Supporting information

Cobalt-Catalyzed Radical Cyclization of Isocyanides Forming Phenanthridine Derivatives

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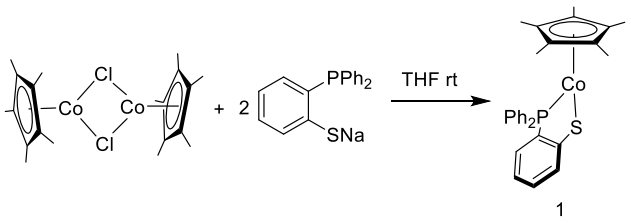
1. General procedure

All reactions were performed in flame-dried glassware using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. Acetonitrile, hexane, DCE and tetrahydrofuran were dried and degassed by Solvent Purification Systems. All reagents were purchased from commercial suppliers, unless specified otherwise, or prepared as described in the literature. All solid heteroarenes were dried under vacuum and liquid heteroarenes were distilled prior to use. The 2-(diphenylphosphino)benzenethiol ($Ph_2PC_6H_4SH$) and $[Cp^*CoCl]_2$ were prepared according to published procedures.[1] NMR spectra were recorded on Bruker 500 (500 MHz for ^1H, 126 MHz for ^{13}C, 471 MHz for ^{19}F) spectrometers. Chemical shifts for ^1H and ^{13}C spectra were referenced to residual solvent resonances and are reported relative to tetramethylsilane. High resolution mass spectra (MS) were obtained using a LC/MSD TOF spectrometer system with electrospray ionization (ESI). UV-vis absorption spectra were recorded with an Agilent Cary 60 spectrophotometer. Steady-state emission spectra were recorded using a Shimadzu RF-6000 spectrofluorimeter.

2. Experimental section

2.1 Synthesis of [Cp*($Ph_2PC_6H_4S$)Co]

$Ph_2PC_6H_4SNa$. NaH (0.09 g, 3.74 mmol) was added to a THF solution of $Ph_2PC_6H_4SH$ (1.0 g, 3.40 mmol) under nitrogen. The mixture was stirred at room temperature for 1 h and filtered through a short pad of celite. The filtrate was concentrated in vacuo and the product was recrystallized in THF/hexane to give $Ph_2PC_6H_4SNa$ as white solid (1.02 g, 95%). ^{1}HNMR (500 MHz, acetone-d_6): δ 7.37 (m, 1H), 7.24 (m, 10H), 6.75 (m, 1H), 6.45 (m, 1H), 6.32 (m, 1H). ^{31}P NMR: δ -15.4.

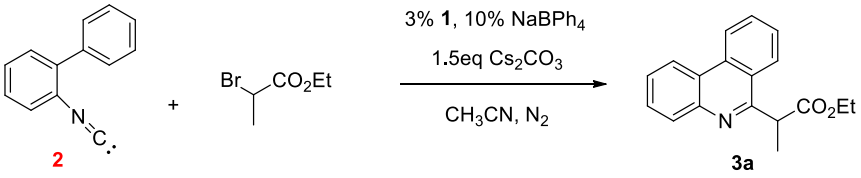


Scheme S1. Synthesis of [Cp*($Ph_2PC_6H_4S$)Co].

[Cp*($Ph_2PC_6H_4S$)Co], **1.** $Ph_2PC_6H_4SNa$ (312 mg, 0.1 mmol) in 10 mL THF was added to the solution of $[Cp^*CoCl]_2$ (230 mg, 0.05 mmol) in 30 mL THF, the color turned to red brown immediately. After stirring for 3 h at room temperature, the volatile was removed under vacuum, and the residue was extracted with hexane (100 mL). The resulting hexane solution was concentrated, cooled at -30 ℃ to give [Cp*($Ph_2PC_6H_4S$)Co] (397 mg, yield 80%) as red solid. MS (ESI) Calcd for $C_{28}H_{29}PSCo$ [M]: 487.1060; Found: 487.1038. Magnetic susceptibility (μ_{eff}, C_6D_6, 23 ^oC): 1.92 μB.

2.2 Survey of reaction conditions

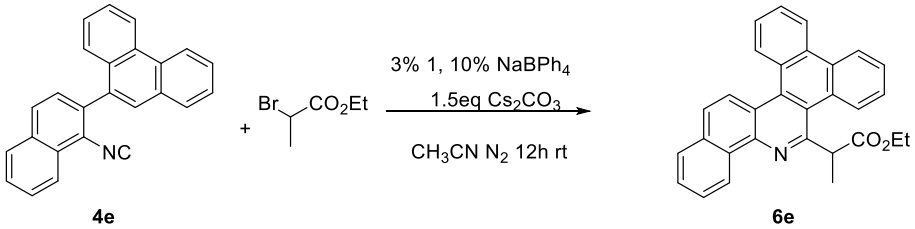
Table S1. Optimization of reaction conditions[a]



Entry	Additive	Base	Solvent	Yield/%[b]
1	NO	Na_2HPO_4	MeCN	23%
2	NO	K_2CO_3	MeCN	42%
3	NO	Cs_2CO_3	MeCN	60%
4	NO	Cs_2CO_3	THF	57%
5	NO	Cs_2CO_3	DCE	38%
6	$NaBF_4$	Cs_2CO_3	MeCN	58%
7	KPF_6	Cs_2CO_3	MeCN	62%
8	$NaBPh_4$	Cs_2CO_3	MeCN	90%
9[c]	NO	Cs_2CO_3	MeCN	0%
10[c]	$NaBPh_4$	Cs_2CO_3	MeCN	0%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **1** (3 % mol), base (0.3 mmol), MeCN (2 mL), rt. [b]Isolated yield. [c]Without **1**.

2.3 The amplified reaction



Scheme S2. The amplified reaction for the synthesis of **6e**.

According to general procedure, isocyanide **4e** (660 mg, 2 mmol, 1 equiv), $CH_3CHBrCO_2Et$ (720 mg, 4 mmol, 2 equiv), $NaBPh_4$ (70.0 mg, 0.2 mmol, 10 mol %), **1** (30 mg, 0.06 mmol, 3 mol %), CS_2CO_3 (975 mg, 3 mmol, 1.5 equiv), were added into 20 mL CH_3CN. After stirring for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridines (523 mg, 61%) as a yellow solid (petroleum ether: EtOAc = 30:1).

2.4 Photophysical properties

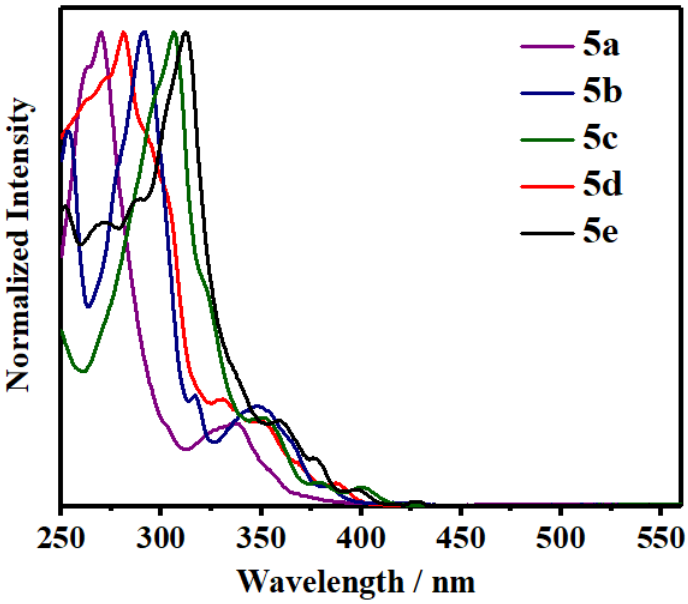


Figure S1. Absorption spectra of **5a-5e** (10^{-5} M) in DCM.

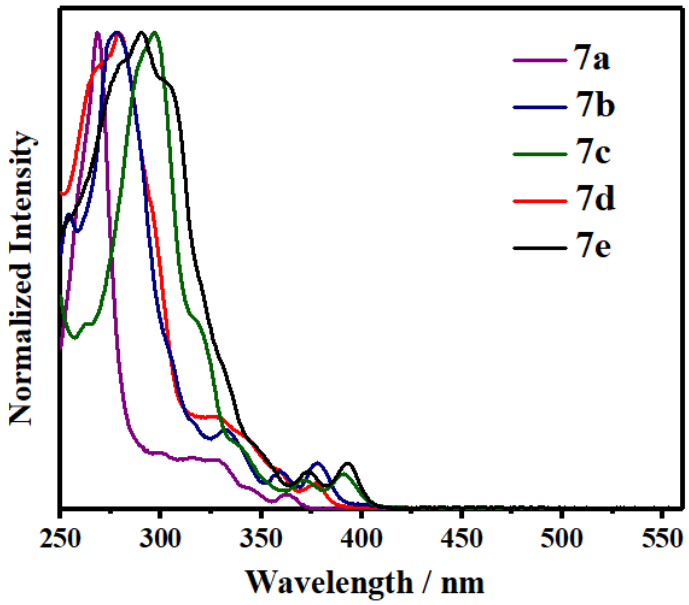


Figure S2. Absorption spectra of **7a-7e** (10^{-5} M) in DCM.

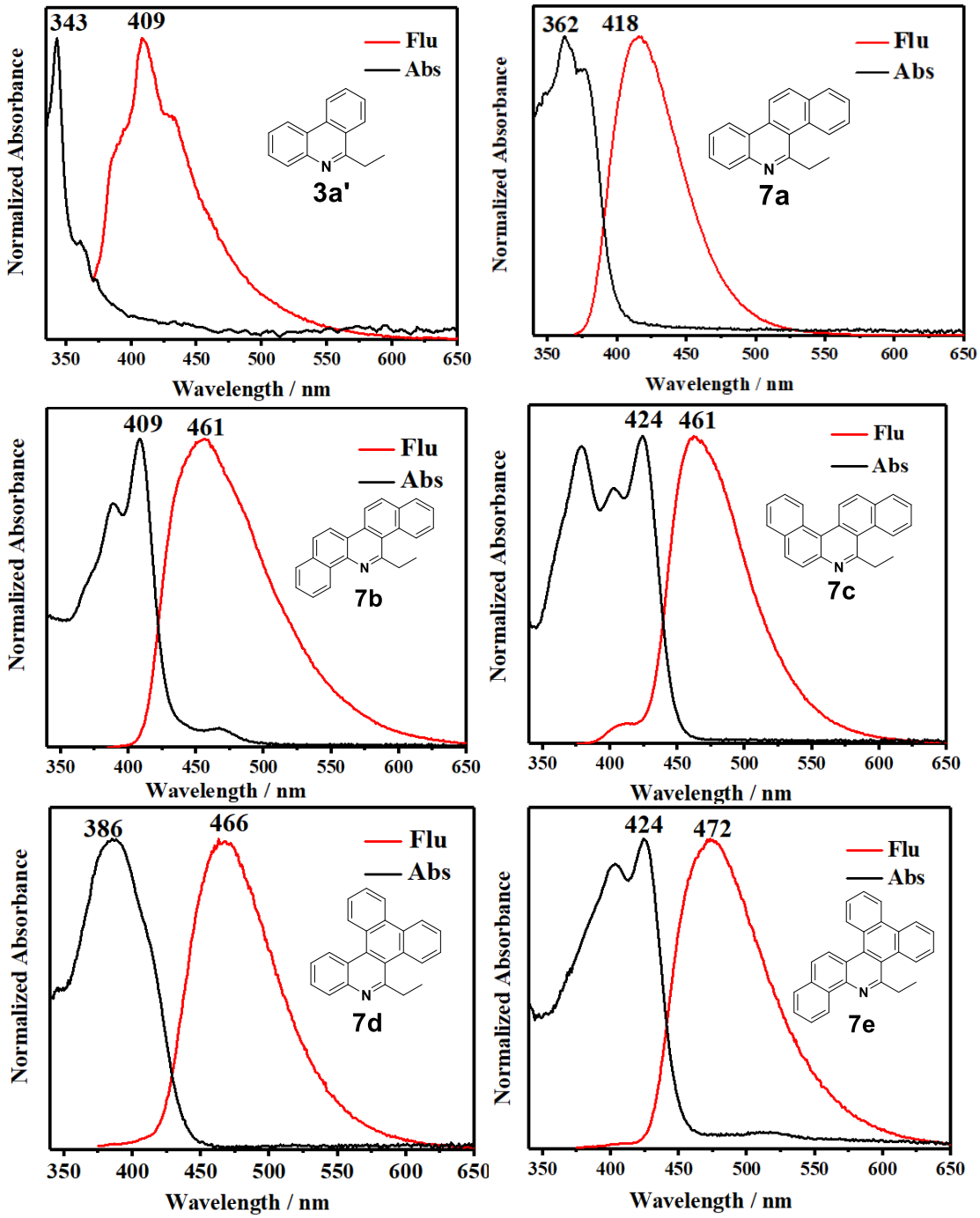
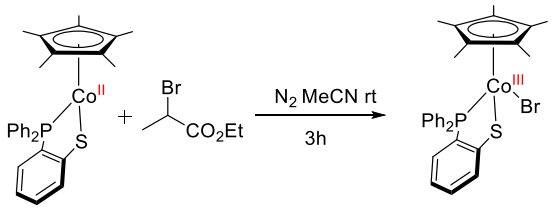


Figure S3. Absorption (black line) and fluorescence (red line) spectra of **3a'** (10^{-5} M) and **7a-7e** (10^{-5} M) in the presence of HBF_4 ($3*10^{-5}$ M) in DCM with λ_{ex} = 365 nm.

2.5 Reaction of [Cp*($Ph_2PC_6H_4S$)Co] with 2-bromopropanoate



Scheme S3. Stoichiometric reaction of [Cp*($Ph_2PC_6H_4S$)Co] with 2-bromopropanoate.

In a glovebox under an N_2 atmosphere, a scintillation vial (with a magnetic stir bar) was charged with (180 mg, 1 mmol) of ethyl 2-bromopropanoate, and a stoichiometric amount of **[Cp*($Ph_2PC_6H_4S$)Co]** in 20 mL acetonitrile. The color turned to purple immediately. After stirring for 3 h at room temperature, the volatile was removed under vacuum, the purple solid was collected by filtration, washed with dried hexane (100 mL) in vacuo to give product **[Cp*($Ph_2PC_6H_4S$)CoBr]**. Yield: (540 mg, 0.095 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.20 (m, 2H), 7.67 – 7.48 (m, 6H), 7.42 – 7.37 (m, 1H), 7.33 (t, J = 6.8 Hz, 2H), 6.94 (t, J = 8.1 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 1.36 (s, 15H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 62.12 (s). MS (ESI) Calcd for $C_{28}H_{29}PS$ Co [M^+]: 487.1060; Found: 487.1032.

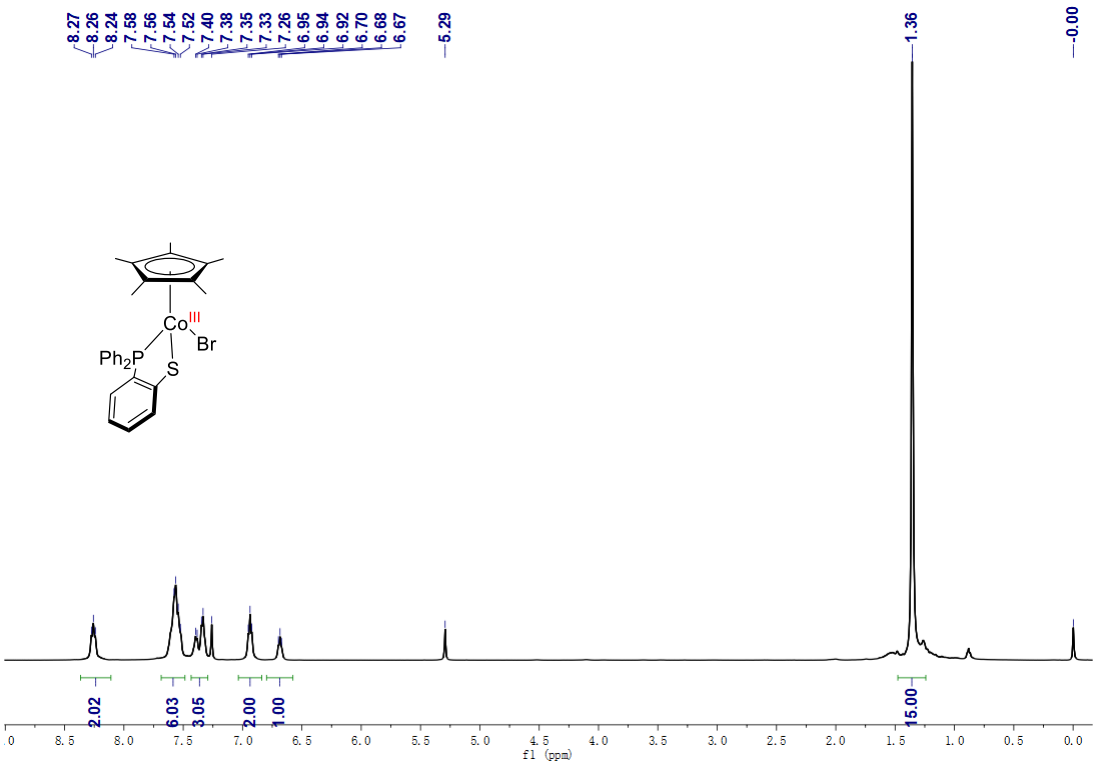


Figure S4. The ^{1}H-NMR spectral copy of compound [**1-Br**].

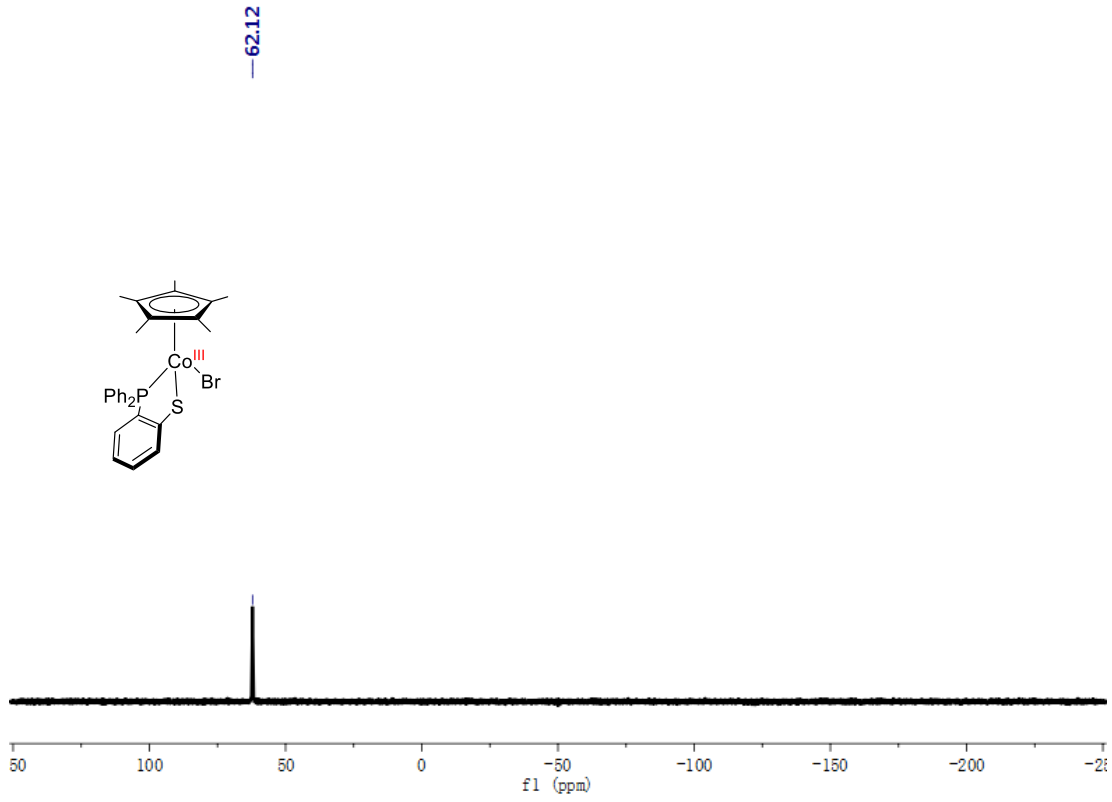
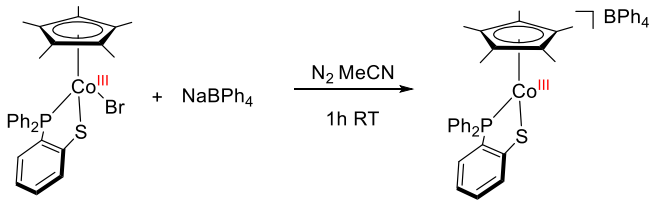


Figure S5. The ^{31}P-NMR spectral copy of compound [**1-Br**].

2.6 Reaction of [Cp*($Ph_2PC_6H_4S$)Co-Br] with $NaBPh_4$



Scheme S4. Reaction of [Cp*($Ph_2PC_6H_4S$)Co-Br] with $NaBPh_4$.

In a glovebox under an N_2 atmosphere, a scintillation vial (with a magnetic stir bar) was charged with **[Cp*($Ph_2PC_6H_4S$)CoBr]** (57 mg 0.1 mmol) and a stoichiometric amount of $NaBPh_4$ (34 mg 0.1 mmol) in 20 mL acetonitrile. The color turned from purple to brown immediately. After stirring for 1 h at room temperature, the volatile was removed under vacuum. The brown solid was collected by filtration, washed with dried hexane (20 mL) in vacuo to give product **[Cp*($Ph_2PC_6H_4S$)Co][BPh_4]**. Yield: (75 mg, 0.094 mmol, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.46 (m, 12H), 7.45-7.32 (br, 8H), 7.12-7.07 (m, 1H), 7.01-6.94 (m, 7H), 6.90-6.65 (m, 6H), 1.21 (s, 15H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 64.95 (s). MS (ESI) Calcd for $C_{28}H_{30}PSCo$ [M^+]: 487.1060; Found: 487.1094.

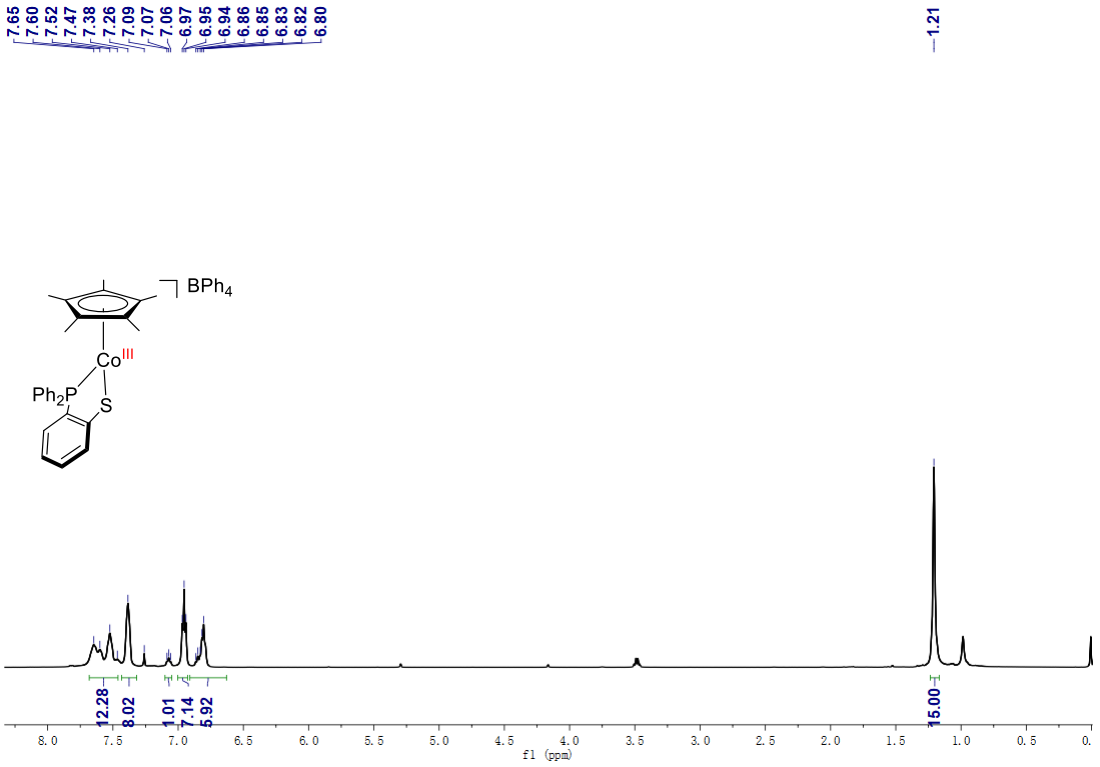


Figure S6. The ^{1}H-NMR spectral copy of compound [**1-BPh$_4$**].

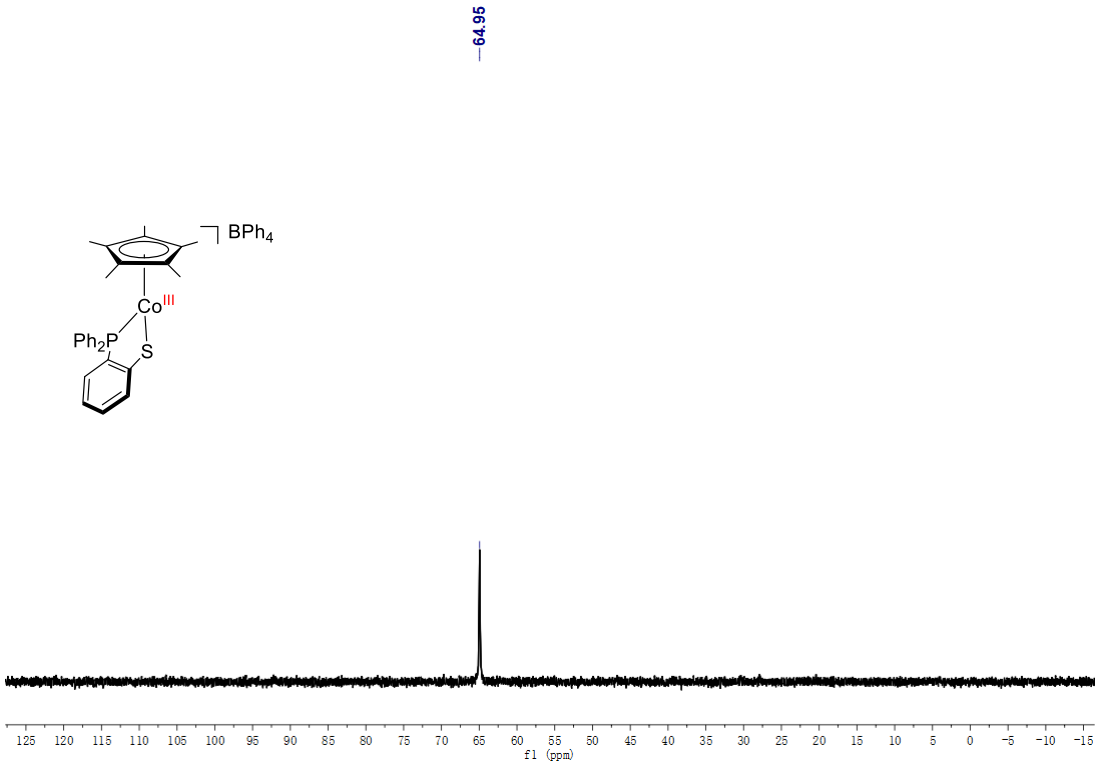


Figure S7. The ^{31}P-NMR spectral copy of compound [**1-BPh$_4$**].

2.7 Characterization data of cyclic voltammogram.

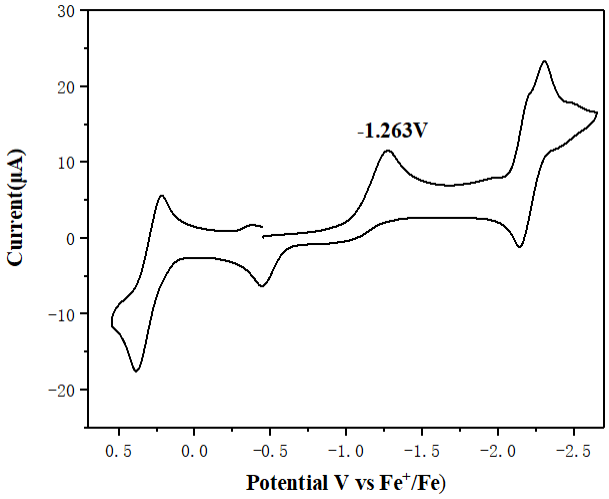


Figure S8. Cyclic voltammogram of [**1-Br]**. Conditions: 1 mM sample in THF, 0.1 M *n*-Bu_4NPF_6; Scan rate: 200 mV s^{-1}. Potential vs $Fc^{+/0.}$ *Results*: $E_{1/2}$[**1-Br**]$^{0/-}$ = -1.263 V.

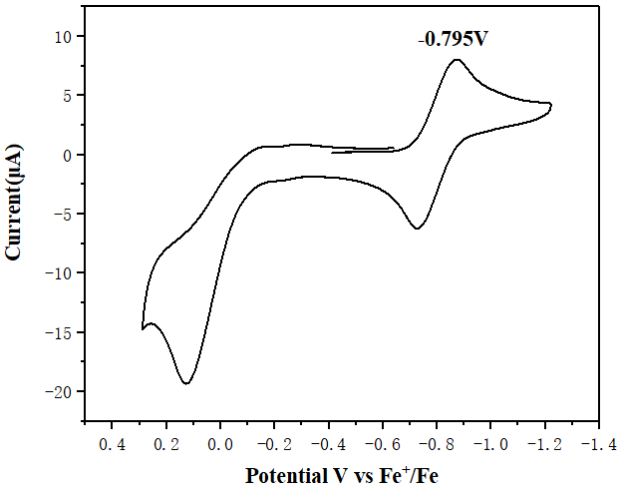
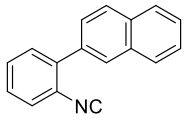


Figure S9. Cyclic voltammogram of [**1-BPh_4]**. Conditions: 1 mM sample in THF, 0.1 M *n*-Bu_4NPF_6; Scan rate: 200 mV s^{-1}. Potential vs $Fc^{+/0.}$ *Results*: $E_{1/2}$[**1-BPh_4**]$^{+/0}$ = -0.795V.

3. Experimental details and characterization data of the products

General Procedure for the Synthesis of Isocyanide Substrates (4a-4e). All isonitriles were prepared according to reported methods.[2]

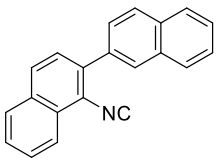
2-(2-Isocyanophenyl)naphthalene (4a).



4a

Synthesized from 2-iodoaniline (2 mmol) and naphthalen-2-ylboronic (2.4 mmol) acid and isolated as white solid (368 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.94-7.91 (m, 2H), 7.66 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.59- 7.52 (m, 4H), 7.50 (td, *J* = 7.6, 1.0 Hz, 1H), 7.41 (td, *J* = 7.8, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.80, 138.77, 134.42, 133.18, 132.92, 130.79, 129.51, 128.31, 128.25, 128.18, 128.15, 127.86, 127.69, 126.59, 126.56, 126.43, 124.81. MS (ESI) Calcd for $C_{17}H_{12}N$ [M+H$^+$]: 230.0970; Found: 230.0961.

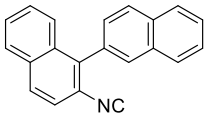
1-Isocyano-2,2'-binaphthalene (4b).



4b

Synthesized from 2-bromonaphthalen-1-amine (2 mmol) and naphthalen-2-ylboronic acid (2.4 mmol) and isolated as white solid (414 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.10 (s, 1H), 8.03-7.98 (m, 2H), 7.97-7.92 (m, 3H), 7.80-7.71 (m, 2H), 7.68-7.61 (m, 2H), 7.59-7.52 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.99, 136.88, 134.93, 133.24, 132.98, 132.64, 129.55, 128.84, 128.54, 128.43, 128.35, 128.30, 128.20, 127.77, 127.54, 127.34, 126.85, 126.73, 126.52, 123.53. MS (ESI) Calcd for $C_{21}H_{14}N$ [M+H$^+$]: 280.1126; Found: 280.1134.

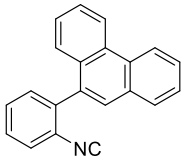
1-Isocyano-1,2'-binaphthalene (4c).



4c

Synthesized from 1-bromonaphthalen-2-amine (2 mmol) and naphthalen-2-ylboronic acid (2.4 mmol) and isolated as white solid (380 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.3 Hz, 1H), 7.96-7.88 (m, 4H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.63-7.55 (m, 4H), 7.52 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.16, 137.47, 133.23, 133.09, 133.04, 132.54, 132.28, 129.44, 129.06, 128.35, 128.20, 128.11, 127.85, 127.57, 127.46, 127.39, 127.08, 126.63, 126.48, 123.60, 122.82. MS (ESI) Calcd for $C_{21}H_{14}N$ [M+H$^+$]: 280.1126; Found: 280.1102.

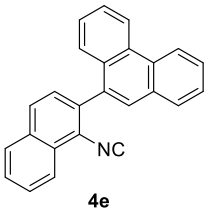
9-(2-Isocyanophenyl) phenanthrene (4d).



4d

Synthesized from 2-iodoaniline (2 mmol) and phenanthren-9-ylboronic (2.4 mmol) acid and isolated as white solid (431 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.3 Hz, 1H), 8.76 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.77-7.68 (m, 3H), 7.67-7.64 (m, 1H), 7.63-7.46 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.46, 138.08, 133.64, 131.75, 131.17, 130.55, 130.52, 130.37, 129.23, 128.86, 128.63, 128.32, 127.21, 127.19, 126.93, 126.80, 126.77, 126.07, 123.09, 122.63. MS (ESI) Calcd for $C_{21}H_{14}N$ [M+H$^+$]: 280.1126; Found: 280.1160.

9-(1-Isocyanonaphthalen-2-yl)phenanthrene (4e).

