Supporting Information

A Catellani and *retro*-Diels-Alder strategy to access 1-amino phenanthrenes via *ortho*- and interannular C-H activations of 2-iodobiphenyls

Mingjie Sun, Xinyang Chen, Zichao Feng, Guobo Deng, Yuan Yang,* and Yun Liang*

National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, China.

E-mail: yuanyang@hunnu.edu.cn; yliang@hunnu.edu.cn.

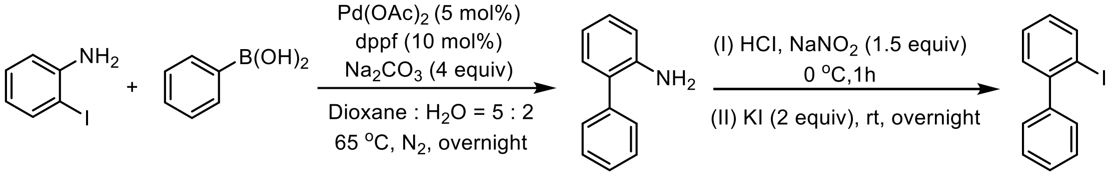
Table of Contents

1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instruments or Avance-400 instruments (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CD(H)Cl_3$ (7.26 ppm), ^{13}C NMR: $CD(H)Cl_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2 Synthetic Methods of Starting Materials

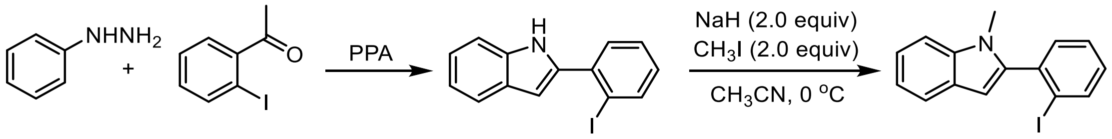
a) General Procedure for the Synthesis of Substrates 1a-1z, 1aa-1gg.[1]



Step I: Under nitrogen atmosphere, a 100 mL schlenk tube was added 2-iodoaniline (5.0 mmol, 1.09 g), phenylboronic acid (6.5 mmol, 0.79 g), $Pd(OAc)_2$ (0.25 mmol, 56.00 mg), dppf (0.5 mmol, 0.28 g), Na_2CO_3 (20.0 mmol, 2.12 g), 1,4-dioxane (15 mL) and water (6 mL). The mixture was heated in an oil bath at 65 °C overnight. After the completion of the reaction, it was allowed to attain to room temperature, then the reaction mixture was filtered and the filtrate diluted in ethyl acetate and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding 2-aminobiphenyls.

Step II: A solution of conc. HCl (36-38%; 2.5 mL) in water (10 mL) was added slowly to the prepared 2-aminobiphenyl (4.8 mmol, 0.81 g) at 0 °C in portions. After stirring for 1 h at 0 °C, the aqueous solution of $NaNO_2$ (7.2 mmol, 0.50 g) was added to the reaction mixture below 5 °C within 10 min and stirred for 1 h. Then an aqueous solution of KI (9.6 mmol, 1.59 g) in ice water (8 mL) was added and the reaction mixture was stirred at room temperature overnight. Ethyl acetate was added to the reaction mixture and the organic phase was treated with saturated $Na_2S_2O_3$ to decolorize. The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether) to give the desired 2-iodobiphenyls (0.87 mg, 65%) as a yellow oil. Procedure for the synthesis of substrates **1b-1z, 1aa-1gg** is similar to **1a**.

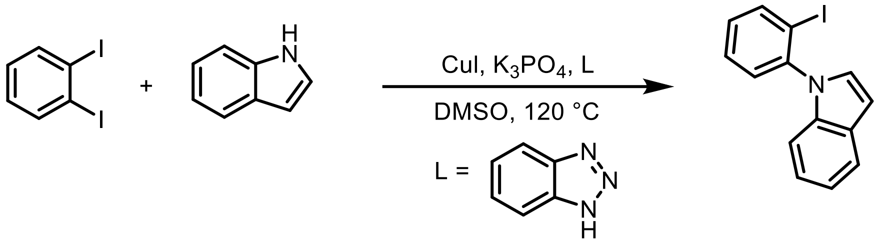
b) General Procedure for the Synthesis of Substrates 1hh.[2]



A mixture of 2-iodoacetophenone (5.0 mmol, 1.23 g), phenyl hydrazine (6.0 mmol, 0.65 g) and polyphosphoric acid PPA (10.00 g) was added to a Schlenk tube equipped with a stir-bar and stirred at 110 °C for 5 h. After the completion of the reaction, the residue was quenched with ice water and extracted into ethyl acetate. The organic phases were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc) to give the corresponding substituted 2-(2-iodophenyl)-1*H*-indole.

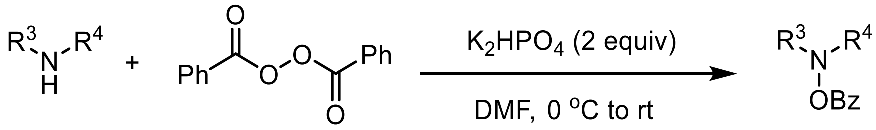
NaH (10.0 mmol, 0.24 g) was added to a solution of the above product in CH_3CN (10 mL) at 0 °C in portions. After stirring for 20 min at 0 °C, CH_3I (10.0 mmol, 1.42 g) was added dropwise and the reaction mixture was allowed to room temperature and stirred for another 2 h. After completion of the reaction (monitored by TLC), the residue was quenched with water and extracted into ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and the solution was evaporated to dryness. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 10:1) to provide **1hh.**

c) General Procedure for the Synthesis of Substrates 1ii.[3]



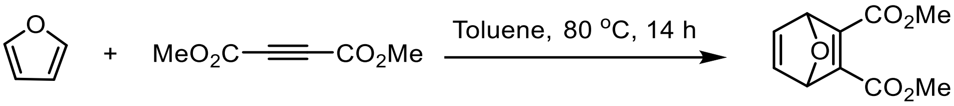
CuI (0.5 mmol, 95.00 mg) and benzotriazole (1.0 mmol, 0.12 g) ligand were added to a 5 mL round bottom flask containing the 1,2-diiodobenzene (5.0 mmol, 1.65 g), indole (5.5 mmol, 0.64 g), and K_3PO_4 (10.0 mmol, 2.12 g) in 20.0 mL of DMSO. The flask was sealed with a cap containing a PTFE septum. The mixture was heated at 120 °C until the 1,2-diiodobenzene were consumed, as determined by TLC. The reaction mixture was washed with ethyl acetate and water. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo and the crude residue was purified by column chromatography on silica gel using a mixture of hexane and ethylacetate as eluent.

d) General Procedure for the Synthesis of Substrates 2a-2g.[4]



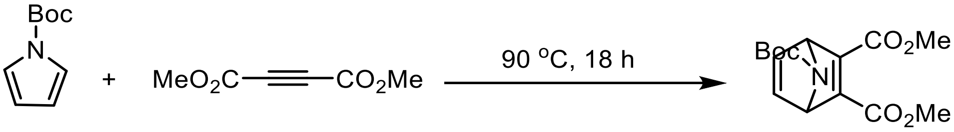
To a reaction flask under argon was added dipotassium hydrogen phosphate (20.0 mmol, 3.48 g) and benzoyl peroxide (10.0 mmol, 2.42 g), followed by DMF (20 mL). With vigorous stirring, the secondary amine (15.0 mmol) was added, and the resulting mixture stirred at 0 °C or room temperature until complete conversion of the benzoyl peroxide, as indicated by TLC. After the reaction was completed, water was added and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was washed with water and brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then chromatographed on silica gel to afford the desired compound.

e) General Procedure for the Synthesis of Substrates 3b.[5]



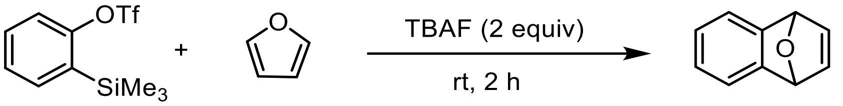
A soln of furan (2.0 mmol, 0.15 mL) and dimethyl acetylenedicarboxylate (2.2 mmol, 0.26 mL) in toluene (2 mL), was stirred at 80 °C for 14 h. The solvent was evaporated under vacuum and the crude product was purified by column chromatography [petroleum ether : ethyl acetate = 20:1] to afford the product **3b**.

f) General Procedure for the Synthesis of Substrates 3c.[5]



N-Boc-pyrrole (2.0 mmol, 0.33 g) and dimethyl acetylenedicarboxylate (16.0 mmol, 0.23 g) were combined and heated at 90 °C for 18 h. The mixture became dark brown. The reaction mixture was cooled to room temperature. And some excess alkyne was removed under high vacuum. The dark brown oil was purified by column chromatography [petroleum ether : ethyl acetate = 10:1] to afford the product **3c**.

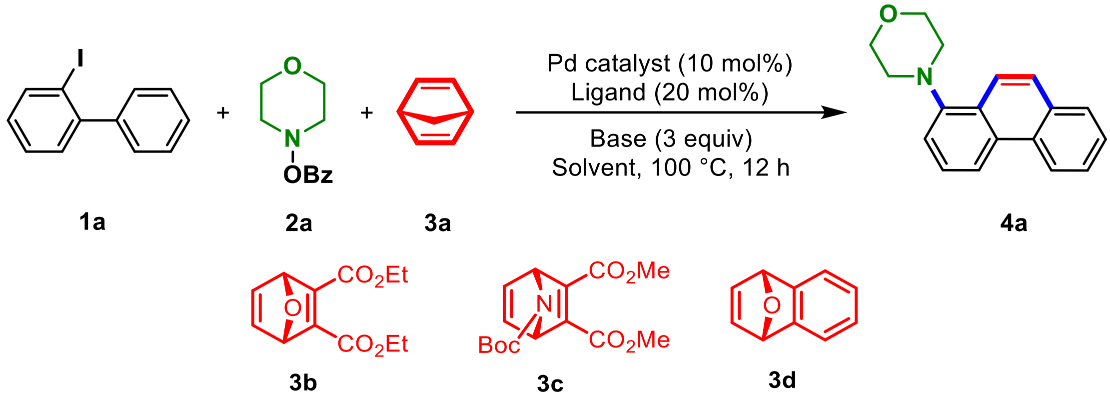
g) General Procedure for the Synthesis of Substrates 3d.[6]



Arylsilyl triflate (2.0 mmol, 0.60 g) was dissolved in furan (0.8 mL) and placed in a 2 mL vial. TBAF (2 equiv, 1 M in THF) was added into the reaction mixture at rt. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at rt for 2 h. The reaction was quenched by adding saturated aqueous ammonium chloride. The reaction mixture was extracted with diethyl ether and concentrated in vacuo to afford the crude mixture, which was purified by column chromatography [petroleum ether : ethyl acetate = 10:1] to afford the product **3d**.

3 Typical Procedures

a) Table S1. Screening of Optimal Reaction Conditions.

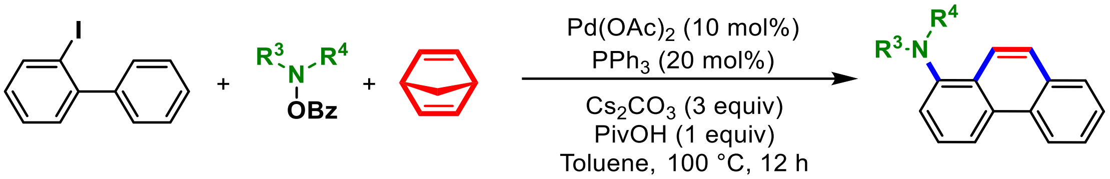


Entry	Pd catalyst	Ligand	Base	Solvent	Yield/%
1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	63
2	$PdCl_2$	PPh_3	Cs_2CO_3	Toluene	37
3	$[Pd(\pi\text{-ally})Cl]_2$	PPh_3	Cs_2CO_3	Toluene	34
4	$Pd(CF_3COO)_2$	PPh_3	Cs_2CO_3	Toluene	8
5	$Pd(dba)_2$	PPh_3	Cs_2CO_3	Toluene	30
6	$Pd(PPh_3)_4$	PPh_3	Cs_2CO_3	Toluene	55
7	$Pd(OAc)_2$	$(4\text{-OMeC}_6H_4)_3P$	Cs_2CO_3	Toluene	44
8	$Pd(OAc)_2$	TFP	Cs_2CO_3	Toluene	18
9	$Pd(OAc)_2$	$(4\text{-FC}_6H_4)_3P$	Cs_2CO_3	Toluene	15
10	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	Toluene	19
11	$Pd(OAc)_2$	dppb	Cs_2CO_3	Toluene	54
12	$Pd(OAc)_2$	PPh_3	K_2CO_3	Toluene	trace
13	$Pd(OAc)_2$	PPh_3	LiO^tBu	Toluene	trace
14	$Pd(OAc)_2$	PPh_3	NaOAc	Toluene	trace
15	$Pd(OAc)_2$	PPh_3	Et_3N	Toluene	trace
16	$Pd(OAc)_2$	PPh_3	CsOPiv	Toluene	trace
17	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	MeCN	20
18	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Dioxane	33
19	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	36
20	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Mesitylene	48
21[c]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	53
22[d]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	62

23[e]	**Pd(OAc)$_2$**	**PPh$_3$**	**Cs$_2$CO$_3$**	**Toluene**	**82**
24[f]	Pd(OAc)$_2$	PPh$_3$	Cs$_2$CO$_3$	Toluene	52
23[g]	Pd(OAc)$_2$	PPh$_3$	Cs$_2$CO$_3$	Toluene	54
23[h]	Pd(OAc)$_2$	PPh$_3$	Cs$_2$CO$_3$	Toluene	trace
23[i]	Pd(OAc)$_2$	PPh$_3$	Cs$_2$CO$_3$	Toluene	70

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), NBD (3.0 equiv), Pd catalyst (10 mol%), Ligand (20 mol%), Base (3.0 equiv), and Solvent (2 mL) at 100 °C under N$_2$ for 12 h. [b] Isolated yield. [c] 90 °C, [d] 110 °C. [e] Trimethylacetic acid was added (1.0 equiv). [f] Trimethylacetic acid was added (0.4 equiv). [g] **3b** instead of **3a**. [h] **3c** instead of **3a**. [i] **3d** instead of **3a**.

b) General Procedure for the Synthesis of 1-Amino Phenanthrenes Derivatives.



1a **2a** **3a**

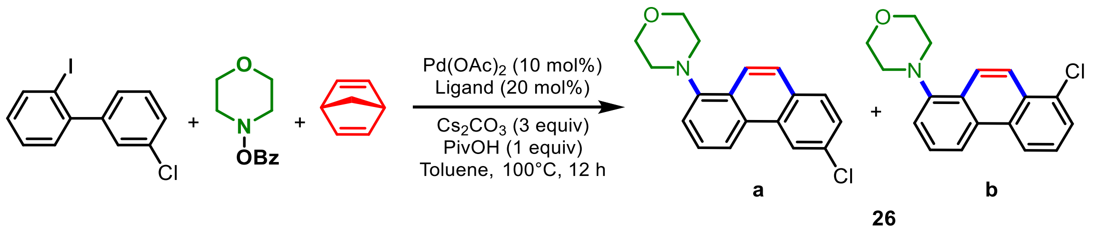
To a Schlenk tube were added Pd(OAc)$_2$ (0.02 mmol, 10 mol%, 4.50 mg), PPh$_3$ (20 mol%), Cs$_2$CO$_3$ (0.6 mmol, 3.0 equiv, 195.40 mg), PivOH (0.2 mmol, 1.0 equiv, 20.40 mg), 2-Iodobiphenyl (0.2 mmol, 1.0 equiv), morpholino benzoate (0.6 mmol, 3.0 equiv), NBD (0.6 mmol, 3.0 equiv), and Toluene (2 mL). Then the tube was charged with nitrogen, and was stirred at 100 ºC (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography to give target product.

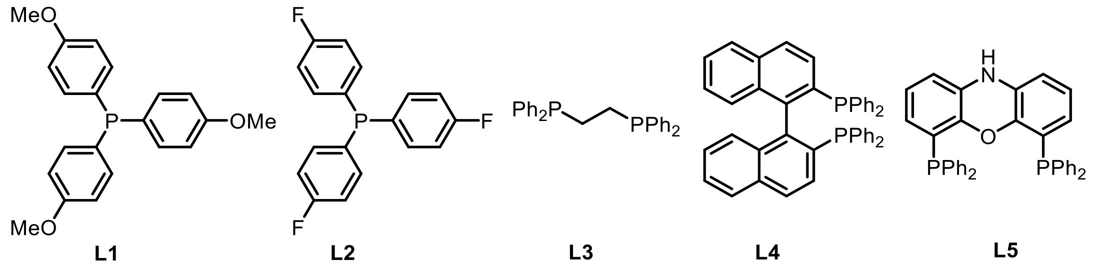
c) Gram-scale experiment of 1a.

To a Schlenk tube were added Pd(OAc)$_2$ (0.36 mmol, 10 mol%, 82.80 mg), PPh$_3$ (0.72 mmol, 20 mol%, 194.40 mg), Cs$_2$CO$_3$ (10.8 mmol, 3.0 equiv, 3.52 g), PivOH (3.6 mmol, 1.0 equiv, 367.20 mg), 2-Iodobiphenyl (3.6 mmol, 1.01 g), morpholino benzoate (10.8 mmol, 2.24 g), NBD (10.8 mmol, 993.60 mg), and Toluene (30 mL). Then the tube was charged with nitrogen, and was stirred at 100 ºC (oil bath temperature) for the indicated time until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography to afford the product **4** (482.87 mg, 51% yield).

d) Regioselective experiment of substrate 1q.

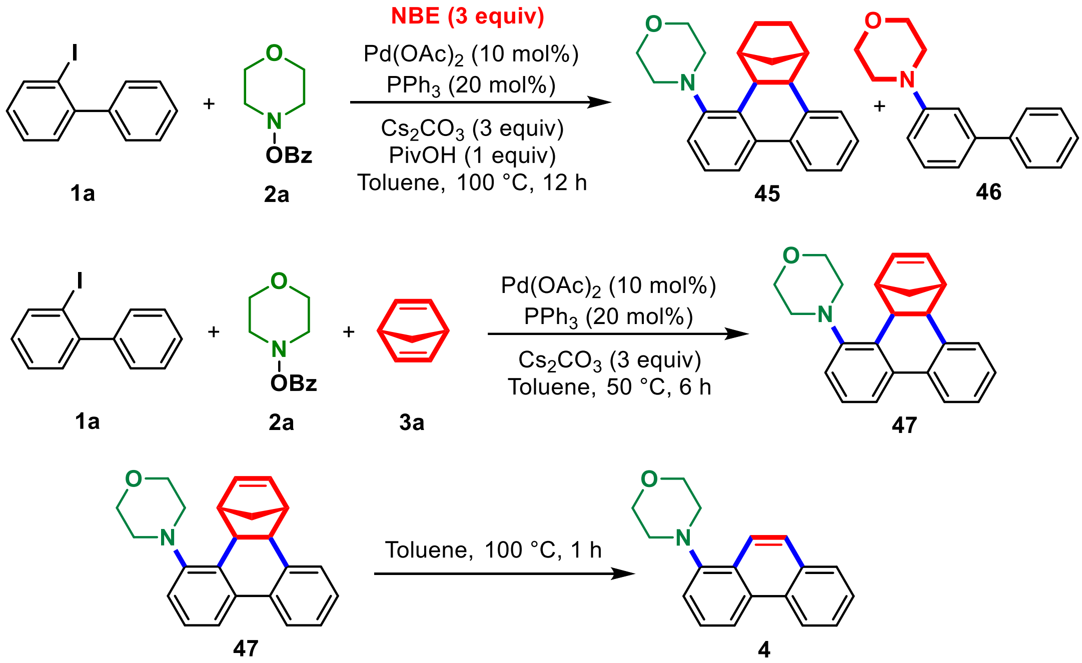
We attempted some ligands (**L1-L5**) to improve the regioselectivity of C-H activation. In terms of yield, their reaction efficiency was lower than PPh_3. For regioselectivity, both electron-rich (**L1**) and electron-deficient monodentate ligands (**L2**) have no effect on the ratio of isomers **a** and **b**. Bidentate ligands can improve regioselectivity, in which the flexible ligand **L3** promoted the formation of **b**, whereas rigid ligand **L5** was easier to afford compound **a**.





Entry	Ligand	Yield **26** (%)	Ratio of **a**:**b**
1	**L1**	44	1:1
2	**L2**	31	1:1
3	**L3**	56	2:3
4	**L4**	Trace	-
5	**L5**	39	1.6:1

4 Mechanistic Studies

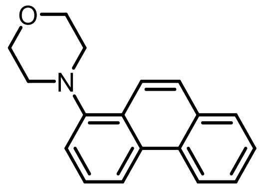


To a 25 mL Schlenk tube was added Pd(OAc)$_2$ (0.02 mmol, 10 mol%, 4.50 mg), PPh$_3$ (20 mol%), Cs$_2$CO$_3$ (0.6 mmol, 3.0 equiv, 195.40 mg), 2-Iodobiphenyl (0.2 mmol, 1.0 equiv), morpholino benzoate (0.6 mmol, 3.0 equiv), NBE (0.6 mmol, 3.0 equiv) and Toluene (2 mL). Then the tube was charged with nitrogen, and was stirred at 100 ºC (oil bath temperature) for 12 h until complete consumption of starting material as monitored by TLC analysis. The reaction mixture was cooled to room temperature. Once cooled, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography to give 4-((1S,4R)-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylen-5-yl)morpholine **45** (13.24 mg, 20%) and 4-([1,1'-biphenyl]-3-yl)morpholine **46** (23.90 mg, 50%).

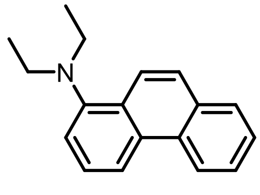
To a 25 mL Schlenk tube was added Pd(OAc)$_2$ (0.02 mmol, 10 mol%, 4.50 mg), PPh$_3$ (20 mol%), Cs$_2$CO$_3$ (0.6 mmol, 3.0 equiv, 195.40 mg), 2-Iodobiphenyl (0.2 mmol, 1.0 equiv), morpholino benzoate (0.6 mmol, 3.0 equiv), NBD (0.6 mmol, 3.0 equiv) and Toluene (2 mL). Then the tube was charged with nitrogen, and was stirred at 50 ºC (oil bath temperature) for 6 h until complete consumption of starting material as monitored by TLC analysis. The reaction mixture was cooled to room temperature. Once cooled, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography to give (tetrahydro-1,4-methanotriphenylen-5-yl) morpholine **47** (11.85 mg, 18%).

To a 25 mL Schlenk tube was added (tetrahydro-1,4-methanotriphenylen-5-yl) morpholine **47** (0.1 mmol, 32.92 mg), and Toluene (1 mL). Then the tube was charged with nitrogen, and was stirred at 100 °C (oil bath temperature) for 1 h until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silica-gel column chromatography to give product **4** (25.26 mg, 96%).

5 Characterization Data

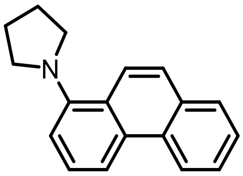


4-(phenanthren-1-yl)morpholine (4)[4]: white solid, isolated yield 82% (43.13 mg), 45% (23.67 mg, 2-bromo-1,1'-biphenyl was used); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.65 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.63-7.56 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 3.98 (t, *J* = 4.0 Hz, 4H), 3.10 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.9, 131.8, 131.6, 130.6, 128.4, 126.9, 126.6, 126.5, 126.4, 126.3, 123.0, 122.0, 118.3, 116.0, 67.4, 53.5.

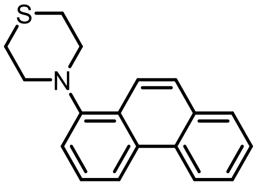


N,N-diethylphenanthren-1-amine (5): yellow liquid, isolated yield 62% (31.10 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.69 (d, *J* =

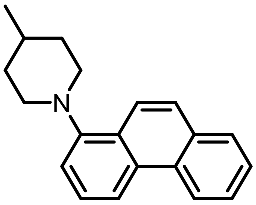
8.0 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.64-7.57 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H), 3.22 (q, *J* = 7.0 Hz, 4H), 1.06 (t, *J* = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.6, 131.9, 131.6, 130.6, 129.7, 128.3, 126.4, 126.2, 126.1, 125.9, 123.1, 122.9, 119.4, 117.9, 48.2, 12.3. HRMS (ESI) m/z calcd for $C_{18}H_{20}N^+$ $(M+H)^+$ 250.1590, found 250.1589.



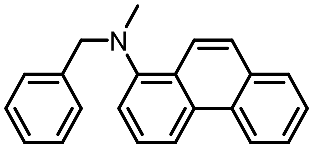
1-(phenanthren-1-yl)pyrrolidine (6): brown solid, isolated yield 45% (22.23 mg); mp: 60.5-63.5 °C (uncorrected); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 1H), 7.71 (d, *J* = 9.5 Hz, 1H), 7.64-7.53 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.36 (s, 4H), 2.05 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.4, 131.8, 131.7, 130.6, 128.2, 126.5, 126.4, 126.2, 126.0, 124.9, 123.4, 123.2, 116.1, 113.3, 52.9, 24.7.HRMS (ESI) m/z calcd for $C_{18}H_{18}N^+$ $(M+H)^+$ 248.1434, found 248.1432.



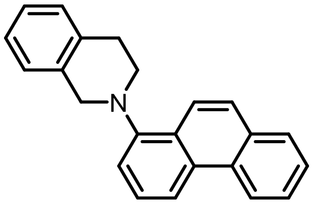
4-(phenanthren-1-yl)thiomorpholine (7): yellow liquid, isolated yield 52% (20.02 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.67-7.59 (m, 3H), 7.27 (dd, *J* = 7.5, 1.0 Hz, 1H), 3.78-2.34 (m, 8H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.3, 131.8, 131.6, 130.5, 128.4, 127.3, 126.5, 126.5, 126.5, 126.4, 122.9, 121.9, 118.4, 117.0, 55.6, 28.6. HRMS (ESI) m/z calcd for $C_{18}H_{18}NS^+$ $(M+H)^+$ 280.1154, found 280.1154.



4-methyl-1-(phenanthren-1-yl)piperidine (8): white solid, isolated yield 80% (44.00 mg); mp: 95.9-98.0 ^{o}C (uncorrected); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 8.69 (d, *J* = 8.2 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 9.1 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.66-7.58 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 3.40 (d, *J* = 11.5 Hz, 2H), 2.80 (t, *J* = 10.0 Hz, 2H), 1.84 (d, *J* = 9.3 Hz, 2H), 1.67-1.57 (m, 3H), 1.10 (d, *J* = 5.5 Hz, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ =151.5, 131.9, 131.6, 130.7, 128.4, 127.3, 126.6, 126.4, 126.3, 126.0, 123.1, 122.6, 117.5, 115.9, 55.7, 54.2, 35.1, 31.1, 28.6, 22.2. HRMS (ESI) m/z calcd for $C_{20}H_{22}N^{+}$ (M+H)$^{+}$ 276.1747, found 276.1745.

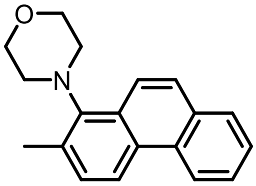


N-benzyl-N-methylphenanthren-1-amine (9): yellow liquid, isolated yield 53% (31.48 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 8.75 (d, *J* = 8.5 Hz, 1H), 8.50-8.44 (m, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.84-7.83 (m, 1H), 7.72-7.68 (m, 1H), 7.67-7.62 (m, 2H), 7.52-7.50 (m, 2H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 2H), 4.36 (s, 2H), 2.87 (s, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ = 150.8, 138.6, 131.9, 131.6, 130.6, 128.4, 128.3, 128.3, 127.3, 127.0, 126.4, 126.4, 126.3, 126.2, 123.0, 122.4, 117.8, 117.0, 61.7, 41.9. HRMS (ESI) m/z calcd for $C_{22}H_{20}N^{+}$ (M+H)$^{+}$ 298.1590, found 298.1591.

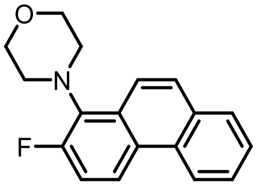


2-(phenanthren-1-yl)-1,2,3,4-tetrahydroisoquinoline (10): brown solid, isolated yield 53% (43.26 mg); mp: 90.4-92.8 ^{o}C (uncorrected); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 8.71 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.68-7.60 (m, 3H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.27-7.25 (m, 2H), 7.24-7.21 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 1H), 4.35 (s, 2H), 3.67-3.41 (m, 2H), 3.26-2.89 (m, 2H); **^{13}C NMR** (125

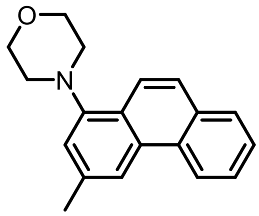
MHz, $CDCl_3$) δ = 150.3, 135.3, 134.5, 131.9, 131.6, 130.6, 129.0, 128.4, 127.3, 126.6, 126.5, 126.4, 126.4, 126.3, 126.3, 125.8, 123.0, 122.4, 118.1, 116.3, 55.6, 51.6, 29.7. HRMS (ESI) m/z calcd for $C_{23}H_{20}N^+$ $(M+H)^+$ 310.1590, found 310.1586.



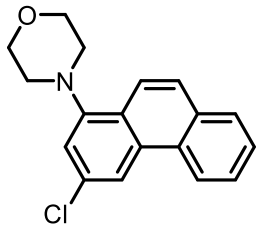
4-(2-methylphenanthren-1-yl)morpholine (11): white solid, isolated yield 20% (11.08 mg); mp: 116.6-120.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.65 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.41 (d, *J* = 9.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.64-7.56 (m, 2H), 7.44 (d, J = 8.5 Hz, 1H), 4.00-3.94 (m, 4H), 3.51-3.47 (m, 2H), 3.13 (d, *J* = 12.0 Hz, 2H), 2.59 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 145.3, 134.3, 131.4, 131.2, 130.5, 130.4, 130.0, 128.3, 126.7, 126.4, 126.2, 122.9, 122.6, 120.3, 68.2, 50.5, 19.8. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO^+$ $(M+H)^+$ 278.1539, found 278.1538.



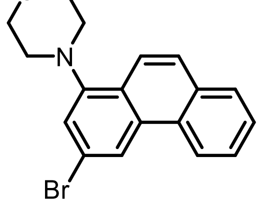
4-(2-fluorophenanthren-1-yl)morpholine (14): white solid, isolated yield 38% (21.36 mg); mp: 96.7-98.6 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 8.0 Hz, 1H), 8.49 (dd, *J* = 9.5, 5.0 Hz, 1H), 8.42 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 11.5, 9.0 Hz, 1H), 4.00-3.92 (m, 4H), 3.60 (t, *J* = 11.0 Hz, 2H), 2.96 (d, *J* = 11.5 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.9 (d, C-F, $^1J_{C\text{-}F}$ = 248.1 Hz), 133.2 (d, C-F, $^3J_{C\text{-}F}$ = 10.0 Hz), 131.6, 131.4, 130.2, 128.5, 127.9, 127.8, 126.8, 126.4, 122.6, 122.1 (d, C-F, $^4J_{C\text{-}F}$ = 4.6 Hz), 121.5 (d, C-F, $^3J_{C\text{-}F}$ = 9.1 Hz,), 116.3 (d, C-F, $^2J_{C\text{-}F}$ = 23.3 Hz), 67.9, 51.8, 51.8. HRMS (ESI) m/z calcd for $C_{18}H_{17}FNO^+$ $(M+H)^+$ 282.1289, found 282.1288.



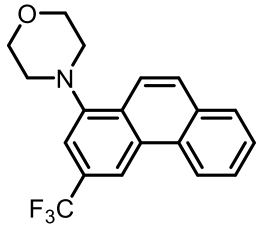
4-(3-methylphenanthren-1-yl)morpholine (16): white solid, isolated yield 70% (38.78 mg); mp: 118.0-121.3 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H), 8.17 (d, *J* = 9.5 Hz 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.65-7.58 (m, 2H), 7.11 (s, 1H), 4.02 (t, *J* = 4.5 Hz, 4H), 3.14 (s, 4H), 2.63 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.9, 136.3, 132.0, 131.7, 130.3, 128.3, 126.4, 126.2, 125.4, 124.8, 122.9, 121.9, 118.1, 117.7, 67.4, 53.6, 22.4. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO^+$ $(M+H)^+$ 278.1539, found 278.1539.



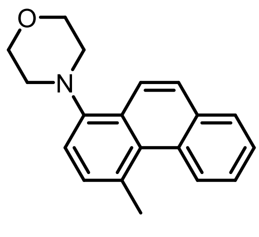
4-(3-chlorophenanthren-1-yl)morpholine (17): yellow solid, isolated yield 67% (39.79 mg); mp: 112.4-114.5 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 8.0 Hz, 1H), 8.39 (s, 1H), 8.10 (d, *J* = 9.5 Hz, 1H), 7.89 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.66-7.61 (m, 2H), 7.19 (s, 1H), 4.00 (t, *J* = 4.0 Hz, 4H), 3.11 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =151.2, 132.6, 132.5, 132.2, 129.6, 128.4, 127.1 126.7, 126.5, 125.2, 123.0, 121.6, 117.9, 116.9, 67.2, 53.4. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClNO^+$ $(M+H)^+$ 298.0993, found 298.0993.



4-(3-bromophenanthren-1-yl)morpholine (18): yellow solid, isolated yield 42% (28.64 mg); mp: 139.8-141.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.59-8.57 (m, 2H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.67-7.61 (m, 2H), 7.33 (s, 1H), 4.00 (t, *J* = 4.0 Hz, 4H), 3.12 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.3, 132.9, 132.2, 129.6, 128.5, 127.2, 126.8, 126.7, 125.6, 123.0, 121.7, 121.1, 120.9, 119.7, 67.3, 53.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}BrNO^+$ $(M+H)^+$ 342.0488, found 342.0488.

