Supporting Information

Molecular Engineering of Locked Alkyl Aryl Carbonyl-Based Thermally Activated Delayed Fluorescence Emitters *via* a Cascade C–H Activation Process

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I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $AgSbF_6$ was purchased from Beijing Ou He Chemical Engineering (China) Co., Ltd. 9,9-Dimethylcarbazine was obtained from Suzhou GeAo New Materials Co., Ltd. Ketone derivatives were purchased from Energy Chemical Technology (Shanghai) Co., Ltd. $[Cp^*RhCl_2]_2$ was prepared according to the literature procedures.[1] Solvents were dried with an innovative technology solvent purification system (model no.: PS-MD-5).

Measurements: NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal standard (CDCl3: δ = 7.26 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal reference ($CDCl_3$: δ = 77.16 ppm). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). X-ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single crystal diffractometer. UV/Vis spectra were measured on a HITACHI U-2910. Fluorescence spectra and phosphorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-3 fluorescence spectrometer. Thermogravimetric analysis (TGA) was carried out using DTG-60(H) at a rate of 10 ^oC/min under nitrogen atmosphere. Cyclic voltammogram (CV) measurements were performed on LK2005A with a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in dry dichloromethane (DCM) as electrolyte and ferrocene/ferrocenium (Fc/Fc^+) as standard. Three-electrode system (Ag/Ag^+, platinum wire and glassy carbon electrode as reference, counter and work electrode respectively) was used in the CV measurements.

OLED fabrication and characterization: Indium-tin-oxide (ITO) coated glass with a sheet resistance of 15 Ω sq^{-1} was used as the anode substrate. Prior to film deposition, patterned ITO substrates were cleaned with alkaline detergent, boiled deionized water in ultrasonic bath, dried in an oven, and finally treated with oxygen plasma for 10 min

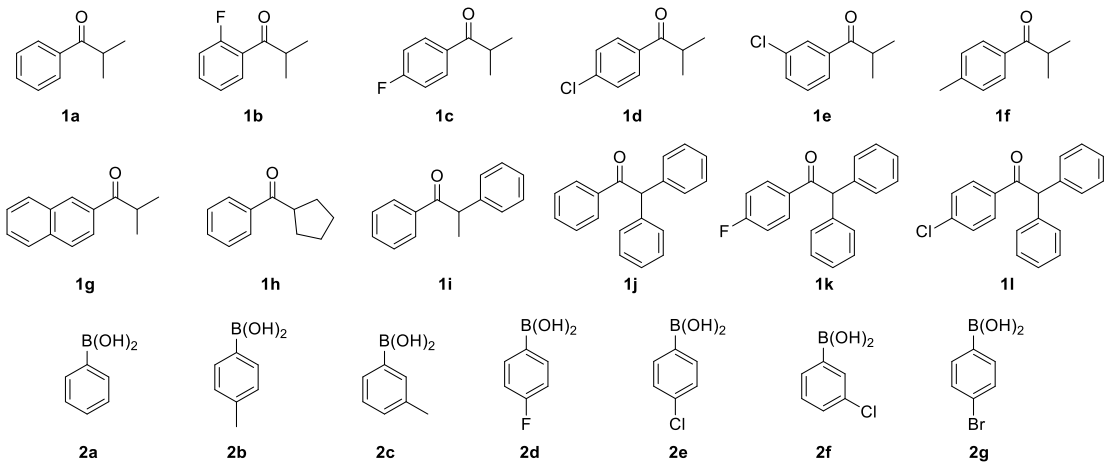
to enhance the surface work function of ITO anode. The organic layers were deposited with the rate of 0.1 nm·s^{-1} under high vacuum. The doped and co-doped layers were prepared by co-evaporating dopant and host material from two individual sources, and the doping concentrations were modulated by controlling the evaporation rates of dopant.

Current density-voltage-luminance (*J-V-L*) characteristics were measured by using KEYSIGHT B1500A. The luminance and electroluminescence spectra were collected with model DLM-100Z photometer and OPT2000 spectrophotometer, respectively.

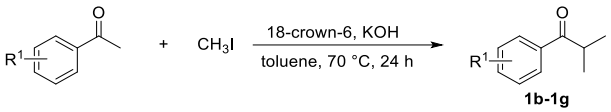
Method of theoretical calculations: All density functional theory (DFT) calculations were performed using Gaussian 09 serials software. The ground-state structures and frontier molecular orbital (FMO) distributions were obtained by B3LYP density functional method with basis set 6-31G*. The singlet (S_1) and triplet (T_1) energies were calculated by time-dependent DFT (TD-DFT) method with the same parameters for ground-state calculations. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) distributions and spin density distribution (SDD) of T_1 state were visualized using Gaussview 5.0 software.

II. Preparation of substrates

1a, **1h** and **2a-2g** were purchased from Energy Chemical (China) CO., Ltd. and used without any further purification.

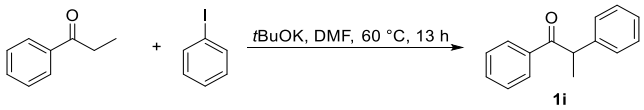


1) General procedure for the synthesis of 1b-1g[2]



To a stirred suspension of KOH (5.6 g, 0.1 mol) in toluene (10.0 mL) containing acetophenone (0.01 mol) and 18-crown-6 (60.0 mg) was added CH_3I (5.0 mL) dropwise. The mixture was stirred at 70 °C for 24 h. After being cooled to room temperature, the solid phase was separated by filtration and toluene was evaporated. The remainder was purified by column chromatography on silica gel to afford corresponding product.

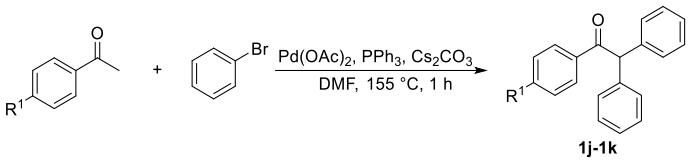
2) Procedure for the synthesis of 1i[3]



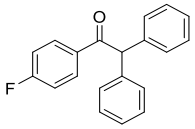
A 25 mL Schlenk tube with a magnetic stir bar was charged with propiophenone (268.4 mg, 2.0 mmol), iodobenzene (204.0 mg, 1.0 mmol), *t*BuOK (561.1 mg, 5.0 mmol), and *N*,*N*-dimethylformamide (DMF, 3.0 mL) under N_2 atmosphere. The resulting mixture was stirred at 60 °C (oil bath) for 13 h. After completion of the reaction, the mixture was cooled to room

temperature and extracted with ethyl acetate (EtOAc, 3 × 20.0 mL). The combined organic phases were dried over Na_2SO_4 and then filtered. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to provide the desired product.

3) General procedure for the synthesis of 1j and 1k[4]



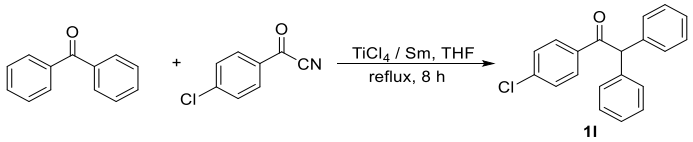
A 25 mL Schlenk tube with a magnetic stir bar was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), PPh_3 (52.5 mg, 0.2 mmol), Cs_2CO_3 (977.5 mg, 3.0 mmol), acetophenone (1.0 mmol), bromobenzene (0.36 mL, 3.4 mmol), and DMF (5.0 mL) under N_2 atmosphere. The resulting mixture was stirred at 155 °C (oil bath) for 1 h. After completion of the reaction, the mixture was cooled to room temperature and extracted with EtOAc (3 × 20.0 mL). The combined organic phases were dried over Na_2SO_4 and then filtered. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to provide the desired product.



1-(4-fluorophenyl)-2,2-diphenylethan-1-one (1k)

Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 100/1 to 80/1, v/v) afforded the desired product **1k** as a white solid (208.8 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.98 (m, 2H), 7.34-7.29 (m, 4H), 7.25 (d, J = 7.4 Hz, 6H), 7.05 (t, J = 8.7 Hz, 2H), 5.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 165.8 (d, J = 255.2 Hz), 139.0, 133.4 (d, J = 3.0 Hz), 131.8 (d, J = 9.3 Hz), 129.3, 128.9, 127.4, 115.9 (d, J = 21.9 Hz), 59.6 ppm. HRMS (ESI^+): calcd for $C_{20}H_{15}O$ $[M+H]^+$ 291.1180, found 291.1181.

4) Procedure for the synthesis of 1l[5]



1l

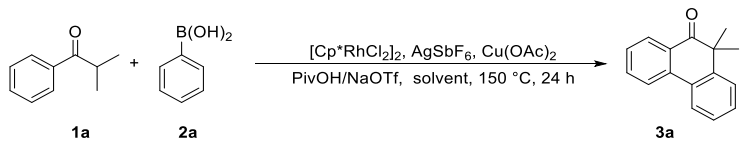
Under N_2 atmosphere, $TiCl_4$ (0.22 mL, 2.0 mmol) was added dropwise using a syringe to stirred suspension of powdered samarium (300.7 mg, 2.0 mmol) in freshly distilled dry tetrahydrofuran (THF, 20.0 mL) at room temperature. After the completion of addition, the mixture was refluxed for 2 h. Then a solution of benzophenone (182.2 mg, 1.0 mmol) and 4-chlorobenzoyl cyanide (165.6 mg, 1.0 mmol) in THF (3.0 mL) was added dropwise. The mixture was stirred at reflux temperature for 8 h. Then, dilute HCl (5%, 4.0 mL) solution was added and the mixture was extracted with ether (3 × 3.0 mL). The combined organic phases were dried over Na_2SO_4 and then filtered. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to provide the desired product.

III. Optimization of the reaction

Optimization of tandem cyclization reactions of aromatic ketone with phenylboronic acid

A 25 mL flame-dried Schlenk test tube with a magnetic stirring bar was charged with isobutyrophenone **1a** (0.2 mmol), phenylboronic acid **2a** (3.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), oxidant (2.0 equiv), additive (1.0-1.4 equiv), and solvent (1.0 mL). The reaction mixture was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature, and diluted with 5.0 mL of CH_2Cl_2. The mixture was filtered through a celite pad and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc =120/1, v/v) to provide the desired product **3a.**

***Table S1*. Screening of solvent**[a]



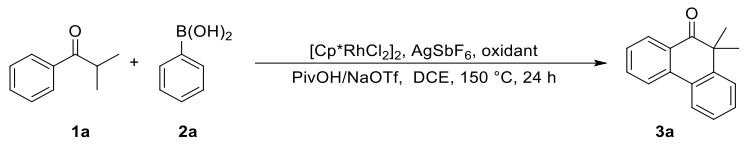
1a 2a 3a

entry	solvent	yield[b]
1	MeCN	N.R.
2	dioxane	8%
3	toluene	N.R.
4	THF	5%
5	DMF	N.R.
6	DMSO	N.R.
7	DCM	45%
8	HFIP	N.R.
9	*t*BuOH	N.R.
10	NMP	N.R.

11	**DCE**	**66%**
12	1,2-dichlorobenzene	N.R.

[a] Conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (2.0 equiv), PivOH (0.5 equiv), NaOTf (0.5 equiv) and solvent (1.0 mL) under N_2, 24 h, 150 °C. [b] The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard. MeCN = acetonitrile, DMSO = dimethyl sulfoxide, DCM = dichloromethane, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, NMP = *N*-methyl pyrrolidone, DCE = 1,2-dichloroethane.

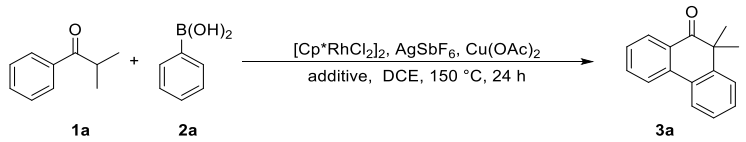
***Table S2*. Screening of oxidant**[a]



entry	oxidant	yield[b]
1	O_2	12%
2	$Cu(NO_3)_2$	N.R.
3	$Cu(acac)_2$	16%
4	$Cu(OTf)_2$	N.R.
5	**$Cu(OAc)_2$**	**66%**
6	CuCl	N.R.
7	AgOAc	N.R.
8	Ag_2CO_3	N.R.
9	Ag_2O	N.R.
10	$AgNO_3$	8%
11	$PhI(OAc)_2$	N.R.

[a] Conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), oxidant (2.0 equiv), PivOH (0.5 equiv), NaOTf (0.5 equiv) and DCE (1.0 mL) under N_2, 24 h, 150 °C. [b] The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard.

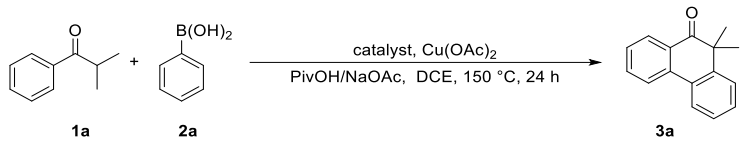
***Table S3*. Screening of additive**[a]



entry	additive	yield[b]
1	/	trace
2	CsOAc	N.R.
3	NaOAc	33%
4	LiOAc	46%
5	$Zn(OTf)_2$	37%
6	LiOTf	60%
7	NaOTf	60%
8	KF	N.R.
9	NaF	52%
10	PivOH	44%
11	PivOH/LiOTf	56%[c]
12	PivOH/NaOTf	66%[c]
13	PivOH/NaF	61%[c]
14	PivOH/LiOAc	67%[d]
15	PivOH/NaOAc	72%[d]
16	**PivOH/NaOAc**	**84%**[e]

[a] Conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (2.0 equiv), additive (1.0 equiv) and DCE (1.0 mL) under N_2, 24 h, 150 ℃. [b] The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard. [c] PivOH/LiOTf, PivOH/NaOTf and PivOH/NaF (0.5 equiv/0.5 equiv). [d] PivOH/LiOAc and PivOH/NaOAc(1.0 equiv/0.2 equiv). [e] PivOH/NaOAc (1.2 equiv/0.2 equiv).

***Table S4*. Screening of catalyst**[a]



entry	catalyst	yield[b]
1	/	N.R.
2	$[Cp^*RhCl_2]_2/AgSbF_6$	41%[c]
3	**$[Cp^*RhCl_2]_2/AgSbF_6$**	**84%**

[a] Conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol%), $Cu(OAc)_2$ (2.0 equiv), PivOH/NaOAc (1.2 equiv/0.2 equiv) and DCE (1.0 mL) under N_2, 24 h, 150 ℃. [b] The yield was determined by ^1H NMR analysis of crude product using CH_2Br_2 as an internal standard. [c] $[Cp^*RhCl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol%).

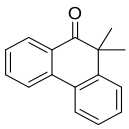
IV. General procedure for tandem cyclization reactions of aromatic ketones with phenylboronic acids

A 25 mL flame-dried Schlenk test tube with a magnetic stirring bar was charged with aromatic ketones **1** (0.2 mmol), phenylboronic acid **2** (3.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol%), $AgSbF_6$ (13.7 mg, 20 mol%), $Cu(OAc)_2$ (72.7 mg, 2.0 equiv), PivOH (24.5 mg, 1.2 equiv), NaOAc (3.3 mg, 0.2 equiv) and DCE (1.0 mL). The reaction mixture was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature, and diluted with 5.0 mL of CH_2Cl_2. The mixture was filtered through a celite pad and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography to provide the desired product **3**.

V. Procedure for the synthesis of 3j on 1.0 mmol scale

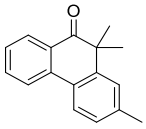
A 100 mL flame-dried Schlenk test tube with a magnetic stirring bar was charged with 1-(4-chlorophenyl)-2-methylpropan-1-one **1d** (167.2 μL, 1.0 mmol) and 4-chlorophenylboronic acid **2e** (468.0 mg, 3.0 mmol), $[Cp^*RhCl_2]_2$ (30.9 mg, 5 mol%), $AgSbF_6$ (68.7 mg, 20 mol%), $Cu(OAc)_2$ (363.3 mg, 2.0 equiv), PivOH (122.5 mg, 1.2 equiv), NaOAc (16.5 mg, 0.2 equiv) and DCE (5.0 mL). The reaction mixture was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere. The reaction mixture was then cooled to room temperature, and diluted with 25.0 mL of CH_2Cl_2. The mixture was filtered through a celite pad and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were concentrated under reduced pressure. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3j** as a white solid (194.6 mg, 67% yield).

VI. Experimental data for the described substances



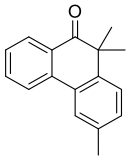
10,10-dimethylphenanthren-9(10*H*)-one (3a)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1, v/v) afforded the desired product **3a** as a colorless oil (36.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (dd, J = 7.8, 1.1 Hz, 1H), 8.03-7.97 (m, 2H), 7.70-7.65 (m, 1H), 7.53-7.50 (m, 1H), 7.45-7.40 (m, 1H), 7.40-7.34 (m, 2H), 1.55 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 144.2, 137.2, 134.4, 129.3, 129.0, 128.3, 128.0, 127.2, 126.5, 124.1, 123.0, 47.5, 27.4 ppm. HRMS (ESI^+): calcd for $C_{16}H_{14}O$ $[M+H]^+$ 223.1117, found 223.1118.



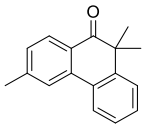
2,10,10-trimethylphenanthren-9(10*H*)-one (3b)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 4-tolylboronic acid **2b** (81.6 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1, v/v) afforded the desired product **3b** as a pale yellow oil (40.1 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.31 (s, 1H), 7.18 (d, J = 8.0 Hz, 1H), 2.42 (s, 3H), 1.54 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 144.1, 139.3, 137.4, 134.3, 128.7, 128.0, 127.9, 127.8, 127.1, 126.5, 124.1, 122.8, 47.4, 27.5, 21.7 ppm. HRMS (ESI^+): calcd for $C_{17}H_{16}O$ $[M+H]^+$ 237.1274, found 237.1274.



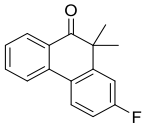
3,10,10-trimethylphenanthren-9(10*H*)-one (3c)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 3-tolylboronic acid **2c** (81.6 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1, v/v) afforded the desired product **3c** as a pale yellow oil (36.8 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.5 Hz, 2H), 7.21 (d, J = 7.9 Hz, 1H), 2.43 (s, 3H), 1.53 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 141.2, 137.3, 136.7, 134.3, 130.1, 129.1, 129.0, 128.2, 128.0, 126.4, 124.7, 123.0, 47.2, 27.5, 21.4 ppm. HRMS (ESI^+): calcd for $C_{17}H_{16}O$ $[M+H]^+$ 237.1274, found 237.1275.



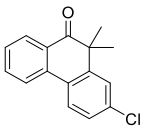
6,10,10-trimethylphenanthren-9(10*H*)-one (3d)

Following the general procedure, 2-methyl-1-(*p*-tolyl)propan-1-one **1f** (33.0 μL, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1, v/v) afforded the desired product **3d** as a pale yellow oil (29.3 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 7.9 Hz, 2H), 7.82 (s, 1H), 7.51 (d, J = 7.1 Hz, 1H), 7.38 (q, J = 5.9, 4.2 Hz, 2H), 7.27-7.21 (m, 1H), 2.50 (s, 3H), 1.54 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.9, 145.1, 144.5, 137.2, 129.3, 129.3, 129.1, 128.1, 127.0, 126.7, 126.5, 124.0, 123.5, 47.3, 27.6, 22.3 ppm. HRMS (ESI^+): calcd for $C_{17}H_{16}O$ $[M+H]^+$ 237.1274, found 237.1273.



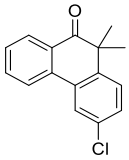
2-fluoro-10,10-dimethylphenanthren-9(10*H*)-one (3e)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 4-fluorobenzeneboronic acid **2d** (84.0 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3e** as a colorless oil (41.3 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.7 Hz, 1H), 7.98-7.90 (m, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 10.2 Hz, 1H), 7.06 (t, J = 8.3 Hz, 1H), 1.53 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 163.4 (d, J = 248.7 Hz), 146.9 (d, J = 7.2 Hz), 136.5, 134.5, 128.5, 128.2, 128.1, 126.1 (d, J = 8.5 Hz), 125.6 (d, J = 3.1 Hz), 122.9, 114.3 (d, J = 21.6 Hz), 113.5 (d, J = 22.4 Hz), 47.7, 27.3 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{13}FO$ $[M+H]^+$ 241.1023, found 241.1024.



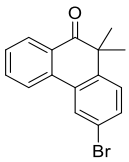
2-chloro-10,10-dimethylphenanthren-9(10*H*)-one (3f)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 4-chlorophenylboronic acid **2e** (93.8 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3f** as a pale yellow solid (33.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.32 (dd, J = 8.5, 2.2 Hz, 1H), 1.53 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 146.0, 136.2, 135.1, 134.5, 128.7, 128.6, 128.1, 127.9, 127.4, 126.7, 125.5, 123.0, 47.5, 27.3 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{13}{}^{35}ClO$ $[M+H]^+$ 257.0728, found 257.0728; calcd for $C_{16}H_{13}{}^{37}ClO$ $[M+H]^+$ 259.0699, found 259.0700.



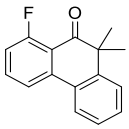
3-chloro-10,10-dimethylphenanthren-9(10*H*)-one (3g)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 3-chlorophenylboronic acid **2f** (93.8 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3g** as a pale yellow oil (32.7 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.7 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.69 (t, J = 7.7 Hz, 1H), 7.50-7.42 (m, 2H), 7.34 (d, J = 8.5 Hz, 1H), 1.52 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.5, 142.5, 135.9, 134.5, 133.3, 131.1, 129.1, 129.0, 128.2, 128.0, 124.1, 123.1, 47.3, 27.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{13}{}^{35}ClO$ $[M+H]^+$ 257.0728, found 257.0731; calcd for $C_{16}H_{13}{}^{37}ClO$ $[M+H]^+$ 259.0699, found 259.0699.



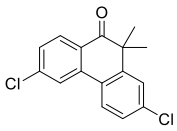
3-bromo-10,10-dimethylphenanthren-9(10*H*)-one (3h)

Following the general procedure, isobutyrophenone **1a** (30.0 μL, 0.2 mmol) and 3-bromophenylboronic acid **2g** (120.5 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3h** as a pale yellow oil (42.6 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 9.7 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.51-7.43 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 1.52 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 143.0, 135.8, 134.5, 132.0, 131.5, 129.0, 128.3, 128.1, 127.1, 123.1, 121.3, 47.3, 27.3 ppm. HRMS (ESI^+): calcd for $C_{16}H_{13}{}^{79}BrO$ $[M+H]^+$ 301.0223, found 301.0223; calcd for $C_{16}H_{13}{}^{81}BrO$ $[M+H]^+$ 303.0203, found 303.0202.



8-fluoro-10,10-dimethylphenanthren-9(10*H*)-one (3i)

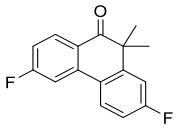
Following the general procedure, 1-(2-fluorophenyl)-2-methylpropan-1-one **1b** (32.0 μL, 0.2 mmol) and fhenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 40/1 to 20/1, v/v) afforded the desired product **3i** as a yellow solid (10.6 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.59 (td, J = 8.1, 5.4 Hz, 1H), 7.49 (d, J = 7.3 Hz, 1H), 7.43-7.32 (m, 2H), 7.10 (t, J = 8.0 Hz, 1H), 1.54 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 161.7 (d, J = 262.3 Hz), 143.6, 139.6, 134.7 (d, J = 10.0 Hz), 129.9, 129.4 (d, J = 3.1 Hz), 127.4, 125.9, 124.9, 119.1 (d, J = 3.8 Hz), 118.3 (d, J = 7.9 Hz), 116.2 (d, J = 21.9 Hz), 48.8, 26.0 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{13}FO$ $[M+H]^+$ 241.1024, found 241.1022.



2,6-dichloro-10,10-dimethylphenanthren-9(10*H*)-one (3j)

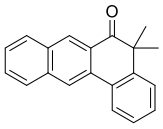
Following the general procedure, 1-(4-chlorophenyl)-2-methylpropan-1-one **1d** (34.0 μL, 0.2 mmol) and 4-chlorophenylboronic acid **2e** (93.8 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3j** as a white solid (46.4 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.3 Hz, 1H), 7.91 (s, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.48 (s, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 1.53 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 146.4, 141.2, 137.9, 136.0, 129.9, 128.8, 127.6, 127.0, 126.9, 126.7, 125.7, 123.2, 47.6, 27.4 ppm. HRMS (ESI$^+$): calcd for $C_{16}H_{12}{}^{35}Cl^{35}ClO$ $[M+H]^+$ 291.0338, found 291.0338; calcd for

$C_{16}H_{12}{}^{35}Cl^{37}ClO$ $[M+H]^+$ 293.0309, found 293.0308, calcd for $C_{16}H_{12}{}^{37}Cl^{37}ClO$ $[M+H]^+$ 295.0276, found 295.0273.



2,6-difluoro-10,10-dimethylphenanthren-9(10*H*)-one (3k)

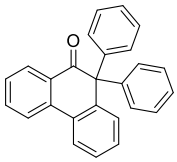
Following the general procedure, 1-(4-fluorophenyl)-2-methylpropan-1-one **1c** (32.0 μL, 0.2 mmol) and 4-fluorobenzeneboronic acid **2d** (84.0 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3k** as a white solid (42.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (t, *J* = 8.0 Hz, 1H), 7.87 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.56 (d, *J* = 10.5 Hz, 1H), 7.21 (dd, *J* = 10.1, 2.1 Hz, 1H), 7.08 (q, *J* = 7.0, 6.5 Hz, 2H), 1.53 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 167.1 (d, *J* = 254.0 Hz), 163.8 (d, *J* = 249.9 Hz), 147.5 (d, *J* = 7.4 Hz), 139.4 (d, *J* = 9.0 Hz), 131.4 (d, *J* = 9.9 Hz), 126.3 (d, *J* = 8.7 Hz), 125.0, 124.6, 115.7 (d, *J* = 22.3 Hz), 114.6 (d, *J* = 21.8 Hz), 113.7 (d, *J* = 22.5 Hz), 109.5 (d, *J* = 24.2 Hz), 47.6, 27.5 ppm. HRMS (ESI^+): calcd for $C_{16}H_{12}F_2O$ $[M+H]^+$ 259.0929, found 259.0928.



5,5-dimethyltetraphen-6(5*H*)-one (3l)

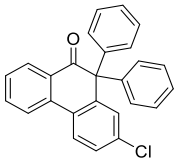
Following the general procedure, 2-methyl-1-(naphthalen-2-yl)propan-1-one **1g** (39.6 mg, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 100/1, v/v) afforded the desired product **3l** as a white solid (22.3 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.40 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 8.01-7.92 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.52 (q, *J* = 7.1 Hz, 2H), 7.45-7.37 (m, 2H), 1.58 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.3, 143.2, 136.5, 133.2, 132.6, 130.1,

129.8, 129.2, 128.8, 128.4, 127.8, 127.4, 126.9, 126.3, 124.5, 122.1, 47.8, 27.2 ppm. HRMS (ESI^+): calcd for $C_{20}H_{16}O$ $[M+H]^+$ 273.1274, found 273.1274.



10,10-diphenylphenanthren-9(10*H*)-one (3m)

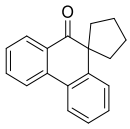
Following the general procedure, 1,2,2-triphenylethan-1-one **1j** (54.4 mg, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 100/1 to 80/1, v/v) afforded the desired product **3m** as a white solid (49.8 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.9 Hz, 1H), 7.96-7.86 (m, 2H), 7.56 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.28-7.19 (m, 7H), 6.96 (s, 4H), 6.75 (d, J = 7.9 Hz, 1H). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5, 141.9, 141.3, 136.7, 134.2, 132.2, 131.5, 130.8, 130.3, 128.7, 128.5, 128.2, 128.0, 127.5, 124.3, 123.0, 68.4 ppm. HRMS (ESI^+): calcd for $C_{26}H_{18}O$ $[M+H]^+$ 347.1431, found 347.1429.



2-chloro-10,10-diphenylphenanthren-9(10*H*)-one (3n)

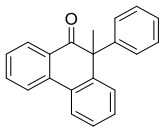
Following the general procedure, 1,2,2-triphenylethan-1-one **1j** (54.4 mg, 0.2 mmol) and 4-chlorophenylboronic acid **2e** (93.8 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1 to 80/1, v/v) afforded the desired product **3n** as a yellow solid (48.6 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.91 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.0 Hz, 1H), 7.40 (dd, J = 8.5, 2.2 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.28-7.24 (m, 6H), 6.99-6.93 (m, 4H), 6.76 (d, J = 2.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 143.3, 141.2, 135.8, 134.8, 134.4, 132.0, 130.3, 130.2, 130.1, 128.8, 128.4, 127.8,

125.7, 123.0, 68.4 ppm. HRMS (ESI^+): calcd for $C_{26}H_{17}{}^{35}ClO$ $[M+H]^+$ 381.1041, found 381.1041; calcd for $C_{26}H_{17}{}^{37}ClO$ $[M+H]^+$ 383.1012, found 381.1016.



10'*H*-spiro[cyclopentane-1,9'-phenanthren]-10'-one (3o)

Following the general procedure, cyclopentyl(phenyl)methanone **1h** (34.8 mg, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 120/1, v/v) afforded the desired product **3o** as a colorless oil (27.8 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.46-7.30 (m, 4H), 2.49 (s, 2H), 1.93 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7, 144.7, 137.5, 134.1, 129.6, 129.5, 129.2, 128.1, 127.8, 126.9, 126.8, 123.9, 123.0, 59.0, 39.5, 27.0 ppm. HRMS (ESI^+): calcd for $C_{18}H_{16}O$ $[M+H]^+$ 249.1274, found 249.1275.