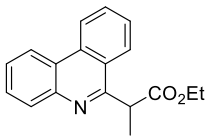


4e

Synthesized from 2-bromonaphthalen-1-amine (2 mmol) and phenanthren-9-ylboronic acid (2.4 mmol) and isolated as white solid (370 mg, 56% yield). ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.4 Hz, 1H), 8.79 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.02 (dd, *J* = 8.1, 5.6 Hz, 2H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.83 (s, 1H), 7.72 (m, 5H), 7.63 – 7.47 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.69, 136.23, 134.00, 132.89, 131.18, 130.61, 130.50, 130.31, 129.10, 128.92, 128.57, 128.41, 128.29, 128.27, 127.47, 127.24, 126.97, 126.82, 126.79, 126.19, 123.43, 123.13, 122.64. MS (ESI) Calcd for $C_{25}H_{16}N$ [M+H^{+}]: 330.1283; Found: 330.1283.

General Procedure for the Synthesis of Phenanthridines (3a-3l). A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (3 mg, 0.01 mmol, 3 mol%), $NaBPh_4$ (14.0 mg, 0.10 mmol, 10 mol%) in a glovebox, and this was followed by addition of CS_2CO_3 (98 mg, 0.4 mmol, 1.5 equiv). The isocyanide **2** (36 mg, 0.2 mmol, 1 equiv), R-X (0.4 mmol, 2 equiv) and anhydrous MeCN (2 mL) were then added. After stirring for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridines.

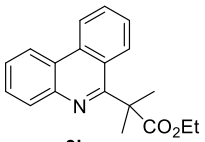
Ethyl 2-(phenanthridin-6-yl)propanoate (3a).



3a

Yellow solid, 50 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.58-8.50 (m, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 8.16 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.74-7.62 (m, 3H), 4.74 (q, *J* = 7.1 Hz, 1H), 4.30-4.11 (m, 2H), 1.79 (d, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.66, 159.48, 143.52, 133.23, 130.28, 130.17, 128.53, 127.33, 126.78, 125.56, 124.64, 123.68, 122.63, 121.80, 60.90, 45.54, 16.39, 14.09. MS (ESI) Calcd for $C_{18}H_{18}NO_2$ [M+H$^+$]: 280.1338; Found: 280.1335.

Ethyl 2-methyl-2-(phenanthridin-6-yl)propanoate (3b).

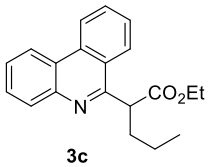


3b

Yellow liquid, 45 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.18 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.80 – 7.77 (m, 1H), 7.74 – -7.71 (m, 1H), 7.66 – 7.60 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.88 (s, 6H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.07,

161.22, 143.06, 133.49, 130.35, 129.68, 128.45, 126.81, 126.05, 124.30, 123.79, 122.81, 121.75, 60.98, 49.93, 26.56, 13.85. MS (ESI) Calcd for $C_{19}H_{20}NO_2$ [M+H$^+$]: 294.1489; Found: 294.1492.

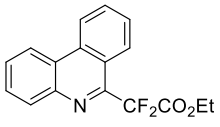
2-(phenanthridin-6-yl)pentanoate (3c).



3c

Yellow liquid, 47 mg, 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.6 Hz, 1H), 8.53 (d, *J* = 7.4 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.77 (m, 1H), 7.74 – 7.67 (m, 2H), 7.65 – 7.58 (m, 1H), 4.65 (t, *J* = 7.2 Hz, 1H), 4.38 – 3.92 (m, 2H), 2.53 – 2.16 (m, 2H), 1.62 – 1.36 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.88, 158.45, 143.49, 133.14, 130.21, 130.20, 128.45, 127.27, 126.71, 125.54, 125.01, 123.56, 122.53, 121.73, 60.74, 50.87, 33.28, 21.24, 14.06, 14.01. MS (ESI) Calcd for $C_{20}H_{22}NO_2$ [M+H$^+$]: 308.1651; Found: 308.1639.

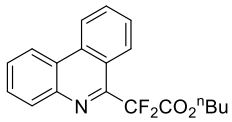
Ethyl 2,2-difluoro-2-(phenanthridin-6-yl)acetate (3d).



3d

White solid, 41 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.1 Hz, 1H), 8.58 – 8.56 (m, 2H), 8.12 (dd, *J* = 5.8, 3.6 Hz, 1H), 7.95 – 7.87 (m, 1H), 7.83 – 7.68 (m, 3H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.78 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.66 (t, *J* = 30.9 Hz), 150.19 (t, *J* = 29.0 Hz), 141.75, 133.87, 131.20, 130.86, 128.99, 128.88, 127.86, 126.27 (t, *J* = 4.9 Hz), 124.84, 122.49, 122.31, 122.03, 117.84, 115.82, 113.80, 62.98, 14.08. MS (ESI) Calcd for $C_{17}H_{13}F_2NO_2$ [M+H$^+$]: 302.0993; Found: 302.0990.

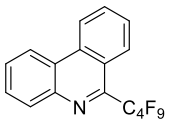
Butyl 2,2-difluoro-2-(phenanthridin-6-yl)acetate (3e).



3e

Yellow liquid, 48 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.59 – 8.50 (m, 2H), 8.14 – 8.05 (m, 1H), 7.92 – 7.83 (m, 1H), 7.79 – 7.66 (m, 3H), 4.53 (t, *J* = 6.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.53 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.39 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.75 (t, *J* = 30.8 Hz), 150.14 (t, *J* = 29.0 Hz), 141.68, 133.80, 131.14, 130.74, 128.92, 128.81, 127.7, 126.19 (t, *J* = 4.9 Hz), 124.77, 122.43, 122.25 (t, *J* = 2.0 Hz), 121.98, 117.98, 115.96, 113.94, 66.70, 30.39, 18.98, 13.55. MS (ESI) Calcd for $C_{19}H_{18}F_2NO_2$ [M+H$^+$]: 330.1306; Found: 330.1307.

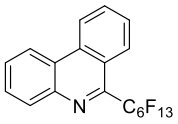
6-(Perfluorobutyl)phenanthridine (3f).



3f

Yellow solid, 65 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.64 – 8.58 (m, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.33 – 8.22 (m, 1H), 7.93-7.90 (m, 1H), 7.85 – 7.69 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.11 – -85.55 (m, 3F), -104.89 – 104.95 (m, 2F), -119.74 – -119.82 (m, 2F), -122.62 – -123.69 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.65 (t, *J* = 25.0 Hz), 141.72, 133.99, 131.18, 131.16, 129.38, 129.28, 127.97, 126.13 (t, *J* = 6.8 Hz), 124.80, 122.94, 122.60, 122.00，120 – 100 (m). MS (ESI) Calcd for $C_{17}H_9F_9N$ [M+H$^+$]: 398.0591; Found: 398.0586.

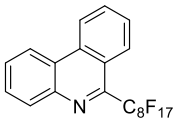
6-(Perfluorohexyl)phenanthridine (3g).



3g

White solid, 90 mg, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.50 – 8.40 (m, 2H), 8.24 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.75 – 7.67 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.77 – -80.81 (m, 3F), -104.91 (t, *J* = 13.8 Hz, 2F), -118.99 – 119.08 (m, 2F), -119.89 (s, 2F), -122.48 – -123.36 (m, 2F), -125.58 – -126.41 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.63 (t, *J* = 24.8 Hz), 141.70, 133.88, 131.10, 130.98, 129.23, 129.14, 127.84, 126.02 (t, *J* = 6.9 Hz), 124.69, 122.92, 122.43, 121.84, 120 – 100 (m). MS (ESI) Calcd for $C_{19}H_9F_{13}N$ [M+H$^+$]: 498.0527; Found: 498.0532.

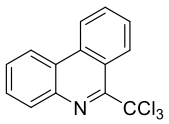
6-(Perfluorooctyl)phenanthridine (3h).



3h

Grey solid, 108 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.67 – 8.56 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.38 – 8.22 (m, 1H), 7.94 – 7.90(m, 1H), 7.87 – 7.69 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.78 (t, *J* = 10.6 Hz, 3F), -102.11 – -108.81 (m, 2F), -118.96 – -119.04 (m, 2F), -119.71 (s, 2F), -121.17 – -122.22 (m, 4F), -122.25 – -123.49 (m, 2F), -125.59 – -126.73 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.68 (t, *J* = 24.5 Hz), 141.80, 134.01, 131.23, 131.15, 129.38, 129.29, 127.98, 126.19 (t, *J* = 6.9 Hz), 124.82, 123.04, 122.60, 122.00, 120 – 100(m). MS (ESI) Calcd for $C_{21}H_9F_{17}N$ [M+H$^+$]: 598.0464; Found: 598.0465.

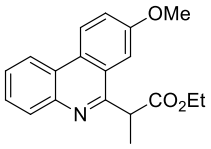
6-(Trichloromethyl)phenanthridine (3i).



3i

White solid, 44 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, *J* = 8.5 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.64-8.50 (m, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.82 – 7.73 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 152.85, 140.80, 134.92, 131.26, 130.72, 129.24, 129.06, 128.42, 126.71, 125.02, 122.81, 121.87, 120.71, 98.45. MS (ESI) Calcd for $C_{14}H_9Cl_3N$ [M+H$^+$] 295.9801; Found 295.9800.

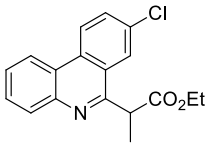
Ethyl 2-(8-methoxyphenanthridin-6-yl)propanoate (3j).



3j

White solid, 57 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.1 Hz, 1H), 8.43 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.13 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.62 (m, 2H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.44 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.68 (q, *J* = 7.1 Hz, 1H), 4.28 – 4.13 (m, 2H), 3.96 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.72, 158.64, 158.35, 142.68, 130.09, 127.50, 126.80, 125.91, 124.24, 123.76, 121.28, 120.75, 105.76, 60.90, 55.43, 45.89, 16.09, 14.11. MS (ESI) Calcd for $C_{19}H_{20}NO_3$ [M+H$^+$]: 310.1443; Found: 310.1443.

Ethyl 2-(8-chlorophenanthridin-6-yl)propanoate (3k).

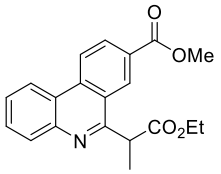


3k

Yellow solid, 56 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.62 (m, 1H), 4.67 (q, *J* = 7.1 Hz, 1H), 4.32 – 4.13 (m, 2H), 1.78 (d, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.21, 158.21, 143.41, 133.30, 131.55, 130.77, 130.30, 128.84, 127.18, 125.61, 124.91, 124.35, 123.02, 121.65, 61.01, 45.12, 16.28, 14.08. MS (ESI) Calcd for $C_{18}H_{17}ClNO_2$

[M+H$^+$]: 314.0948; Found: 314.0952.

Methyl 6-(1-ethoxy-1-oxopropan-2-yl)phenanthridine-8-carboxylate (3l).

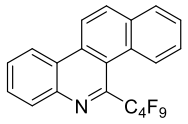


3l

Yellow solid, 55 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (d, *J* = 1.4 Hz, 1H), 8.71 (d, *J* = 8.7 Hz, 1H), 8.57 (d, *J* = 8.2 Hz, 1H), 8.44 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.16 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.71 – 7.64 (m, 1H), 4.84 (q, *J* = 7.1 Hz, 1H), 4.30 – 4.14 (m, 2H), 4.03 (s, 3H), 1.79 (d, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.31, 166.47, 159.98, 144.34, 136.29, 130.39, 130.14, 129.74, 128.74, 127.95, 127.21, 124.22, 123.04, 123.01, 122.43, 61.03, 52.52, 44.98, 16.54, 14.10. MS (ESI) Calcd for $C_{20}H_{20}NO_4$ [M+H$^+$]: 338.1392; Found: 338.1394.

General Procedure for the Synthesis of Phenanthridines (5a-5e), (6a-6e). A 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1** (3 mg, 0.01 mmol, 3 mol%), $NaBPh_4$ (14.0 mg, 0.10 mmol, 10 mol%) in a glovebox, and this was followed by addition of CS_2CO_3 (98 mg, 0.4 mmol, 1.5 equiv). The isocyanide **4a-4e** (0.2 mmol, 1 equiv), C_4F_9I or $CH_3CHBrCO_2Et$ (0.4 mmol, 2 equiv) and anhydrous MeCN (2 mL) were then added. After stirring for 12 h, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridines.

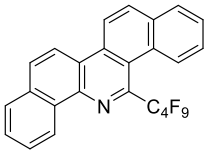
5-(Perfluorobutyl)benzo[i]phenanthridine (5a).



5a

Yellow solid, 77 mg, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.4 Hz, 1H), 8.73 – 8.53 (m, 2H), 8.30-8.23 (m, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.76 – 7.96 m, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.37 (t, *J* = 11.5 Hz, 3F), -99.29 – -102.86 (m, 2F), -115.87 (s, 2F), -120.60 – -120.67 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.31 (t, *J* = 29.6 Hz), 141.63, 135.31, 133.15, 132.96, 130.15, 129.59, 129.30, 128.47, 128.37, 128.33, 128.24, 128.14, 127.50, 127.23, 124.56, 122.60, 120.54, 119.74, 119 – 100 (m). MS (ESI) Calcd for $C_{21}H_{11}F_9N$ [M+H$^+$]: 448.0748; found: 448.0739.

14-(Perfluorobutyl)dibenzo[c,i]phenanthridine (5b).

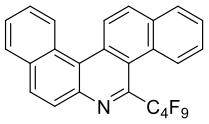


5b

Pale yellow solid, 74 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.2 Hz, 1H), 8.92 (d, *J* = 8.2 Hz, 1H), 8.58 (d, *J* = 9.0 Hz, 1H), 8.50 (d, *J* = 9.1 Hz, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 7.98 (t, *J* = 7.0 Hz, 2H), 7.84 –

7.81(m, 1H), 7.77 – 7.72 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.16 (t, *J* = 11.1 Hz, 3F), -100.95 – -101.47 (m, 2F), -115.75 (d, *J* = 9.9 Hz, 2F), -122.34 – -122.61 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.61 (t, *J* = 31.1 Hz), 139.66, 135.38, 133.27, 132.86, 132.76, 131.31, 130.41, 128.78 (t, *J* = 11.2 Hz), 128.42, 128.25, 127.89, 127.74, 127.65, 127.04, 125.18, 122.32, 121.47, 119.95, 119.64, 119-100 (m). MS (ESI) Calcd for [M+H$^+$]: $C_{25}H_{13}F_9N$: 498.0904; found: 498.0903.

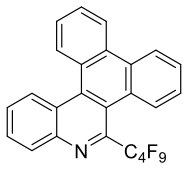
5-(Perfluorobutyl)dibenzo[a,i]phenanthridine (5c).



5c

White solid, 72 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 – 8.94 (m, 1H), 8.93 – -8.84 (m, 2H), 8.12 – 8.02 (m, 5H), 7.79 – 7.67 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.35 (t, *J* = 11.6 Hz, 3F), -100.90 – -101.11 (m, 2F), -115.72 (s, 2F), -120.32 – 120.38 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.97 (t, *J* = 29.1 Hz), 141.76, 135.86, 134.21, 132.37, 131.54, 131.14, 129.00, 128.80, 128.74, 128.69, 128.65, 128.56, 127.90, 127.86, 127.66, 127.14, 127.01, 126.95, 124.86, 122.71, 122.40, 120-100 (m). MS (ESI) Calcd for [M+H$^+$]: $C_{25}H_{13}F_9N$: 498.0904; found: 498.0910.

5-(Perfluorobutyl)dibenzo[i,k]phenanthridine (5d).

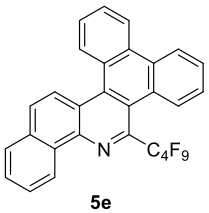


5d

White solid, 83 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 – 8.65 (m, 3H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.48 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.75 – 7.64 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -81.08 (t, *J* = 11.2 Hz, 3F), -100.93 – -101.27 (m, 2F), -116.82 – -116.89 (m, 2F), -121.62 – -125.67 (m,

2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.49 (t, *J* = 28.3 Hz), 143.67, 137.01, 132.68, 130.22, 129.82, 129.50, 129.41, 129.40, 129.36, 128.52, 128.15, 127.64, 127.49, 127.30, 127.23, 127.01, 123.95, 123.53, 123.19, 121.07, 120 – 100(m). MS (ESI) Calcd for [M+H$^+$]: $C_{25}H_{13}F_9N$: 498.0904; found: 498.0900.

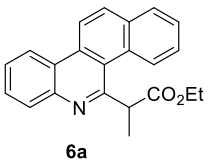
16-(Perfluorobutyl)tribenzo[c,i,k]phenanthridine (5e).



5e

White solid, 82 mg, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 (d, *J* = 8.1 Hz, 1H), 8.69 (dd, *J* = 22.4, 8.1 Hz, 2H), 8.61 – 8.58 (m, 2H), 8.51 (d, *J* = 7.9 Hz, 1H), 7.99 (dd, *J* = 15.1, 8.5 Hz, 2H), 7.87 – 7.64 (m, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -80.97 (t, *J* = 10.0 Hz, 3F), -100.84 (s, 2F), -116.50 (dd, *J* = 9.1, 5.2 Hz, 2F), -123.59 (td, *J* = 12.3, 5.5 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.21 (t, *J* = 27.7 Hz), 141.73, 137.53, 132.94, 132.67, 130.83, 130.40, 130.16, 129.76 (t, *J* = 9.0 Hz), 129.42, 129.27, 128.62, 128.33, 127.84, 127.79, 127.46, 127.41, 127.14, 127.07, 125.40, 124.18, 123.99, 123.21, 122.58, 121.62, 120 –100 (m). MS (ESI) Calcd for [M+H$^+$] $C_{29}H_{15}F_9N$: 548.1061; found: 548.1058.

Ethyl 2-(benzo[i]phenanthridin-5-yl)propanoate (6a).

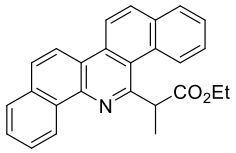


6a

Pale yellow solid, 54 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.5 Hz, 1H), 8.61 (t, *J* = 8.5 Hz, 2H), 8.16 (dd, *J* = 20.0, 8.5 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.65 (m, 4H), 5.24 (q, *J* = 6.8 Hz, 1H), 4.25 – 4.06 (m, 2H), 1.86 (d, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.57, 159.02, 144.02, 134.12, 133.27, 131.79, 129.62, 129.51, 129.08, 128.81, 127.09, 126.55,

123.16, 122.39, 121.84, 120.33, 60.72, 47.95, 17.78, 14.09. MS (ESI) Calcd for [M+H$^+$] $C_{22}H_{20}NO_2$: 330.1494; Found: 330.1497.

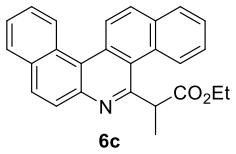
Ethyl 2-(dibenzo[c,i]phenanthridin-14-yl)propanoate (6b).



6b

Pale yellow solid, 51 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 8.2 Hz, 1H), 8.83 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 9.1 Hz, 1H), 8.47 (d, *J* = 9.2 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 8.03 – 7.99 (m, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.80 – 7.66 (m, 4H), 5.33 (q, *J* = 6.8 Hz, 1H), 4.40 – 3.97 (m, 2H), 1.98 (d, *J* = 6.9 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.69, 157.62, 141.13, 134.37, 133.17, 133.00, 131.62, 131.40, 129.61, 129.04, 127.68, 127.43, 127.35, 127.15, 126.94, 126.62, 126.59, 125.12, 60.68, 48.24, 18.15, 14.10. MS (ESI) Calcd for [M+H$^+$] $C_{26}H_{22}NO_2$: 380.1651; Found: 380.1648.

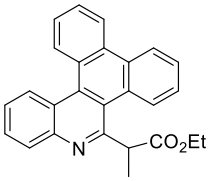
Ethyl 2-(dibenzo[a,i]phenanthridin-5-yl)propanoate (6c).



6c

Pale yellow solid, 46 mg, 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (t, *J* = 8.1 Hz, 1H), 8.74 (d, *J* = 8.2 Hz, 1H), 8.10 – 8.03 (m, 5H), 7.77 – 7.64 (m, 4H), 5.26 (q, *J* = 6.9 Hz, 1H), 4.28 – 4.04 (m, 2H), 1.88 (d, *J* = 6.9 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.70, 158.08, 144.25, 134.83, 133.17, 132.69, 130.25, 130.09, 129.49, 129.28, 128.77, 128.41, 128.15, 127.93, 126.88, 126.77, 126.41, 126.38 125.40, 123.48, 119.95, 60.76, 47.47, 17.88, 14.10. MS Calcd for [M+H$^+$] $C_{26}H_{22}NO_2$: 380.1651; Found: 380.1646.

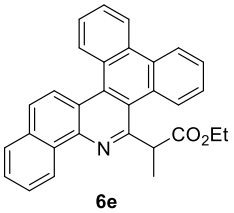
Ethyl 2-(dibenzo[i,k]phenanthridin-5-yl)propanoate (6d).



6d

Pale yellow solid, 55 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.1 Hz, 1H), 8.71 – 8.63 (m, 3H), 8.60 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.63 (m, 5H), 7.60 – 7.57 (m, 1H), 5.15 (q, *J* = 6.8 Hz, 1H), 4.30-4.15 (m, 2H), 1.72 (d, *J* = 6.9 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.56, 157.85, 145.69, 134.94, 132.18, 130.77, 129.69, 128.70, 128.57, 128.52, 128.38, 128.13, 127.35, 127.26, 127.04, 127.02, 125.95, 123.65, 122.37, 121.89, 60.84, 46.87, 18.44, 14.11. MS (ESI) Calcd for [M+H$^+$] $C_{26}H_{22}NO_2$: 380.1651; Found: 380.1654.

Ethyl 2-(tribenzo[c,i,k]phenanthridin-16-yl)propanoate (6e).

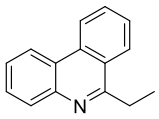


6e

Pale yellow solid, 62 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.1 Hz, 1H), 8.78 (d, *J* = 8.1 Hz, 1H), 8.72 – 8.63 (m, 3H), 8.60 – 8.58 (m, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.81 – 7.64 (m, 6H), 5.23 (q, *J* = 6.8 Hz, 1H), 4.31 – 4.18 (m, 2H), 1.82 (d, *J* = 6.8 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.76, 156.07, 143.07, 135.71, 132.94, 132.28, 131.05, 130.91, 130.15, 128.80, 128.58, 128.48, 127.87, 127.50, 127.38, 127.19, 127.17, 126.95, 126.86, 126.44, 125.45, 124.63, 123.74, 123.69, 122.73, 119.56, 60.82, 47.07, 18.87, 14.16. MS (ESI) Calcd for [M+H$^+$] $C_{30}H_{24}NO_2$: 430.1807; Found: 430.1806.

General Procedure for the Hydrolysis of Phenanthridine Esters. The compound **6** (0.1 mmol) was treated by 2 mL 60% KOH in MeOH (2 mL), and stirred at room temperature for 12 h. After saponification, the pH value was adjusted to 2~4 with HCl, then the mixture was poured into a separatory funnel containing 10 mL H_2O and 10 mL EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel to afford the desired product phenanthridine derivatives **7**.

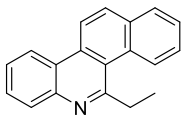
6-Ethylphenanthridine (3a').



3a'

White solid, 18 mg, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.14 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.82 – 7.92 (m, 1H), 7.75-7.54 (m, 3H), 3.41 (q, *J* = 7.6 Hz, 2H), 1.52 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.10, 143.80, 132.88, 130.17, 129.58, 128.49, 127.16, 126.20, 126.14, 125.00, 123.62, 122.44, 121.85, 29.32, 13.45. MS (ESI) Calcd for [M+H$^+$] $C_{15}H_{14}N$: 208.1126; Found: 208.1126.

5-Ethylbenzo[i]phenanthridine (7a).

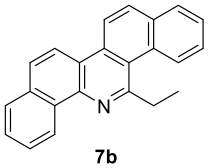


7a

Pale yellow solid, 24 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.6 Hz, 1H), 8.65 – 8.52 (m, 2H), 8.19 (dd, *J* = 8.2, 0.7 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 8.01 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.67 – 7.63 (m, 2H), 3.75 (q, *J* = 7.4 Hz, 2H), 1.66 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.59, 143.98,

133.76, 133.25, 131.66, 130.23, 129.02, 128.94, 128.75, 127.21, 126.83, 126.30, 126.12, 123.21, 122.68, 122.45, 120.30, 34.56, 13.62. MS (ESI) Calcd for $C_{19}H_{16}N$ [M+H$^+$]: 258.1283; Found: 258.1280.

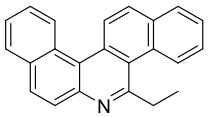
14-Ethyldibenzo[c,i]phenanthridine (7b).



7b

Pale yellow solid, 26 mg, 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (d, *J* = 8.1 Hz, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 8.64 (d, *J* = 8.9 Hz, 1H), 8.54 (d, *J* = 9.0 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.81 – 7.68 (m, 4H), 3.87 (q, *J* = 7.4 Hz, 2H), 1.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.84, 141.02, 133.87, 133.29, 133.07, 131.70, 131.39, 130.42, 128.89, 127.52, 127.48, 126.88, 126.79, 126.33, 124.96, 123.32, 120.73, 120.29, 119.87, 34.81, 13.49. MS (ESI) Calcd for $C_{23}H_{18}N$ [M+H$^+$]: 308.1439; Found: 308.1440.

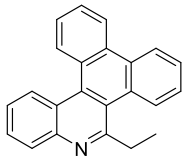
5-Ethyldibenzo[a,i]phenanthridine (7c).



7c

Pale yellow solid, 28 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 –8.90 (m, 2H), 8.83 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.06 – 8.03 (m, 4H), 7.77 – 7.63(m, 4H), 3.78 (q, *J* = 7.4 Hz, 2H), 1.70 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.70, 144.04, 134.49, 132.99, 132.67, 130.16, 130.11, 130.03, 129.39, 128.74, 128.32, 128.07, 127.66, 127.48, 126.65, 126.51, 126.34, 126.13, 125.41, 124.13, 119.90, 33.89, 13.83. MS (ESI) Calcd for [M+H$^+$] $C_{23}H_{18}N$: 308.1439; Found: 308.1442.

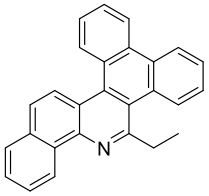
5-Ethyldibenzo[i,k]phenanthridine (7d).



7d

Pale yellow solid, 29 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.2 Hz, 1H), 8.69 – 8.57 (m, 3H), 8.43 (dd, *J* = 7.8, 0.7 Hz, 1H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.68 – 7.60 (m, 3H), 7.58 – 7.53 (m, 1H), 3.61 (q, *J* = 7.4 Hz, 2H), 1.61 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.34, 145.55, 134.41, 132.09, 130.58, 129.66, 129.04, 128.36, 128.33, 128.14, 128.09, 127.50, 127.17, 127.08, 126.85, 126.75, 125.47, 123.60, 123.44, 123.00, 122.43, 32.81, 14.19. MS (ESI) Calcd for $C_{23}H_{18}N$ [M+H$^+$]: 308.1439; Found: 308.1432.

16-Ethyltribenzo[c,i,k]phenanthridine (7e).



7e

Pale yellow solid, 33 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, *J* = 8.2 Hz, 1H), 8.76 (dd, *J* = 8.2, 0.9 Hz, 1H), 8.65 (td, *J* = 7.8, 1.0 Hz, 2H), 8.59 (d, *J* = 9.1 Hz, 1H), 8.51 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.77 – 7.60 (m, 5H), 3.73 (q, *J* = 7.3 Hz, 2H), 1.74 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.34, 142.85, 134.96, 133.00, 132.17, 131.15, 130.74, 130.15, 129.37, 128.53, 128.37, 127.72, 127.66, 127.29, 127.13, 126.88, 126.77, 126.70, 125.82, 125.19, 124.85, 123.85, 123.70, 123.49, 119.44, 33.03, 14.07. MS (ESI) Calcd for $C_{27}H_{20}N$ [M+H$^+$]: 358.1596; Found: 358.1597.

4. Copies of ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR spectra of products

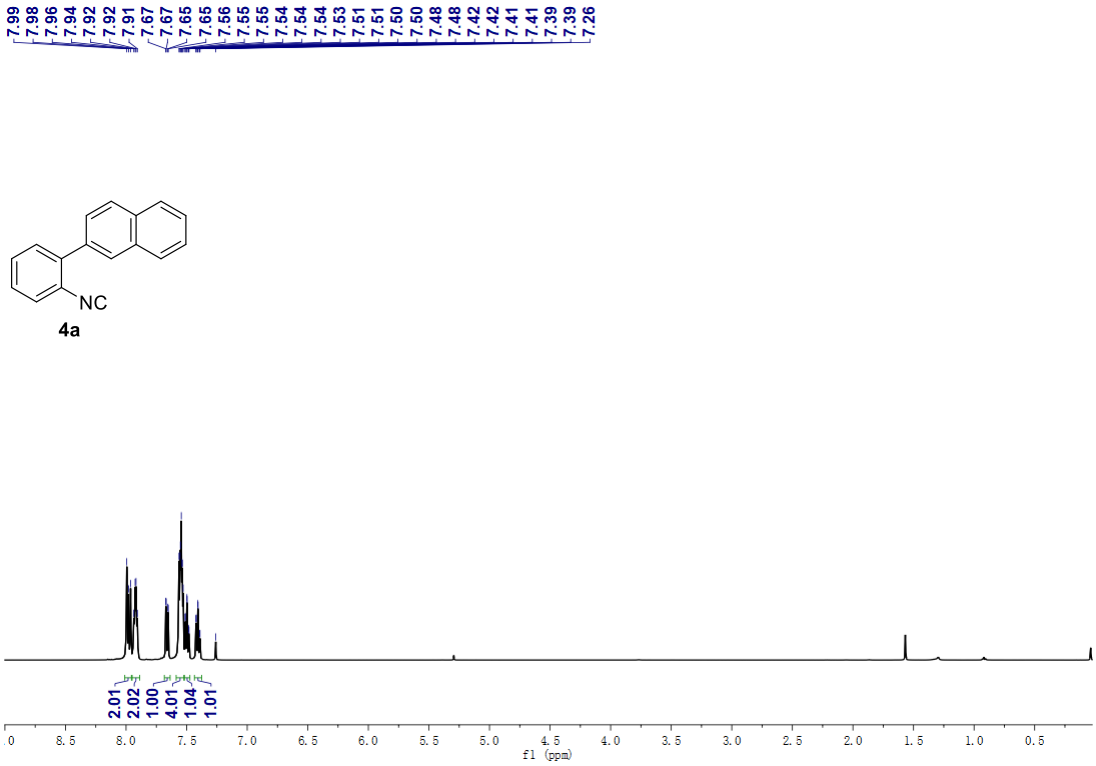


Figure S10. The ^{1}H-NMR spectral copy of compound **4a**.

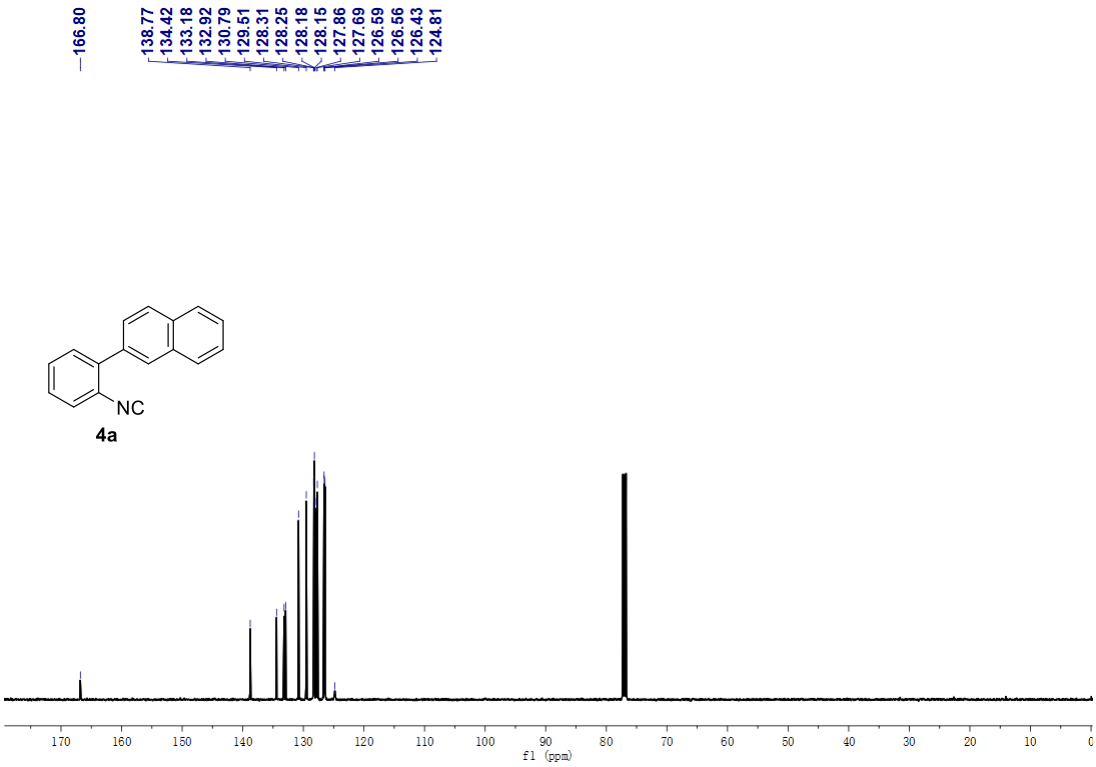


Figure S11. The ^{13}C-NMR spectral copy of compound **4a**.