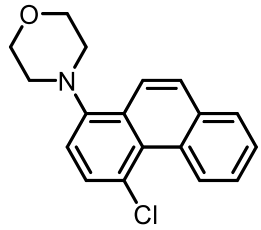


4-(3-(trifluoromethyl)phenanthren-1-yl)morpholine (19): white solid, isolated yield 80% (53.00 mg); mp: 114.4-117.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.71-7.64 (m, 2H), 7.41 (s, 1H), 4.03 (t, *J* = 4.0 Hz, 4H), 3.16 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =150.8, 132.0, 131.2, 130.5, 128.8, 128.6, 128.5, 128.2 (d, C-F, $^2J_{C\text{-}F}$ = 31.8 Hz), 124.6 (q, C-F, $^1J_{C\text{-}F}$ = 270.0 Hz), 123.5, 123.0, 121.5, 121.3, 115.6 (q, C-F, $^4J_{C\text{-}F}$ = 4.25 Hz), 111.7 (q, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 67.2, 53.4. HRMS (ESI) m/z calcd for $C_{19}H_{17}F_3NO^+$ $(M+H)^+$ 332.1257, found 332.1256.

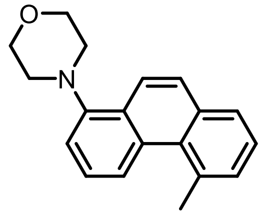


4-(4-methylphenanthren-1-yl)morpholine (20): white solid, isolated yield 78% (43.21 mg); mp: 50.2-52.0 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.88 (t, *J* = 4.0 Hz, 1H), 8.35(d, *J* = 9.0 Hz, 1H), 7.94 (t, *J* = 5.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.64-7.60 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 4.5 Hz, 4H), 3.11 (s, 7H); **^{13}C NMR** (125

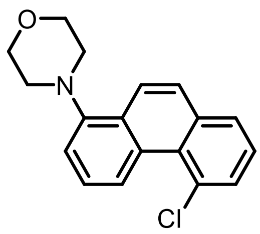
MHz, $CDCl_3$) δ =148.2, 133.3, 131.8, 131.4, 130.9, 130.7, 128.3, 128.3, 127.5, 126.5, 125.8, 125.2, 122.5, 115.5, 67.5, 53.6, 26.9. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO^+$ $(M+H)^+$ 278.1539, found 278.1539.



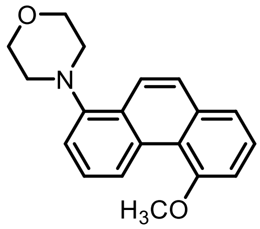
4-(4-chlorophenanthren-1-yl)morpholine (21): white solid, isolated yield 77% (46.00 mg); mp: 90.5-92.5 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.84 (m, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 7.90 (m, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.67-7.63 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.99 (t, *J* = 4.0 Hz, 4H), 3.08 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =148.9, 133.3, 130.3,129.9, 129.7, 128.5, 128.2, 127.6, 127.3, 126.9, 126.5, 125.5, 122.0, 116.2, 67.3, 53.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClNO^+$ $(M+H)^+$ 298.0993, found 298.0993.



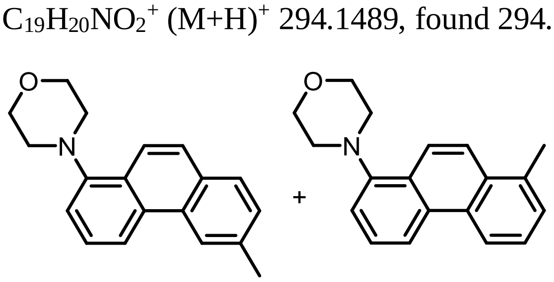
4-(5-methylphenanthren-1-yl)morpholine (22): white solid, isolated yield 73% (40.44 mg); mp: 64.5-66.2 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 8.5 Hz, 1H), 8.27 (d, *J* = 9.5 Hz, 1H), 7.79 (t, *J* = 4.5 Hz, 1H), 7.74 (d, *J* = 9.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 5.0 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 4.02 (t, *J* = 4.5 Hz, 4H), 3.15 (s, 3H), 3.13 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =149.6, 135.4, 133.5, 132.9, 131.1, 130.6, 128.4, 127.4, 127.1, 125.9, 125.2, 123.3, 122.0, 115.2, 67.5, 53.6, 27.2. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO^+$ $(M+H)^+$ 278.1539, found 278.1539.



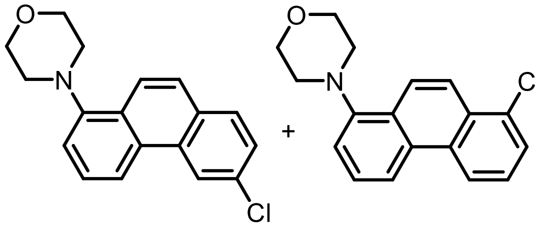
4-(5-chlorophenanthren-1-yl)morpholine (23): white solid, isolated yield 76% (45.14 mg); mp: 91.8-92.3 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.57 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 4.01 (t, J = 4.5 Hz, 4H), 3.12 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =149.5, 134.9, 131.6, 130.9, 130.5, 128.4, 127.9, 127.8, 126.6, 126.3, 125.6, 123.2, 122.9, 116.4, 67.4, 53.6. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClNO^+$ $(M+H)^+$ 298.0993, found 298.0993.



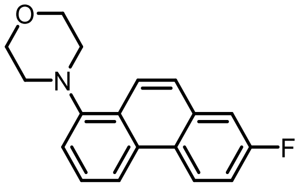
4-(5-methoxyphenanthren-1-yl)morpholine (24): white solid, isolated yield 80% (46.88 mg); mp: 100.8-103.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.48 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.56-7.55 (m, 2H), 7.30 (d, J = 7.5 Hz, 1H), 7.17-7.13 (m, 1H), 4.12 (s, 3H), 4.03 (t, J = 4.5 Hz, 4H), 3.13 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.6, 149.2, 134.4, 131.5, 127.7, 126.6, 126.5, 126.1, 124.3, 122.7, 121.3, 121.1, 115.6, 108.1, 67.4, 55.6, 53.6. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_2^+$ $(M+H)^+$ 294.1489, found 294.1488.



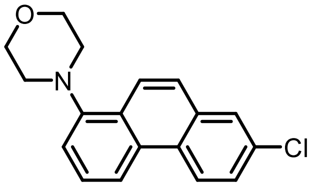
4-(6-methylphenanthren-1-yl)morpholine and 4-(8-methylphenanthren-1-yl)morpholine (25): white solid, isolated yield 74% (40.99 mg, 6:1); mp: 105.4-106.2 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); Major isomer **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.59 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 3.97 (t, *J* = 4.5 Hz, 4H), 3.09 (s, 4H), 2.59 (s, 3H) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.9, 136.1, 131.4, 130.6, 129.8, 128.3, 128.2, 127.1, 126.3, 126.2, 122.7, 120.9, 118.3,115.8, 67.4, 53.5, 22.1. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO^+$ $(M+H)^+$ 278.1539, found 278.1539.



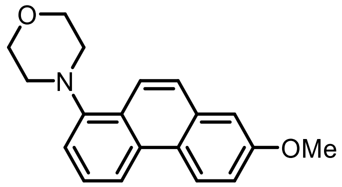
4-(6-chlorophenanthren-1-yl)morpholine and 4-(8-chlorophenanthren-1-yl)morpholine (26): brown liquid, isolated yield 72% (42.77 mg, 1:1); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.26-8.23 (m, 2H), 8.19 (d, *J* = 9.5 Hz, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.63-7.61 (m, 2H), 7.55-7.42 (m, 4H), 7.19 (dd, *J* = 7.5 Hz, 2.5 Hz, 2H), 3.95 (t, *J* = 4.0 Hz, 8H), 3.04 (s, 8H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.0, 149.9, 132.5, 132.3, 132.1, 131.6, 131.2, 130.6, 129.9, 129.7, 129.0, 127.1, 127.0, 126.9, 126.9, 126.80, 126.7, 126.2, 125.5, 123.3, 122.6, 122.3, 121.9, 121.8, 118.4, 118.2, 116.5, 116.3, 67.3, 67.2, 53.4. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClNO^+$ $(M+H)^+$ 298.0993, found 298.0993.



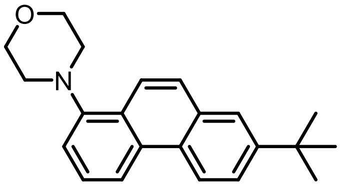
4-(7-fluorophenanthren-1-yl)morpholine (27): white solid, isolated yield 85% (48.01 mg); mp: 97.1-98.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.59 (dd, *J* = 9.0, 5.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.21 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.49 (dd, J = 9.0, 2.5 Hz, 1H), 7.33 (td, J = 8.5, 2.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 3.98 (t, J = 4.5 Hz, 4H), 3.08 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 161.2 (d, C-F, $^{1}J_{C\text{-}F}$ = 244.9 Hz), 150.2, 133.2 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 131.5, 127.2, 126.9, 126.5, 125.5 (d, C-F, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 125.3 (d, C-F, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 123.3, 118.1, 115.8, 115.4 (d, C-F, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 112.3 (d, C-F, $^{2}J_{C\text{-}F}$ = 20.1 Hz), 67.4, 53.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}FNO^+$ $(M+H)^+$ 282.1289, found 282.1288.



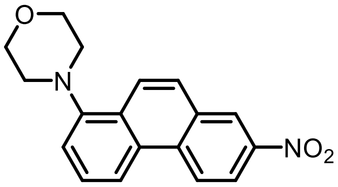
4-(7-chlorophenanthren-1-yl)morpholine (28): yellow solid, isolated yield 82% (48.71 mg); mp: 78.8-81.3 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H), 8.24 (d, J = 9.5 Hz, 1H), 7.86 (s, 1H), 7.65 (d, J = 9.0Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.56 (dd, J = 9.0 Hz, 2.0 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 4.01(t, J = 4.0 Hz, 4H), 3.12 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.1, 132.8, 132.3, 131.3, 128.9, 127.3, 127.0, 126.8(2C), 125.2, 124.7, 123.3, 118.2, 116.3, 67.4, 53.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}ClNO^+$ $(M+H)^+$ 298.0993, found 298.0993.



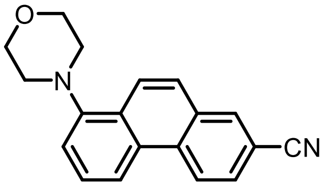
4-(7-methoxyphenanthren-1-yl)morpholine (29): yellow solid, isolated yield 57% (33.40 mg); mp: 123.3-125.0 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.28-7.25 (m, 2H), 7.20 (d, J = 7.5 Hz, 1H), 4.01 (t, J = 4.0 Hz, 4H), 3.96 (s, 3H), 3.13 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.2, 150.0, 133.2, 131.8, 126.7, 125.9, 125.9, 124.9, 124.6, 122.6, 117.9, 117.1, 115.0, 108.2, 67.4, 55.4, 53.6. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_2^+$ $(M+H)^+$ 294.1489, found 294.1488.



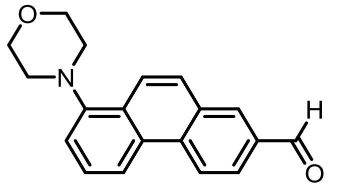
4-(7-(tert-butyl)phenanthren-1-yl)morpholine (30): white solid, isolated yield 72% (45.94 mg); mp: 115.7-117.2 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.60 (d, *J* = 8.5 Hz, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 9.5 Hz, 1H), 7.84 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.13 (s, 4H), 1.46 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.9, 149.4, 131.7, 131.6, 128.4, 126.7, 126.6, 126.4, 124.8, 124.0, 122.8, 121.8, 118.2, 115.5, 67.5, 53.6, 34.7, 31.3. HRMS (ESI) m/z calcd for $C_{22}H_{26}NO^+$ $(M+H)^+$ 320.2009, found 320.2008.



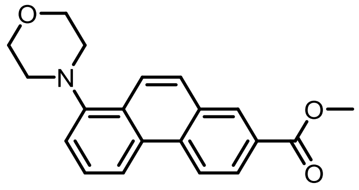
4-(7-nitrophenanthren-1-yl)morpholine (31): yellow solid, isolated yield 52% (32.03 mg); mp: 193.4-195.0 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.78 (d, *J* = 2.0 Hz, 1H), 8.76 (d, *J* = 9.5 Hz, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.38 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.36 (d, *J* = 9.5 Hz, 1H), 7.85 (d, *J* = 9.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 4.02 (t, *J* = 4.5 Hz, 4H), 3.14 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 150.4, 145.8, 134.5, 131.3, 130.7, 128.4, 127.7, 126.3, 124.5, 124.5, 124.1, 120.0, 119.0, 118.0, 67.3, 53.6. HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2O_3^+$ $(M+H)^+$ 309.1234, found 309.1233.



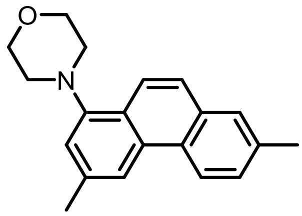
8-morpholinophenanthrene-2-carbonitrile (32): brown solid, isolated yield 40% (23.04 mg); mp: 170.3-171.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.70 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.22 (s, 1H), 7.77 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.12 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 150.3, 133.4, 133.0, 131.2, 130.7, 127.9, 127.7, 127.5, 125.3, 124.1, 124.0, 119.1, 118.7, 117.6, 109.8, 67.3, 53.5. HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2O^+$ (M+H)$^+$ 289.1335, found 289.1335.



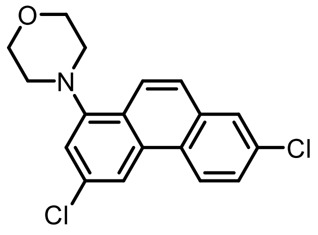
8-morpholinophenanthrene-2-carbaldehyde (33): yellow solid, isolated yield 38% (22.12 mg); mp: 128.6-130.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.22 (s, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 8.5 Hz, 1H), 8.40 (s, 1H), 8.32 (d, *J* = 9.0 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 4.5 Hz, 4H), 3.14 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 192.1, 150.2, 134.7, 134.2, 132.9, 131.4, 131.1, 128.3, 127.2, 126.5, 124.5, 124.0, 123.4, 119.0, 117.5, 67.4, 53.5. HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_2^+$ (M+H)$^+$ 292.1332, found 292.1332.



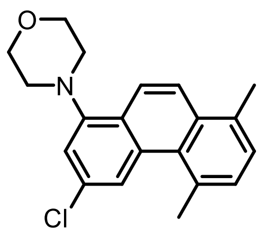
methyl 8-morpholinophenanthrene-2-carboxylate (34): brown solid, isolated yield 47% (30.17 mg); mp: 151.8-153.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 9.0 Hz, 1H), 8.60 (s, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 9.5 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.80 (d, *J* = 9.5 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 4.01-3.99 (m, 7H), 3.11 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 167.0, 150.0, 133.5, 131.1, 131.0, 130.7, 127.9, 127.8, 126.9, 126.5, 126.2, 123.2, 122.8, 118.8, 117.0, 67.3, 53.5, 52.2. HRMS (ESI) m/z calcd for $C_{20}H_{20}NO_3^+$ (M+H)$^+$ 322.1438, found 322.1437.



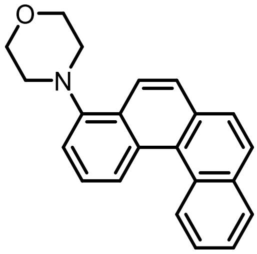
4-(3,7-dimethylphenanthren-1-yl)morpholine (35): yellow solid, isolated yield 68% (39.58 mg); mp: 91.8-95.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 8.5 Hz, 1H), 8.21 (s, 1H), 8.13 (d, *J* = 9.5 Hz, 1H), 7.67 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.07 (s, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.13 (s, 4H), 2.61 (s, 3H), 2.57 (s, 3H); **^{13}C NMR** (125 MHz, CDCl3) δ = 149.8, 136.2, 136.1, 132.2, 131.7, 128.2, 128.0, 127.9, 125.1, 124.4, 122.8, 121.9, 117.9, 117.3, 67.5, 53.6, 22.3, 21.4. HRMS (ESI) m/z calcd for $C_{20}H_{22}NO^+$ $(M+H)^+$ 292.1696, found 292.1696.



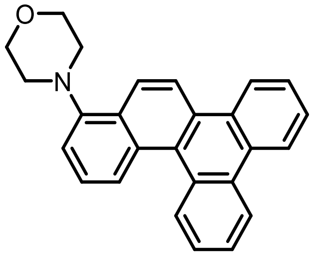
4-(3,7-dichlorophenanthren-1-yl)morpholine (36): white solid, isolated yield 66% (43.69 mg); mp: 91.8-92.7 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 9.0 Hz, 1H), 8.26 (s, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.83 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.54 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.18 (s, 1H), 3.99 (t, *J* = 4.0 Hz, 4H), 3.09 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 151.3, 133.1, 133.0, 132.9, 132.1, 127.9, 127.3, 127.1, 125.3, 125.1, 124.6, 122.9, 117.7, 117.2, 67.2, 53.4. HRMS (ESI) m/z calcd for $C_{18}H_{16}ClNO^+$ $(M+H)^+$ 332.0603, found 332.0603.



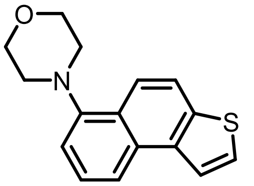
4-(3-chloro-5,8-dimethylphenanthren-1-yl)morpholine (37): white solid, isolated yield 77% (50.05 mg); mp: 142.7-145.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 8.52 (s, 1H), 8.18 (d, *J* = 9.5 Hz, 1H), 7.94 (d, *J* = 9.5 Hz, 1H), 7.37 (dd, *J* = 10.5,7.5 Hz, 1H), 7.18 (s, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.13 (s, 4H), 3.06 (s, 3H), 2.74 (s, 3H); **^{13}C NMR** (125 MHz, CDCl3) δ = 150.6, 133.9, 133.2, 132.6, 132.4, 130.8, 130.7, 130.0, 127.8, 126.3, 123.1, 122.8, 121.5, 115.8, 67.2, 53.4, 26.9, 20.1. HRMS (ESI) m/z calcd for $C_{20}H_{21}ClNO^+$ $(M+H)^+$ 326.1306, found 326.1305.



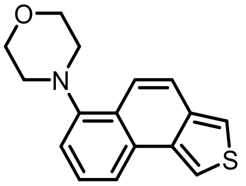
4-(benzo[c]phenanthren-4-yl)morpholine (38): white solid, isolated yield 53% (33.18 mg); mp: 154.1-156.8 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 9.12 (d, *J* = 8.5 Hz, 1H), 8.85 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.86 (dd, *J* = 8.5 Hz, 3.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.67-7.61 (m, 2H), 7.26(d, *J* = 7.5 Hz, 1H), 4.07 (t, *J* = 4.5 Hz, 4H), 3.25 (s, 4H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ = 149.6, 133.4, 131.8, 130.8, 130.3, 128.6, 128.5, 128.2, 127.9, 127.5, 126.6, 126.4, 126.0, 125.9, 125.8, 123.6, 122.8, 114.4, 67.4, 53.6. HRMS (ESI) m/z calcd for $C_{22}H_{20}NO^+$ $(M+H)^+$ 314.1539, found 314.1515.



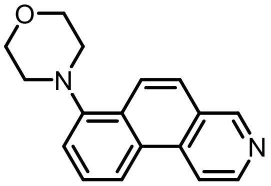
4-(benzo[g]chrysen-7-yl)morpholine (39): brown liquid, isolated yield 36% (26.14 mg); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, CDCl$_3$) δ = 8.86 (d, *J* = 8.0 Hz, 1H), 8.74-8.67 (m, 3H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.61 (d, *J* = 9.5 Hz, 1H), 8.47 (d, *J* = 9.0 Hz, 1H), 7.72 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.06 (t, *J* = 4.5 Hz, 4H), 3.24 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 149.4, 131.9, 130.8, 130.0, 129.8, 129.6, 129.5, 128.9, 127.9, 127.3, 127.1, 126.6, 126.0, 125.8, 124.2, 123.6, 123.4, 123.2, 123.1, 120.3, 114.3, 67.5, 53.6. HRMS (ESI) m/z calcd for $C_{26}H_{22}NO^+$ $(M+H)^+$ 364.1696, found 364.1696.



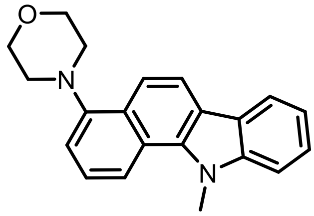
4-(naphtho[2,1-b]thiophen-6-yl)morpholine (40): yellow solid, isolated yield 45% (24.21 mg); mp: 78.3-80.4 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.46 (d, *J* = 5.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.15 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =150.5, 138.0, 137.4, 130.3, 126.8, 125.9, 125.3, 125.0, 121.4, 120.7, 119.4, 114.8, 67.4, 53.6. HRMS (ESI) m/z calcd for $C_{16}H_{16}NOS^+$ $(M+H)^+$ 270.0947, found 270.0947.



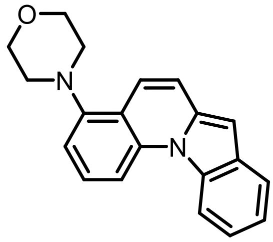
4-(naphtho[1,2-c]thiophen-6-yl)morpholine (41): white solid, isolated yield 42% (22.60 mg); mp: 127.9-128.3 °C (uncorrected); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 9.0 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 5.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.58-7.54 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.15 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =150.2, 137.4, 136.4, 130.7, 126.6, 126.1, 125.7, 122.3, 120.4, 120.1, 119.4, 114.5, 67.5, 53.6. HRMS (ESI) m/z calcd for $C_{16}H_{16}NOS^+$ $(M+H)^+$ 270.0947, found 270.0947.



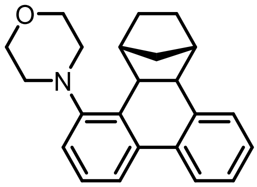
4-(benzo[f]isoquinolin-7-yl)morpholine (42): brown solid, isolated yield 75% (39.60 mg); mp: 109.1-112.1 °C (uncorrected); (eluent: petroleum ether/EtOAc = 3:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.25 (s, 1H), 8.73 (*d*, *J* = 6.0 Hz, 1H), 8.42-8.39 (m, 2H), 8.31 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 9.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 4.01 (t, *J* = 4.5 Hz, 4H), 3.13 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 151.6, 150.2, 144.9, 135.1, 129.8, 128.6, 127.3, 126.8, 124.1, 123.6, 118.7, 118.2, 116.4, 67.3, 53.5. HRMS (ESI) m/z calcd for $C_{17}H_{17}N_2O^+$ $(M+H)^+$ 265.1335, found 265.1335.



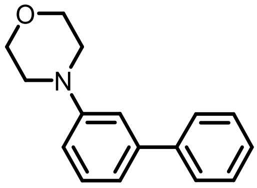
4-(11-methyl-11*H*-benzo[a]carbazol-4-yl)morpholine (43): brown solid, isolated yield 65% (41.08 mg); mp: 166.8-168.3 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.45 (d, *J* = 8.0 Hz, 1H), 8.22-8.16 (m, 3H), 7.55-7.51 (m, 3H), 7.36-7.33 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.35 (s, 3H), 4.06 (t, *J* = 4.5 Hz, 4H), 3.20 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ =150.3, 140.8, 136.1, 128.5, 125.0, 124.7, 123.8, 122.8, 119.6, 119.4, 119.0, 118.6, 117.9, 115.4, 113.9, 109.0, 67.5, 53.5, 34.0. HRMS (ESI) m/z calcd for $C_{21}H_{21}N_2O^+$ $(M+H)^+$ 317.1648, found 317.1648.



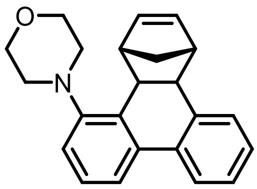
4-(indolo[1,2-a]quinolin-4-yl)morpholine (44): yellow solid, isolated yield 63% (38.05 mg); mp: 112.8-114.6 °C (uncorrected); (eluent: petroleum ether/EtOAc = 10:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.45 (d, *J* = 7.5 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.0 Hz, 1H), 7.59-7.52 (m, 2H), 7.40-7.34 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.80 (s, 1H), 3.97 (s, 4H), 3.10 (s, 4H); **^{13}C NMR** (125 MHz, CDCl3) δ = 150.6, 137.9, 136.2, 133.0, 130.3, 128.6, 121.8, 121.5, 121.0, 119.3, 118.8, 118.7, 114.3, 113.1, 111.3, 96.5, 67.3, 53.5. HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O^+$ $(M+H)^+$ 303.1492, found 303.1492.



4-((1S,4R)-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylen-5-yl)morpholine (45): brown solid, isolated yield 20% (13.24 mg); mp: 174.8-177.9 °C (uncorrected); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.29-7.21 (m, 4H), 7.14 (d, *J* = 7.0 Hz, 1H), 3.88 (s, 4H), 3.33-3.25 (m, 2H), 3.08 (s, 2H), 2.79 (s, 2H), 2.41 (s, 1H), 2.32 (s, 1H), 1.79-1.68 (m, 4H), 1.36 (d, *J* = 9.5 Hz, 1H), 1.03 (d, *J* = 9.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.9, 137.8, 134.8, 132.9, 131.9, 129.8, 127.7, 126.9, 126.1, 122.4, 121.4, 119.3, 67.9, 49.4, 49.2, 46.2, 42.0, 33.2, 31.5, 29.7. HRMS (ESI) m/z calcd for $C_{23}H_{26}NO^+$ $(M+H)^+$ 332.2009, found 332.2007.



4-([1,1'-biphenyl]-3-yl)morpholine (46)[7]: White solid, isolated yield 50% (23.90 mg); (eluent: petroleum ether/EtOAc = 20:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 6.5 Hz, 2H), 7.14 (s, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 3.89 (s, 4H), 3.24 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.6, 142.3, 141.7, 129.5, 128.6, 127.2, 127.2, 119.1, 114.7, 114.6, 66.9, 49.4.



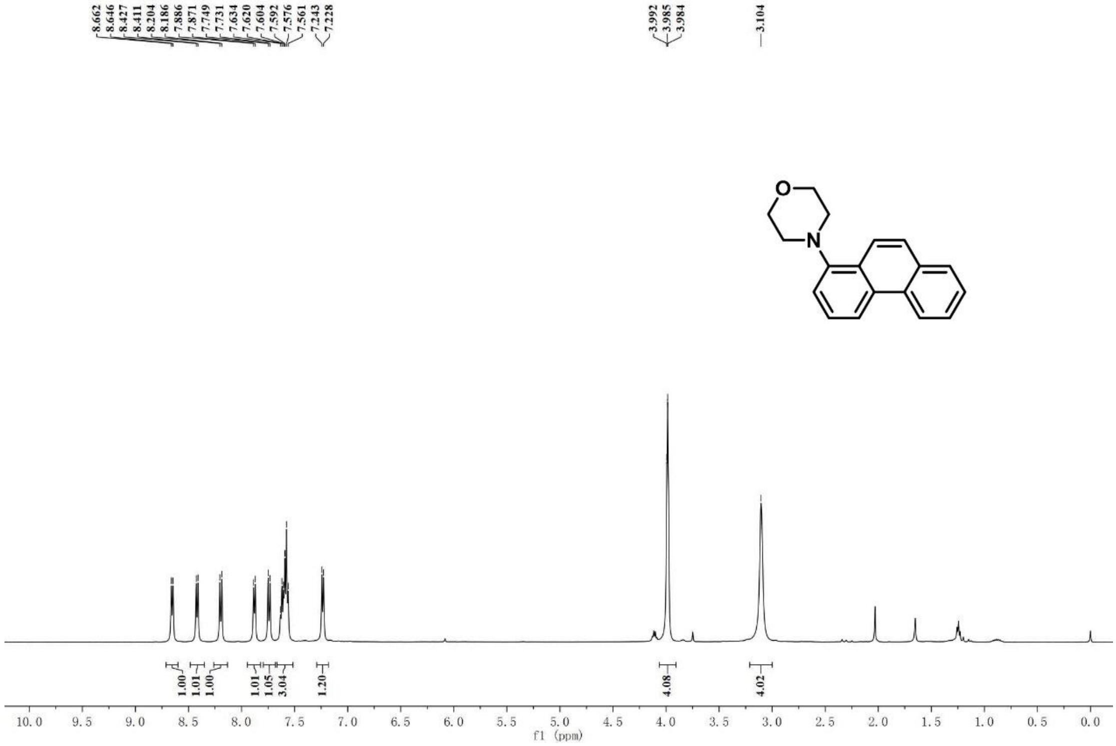
4-((4aS,12bR)-1,4,4a,12b-tetrahydro-1,4-methanotriphenylen-5-yl)morpholine (47)[4]: white solid, isolated yield 96% (63.17 mg); (eluent: petroleum ether/EtOAc = 30:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.27-7.20 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.46 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.34 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.86 (s, 4H), 3.13-2.99 (m, 6H), 2.80-2.76 (m, 2H), 1.30 (d, *J* = 9.0 Hz, 1H), 1.11 (d, *J* = 9.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.89, 138.80, 138.12, 136.89, 134.63, 133.39, 132.33, 129.95, 127.69, 126.99, 126.18, 122.80, 121.10, 119.47, 67.90, 55.46, 54.85, 42.71, 40.78, 38.13.

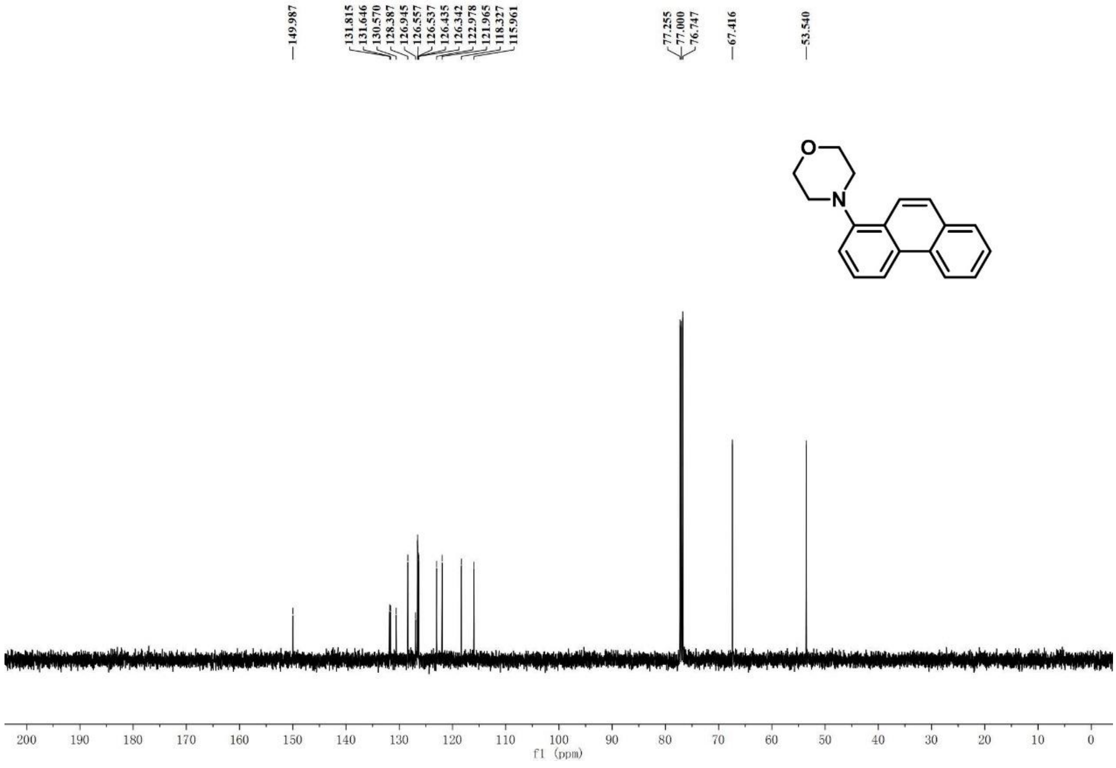
6 References

1. (a) S. Pan, H. Jiang, Y. Zhang, D. Chen, Y. Zhang. *Org. Lett.,* **2016**, *18*, 5192-5195; (b) X. Yang, X. Chen, Y. Xu, M. Zhang, G. Deng, Y. Yang, Y. Liang. *Org. Lett.,* **2021**, *23*, 2610-2615.
2. W. Li, G. Xiao, G. Deng, Y. Liang. *Org. Chem. Front.,* **2018**, *5*, 1488-1492.
3. H. Liu, T. Duan, Z. Zhang, C. Xie, C. Ma. *Org. Lett.,* **2015**, *17*, 2932-2935.
4. L. Fan, J. Liu, L. Bai, Y. Wang, X. Luan. *Angew. Chem. Int. Ed.,* **2017**, *56,* 14257-14261.
5. W. Lv, S. Wen, J. Yu, G. Cheng. *Org. Lett.,* **2018**, *20,* 4984-4987.
6. P. Asgari, U. S. Dakarapu, H. Nguyen, J. Jeon. *Tetrahedron,* **2017**, *73,* 4052-4061.
7. K.-X. Sun, Q.-W. He, B.-B. Xu, X.-T. Wu, J.-M. Lu. *Asian J. Org. Chem.,* **2018**, *7*, 781-787.

