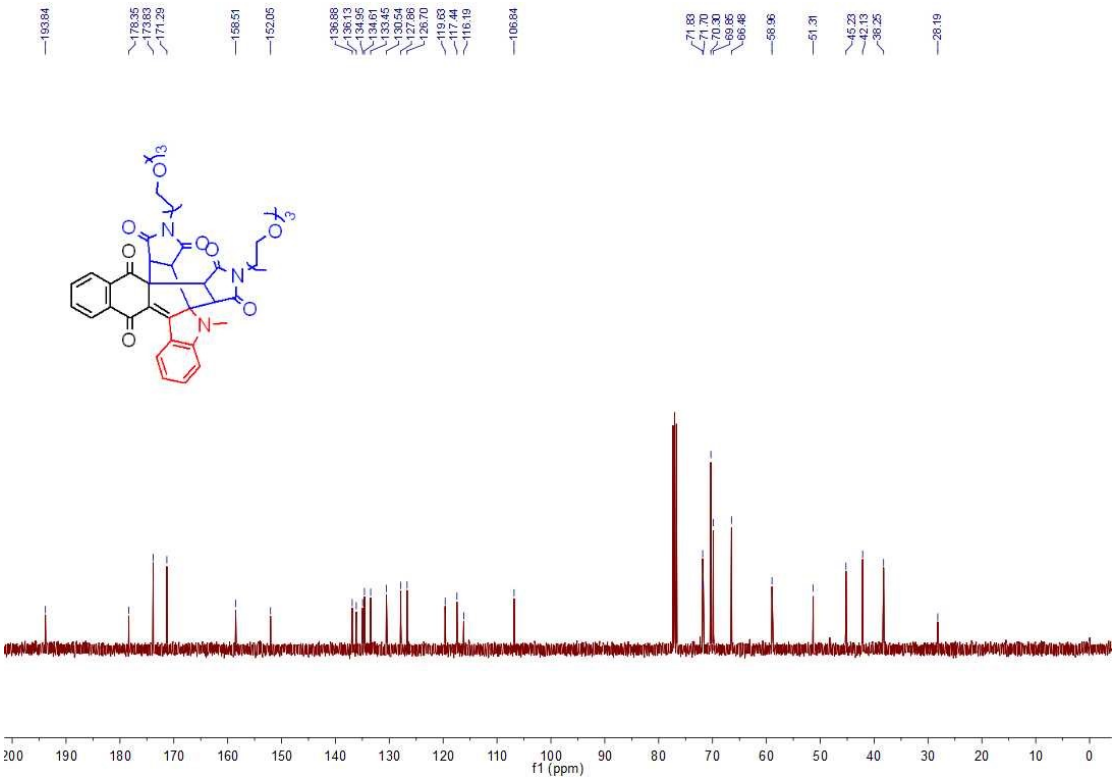


7,17-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5m**)

^{1}H NMR (400 MHz)