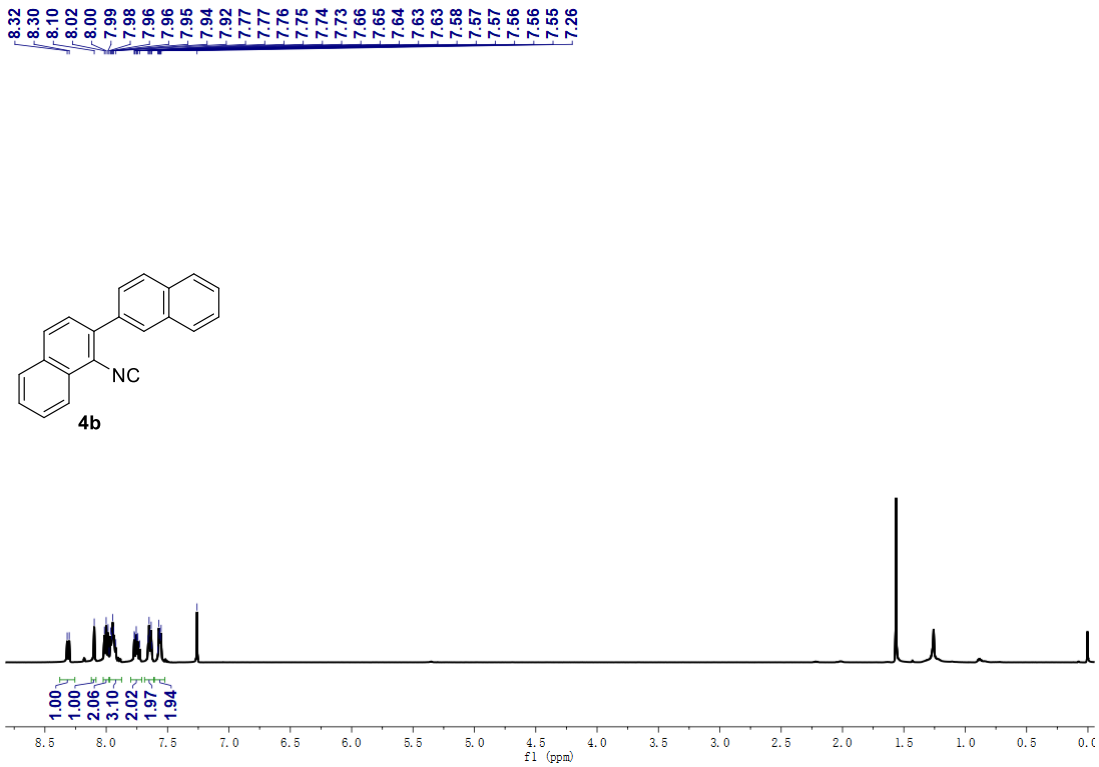


Figure S12. The ^{1}H-NMR spectral copy of compound **4b**.

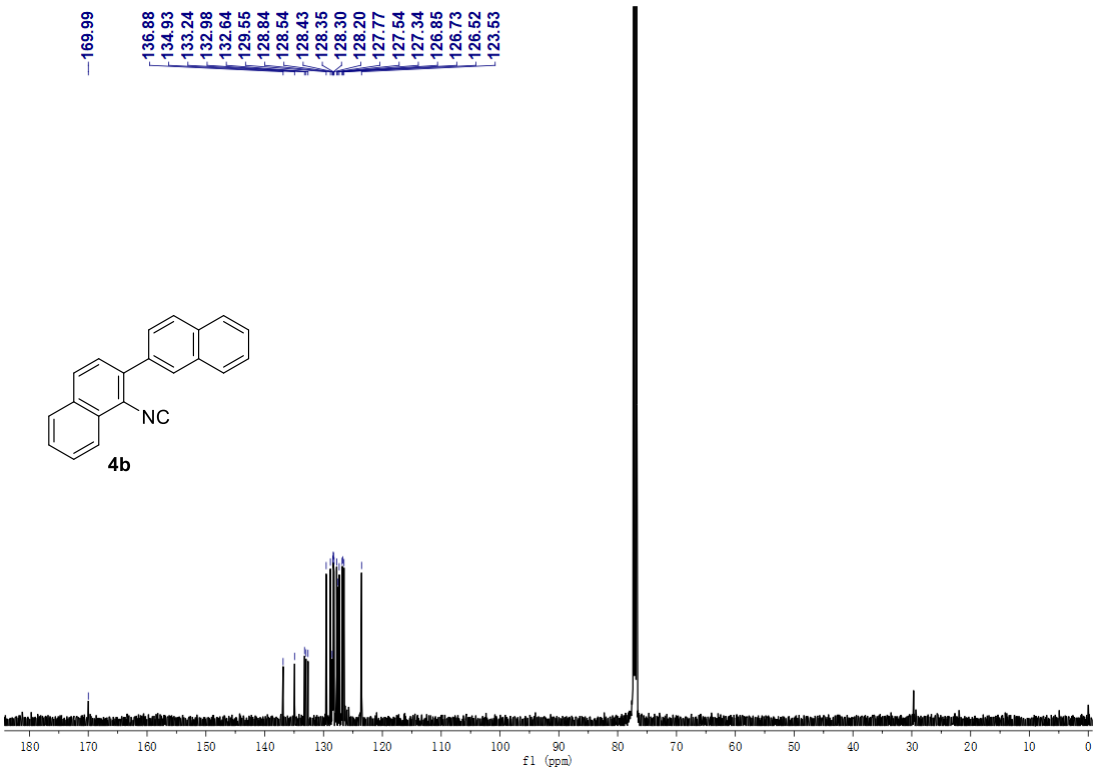


Figure S13. The ^{13}C-NMR spectral copy of compound **4b**.

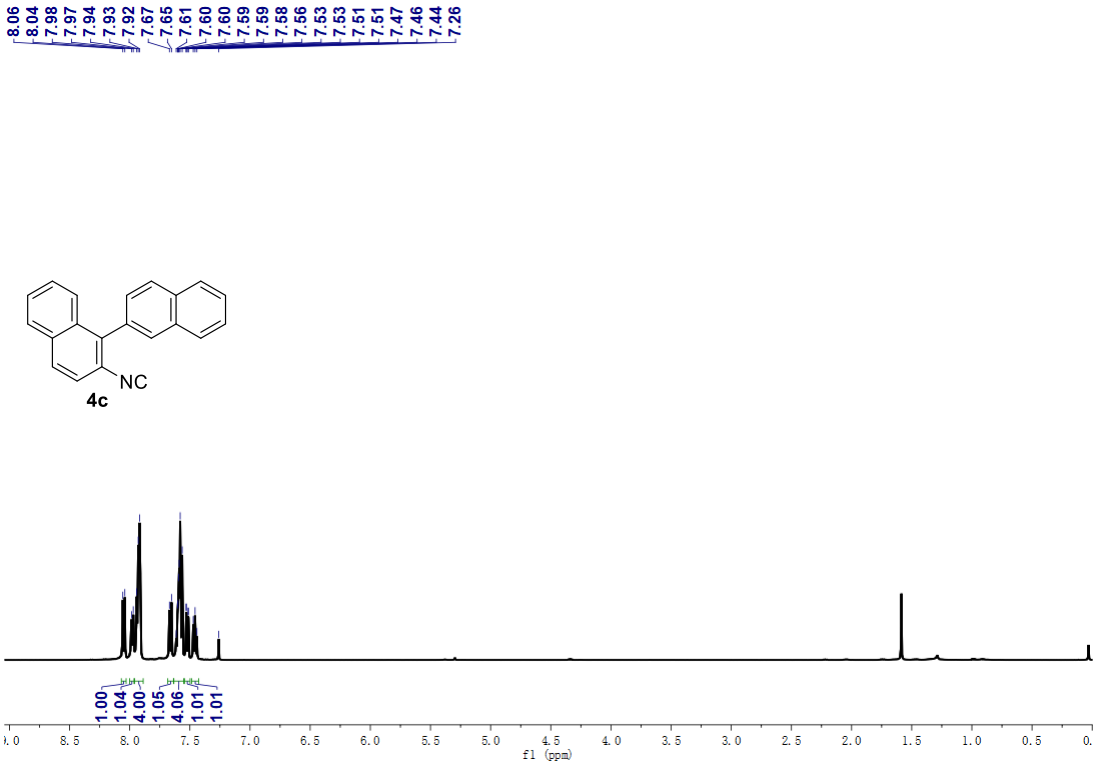


Figure S14. The ^{1}H-NMR spectral copy of compound **4c**.

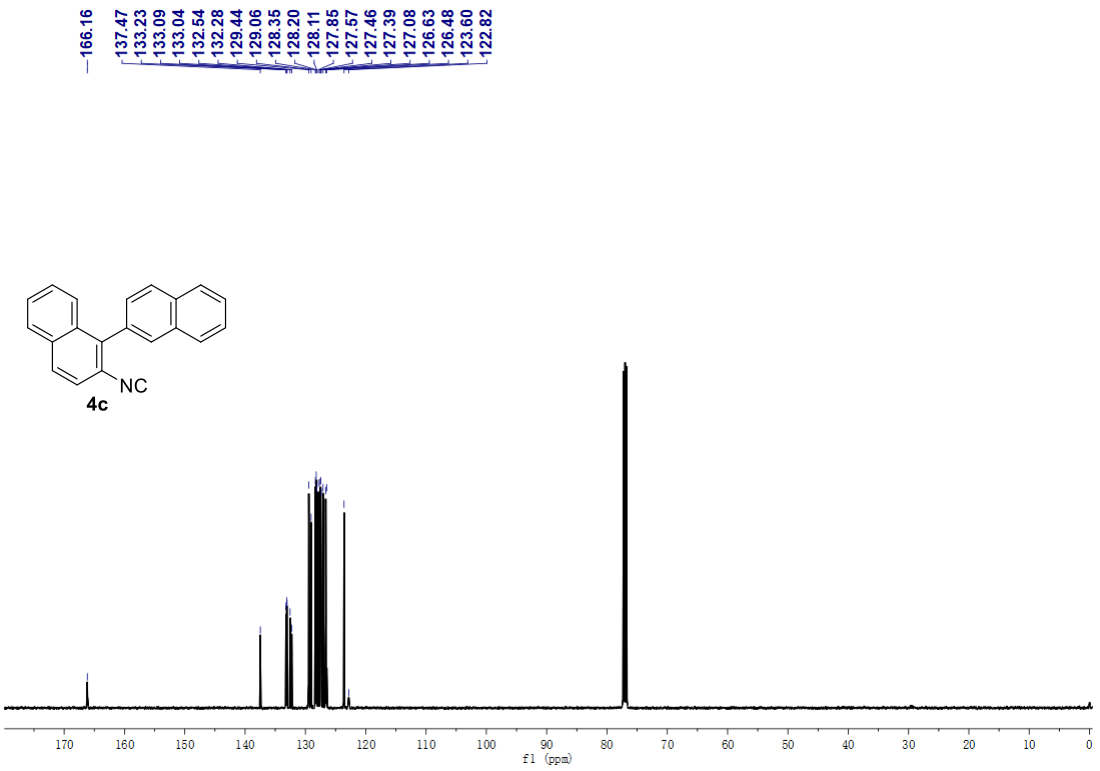


Figure S15. The ^{13}C-NMR spectral copy of compound **4c**.

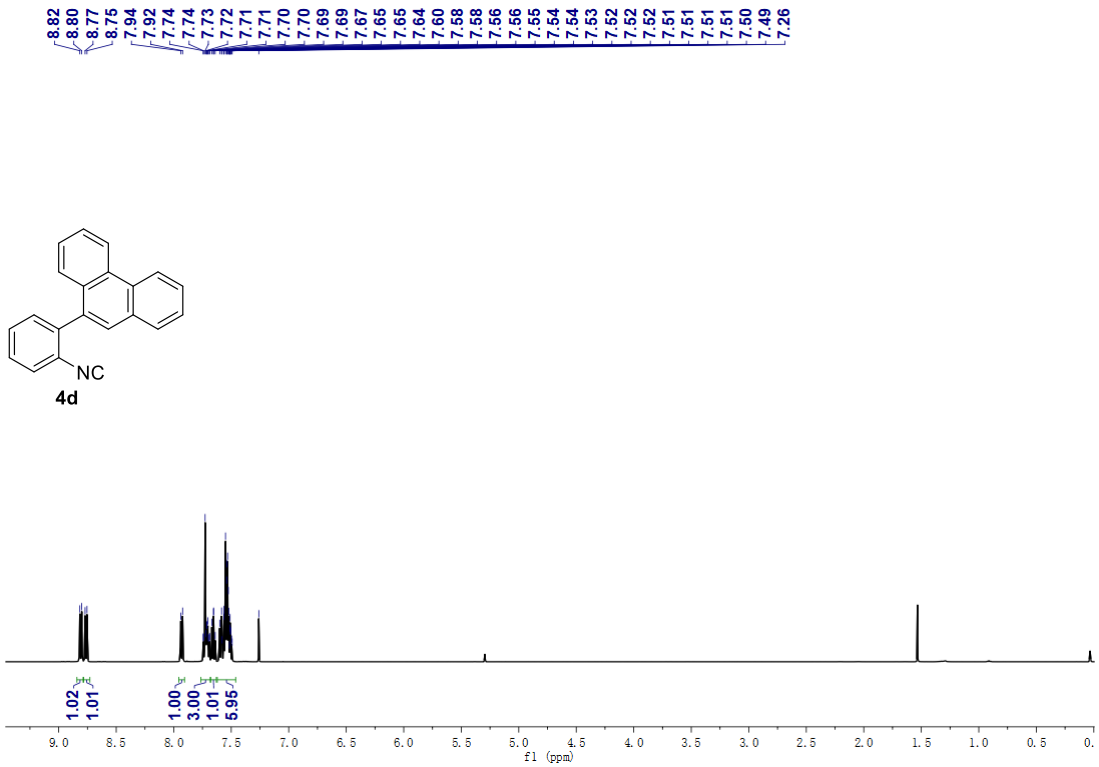


Figure S16. The ^{1}H-NMR spectral copy of compound **4d**.

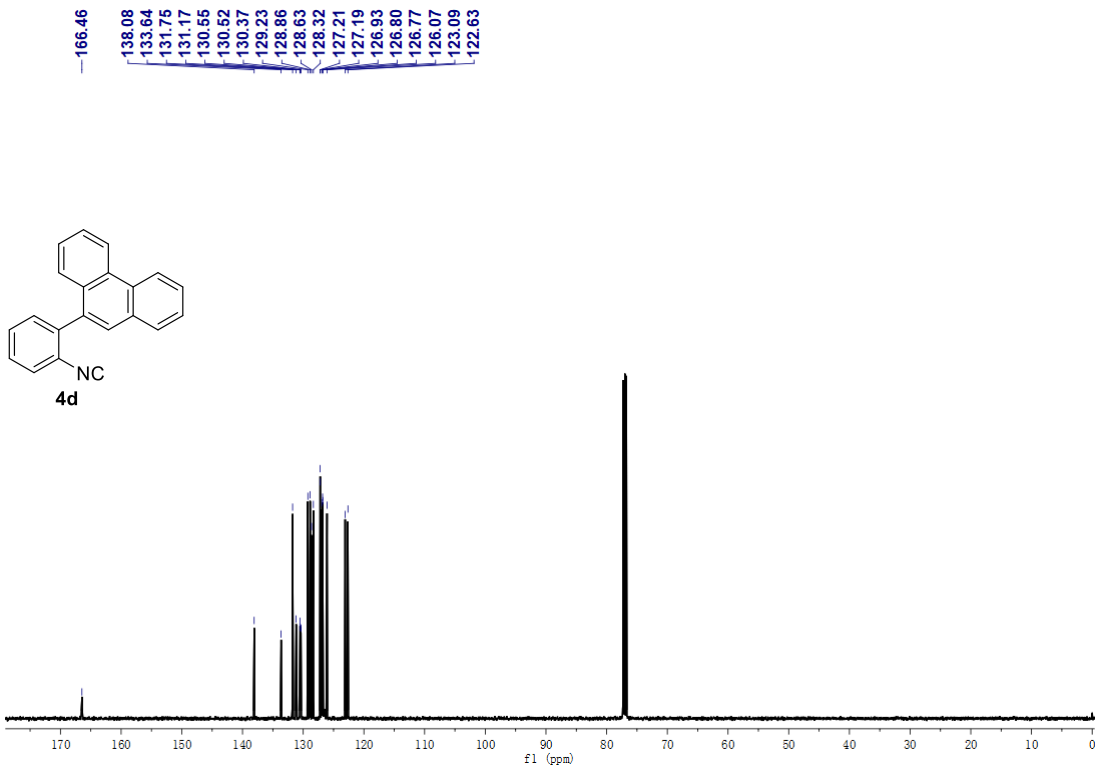


Figure S17. The ^{13}C-NMR spectral copy of compound **4d**.

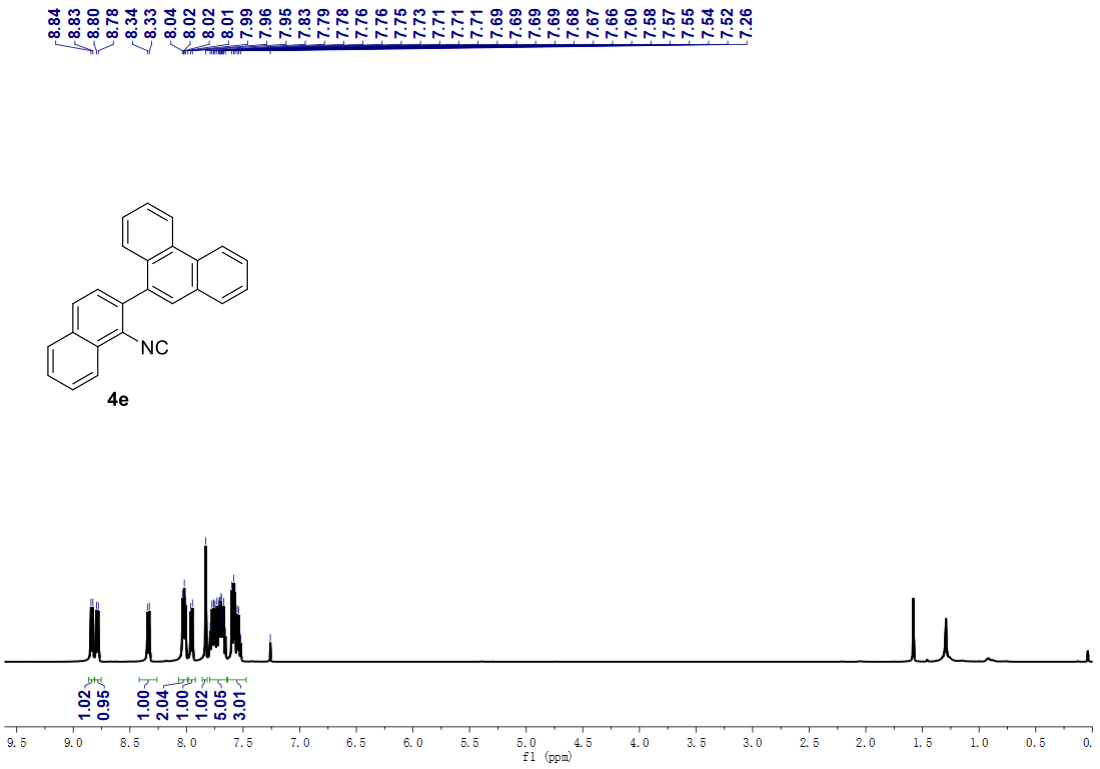


Figure S18. The ^{1}H-NMR spectral copy of compound **4e**.

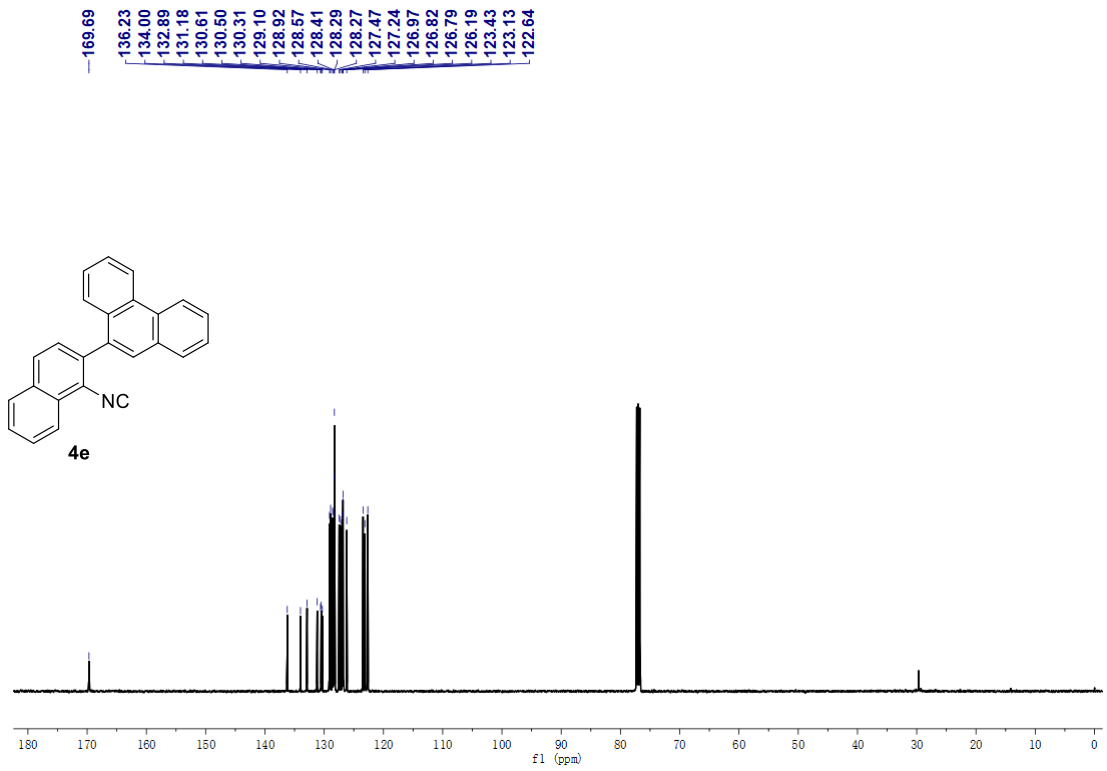


Figure S19. The ^{13}C-NMR spectral copy of compound **4e**.

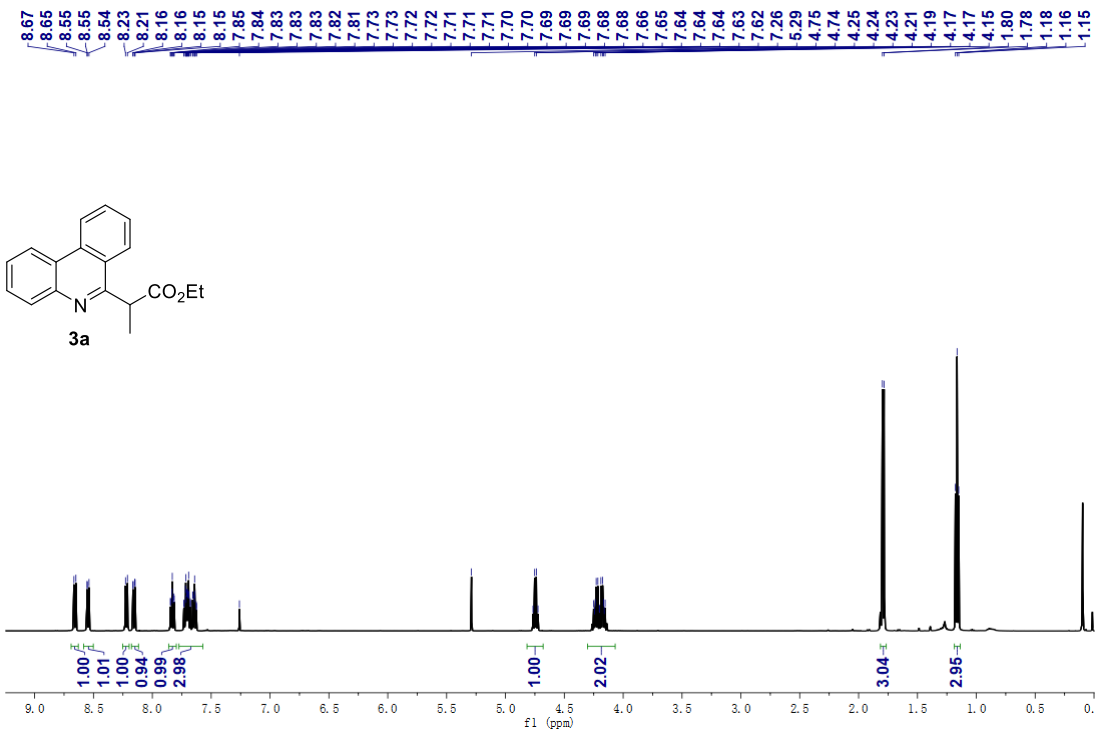


Figure S20. The ^{1}H-NMR spectral copy of compound **3a**.

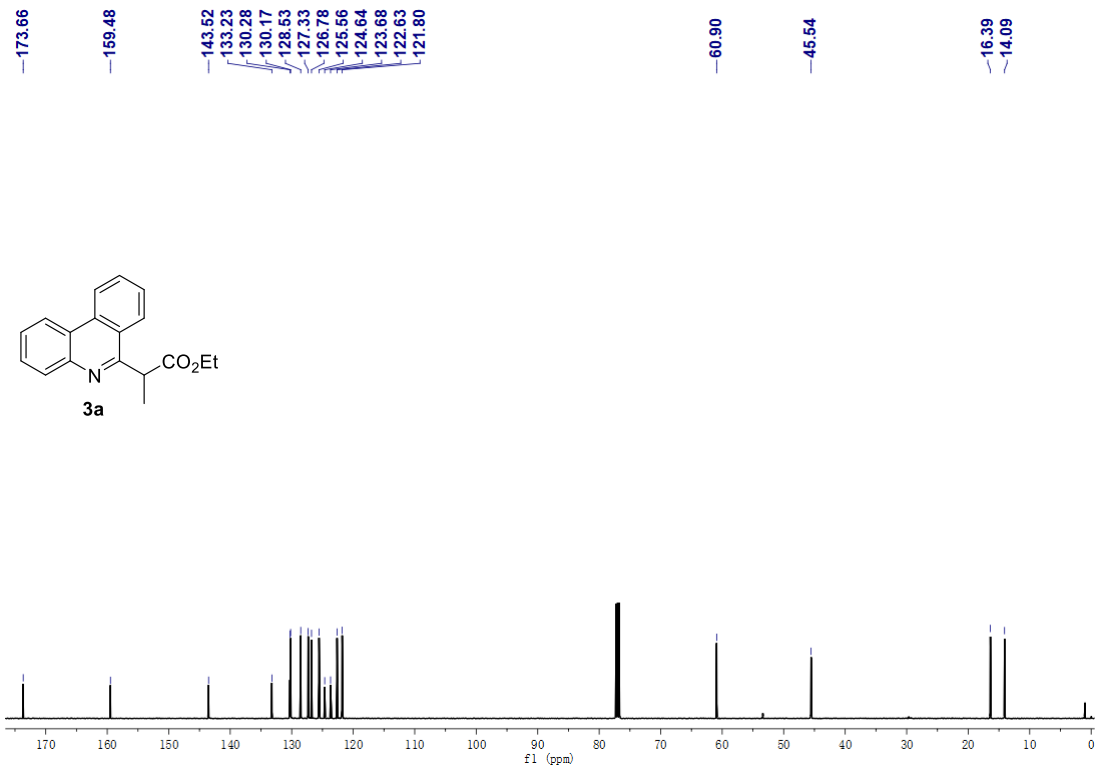


Figure S21. The ^{13}C-NMR spectral copy of compound **3a**.

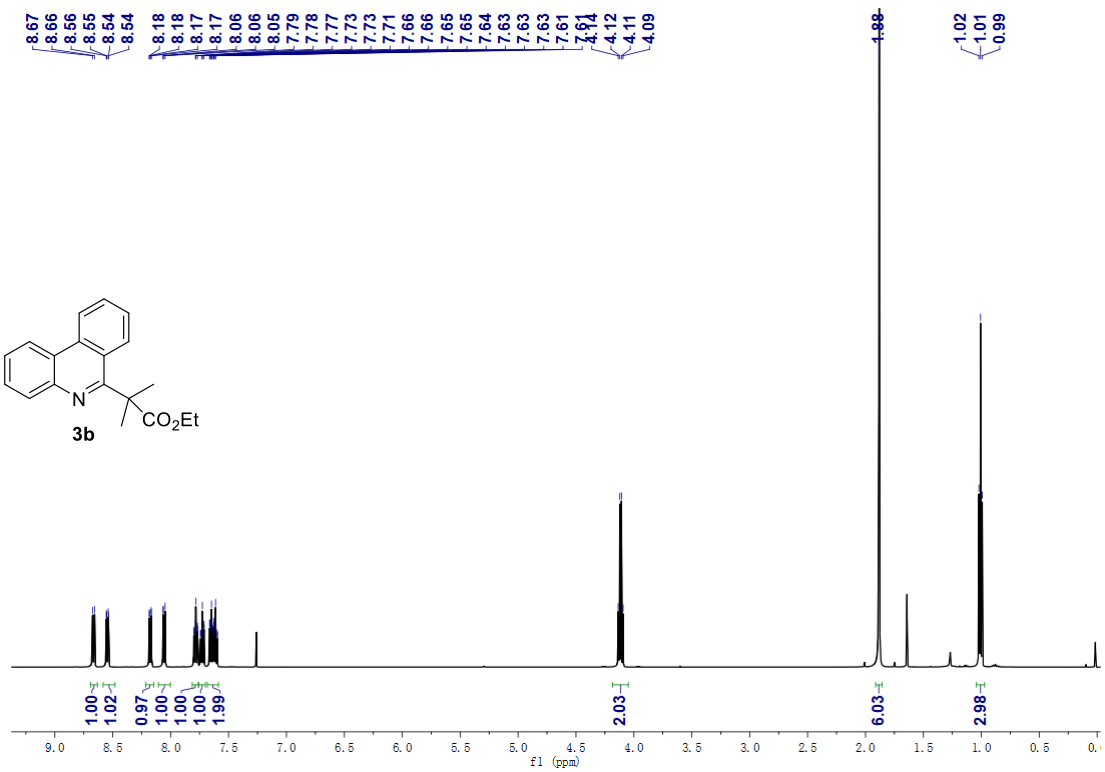


Figure S22. The ^{1}H-NMR spectral copy of compound **3b**.

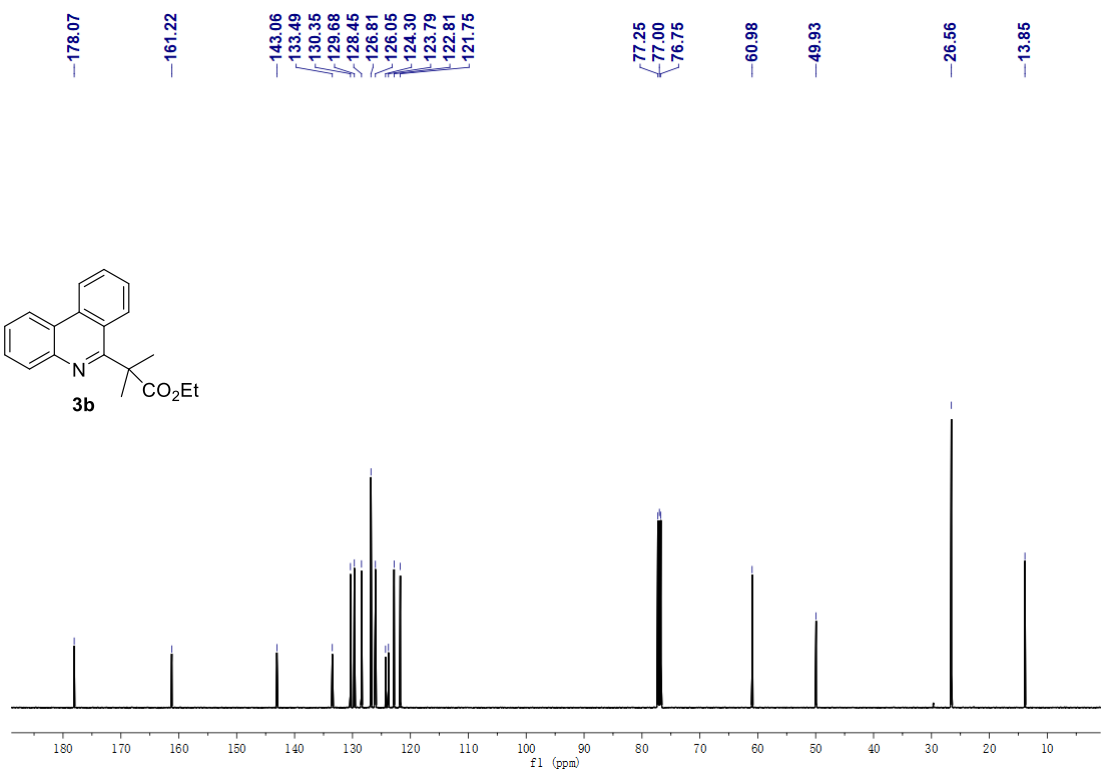


Figure S23. The ^{13}C-NMR spectral copy of compound **3b**.

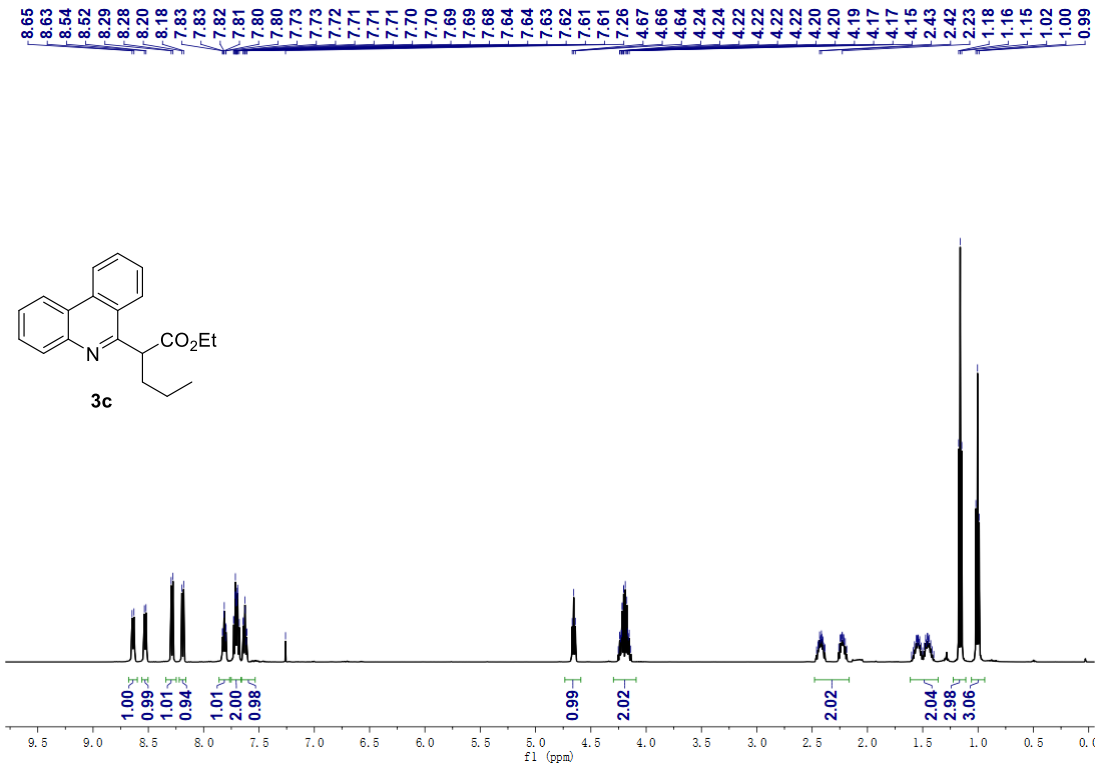


Figure S24. The ^{1}H-NMR spectral copy of compound **3c**.