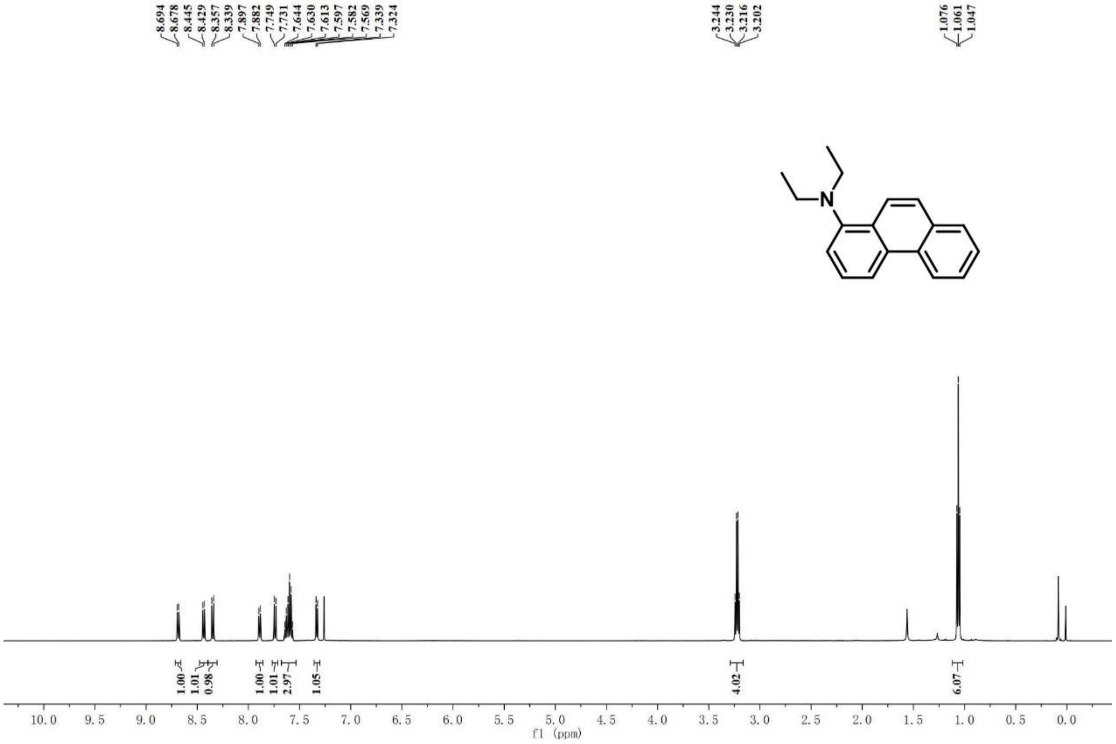
7 Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

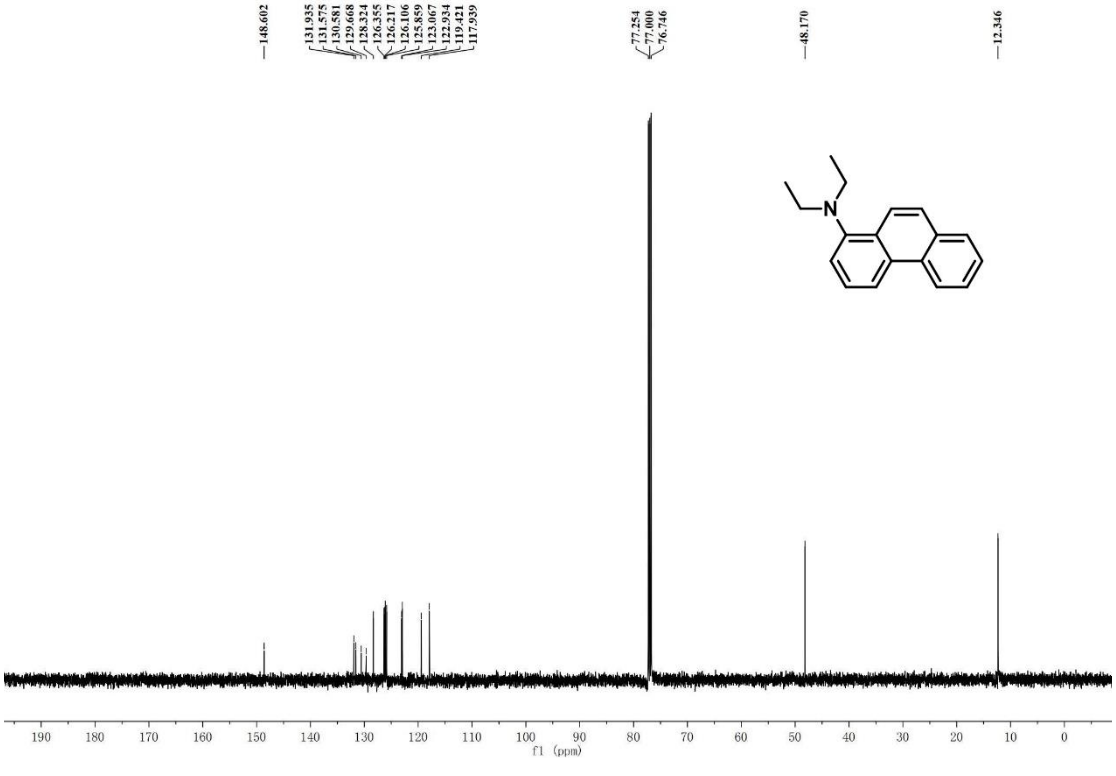
^{1}H NMR of **4** (500 MHz, $CDCl_3$) and ^{13}C NMR of **4** (125 MHz, $CDCl_3$)



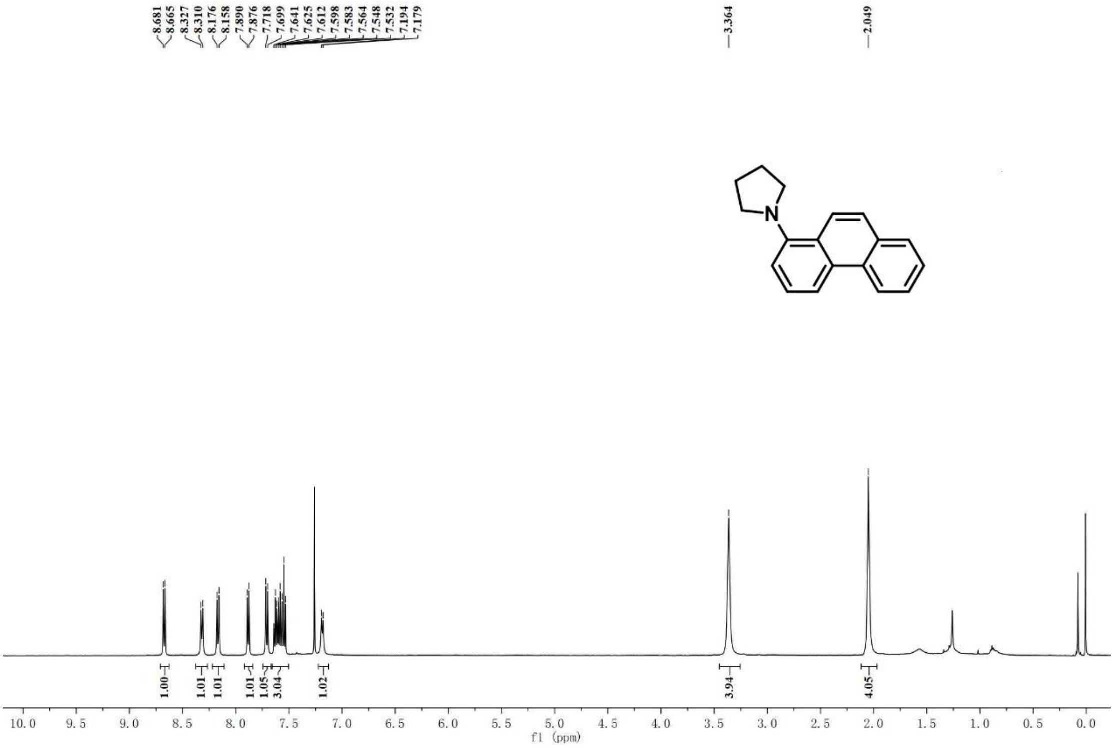


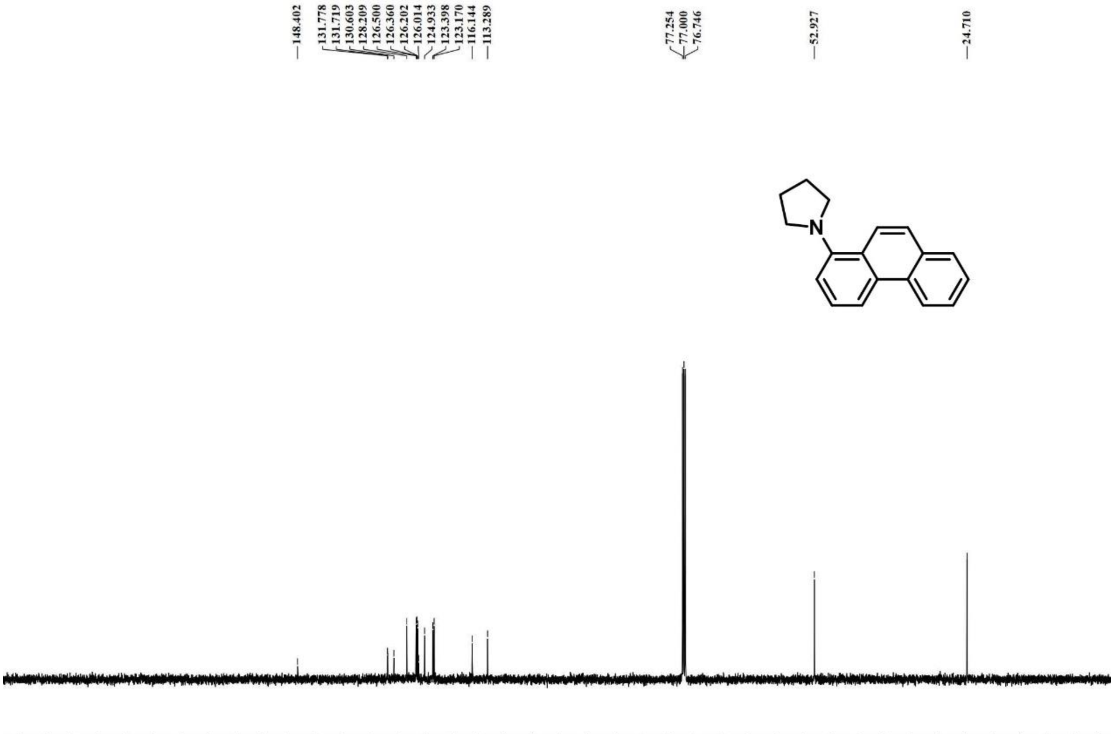
^{1}H NMR of **5** (500 MHz, $CDCl_3$) and ^{13}C NMR of **5** (125 MHz, $CDCl_3$)



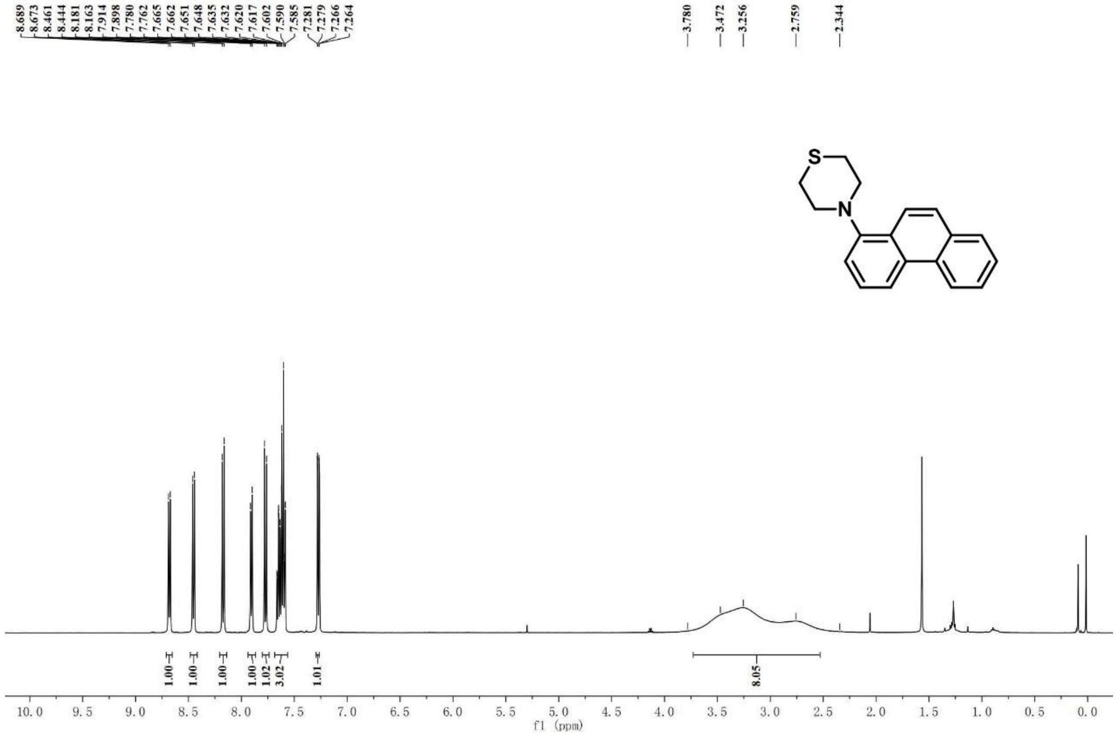


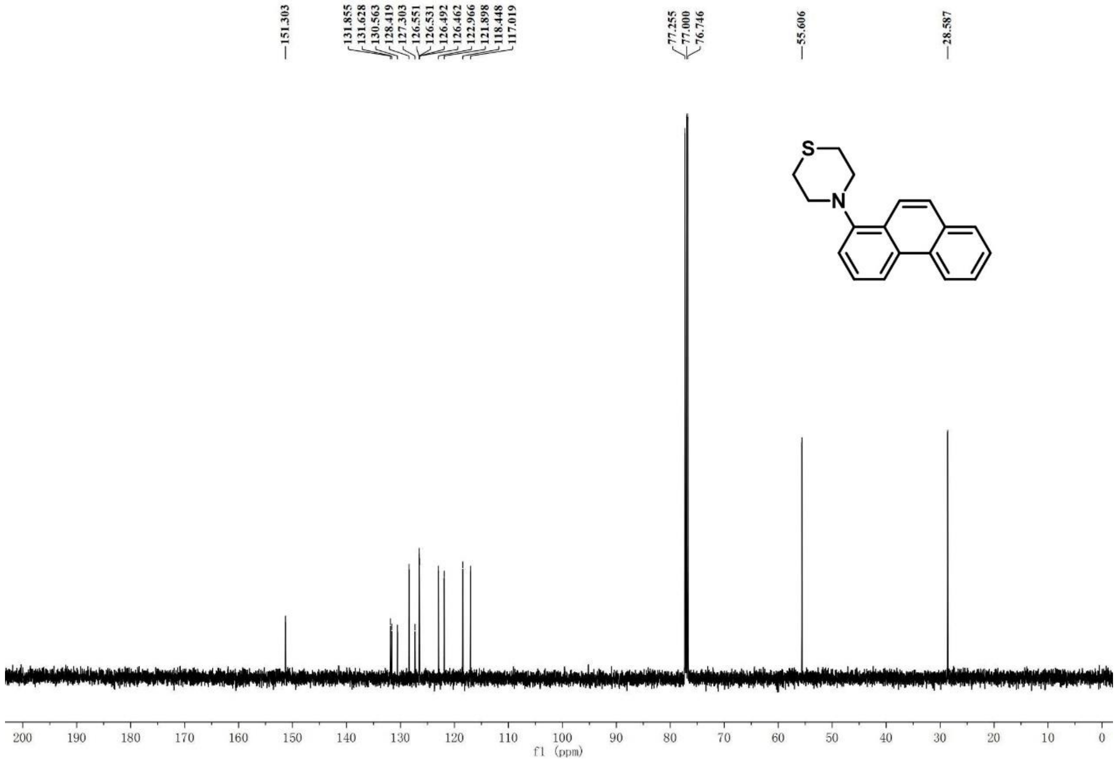
^{1}H NMR of **6** (500 MHz, CDCl$_3$) and ^{13}C NMR of **6** (125 MHz, CDCl$_3$)



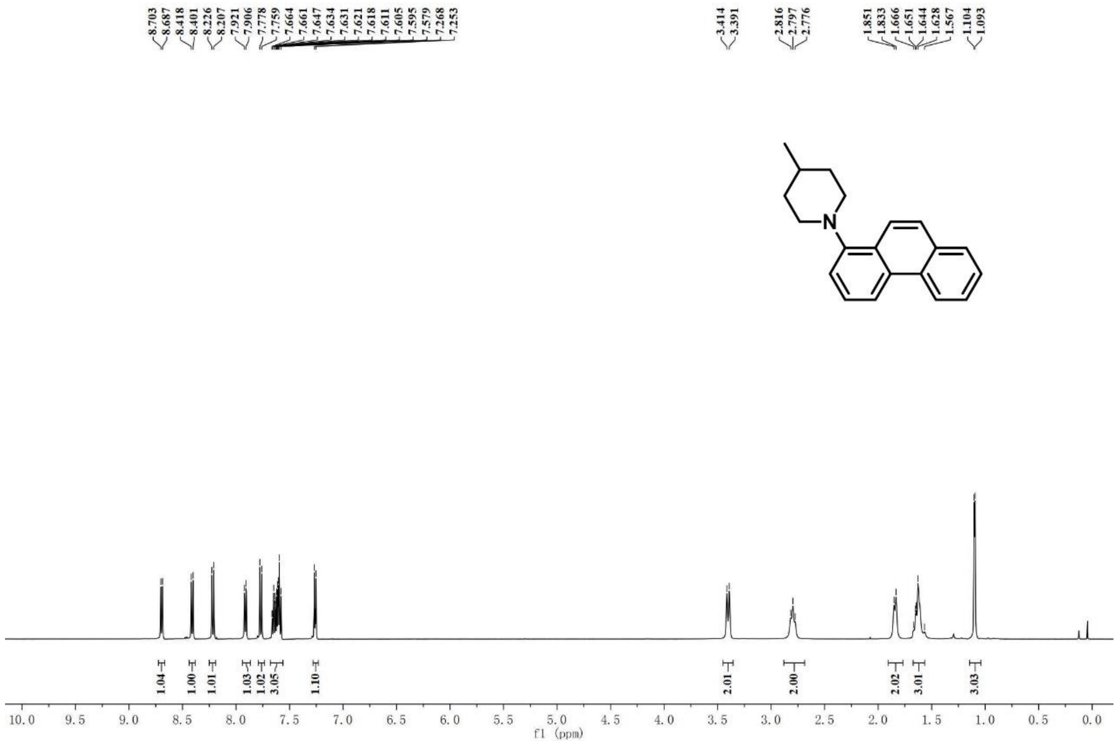


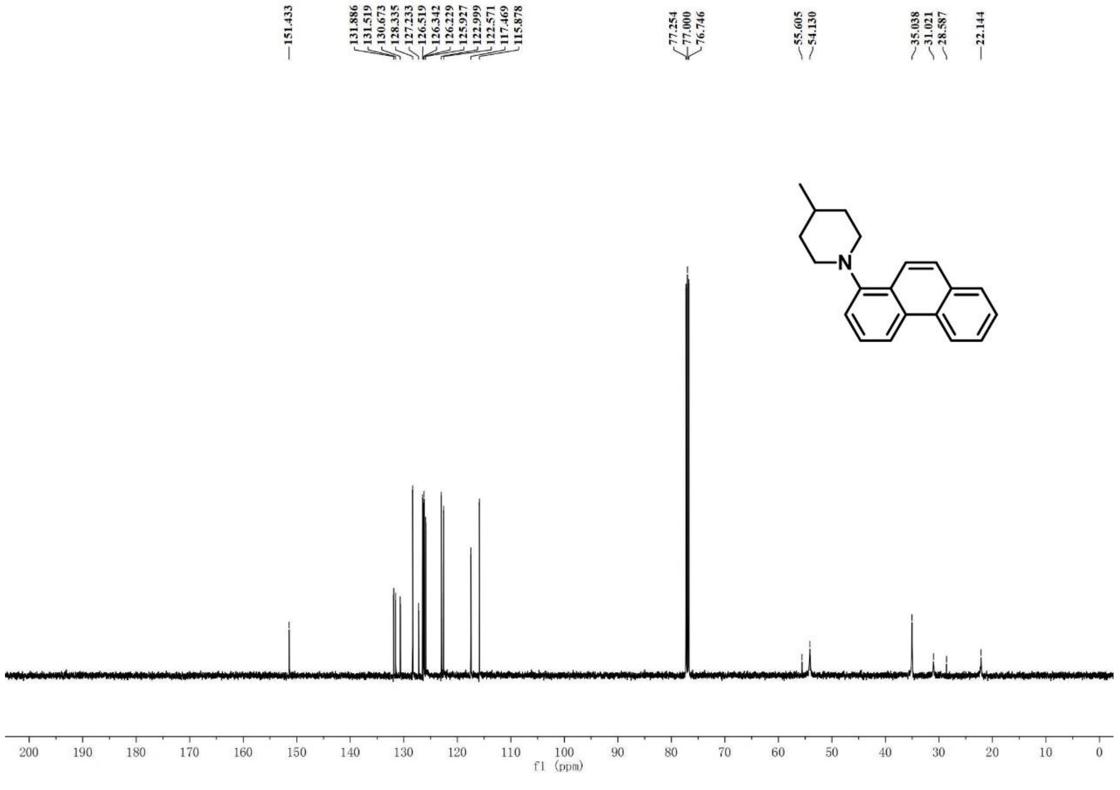
^{1}H NMR of **7** (500 MHz, CDCl$_3$) and ^{13}C NMR of **7** (125 MHz, CDCl$_3$)



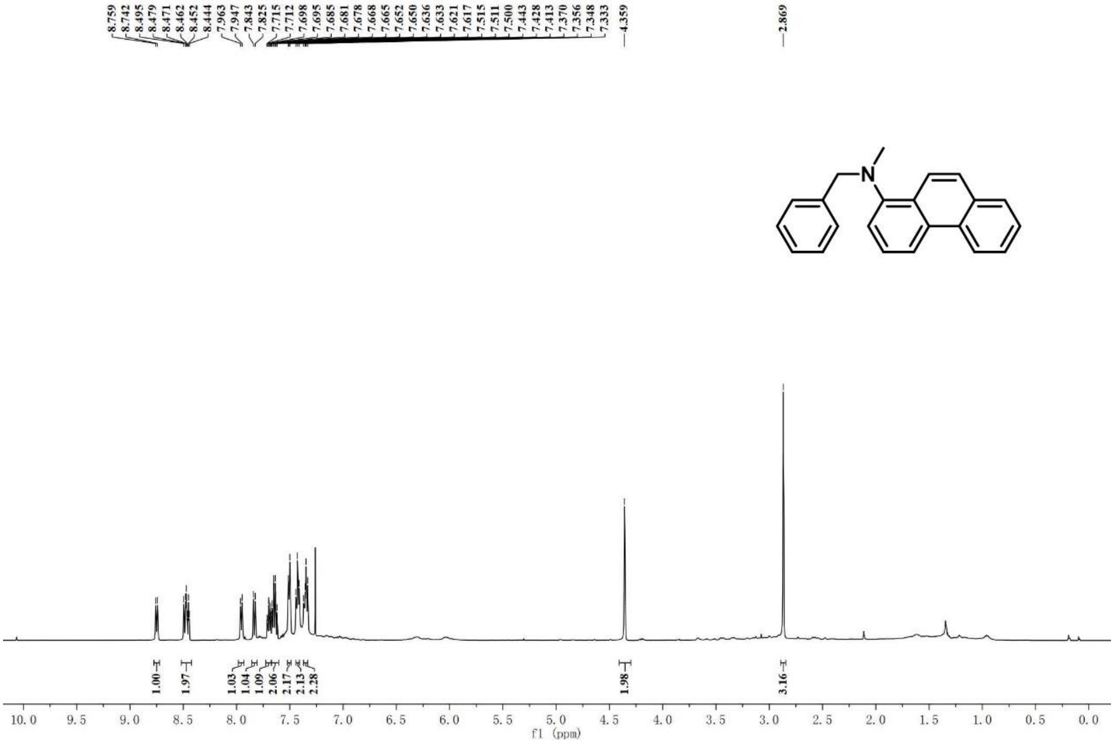


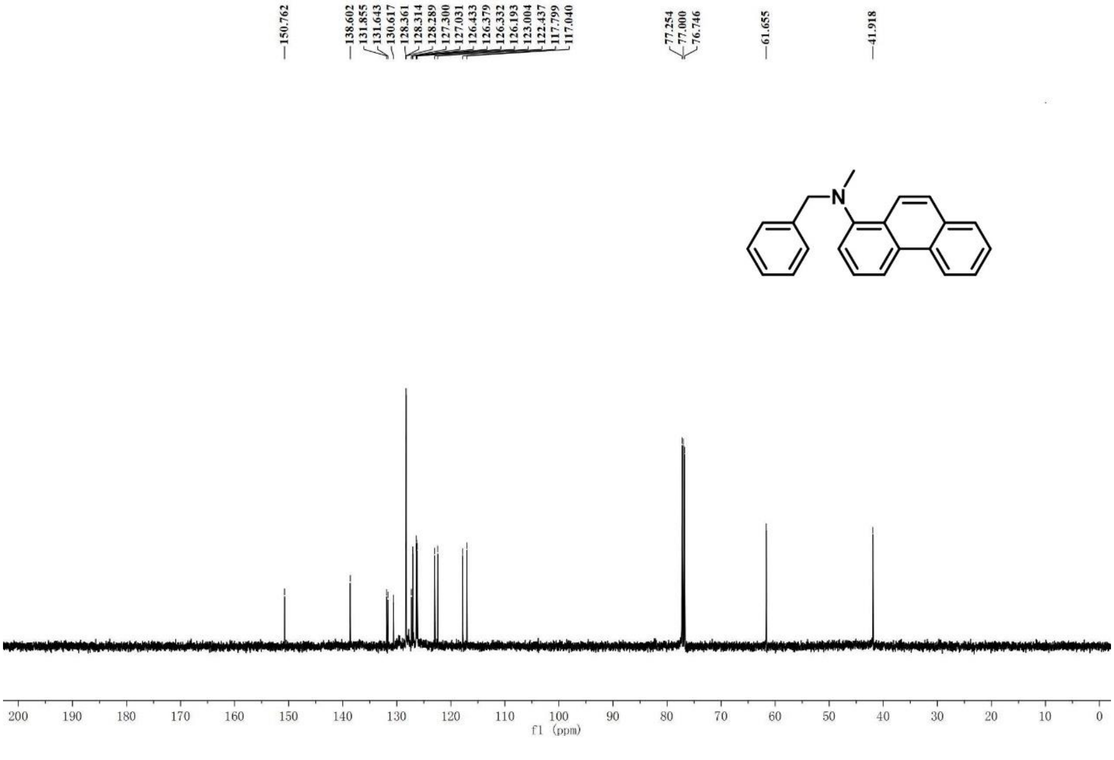
^{1}H NMR of **8** (500 MHz, $CDCl_3$) and ^{13}C NMR of **8** (125 MHz, $CDCl_3$)



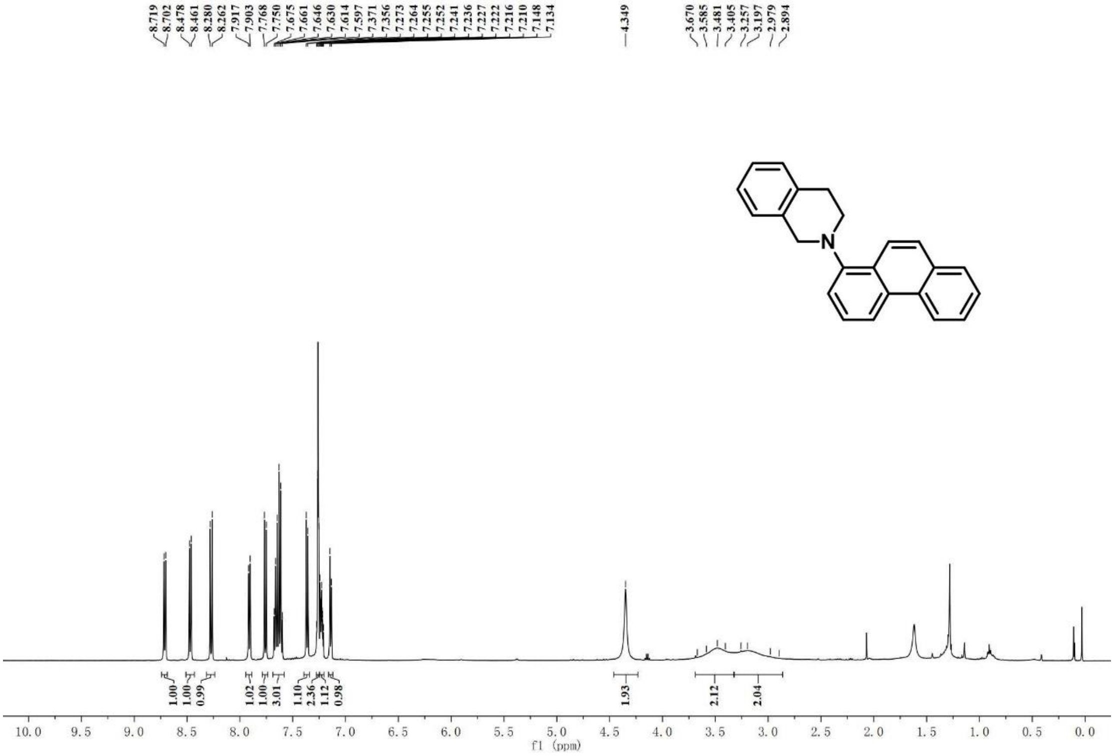


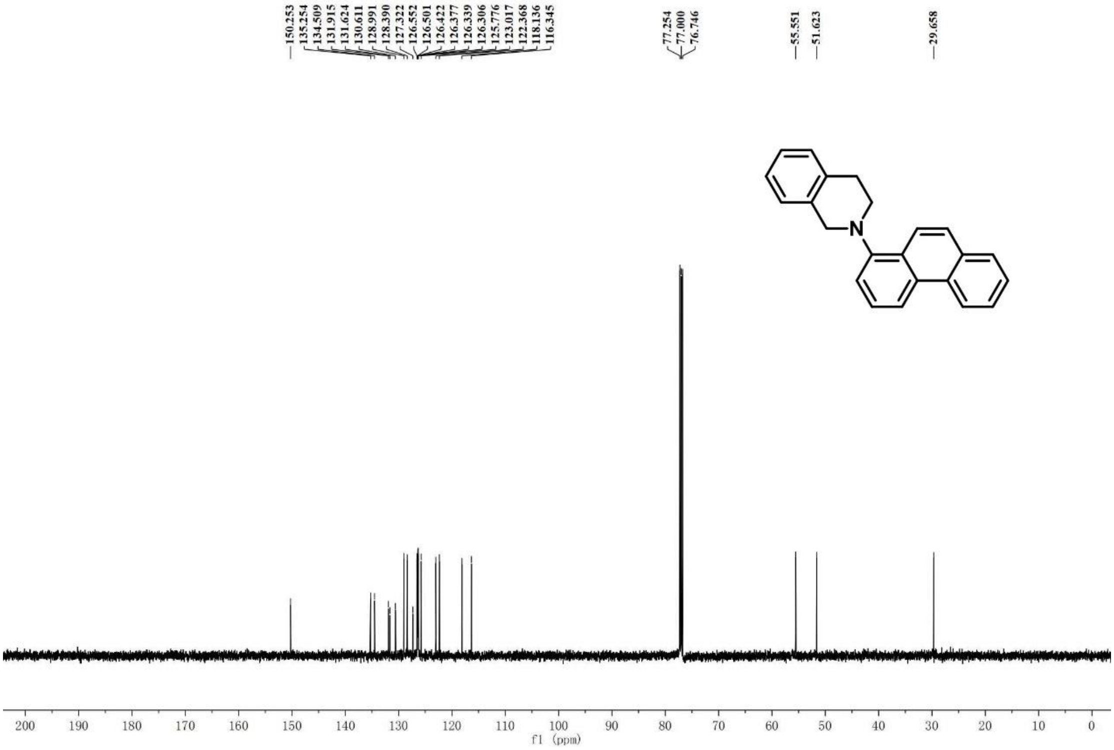
^{1}H NMR of **9** (500 MHz, $CDCl_3$) and ^{13}C NMR of **9** (125 MHz, $CDCl_3$)