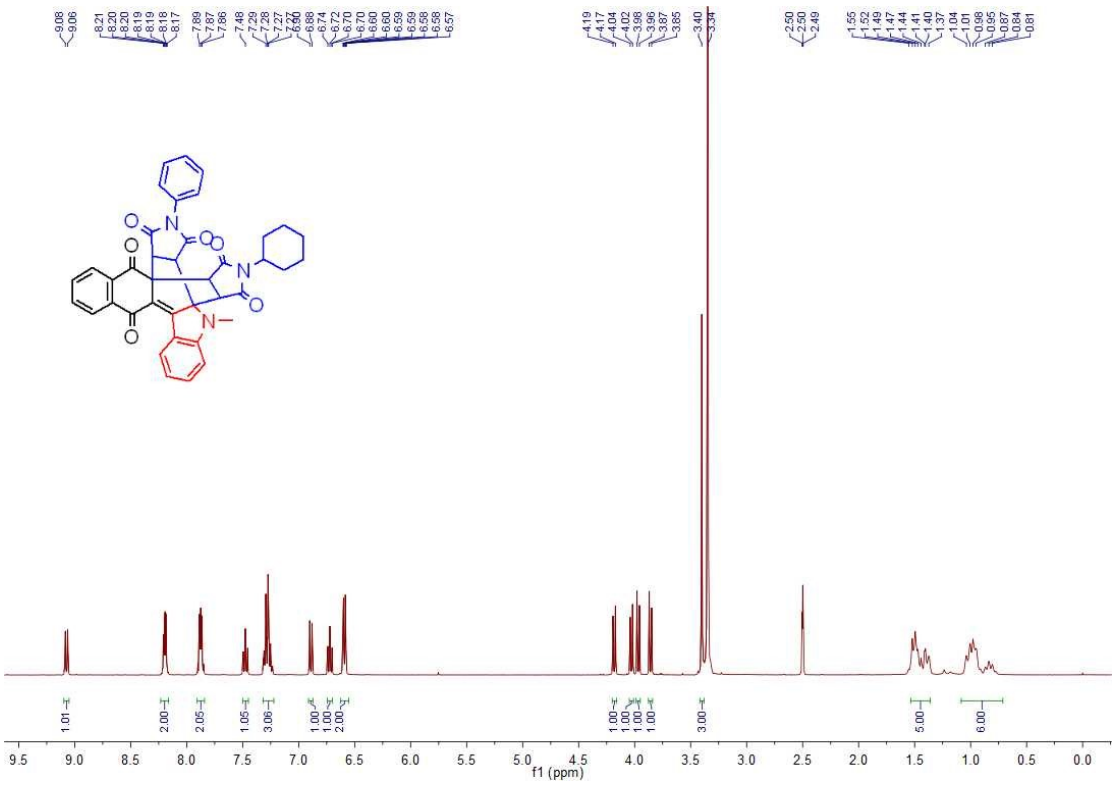
^{13}C NMR (101 MHz)



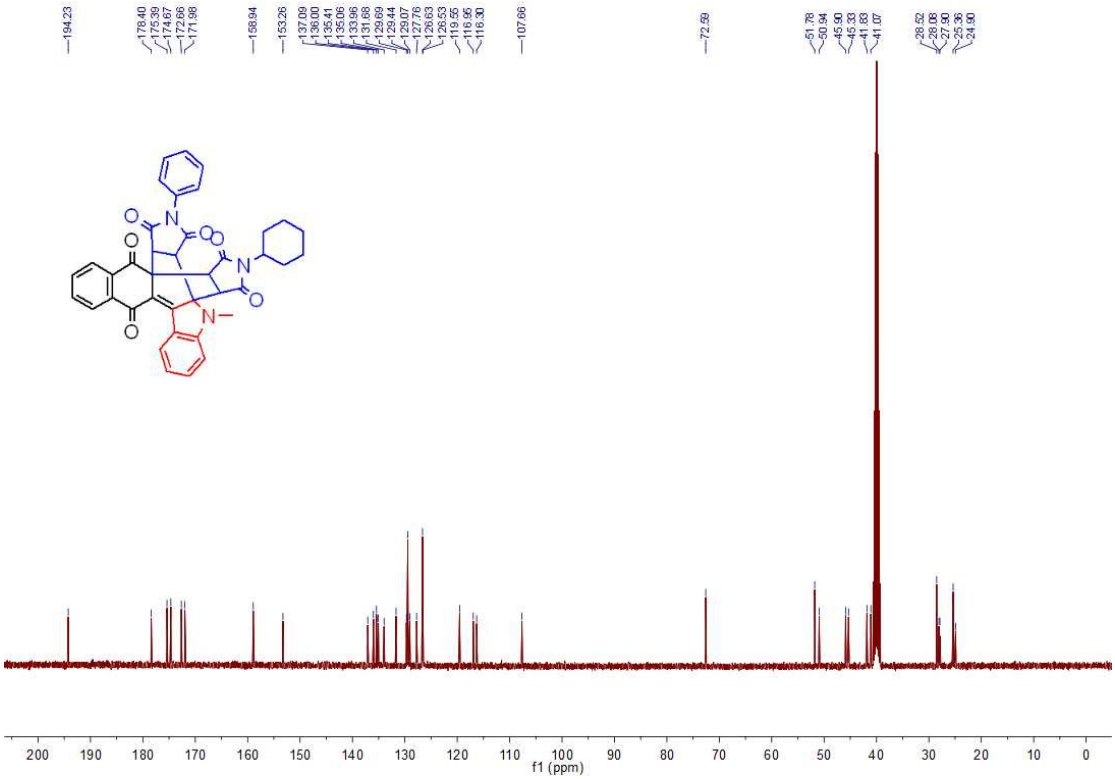
7-cyclohexyl-5-methyl-17-phenyl-5b,8a-dihydro-5H,6H-5a,8b-