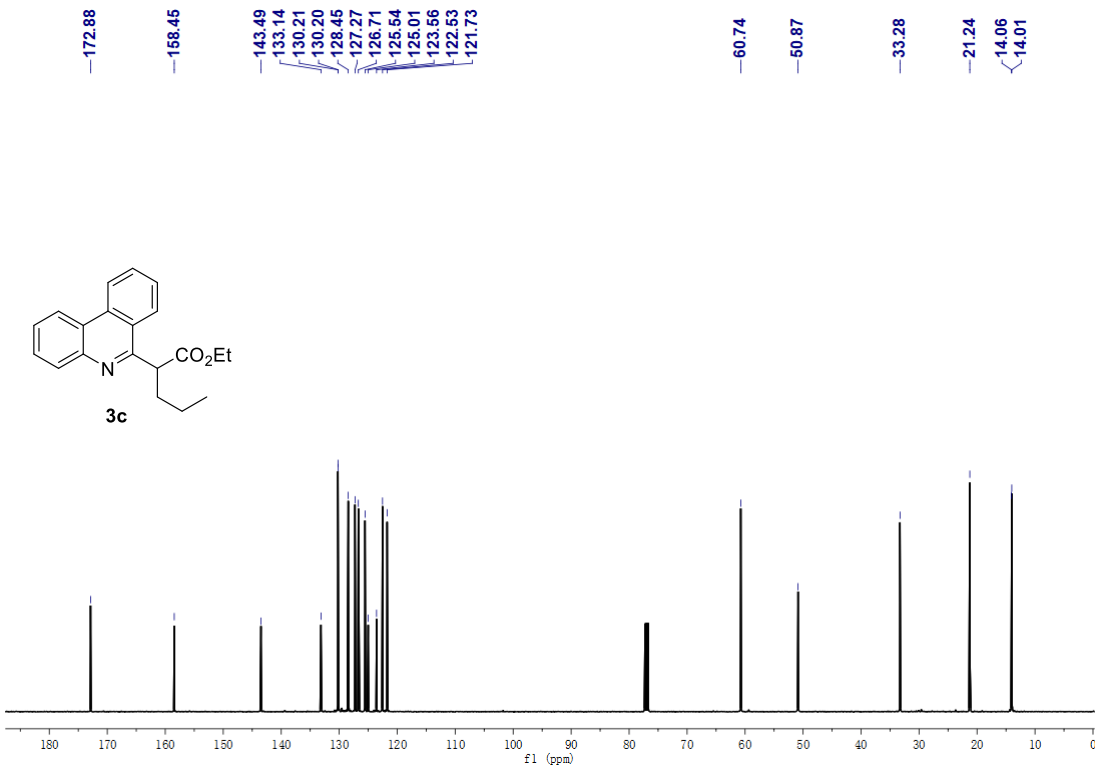


Figure S25. The ^{13}C-NMR spectral copy of compound **3c**.

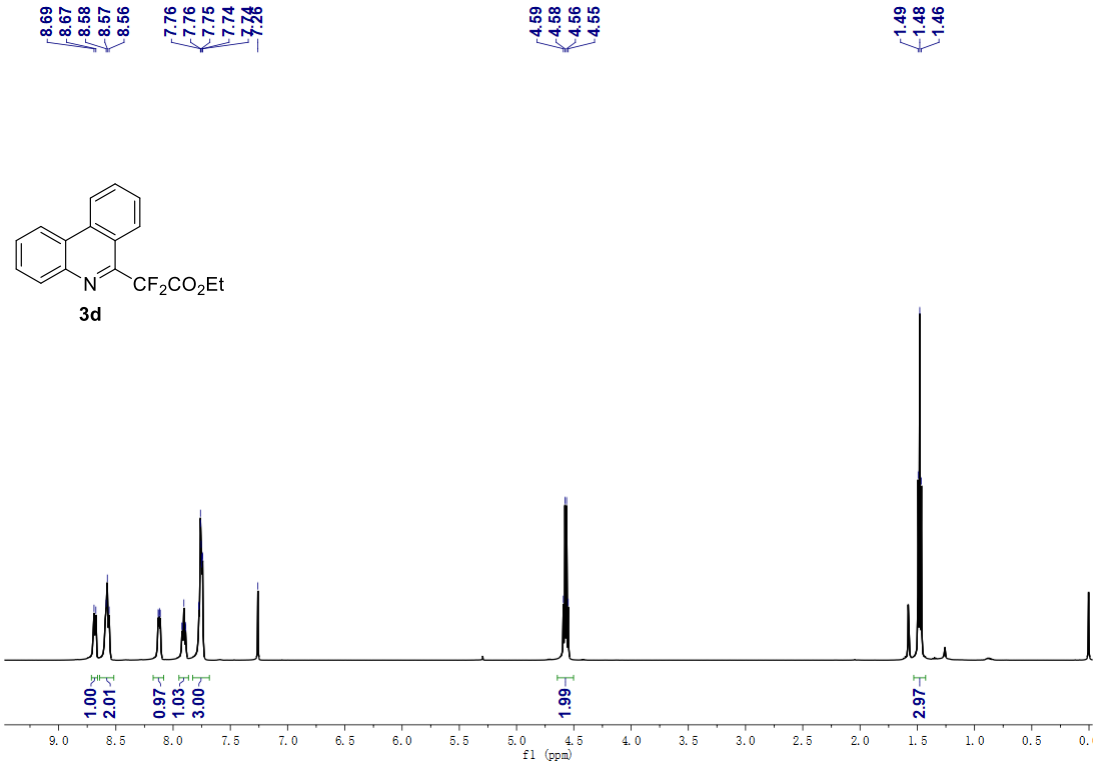


Figure S26. The ^{1}H-NMR spectral copy of compound **3d**.

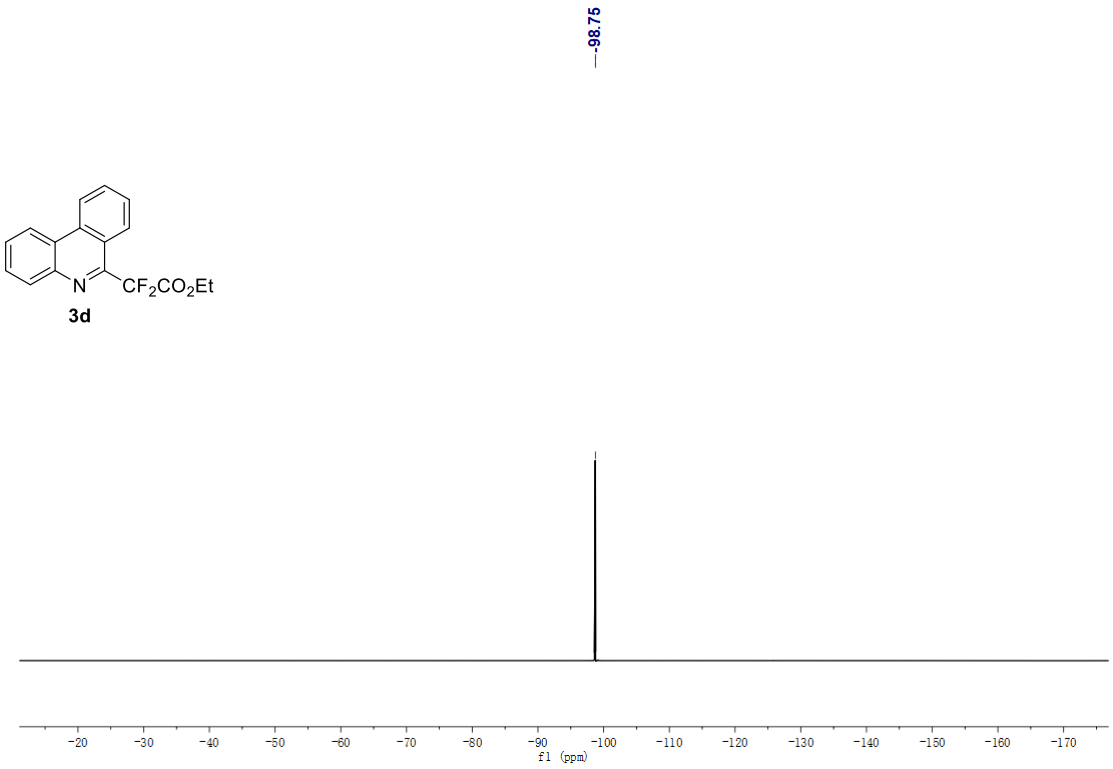


Figure S27. The ^{19}F-NMR spectral copy of compound **3d**.

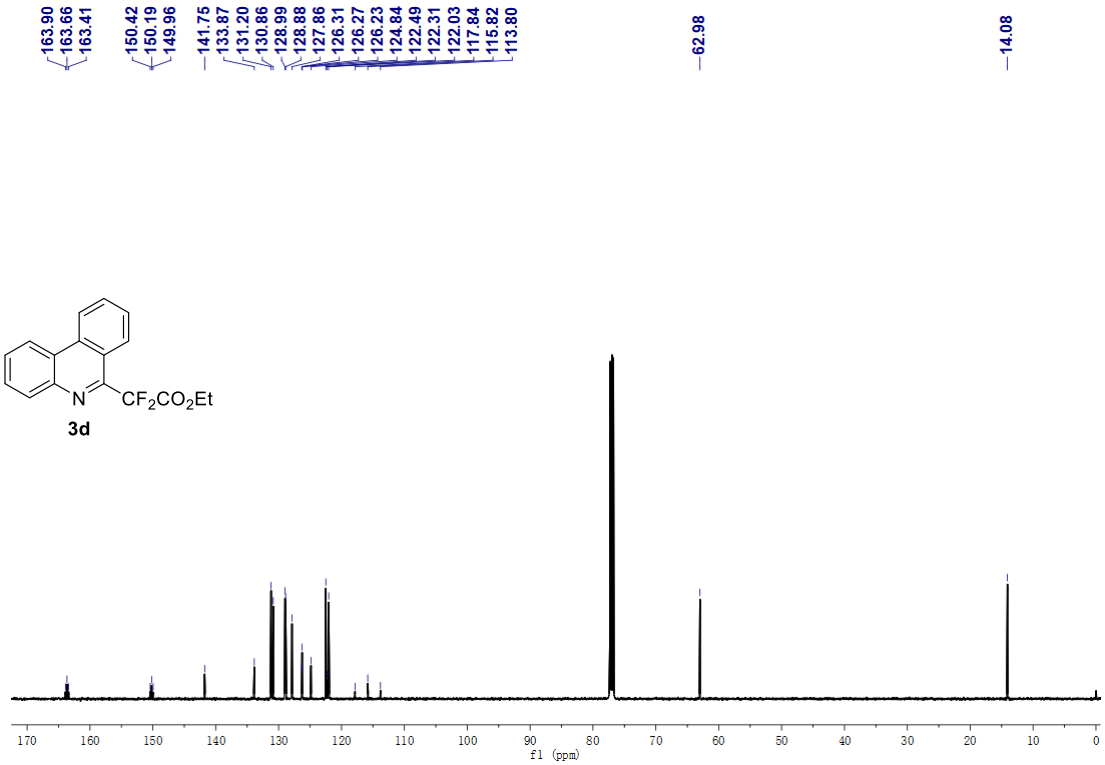


Figure S28. The ^{13}C-NMR spectral copy of compound **3d**.

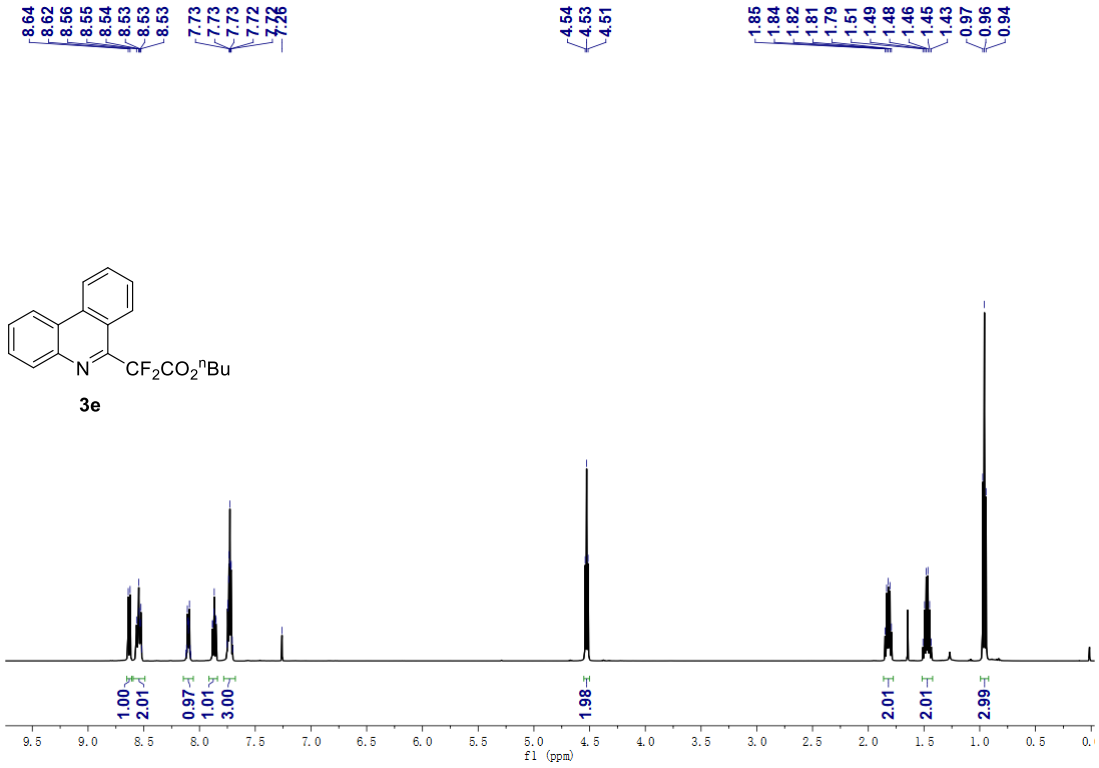


Figure S29. The ^{1}H-NMR spectral copy of compound **3e**.

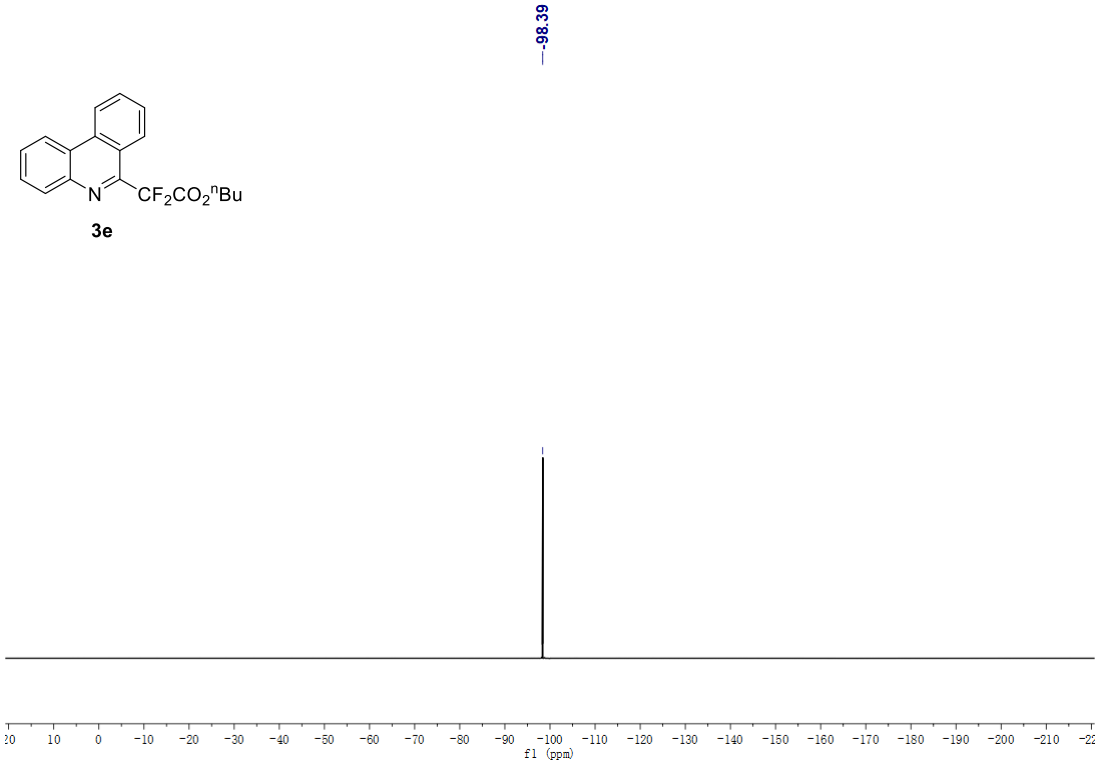


Figure S30. The ^{19}F-NMR spectral copy of compound **3e**.

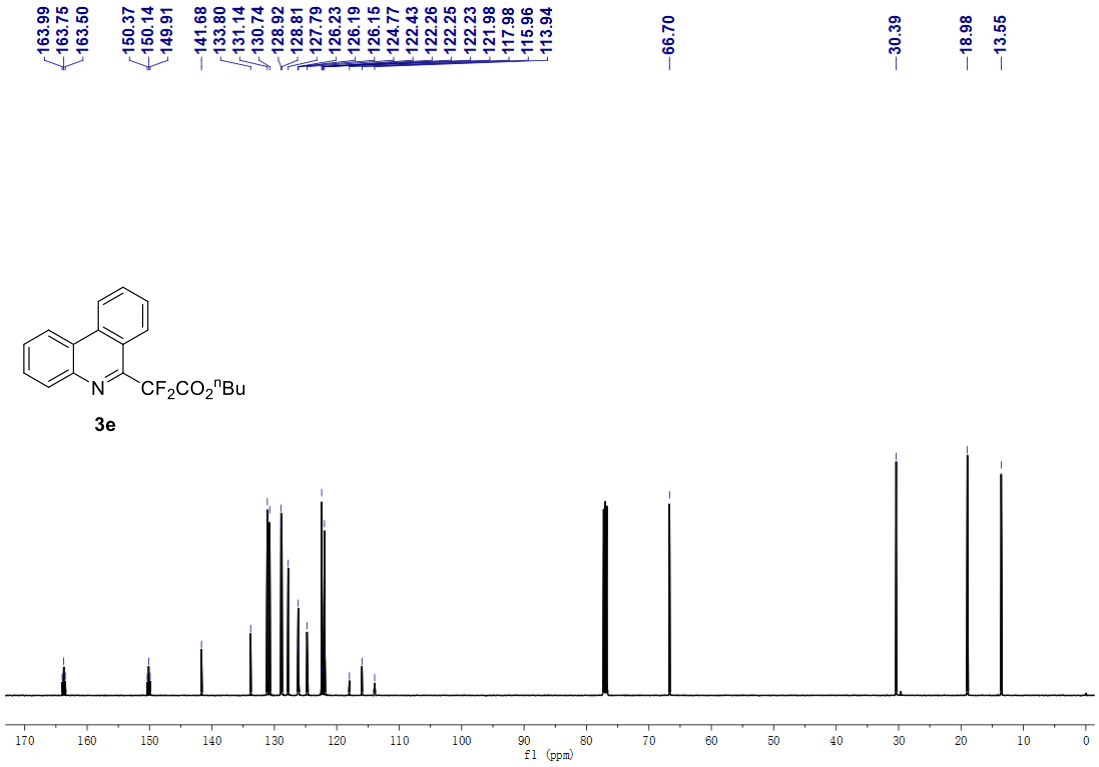


Figure S31. The ^{13}C-NMR spectral copy of compound **3e**.

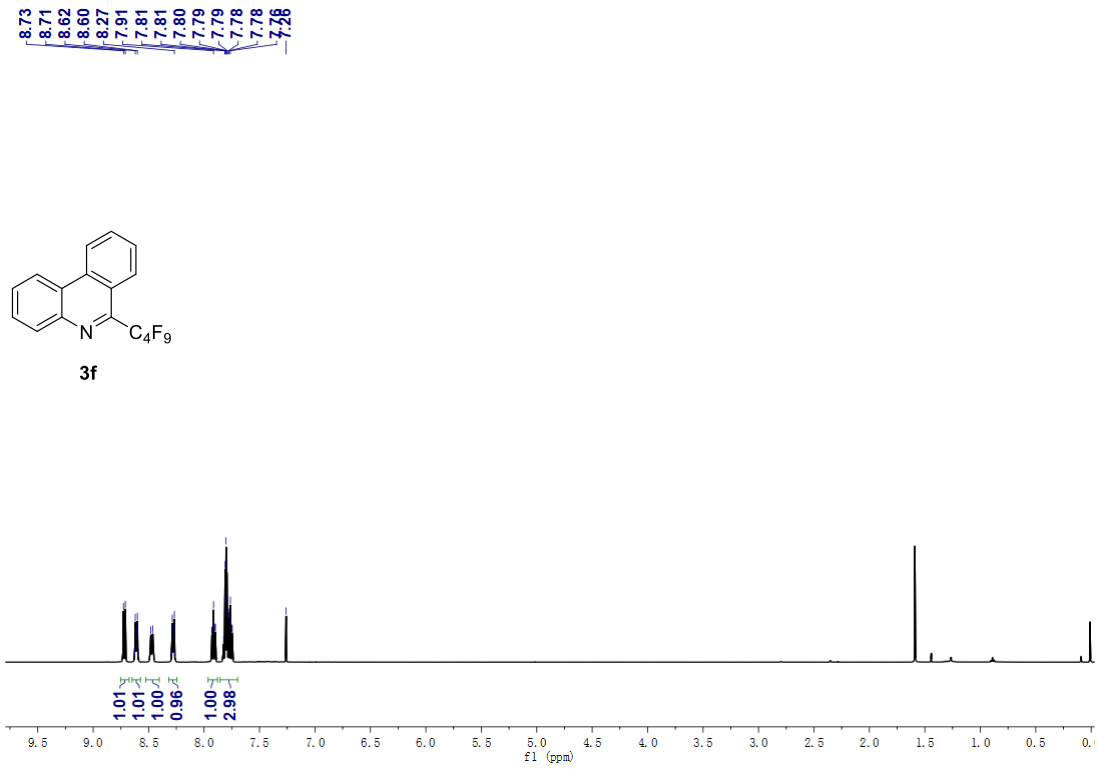


Figure S32. The ^{1}H-NMR spectral copy of compound **3f**.

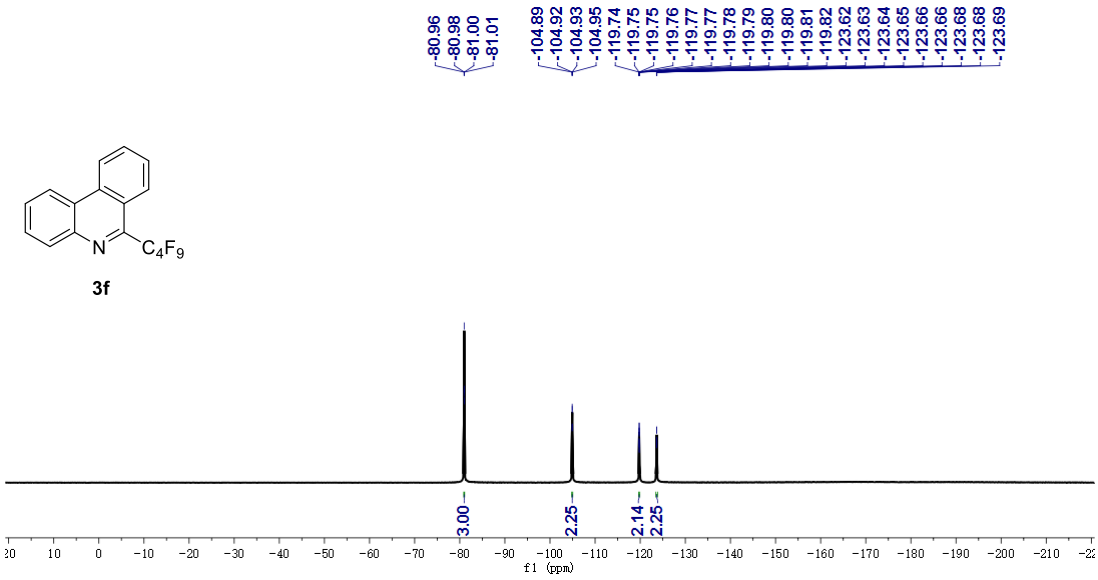


Figure S33. The ^{19}F-NMR spectral copy of compound **3f**.

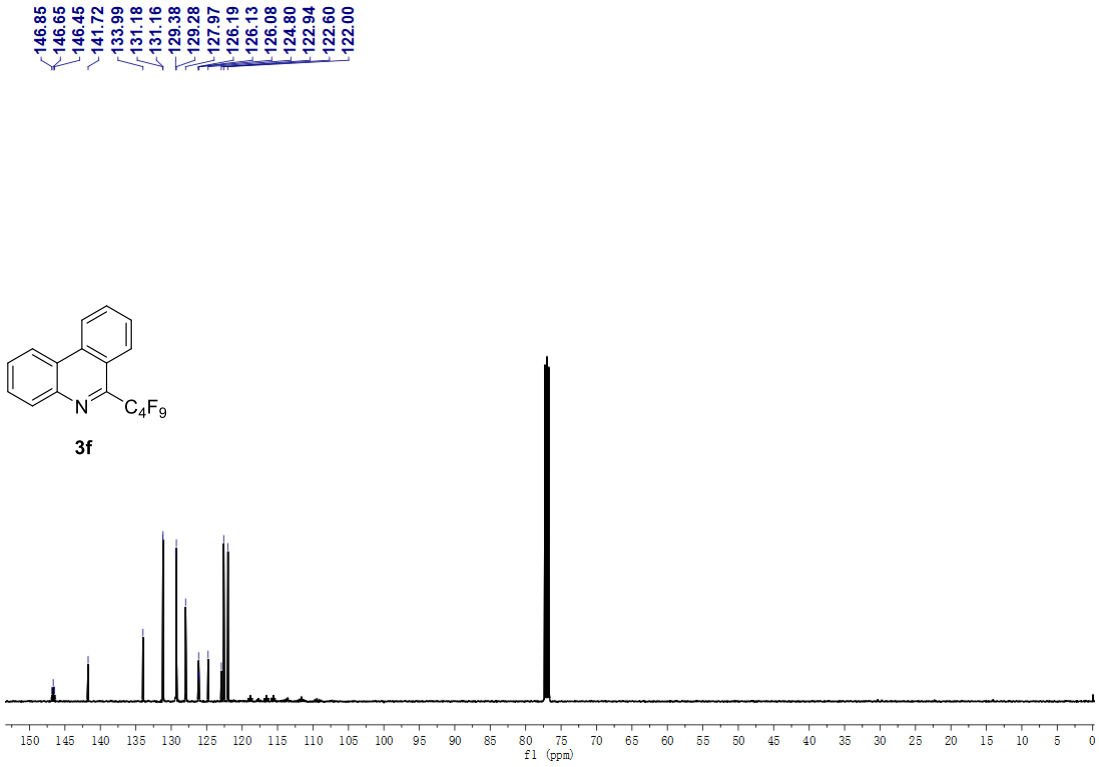


Figure S34. The ^{13}C-NMR spectral copy of compound **3f**.

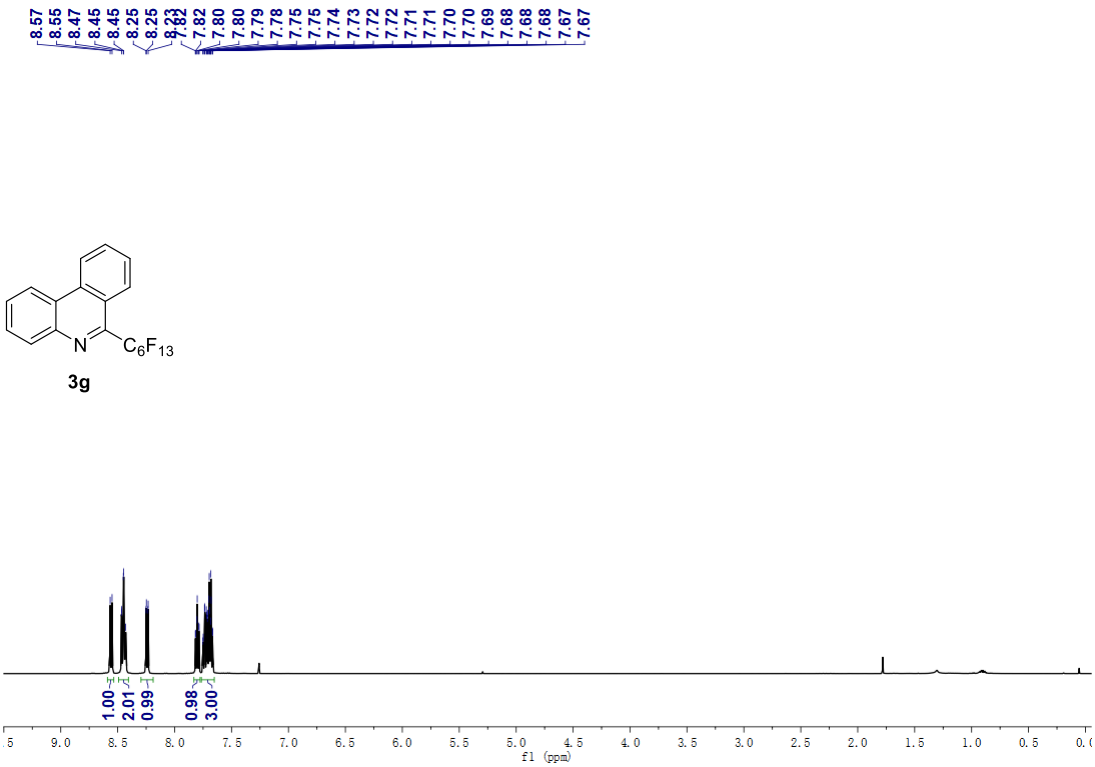


Figure S35. The ^{1}H-NMR spectral copy of compound **3g**.

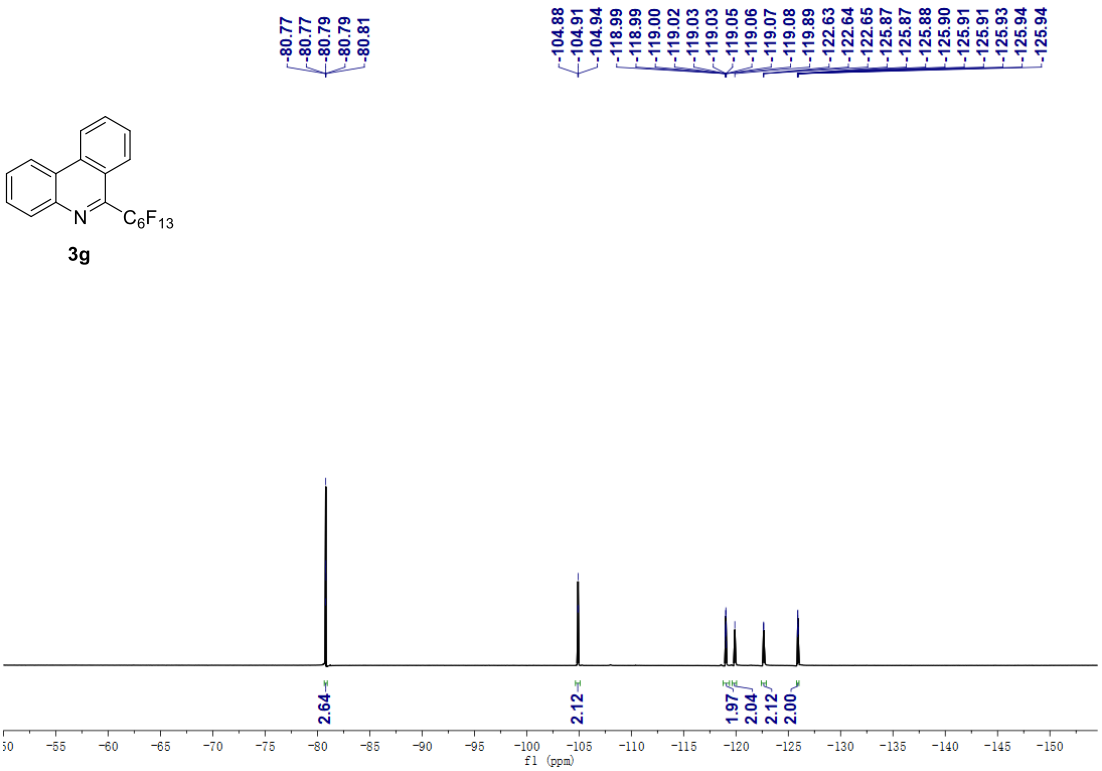


Figure S36. The ^{19}F-NMR spectral copy of compound **3g**.