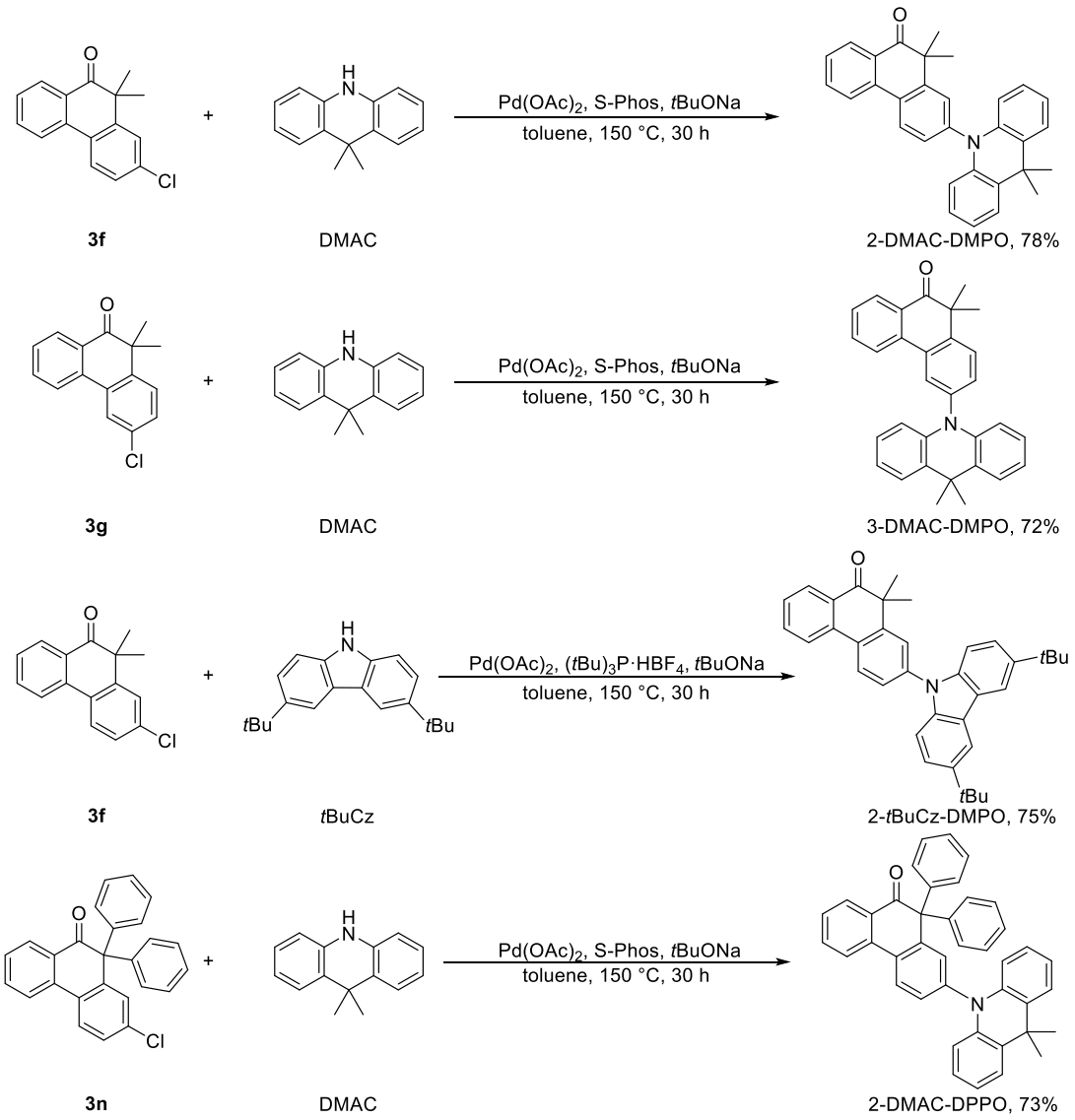
10-methyl-10-phenylphenanthren-9(10*H*)-one (3p)

Following the general procedure, 1,2-diphenylpropan-1-one **1i** (42.0 mg, 0.2 mmol) and phenylboronic acid **2a** (73.2 mg, 0.6 mmol) were used at 150 ºC for 24 h. Purification *via* silica gel column chromatography (petroleum ether/EtOAc = 100/1, v/v) afforded the desired product **3p** as a colorless oil (34.6 mg, 61% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.06-7.95 (m, 3H), 7.63 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.8 Hz, 1H), 7.22-7.12 (m, 3H), 7.08 (d, J = 7.6 Hz, 2H), 1.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.0, 143.9, 142.8, 137.2, 134.5, 130.4, 129.4, 129.3, 129.2, 128.5, 128.4, 128.3, 127.7, 127.5, 127.0, 124.0,

123.0, 56.0, 25.5 ppm. HRMS (ESI^+): calcd for $C_{21}H_{16}O$ $[M+H]^+$ 285.1274, found 285.1275.

VII. Synthesis and characterization of TADF molecules

1) Synthesis of 2-DMAC-DMPO, 3-DMAC-DMPO, 2-*t*BuCz-DMPO and 2-DMAC-DPPO



Synthesis of 2-(9,9-dimethylacridin-10(9*H*)-yl)-10,10-dimethylphenanthren-9(10*H*)-one (2-DMAC-DMPO). A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), S-Phos(30.8 mg, 0.075 mmol), *t*BuONa (96.1 mg, 1.0 mmol), toluene (3.0 mL), **3f** (128.0 mg, 0.5 mmol) and 9,9-dimethyl-9,10-dihydroacridine (DMAC, 104.7 mg, 0.5 mmol) was refluxed under N_2 for 30 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous

Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow solid (167.2 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.54-7.46 (m, 4H), 7.35 (d, *J* = 8.3 Hz, 1H), 6.97 (p, *J* = 8.4, 7.9 Hz, 4H), 6.34 (d, *J* = 8.0 Hz, 2H), 1.73 (s, 6H), 1.57 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 147.3, 142.1, 140.9, 136.5, 134.6, 130.2, 130.0, 129.4, 129.3, 129.1, 128.8, 128.2, 126.7, 126.6, 125.6, 123.3, 120.9, 114.0, 47.8, 36.2, 31.6, 27.4 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{27}NO$ $[M+H]^+$ 430.2165, found 430.2164.

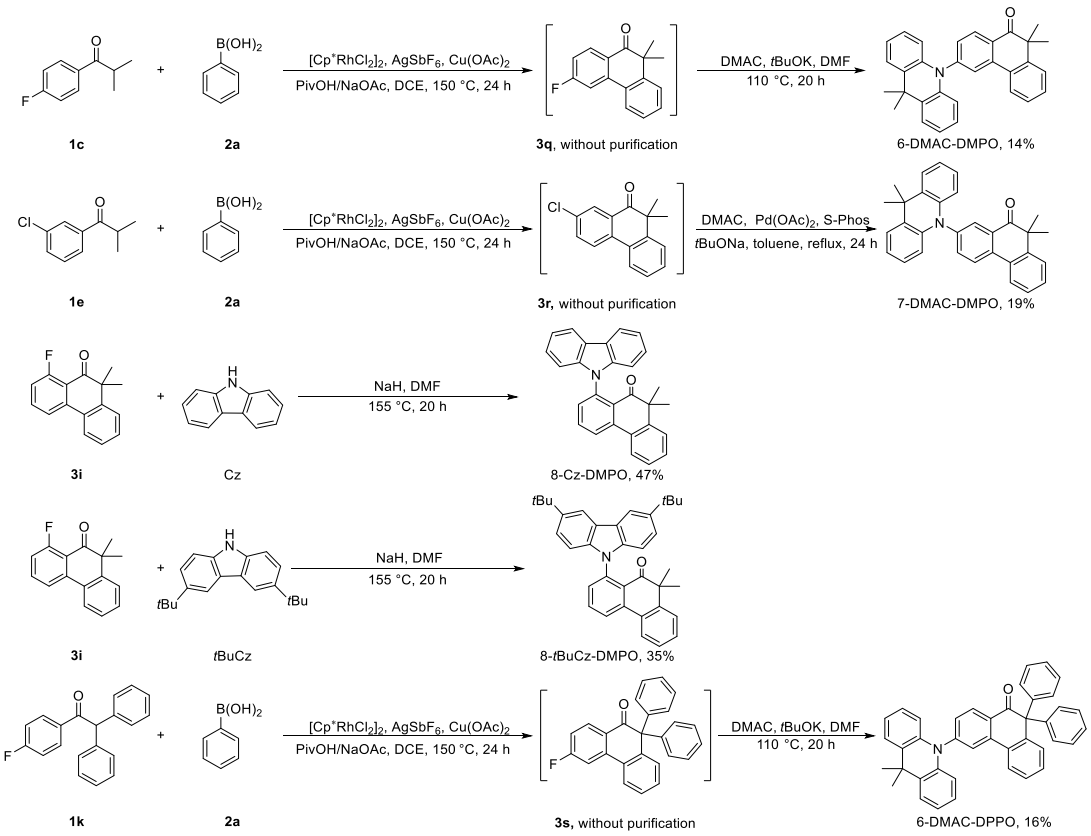
Synthesis of 3-(9,9-dimethylacridin-10(9*H*)-yl)-10,10-dimethylphenanthren-9(10*H*)-one (3-DMAC-DMPO). A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), S-Phos(30.8 mg, 0.075 mmol), *t*BuONa (96.1 mg, 1.0 mmol), toluene (3.0 mL), **3g** (190.0 mg, 0.5 mmol) and DMAC (104.7 mg, 0.5 mmol) was refluxed under N_2 for 30 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow powder (154.6 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.63 (td, *J* = 8.3, 7.9, 1.4 Hz, 1H), 7.51-7.42 (m, 3H), 7.35 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.02-6.90 (m, 4H), 6.34 (dd, *J* = 8.0, 1.4 Hz, 2H), 1.74 (s, 6H), 1.67 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7, 144.2, 140.9, 140.4, 136.4, 134.5, 132.3, 132.0, 130.2, 129.2, 129.0, 128.9, 128.2, 127.0, 126.6, 125.6, 123.3, 120.9, 114.2, 47.6, 36.2, 29.9, 27.6 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{27}NO$ $[M+H]^+$ 5430.2165, found 430.2166.

Synthesis of 2-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-10,10-dimethylphenanthren-9(10*H*)-one (2-*t*BuCz-DMPO). A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), $(t\text{Bu})_3\text{P}\cdot\text{HBF}_4$ (21.8 mg, 0.075 mmol), *t*BuONa (96.1 mg, 1.0 mmol), toluene (3.0 mL), **3f** (128.0 mg, 0.5 mmol) and 3,6-di-*tert*-butyl-9*H*-carbazole (*t*BuCz, 139.7 mg, 0.5 mmol) was refluxed under N_2 for 30 h. After being cooled to room temperature, the

reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow solid (187.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.13 (m, 4H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.76-7.70 (m, 2H), 7.59 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.53-7.46 (m, 3H), 7.43 (d, *J* = 8.7 Hz, 2H), 1.61 (s, 6H), 1.49 (s, 18H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 146.1, 143.4, 139.1, 136.7, 134.6, 128.9, 128.5, 128.2, 127.8, 125.6, 125.1, 124.5, 124.0, 123.8, 123.1, 116.5, 109.3, 47.7, 34.9, 32.2, 27.6 ppm. HRMS (ESI$^+$): calcd for $C_{36}H_{37}NO$ $[M+Na]^+$ 522.2767, found 522.2766.

Synthesis of 2-(9,9-dimethylacridin-10(9*H*)-yl)-10,10-diphenylphenanthren-9(10*H*)-one (2-DMAC-DPPO). A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), S-Phos (30.8 mg, 0.075 mmol), *t*BuONa (96.1 mg, 1.0 mmol), toluene (3.0 mL), **3n** (190.0 mg, 0.5 mmol) and DMAC (104.7 mg, 0.5 mmol) was refluxed under N_2 for 30 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a white solid (201.9 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.64 (td, *J* = 7.7, 1.4 Hz, 1H), 7.40 (ddd, *J* = 12.9, 7.6, 1.9 Hz, 4H), 7.26-7.17 (m, 6H), 7.08-7.01 (m, 4H), 6.99-6.89 (m, 4H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 2H), 1.63 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 144.2, 141.5, 141.5, 140.8, 136.1, 135.3, 134.5, 131.3, 130.5, 130.5, 130.4, 130.2, 129.0, 128.4, 128.4, 127.7, 127.1, 126.5, 125.3, 123.3, 120.9, 114.1, 68.4, 36.1, 31.1 ppm. HRMS (ESI$^+$): calcd for $C_{41}H_{31}NO$ $[M+Na]^+$ 576.2298, found 576.2297.

2) Synthesis of 6-DMAC-DMPO, 7-DMAC-DMPO, 8-Cz-DMPO, 8-*t*BuCz-DMPO and 6-DMAC-DPPO



Synthesis of 6-(9,9-dimethylacridin-10(9*H*)-yl)-10,10-dimethylphenanthren-9(10*H*)-one (6-DMAC-DMPO). A mixture of 1-(4-fluorophenyl)-2-methylpropan-1-one **1c** (64.3 μL, 0.40 mmol), phenylboronic acid **2a** (146.3 mg, 3.0 equiv), $[Cp^*RhCl_2]_2$ (12.4 mg, 5 mol%), $AgSbF_6$ (27.4 mg, 20 mol%), $Cu(OAc)_2$ (145.5 mg, 2.0 equiv), PivOH (49.0 mg, 1.2 equiv), NaOAc (6.6 mg, 0.2 equiv) and DCE (2.0 mL) was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere, and then cooled to room temperature, diluted with 5.0 mL of CH_2Cl_2, filtered through a celite pad, and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were evaporated under reduced pressure for use in the next step. It is worth noting that the pure product **3q** was isolated difficultly, and thus the reaction-treated mixture was directly used for the next reaction step.

DMAC (62.8 mg, 0.3 mmol), *t*BuOK (67.4 mg, 0.6 mmol) and DMF (2.5 mL) were combined and the mixture was allowed to stir at room temperature under N_2 atmosphere

for 30 min. The mixture containing **3q** was dissolved in DMF (2.5 mL) and added to the above stirred solution. The mixture was allowed to heat in a preheated oil bath at 110 °C for 20 h under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was extracted with EtOAc and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (200-300 mesh, petroleum ether/EtOAc = 100:1 to 80:1, v/v) to give a yellow solid (24.0 mg, 14% yield, two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.1 Hz, 1H), 8.01 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.99 (p, *J* = 7.2 Hz, 4H), 6.37 (d, *J* = 8.0 Hz, 2H), 1.73 (s, 6H), 1.64 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 147.2, 144.4, 140.5, 140.2, 131.1, 130.8, 130.6, 129.9, 128.4, 128.3, 127.3, 126.8, 126.7, 125.6, 124.3, 121.3, 114.4, 47.6, 36.2, 31.5, 27.7 ppm. HRMS (ESI^+): calcd for $C_{31}H_{27}NO$ $[M+Na]^+$ 452.1985, found 452.1985.

Synthesis of 7-(10,10-dimethyl-9,10-dihydroanthracen-9-yl)-10,10-dimethylphenanthren-9(10*H*)-one (7-DMAC-DMPO). A mixture of 1-(3-chlorophenyl)-2-methylpropan-1-one **1e** (73.1 mg, 0.40 mmol), phenylboronic acid **2a** (146.3 mg, 3.0 equiv), $[Cp^*RhCl_2]_2$ (12.4 mg, 5 mol%), $AgSbF_6$ (27.4 mg, 20 mol%), $Cu(OAc)_2$ (145.5 mg, 2.0 equiv), PivOH (49.0 mg, 1.2 equiv), NaOAc (6.6 mg, 0.2 equiv) and DCE (2.0 mL) was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere, and then cooled to room temperature, diluted with 5.0 mL of CH_2Cl_2, filtered through a celite pad, and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were evaporated under reduced pressure. Similarly, the pure product **3r** was isolated difficultly, and thus the reaction-treated mixture was directly used for the next reaction step.

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol), S-Phos (24.6 mg, 0.06 mmol), *t*BuONa (76.9 mg, 0.8 mmol), toluene (3.0 mL) and DMAC (62.8 mg, 0.3 mmol) were added to the mixture after the first step of treatment, followed by reflux under N_2 for 24 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the

solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow powder (32.5 mg, 19% yield, two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 2.2 Hz, 1H), 8.11-8.04 (m, 1H), 7.66 (dd, J = 8.4, 2.3 Hz, 1H), 7.62-7.55 (m, 1H), 7.49 (dd, J = 7.3, 1.8 Hz, 2H), 7.47-7.40 (m, 2H), 6.97 (pd, J = 7.2, 1.7 Hz, 4H), 6.34 (dd, J = 7.8, 1.5 Hz, 2H), 1.72 (s, 6H), 1.62 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 144.5, 141.4, 140.8, 137.5, 137.1, 131.4, 130.9, 130.6, 129.8, 128.6, 127.4, 126.7, 126.6, 125.9, 125.4, 124.4, 121.1, 114.2, 47.6, 36.2, 31.2, 27.6 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{27}NO$ $[M+Na]^+$ 452.1985, found 452.1983.

Synthesis of 8-(9*H*-carbazol-9-yl)-10,10-dimethylphenanthren-9(10*H*)-one (8-Cz-DMPO). 9*H*-carbazole (Cz, 83.6 mg, 0.5 mmol), NaH (18.0 mg, 0.75 mmol) and DMF (2.5 mL) were combined and the mixture was allowed to stir at room temperature under N_2 atmosphere for 30 min. **3i** (120 mg, 0.5 mmol) dissolved in DMF (2.5 mL) was added to the stirred mixture and then heated in a preheated oil bath at 155 ℃ for 20 h under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was extracted with EtOAc and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/EtOAc = 40:1 to 20:1, v/v) to give a yellow solid (91.3 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 7.4 Hz, 3H), 8.01 (d, J = 7.6 Hz, 1H), 7.83 (t, J = 7.9 Hz, 1H), 7.48-7.38 (m, 4H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.03 (d, J = 8.1 Hz, 2H), 1.38 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6, 143.7, 142.2, 139.8, 136.8, 134.1, 131.1, 129.9, 129.8, 129.0, 127.5, 125.8, 125.7, 124.9, 124.3, 123.4, 120.6, 119.6, 109.6, 49.0, 25.5 ppm. HRMS (ESI$^+$): calcd for $C_{28}H_{21}NO$ $[M+Na]^+$ 410.1515, found 410.1515.

Synthesis of 8-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-10,10-dimethylphenanthren-9(10*H*)-one (8-*t*BuCz-DMPO). *t*BuCz (139.6 mg, 0.5 mmol), NaH (18.0 mg, 0.75 mmol) and DMF (2.5 mL) were combined and the mixture was allowed to stir at room temperature under N_2 atmosphere for 30 min. **3i** (120.0 mg, 0.5 mmol) dissolved in DMF (2.5 mL) was added to the stirred mixture and then heated in a preheated oil bath

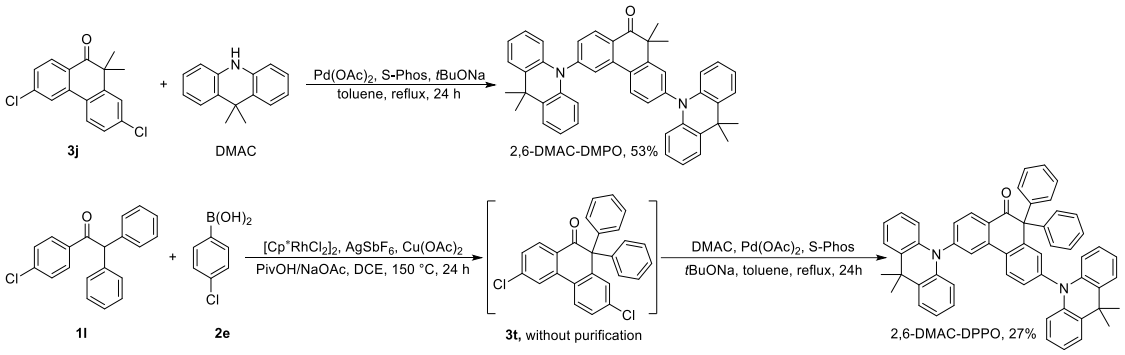
at 155 °C for 20 h under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was extracted with EtOAc and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/EtOAc = 40:1 to 20:1, v/v) to give a yellow solid (87.4 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 2H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 7.48-7.35 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 2H), 1.47 (s, 18H), 1.41 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 143.7, 142.2, 140.7, 139.7, 137.3, 134.0, 131.1, 129.9, 129.8, 129.0, 127.5, 125.7, 124.9, 124.0, 123.5, 123.3, 116.6, 109.0, 49.0, 34.8, 32.2, 25.6 ppm. HRMS (ESI$^+$): calcd for $C_{36}H_{37}NO$ $[M+Na]^+$ 522.2767, found 522.2767.

Synthesis of 6-(9,9-dimethylacridin-10(9*H*)-yl)-10,10-diphenylphenanthren-9(10*H*)-one (6-DMAC-DPPO). A mixture of 1-(4-fluorophenyl)-2,2-diphenylethan-1-one **1k** (116.0 mg, 0.40 mmol), phenylboronic acid **2a** (146.3 mg, 3.0 equiv), $[Cp^*RhCl_2]_2$ (12.4 mg, 5 mol%), $AgSbF_6$ (27.4 mg, 20 mol%), $Cu(OAc)_2$ (145.5 mg, 2.0 equiv), PivOH (49.0 mg, 1.2 equiv), NaOAc (6.6 mg, 0.2 equiv) and DCE (2.0 mL) was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere, then cooled to room temperature, diluted with 5.0 mL of CH_2Cl_2, filtered through a celite pad, and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were evaporated under reduced pressure. Similarly, the pure product **3s** was isolated difficultly, and thus the reaction-treated mixture was directly used for the next reaction step.

DMAC (62.8 mg, 0.3 mmol), *t*BuOK (67.4 mg, 0.6 mmol) and DMF (2.5 mL) were combined and the mixture was allowed to stir at room temperature under N_2 atmosphere for 30 min. The mixture containing **3s** was dissolved in DMF (2.5 mL) and added to the above stirred solution, the mixture was allowed to heat in a preheated oil bath at 110 °C for 20 h under N_2 atmosphere. After being cooled to room temperature, the reaction mixture was extracted with EtOAc and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (200-300 mesh, petroleum ether/EtOAc = 100:1 to 80:1,

v/v) to give a yellow solid (35.4 mg, 16% yield, two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 6.0 Hz, 2H), 7.56-7.50 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39-7.28 (m, 8H), 7.10 (s, 4H), 7.04-6.98 (m, 4H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.38-6.32 (m, 2H), 1.76 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 147.0, 141.8, 141.5, 140.4, 139.7, 132.4, 131.1, 130.8, 130.7, 130.5, 130.4, 129.5, 129.3, 128.3, 128.1, 127.6, 126.6, 125.5, 125.3, 124.5, 121.3, 114.5, 68.4, 36.2, 31.3 ppm. HRMS (ESI$^+$): calcd for $C_{41}H_{31}NO$ $[M+Na]^+$ 576.2298, found 576.2298.

3) Synthesis of 2,6-DMAC-DMPO and 2,6-DMAC-DPPO



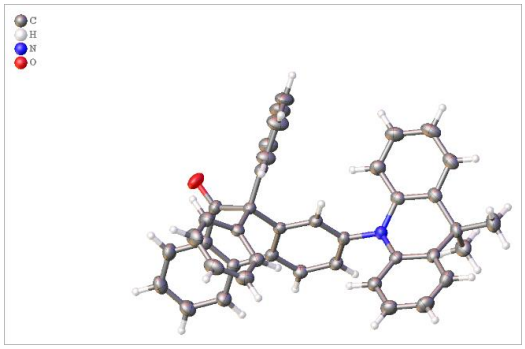
Synthesis of 2,6-bis(9,9-dimethylacridin-10(9*H*)-yl)-10,10-dimethylphenanthren-9(10*H*)-one (2,6-DMAC-DMPO). A mixture of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), S-Phos(61.6 mg, 0.15 mmol), *t*BuONa (192.2 mg, 2.0 mmol), toluene (6.0 mL), **3j** (145.0 mg, 0.5 mmol), and DMAC (209.3mg, 1.0 mmol) was refluxed under N_2 for 24 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow solid (168.6 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.08 (s, 1H), 7.56-7.46 (m, 6H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.06-6.93 (m, 8H), 6.43 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.32 (dd, *J* = 7.6, 1.8 Hz, 2H), 1.74 (d, *J* = 8.3 Hz, 12H), 1.66 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 147.6, 142.7, 140.8, 140.5, 139.4, 131.3, 131.2, 130.9, 130.3, 130.2, 129.7, 128.5, 128.3, 127.0, 126.7, 126.6, 125.8, 125.7, 125.7, 121.4, 121.0, 114.5, 114.0, 47.9, 36.2, 31.6, 27.7 ppm. HRMS (ESI$^+$): calcd for $C_{46}H_{40}N_2O$ $[M+Na]^+$ 659.3033, found 659.3034.

Synthesis of 2,6-bis(9,9-dimethylacridin-10(9*H*)-yl)-10,10-diphenylphenanthren-9(10*H*)-one (2,6-DMAC-DPPO). A mixture of 1-(4-chlorophenyl)-2,2-diphenylethan-1-one **1l** (122.4 mg, 0.4 mmol), (4-chlorophenyl)boronic acid **2e** (187.2 mg, 1.2 mmol), $[Cp^*RhCl_2]_2$ (12.4 mg, 5 mol%), $AgSbF_6$ (27.4 mg, 20 mol%), $Cu(OAc)_2$ (145.5 mg, 2.0 equiv), PivOH (49.0 mg, 1.2 equiv), NaOAc (6.6 mg, 0.2 equiv) and DCE (2.0 mL). The reaction mixture was allowed to heat in a preheated oil bath at 150 °C for 24 h under N_2 atmosphere, then cooled to room temperature, diluted with 5.0 mL of CH_2Cl_2, filtered through a celite pad, and washed with 20.0-30.0 mL of CH_2Cl_2. The combined organic extracts were evaporated under reduced pressure. Similarly, the pure product **3t** was isolated difficultly, and thus the reaction-treated mixture was directly used for the next reaction step.

$Pd(OAc)_2$ (9.0 mg, 0.04 mmol), S-Phos(49.2 mg, 0.12 mmol), *t*BuONa (153.8 mg, 0.16 mmol), toluene (6.0 mL) and DMAC (125.6 mg, 0.6 mmol) were added to the mixture after the first step of treatment, followed by reflux under N_2 for 24 h. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (100-200 mesh, petroleum ether/dichloromethane = 6:1 to 2:1, v/v) to give a yellow powder (82.0 mg, 27% yield, two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 7.98 (s, 1H), 7.50 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 6.3 Hz, 3H), 7.35 (d, J = 8.3 Hz, 1H), 7.28 (t, J = 7.9 Hz, 7H), 7.12 (d, J = 7.3 Hz, 4H), 7.03-6.88 (m, 9H), 6.34 (d, J = 7.4 Hz, 2H), 6.27 (d, J = 7.8 Hz, 2H), 1.72 (s, 6H), 1.62 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 147.4, 144.5, 142.0, 141.4, 140.6, 140.4, 139.0, 135.5, 131.4, 131.1, 131.0, 130.6, 130.4, 130.3, 130.2, 129.4, 128.5, 127.8, 127.3, 126.7, 126.5, 125.6, 125.5, 125.3, 121.4, 121.0, 114.6, 114.1, 68.4, 36.3, 36.1, 31.3, 31.1 ppm. HRMS (ESI^+): calcd for $C_{56}H_{44}N_2O$ $[M+H]^+$ 761.3527, found 761.3525.