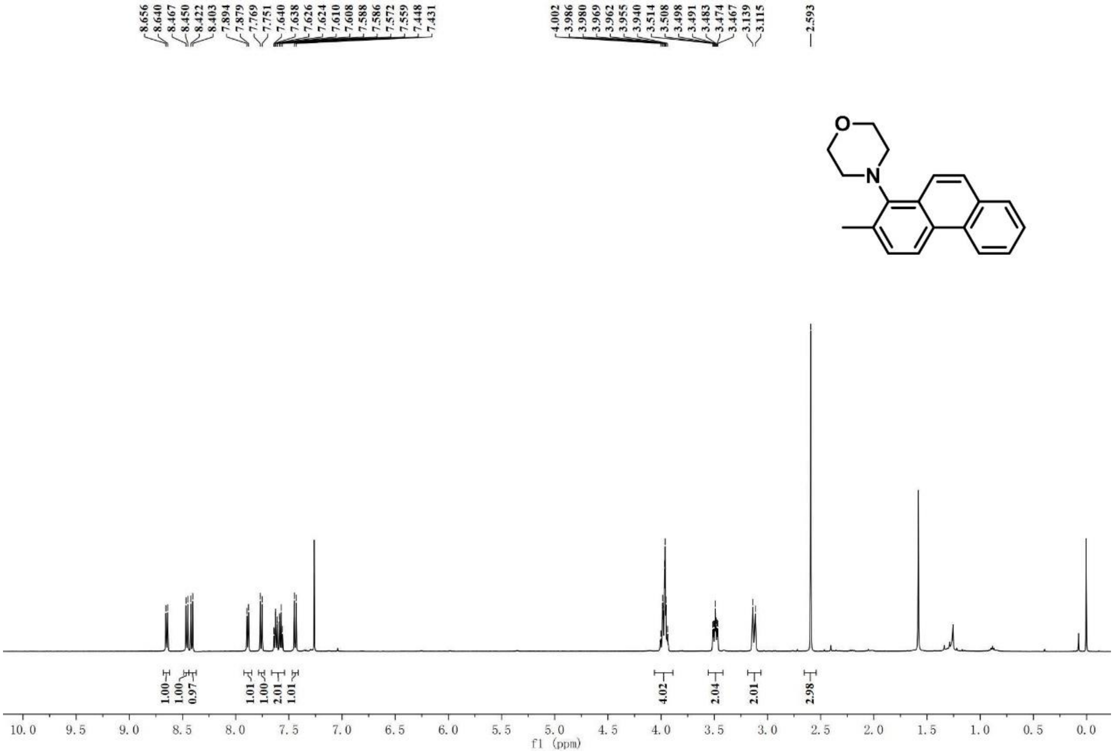


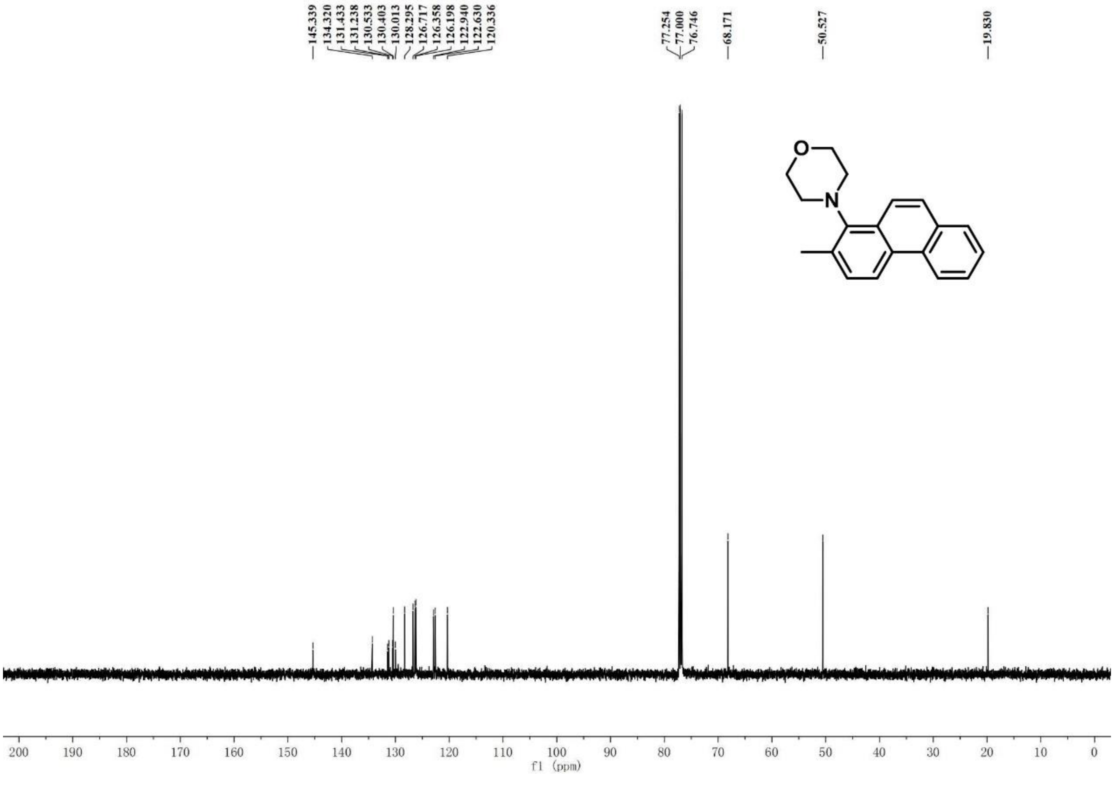
^{1}H NMR of **10** (500 MHz, $CDCl_3$) and ^{13}C NMR of **10** (125 MHz, $CDCl_3$)



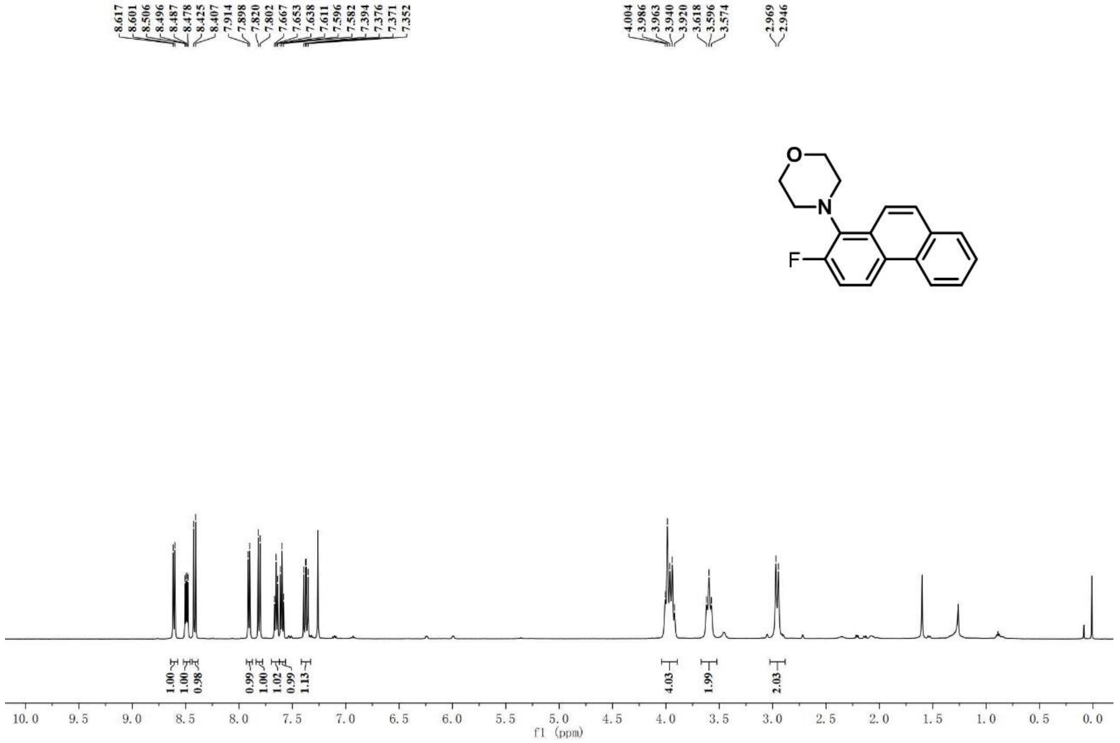


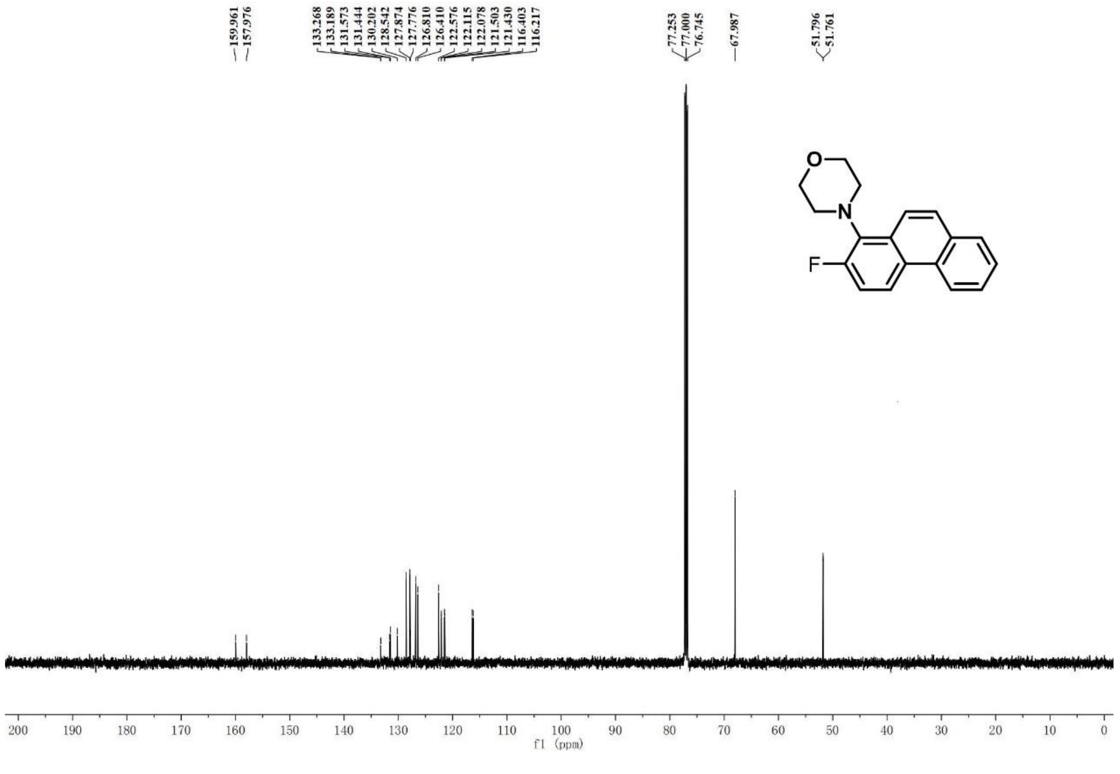
^{1}H NMR of **11** (500 MHz, CDCl$_3$) and ^{13}C NMR of **11** (125 MHz, CDCl$_3$)



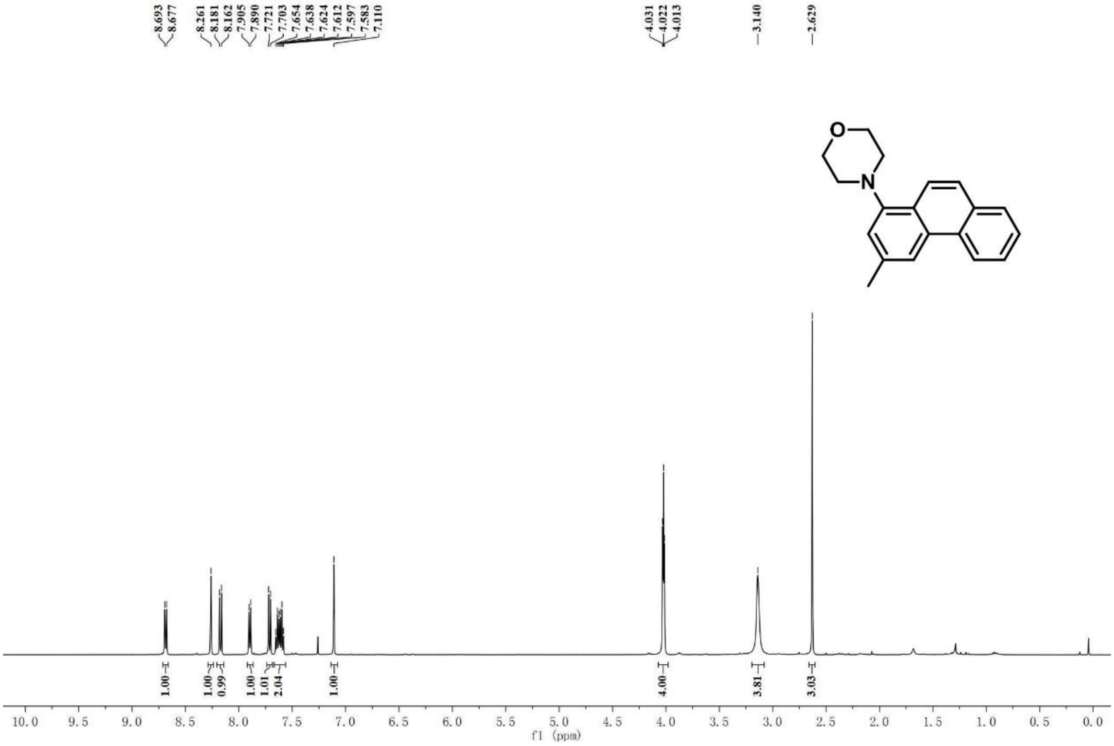


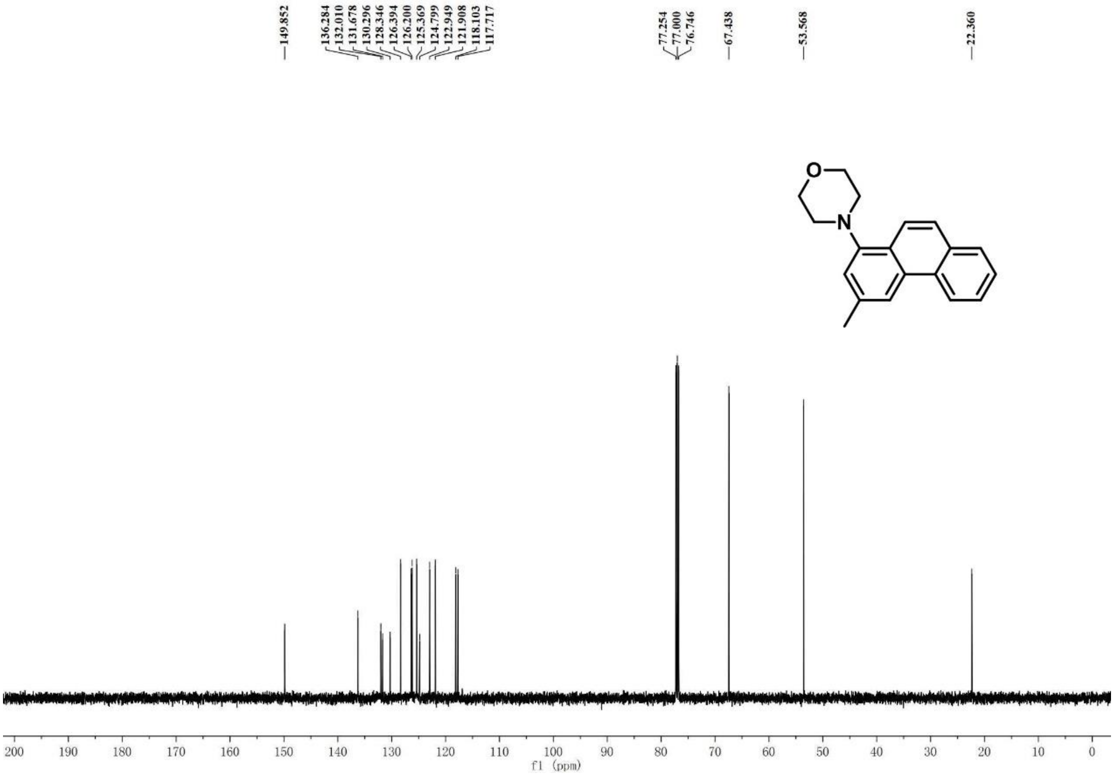
^{1}H NMR of **14** (500 MHz, CDCl$_3$) and ^{13}C NMR of **14** (125 MHz, CDCl$_3$)



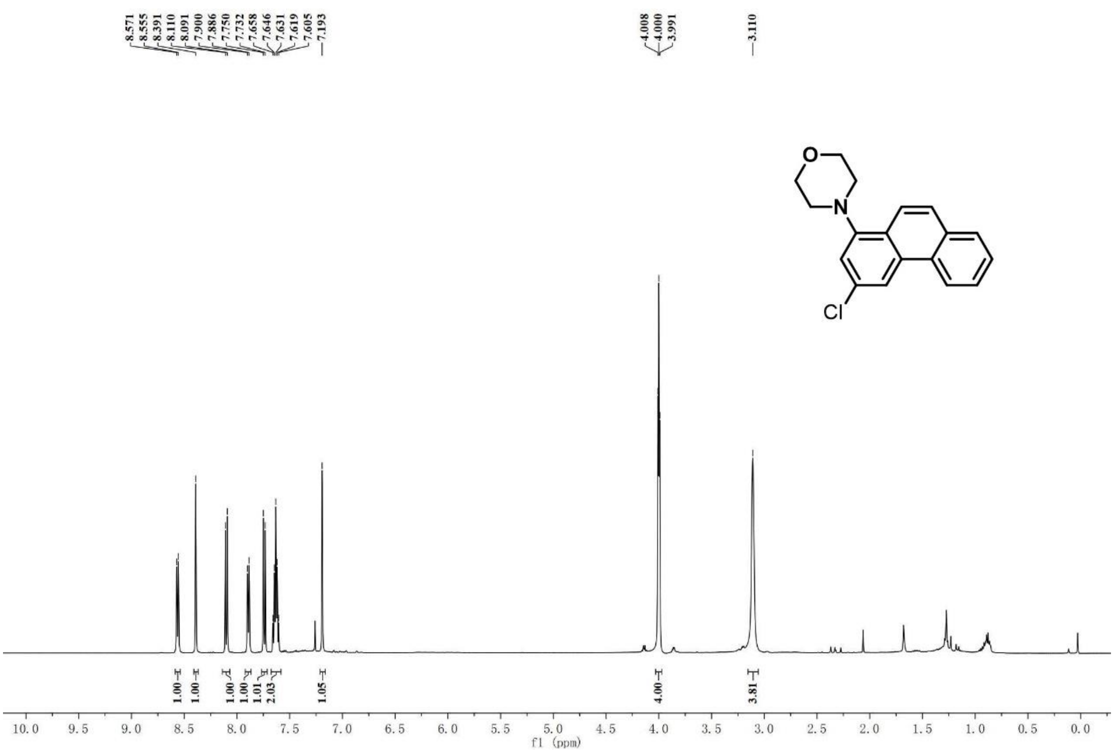


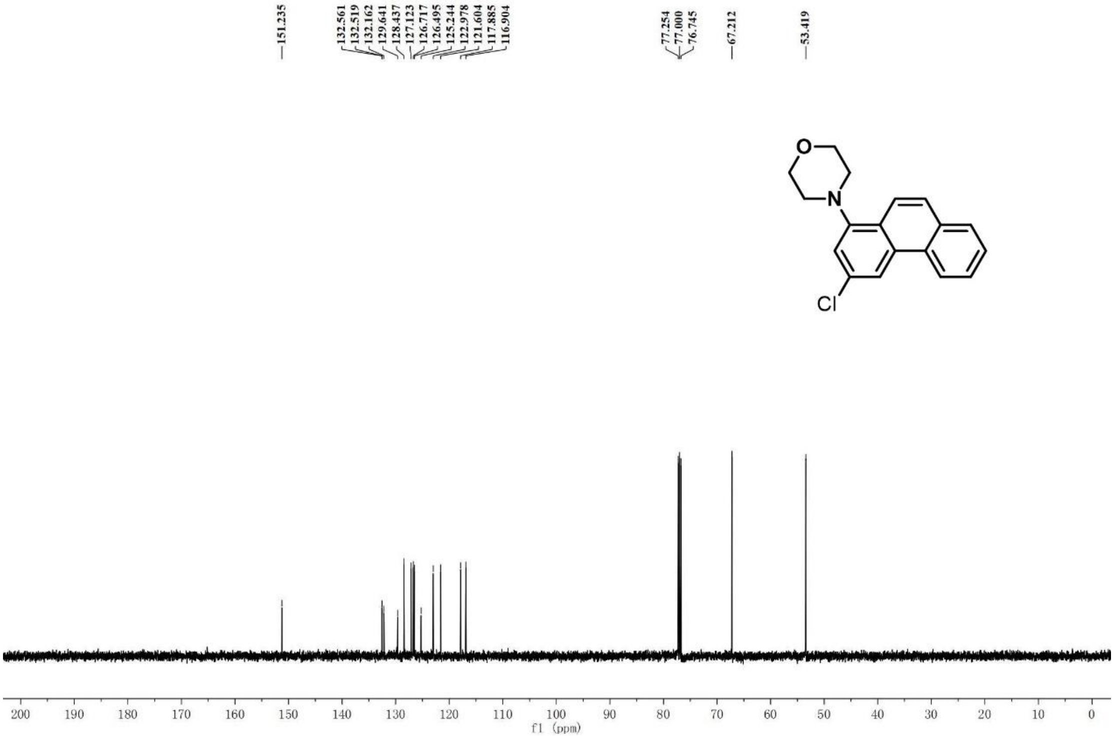
^{1}H NMR of **16** (500 MHz, $CDCl_3$) and ^{13}C NMR of **16** (125 MHz, $CDCl_3$)



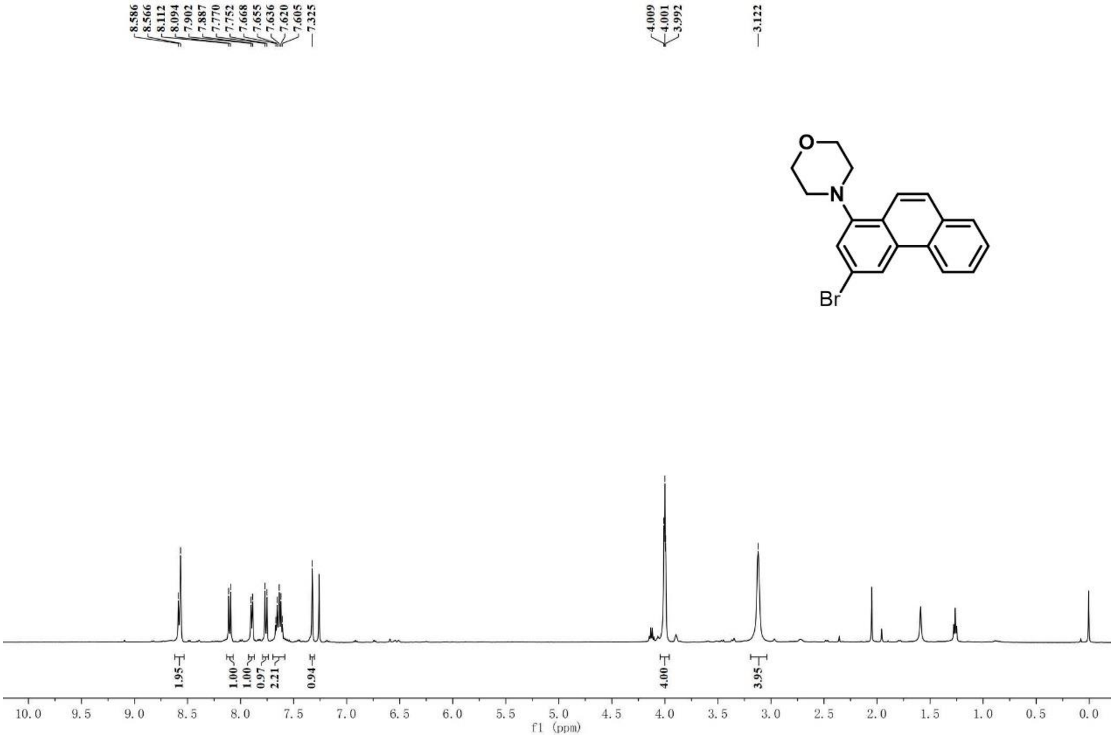


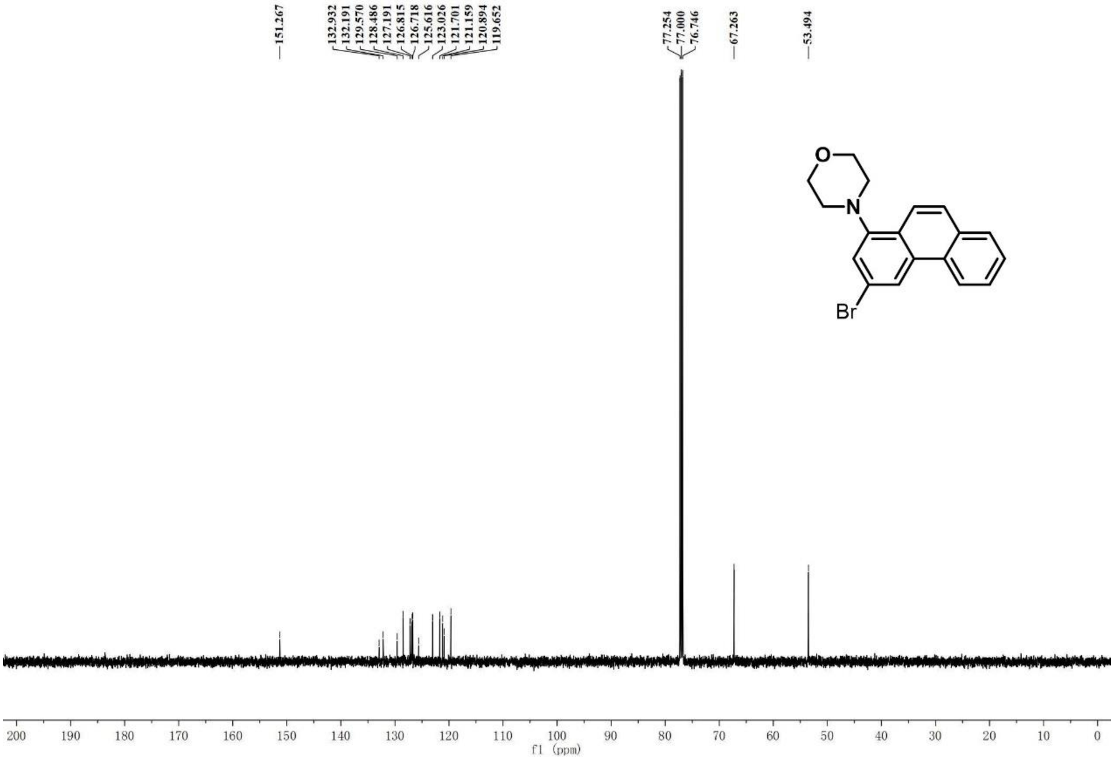
^{1}H NMR of **17** (500 MHz, CDCl$_3$) and ^{13}C NMR of **17** (125 MHz, CDCl$_3$)



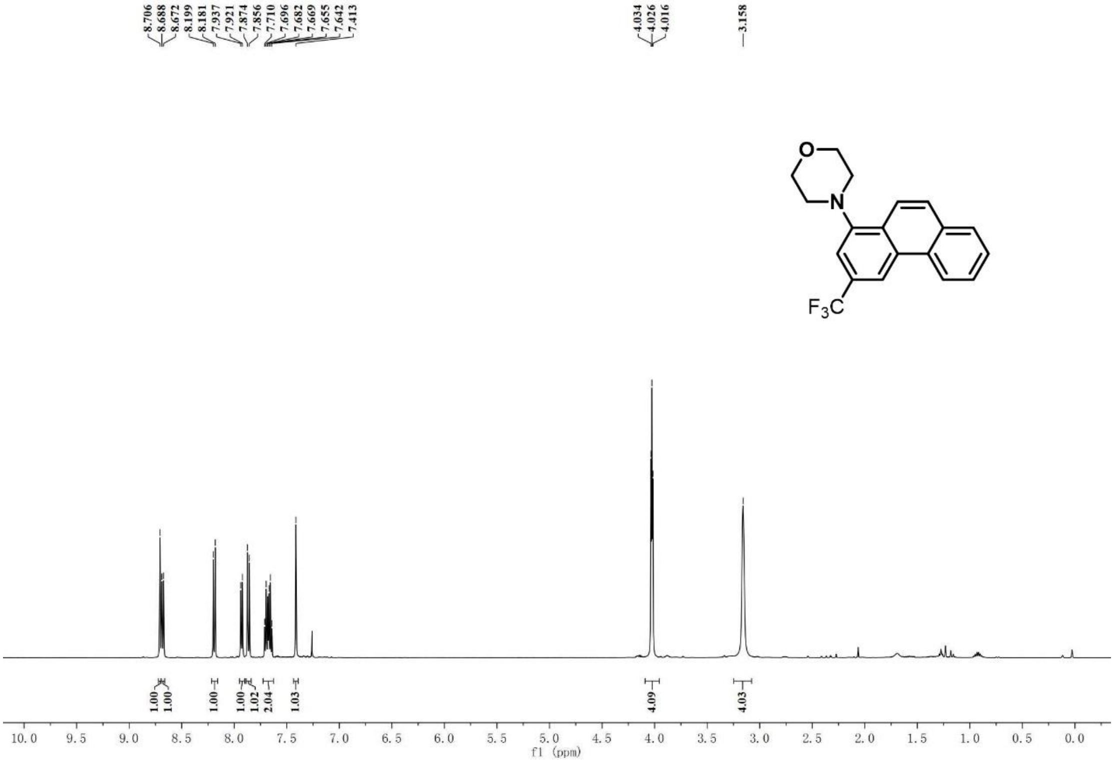


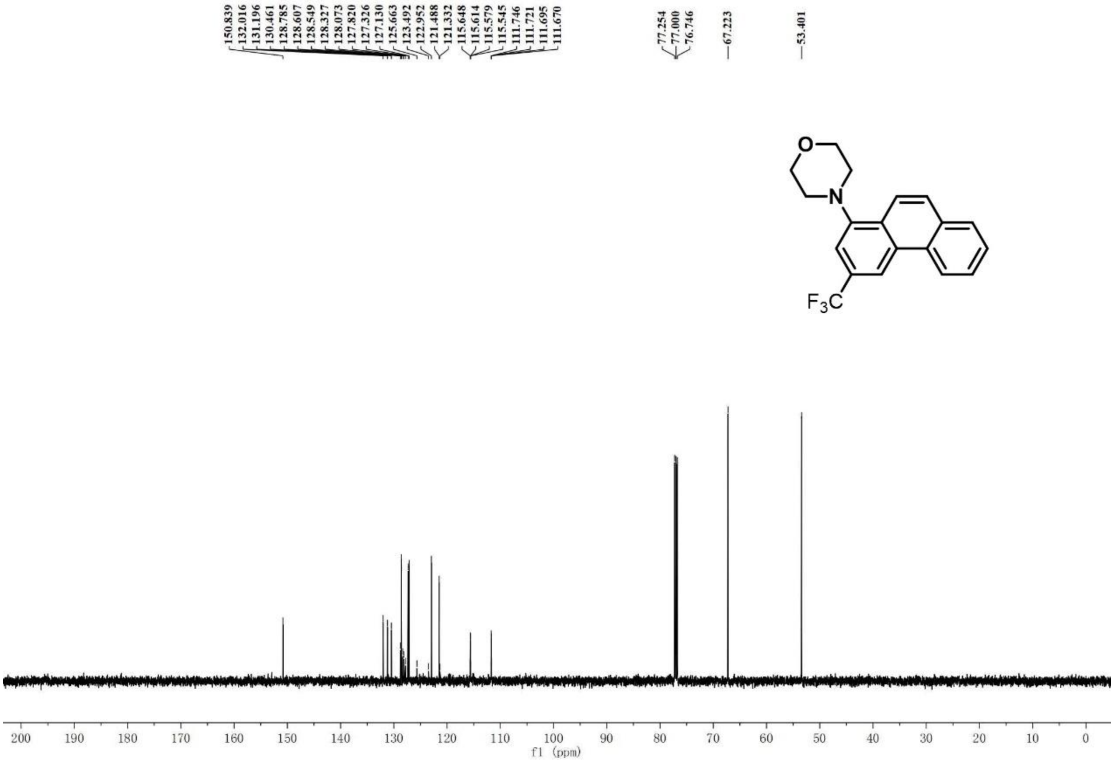
^{1}H NMR of **18** (500 MHz, CDCl$_3$) and ^{13}C NMR of **18** (125 MHz, CDCl$_3$)



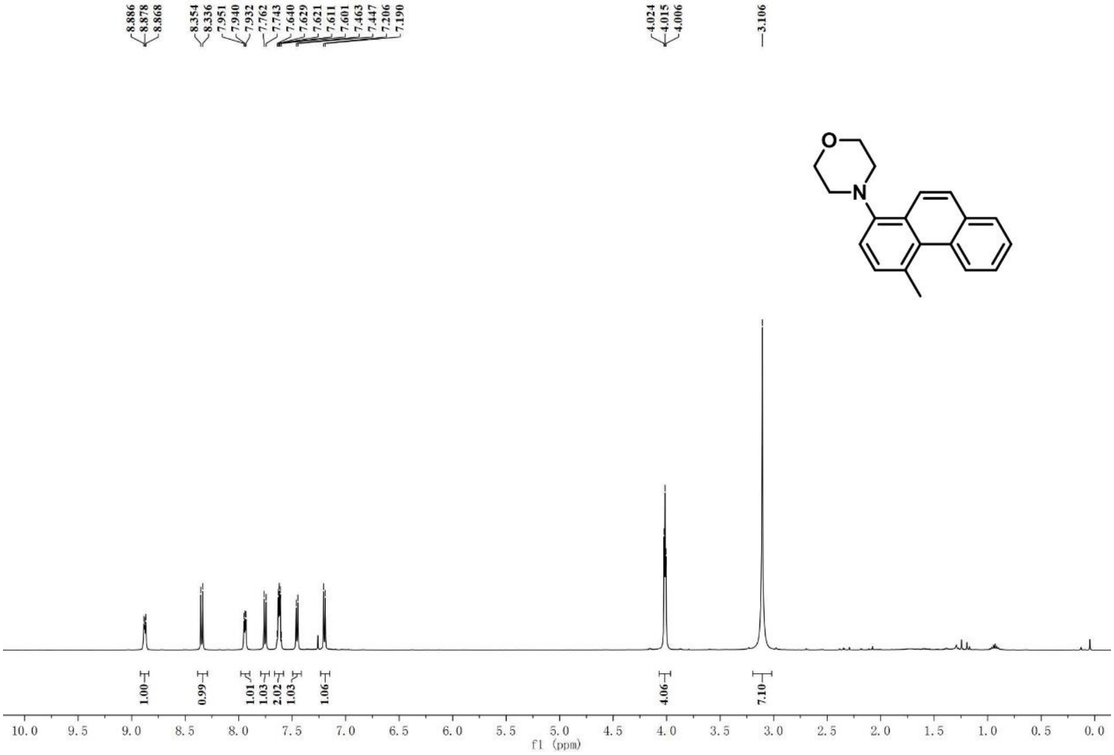


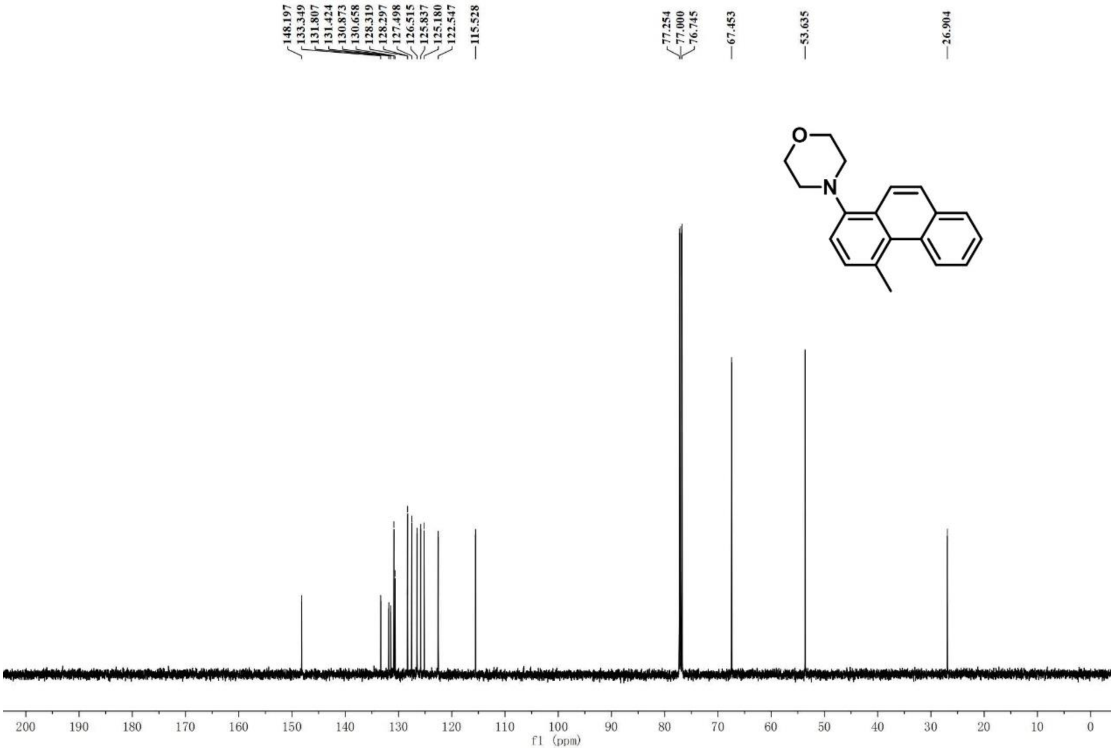
^{1}H NMR of **19** (500 MHz, CDCl$_3$) and ^{13}C NMR of **19** (125 MHz, CDCl$_3$)