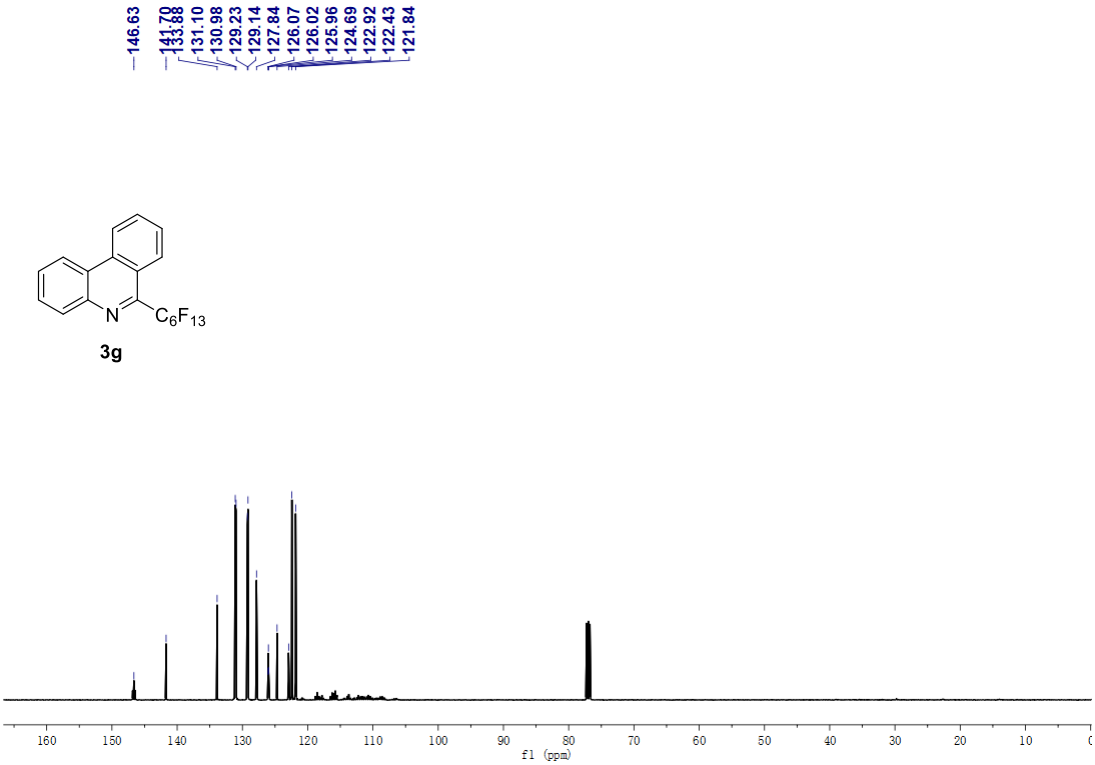


Figure S37. The ^{13}C-NMR spectral copy of compound **3g**.

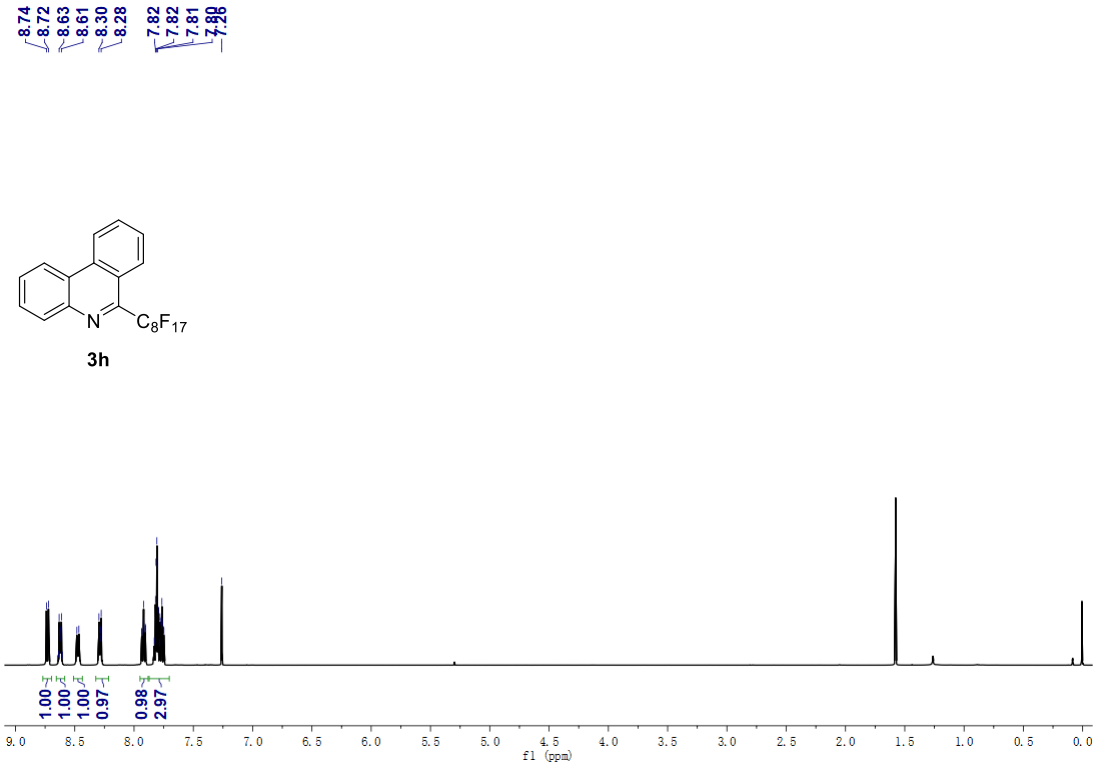


Figure S38. The ^{1}H-NMR spectral copy of compound **3h**.

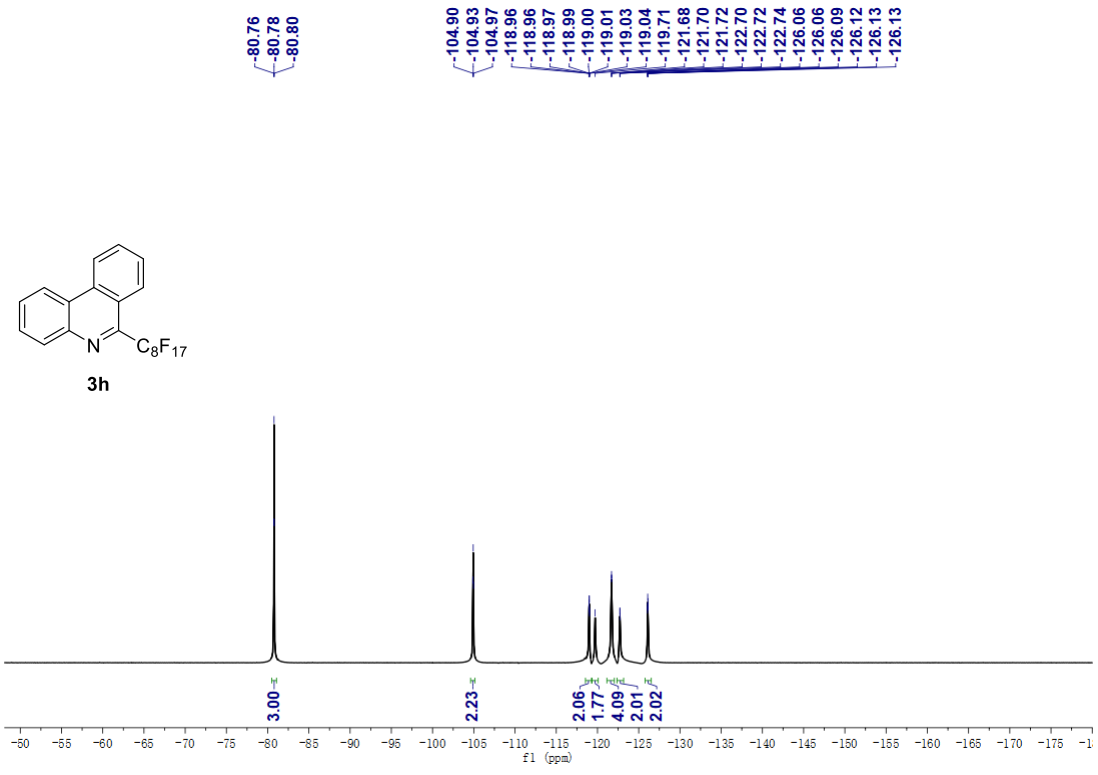


Figure S39. The ^{19}F-NMR spectral copy of compound **3h**.

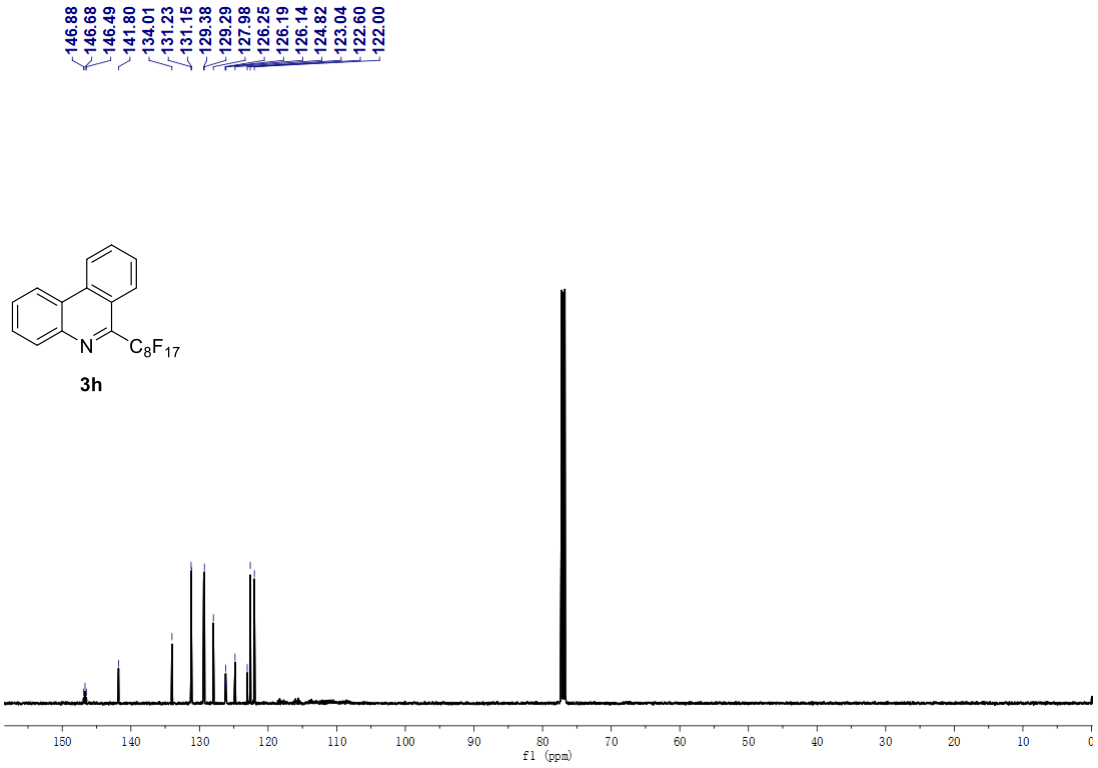


Figure S40. The ^{13}C-NMR spectral copy of compound **3h**.

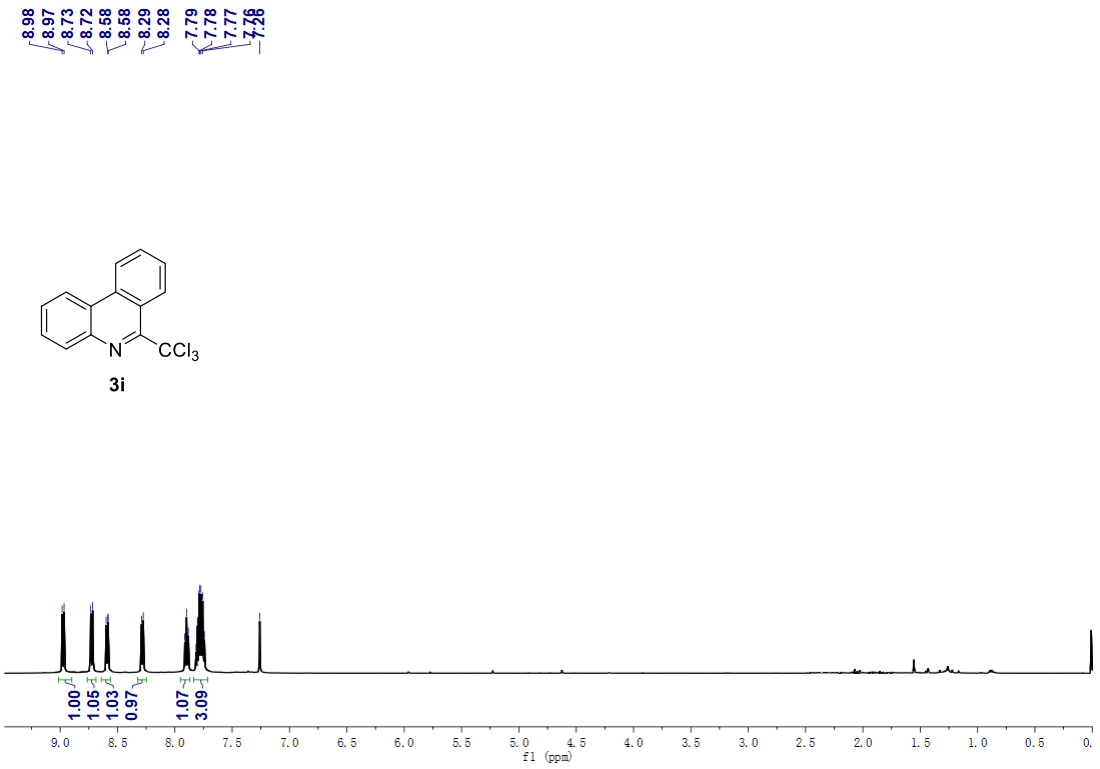


Figure S41. The ^{1}H-NMR spectral copy of compound **3i**.

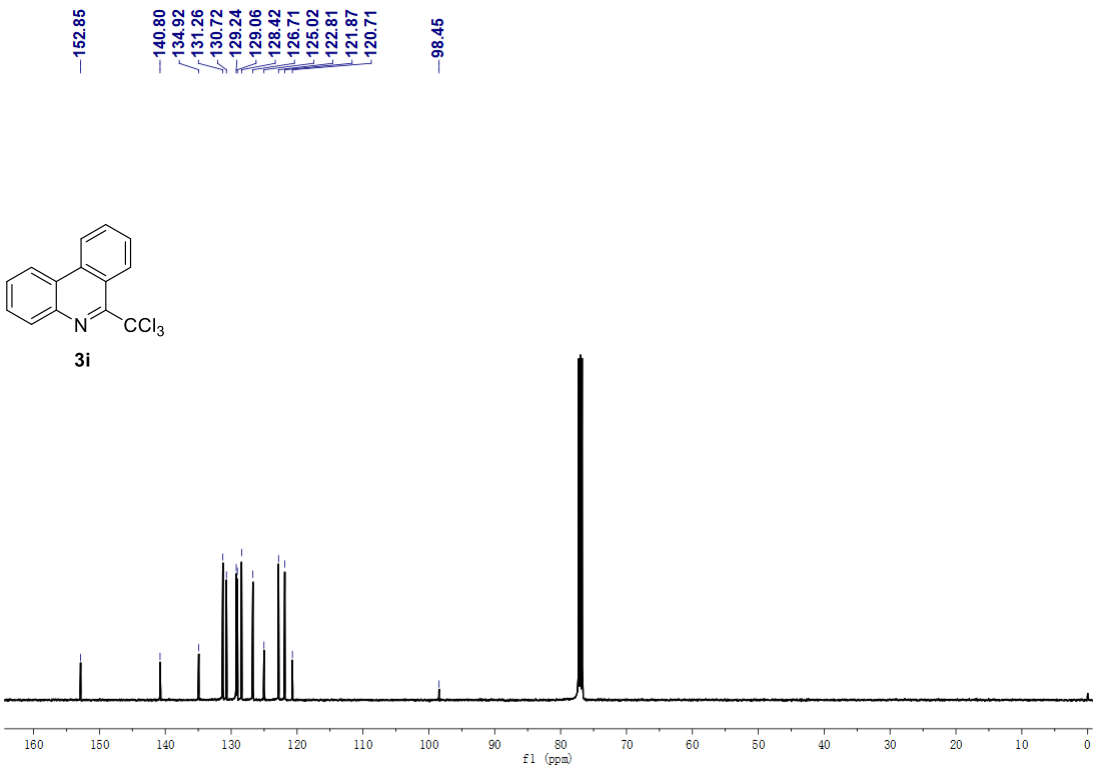


Figure S42. The ^{13}C-NMR spectral copy of compound 3i.

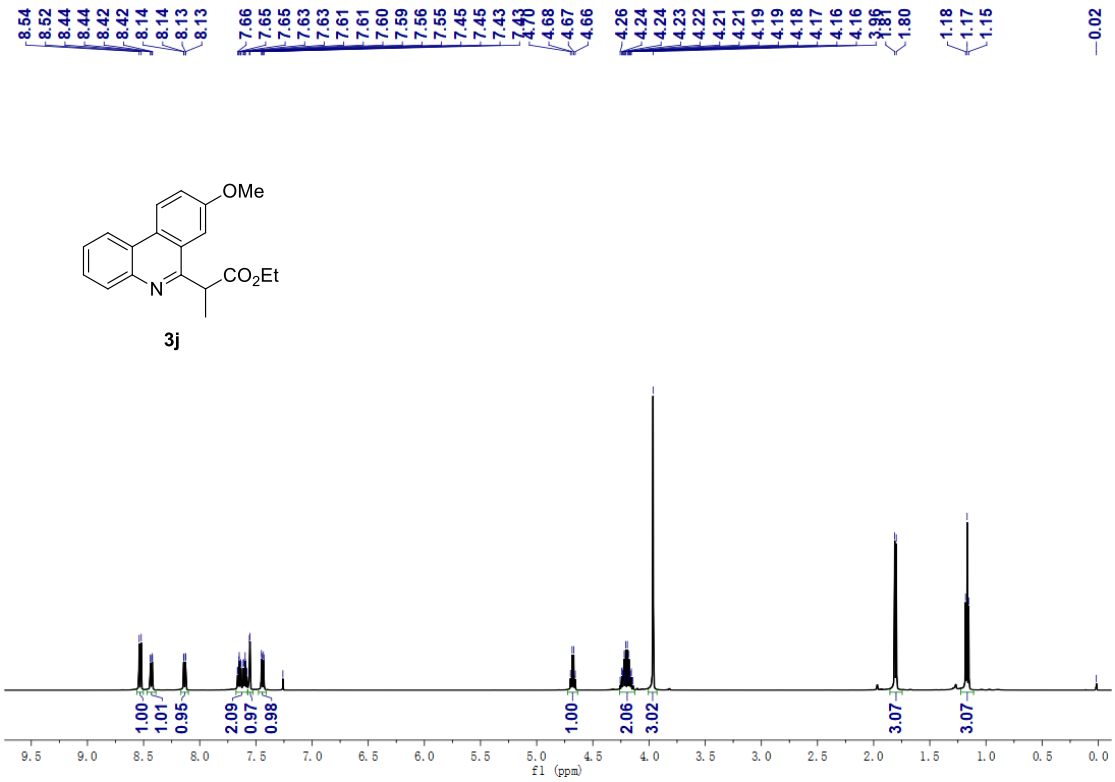


Figure S43. The ^{1}H-NMR spectral copy of compound **3j.**

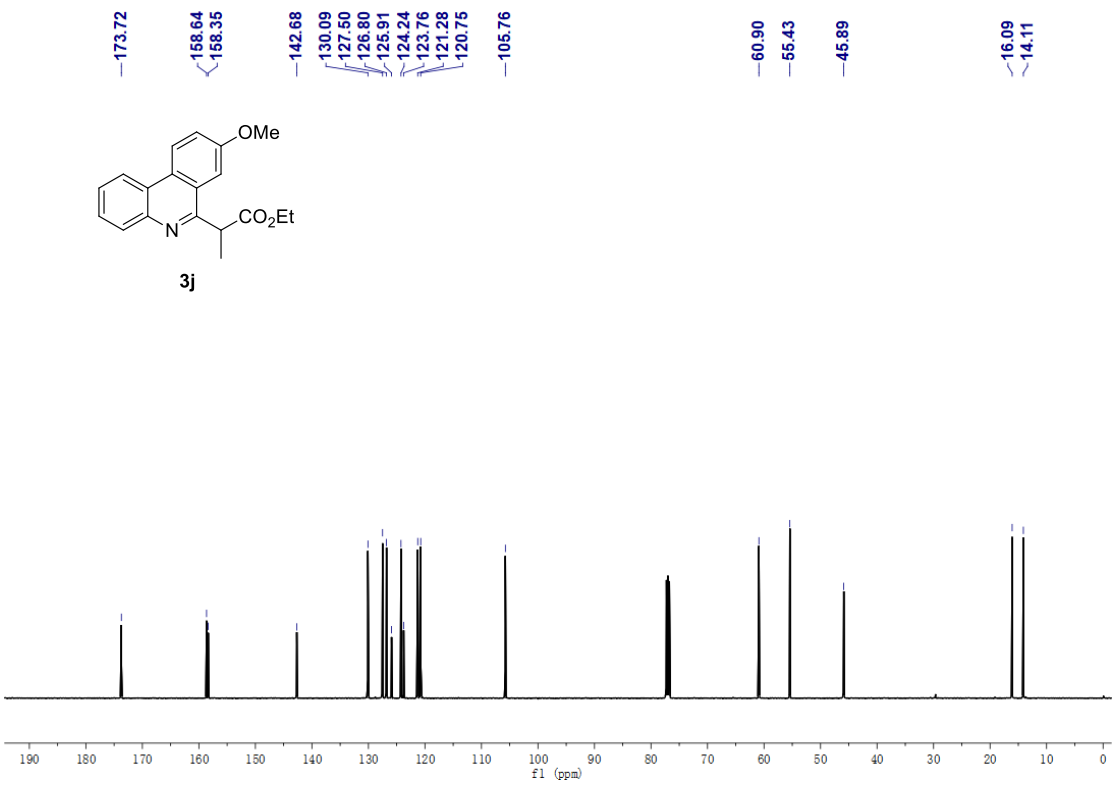


Figure S44. The ^{13}C-NMR spectral copy of compound **3j.**

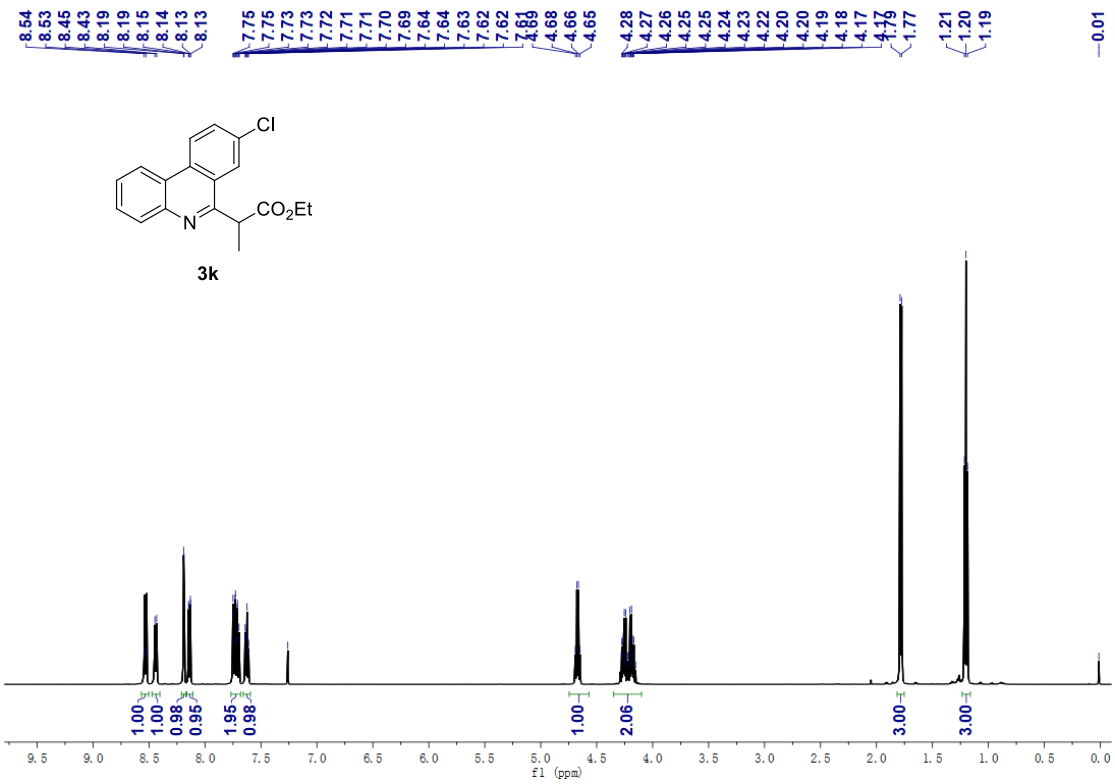


Figure S45. The ^{1}H-NMR spectral copy of compound **3k**.

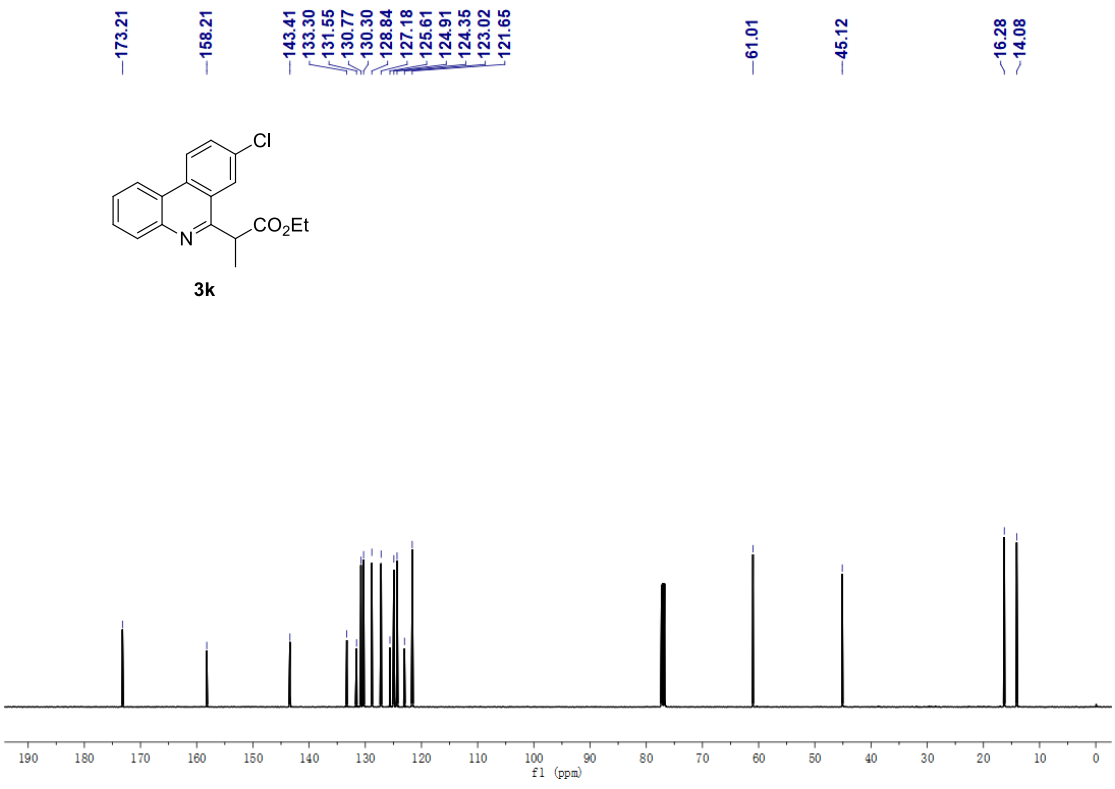


Figure S46. The ^{13}C-NMR spectral copy of compound **3k**.

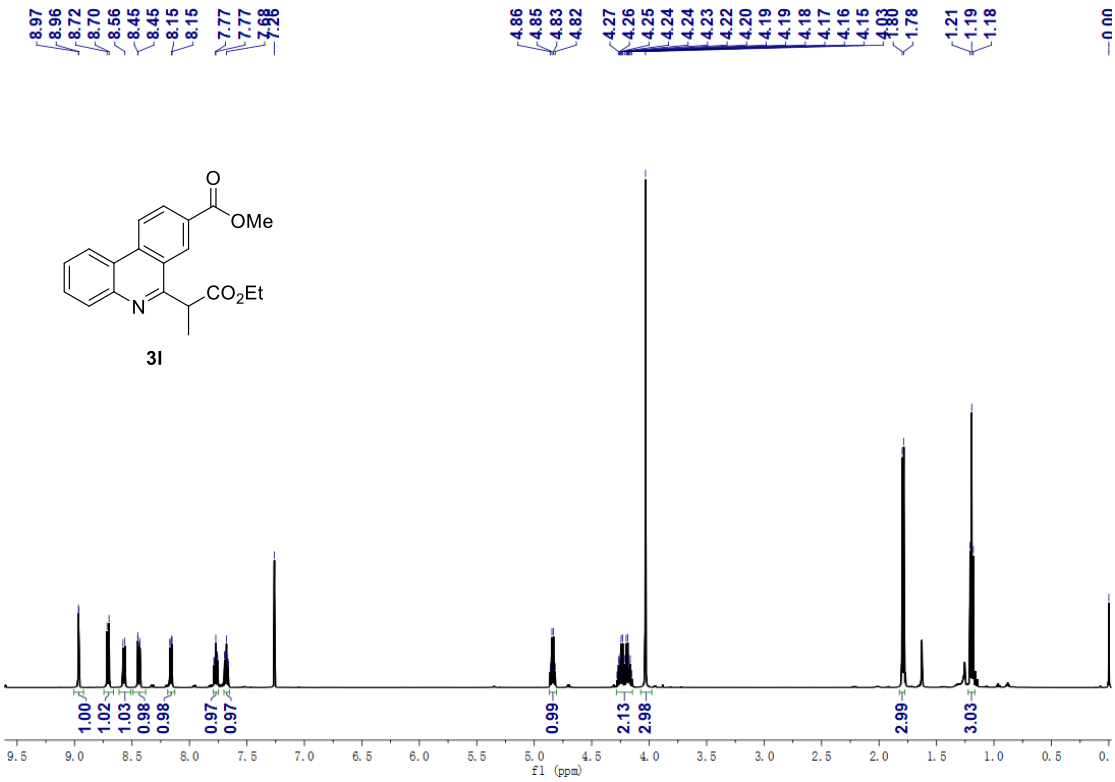


Figure S47. The ^{1}H-NMR spectral copy of compound **3l.**

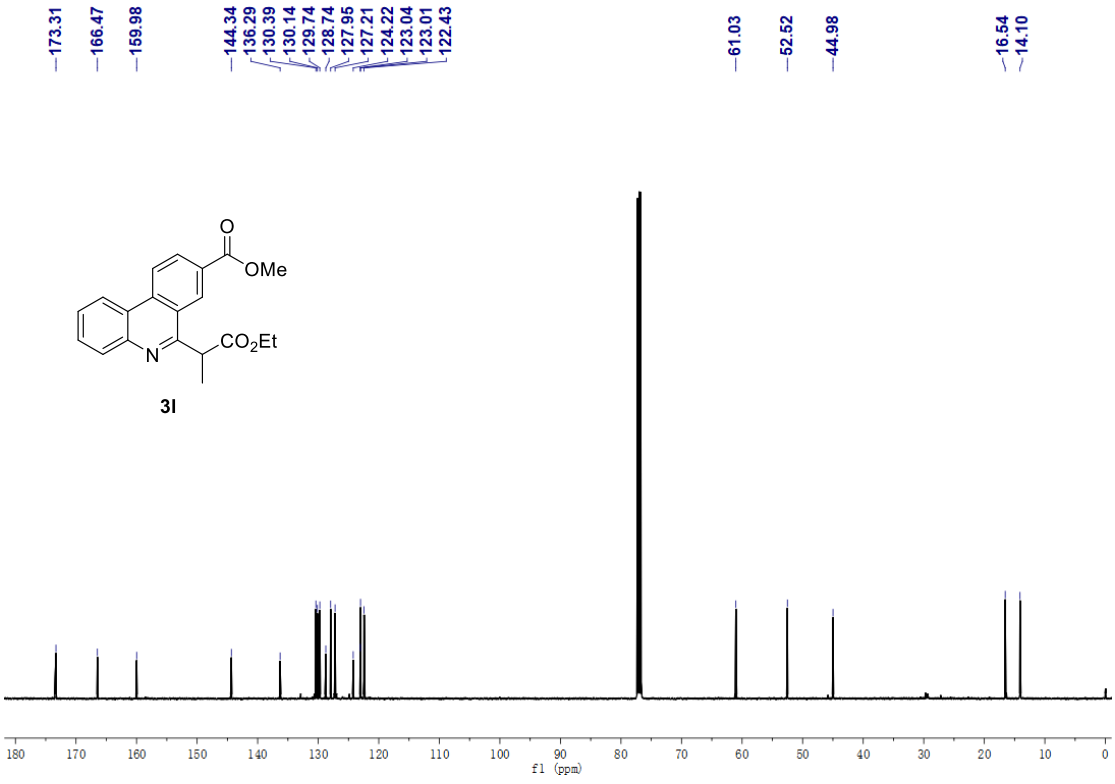


Figure S48. The ^{13}C-NMR spectral copy of compound **3l.**

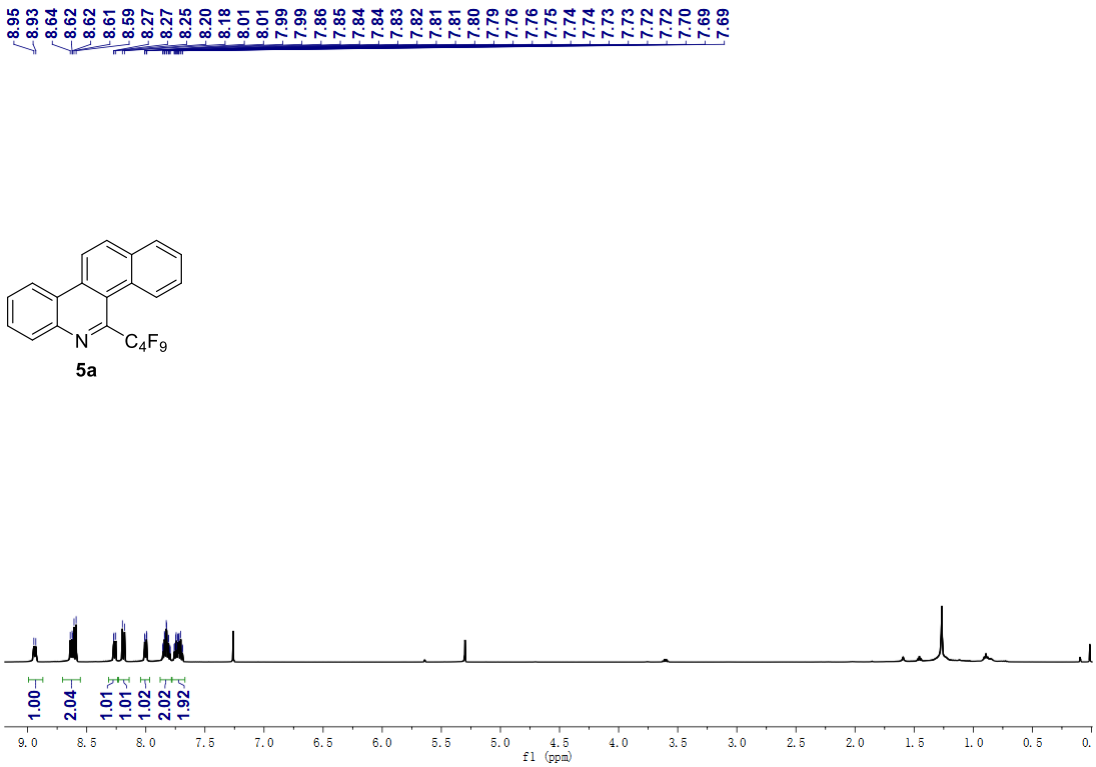


Figure S49. The ^{1}H-NMR spectral copy of compound **5a**.