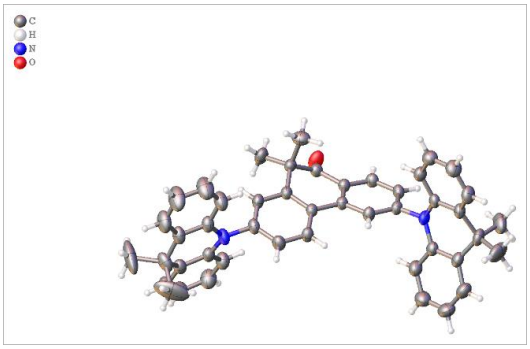
VIII. Crystal data

Table S5. Crystal Data for 2-DMAC-DPPO (CCDC: 2241220)



Identification code	mo_zyx_2_dpac_220k_0m_a
Empirical formula	C41H31NO
Formula weight	553.67
Temperature/K	220.0
Crystal system	triclinic
Space group	P-1
a/Å	8.8902(14)
b/Å	12.895(2)
c/Å	14.568(2)
α/°	67.108(5)
β/°	72.348(6)
γ/°	76.144(6)
Volume/Å3	1451.9(4)
Z	2
ρcalcg/cm3	1.266
μ/mm⁻1	0.075
F(000)	584.0
Crystal size/mm3	0.37 × 0.22 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.856 to 55.03
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	25806
Independent reflections	6579 [Rint = 0.0929, Rsigma = 0.0768]
Data/restraints/parameters	6579/0/390
Goodness-of-fit on F2	1.019
Final R indexes [I>=2σ (I)]	R1 = 0.0516, wR2 = 0.1125
Final R indexes [all data]	R1 = 0.0917, wR2 = 0.1307
Largest diff. peak/hole / e Å-3	0.19/-0.23

Table S6. Crystal Data for 2,6-DMAC-DMPO (CCDC: 2241219)



Identification code	mo_zyx_0530_0m_a
Empirical formula	$C_{46}H_{40}N_2O$
Formula weight	636.80
Temperature/K	302.0
Crystal system	triclinic
Space group	P-1
a/Å	9.4218(5)
b/Å	12.9960(6)
c/Å	14.5646(8)
α/°	90.383(2)
β/°	100.408(2)
γ/°	98.456(2)
Volume/Å^3	1733.95(16)
Z	2
ρ_{calc}g/cm^3	1.220
μ/mm^{-1}	0.072
F(000)	676.0
Crystal size/mm^3	0.25 × 0.18 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.186 to 55.018
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	41314
Independent reflections	7950 [R_{int} = 0.0915, R_{sigma} = 0.0577]
Data/restraints/parameters	7950/0/448
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0522, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0988, wR_2 = 0.1414
Largest diff. peak/hole / e Å^{-3}	0.19/-0.19

IX. Additional spectra and data

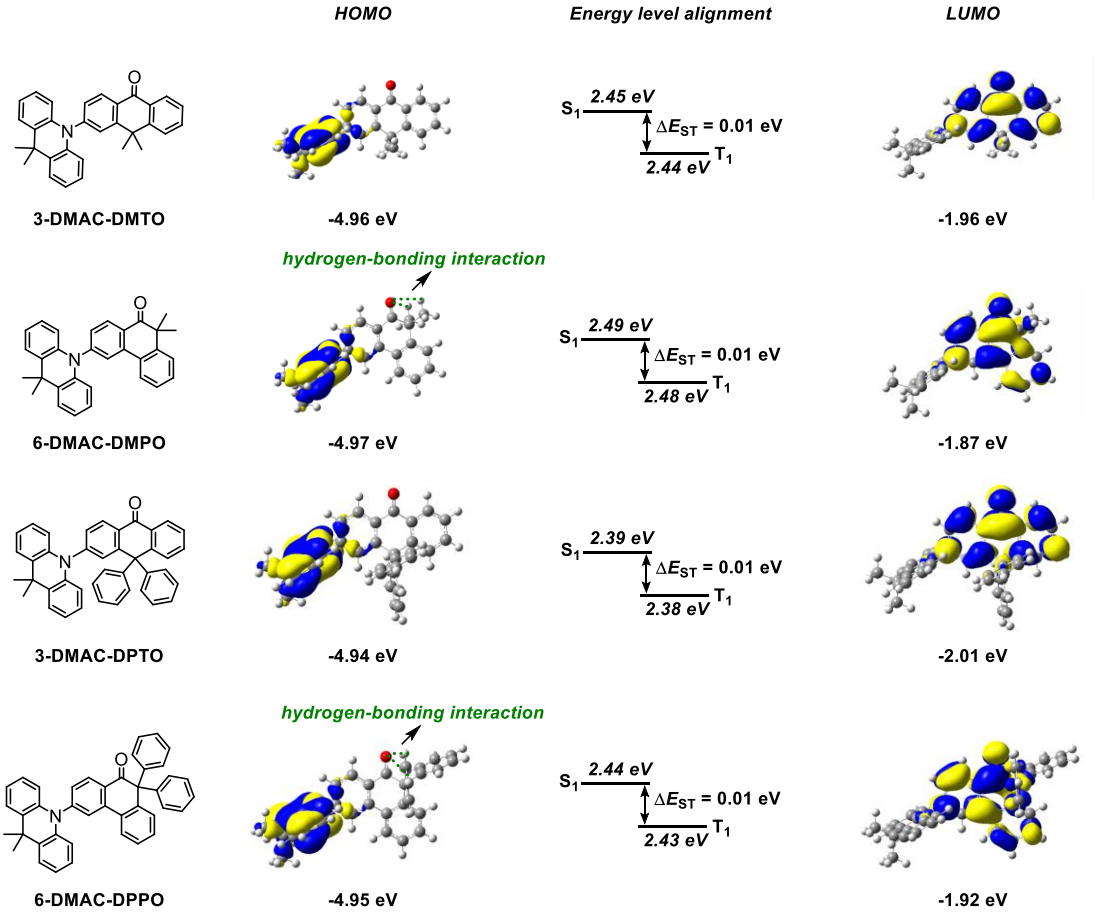


Fig. S1 Molecular structures, frontier molecular orbital distributions, calculated energy levels and hydrogen-bonding interactions of γ-locked diaryl carbonyl-based and α-locked alkyl aryl carbonyl-based TADF molecules.

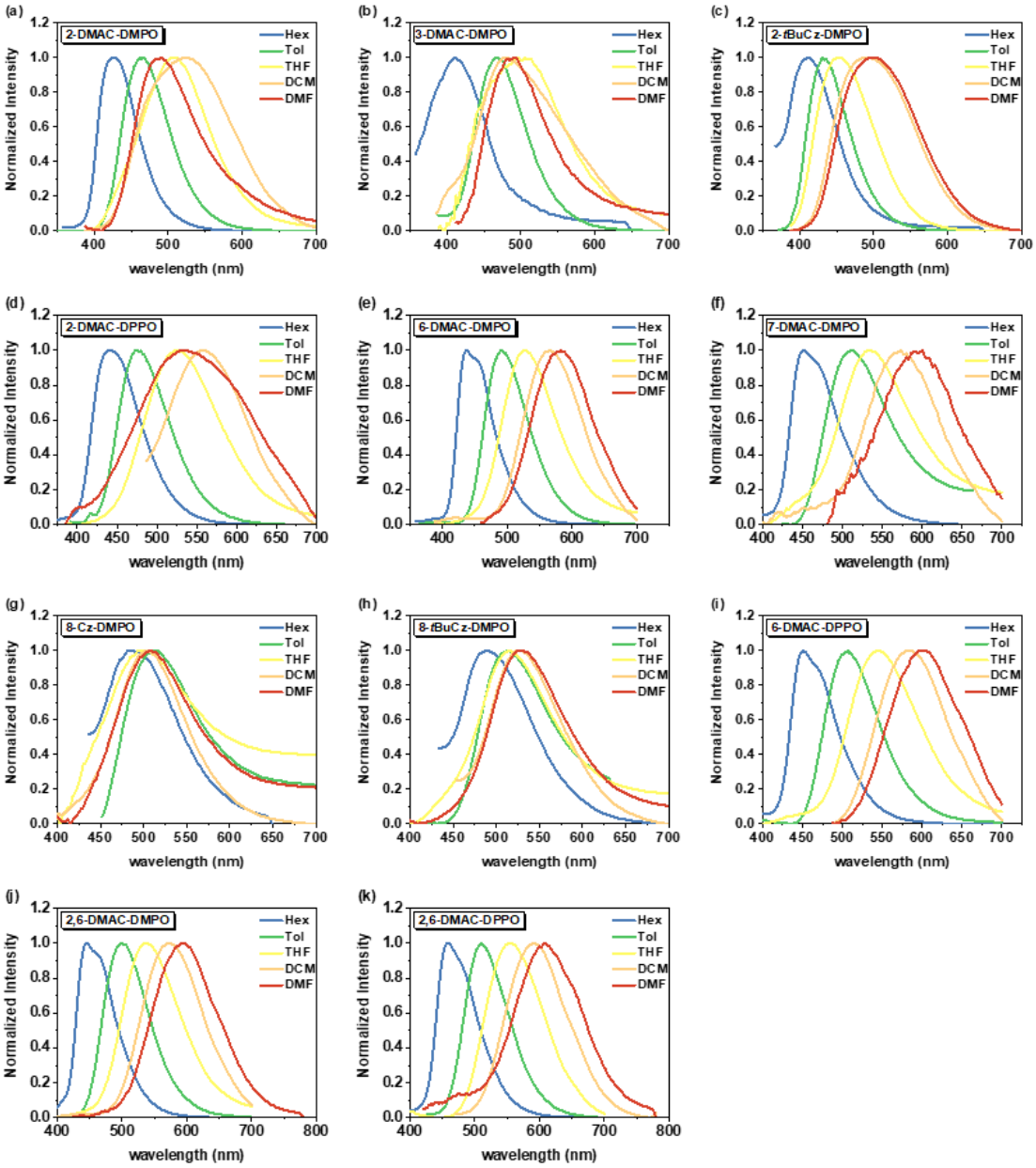
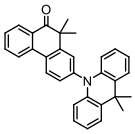
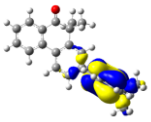
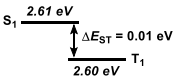
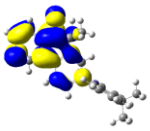
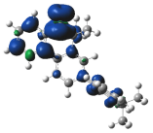
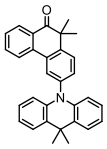
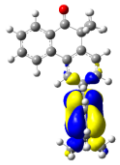
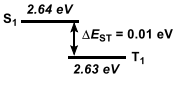
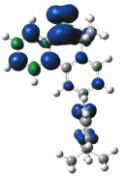
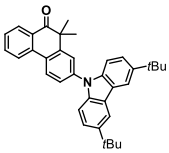
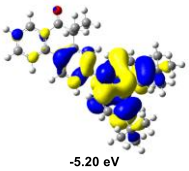
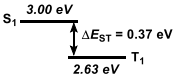
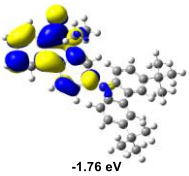
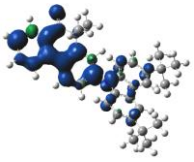
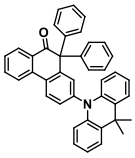
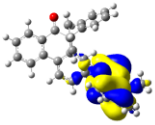
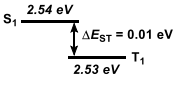
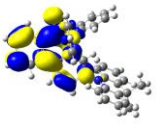
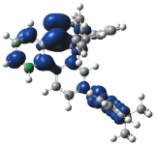
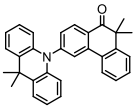
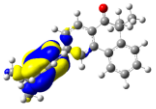
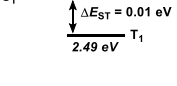
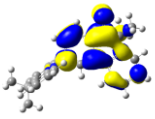
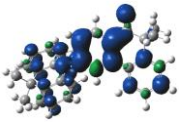
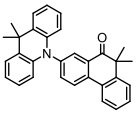
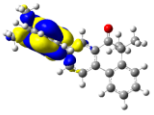
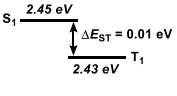
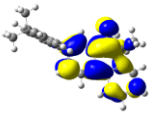
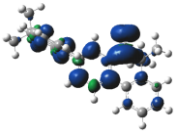
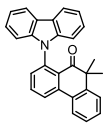
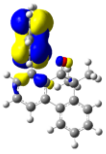
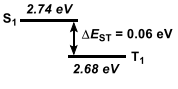
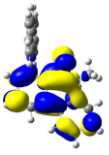
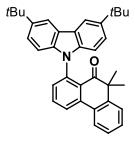
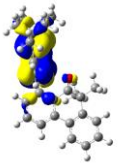
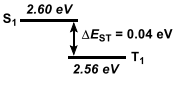
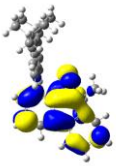
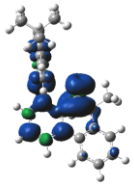


Fig. S2 Photoluminescence spectra in different solvents of the designed TADF molecules. Hex represents *n*-hexane and Tol represents toluene.

	HOMO	Energy level alignment	LUMO	SDD
 2-DMAC-DMPO	 -4.92 eV		 -1.82 eV	
 3-DMAC-DMPO	 -4.94 eV		 -1.84 eV	
 2-*t*BuCz-DMPO	 -5.20 eV		 -1.76 eV	
 2-DMAC-DPPO	 -4.89 eV		 -1.87 eV	
 6-DMAC-DMPO	 -4.97 eV		 -1.87 eV	
 7-DMAC-DMPO	 -4.90 eV		 -1.86 eV	
 8-Cz-DMPO	 -5.23 eV		 -1.79 eV	
 8-*t*BuCz-DMPO	 -5.04 eV		 -1.76 eV	
6-DMAC-DPPO	-4.95 eV		-1.92 eV	

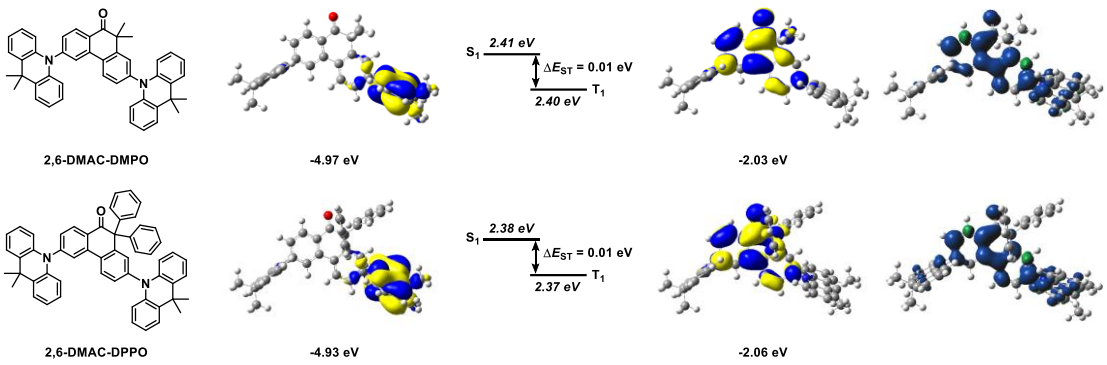


Fig. S3 Molecular structures, frontier molecular orbital distributions, calculated energy levels and spin density distribution (SDD) of T_1 states of the designed TADF molecules.

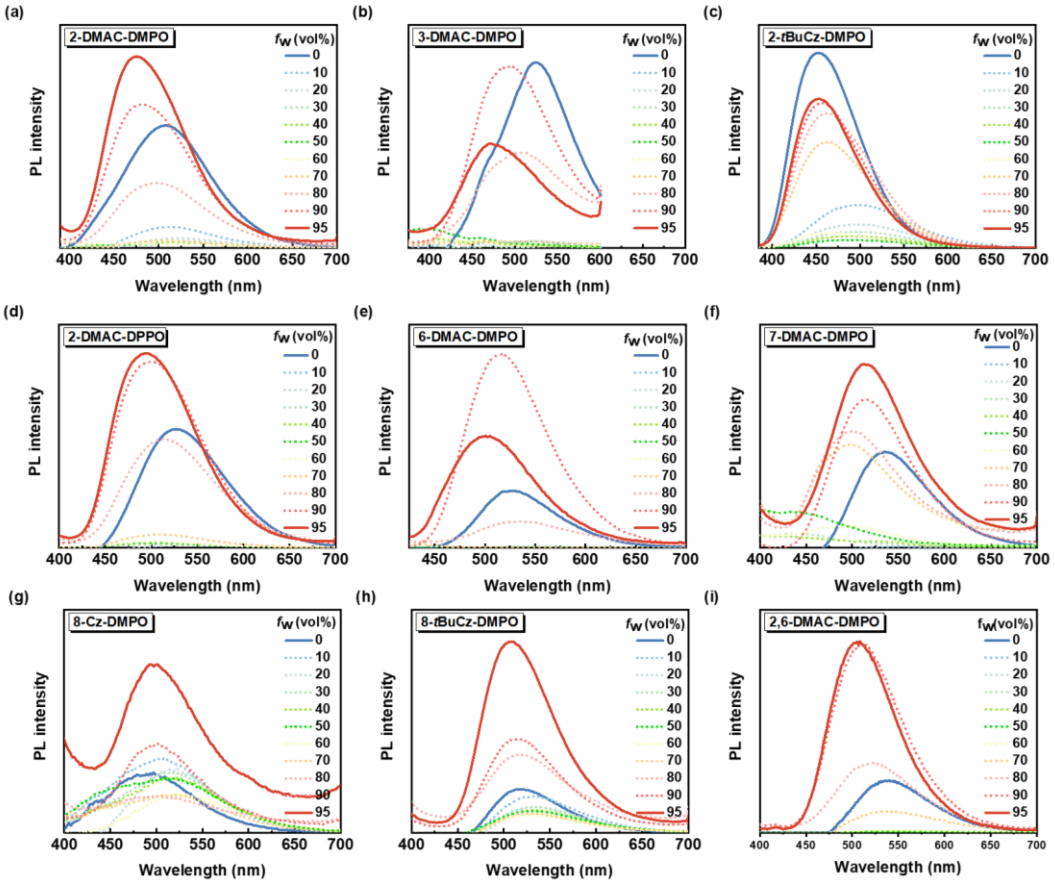


Fig. S4 Fluorescence spectra in THF/ water mixtures with different water fractions (f_w) of the designed TADF molecules.

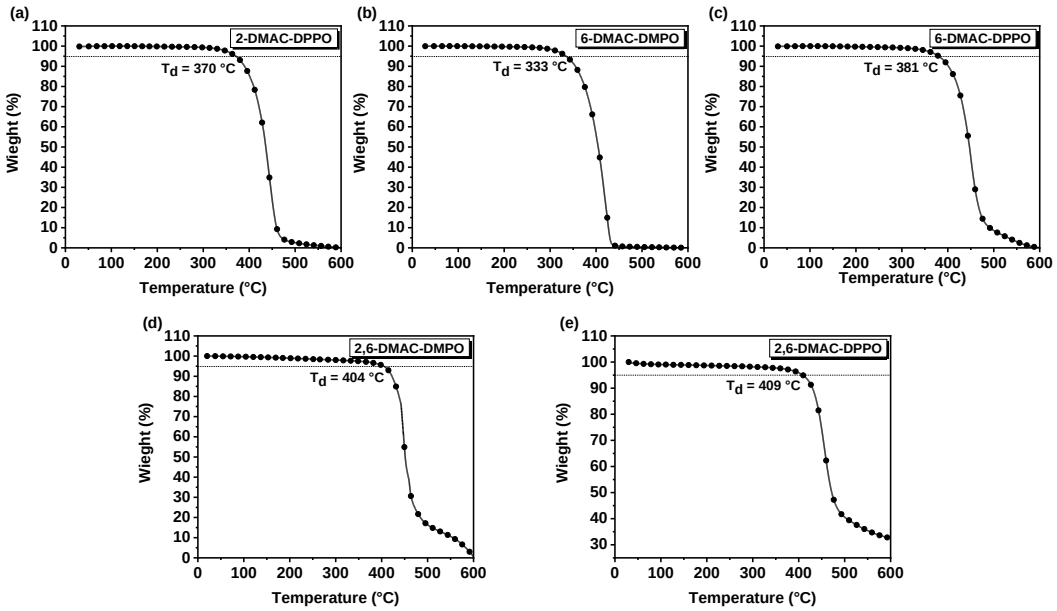


Fig. S5 TGA thermograms of (a) 2-DMAC-DPPO, (b) 6-DMAC-DMPO, (c) 6-DMAC-DPPO, (d) 2,6-DMAC-DMPO and (e) 2,6-DMAC-DPPO recorded at a heating rate of 10 ºC/min.

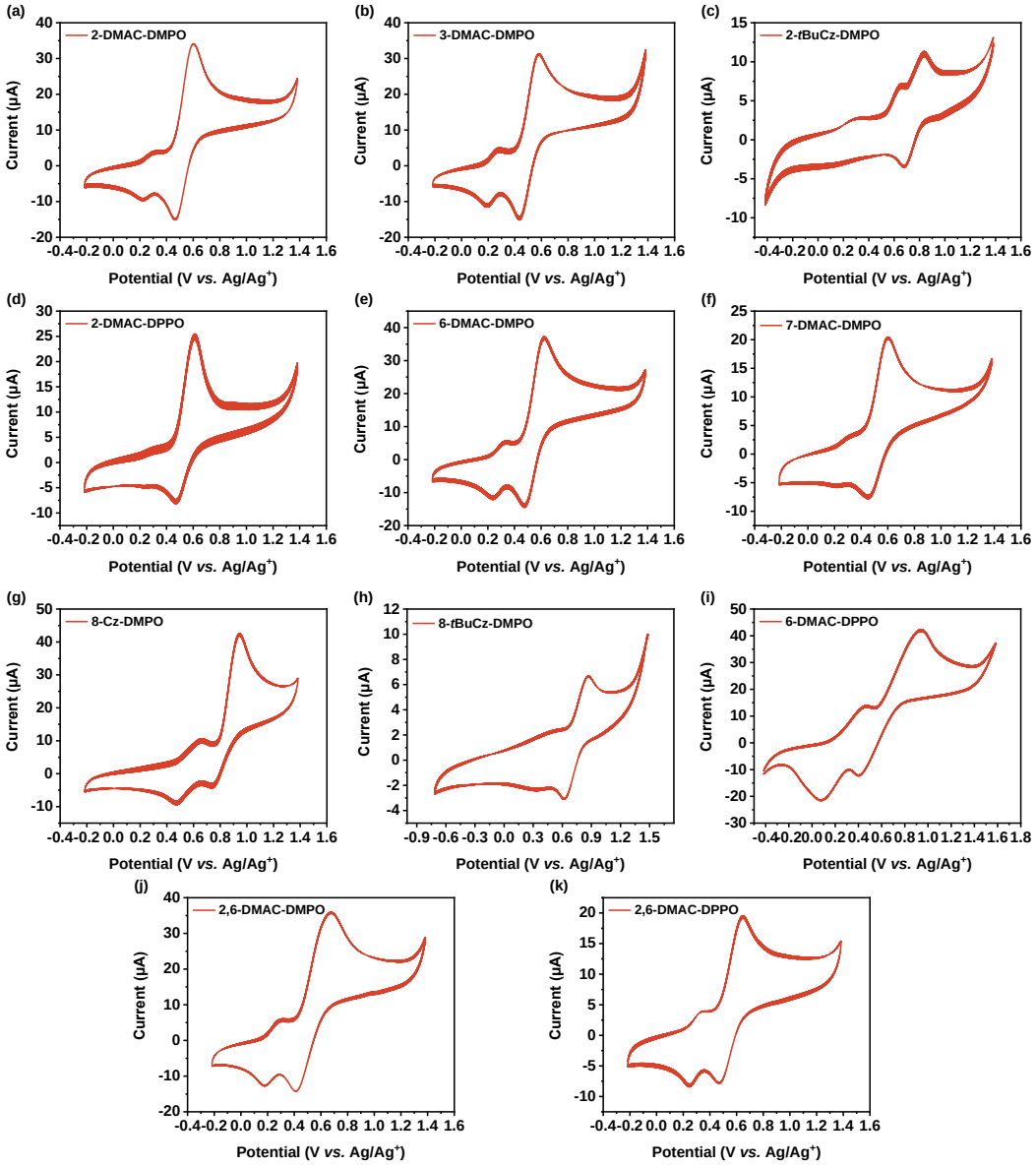


Fig. S6 cyclic voltammograms (CV) measured in dry DCM at 1.0×10^{-5} M containing 0.1 M tetrabutylammonium hexafluorophosphate of (a) 2-DMAC-DMPO, (b) 3-DMAC-DMPO, (c) 2-*t*BuCz-DMPO, (d) 2-DMAC-DPPO, (e) 6-DMAC-DMPO, (f) 7-DMAC-DMPO, (g) 8-Cz-DMPO, (h) 8-*t*BuCz-DMPO, (i) 6-DMAC-DPPO, (j) 2,6-DMAC-DMPO and (k) 2,6-DMAC-DPPO.

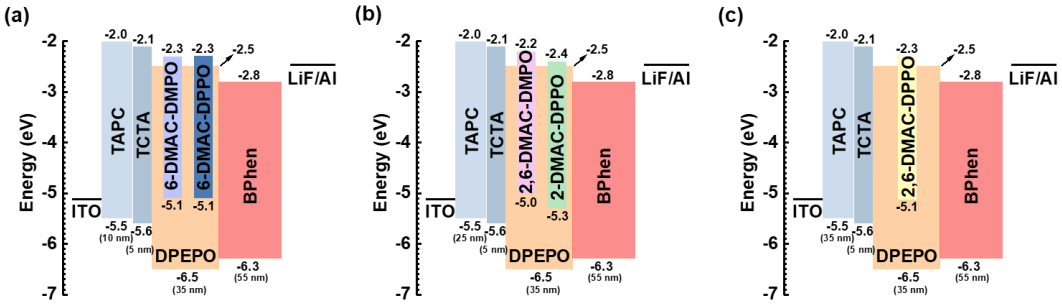


Fig. S7 (a) Optimized device structure for 6-DMAC-DMPO- or 6-DMAC-DPPO-based OLED: ITO/TAPC (10 nm)/TCTA (5 nm)/6-DMAC-DMPO or 6-DMAC-DPPO: DPEPO (40%, 35 nm)/BPhen (55 nm)/LiF (0.8 nm)/Al (100 nm). (b) Optimized device structure for 2,6-DMAC-DMPO- or 2-DMAC-DPPO-based OLED: ITO/TAPC (25 nm)/TCTA (5 nm)/2,6-DMAC-DMPO or 2-DMAC-DPPO: DPEPO (40%, 35 nm)/BPhen (55 nm)/LiF (0.8 nm)/Al (100 nm). (c) Optimized device structure for 2,6-DMAC-DPPO-based OLED: ITO/TAPC (35 nm)/TCTA (5 nm)/2,6-DMAC-DPPO: DPEPO (40%, 35 nm)/BPhen (55 nm)/LiF (0.8 nm)/Al (100 nm).

Table S5. Performance summary of efficient carbonyl-based TADF-OLED.

Emitter	Host	λ_{EL} [nm]	CE_{max} [a] [cd A^{-1}]	PE_{max} [b] [Im W^{-1}]	EQE_{max} [c] [%]	Refs.
2,6-DMAC-DMPO	DPEPO	521	99.2	107.4	31.0	This work
2,6-DMAC-DPPO	DPEPO	545	106.2	123.5	32.6	This work
QAD-2Cz	mCP	530	103.1	104.4	27.3	6
3-CCP-BP-PXZ	CBP	523	100.1	104.8	29.1	7
3,6-DPXZ-AD	CBP	552	98.0	109.9	30.6	8
DTCBPy	CBP	514	94.6	84.5	27.2	9
3,9-CCP-BP-PXZ	CBP	528	92.1	90.4	26.5	7
2,3-PICz-XT	PPF	508	89.2	100.1	32.7	10
2SPBAC-BP	PPF	532	86.8	85.2	26.4	11
TCP-BP-SFAC	DPEPO	480	74.3	68.6	38.6	12
CP-BP-SFAC	DPEPO	484	73.8	72.4	36.6	12
*m*CP-BP-SFAC	DPEPO	478	73.1	67.5	38.0	12
OPDPO	CBP	552	73.1	38.2	26.7	13
BPy3-TXDMAc	DPEPO	506	69.8	58.9	25.6	14
TRZ-*p*-ACRSA	DPEPO	-	69.4	66.1	28.0	15
4BPy-*m*DTC	mCBP	490	67.0	60.1	28.1	16
QAD-mTDPA	CBP	589	66.7	65.4	26.3	6
P-BP-SFAC	DPEPO	492	66.6	69.7	28.9	12
2BPy-*m*DTC	mCBP	490	65.4	50.7	28.0	16
SeDF-G	mCBP	-	64.0	-	30.8	17
3DPyM-*p*DTC	mCBP	464	37.6	37.3	31.9	18
TBP-DMAc	CBP	-	-	-	25.9	19

[a] Maximum current efficiency. [b] Maximum power efficiency. [c] Maximum external quantum efficiency.