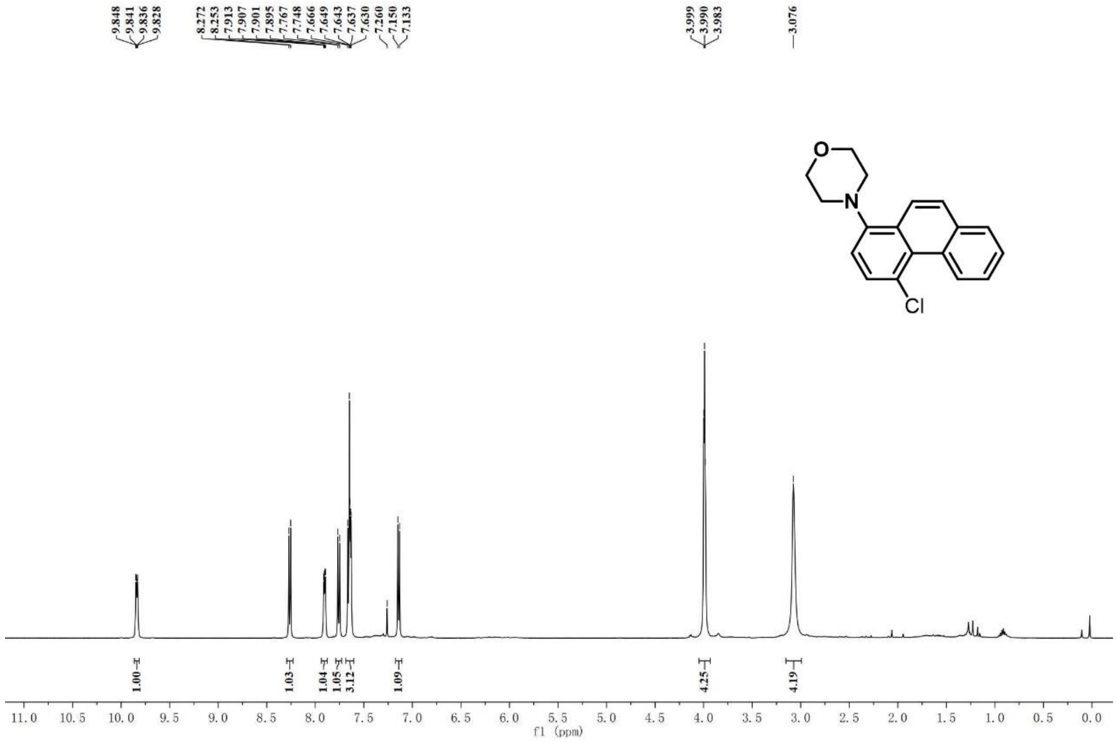


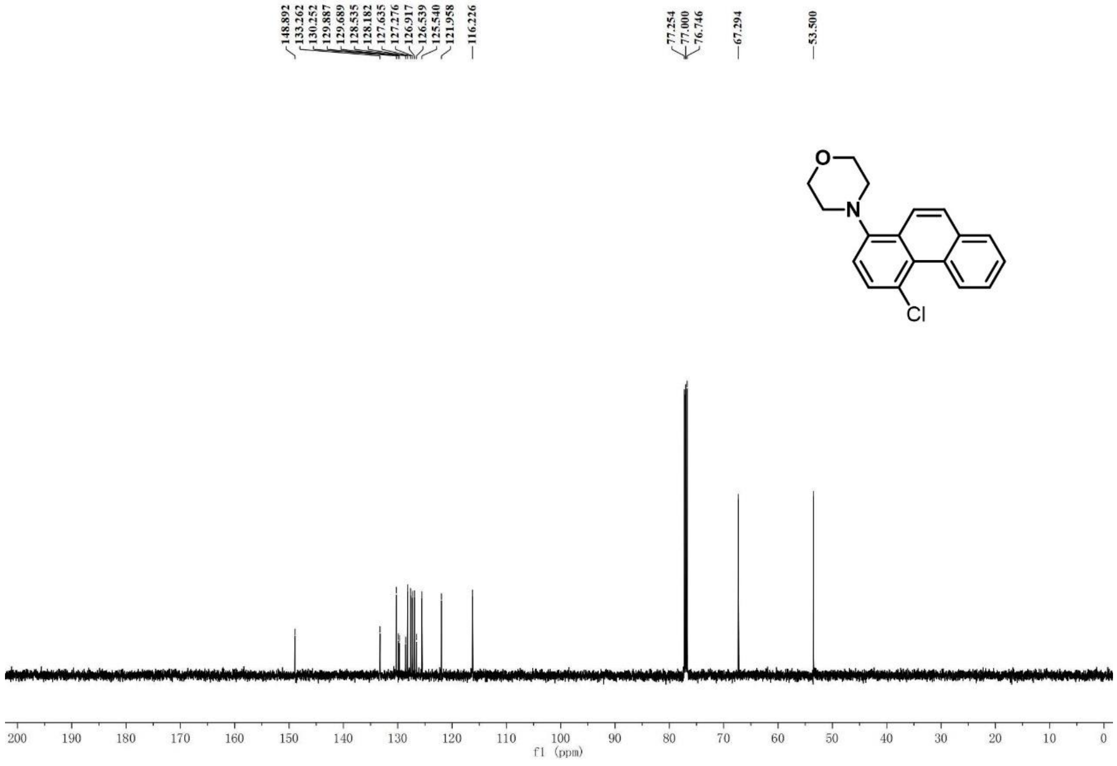
^{1}H NMR of **20** (500 MHz, CDCl$_3$) and ^{13}C NMR of **20** (125 MHz, CDCl$_3$)



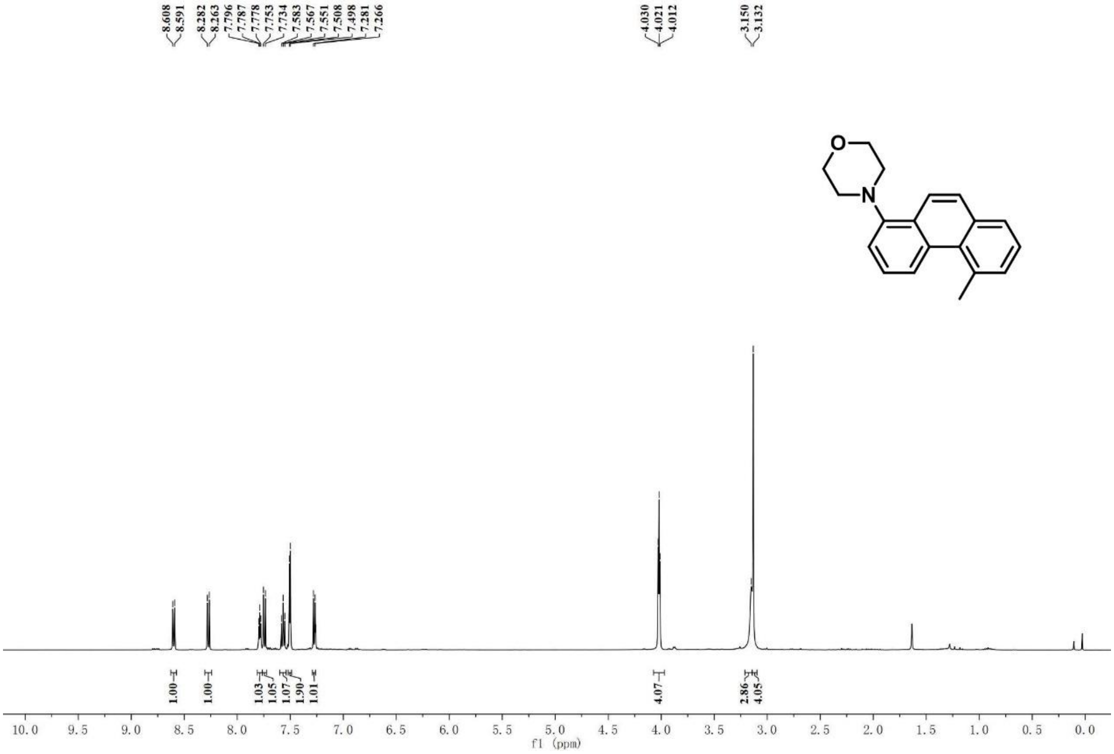


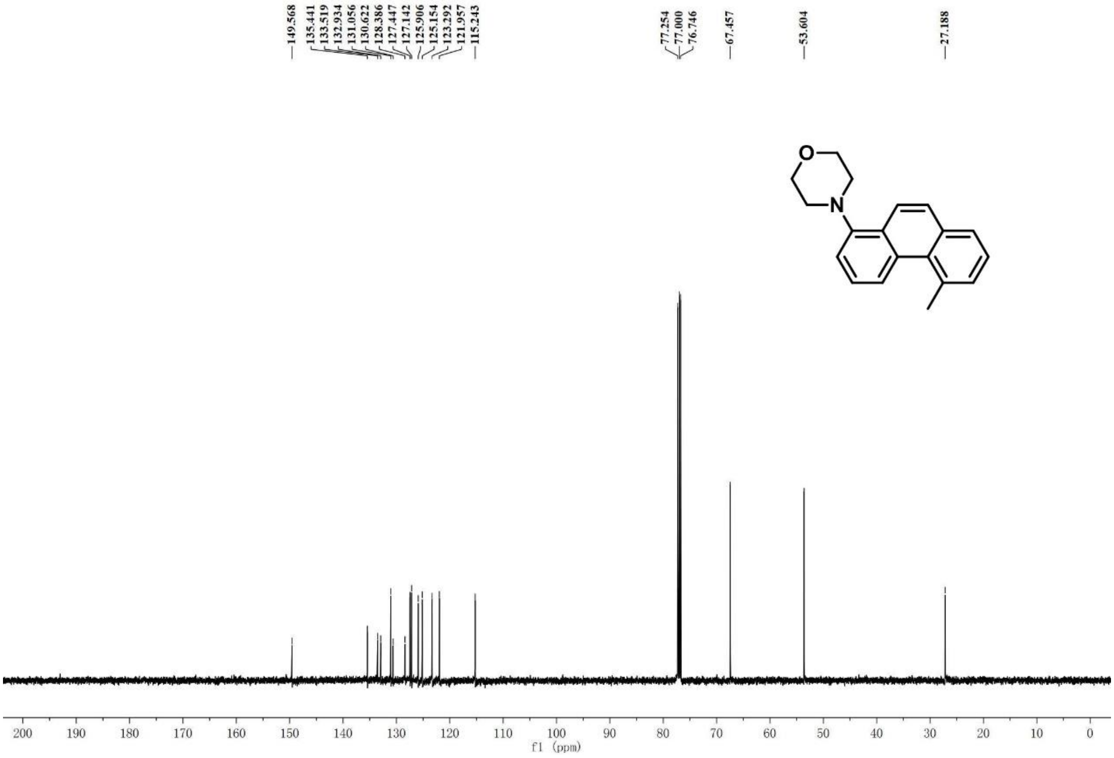
^{1}H NMR of **21** (500 MHz, CDCl$_3$) and ^{13}C NMR of **21** (125 MHz, CDCl$_3$)



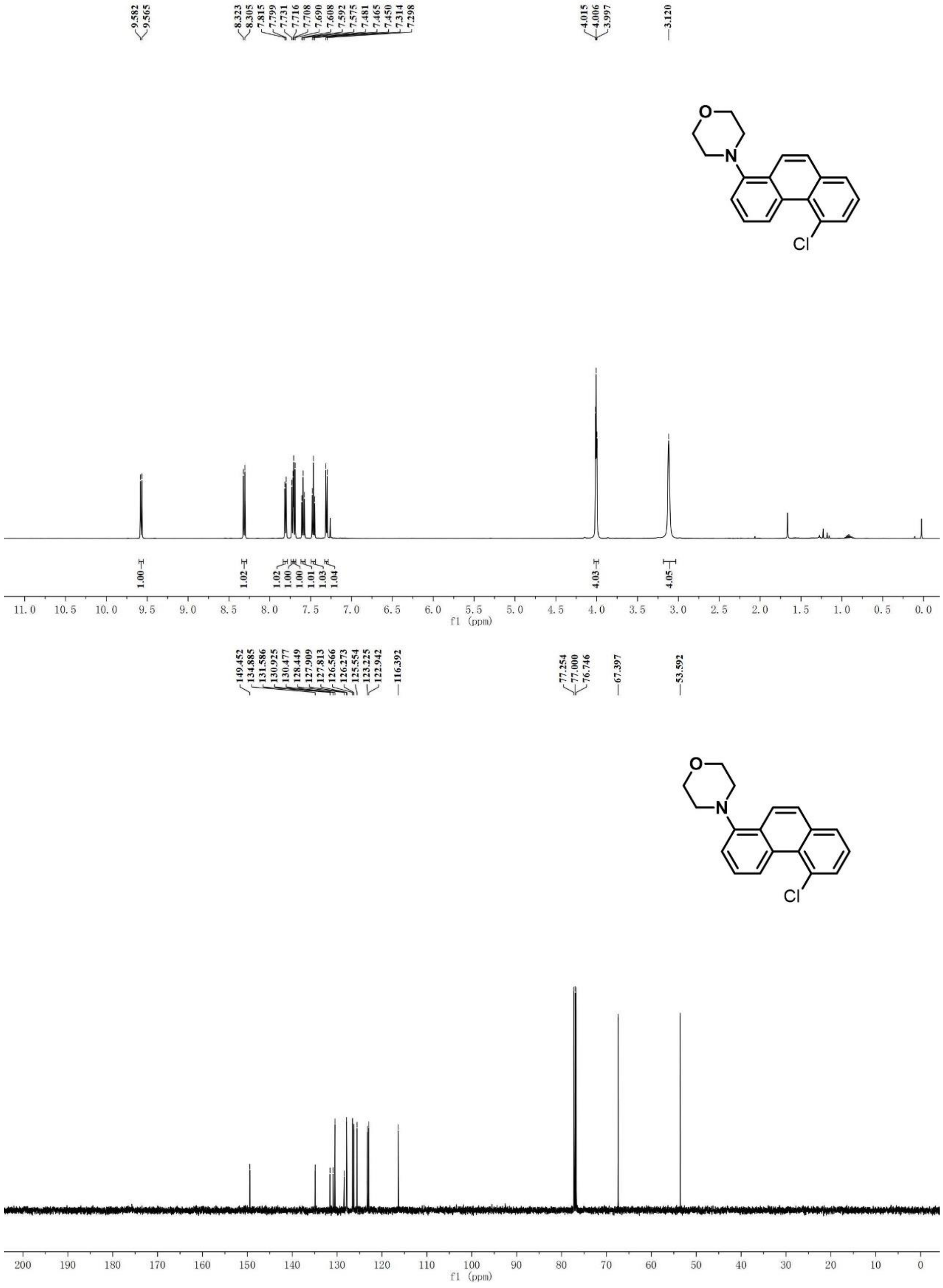


^{1}H NMR of **22** (500 MHz, $CDCl_3$) and ^{13}C NMR of **22** (125 MHz, $CDCl_3$)

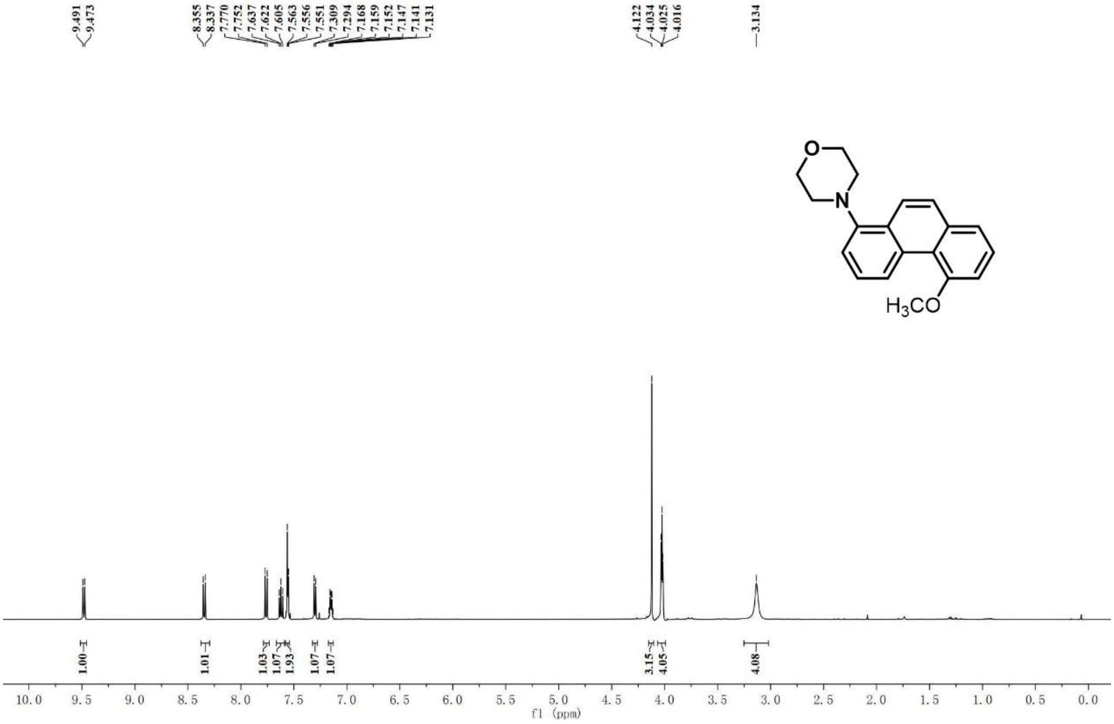


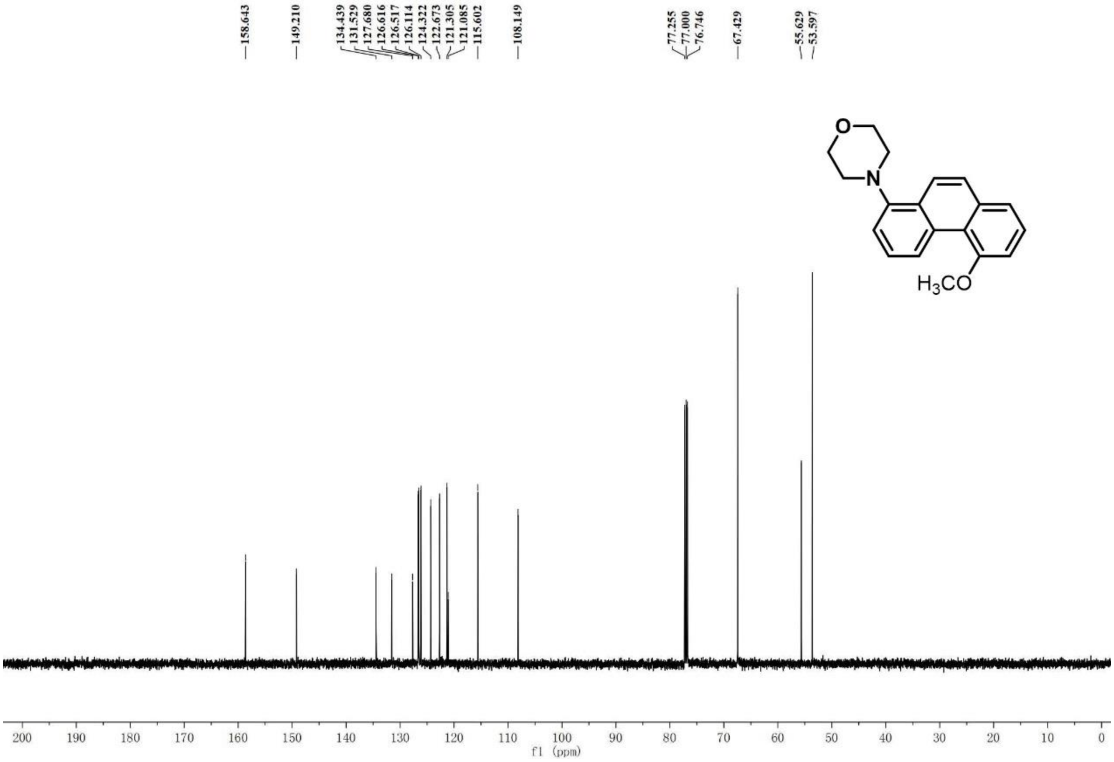


^{1}H NMR of **23** (500 MHz, CDCl$_3$) and ^{13}C NMR of **23** (125 MHz, CDCl$_3$)

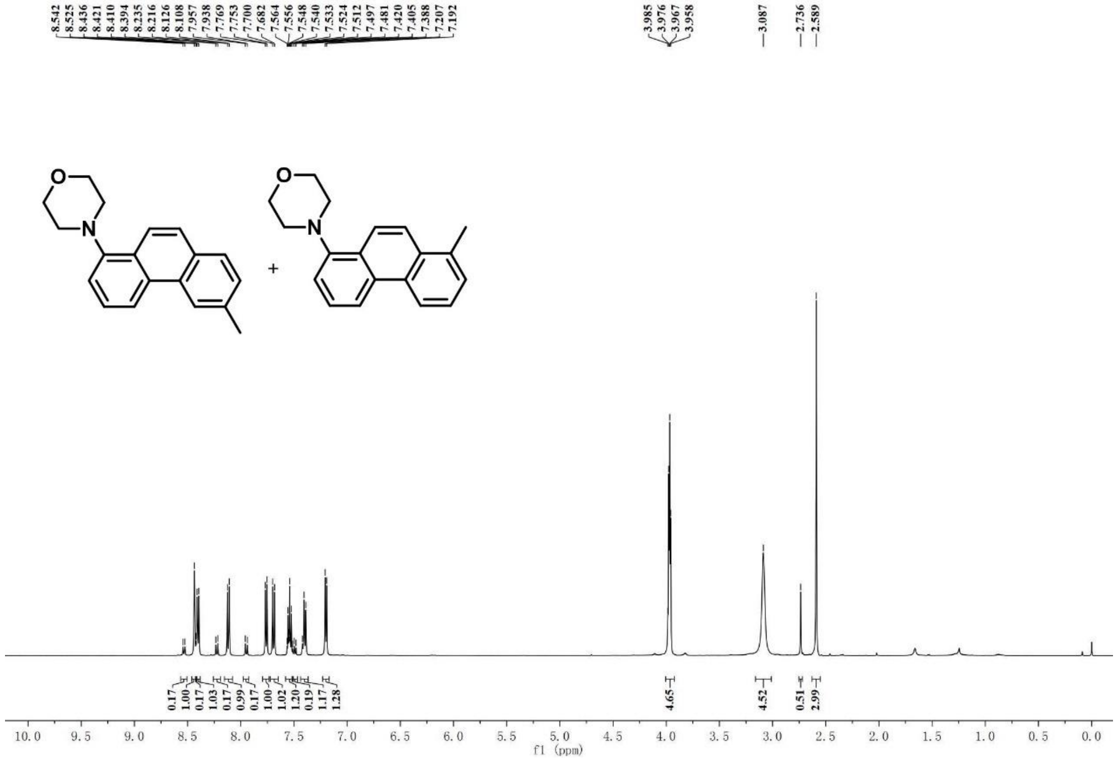


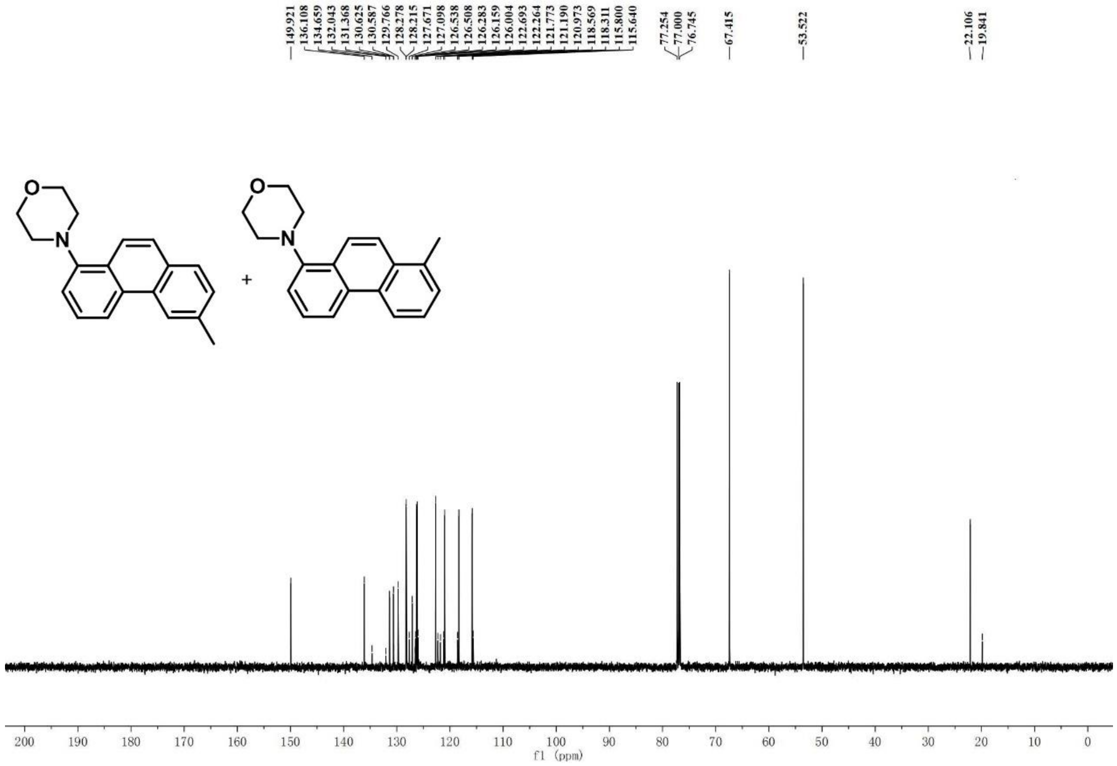
^{1}H NMR of **24** (500 MHz, $CDCl_3$) and ^{13}C NMR of **24** (125 MHz, $CDCl_3$)



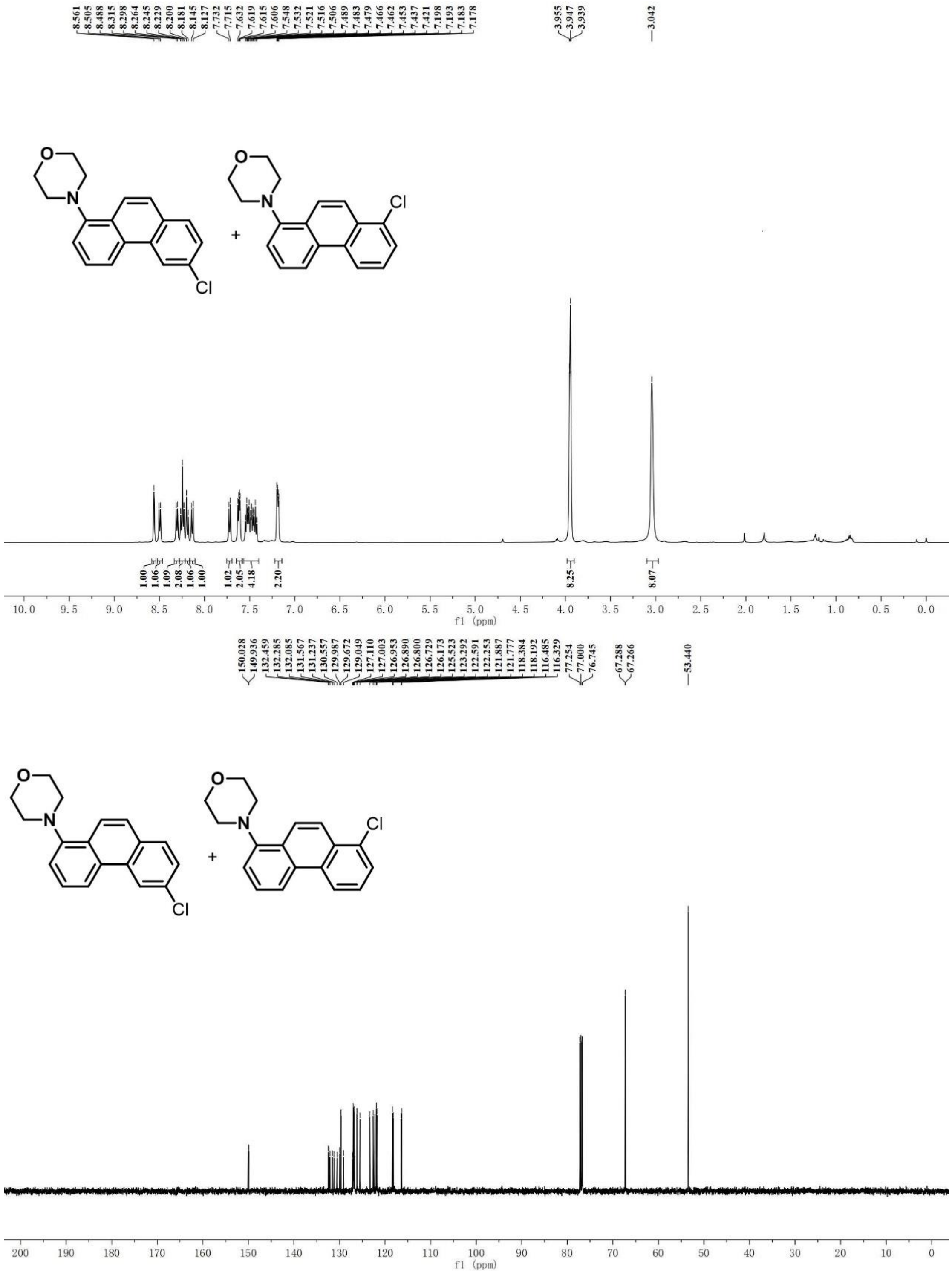


^{1}H NMR of **25** (500 MHz, $CDCl_3$) and ^{13}C NMR of **25** (125 MHz, $CDCl_3$)