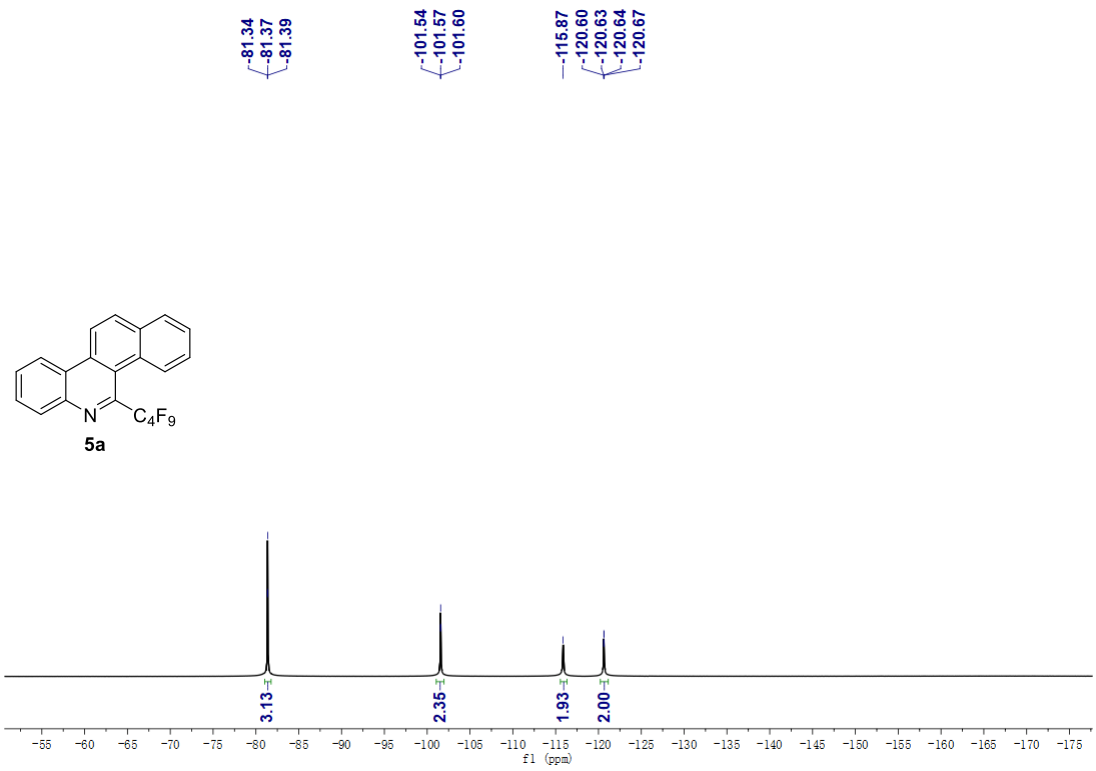


Figure S50. The ^{19}F-NMR spectral copy of compound **5a**.

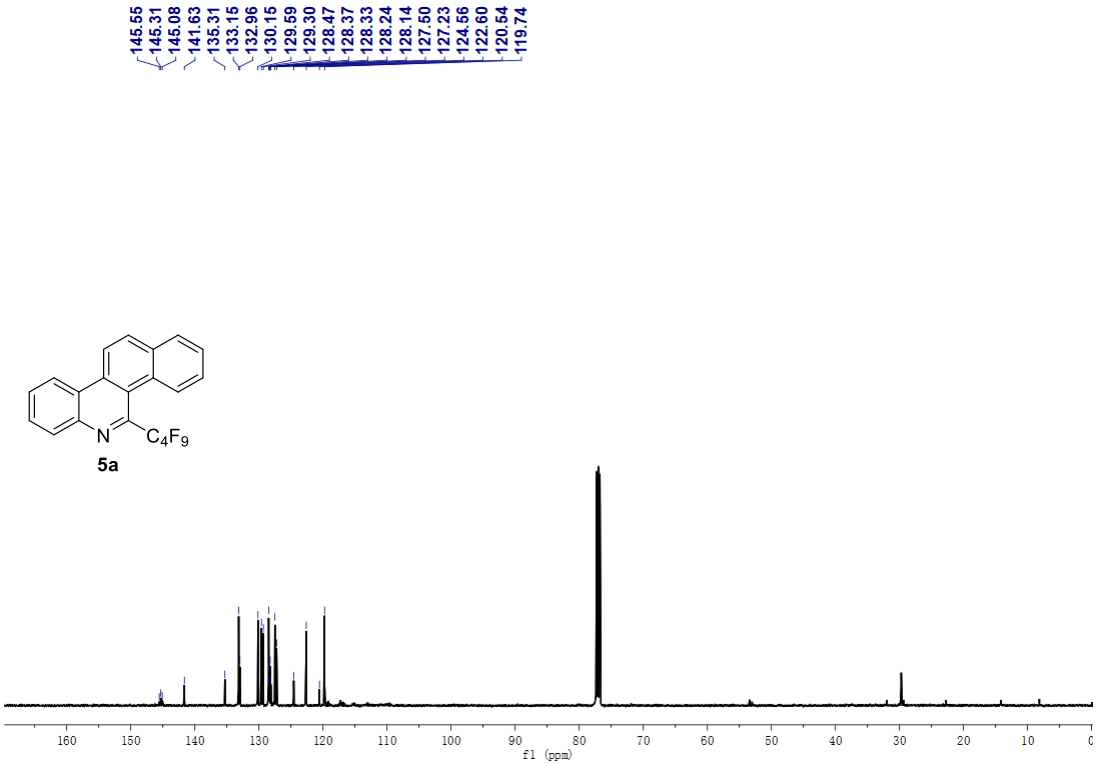


Figure S51. The ^{13}C-NMR spectral copy of compound **5a**

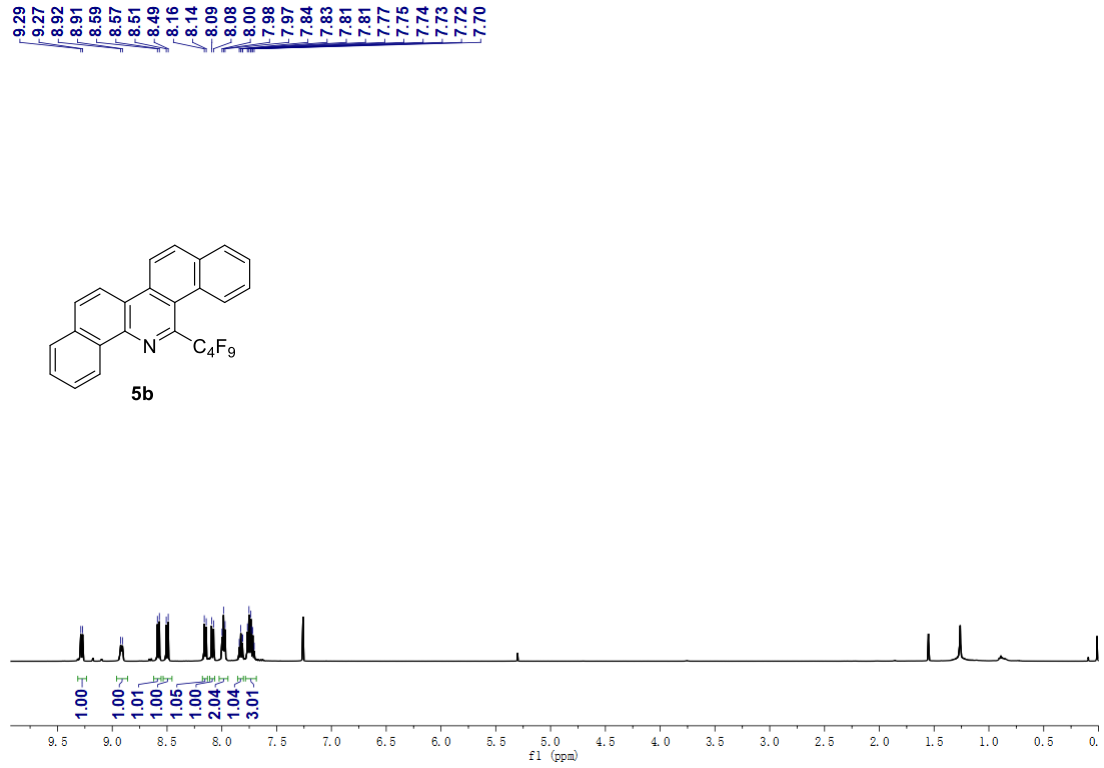


Figure S52. The ^{1}H-NMR spectral copy of compound **5b**.

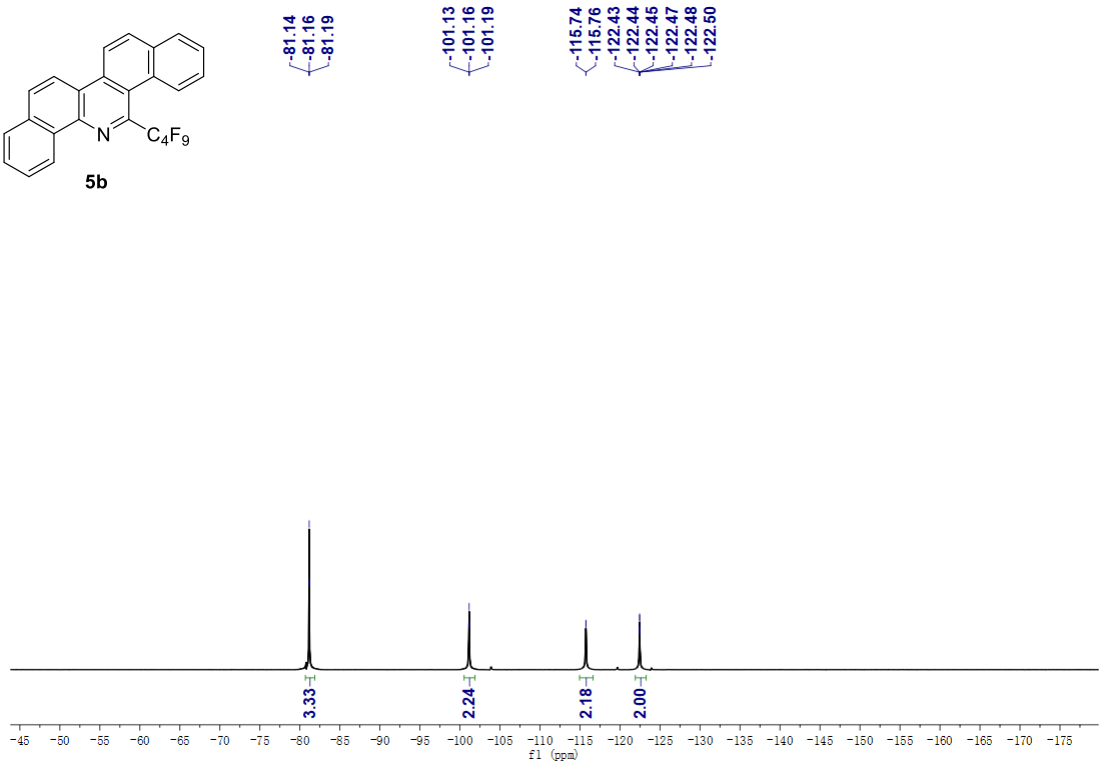


Figure S53. The ^{19}F-NMR spectral copy of compound **5b**.

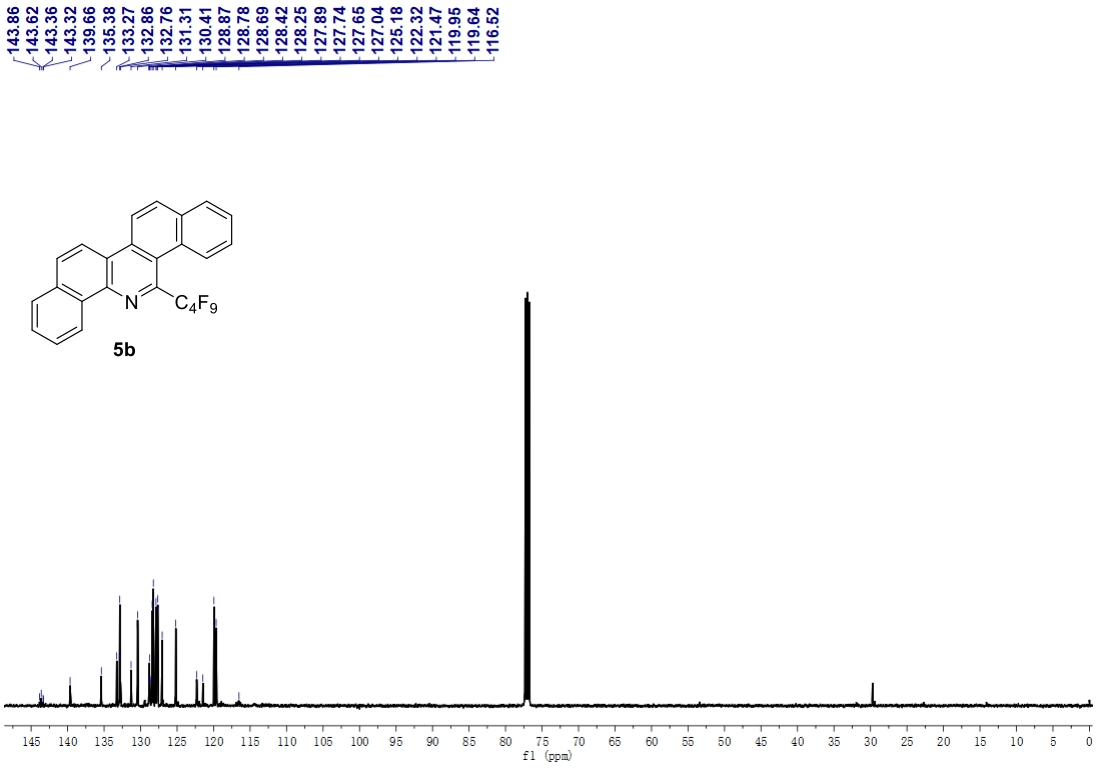


Figure S54. The ^{13}C-NMR spectral copy of compound **5b**.

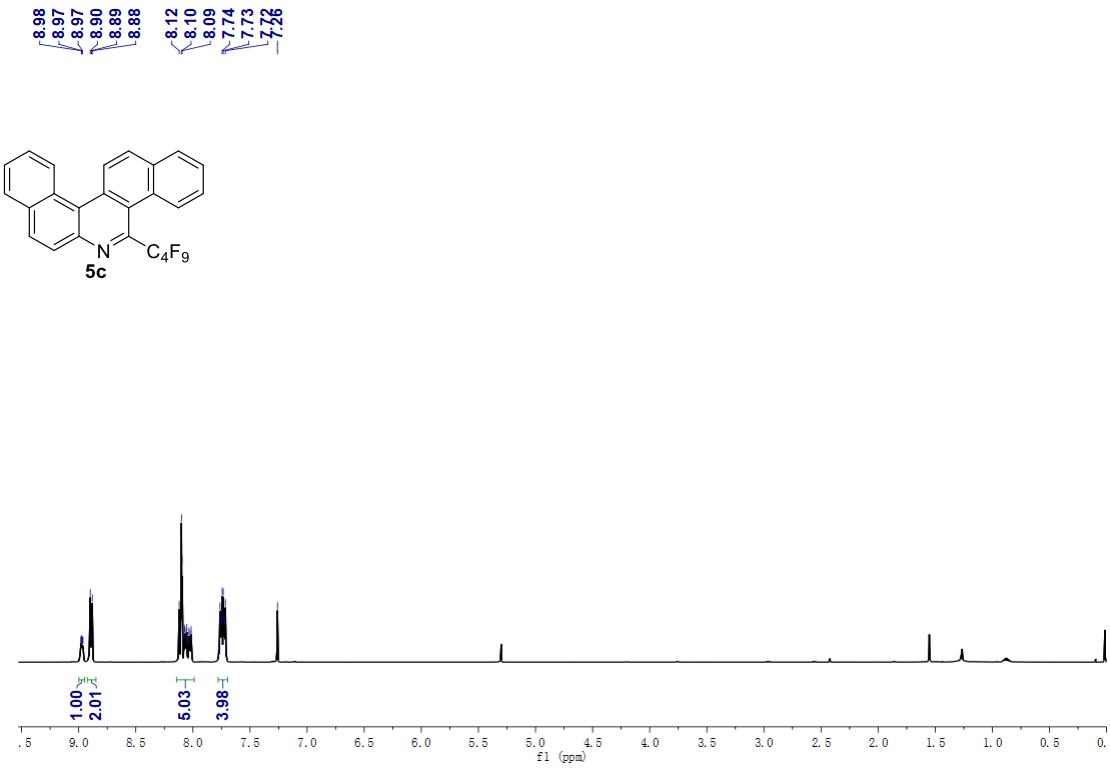


Figure S55. The ^{1}H-NMR spectral copy of compound **5c**.

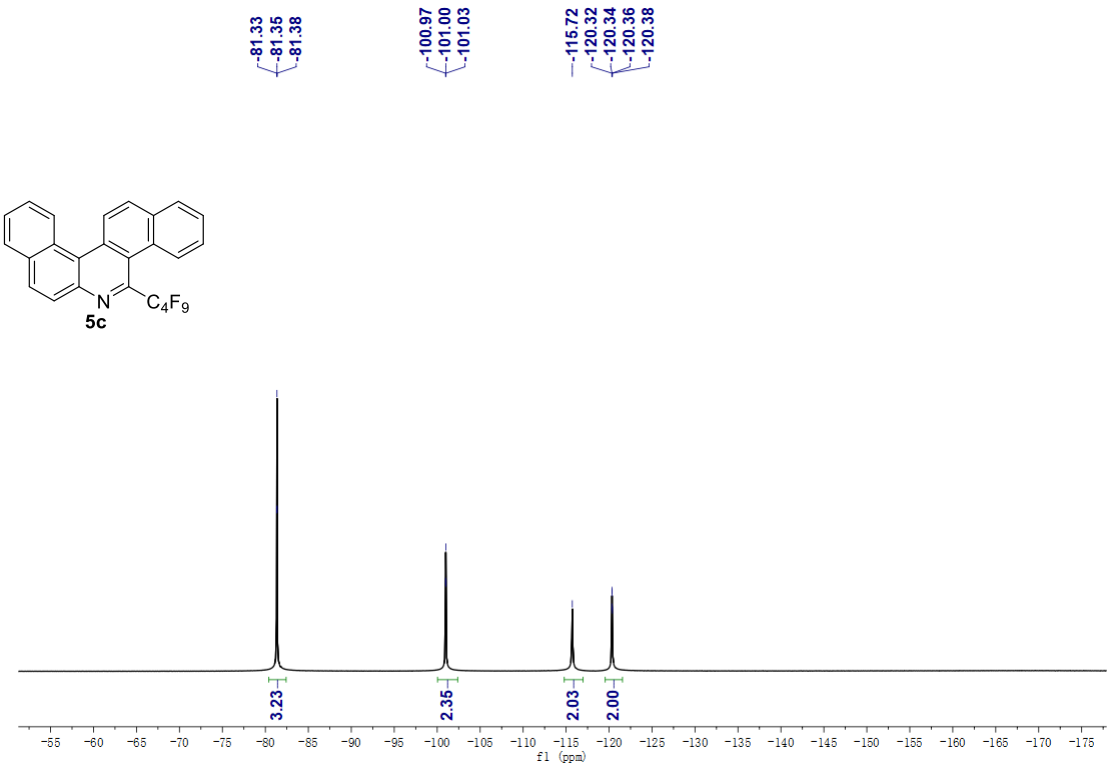


Figure S56. The ^{19}F-NMR spectral copy of compound **5c**.

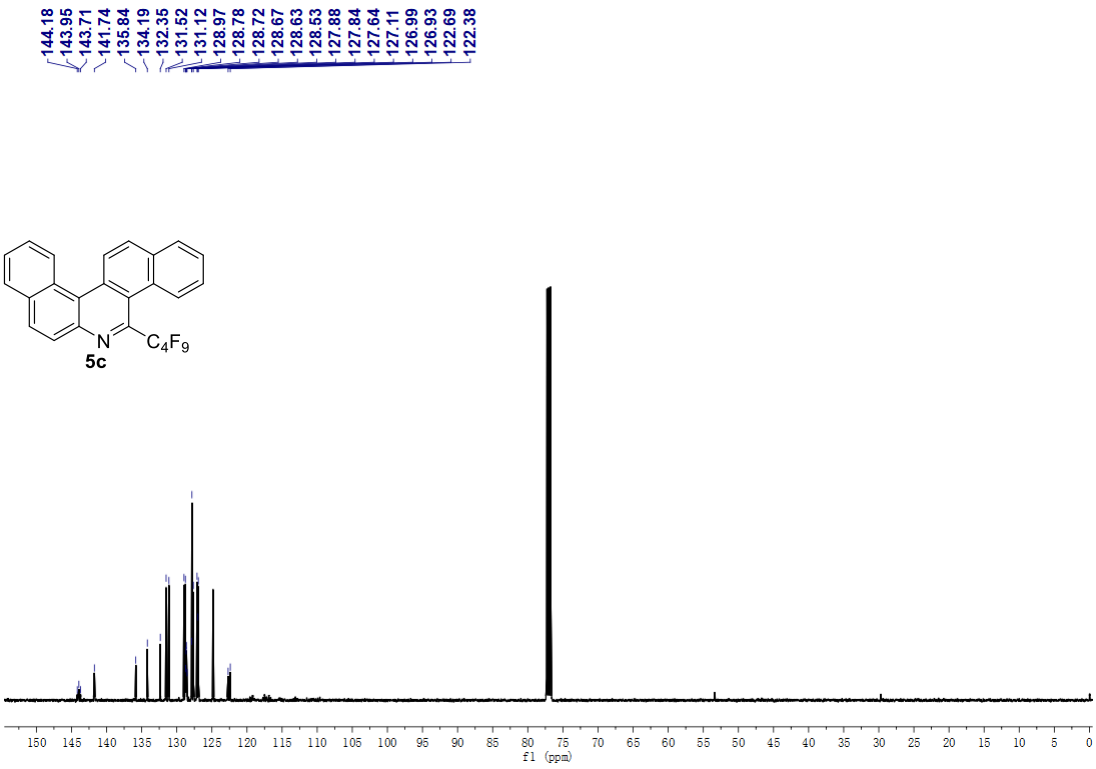


Figure S57. The ^{13}C-NMR spectral copy of compound **5c**.

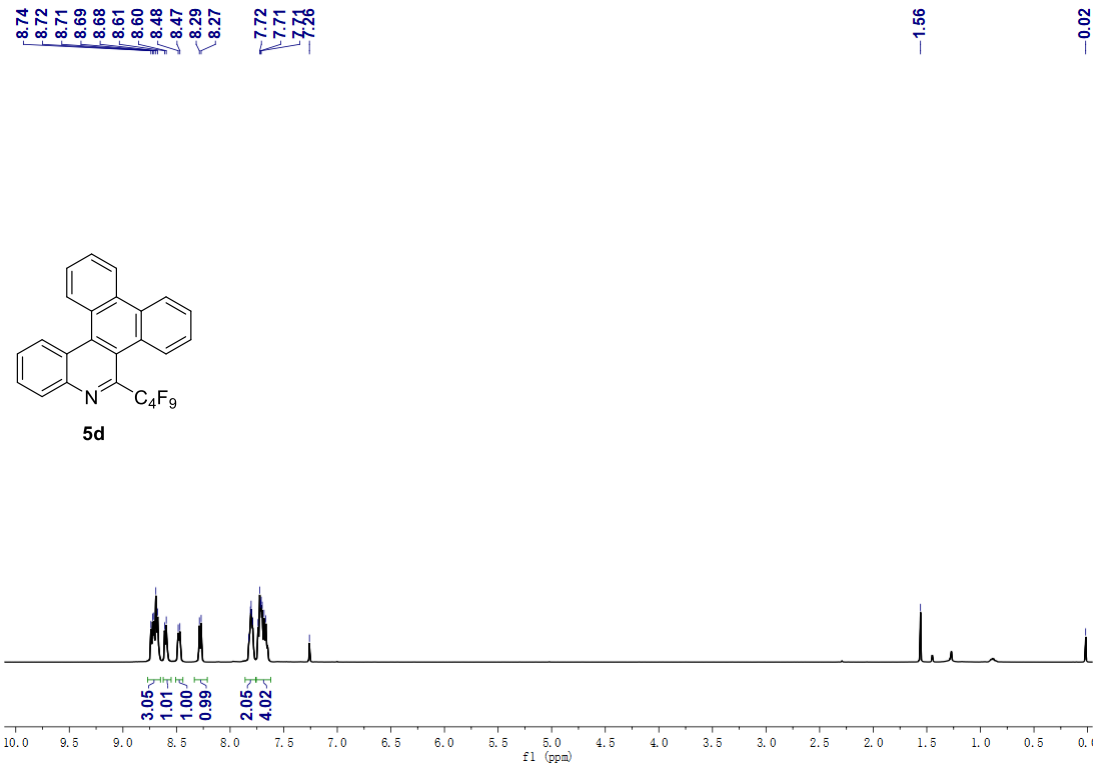


Figure S58. The ^{1}H-NMR spectral copy of compound **5d**.

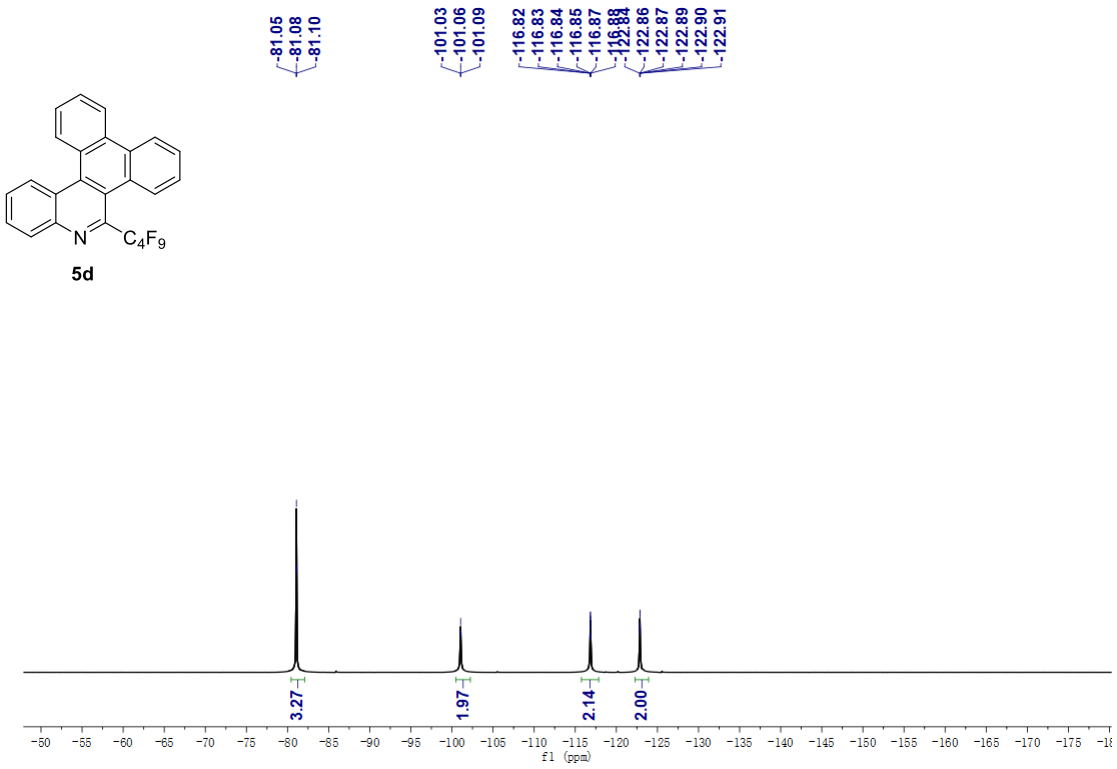


Figure S59. The ^{19}F-NMR spectral copy of compound **5d**.

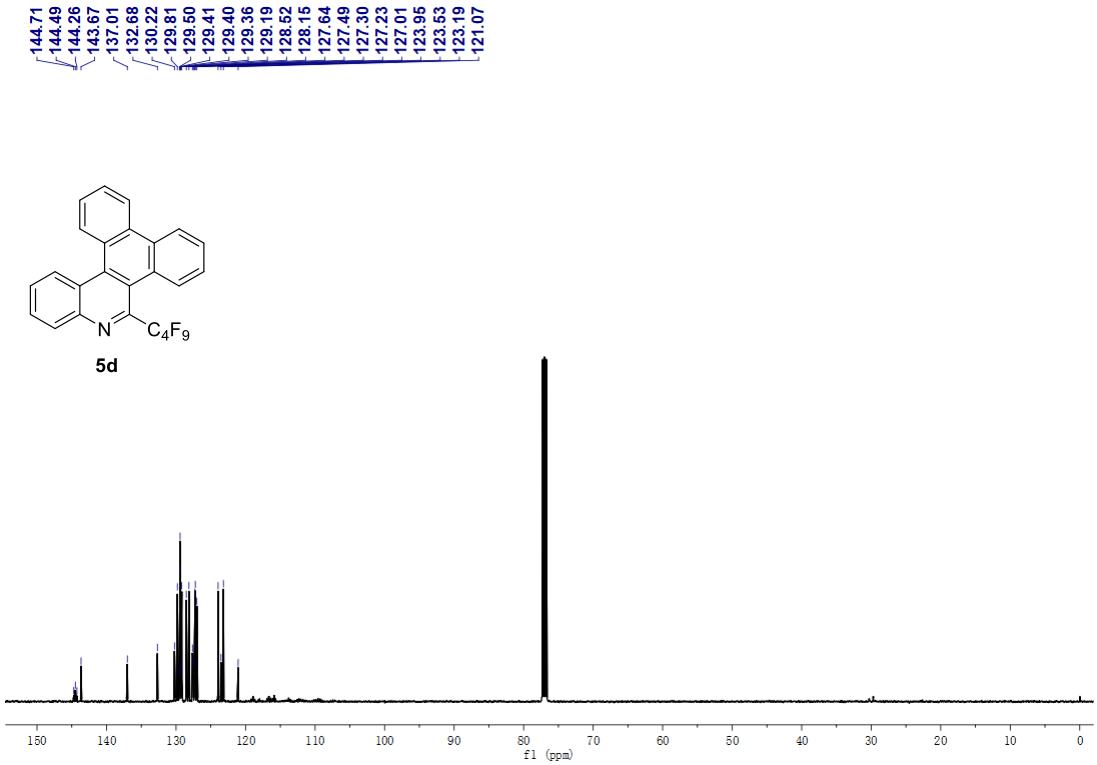


Figure S60. The ^{13}C-NMR spectral copy of compound **5d**.

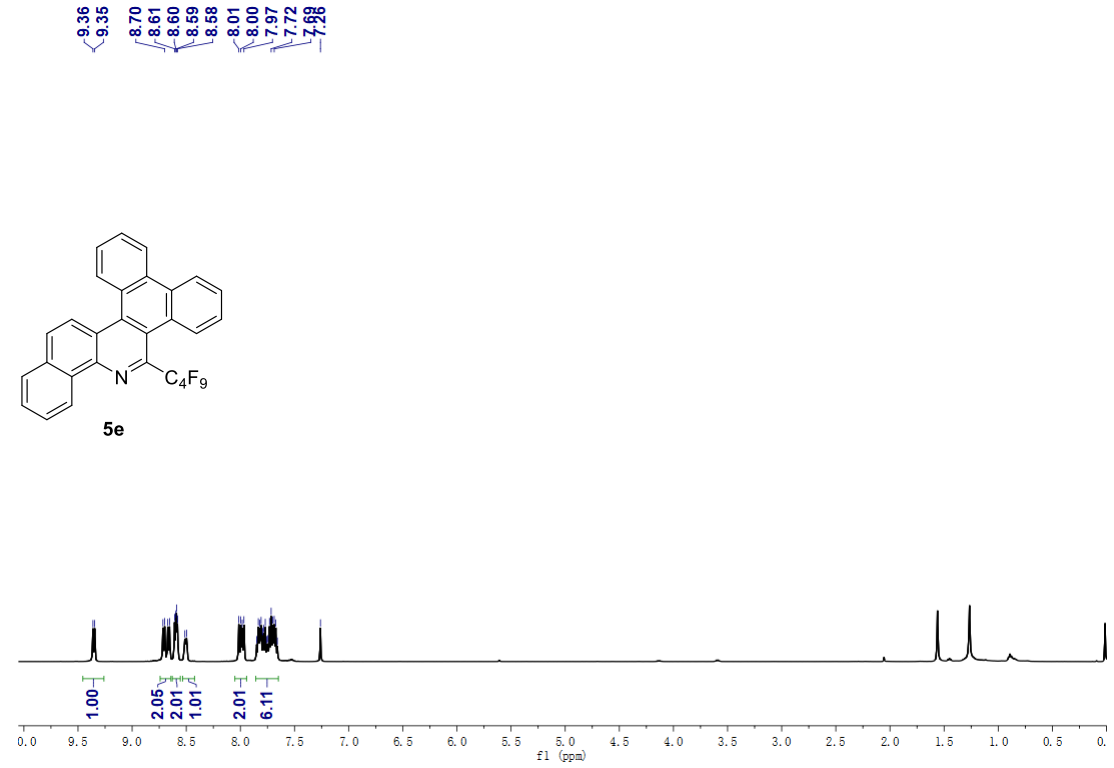


Figure S61. The ^{1}H-NMR spectral copy of compound **5e**.