X. References

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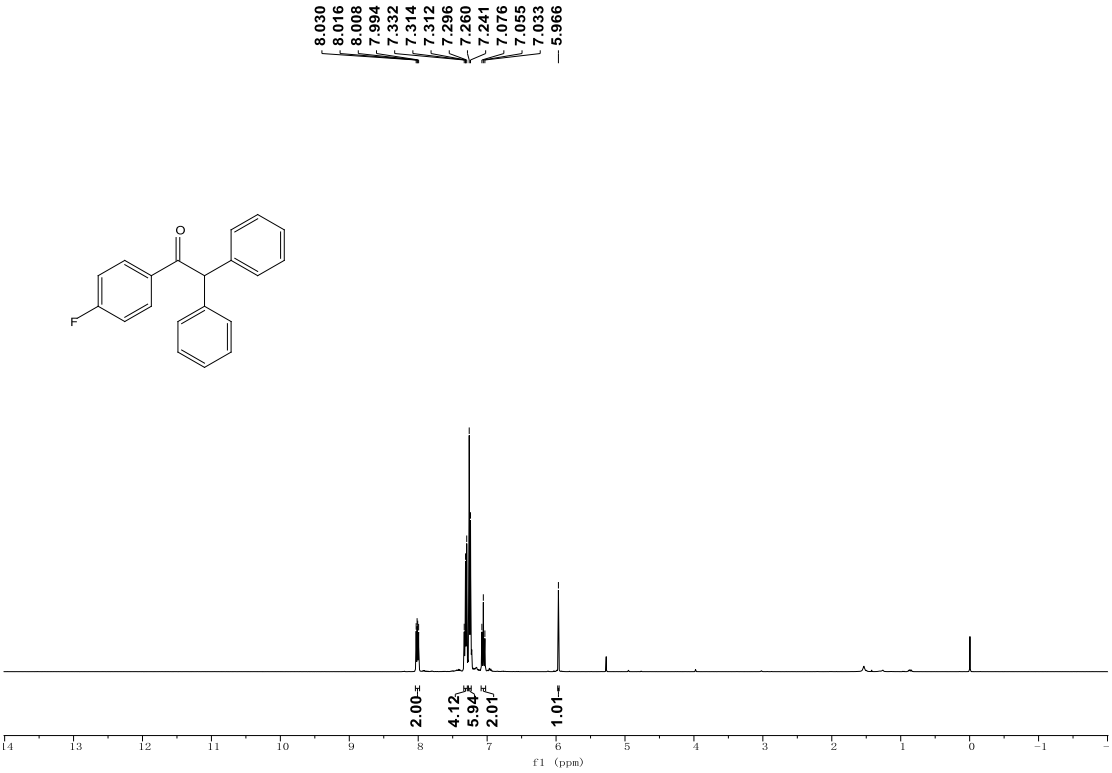
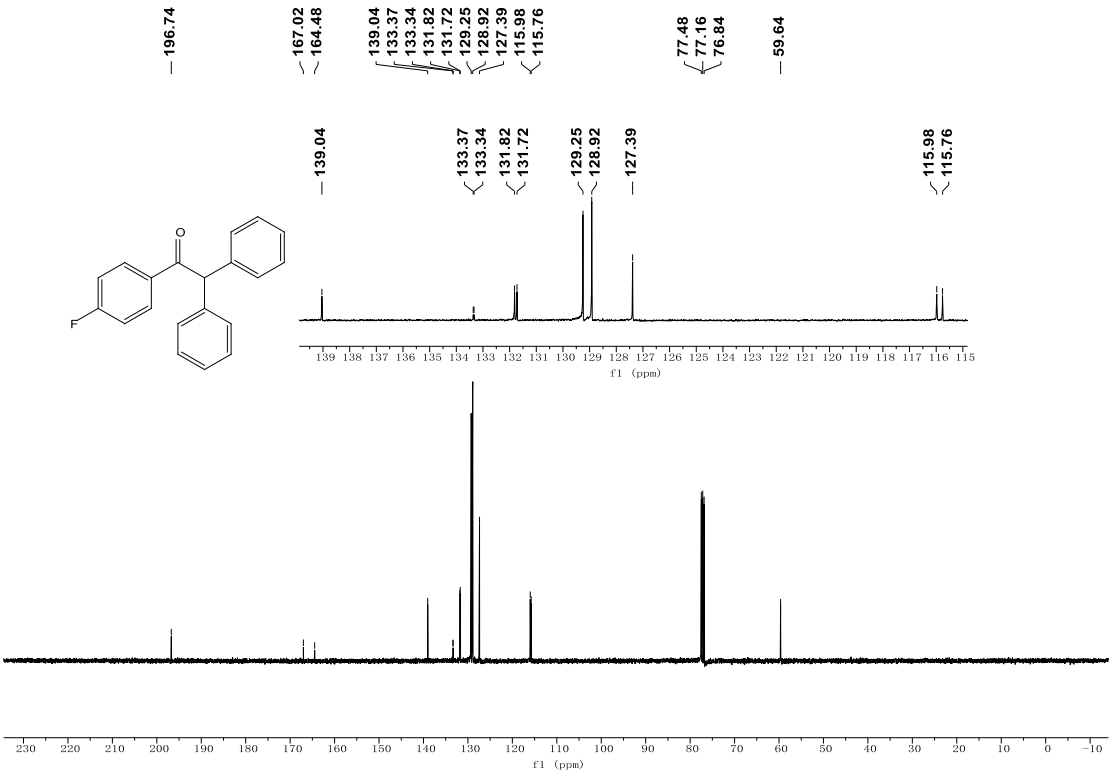
XI. Copies of NMR spectra

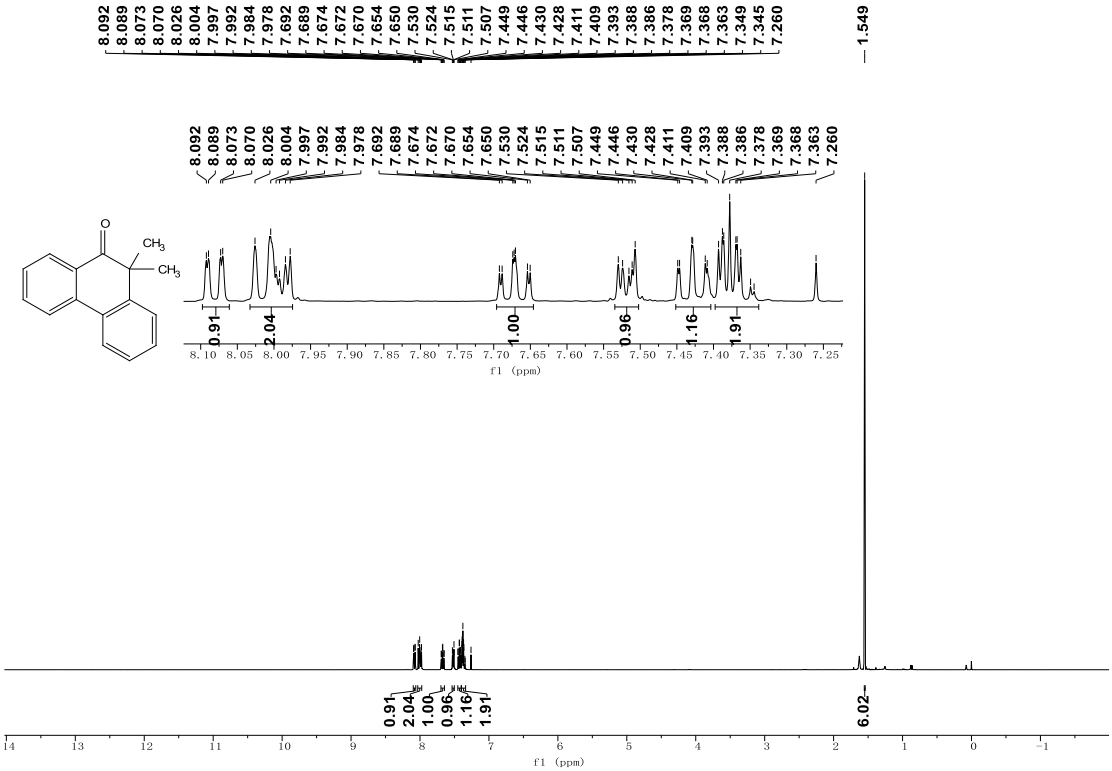
^{1}H NMR spectrum of **1k** ($CDCl_3$)



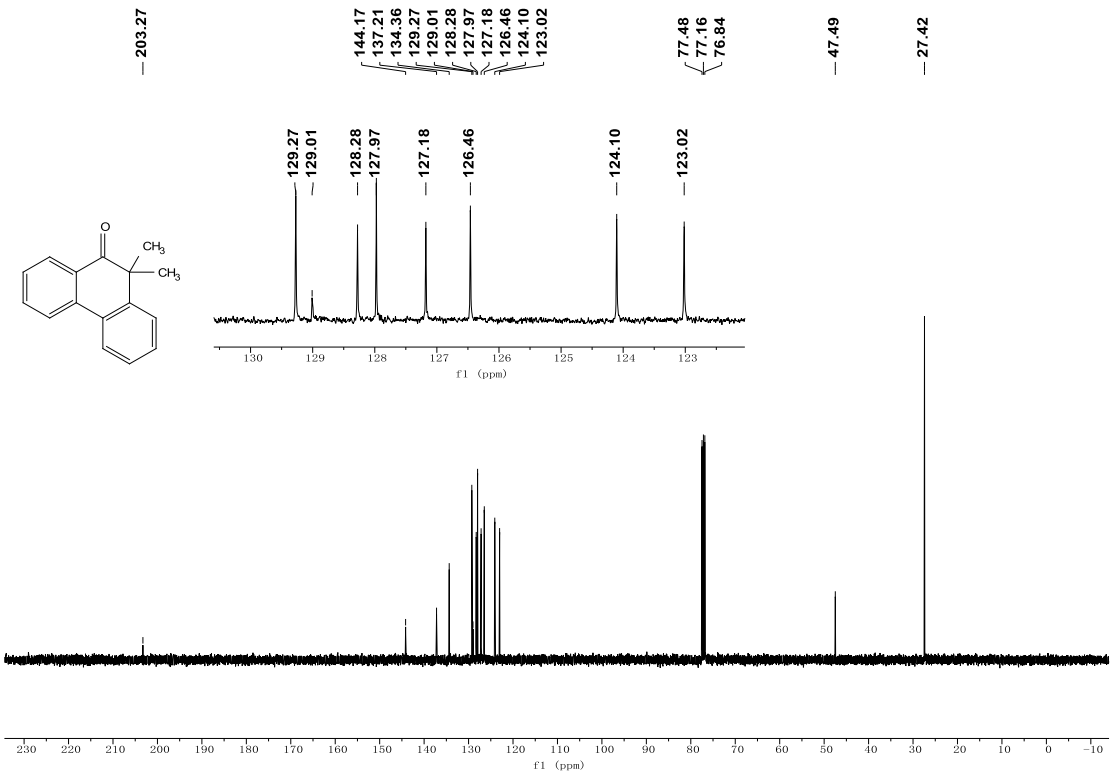
^{13}C NMR spectrum of **1k** ($CDCl_3$)



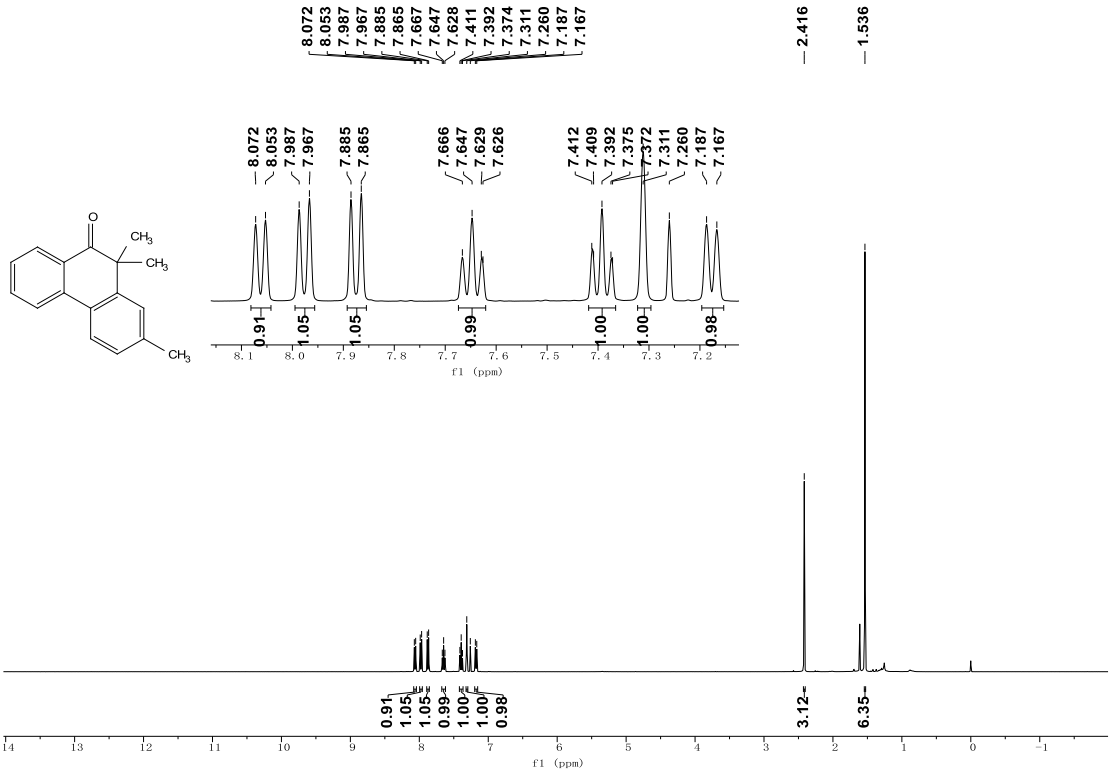
^{1}H NMR spectrum of **3a** ($CDCl_3$)



^{13}C NMR spectrum of **3a** ($CDCl_3$)



^{1}H NMR spectrum of **3b** ($CDCl_3$)



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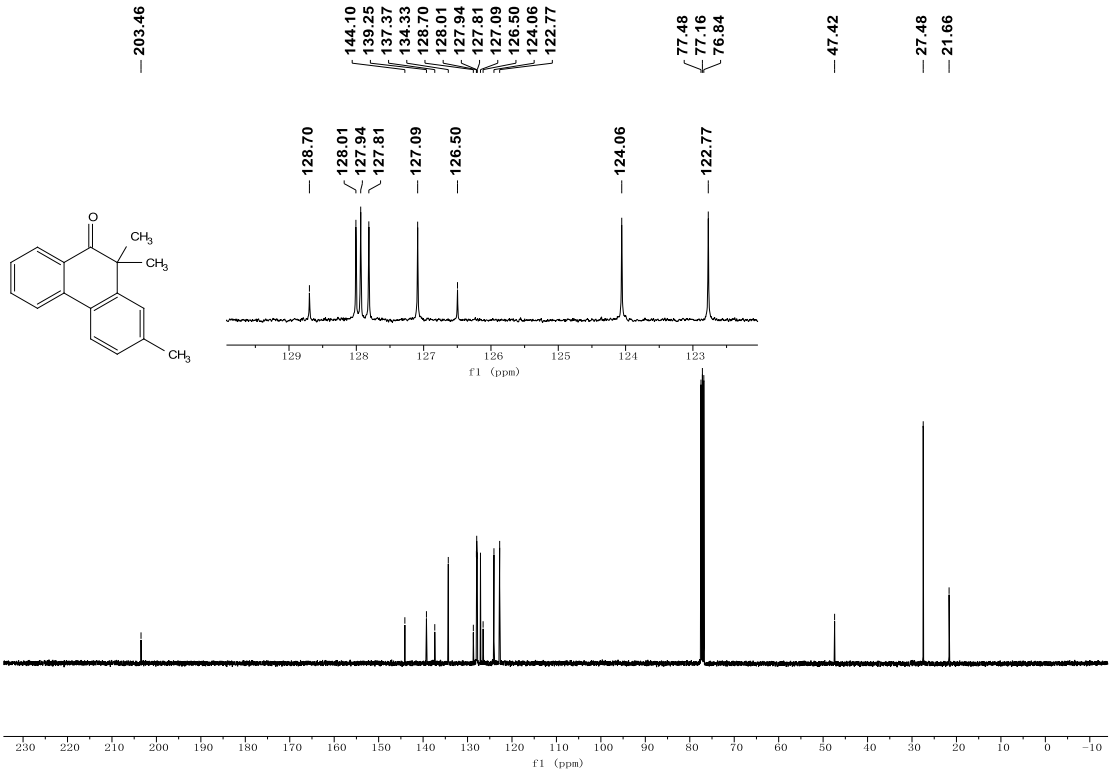

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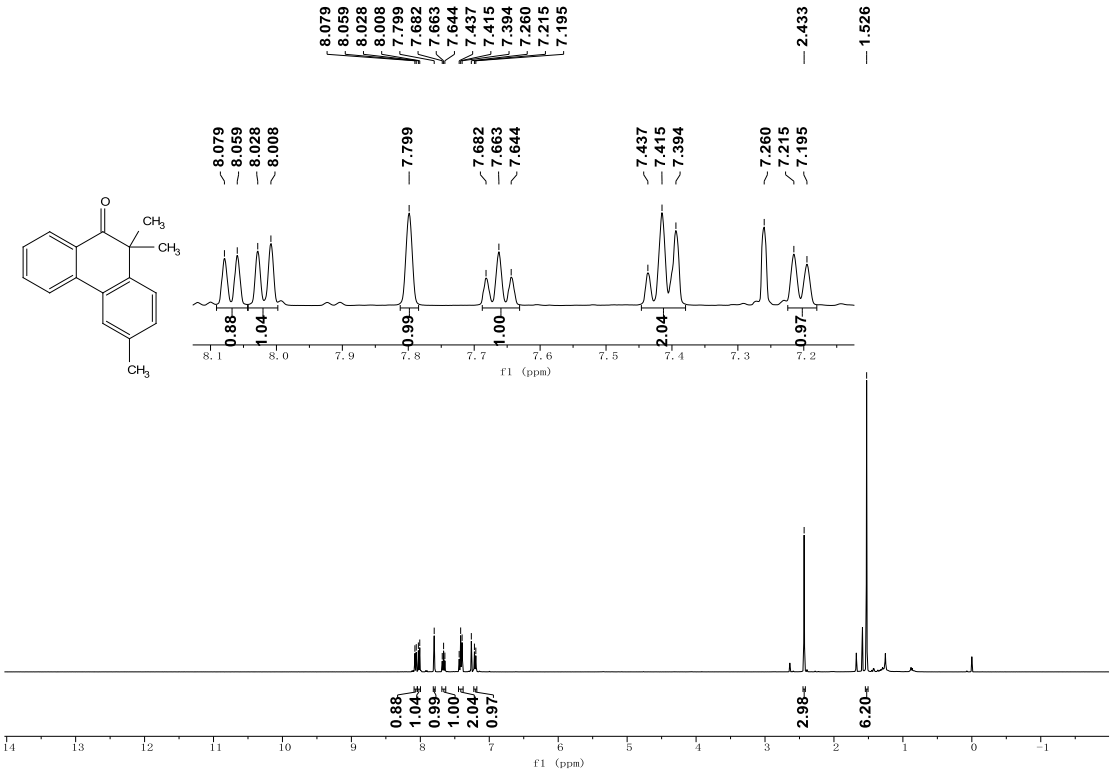

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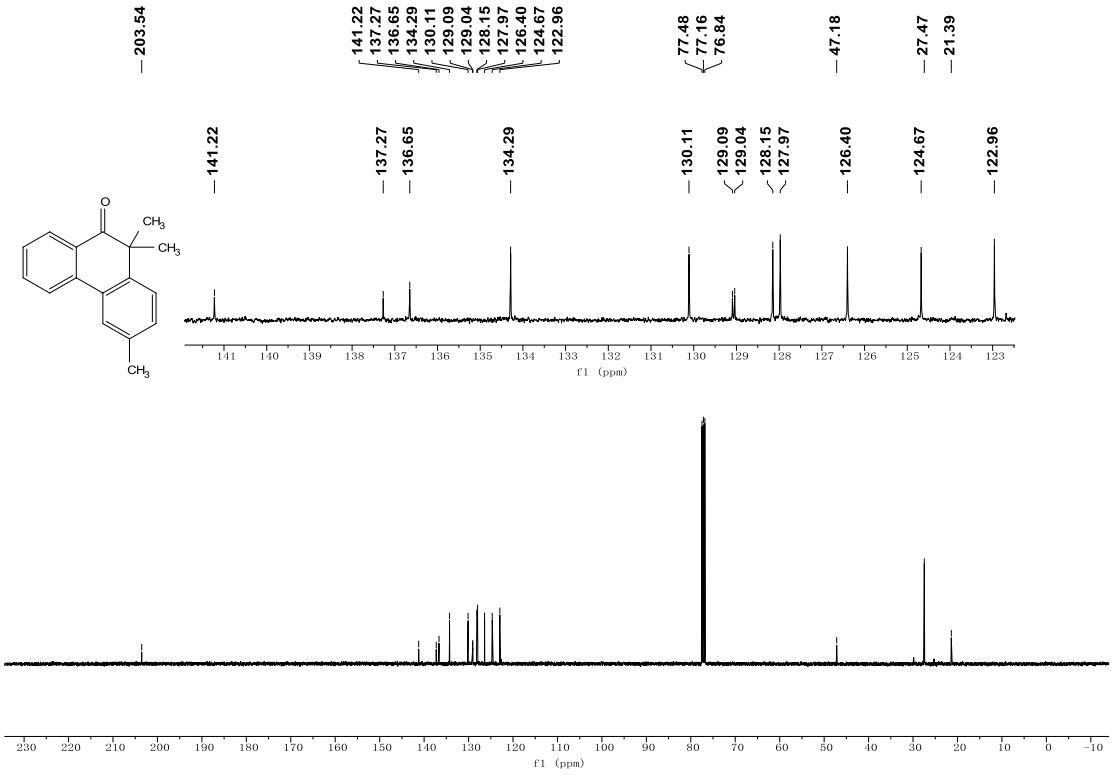
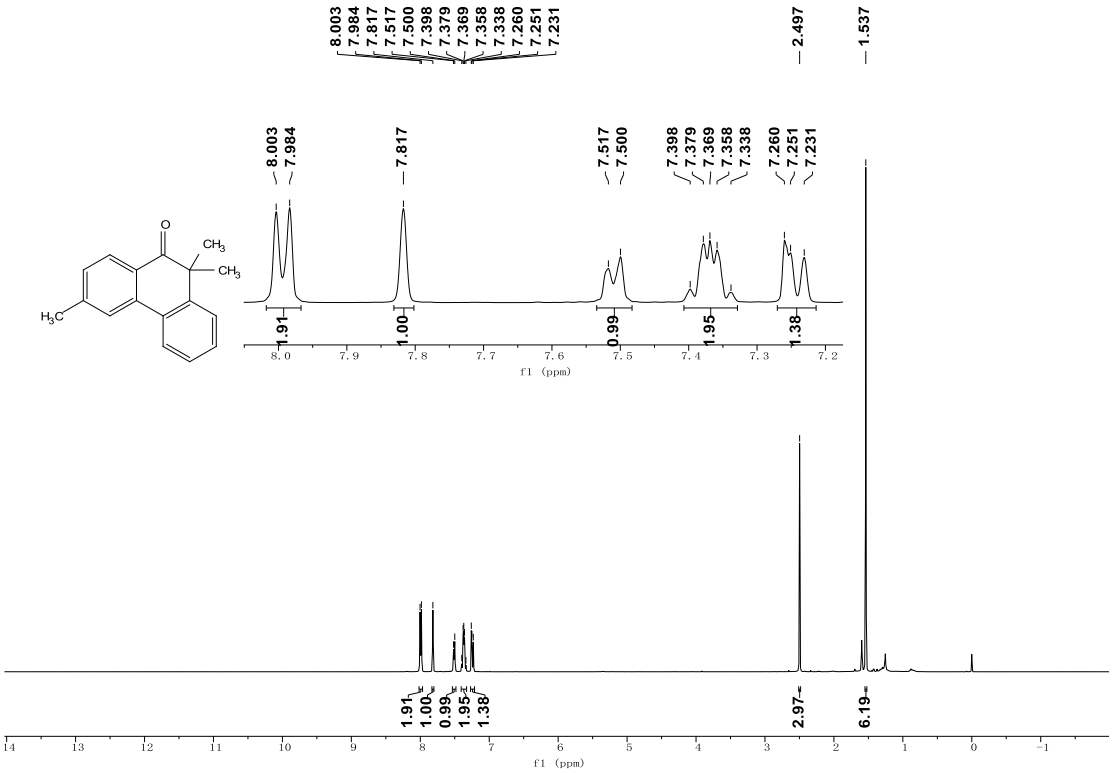
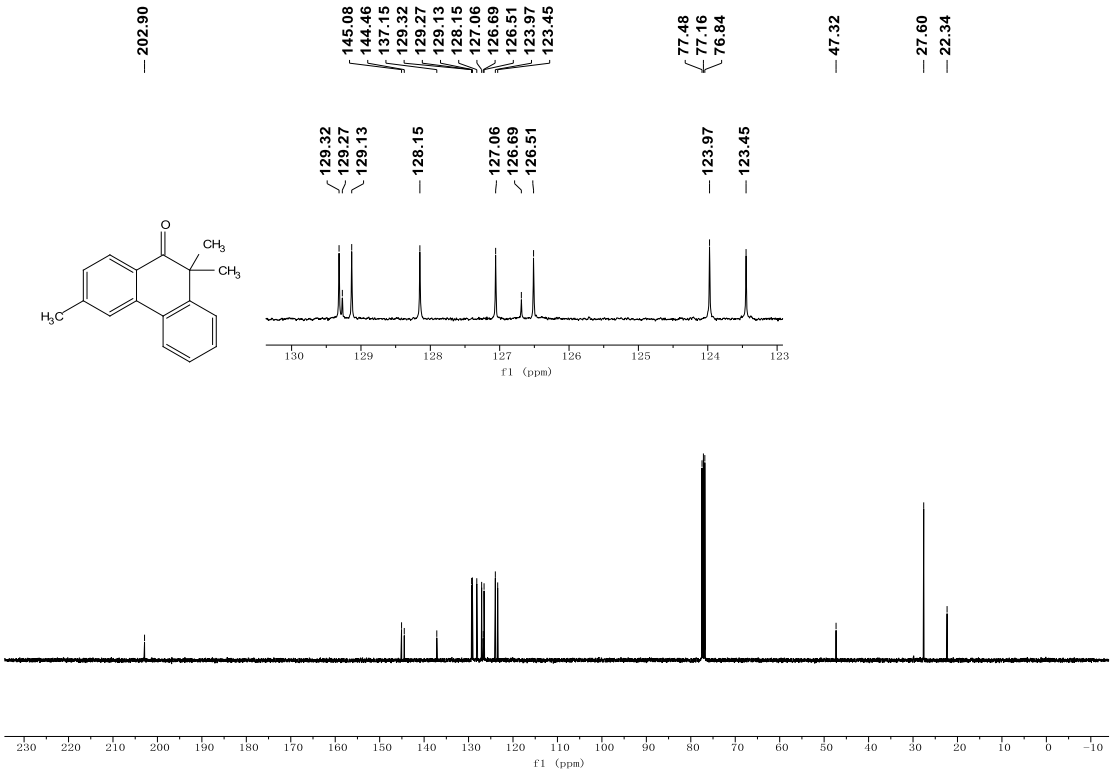


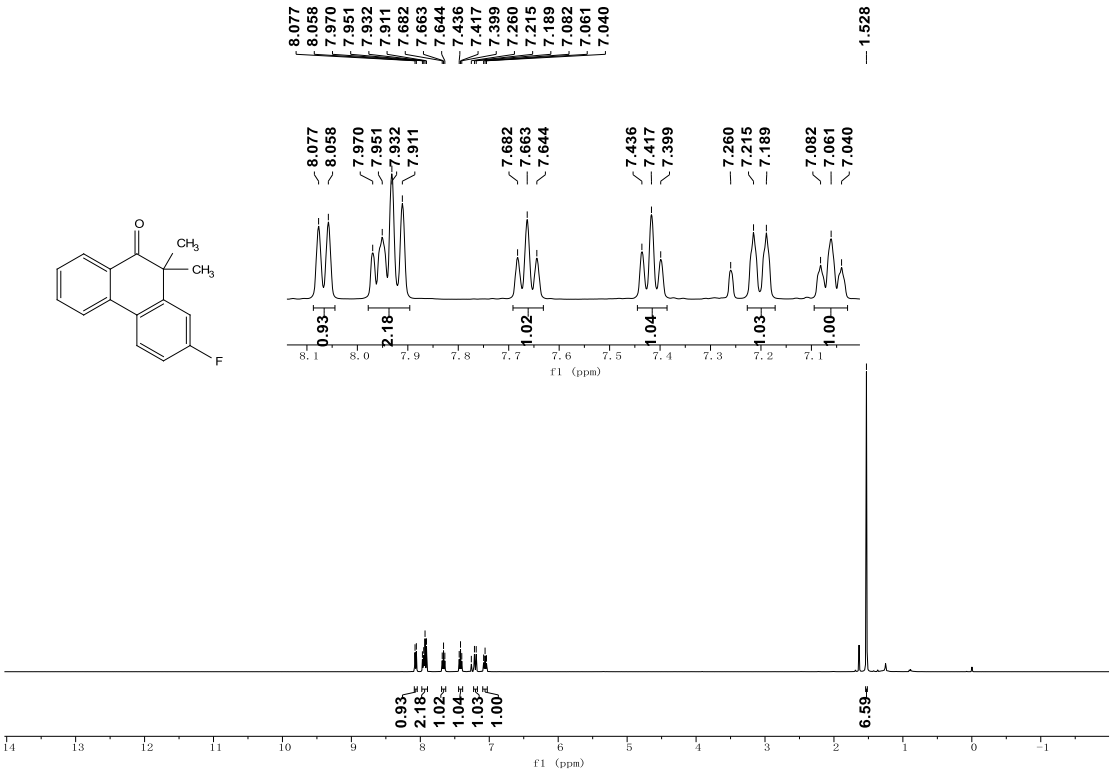
^{1}H NMR spectrum of **3d** ($CDCl_3$)