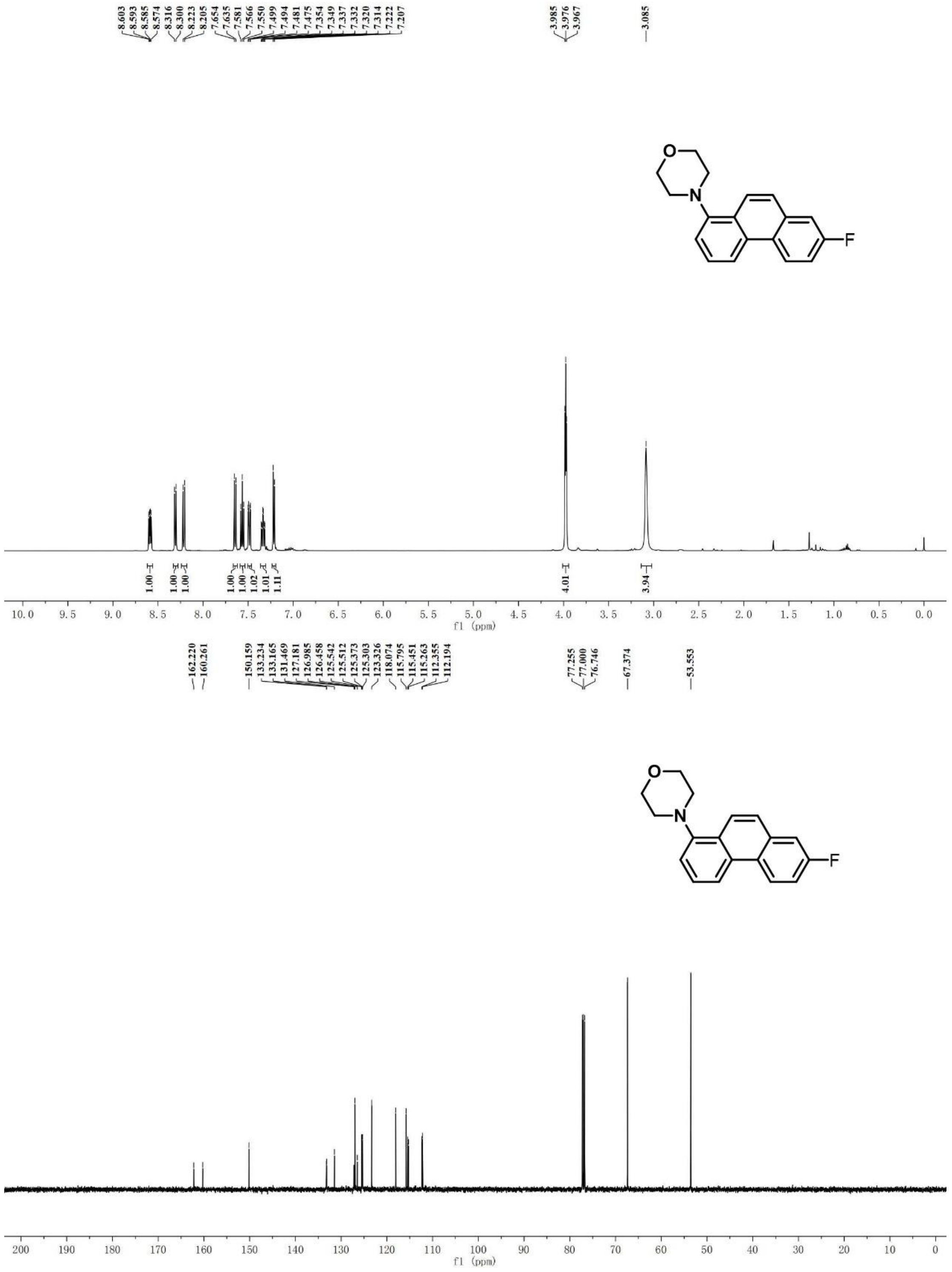




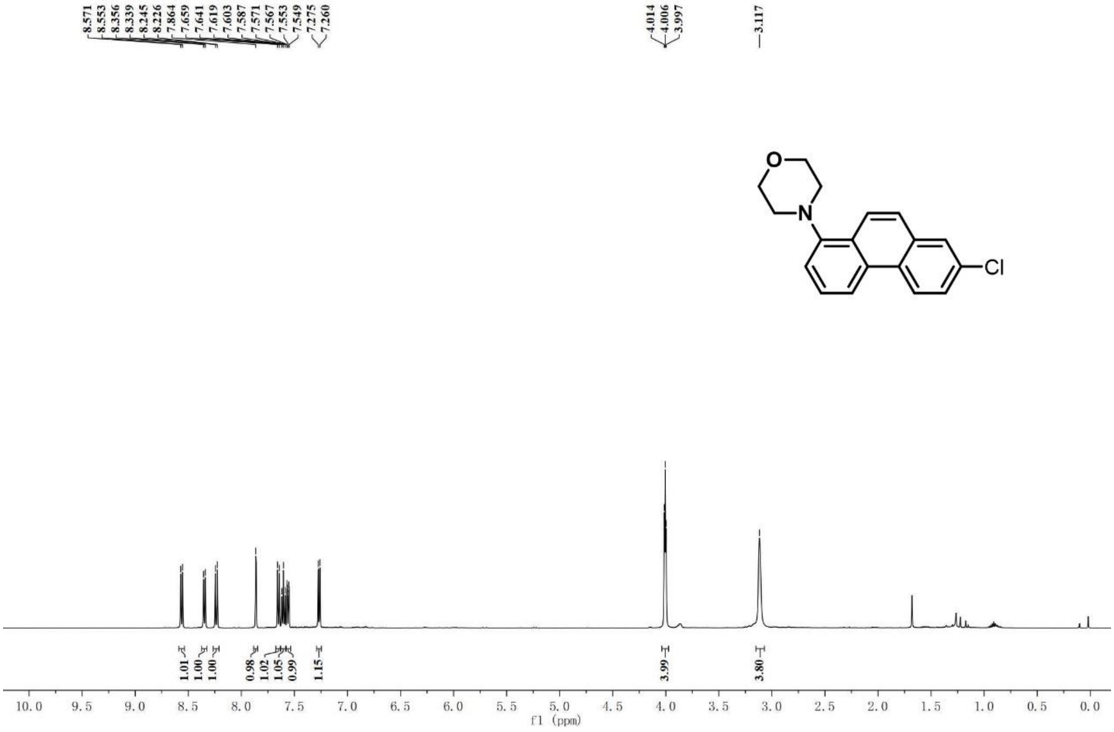
^{1}H NMR of **26** (500 MHz, $CDCl_3$) and ^{13}C NMR of **26** (125 MHz, $CDCl_3$)

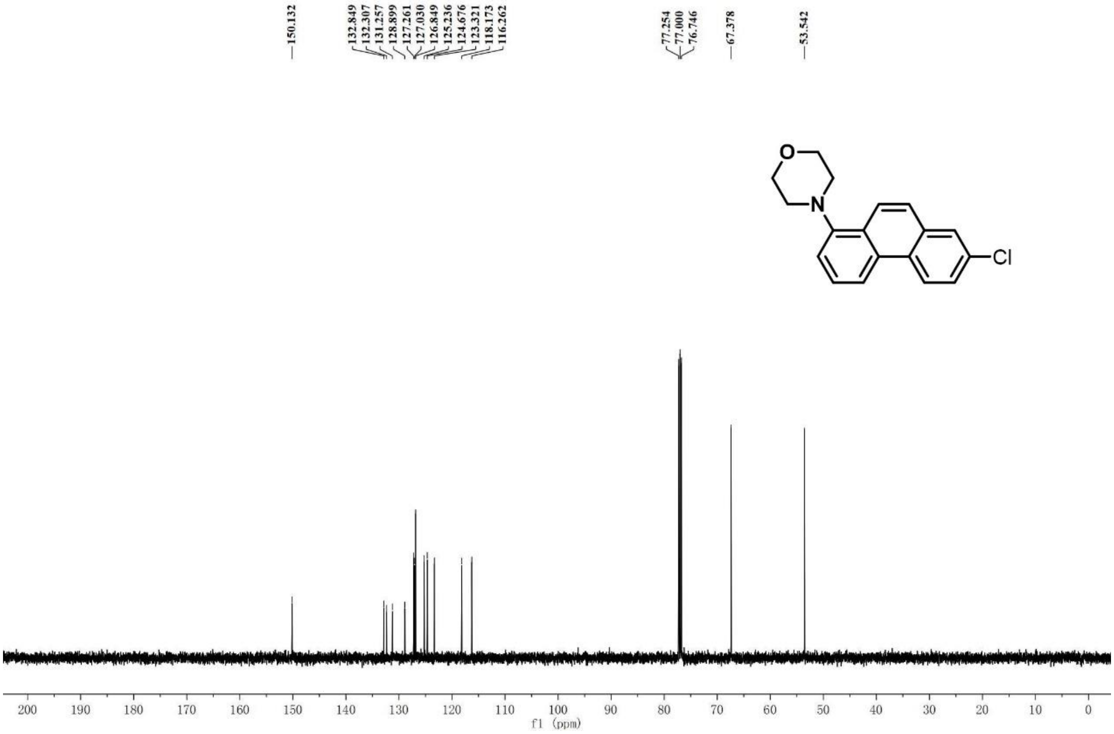


^{1}H NMR of **27** (500 MHz, CDCl$_3$) and ^{13}C NMR of **27** (125 MHz, CDCl$_3$)

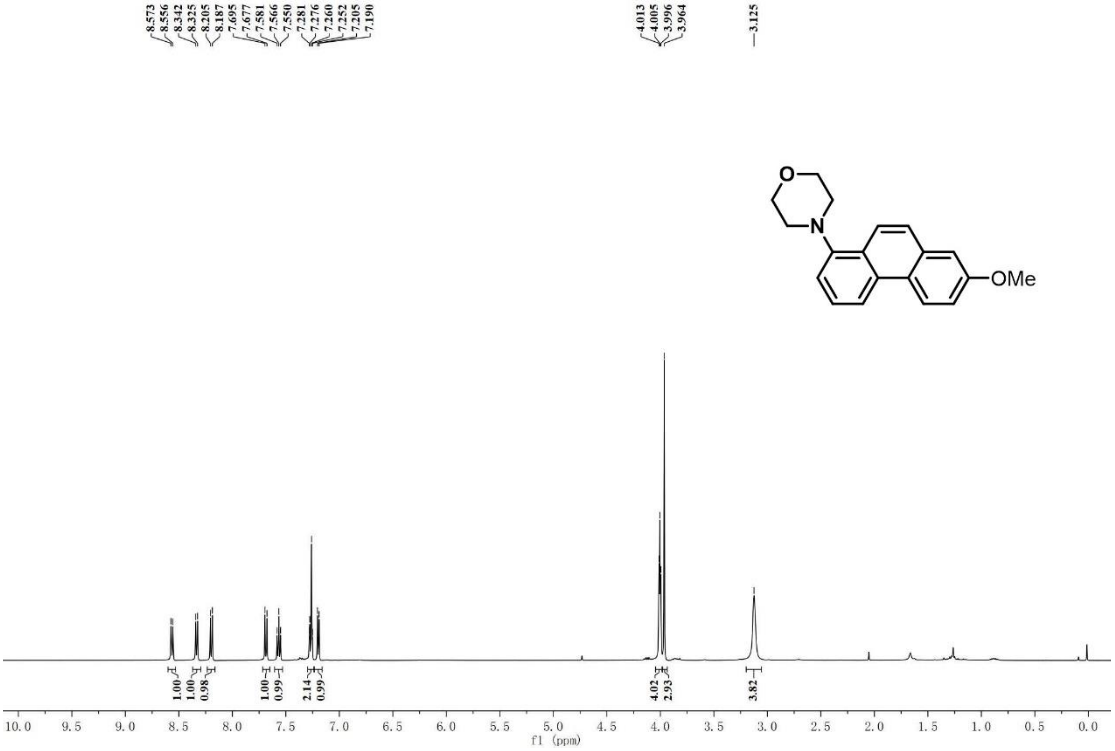


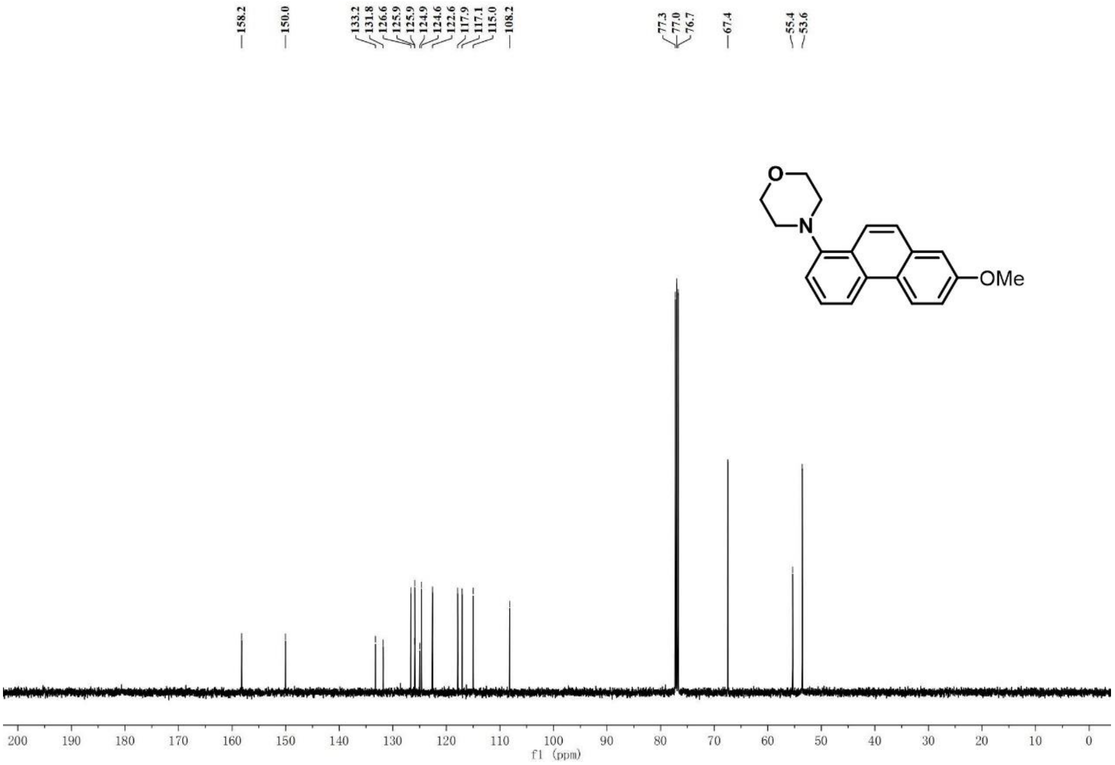
^{1}H NMR of **28** (500 MHz, $CDCl_3$) and ^{13}C NMR of **28** (125 MHz, $CDCl_3$)



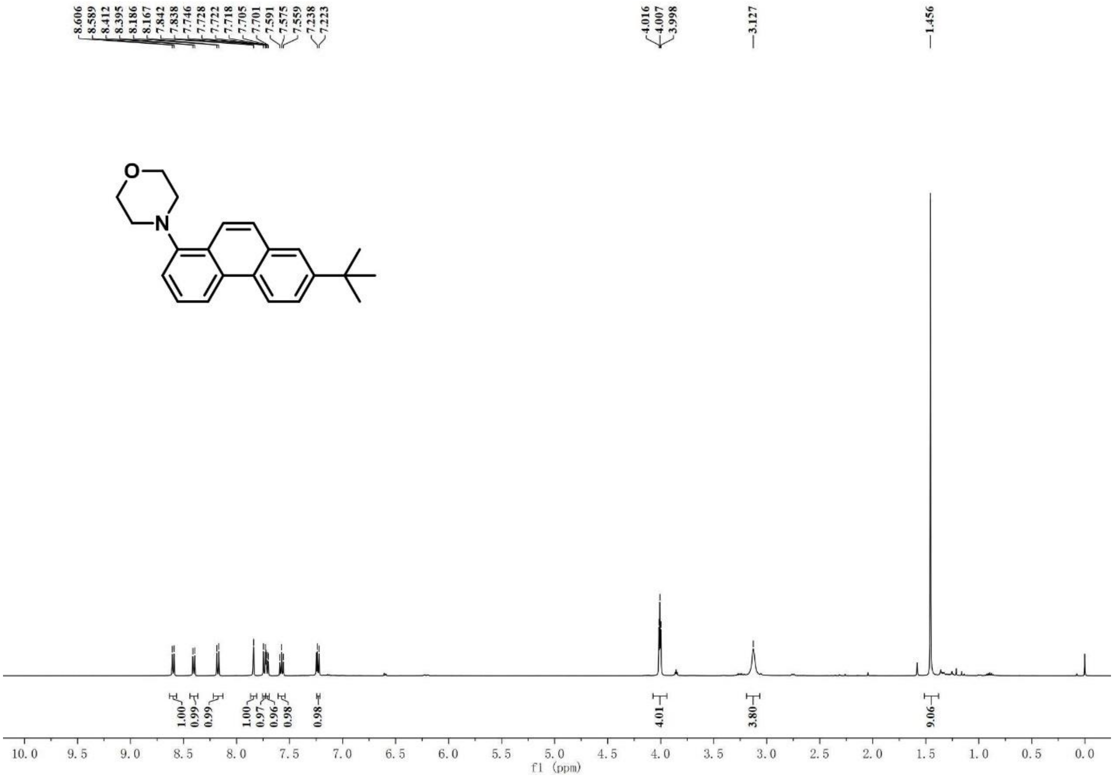


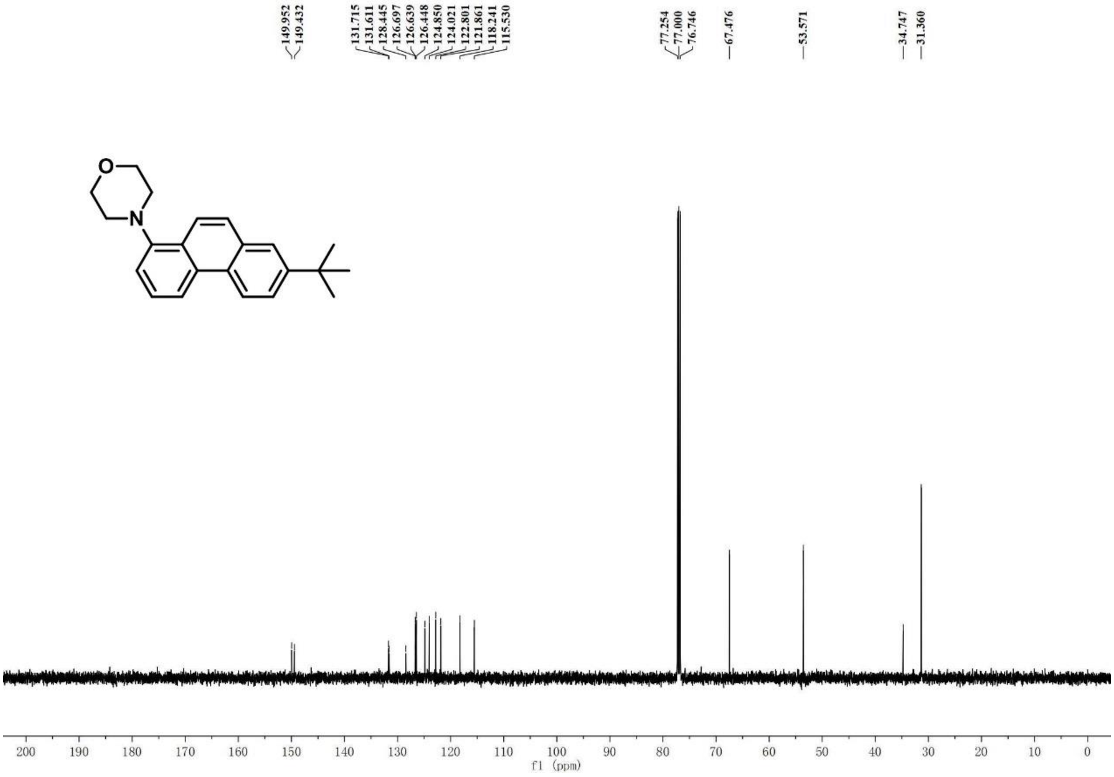
^{1}H NMR of **29** (500 MHz, CDCl$_3$) and ^{13}C NMR of **29** (125 MHz, CDCl$_3$)



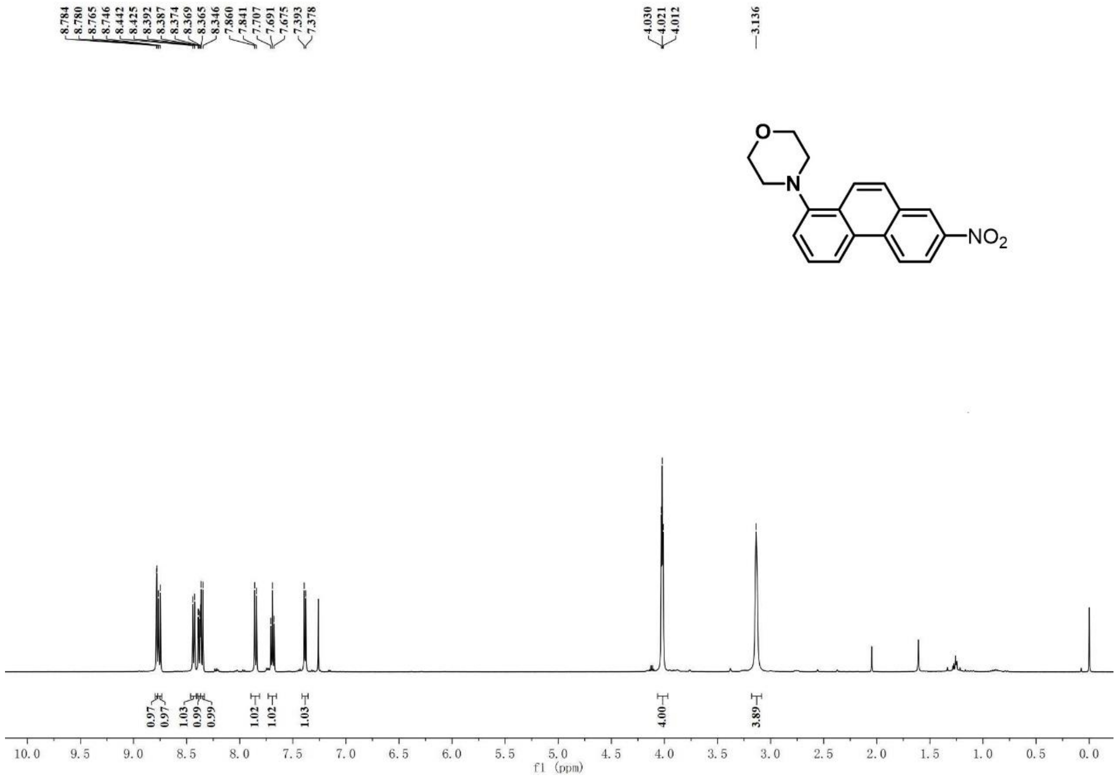


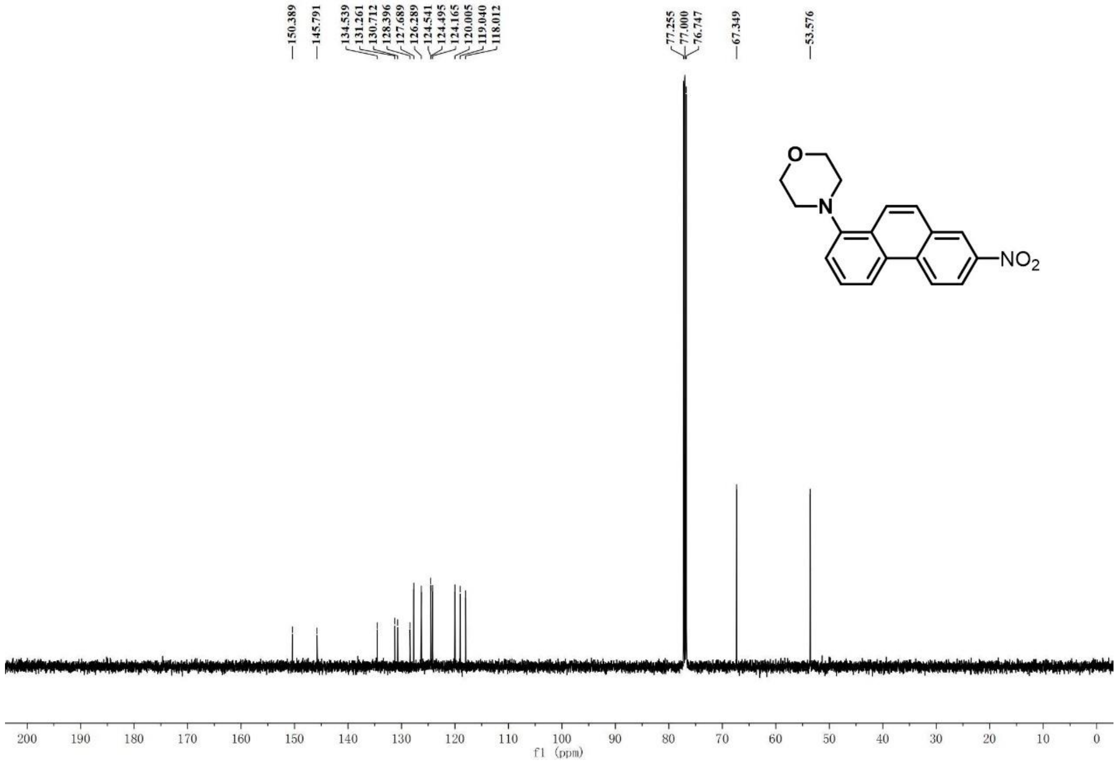
^{1}H NMR of **30** (500 MHz, $CDCl_3$) and ^{13}C NMR of **30** (125 MHz, $CDCl_3$)



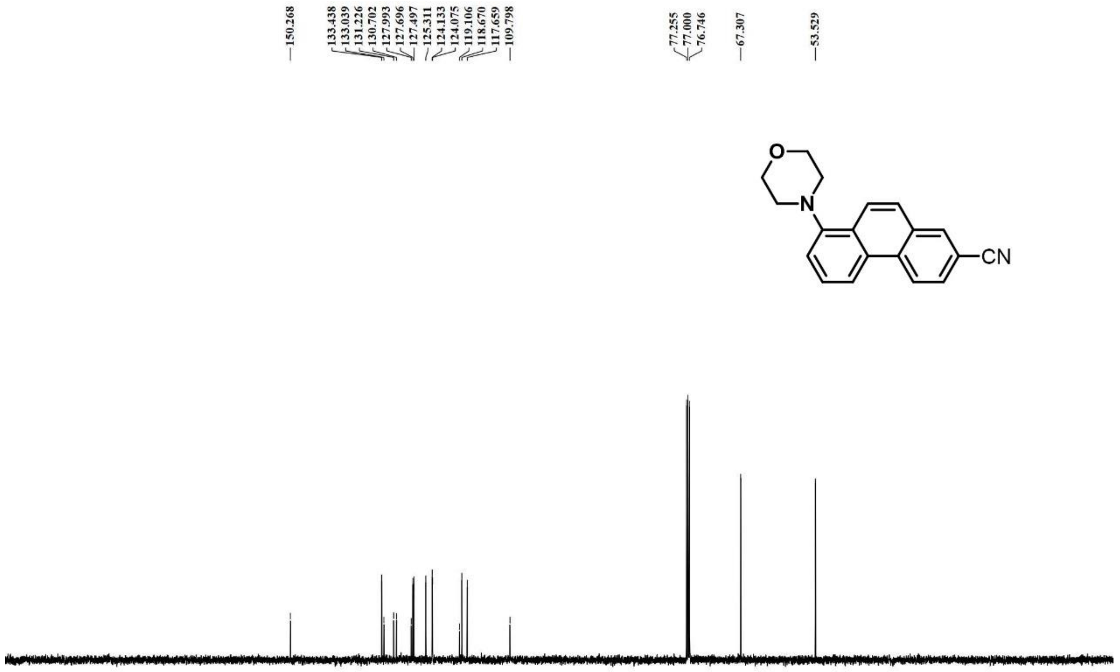


^{1}H NMR of **31** (500 MHz, CDCl$_3$) and ^{13}C NMR of **31** (125 MHz, CDCl$_3$)

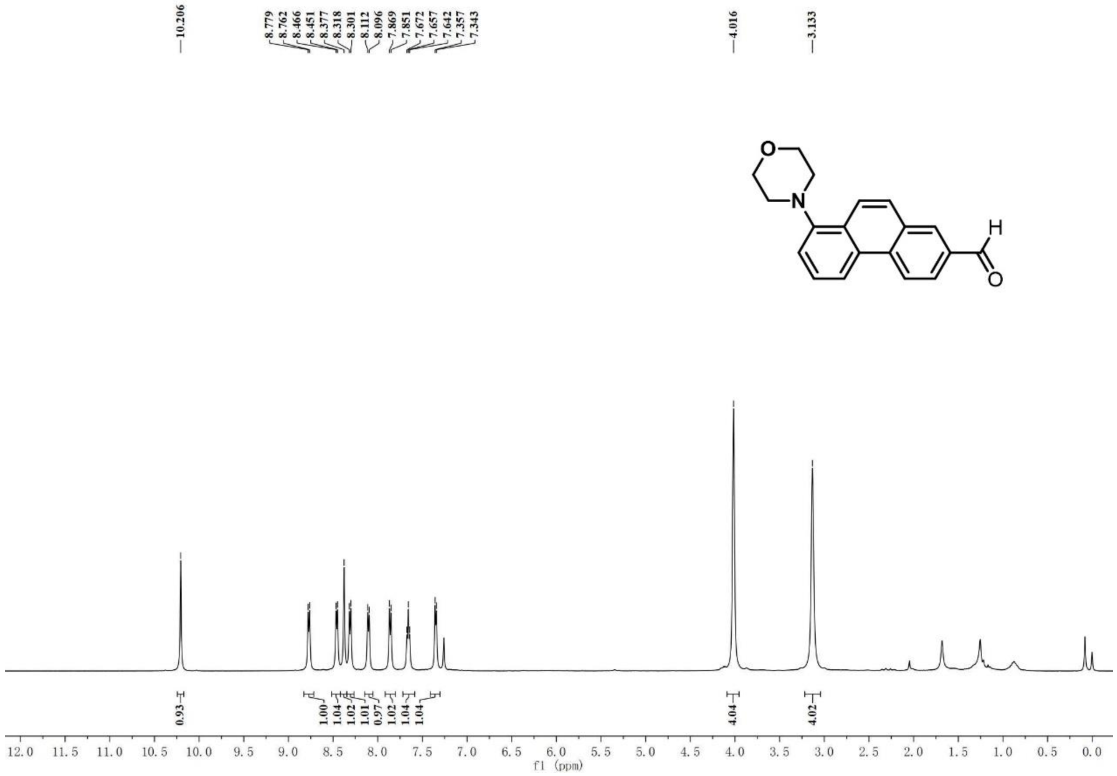


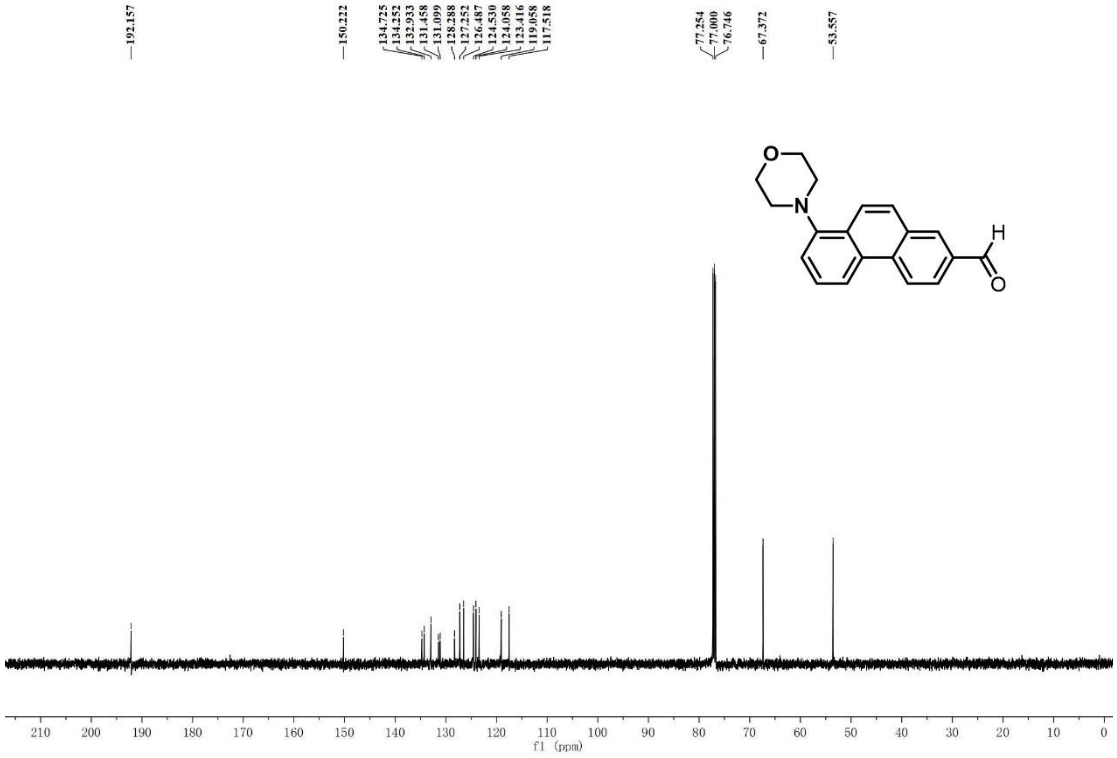


^{1}H NMR of **32** (500 MHz, $CDCl_3$) and ^{13}C NMR of **32** (125 MHz, $CDCl_3$)

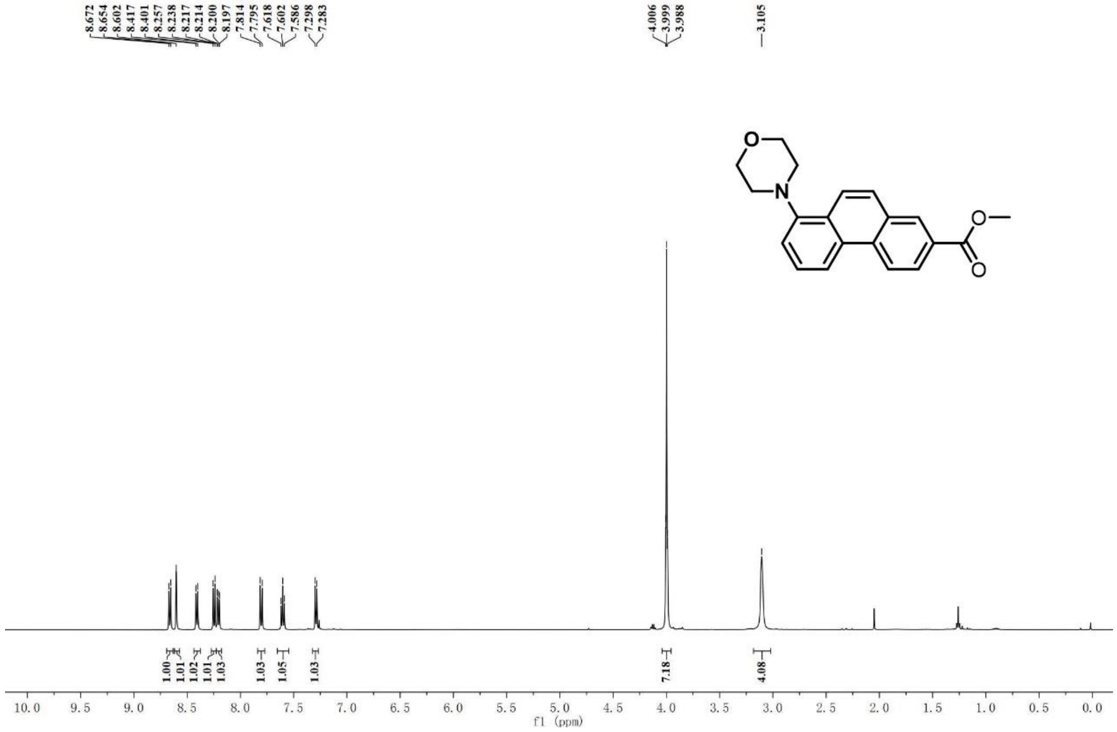


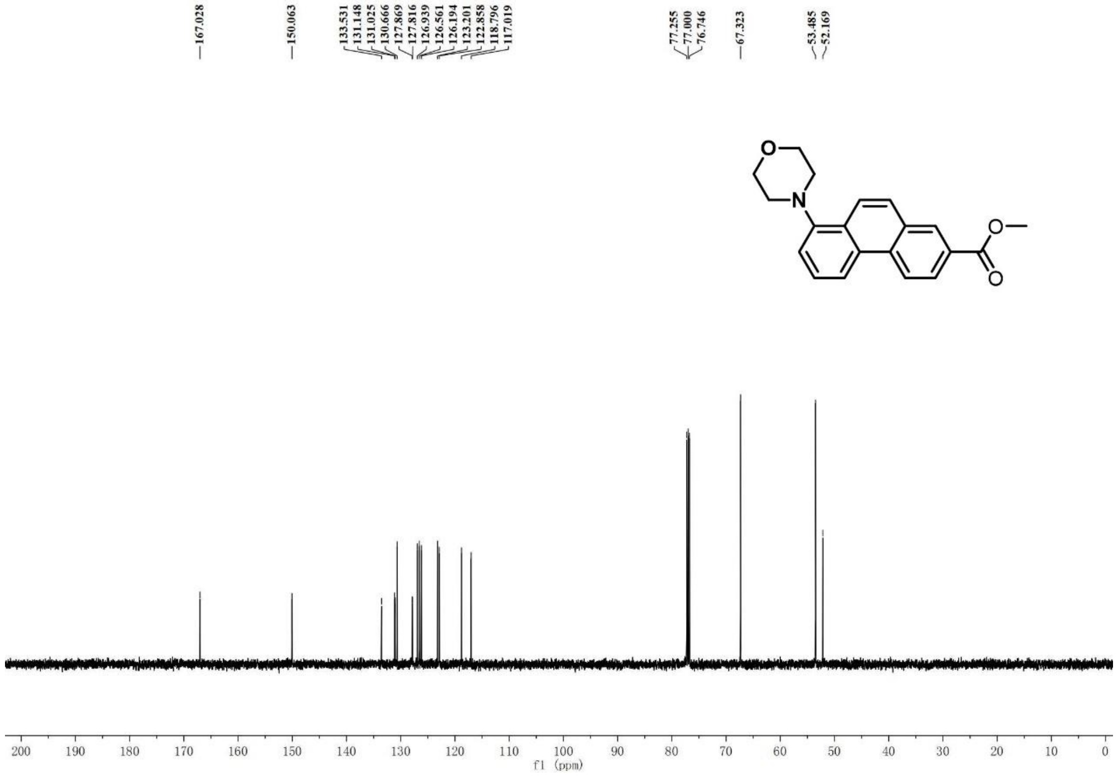
^{1}H NMR of **33** (500 MHz, $CDCl_3$) and ^{13}C NMR of **33** (125 MHz, $CDCl_3$)