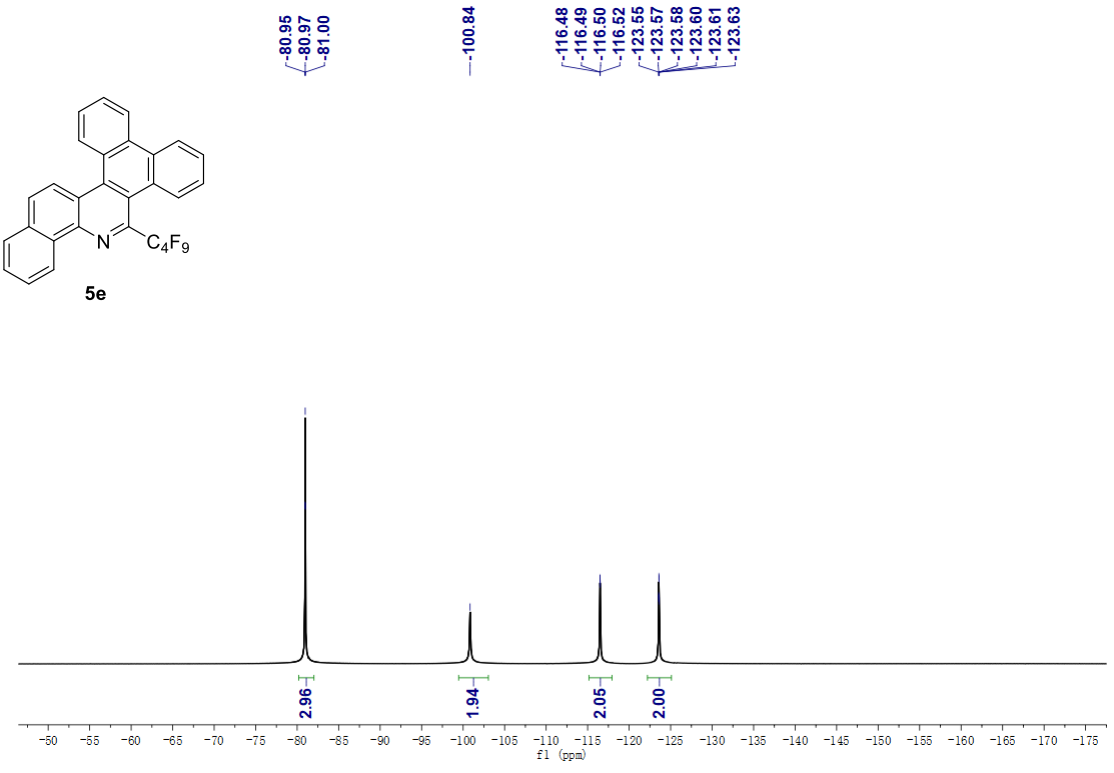


Figure S62. The ^{19}F-NMR spectral copy of compound **5e**.

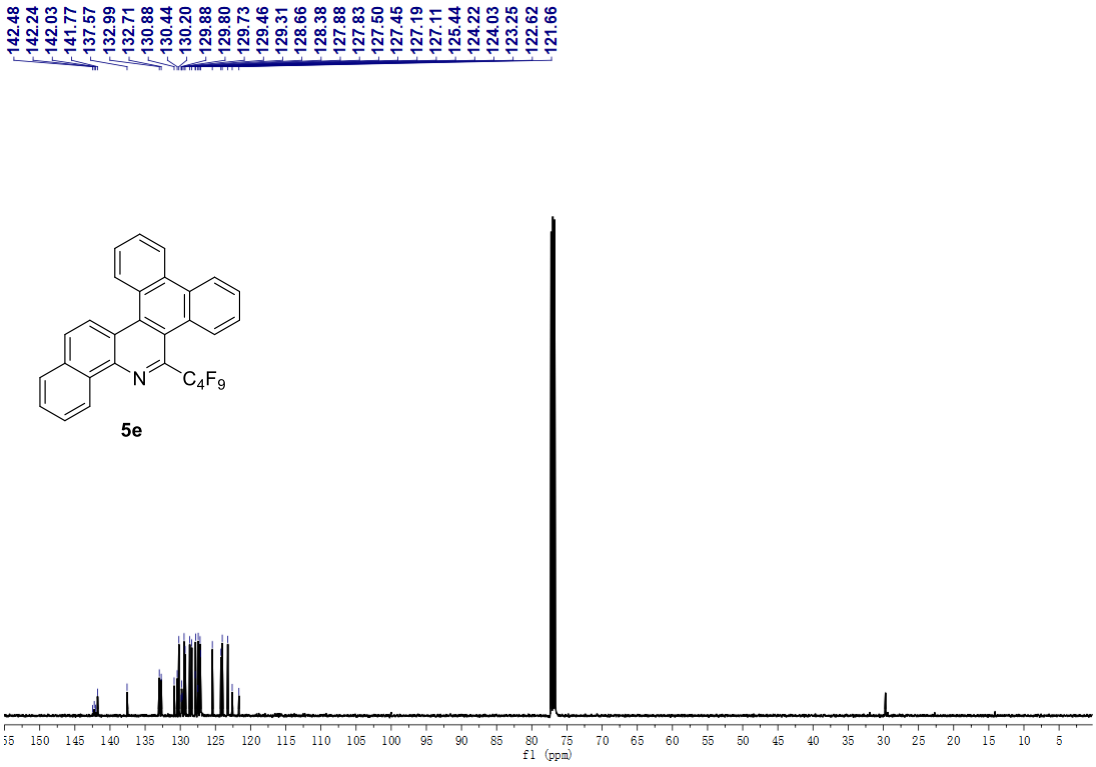


Figure S63. The ^{13}C-NMR spectral copy of compound **5e**.

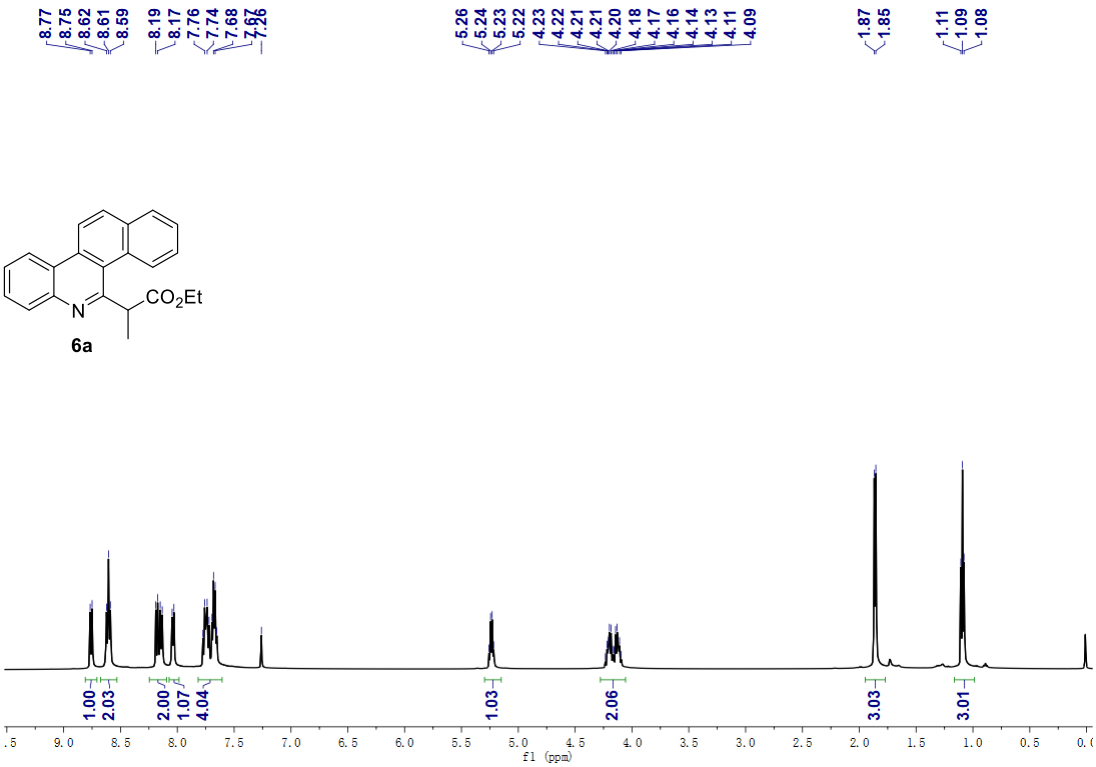


Figure S64. The ^{1}H-NMR spectral copy of compound **6a**.

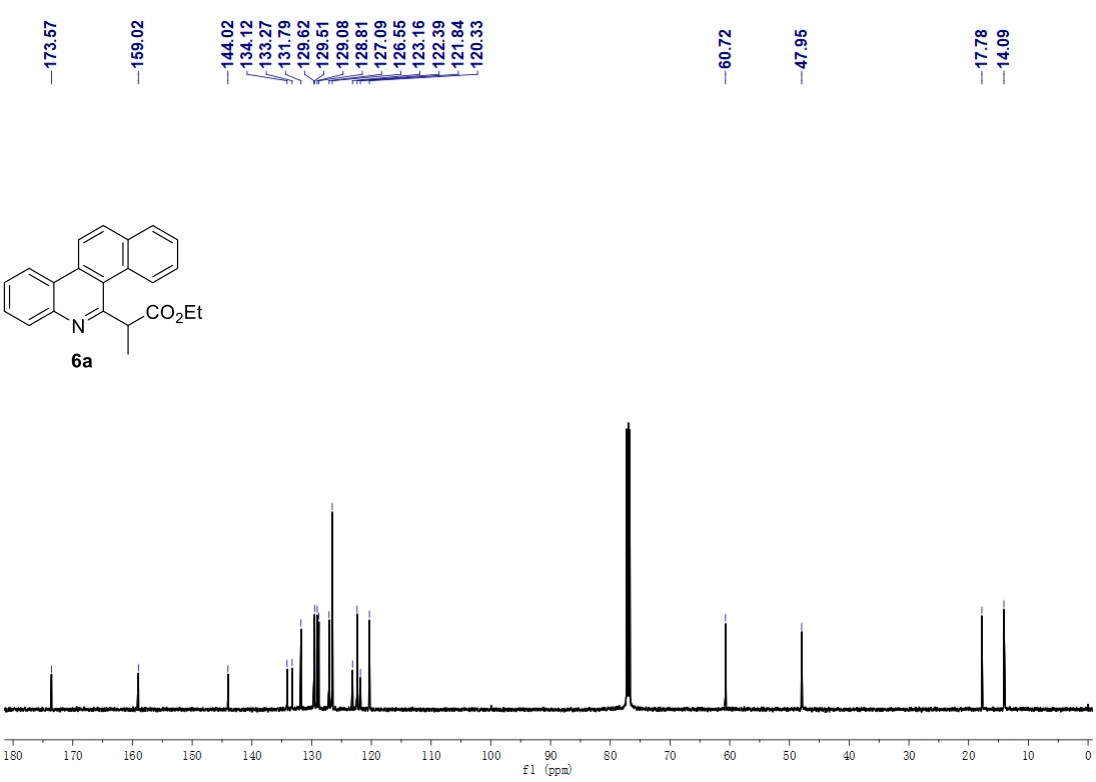


Figure S65. The ^{13}C-NMR spectral copy of compound **6a**.

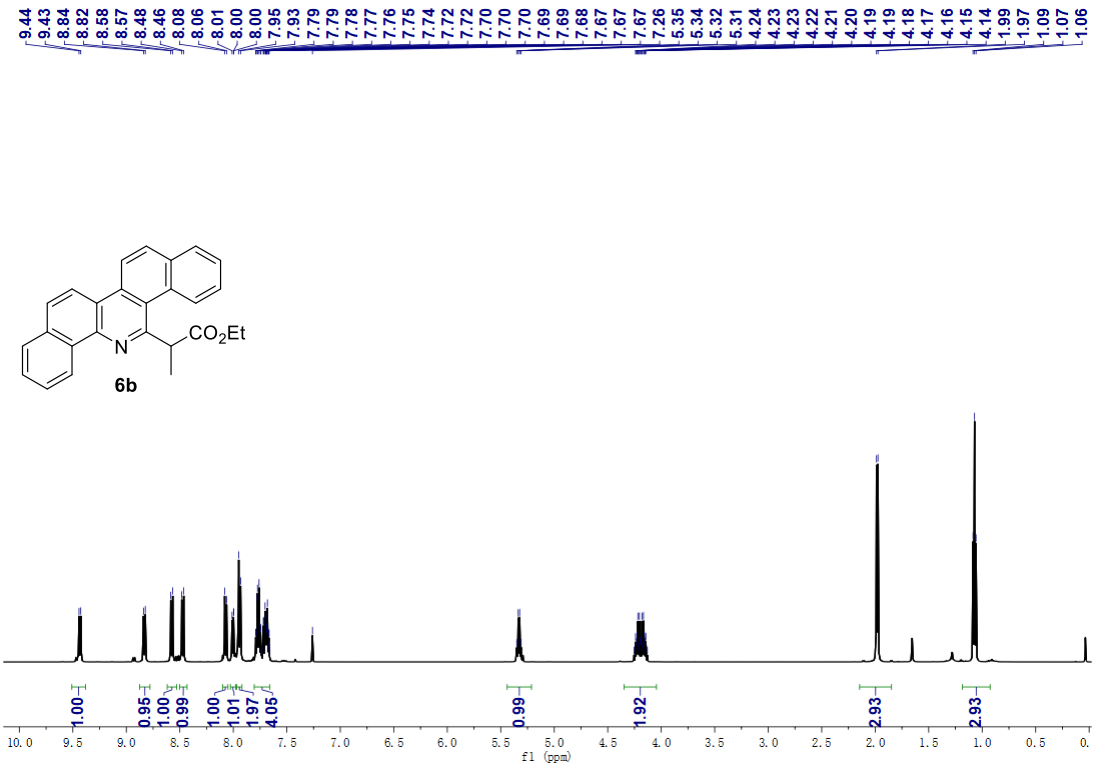


Figure S66. The ^{1}H-NMR spectral copy of compound **6b**.

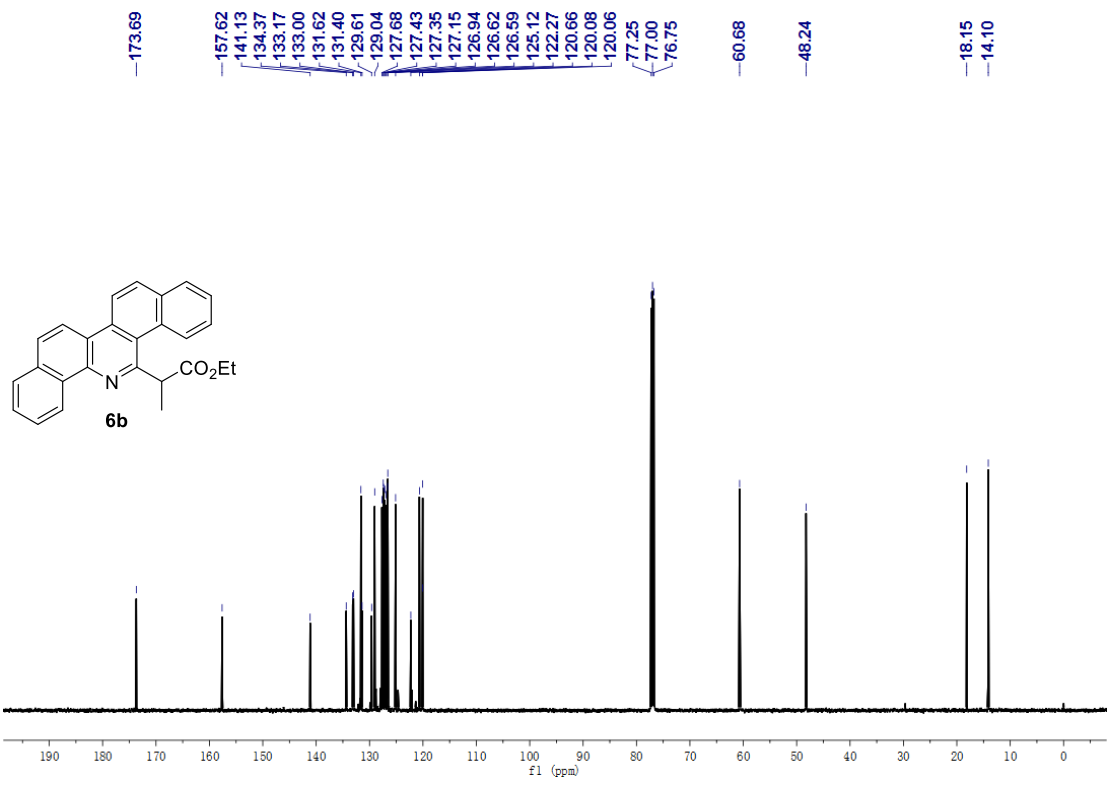


Figure S67. The ^{13}C-NMR spectral copy of compound **6b**.

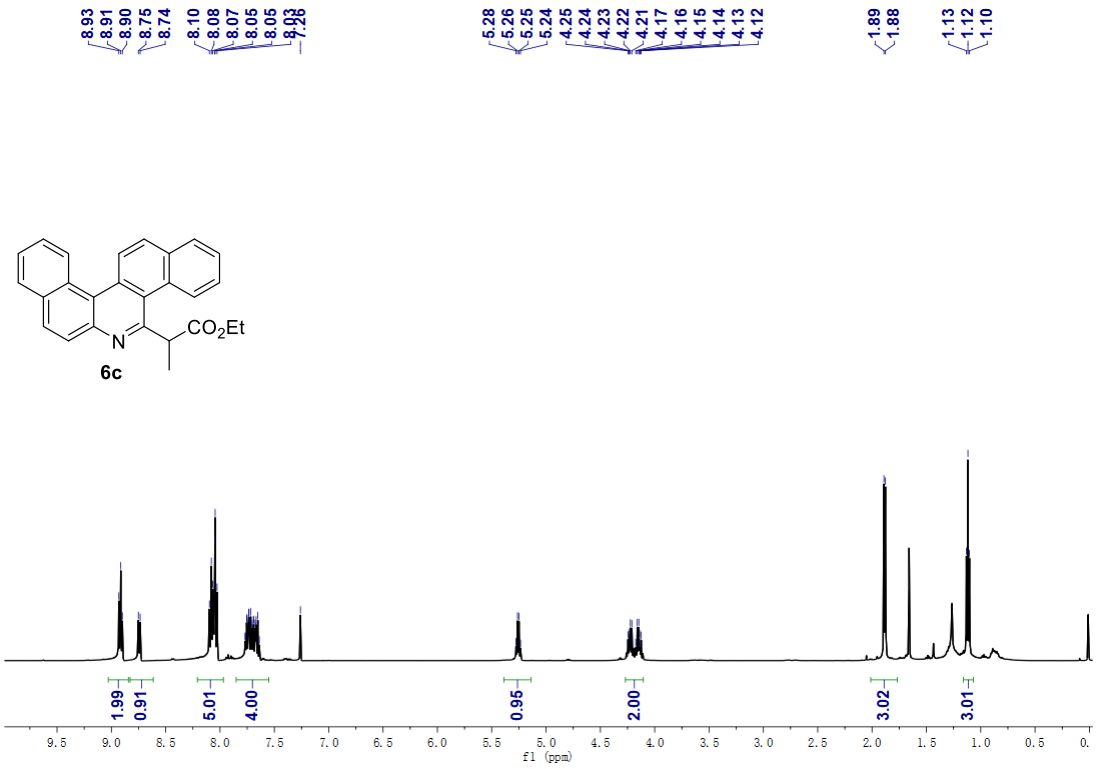


Figure S68. The ^{1}H-NMR spectral copy of compound **6c**.

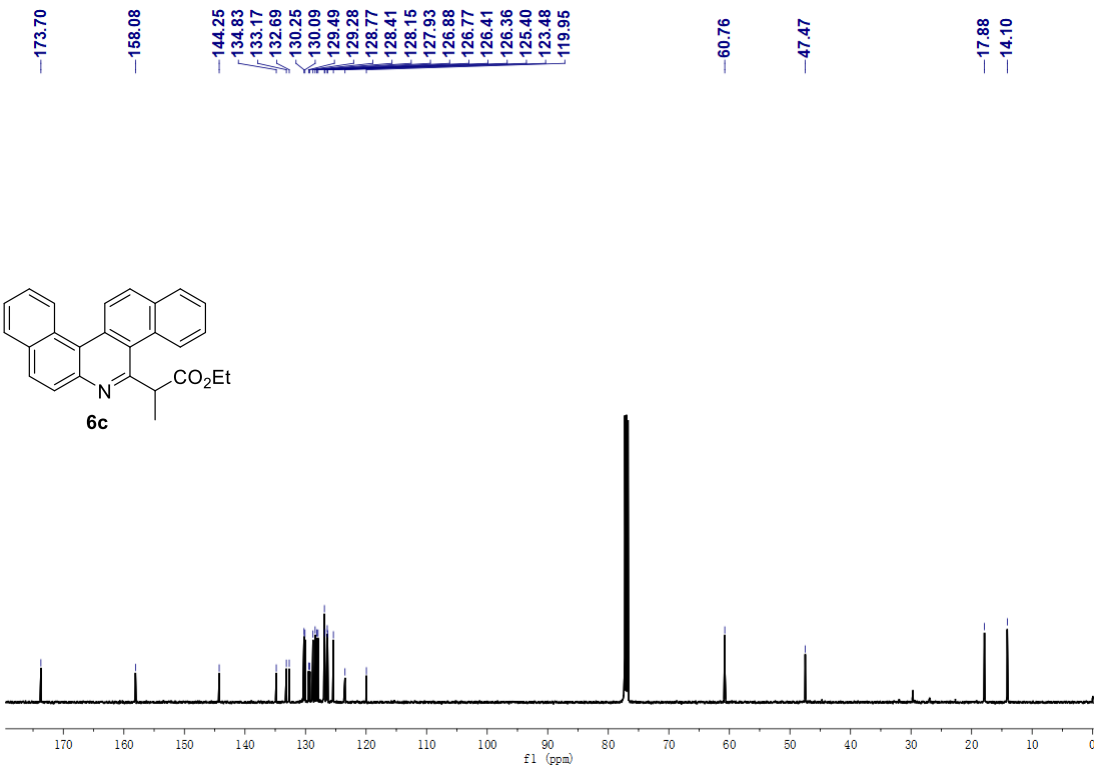


Figure S69. The ^{13}C-NMR spectral copy of compound **6c**

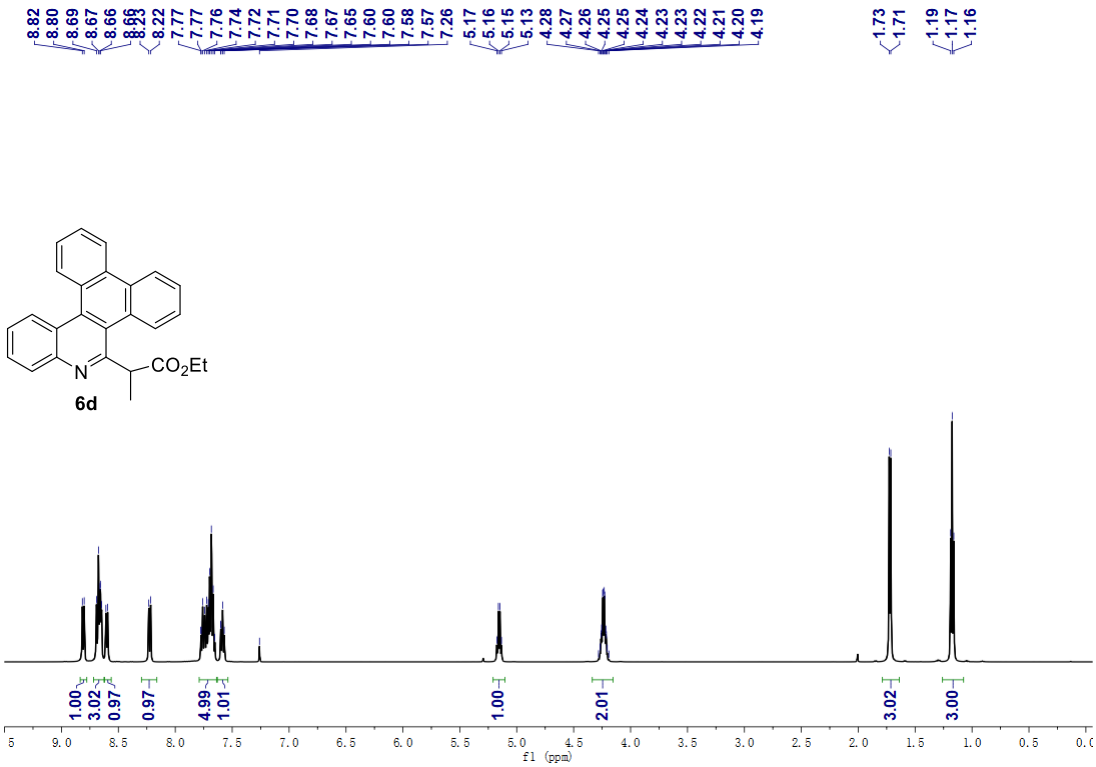


Figure S70. The ^{1}H-NMR spectral copy of compound **6d**.

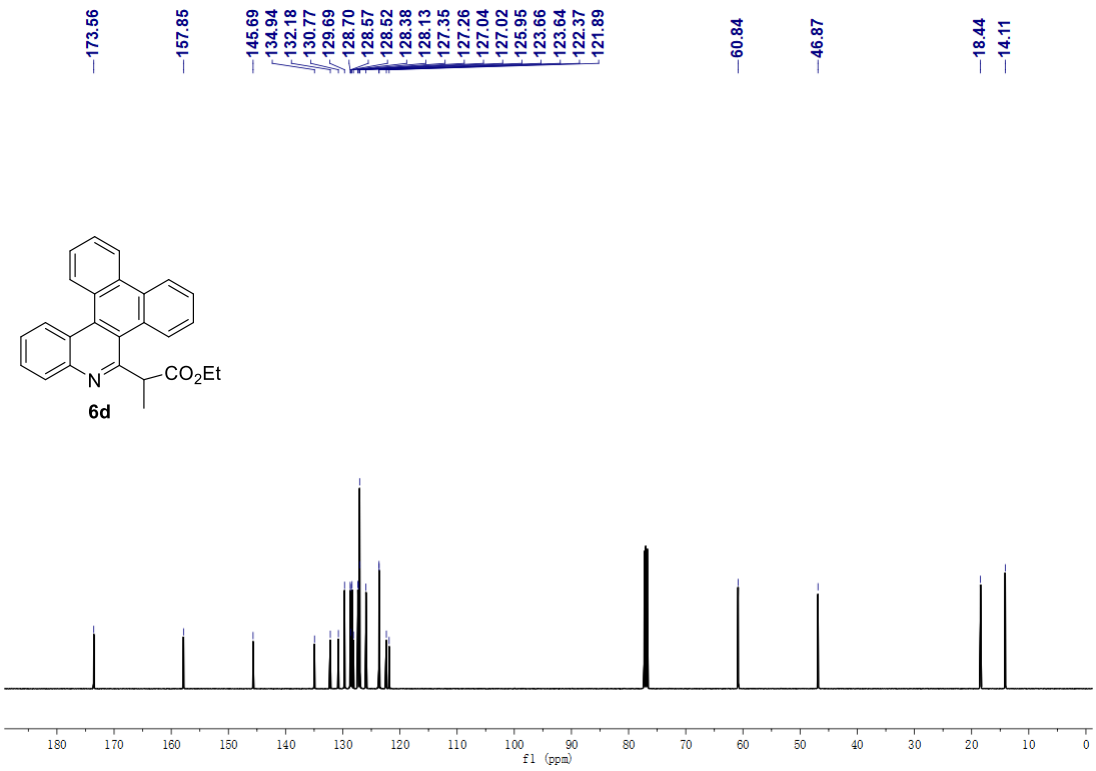


Figure S71. The ^{13}C-NMR spectral copy of compound **6d**.

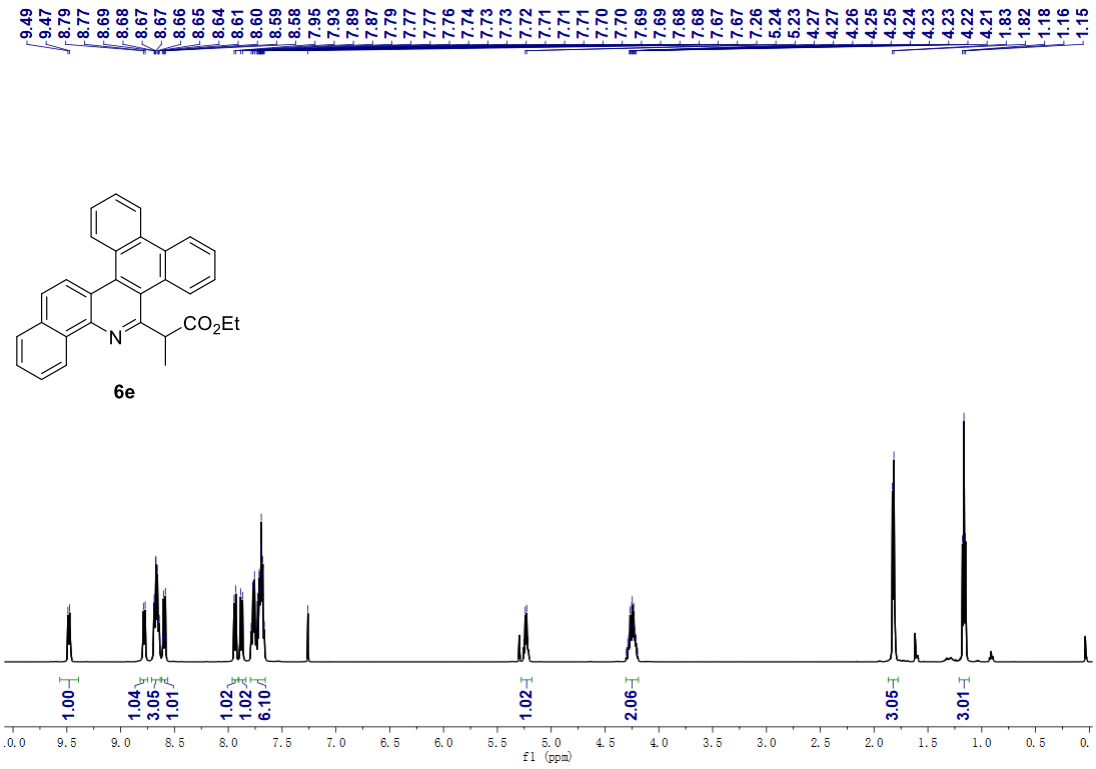


Figure S72. The ^{1}H-NMR spectral copy of compound **6e**.

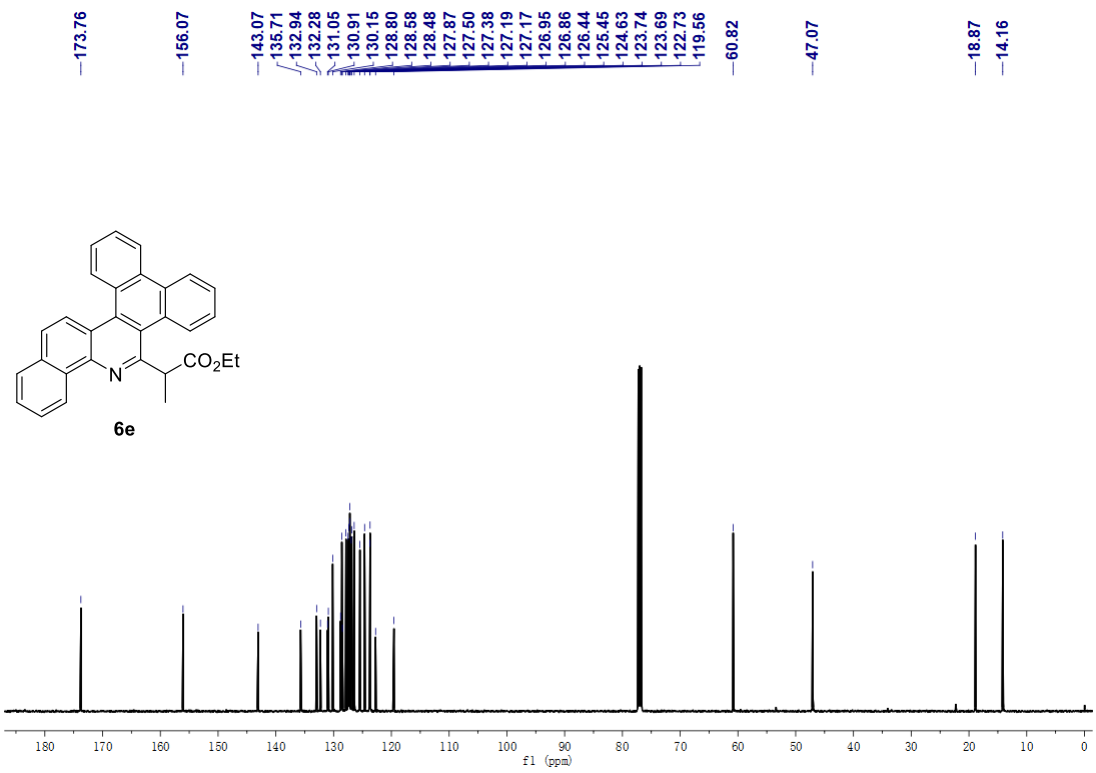


Figure S73. The ^{13}C-NMR spectral copy of compound **6e**.