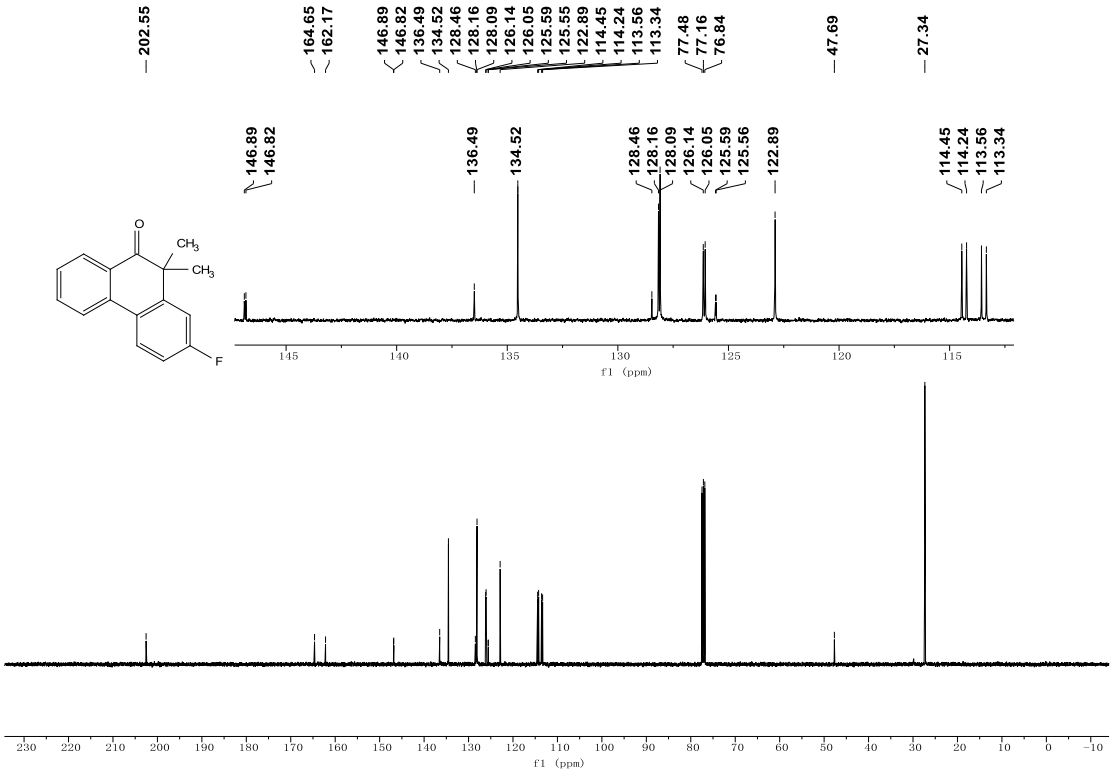
^{13}C NMR spectrum of **3d** ($CDCl_3$)



^{1}H NMR spectrum of **3e** ($CDCl_3$)



^{13}C NMR spectrum of **3e** ($CDCl_3$)



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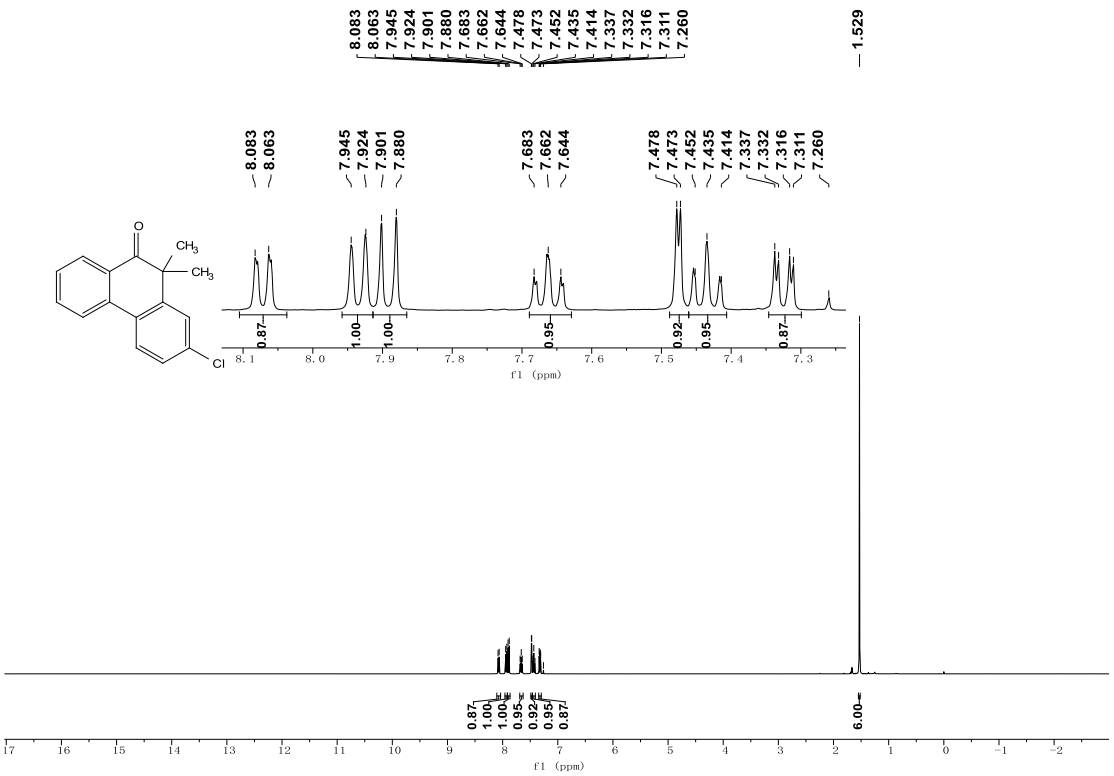
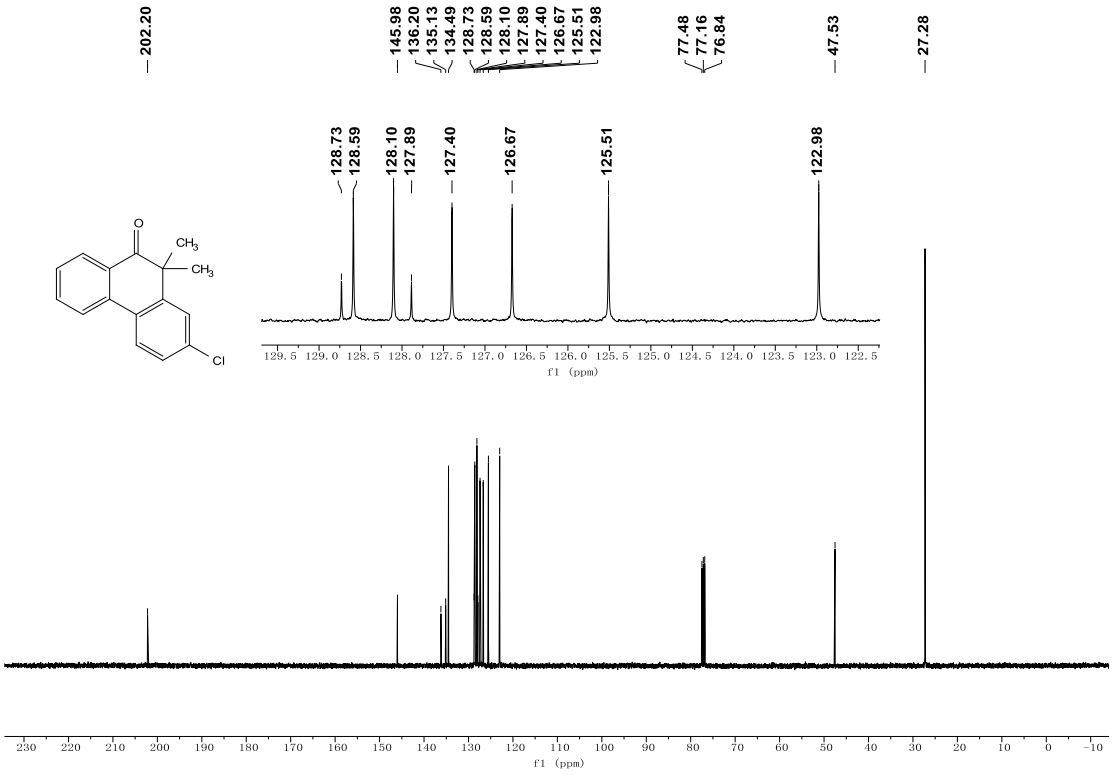


^{13}C NMR spectrum of **3f** ($CDCl_3$)



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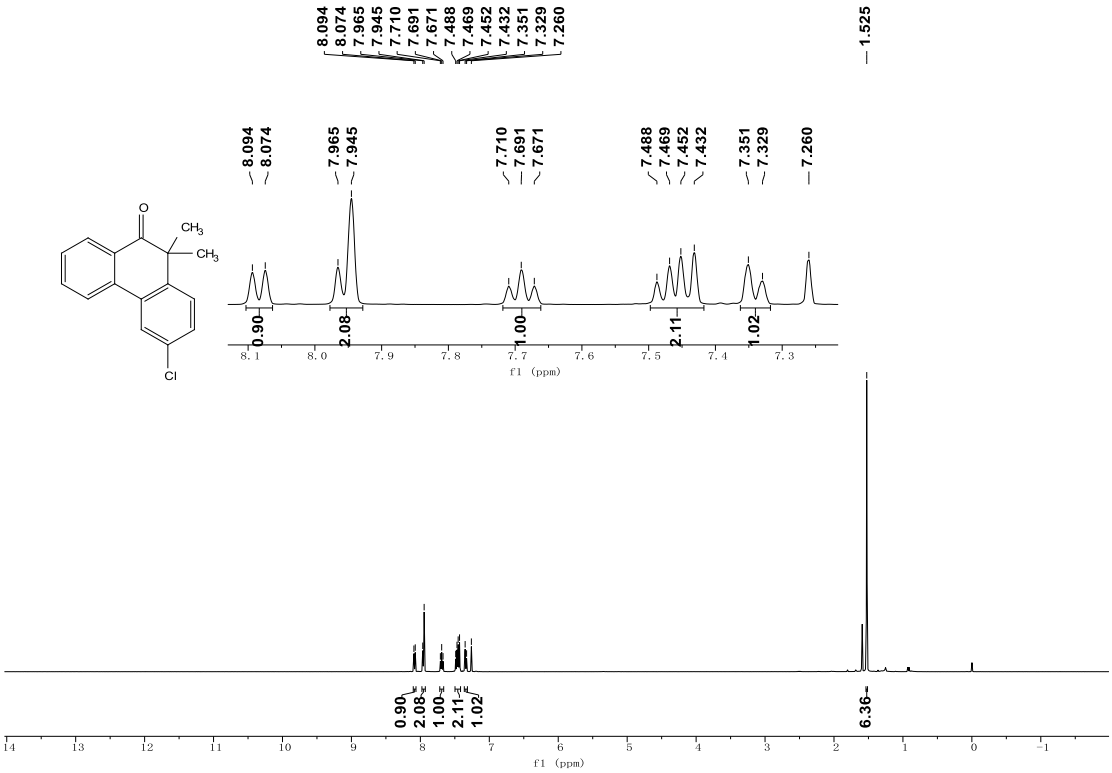

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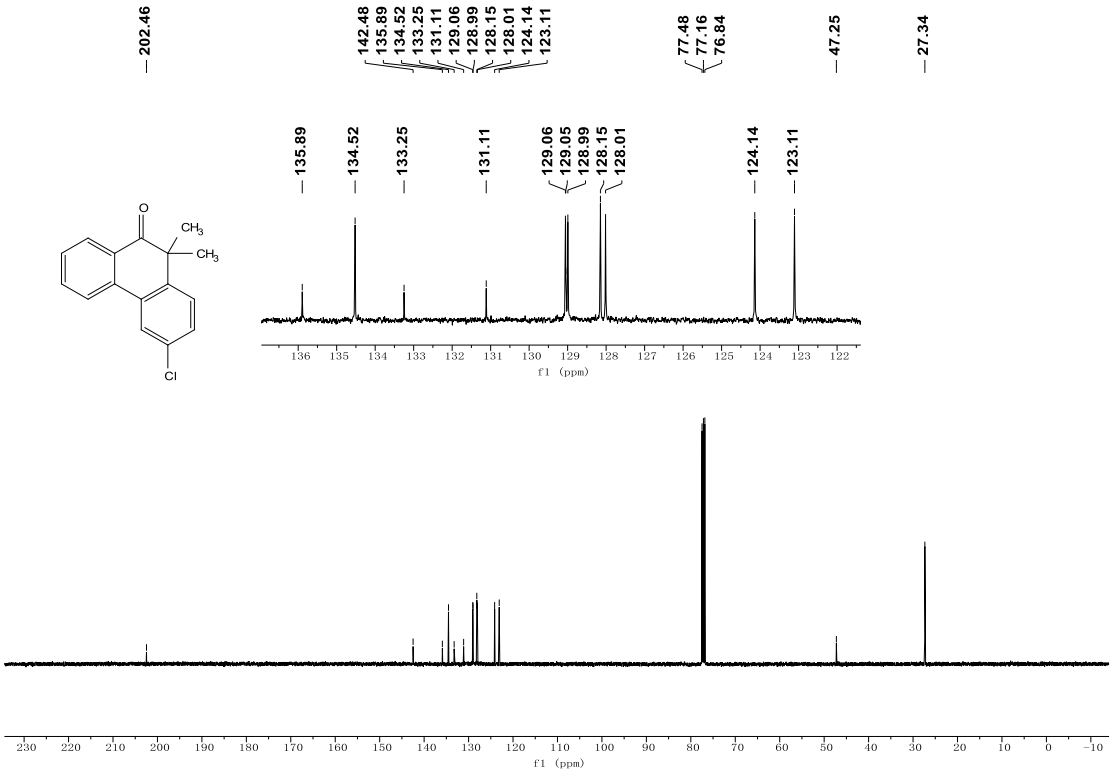
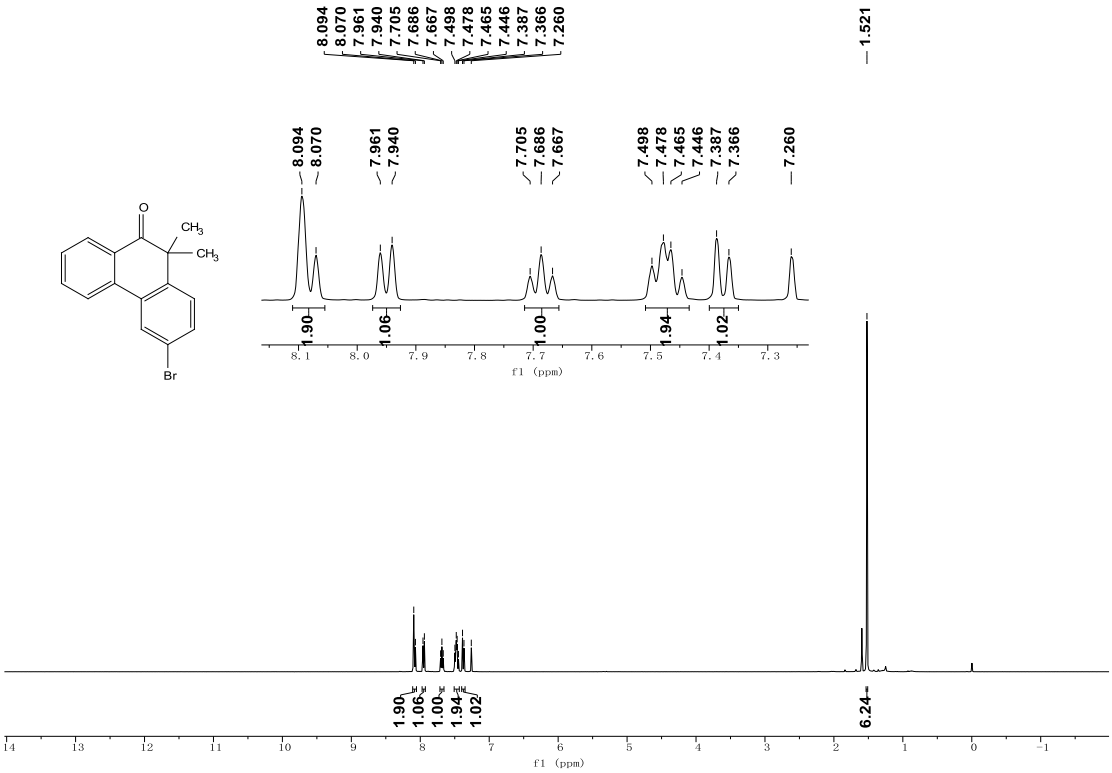
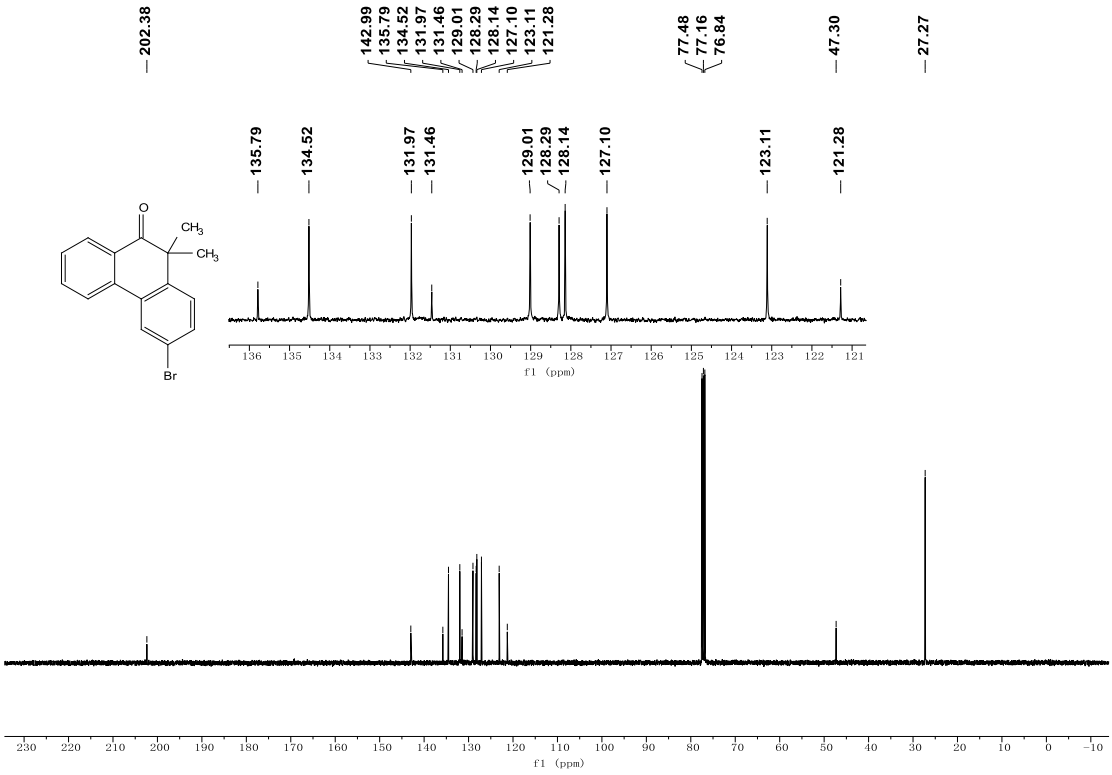


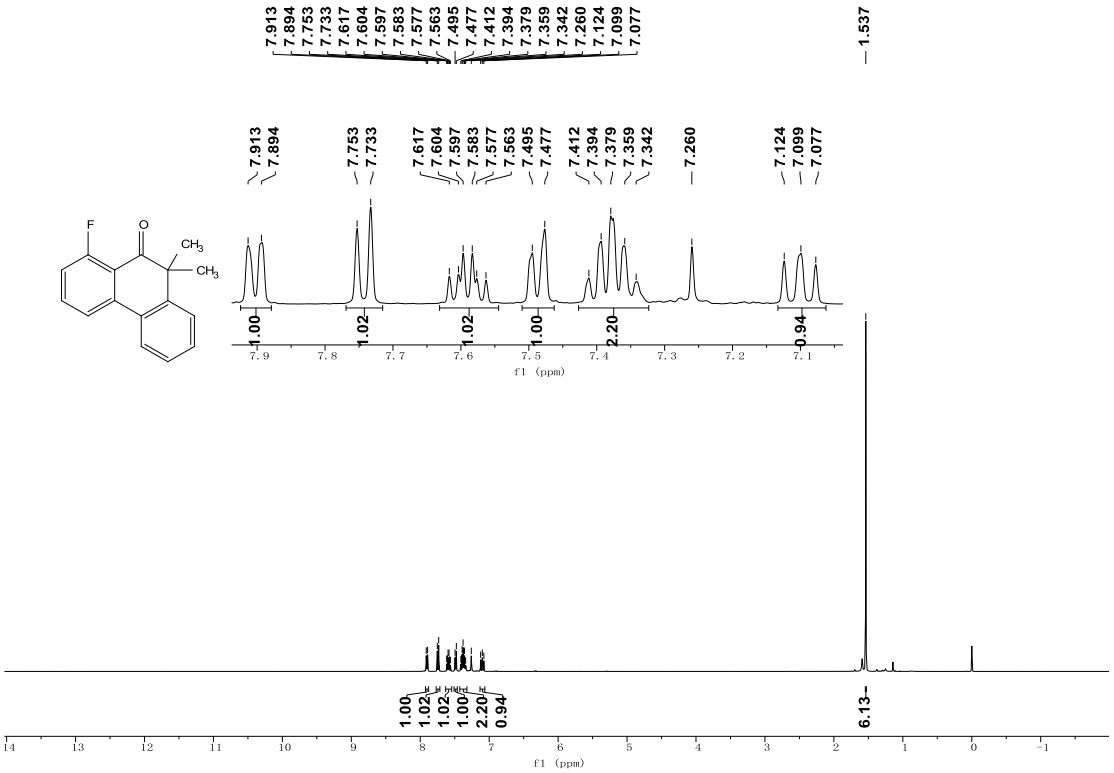
^{1}H NMR spectrum of **3h** ($CDCl_3$)



^{13}C NMR spectrum of **3h** ($CDCl_3$)



^{1}H NMR spectrum of **3i** ($CDCl_3$)



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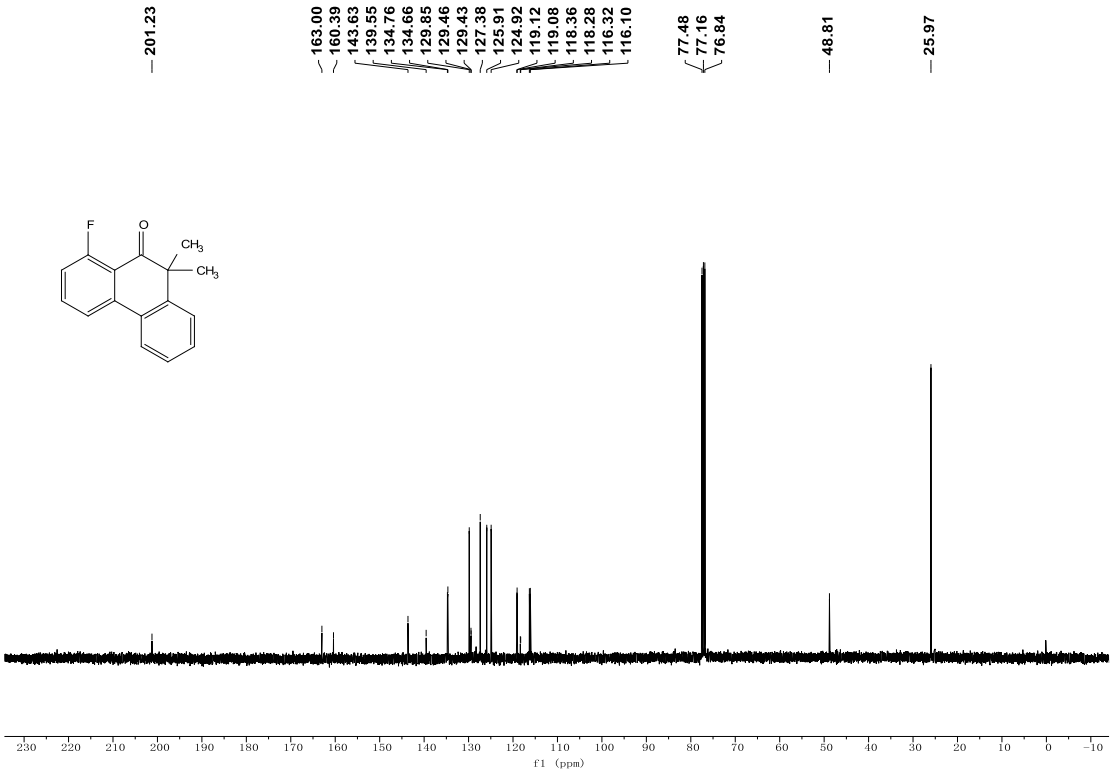

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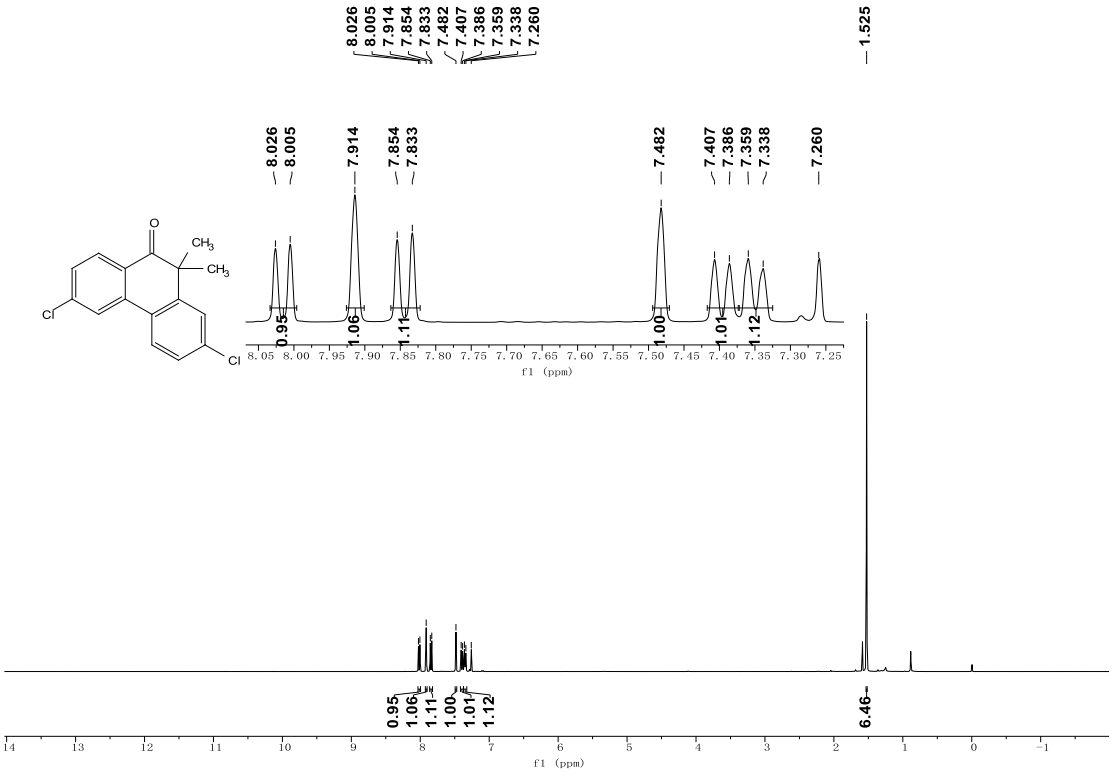

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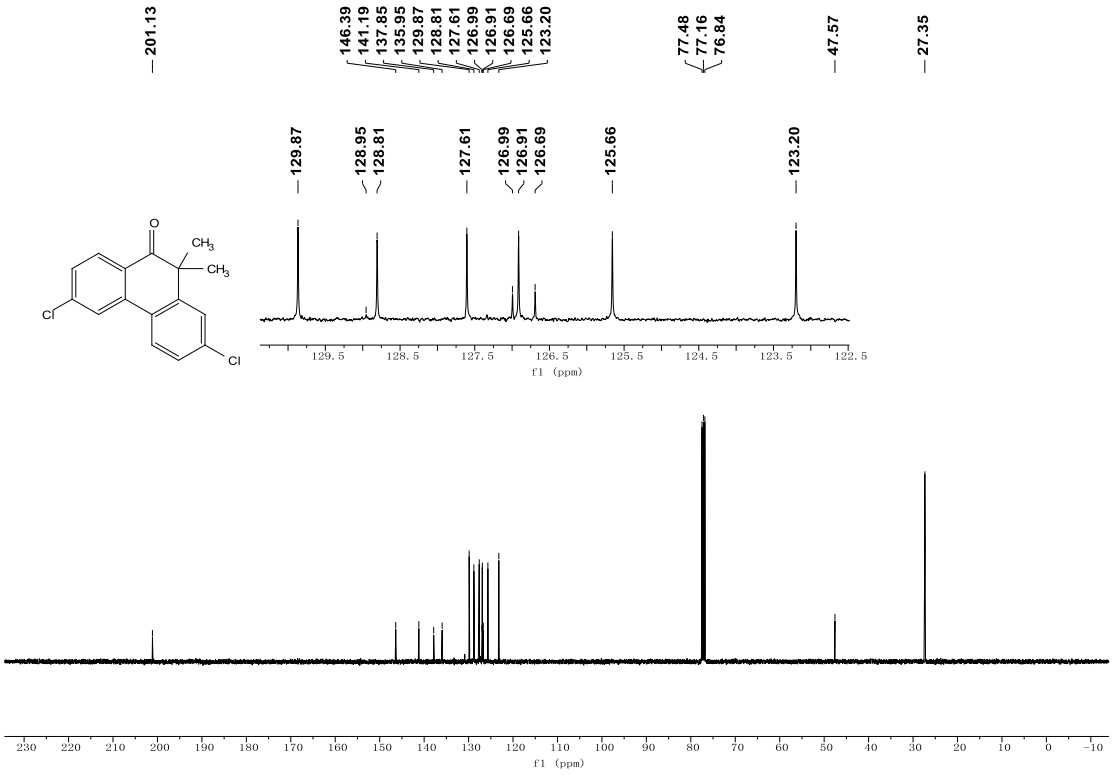