[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5n**)

^{1}H NMR (400 MHz)

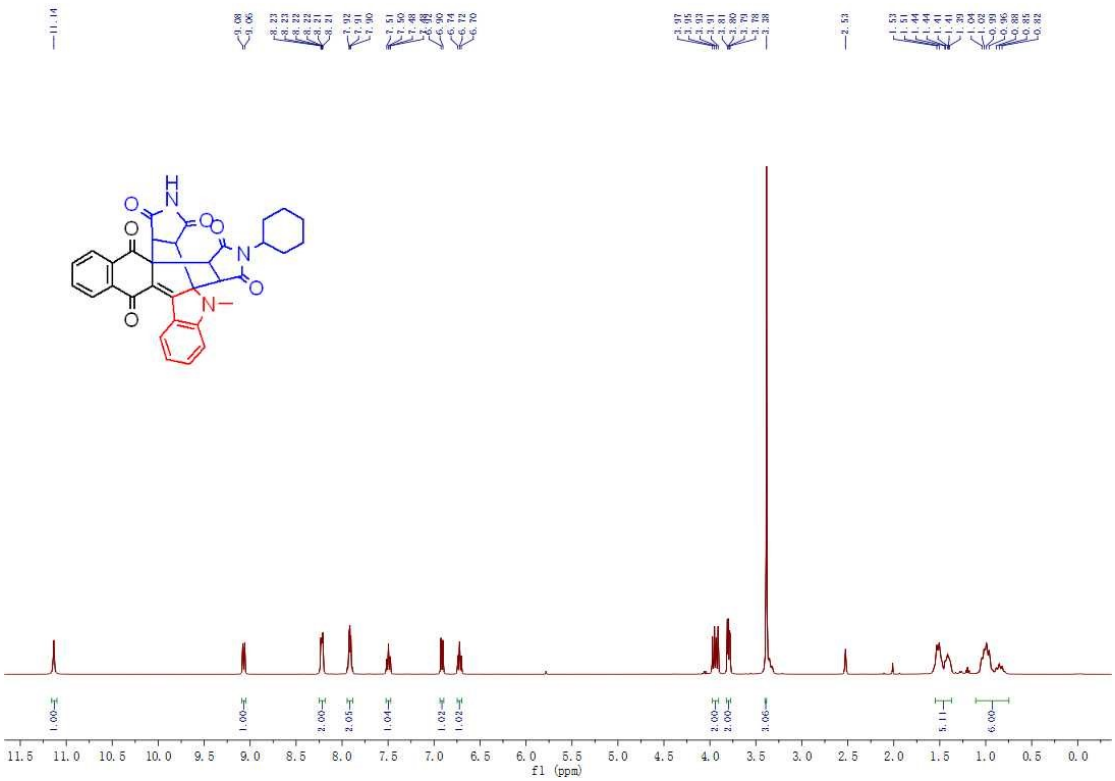


^{13}C NMR (101 MHz)



7-cyclohexyl-5-methyl-5b,8a-dihydro-5H,6H-5a,8b-[3,4]epipyrrolonaphtho[2,3-c]pyrrolo[3,4-a]carbazole-6,8,9,14,16,18(7H)-hexaone (**5o**)

^{1}H NMR (400 MHz)



^{13}C NMR (101 MHz)