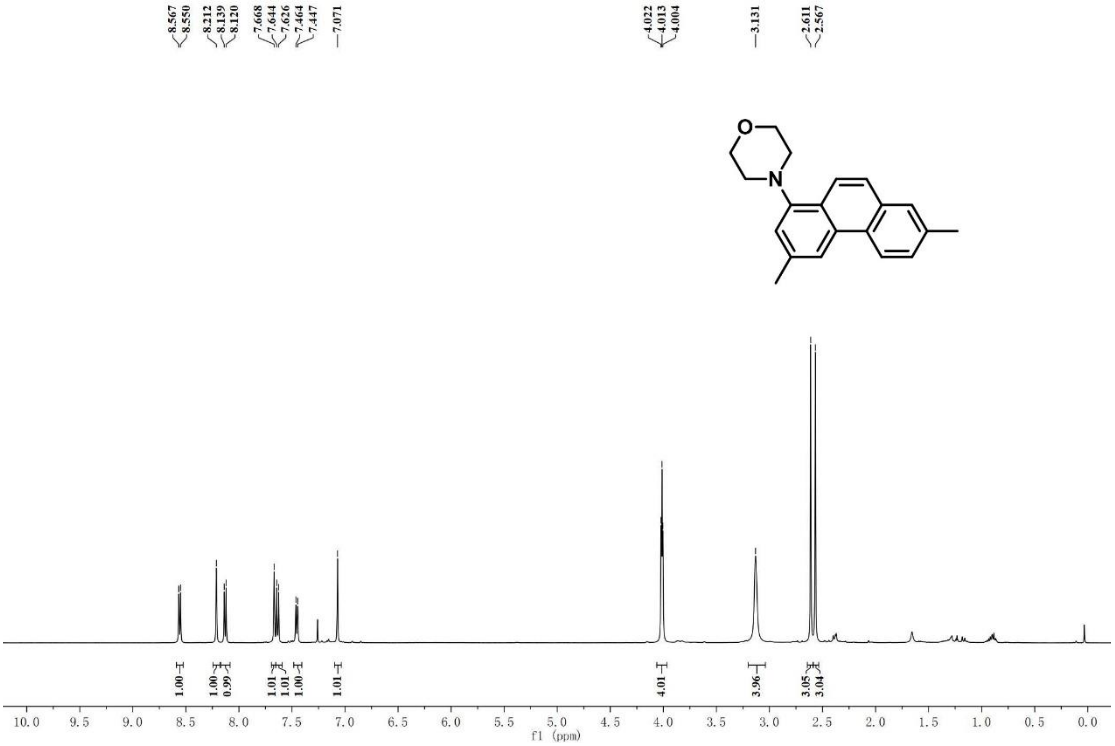


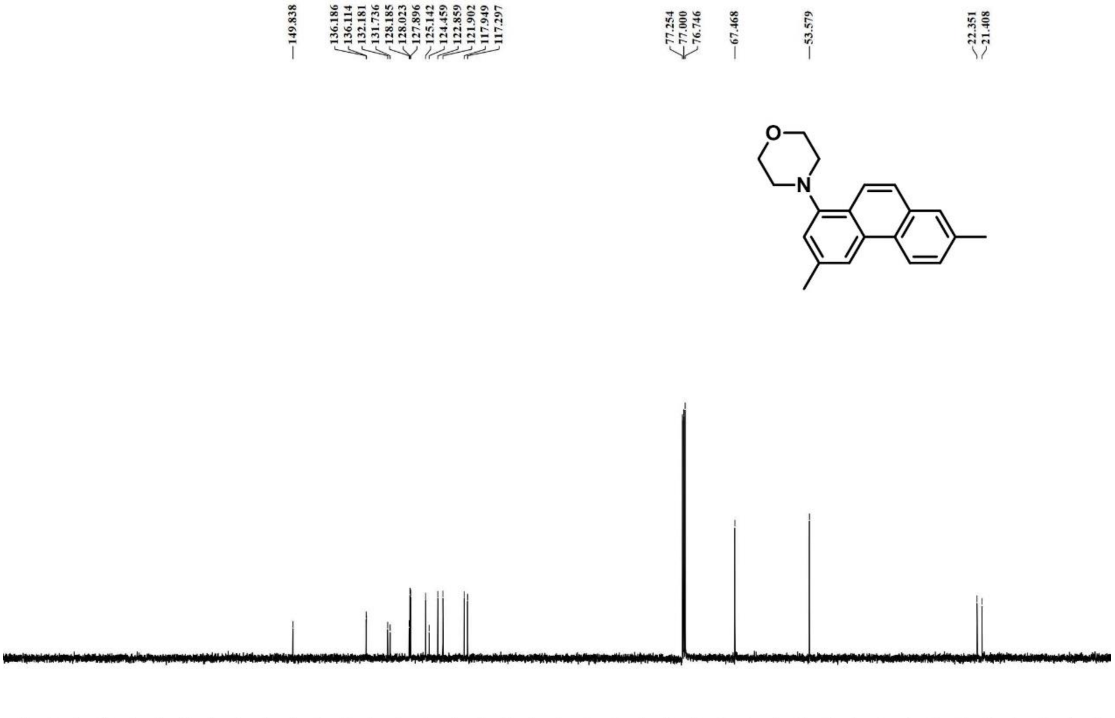
^{1}H NMR of **34** (500 MHz, $CDCl_3$) and ^{13}C NMR of **34** (125 MHz, $CDCl_3$)



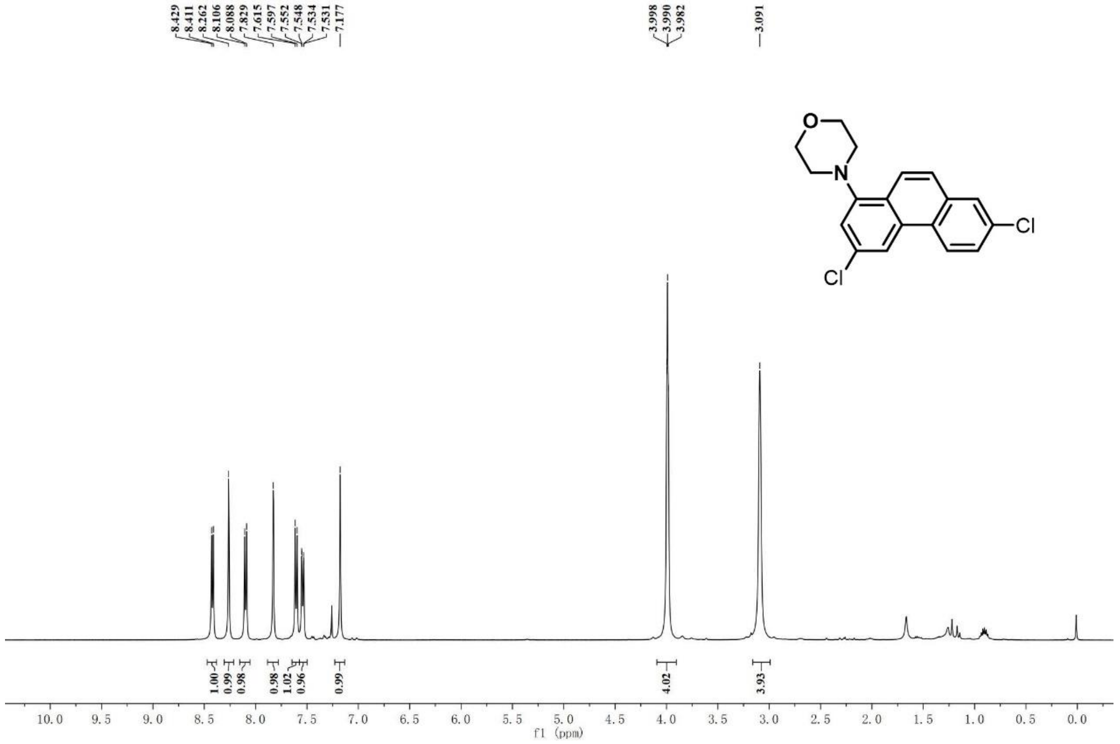


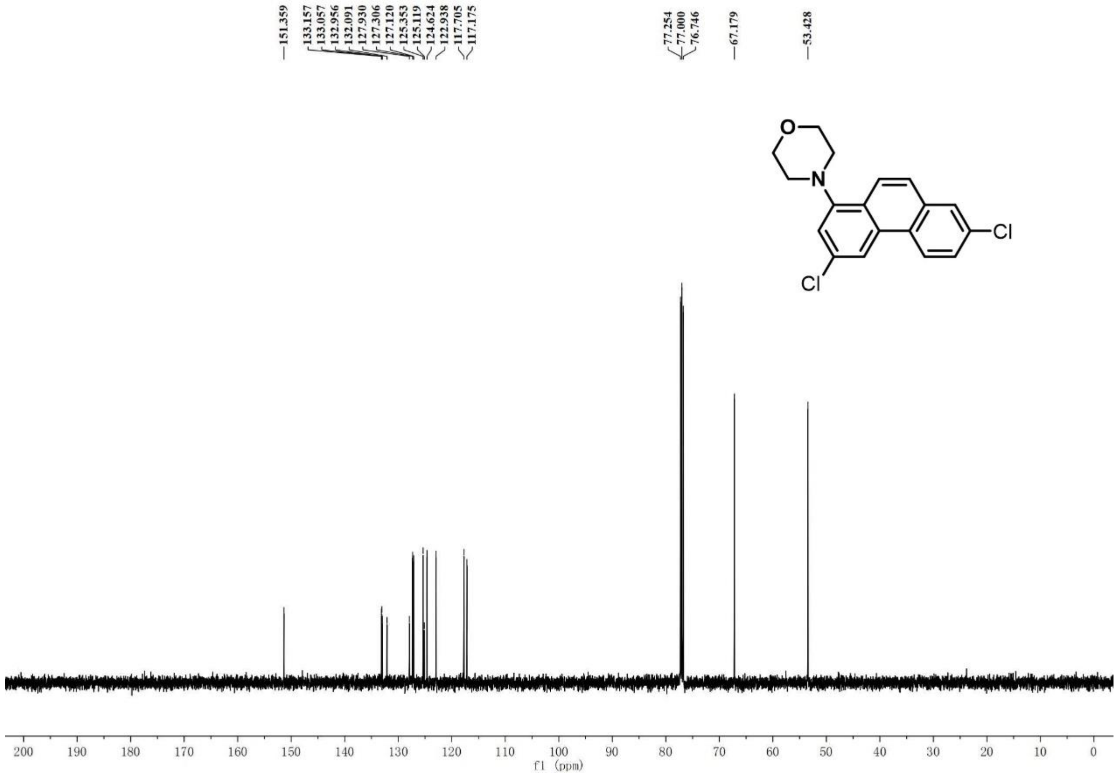
^{1}H NMR of **35** (500 MHz, $CDCl_3$) and ^{13}C NMR of **35** (125 MHz, $CDCl_3$)



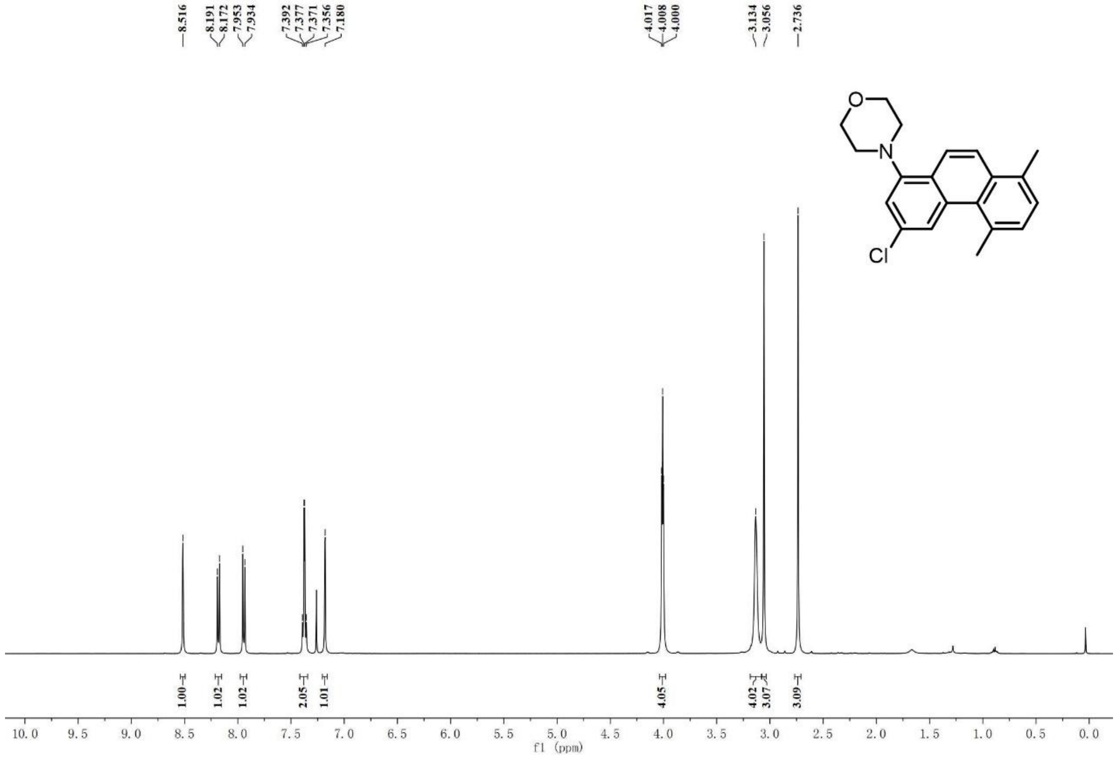


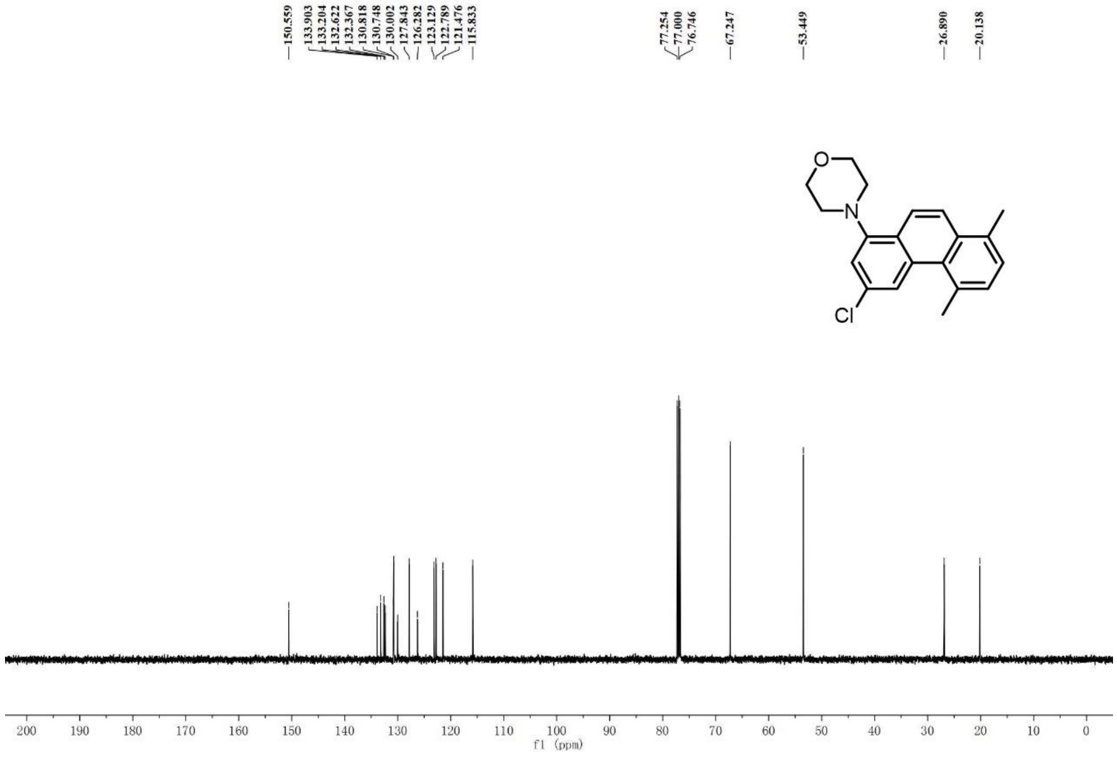
^{1}H NMR of **36** (500 MHz, $CDCl_3$) and ^{13}C NMR of **36** (125 MHz, $CDCl_3$)



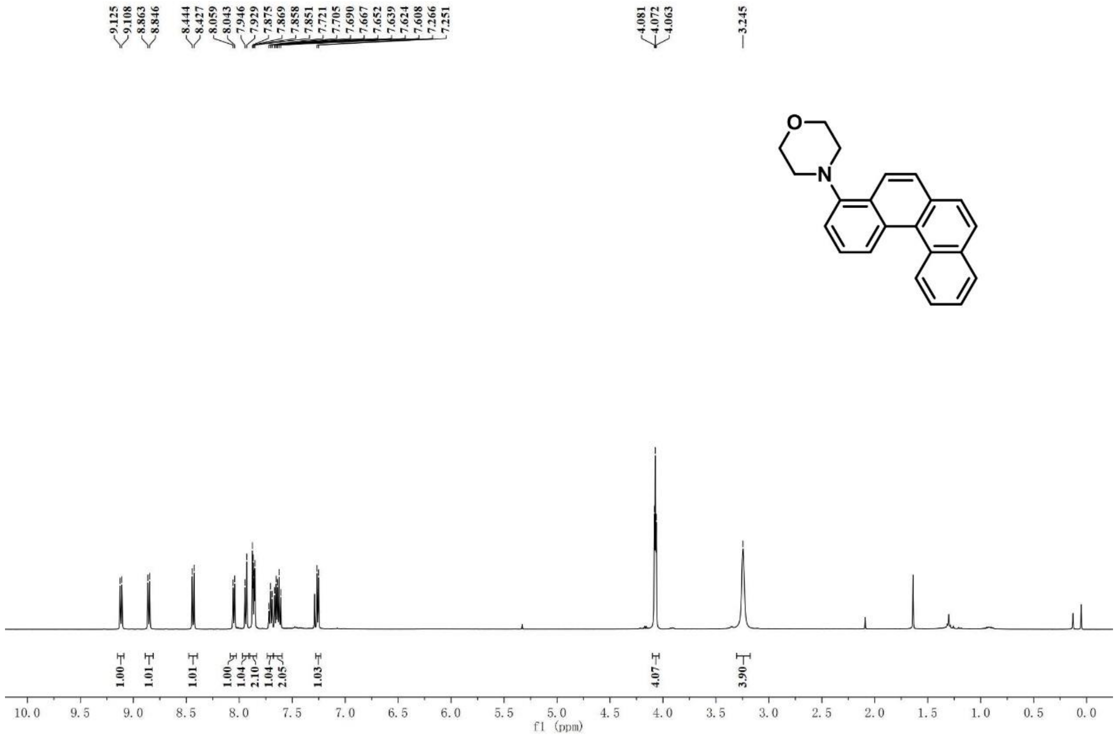


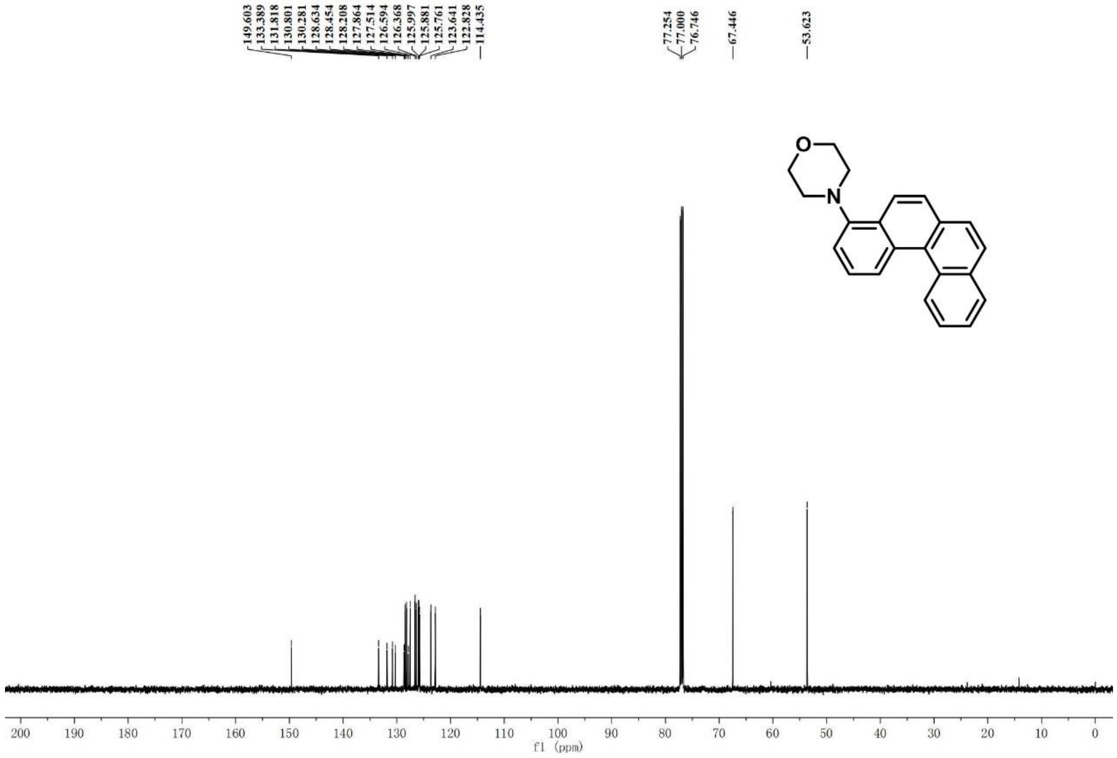
^{1}H NMR of **37** (500 MHz, $CDCl_3$) and ^{13}C NMR of **37** (125 MHz, $CDCl_3$)



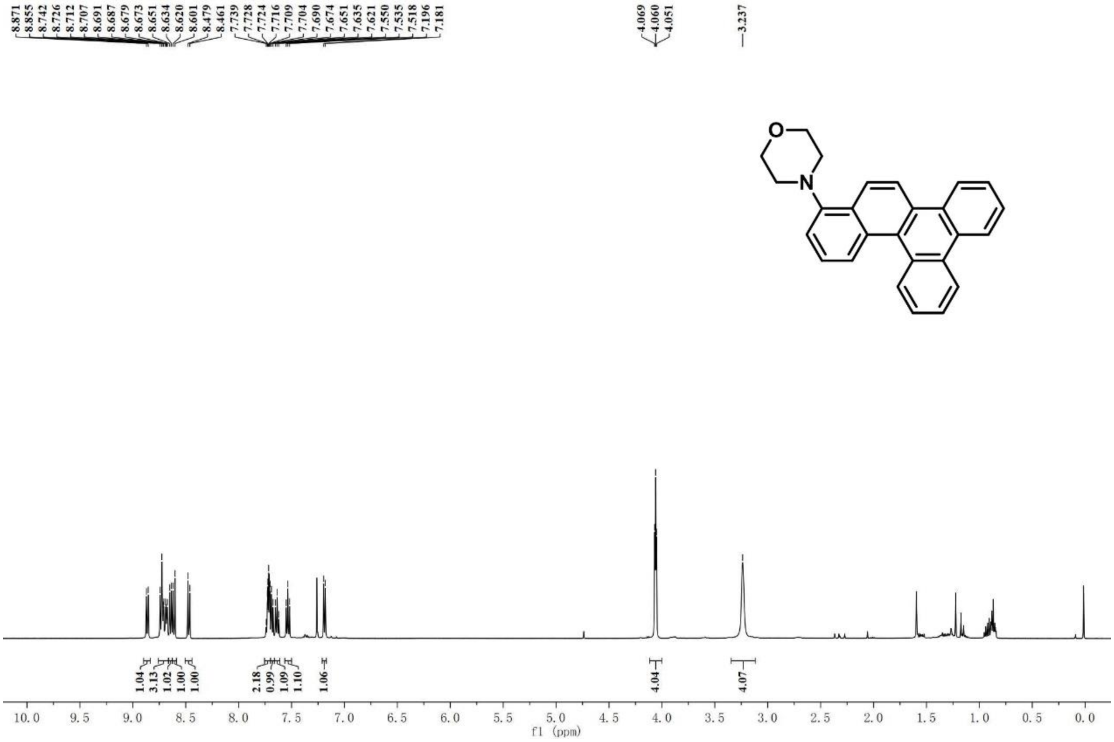


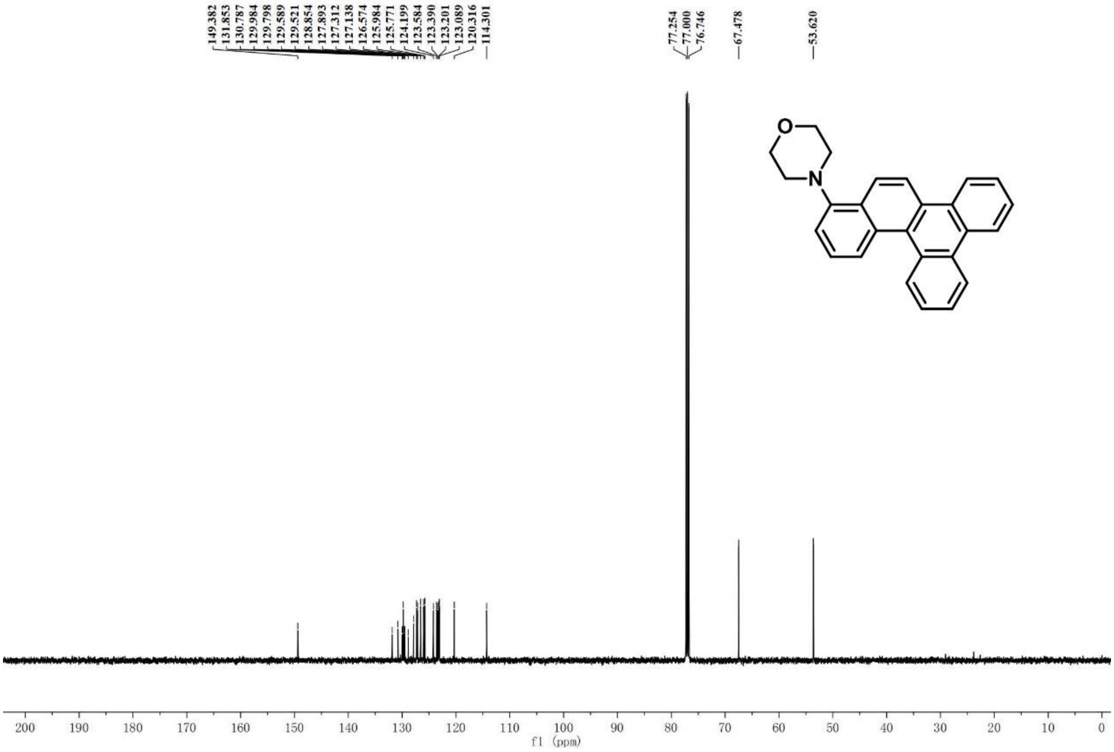
^{1}H NMR of **38** (500 MHz, $CDCl_3$) and ^{13}C NMR of **38** (125 MHz, $CDCl_3$)



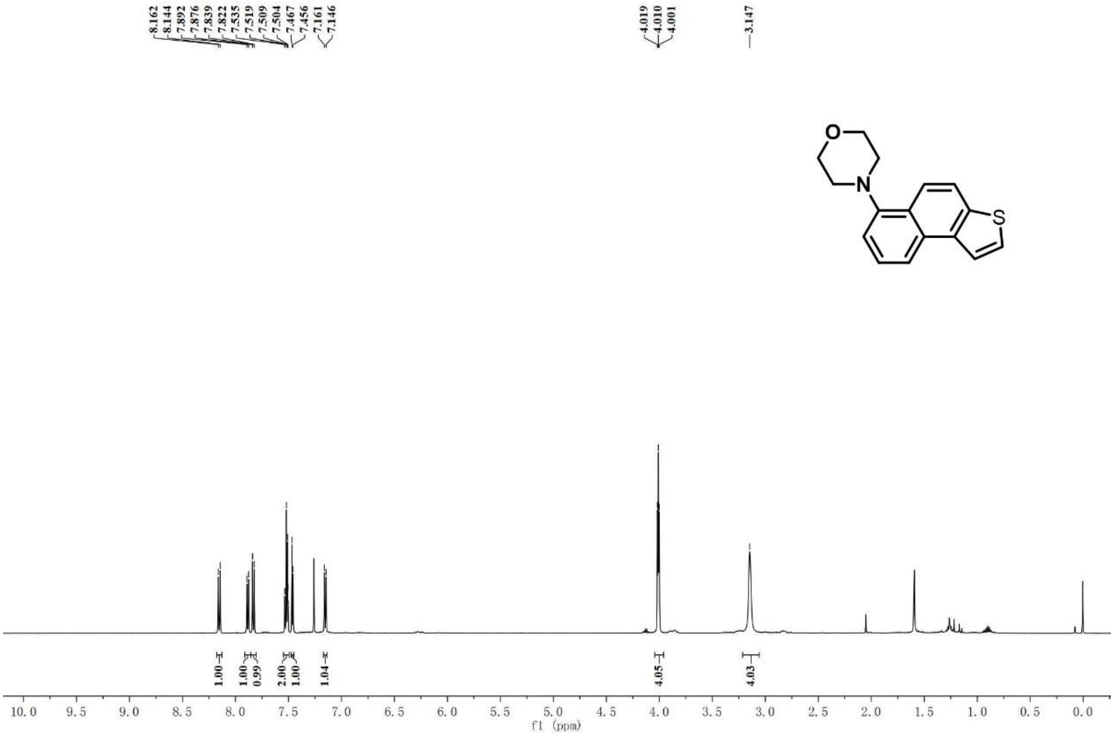


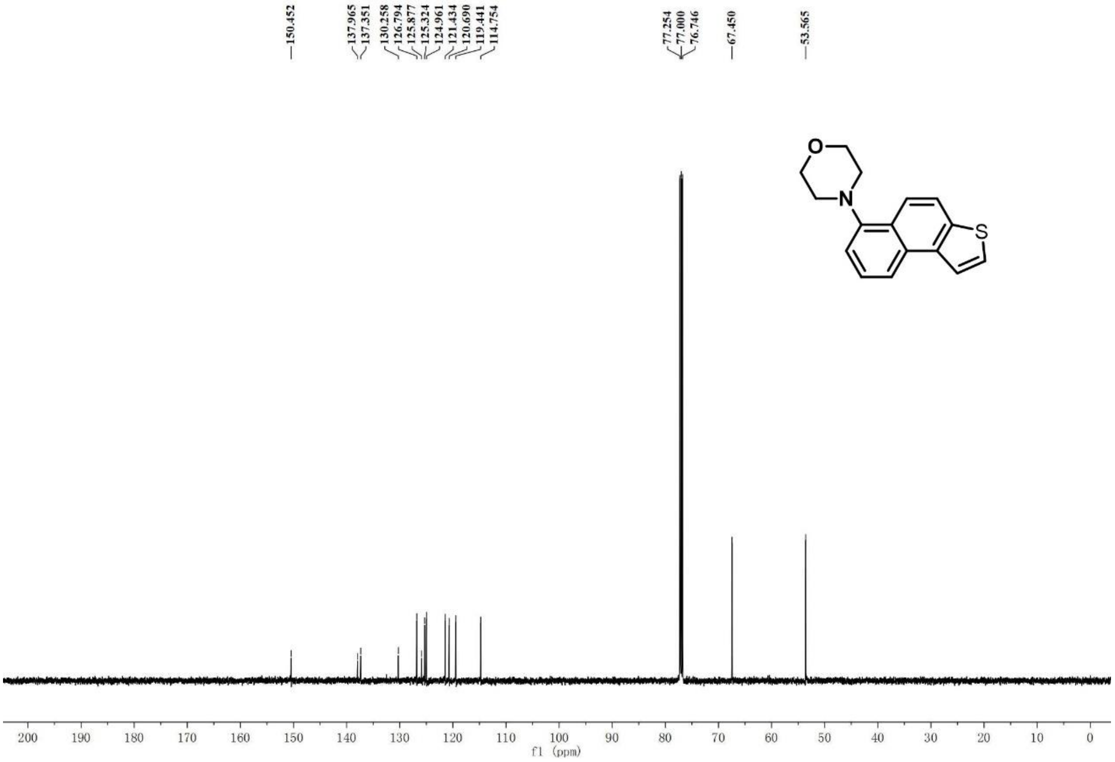
^{1}H NMR of **39** (500 MHz, $CDCl_3$) and ^{13}C NMR of **39** (125 MHz, $CDCl_3$)