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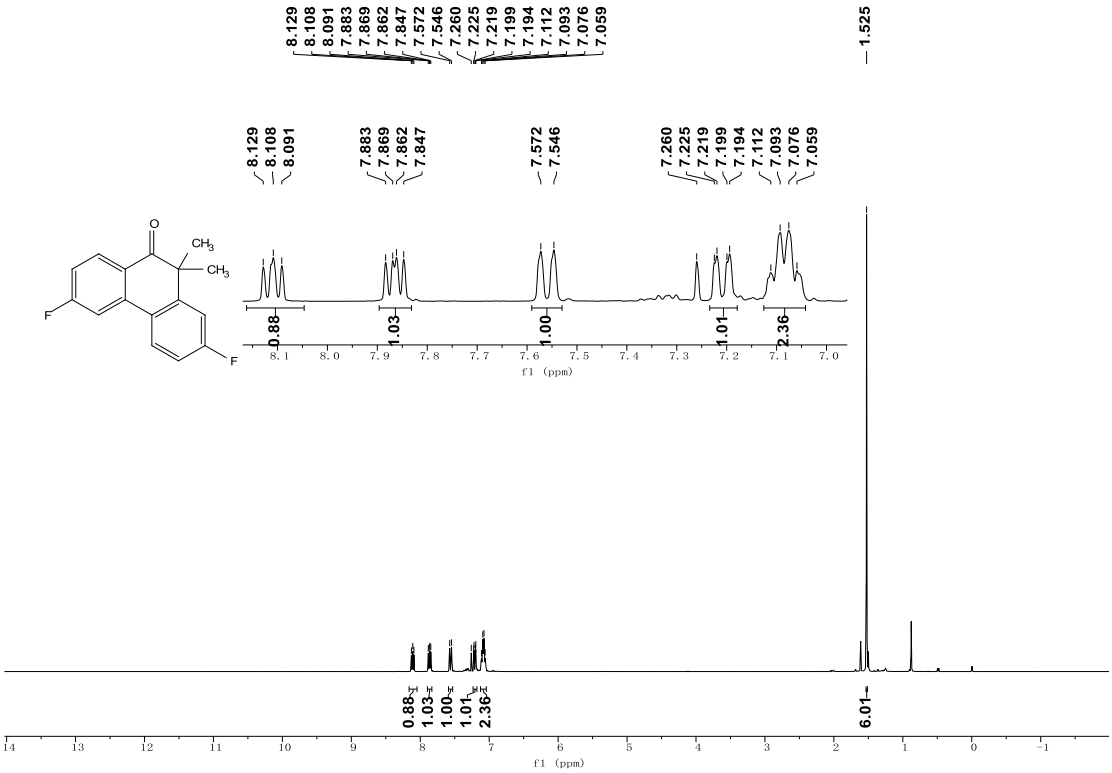

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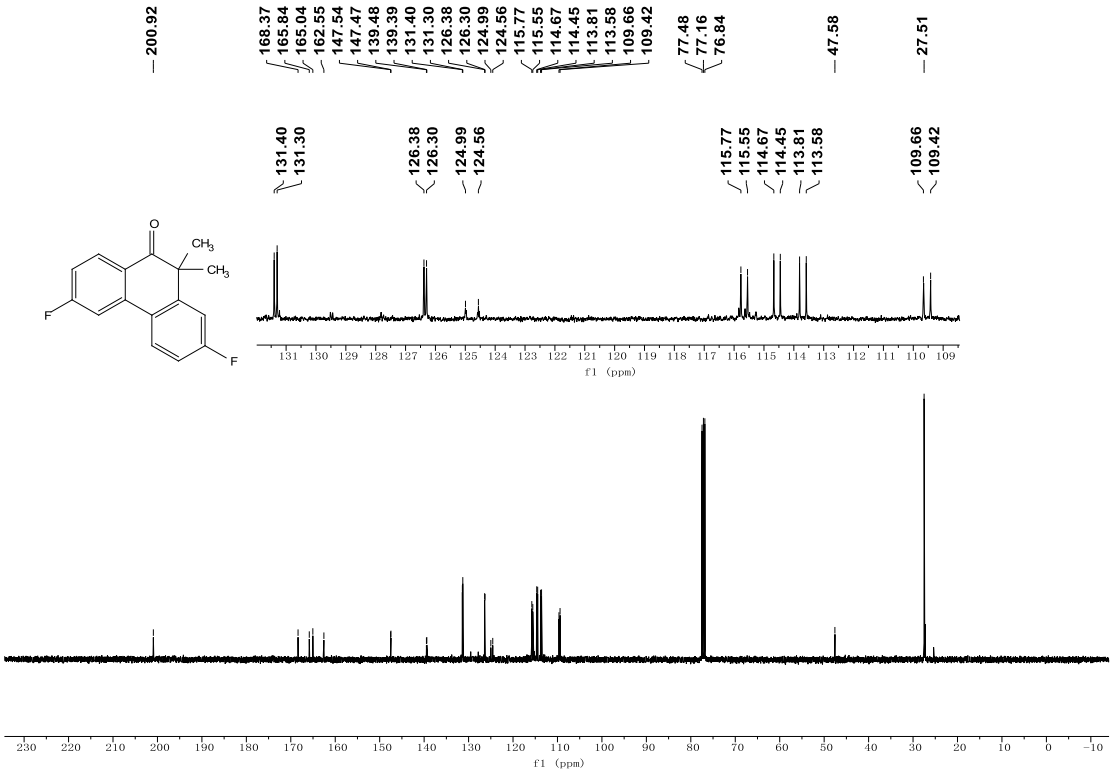

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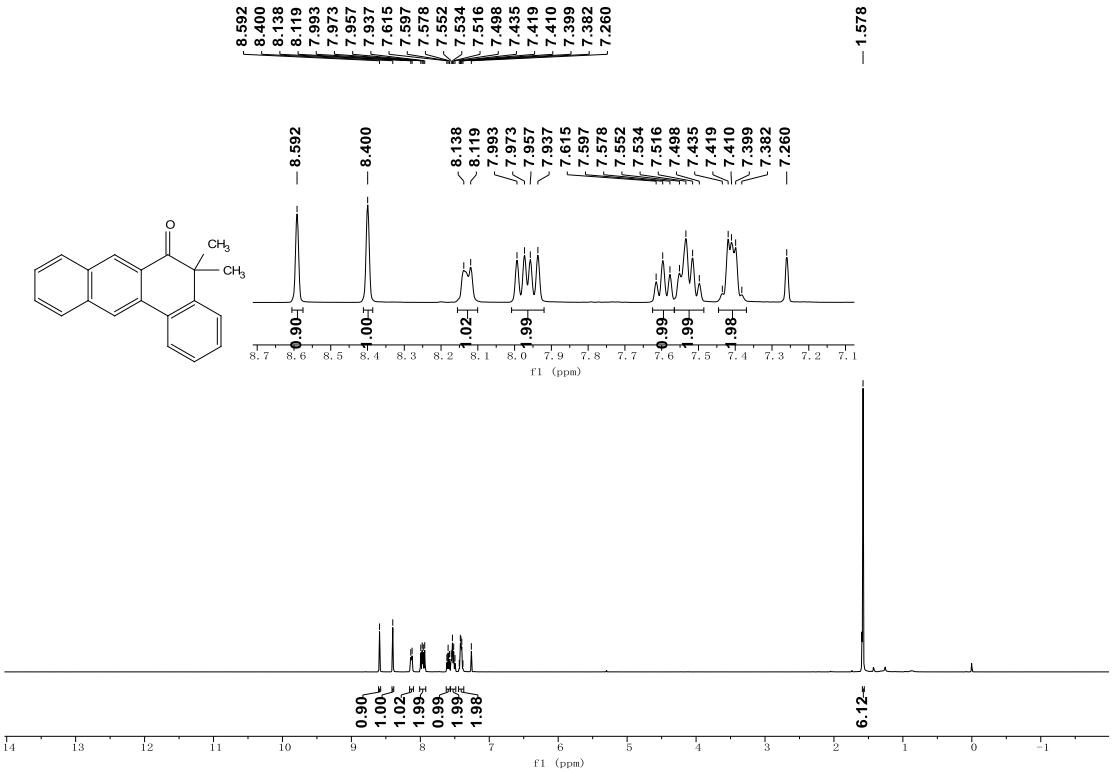
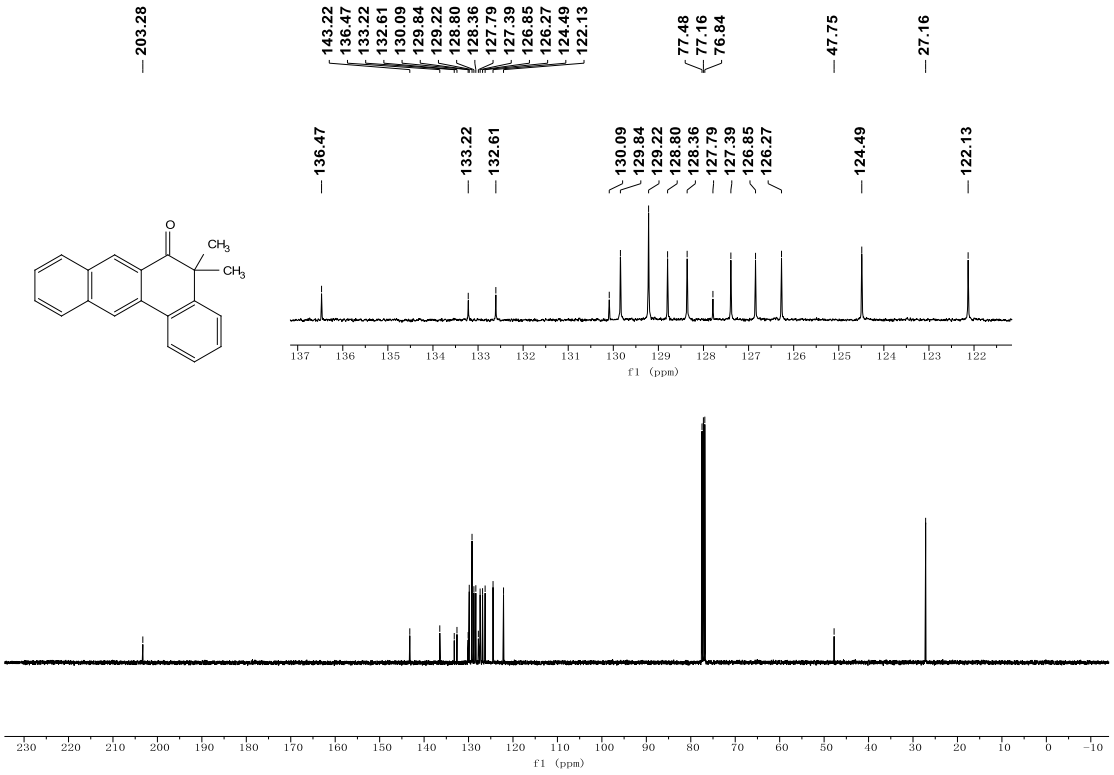


^{13}C NMR spectrum of **3l** ($CDCl_3$)



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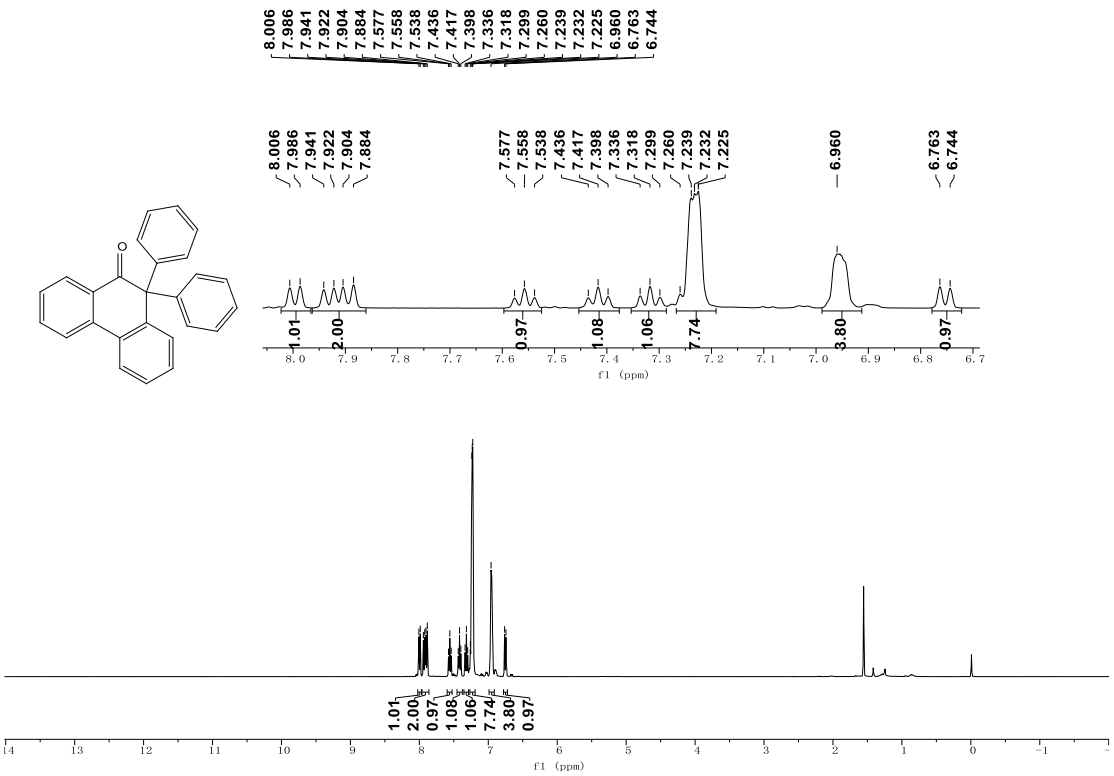

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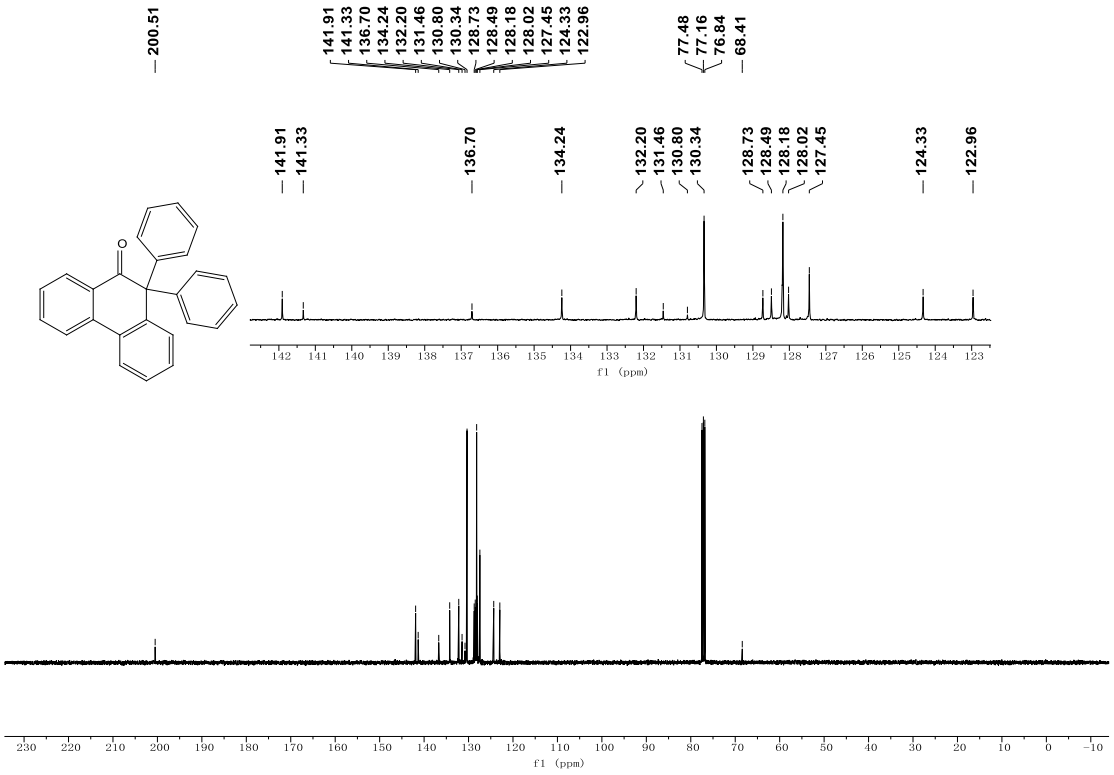

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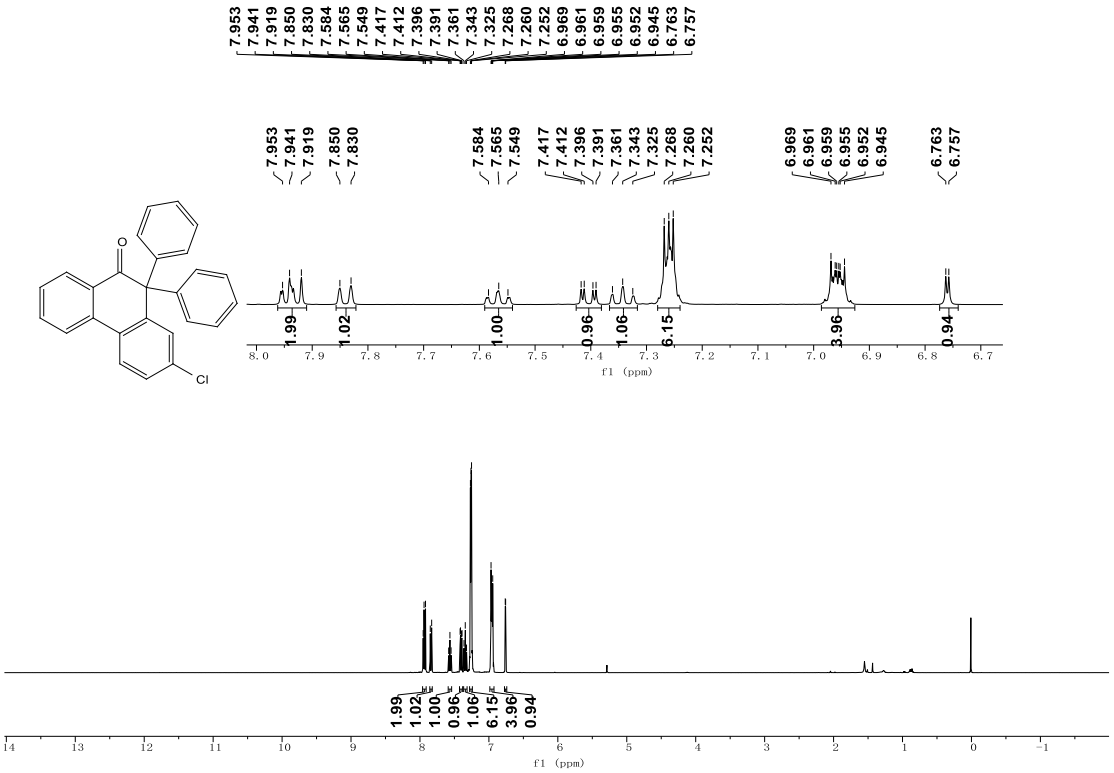

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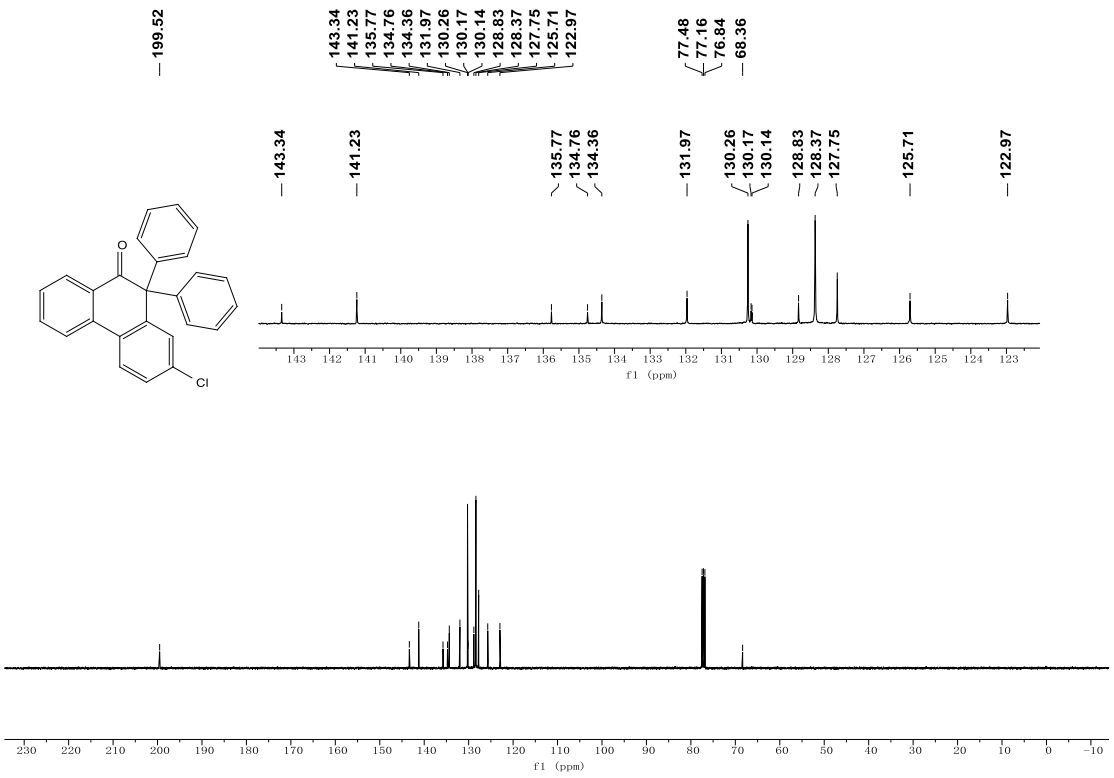
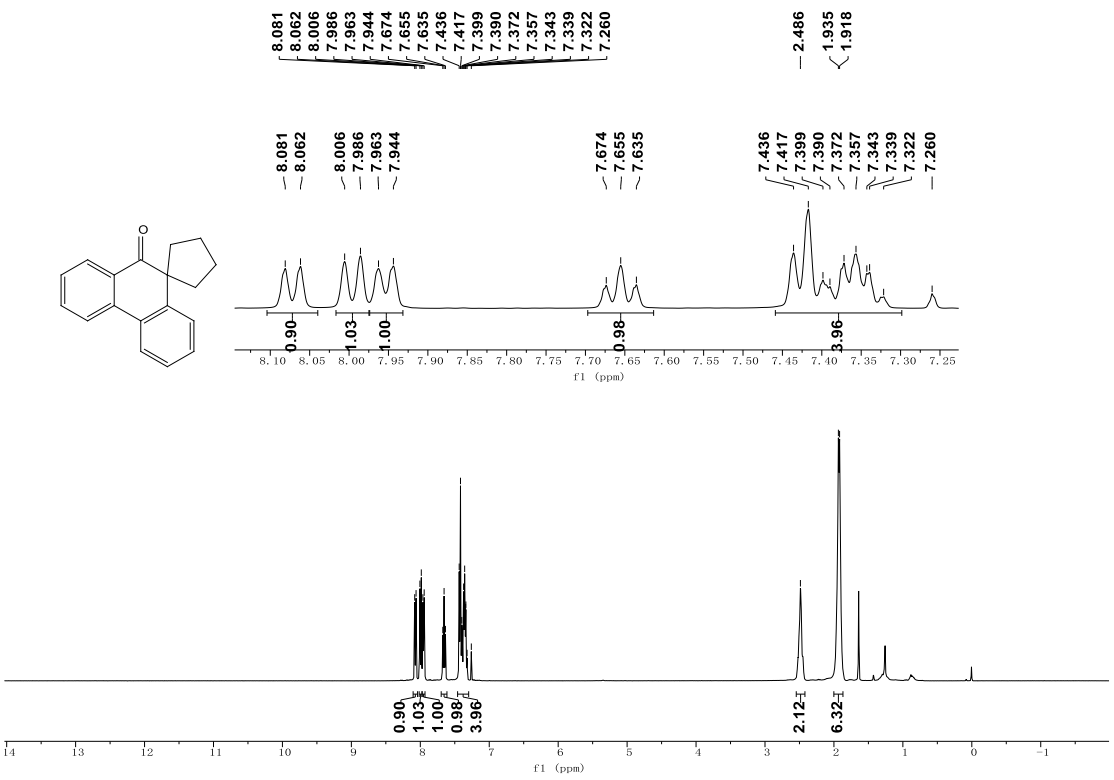


^{1}H NMR spectrum of **3o** ($CDCl_3$)



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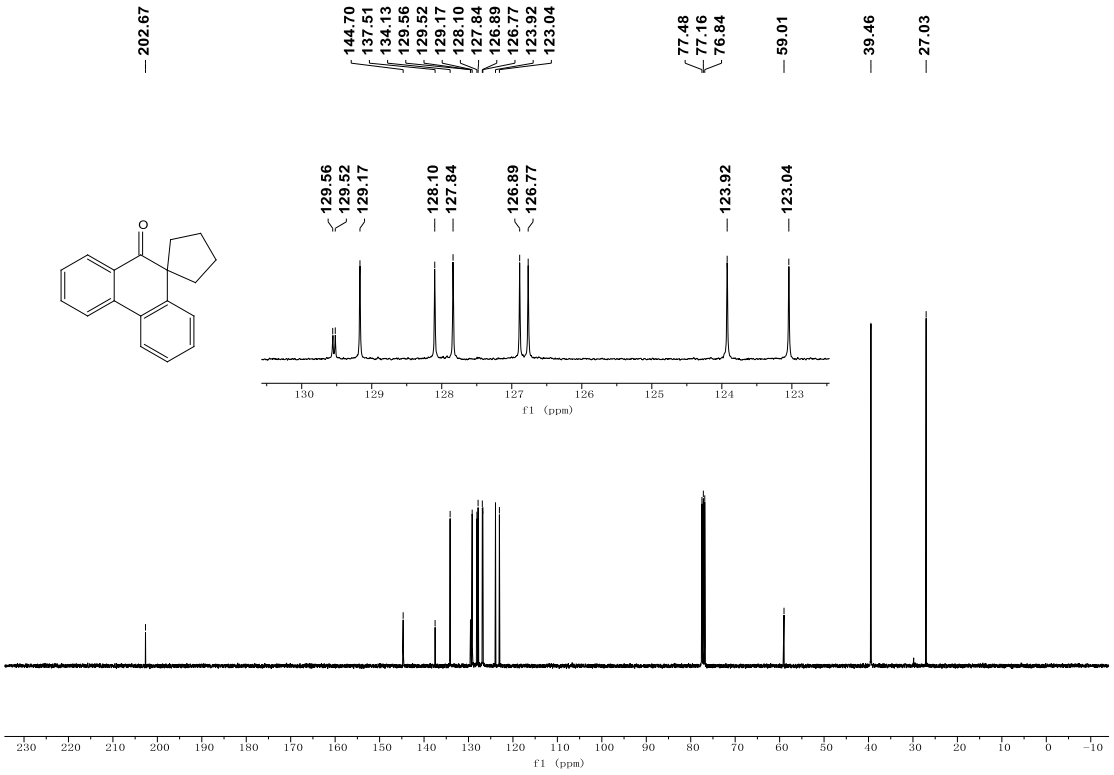

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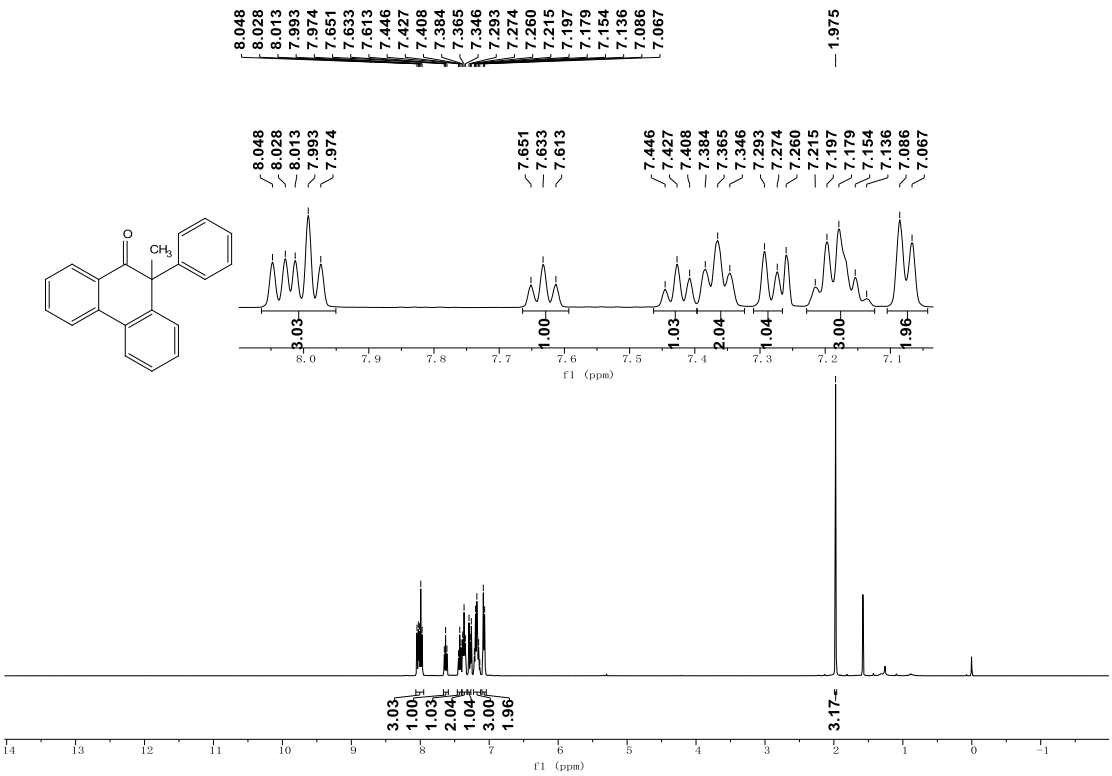

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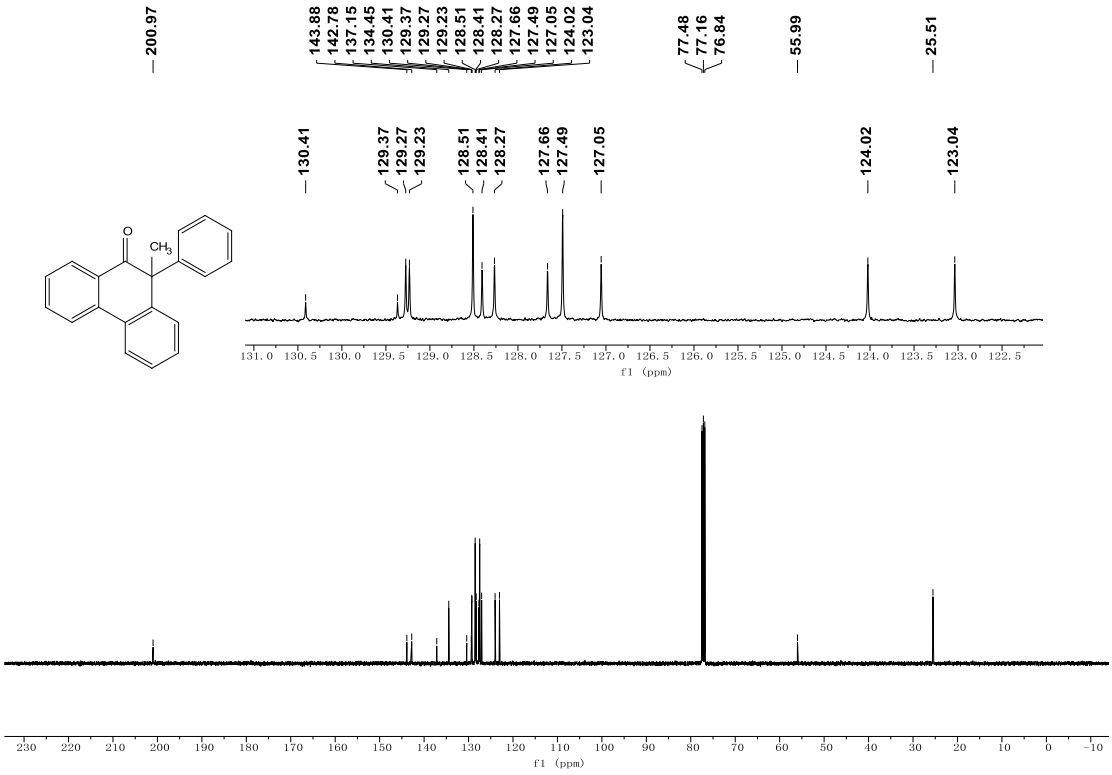
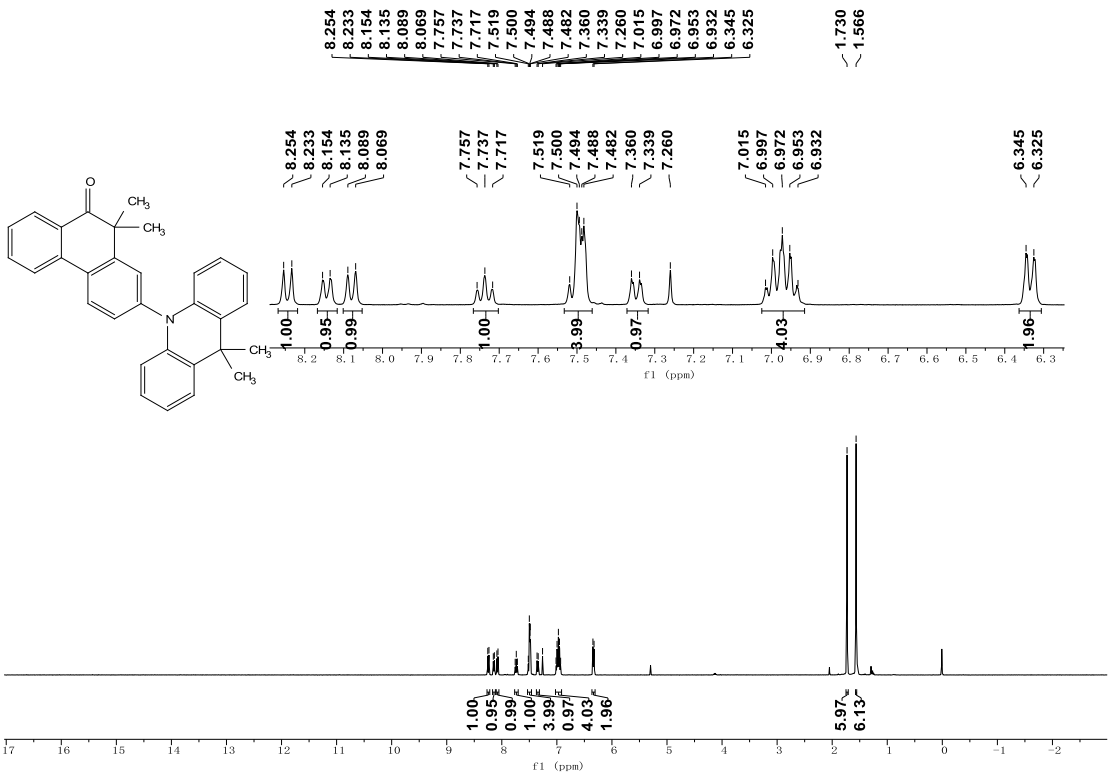
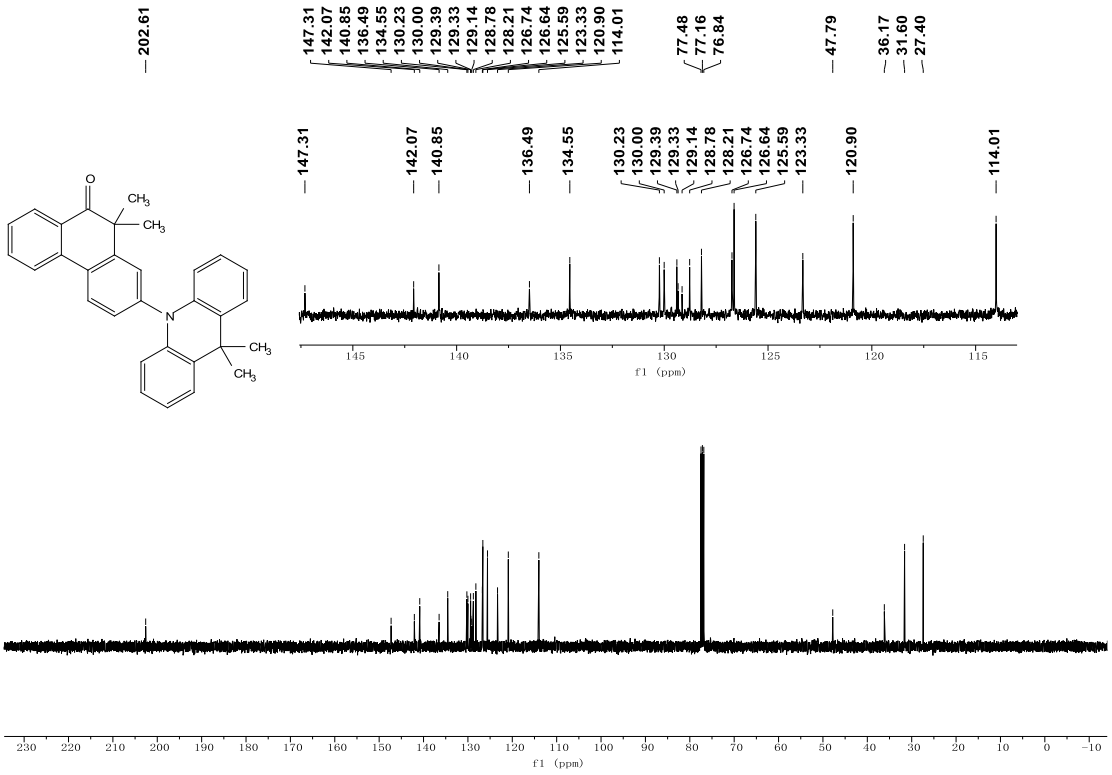


^{1}H NMR spectrum of 2-DMAC-DMPO ($CDCl_3$)



^{13}C NMR spectrum of 2-DMAC-DMPO ($CDCl_3$)



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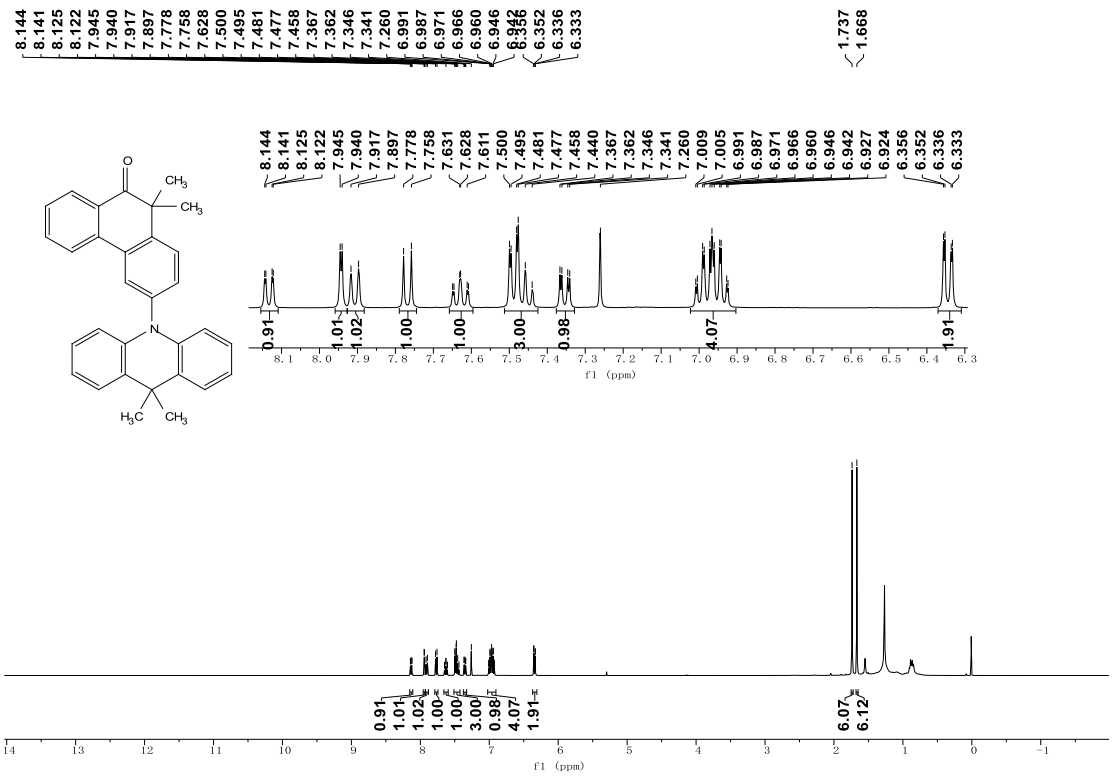

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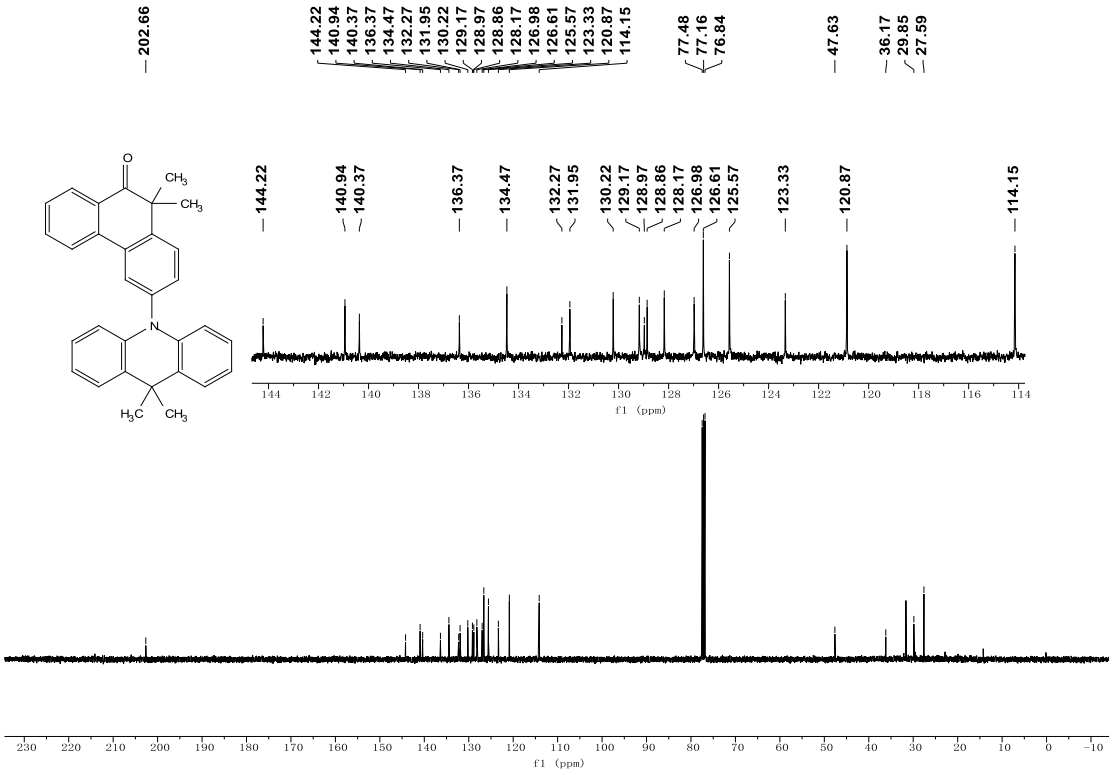
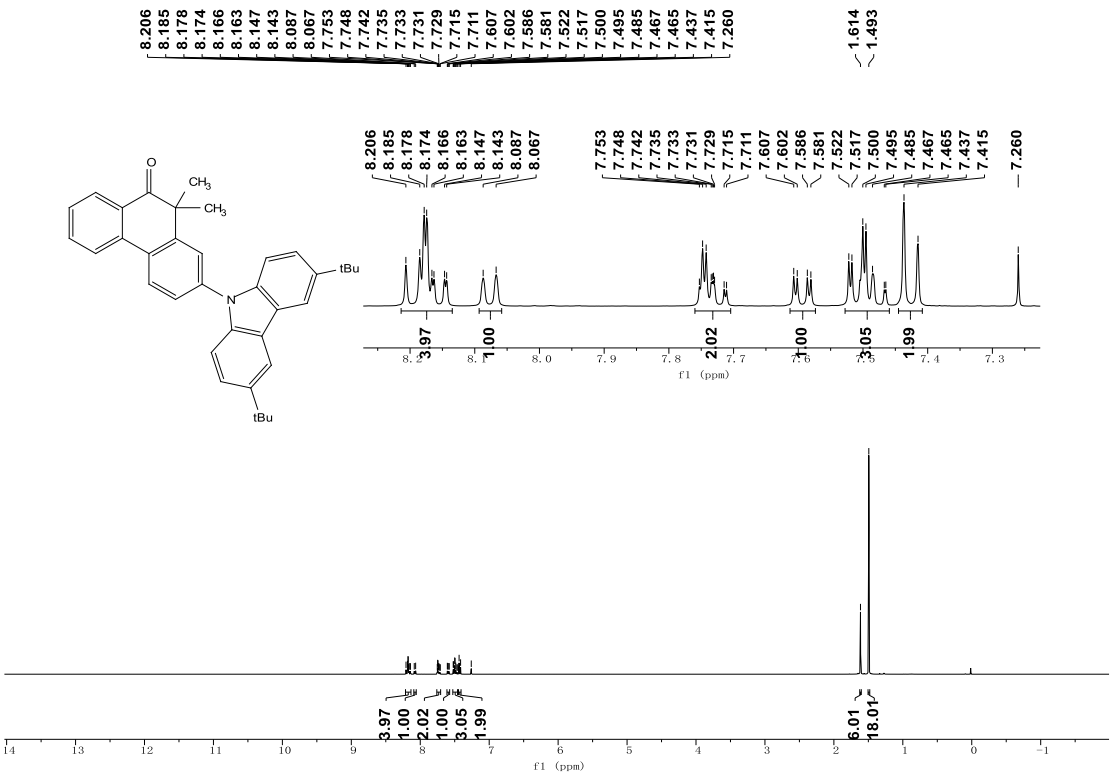
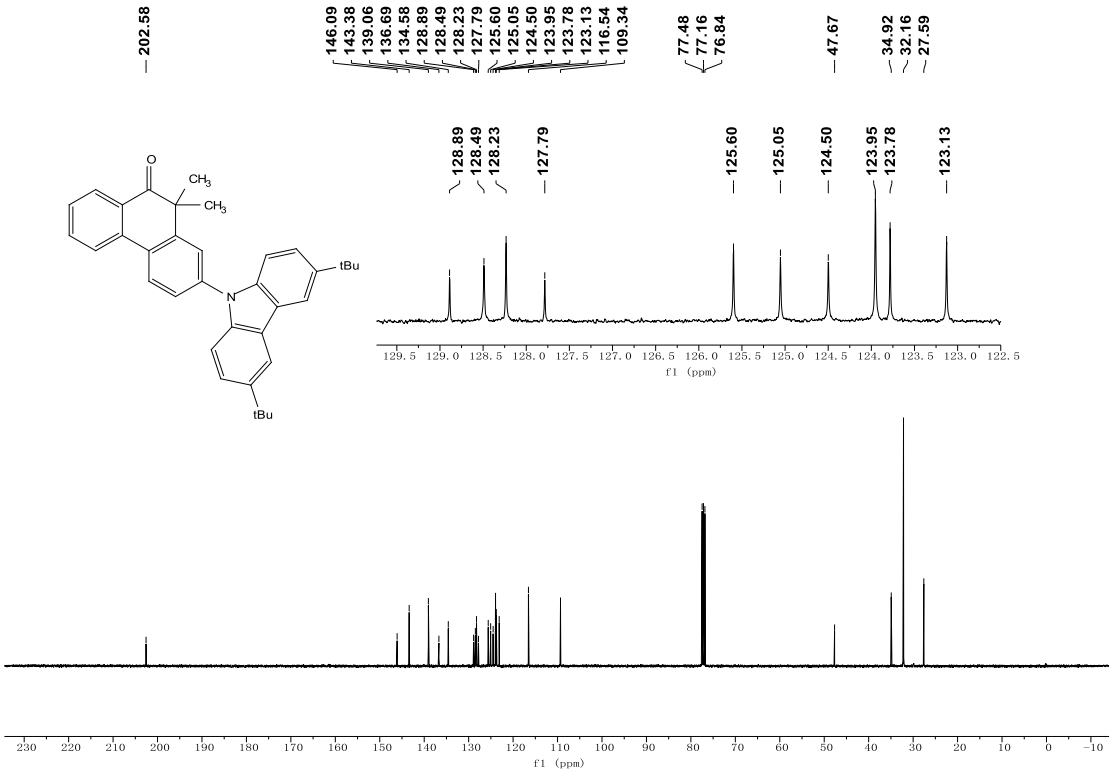


^{1}H NMR spectrum of 2-*t*BuCz-DMPO ($CDCl_3$)



^{13}C NMR spectrum of 2-*t*BuCz-DMPO ($CDCl_3$)



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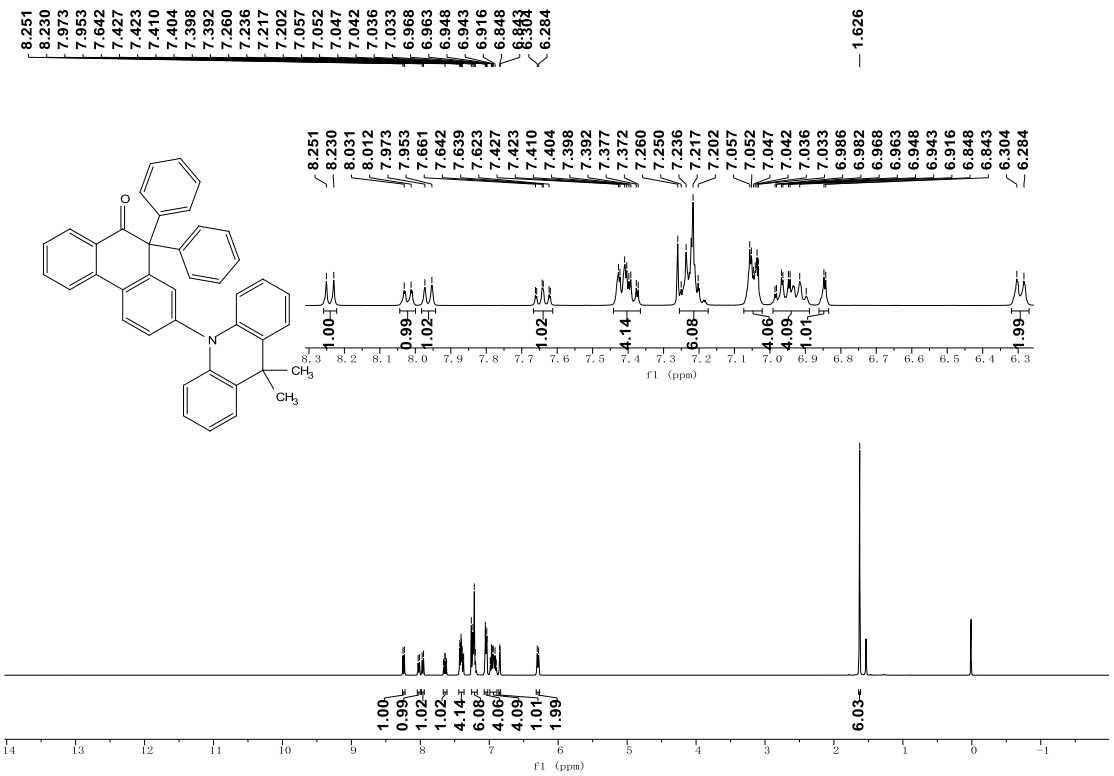

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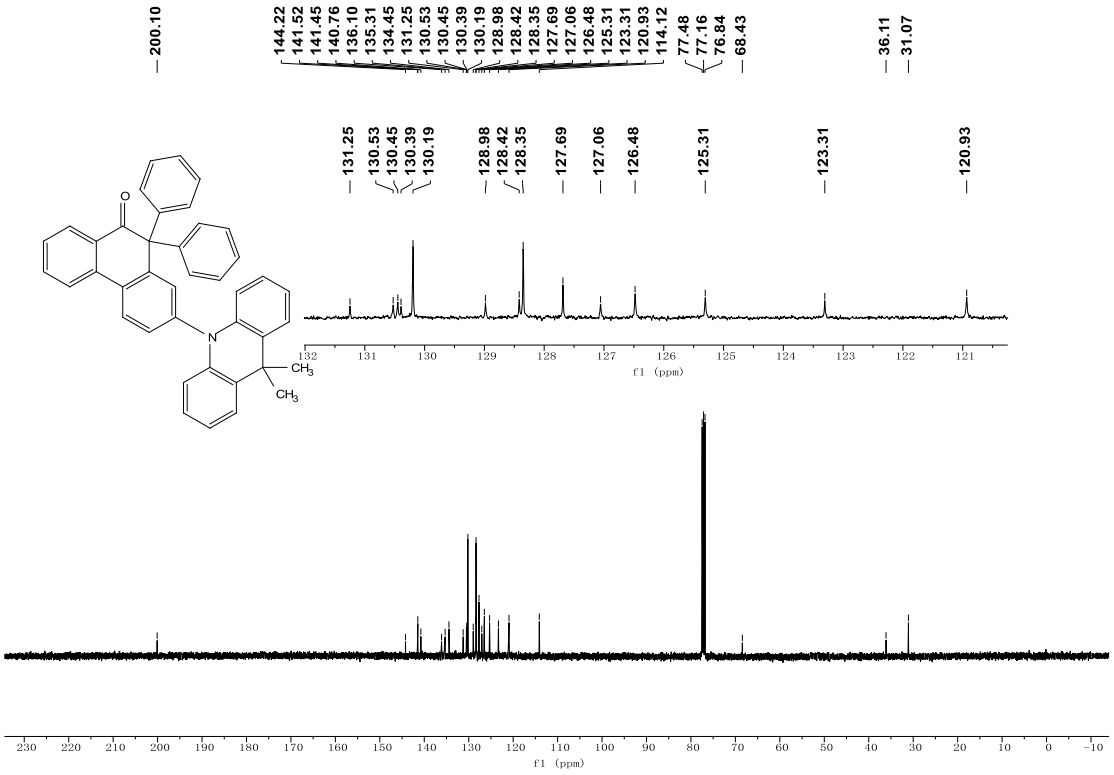

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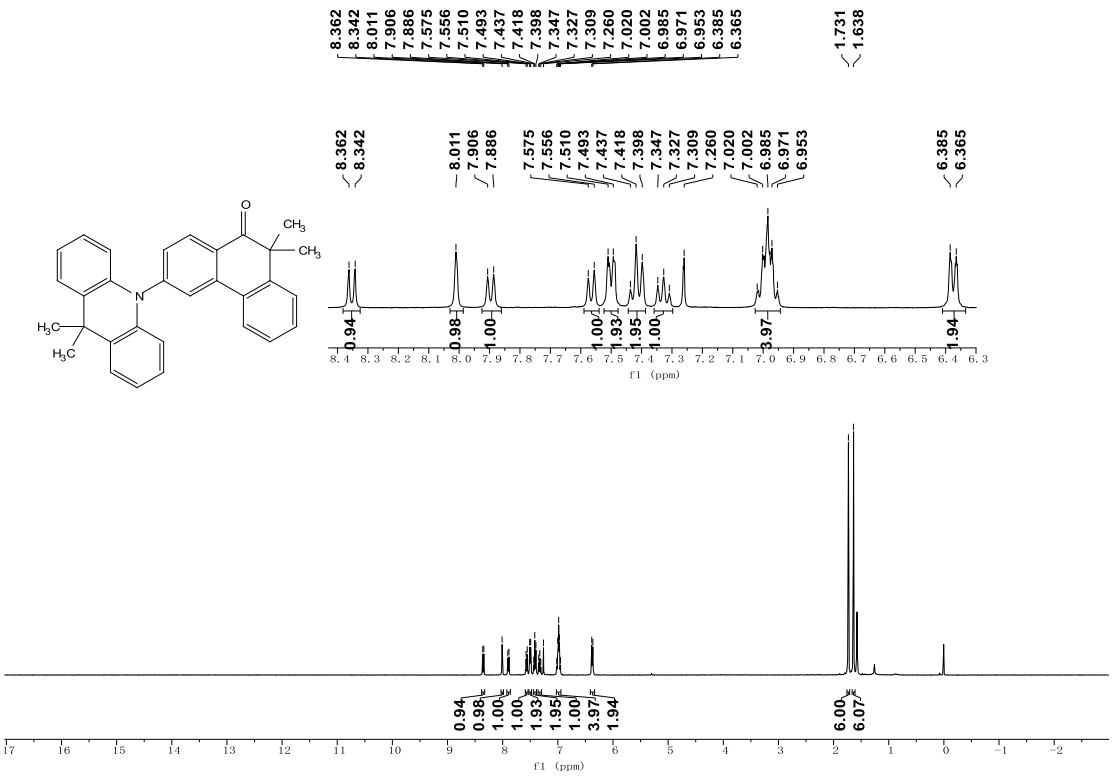

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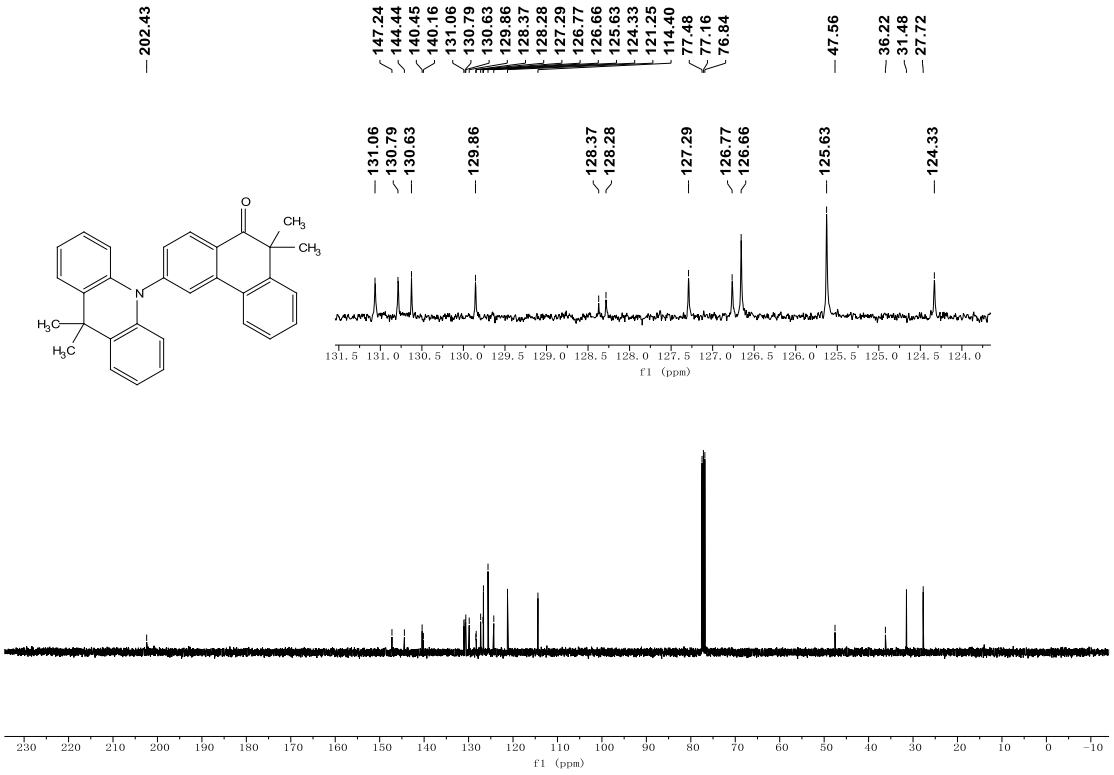