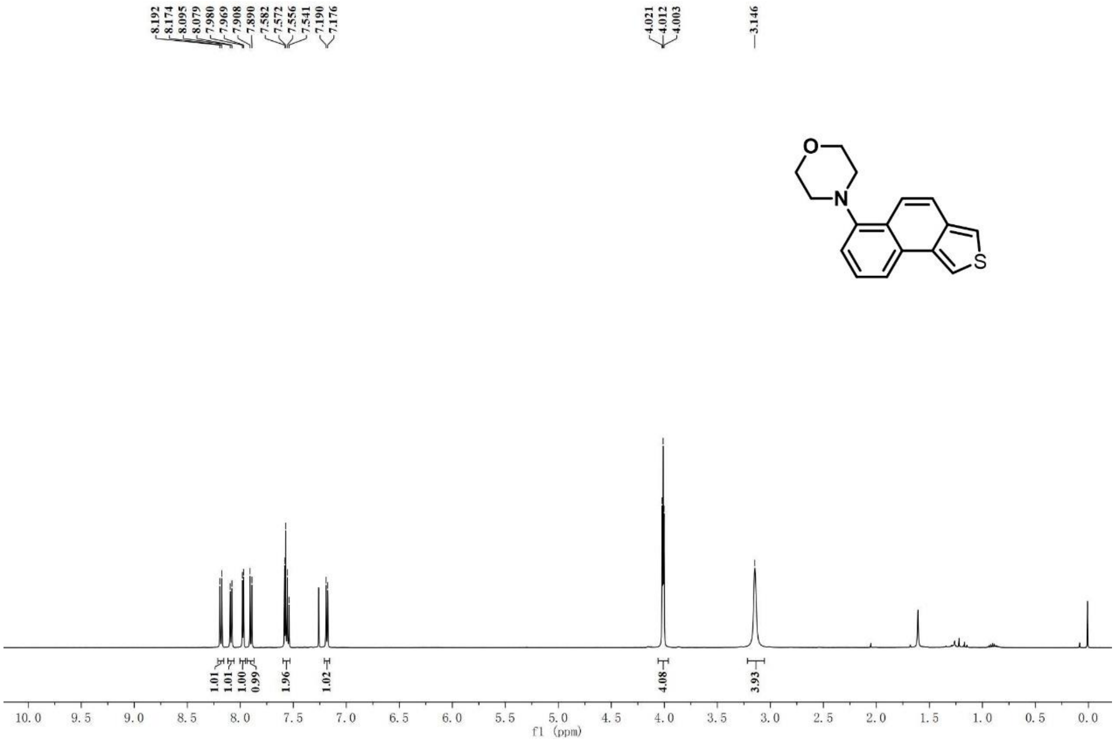


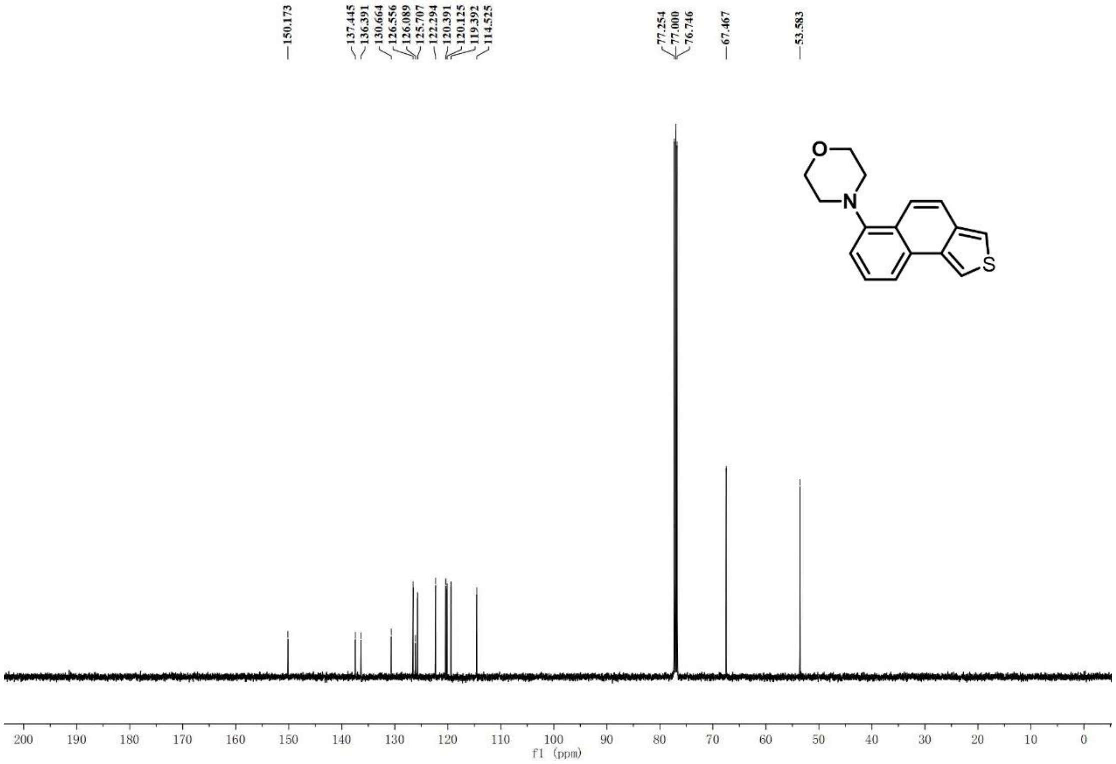
^{1}H NMR of **40** (500 MHz, $CDCl_3$) and ^{13}C NMR of **40** (125 MHz, $CDCl_3$)



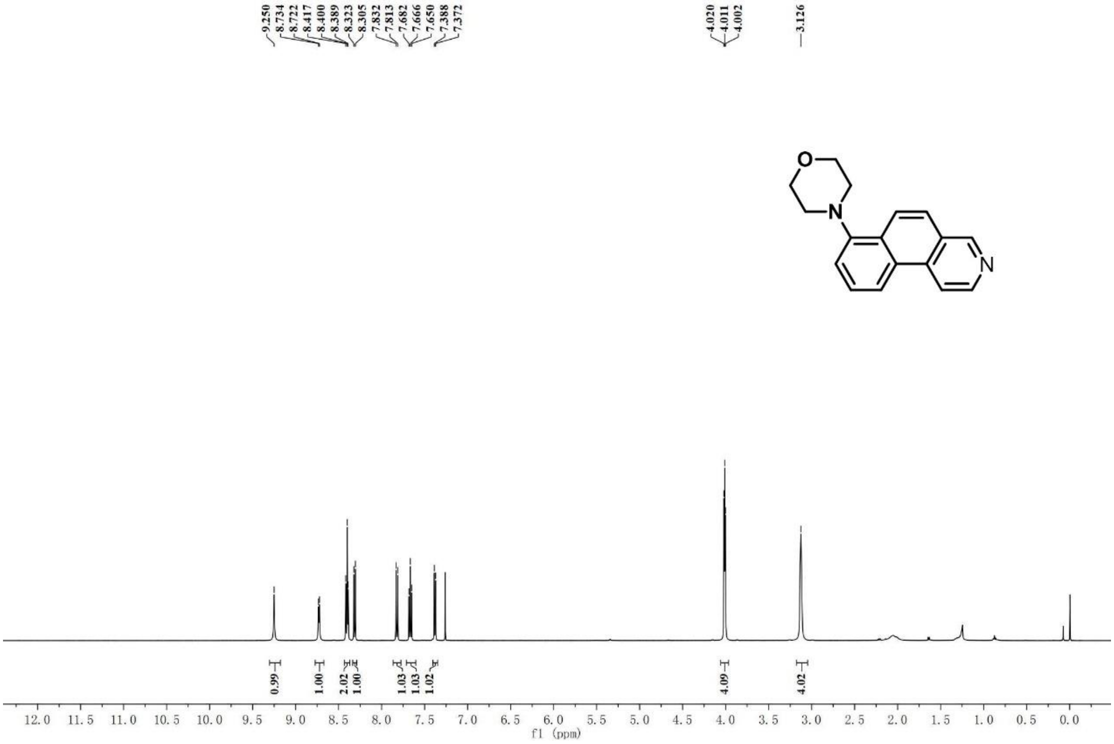


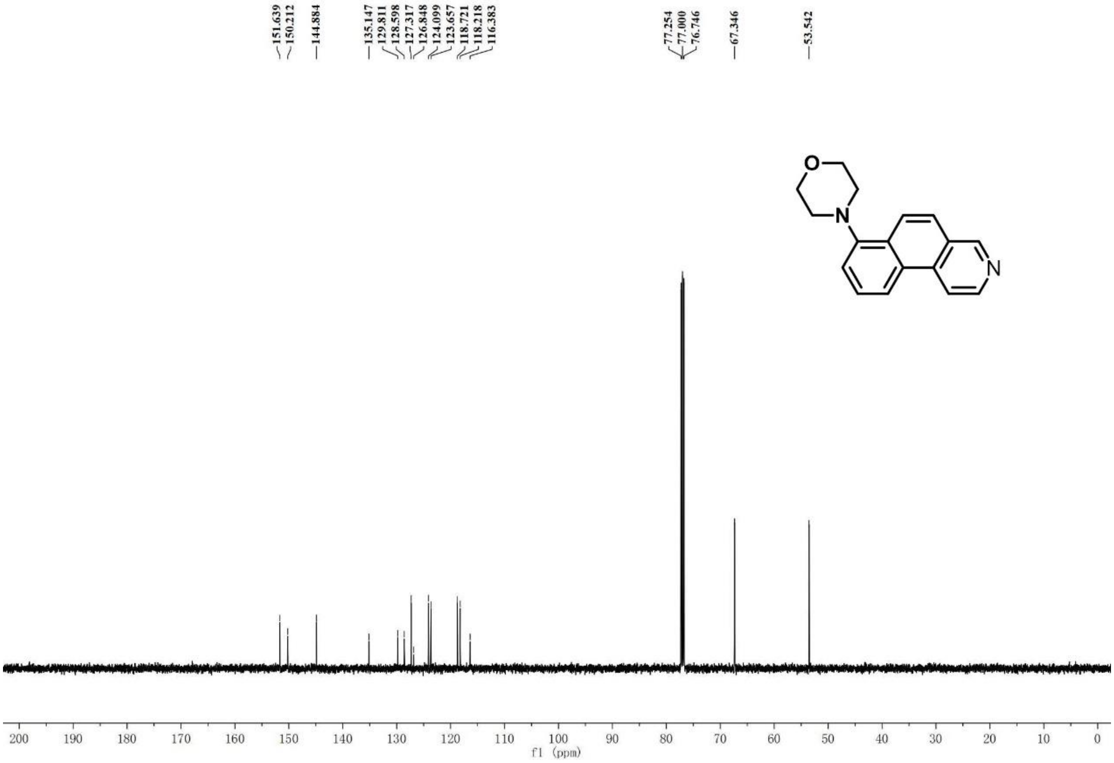
^{1}H NMR of **41** (500 MHz, $CDCl_3$) and ^{13}C NMR of **41** (125 MHz, $CDCl_3$)



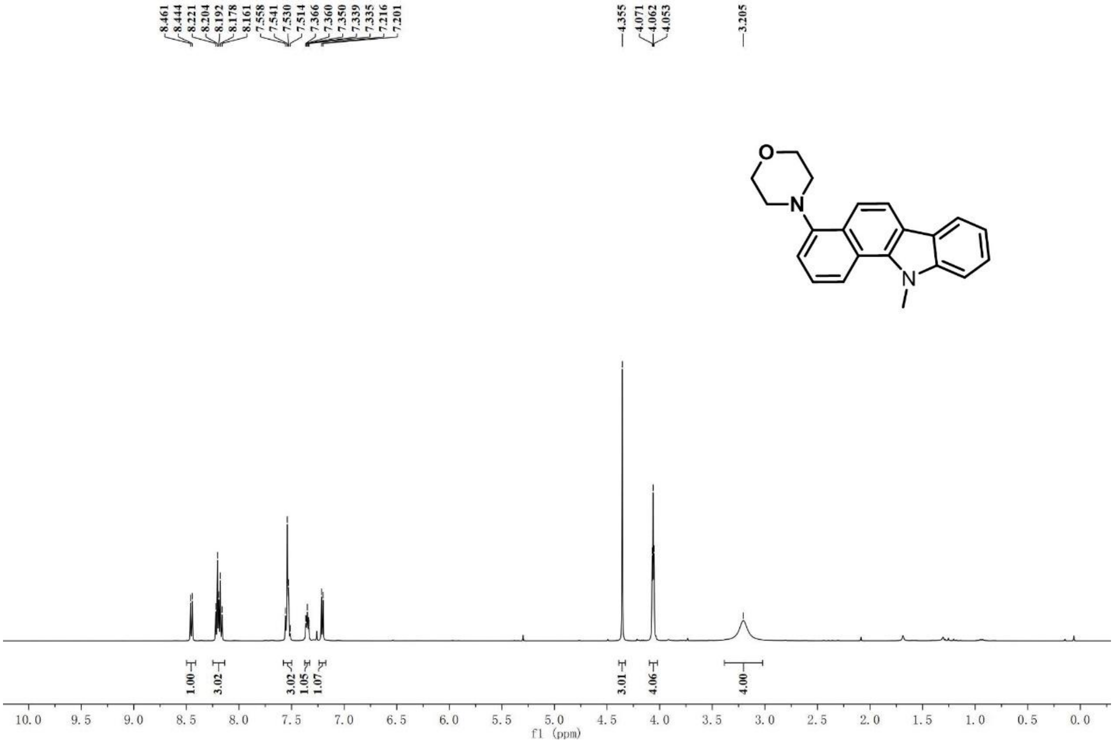


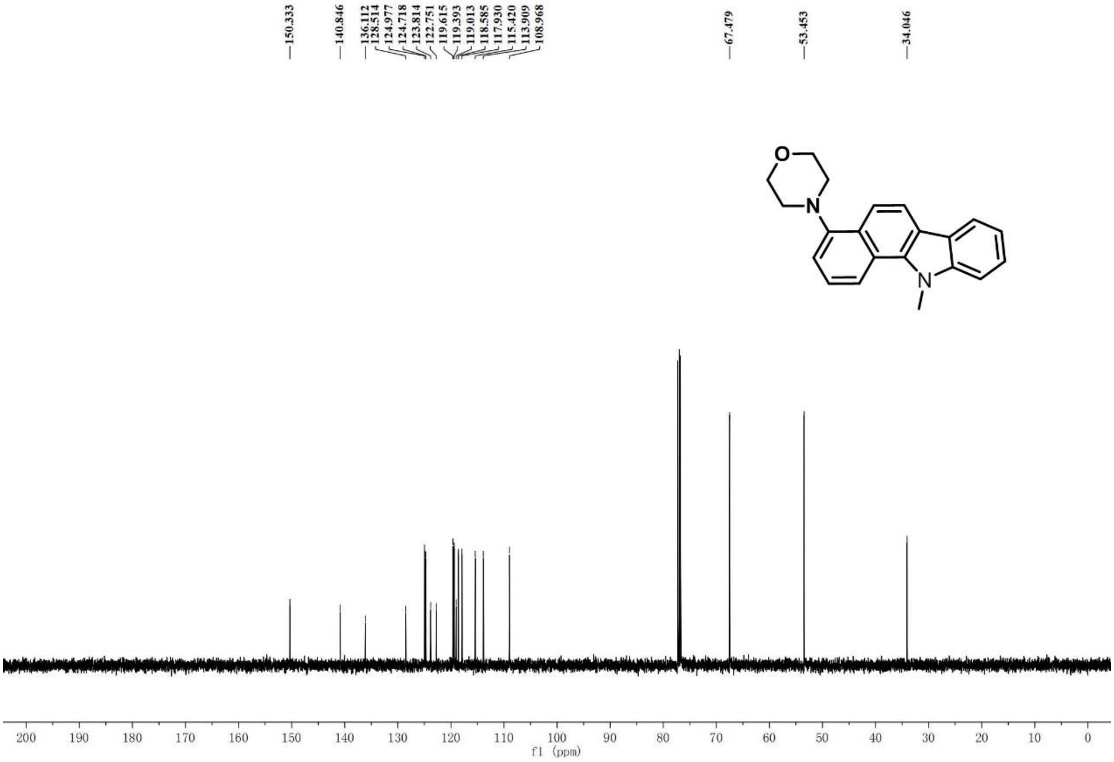
^{1}H NMR of **42** (500 MHz, $CDCl_3$) and ^{13}C NMR of **42** (125 MHz, $CDCl_3$)



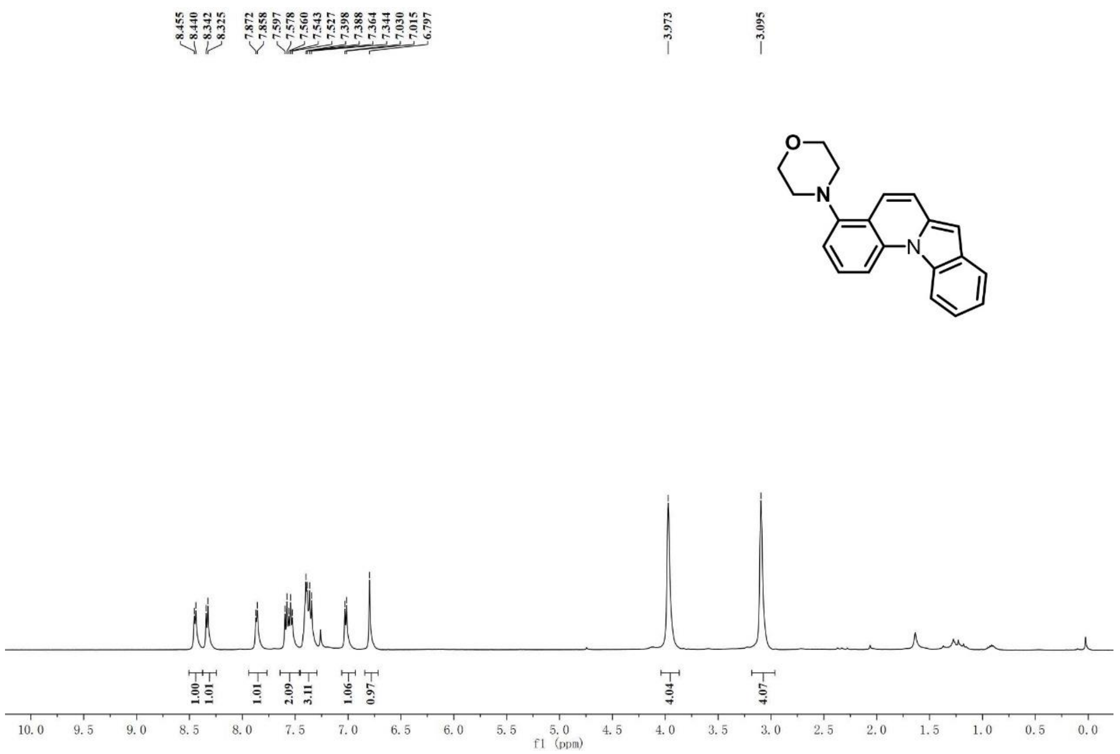


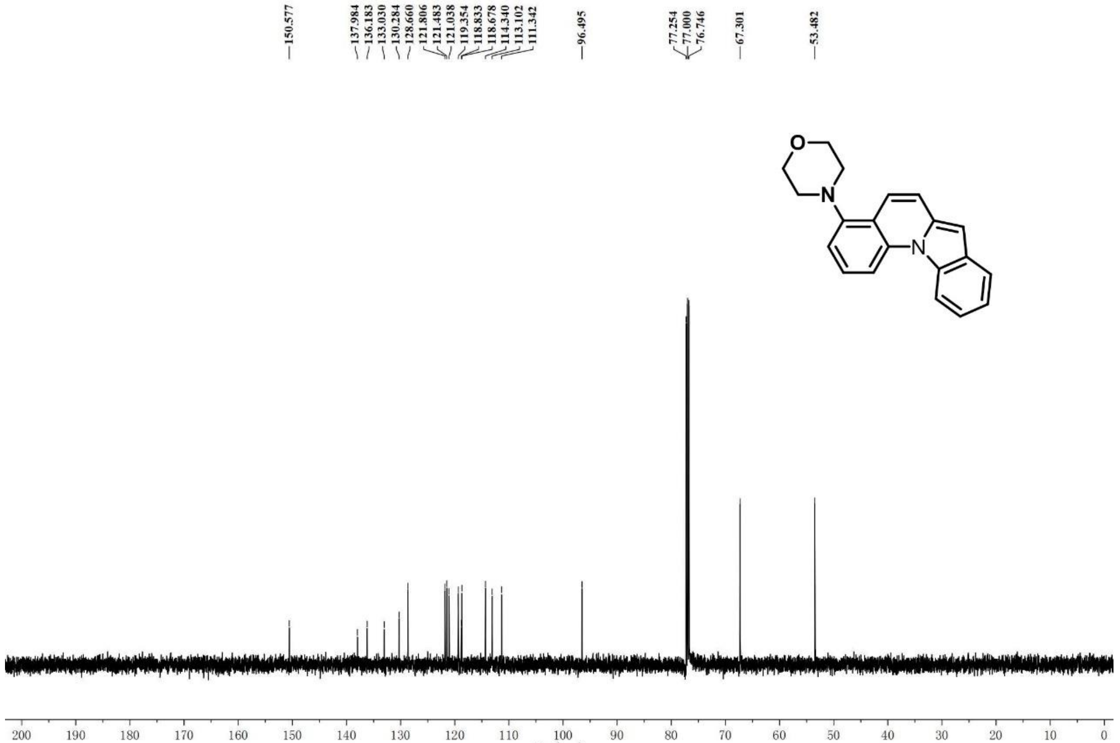
^{1}H NMR of **43** (500 MHz, CDCl$_3$) and ^{13}C NMR of **43** (125 MHz, CDCl$_3$)



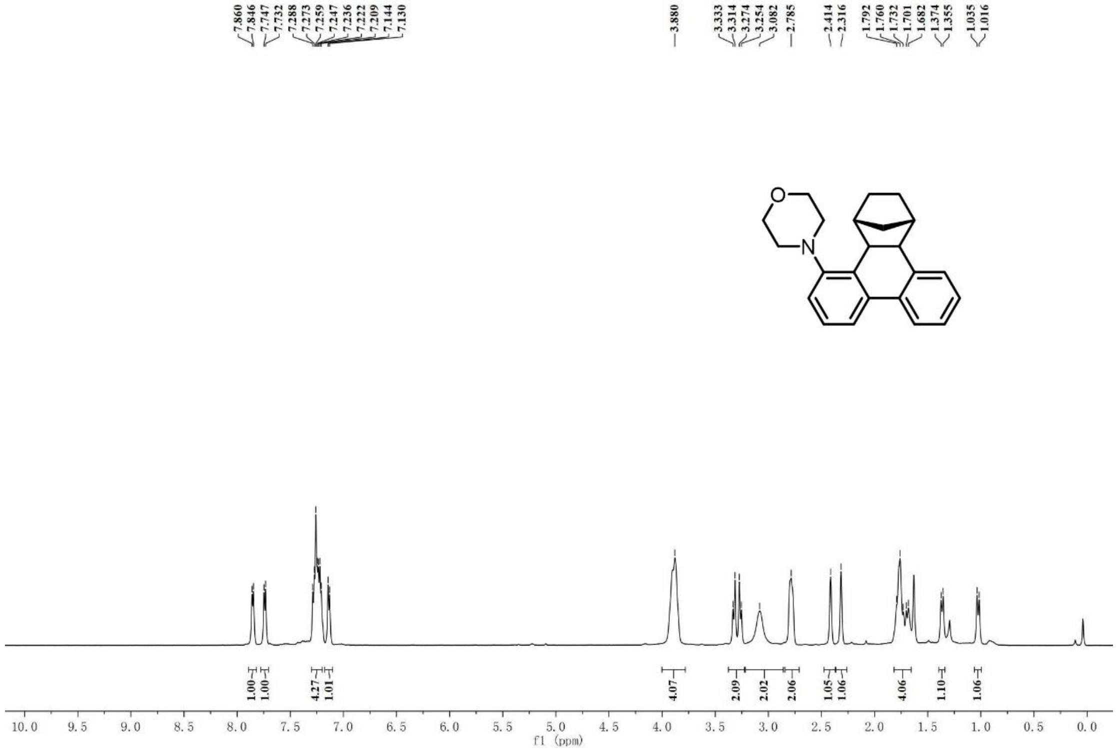


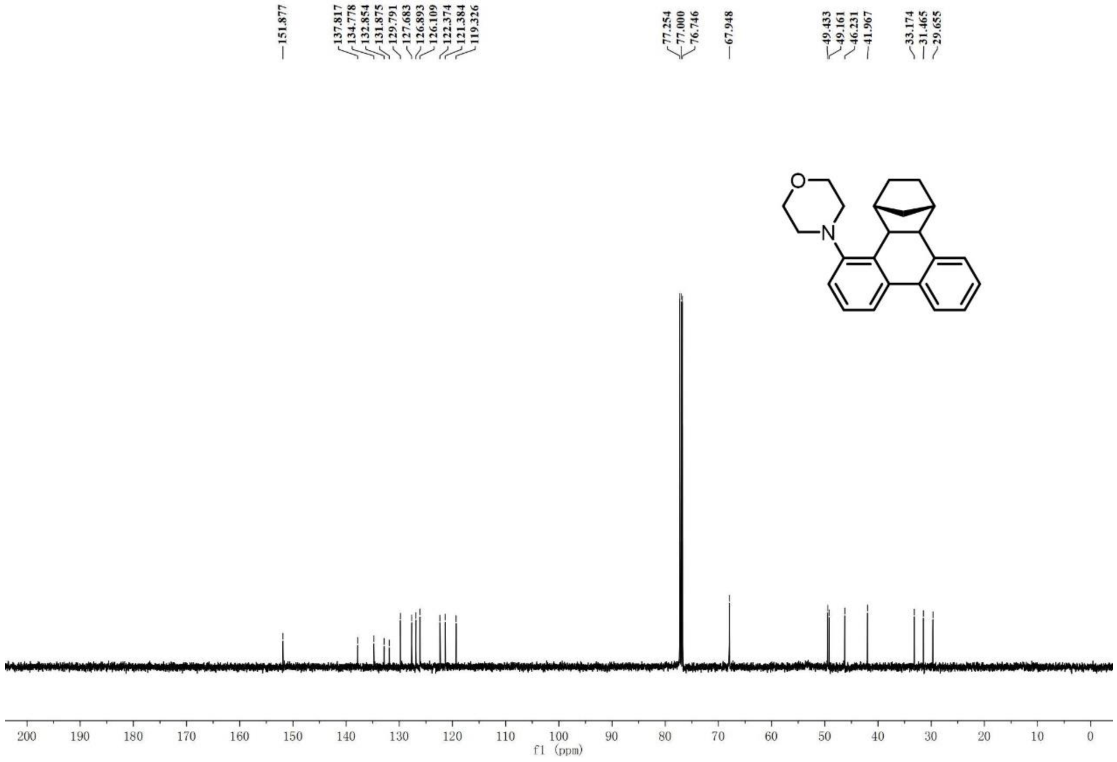
^{1}H NMR of **44** (500 MHz, $CDCl_3$) and ^{13}C NMR of **44** (125 MHz, $CDCl_3$)



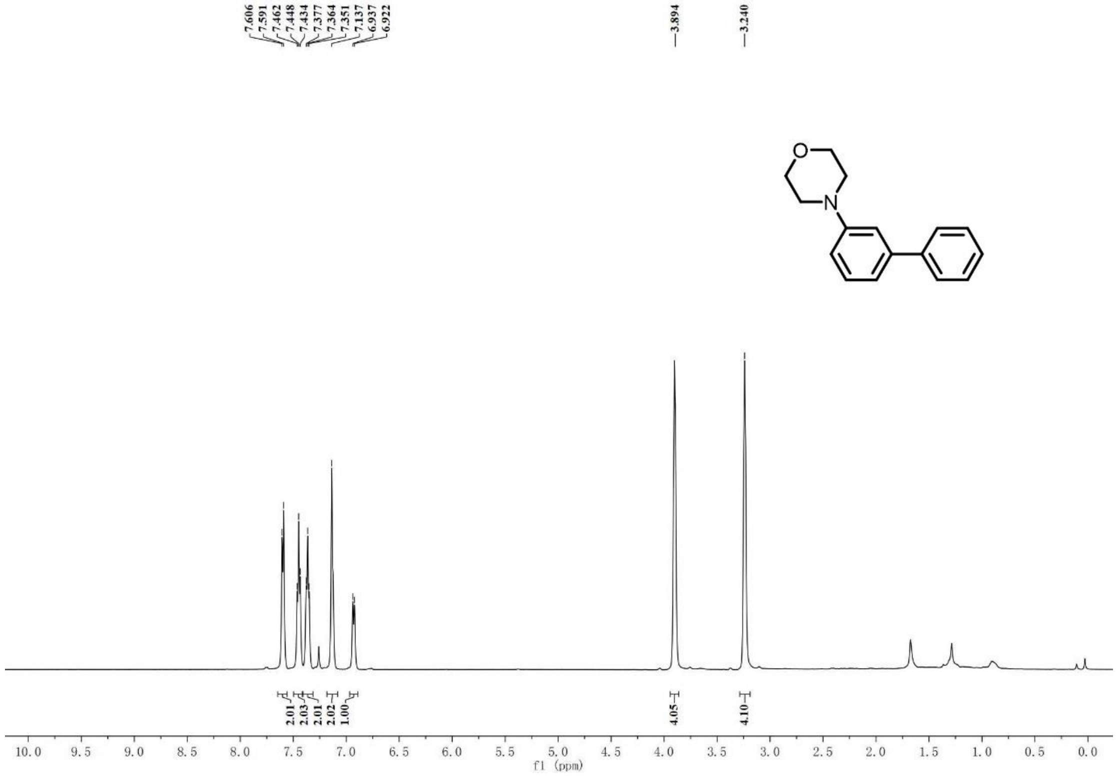


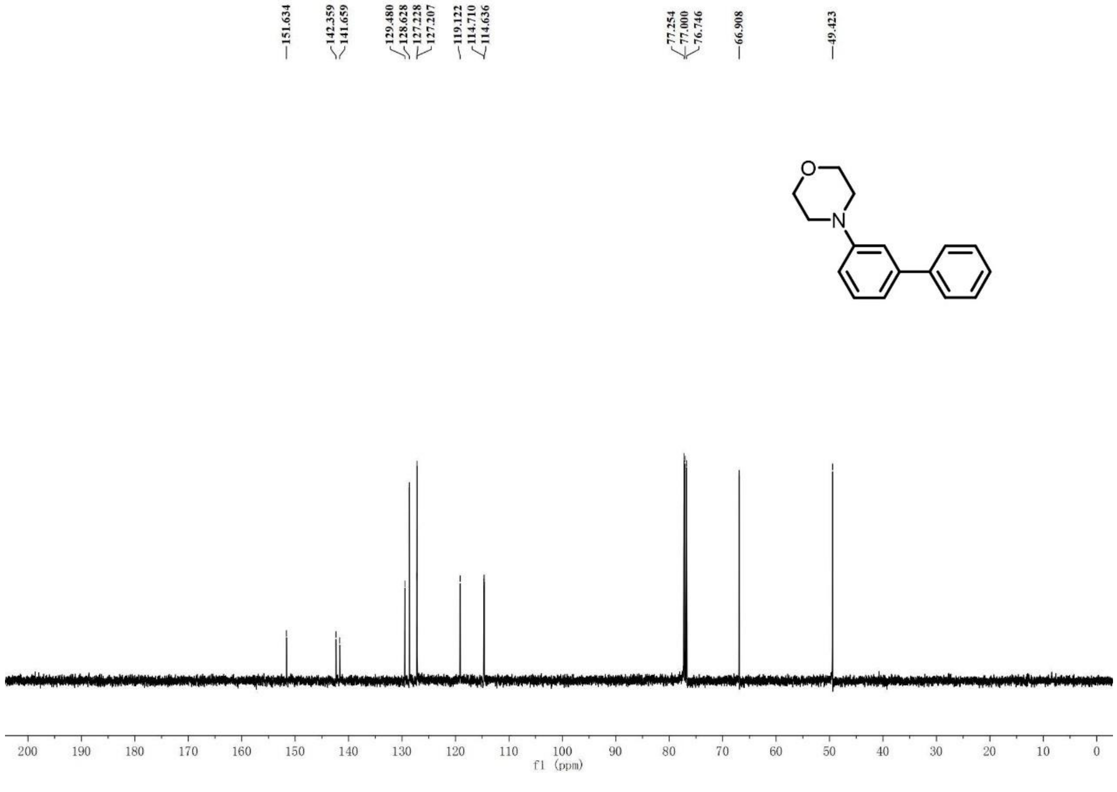
^{1}H NMR of **45** (500 MHz, CDCl$_3$) and ^{13}C NMR of **45** (125 MHz, CDCl$_3$)





^{1}H NMR of **46** (500 MHz, CDCl$_3$) and ^{13}C NMR of **46** (125 MHz, CDCl$_3$)





^{1}H NMR of **47** (500 MHz, $CDCl_3$) and ^{13}C NMR of **47** (125 MHz, $CDCl_3$)