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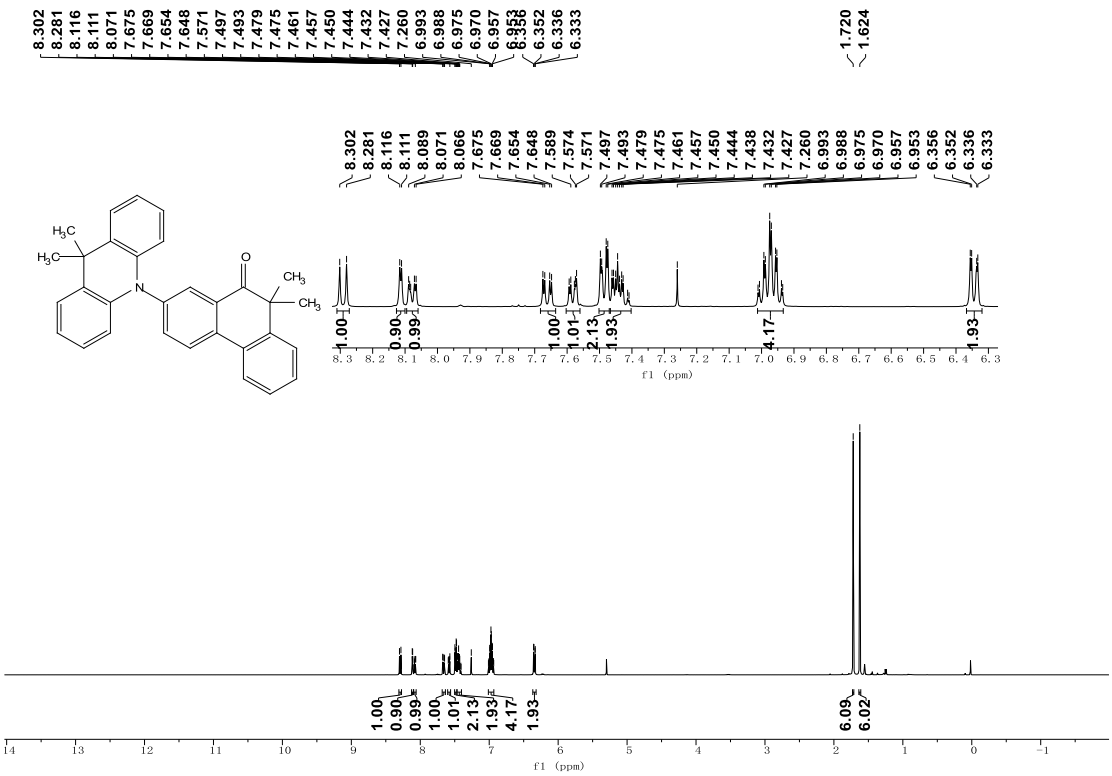
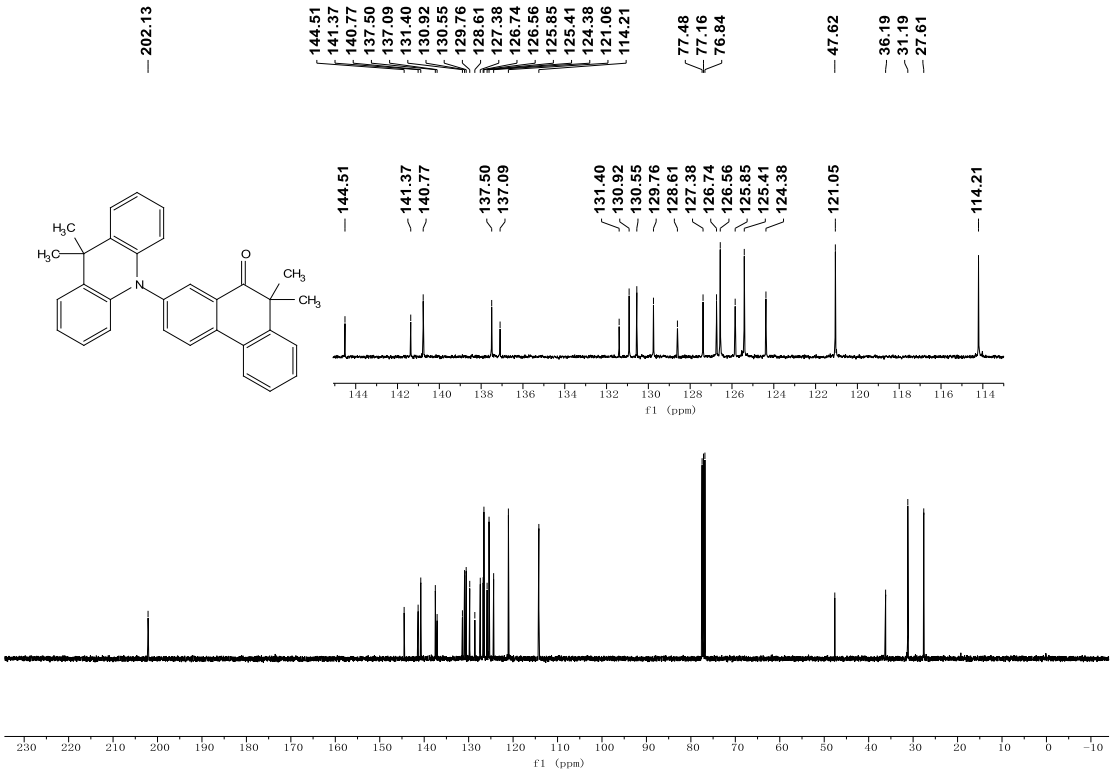
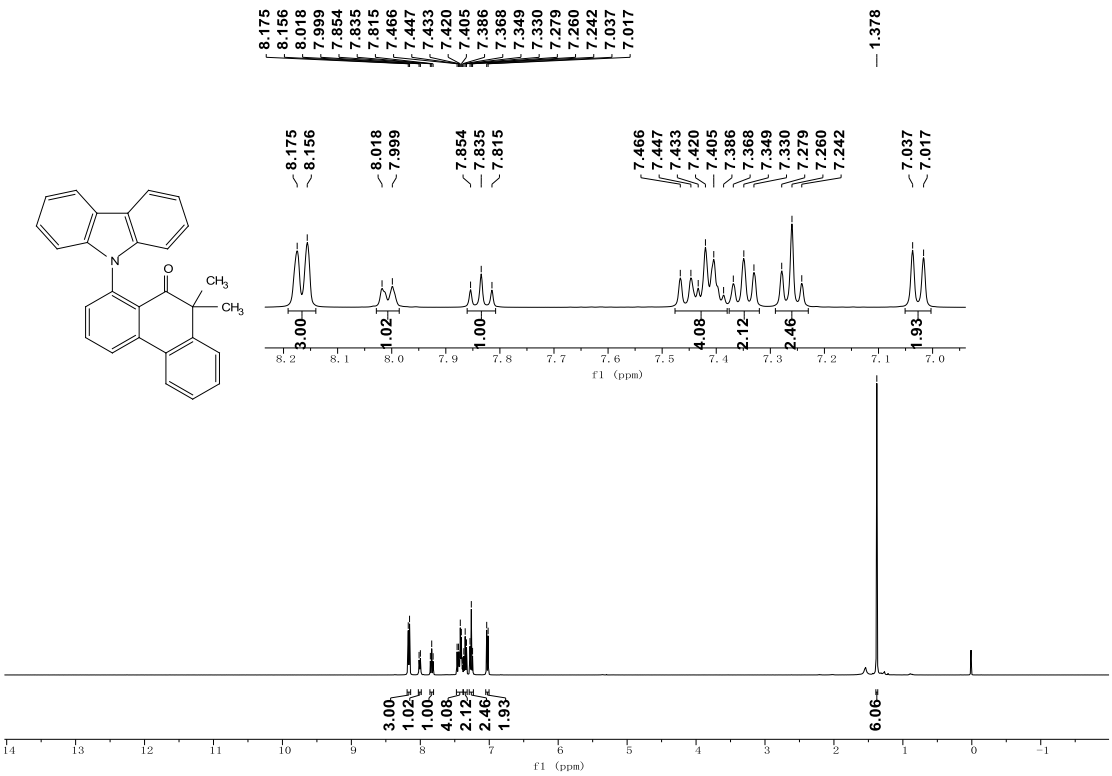


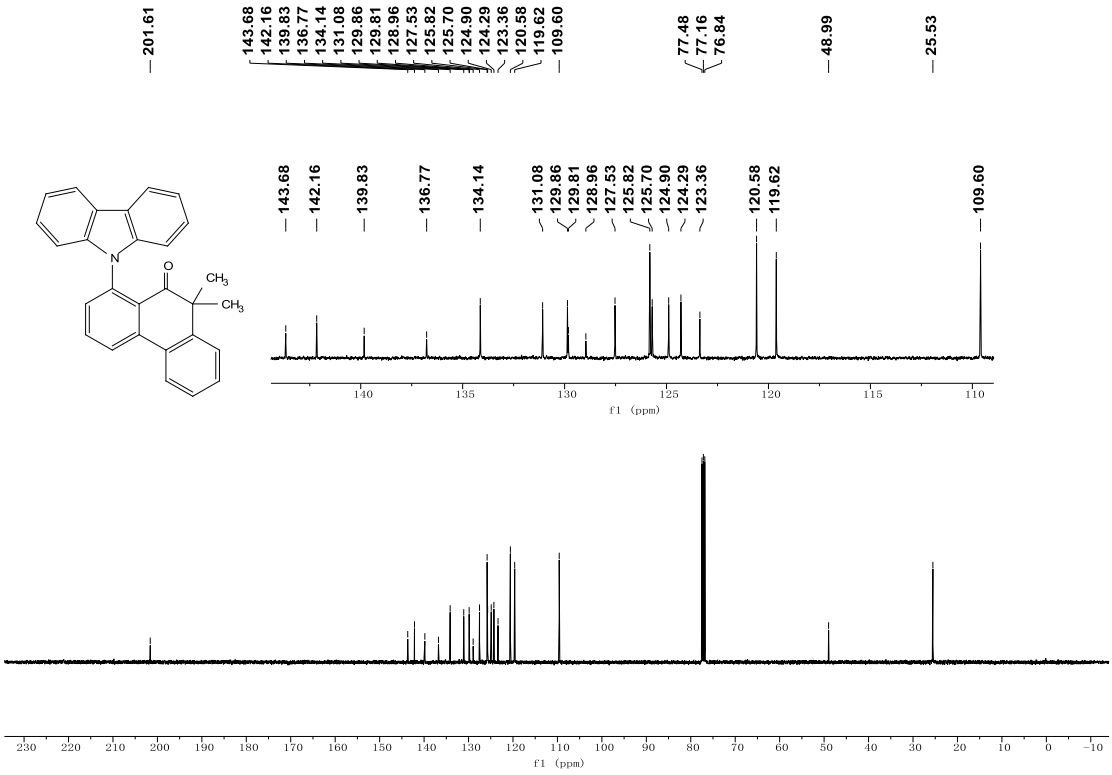
^{13}C NMR spectrum of 7-DMAC-DMPO ($CDCl_3$)



^{1}H NMR spectrum of 8-Cz-DMPO ($CDCl_3$)

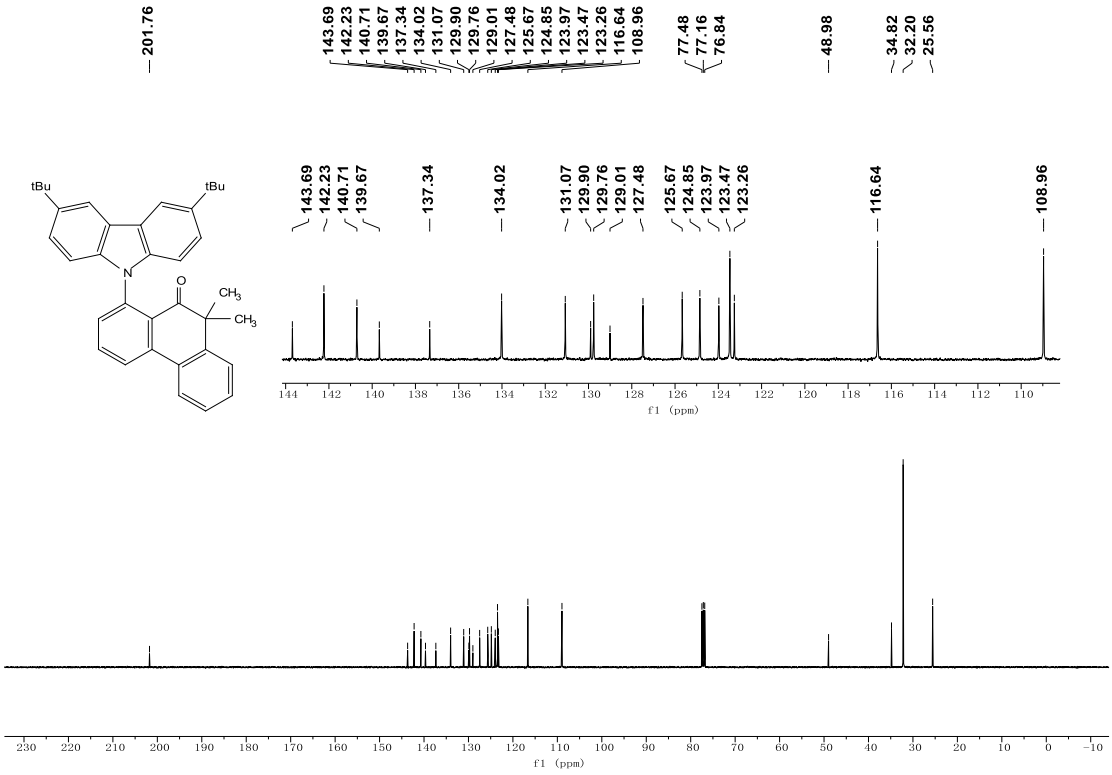


^{13}C NMR spectrum of 8-Cz-DMPO ($CDCl_3$)

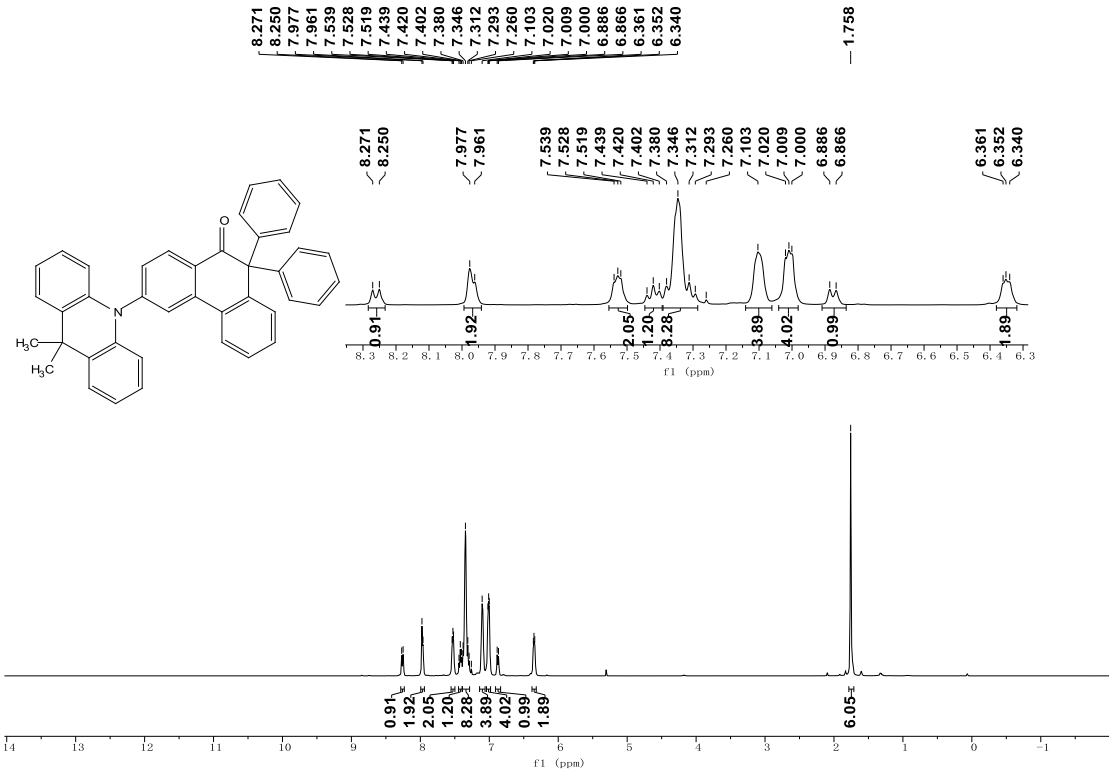


^{1}H NMR spectrum of 8-*t*BuCz-DMPO ($CDCl_3$)

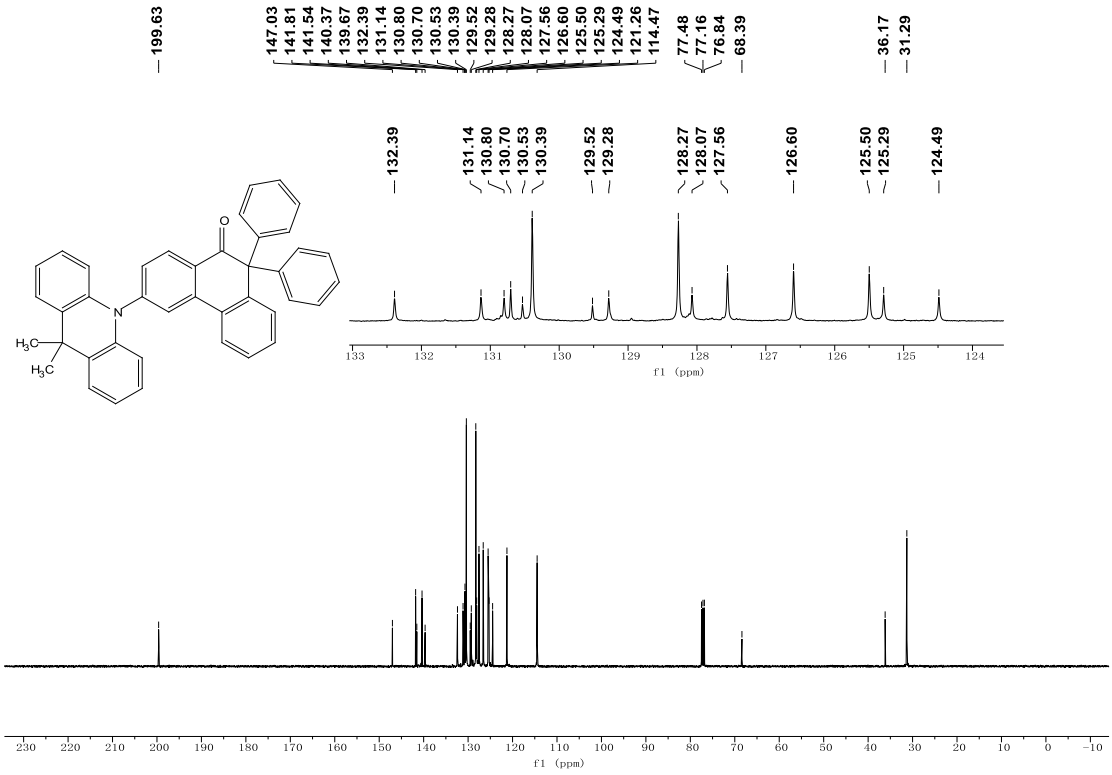
^{13}C NMR spectrum of 8-*t*BuCz-DMPO ($CDCl_3$)



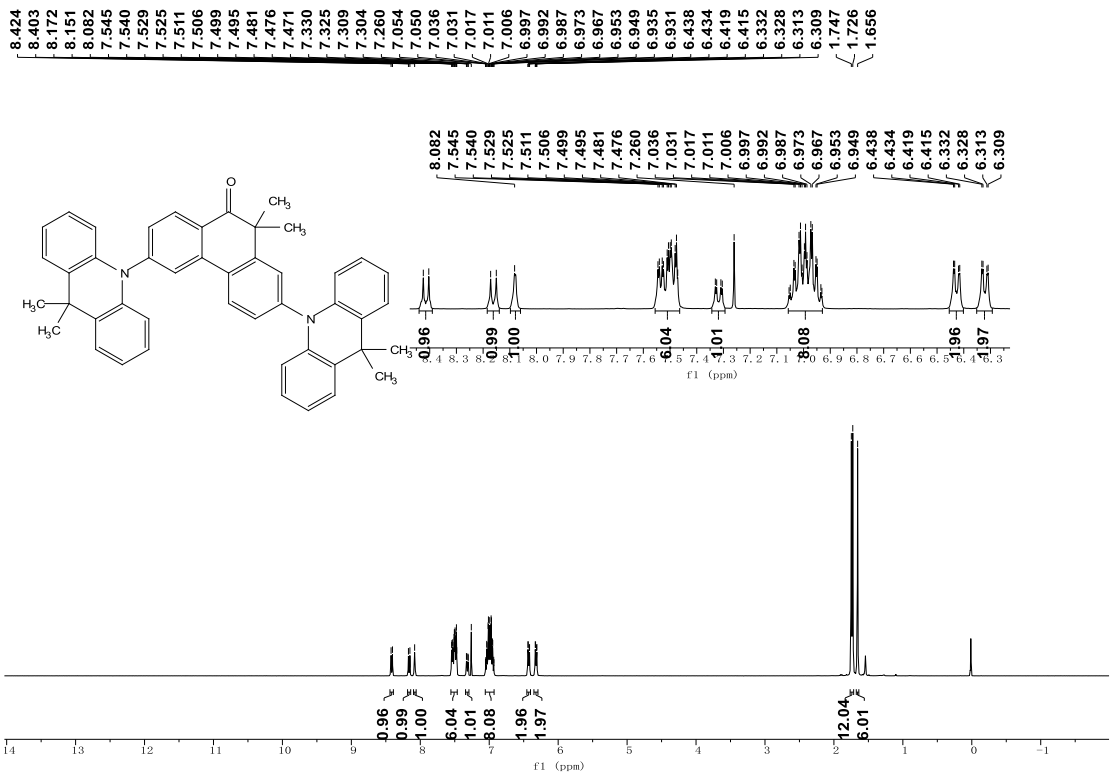
^{1}H NMR spectrum of 6-DMAC-DPPO ($CDCl_3$)



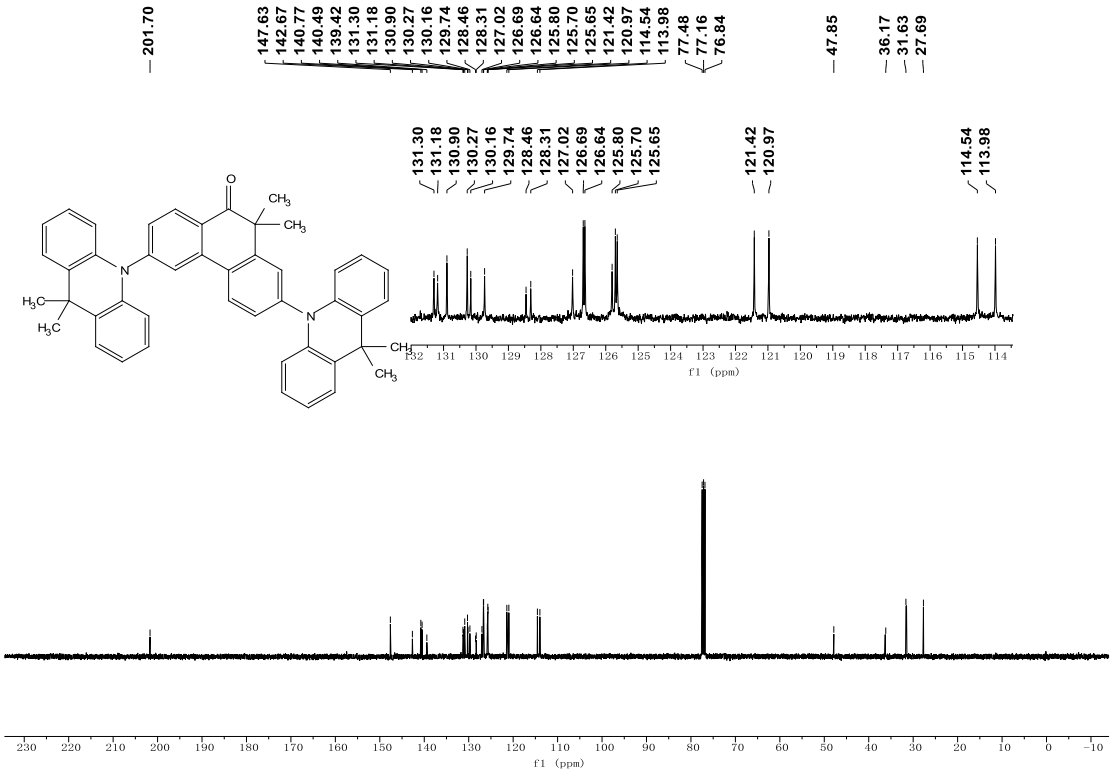
^{13}C NMR spectrum of 6-DMAC-DPPO ($CDCl_3$)



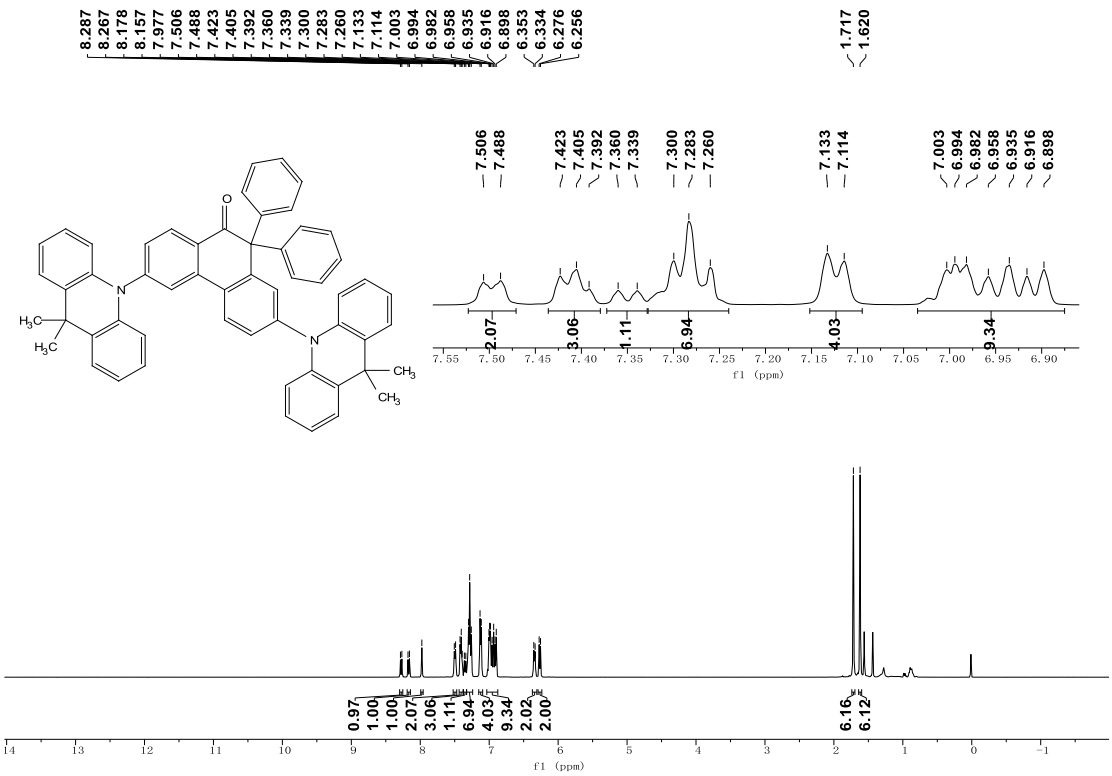
^{1}H NMR spectrum of 2,6-DMAC-DMPO ($CDCl_3$)



^{13}C NMR spectrum of 2,6-DMAC-DMPO ($CDCl_3$)



^{1}H NMR spectrum of 2,6-DMAC-DPPO ($CDCl_3$)



^{13}C NMR spectrum of 2,6-DMAC-DPPO ($CDCl_3$)