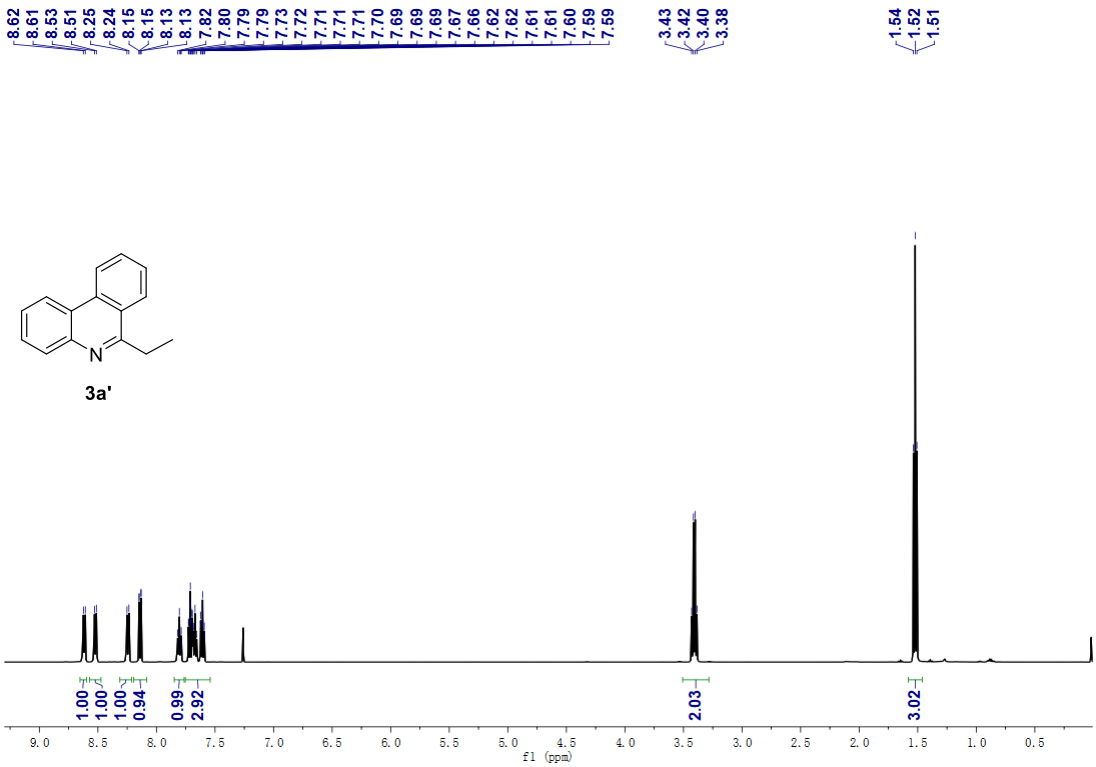


Figure S74. The ^{1}H-NMR spectral copy of compound **3a'**.

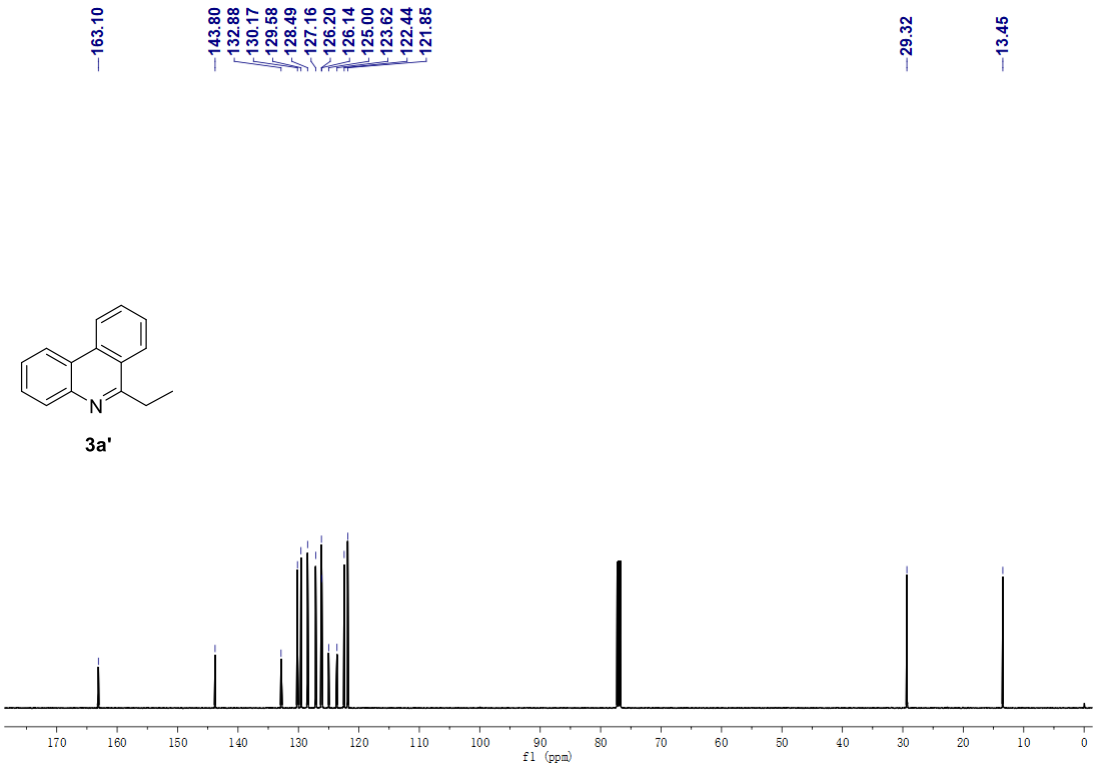


Figure S75. The ^{13}C-NMR spectral copy of compound **3a'**.

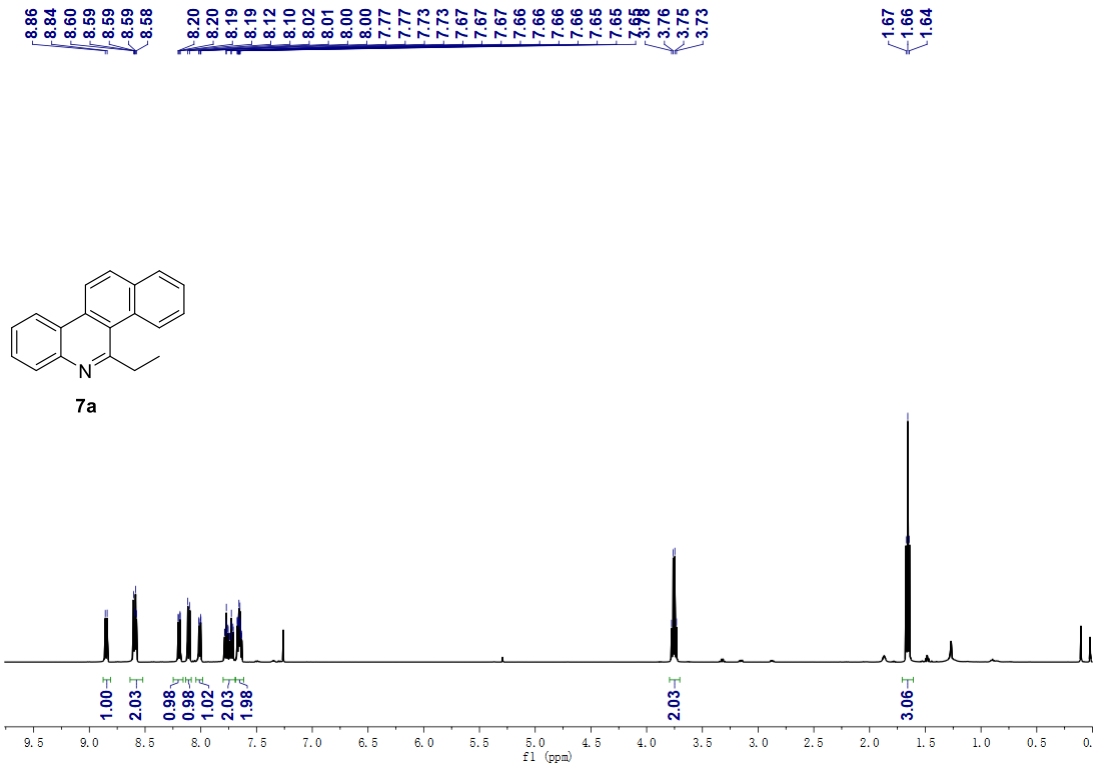


Figure S76. The ^{1}H-NMR spectral copy of compound **7a**.

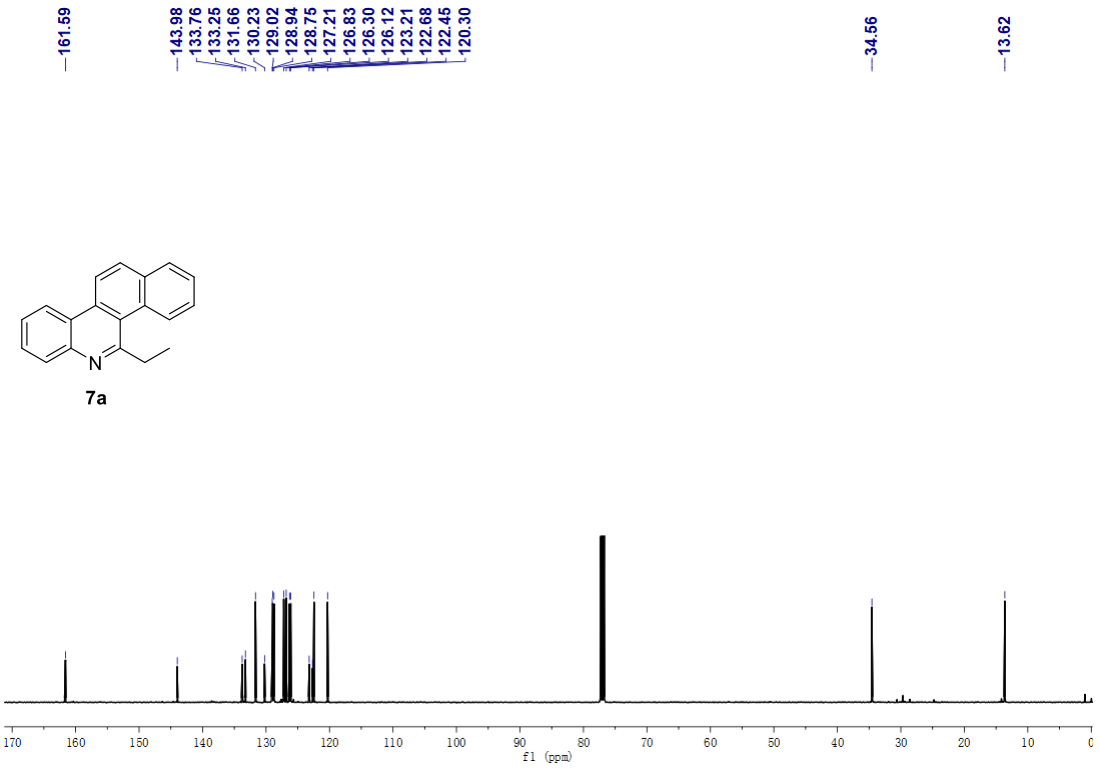


Figure S77. The ^{13}C-NMR spectral copy of compound **7a**.

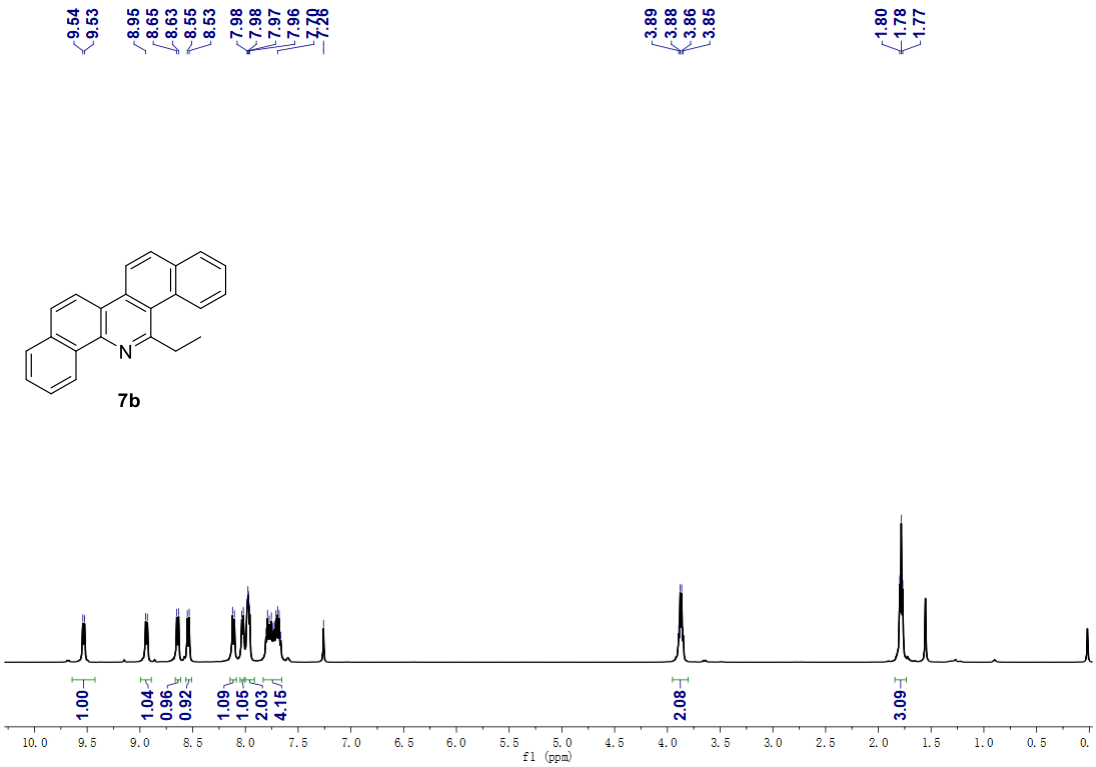


Figure S78. The ^{1}H-NMR spectral copy of compound **7b**.

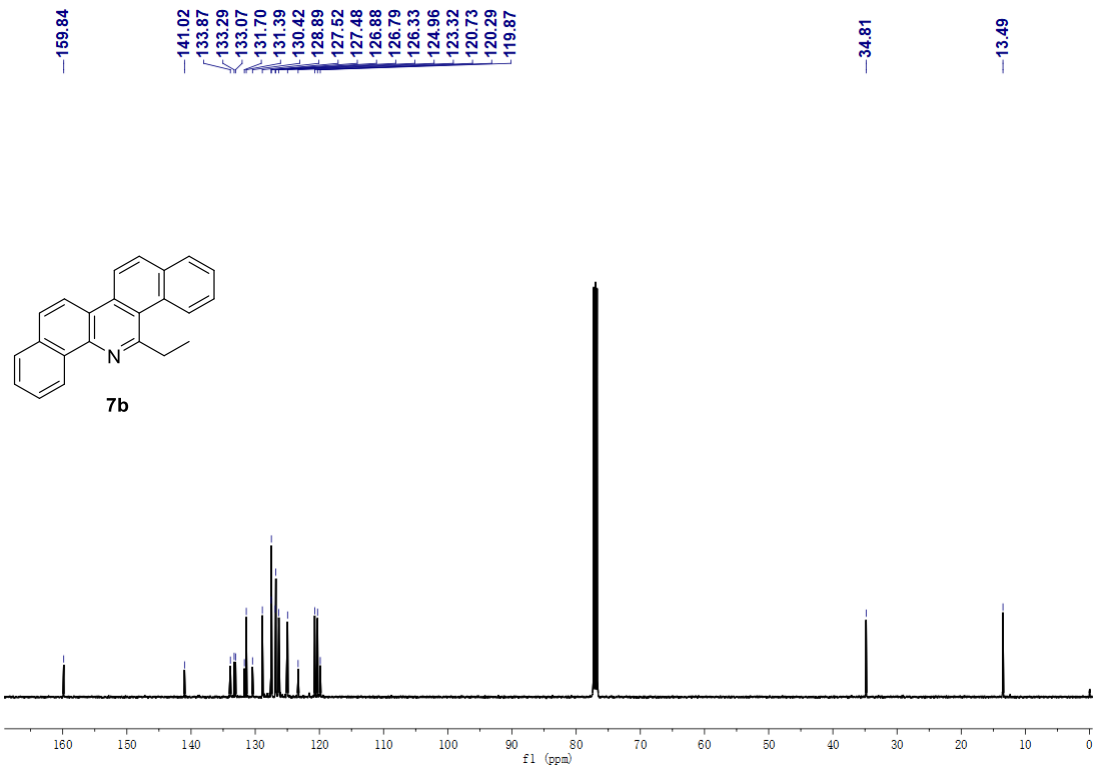


Figure S79. The ^{13}C-NMR spectral copy of compound **7b**.

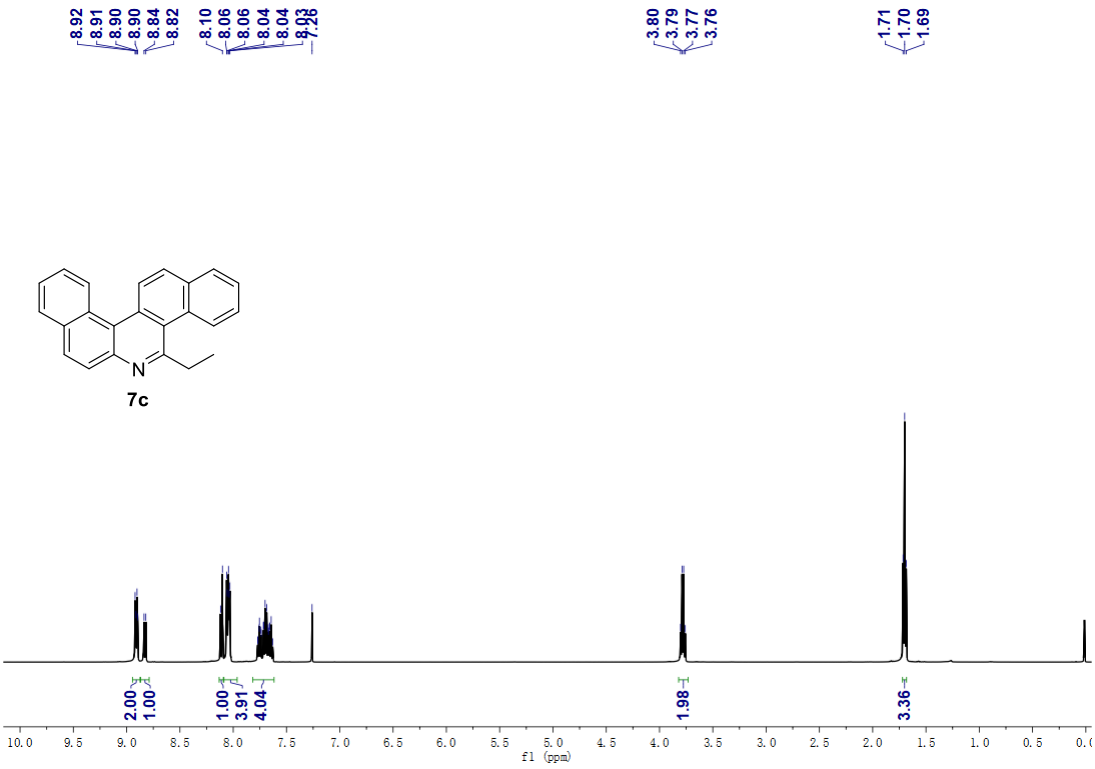


Figure S80. The ^{1}H-NMR spectral copy of compound **7c**.

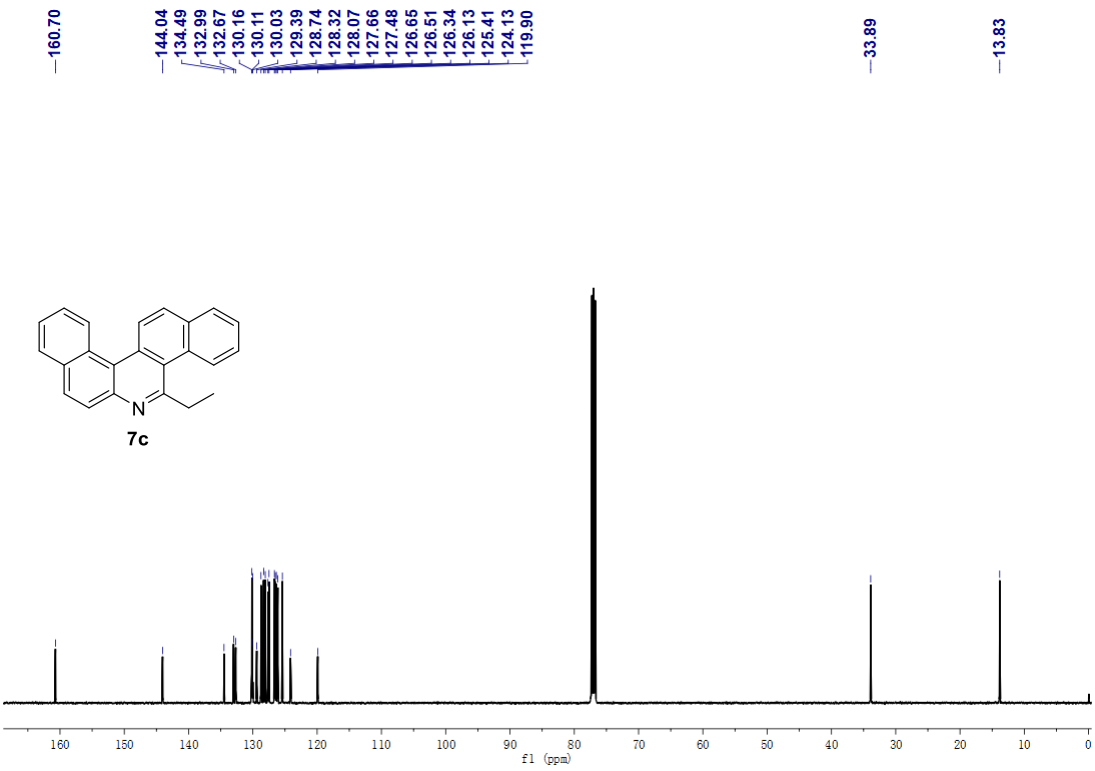


Figure S81. The ^{13}C-NMR spectral copy of compound **7c**.

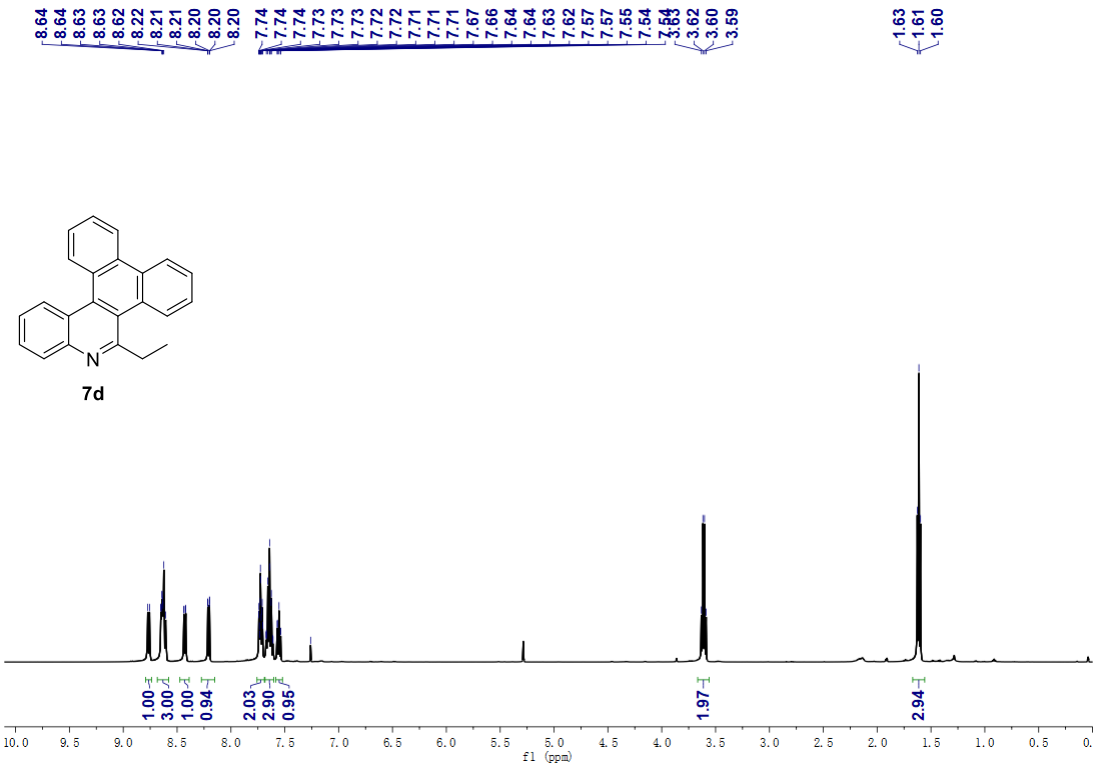


Figure S82. The ^{1}H-NMR spectral copy of compound **7d**.

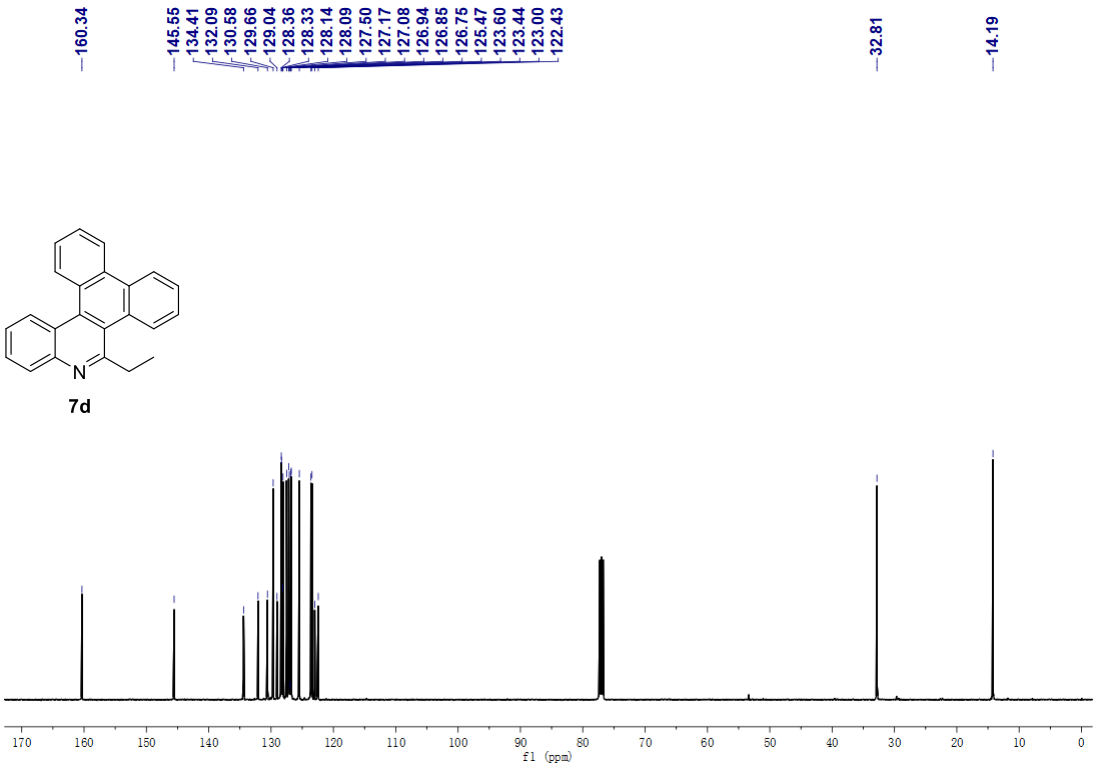


Figure S83. The ^{13}C-NMR spectral copy of compound **7d**.

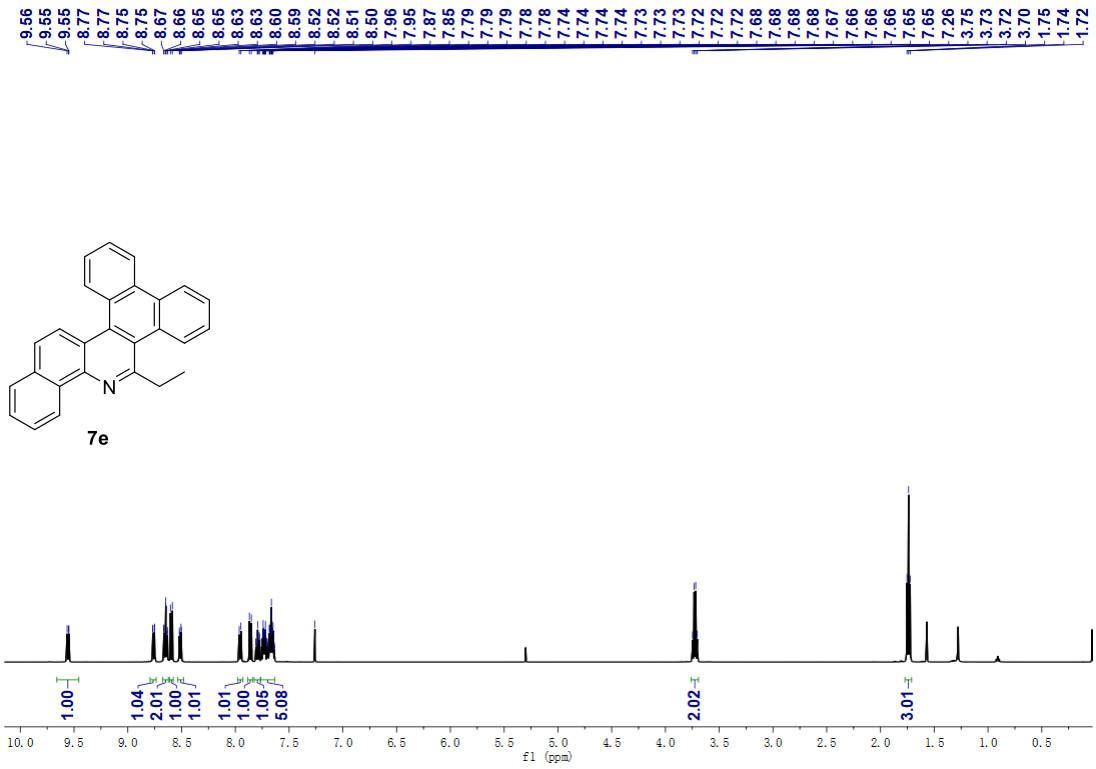


Figure S84. The ^{1}H-NMR spectral copy of compound **7e**.

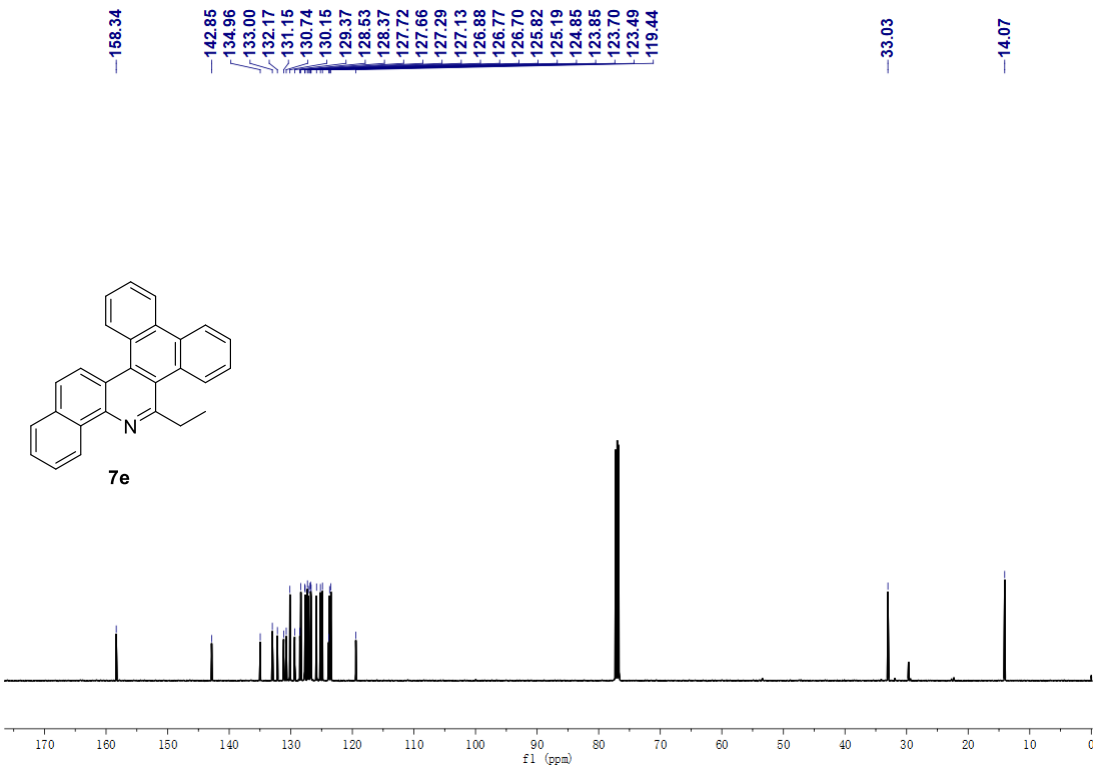


Figure S85. The ^{13}C-NMR spectral copy of compound **7e**.

5. Crystal data and structure refinement parameters

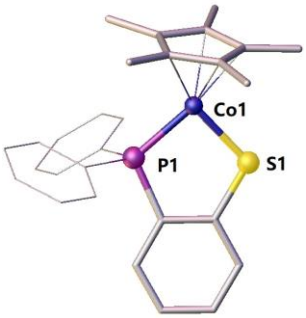


Figure S86. X-ray structure of **1** showing 50% probability ellipsoids.

Table S2. Crystal data and structure refinement for **1**.

Identification code	1
Empirical formula	$C_{28}H_{29}CoPS$
Formula weight	487.47
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.0319(4)
b/Å	18.9034(9)
c/Å	14.4632(7)
α/°	90
β/°	96.640(2)
γ/°	90
Volume/Å^3	2452.8(2)
Z	4
ρ_{calc}g/cm^3	1.320
μ/mm^{-1}	0.863
F(000)	1020.0
Crystal size/mm^3	0.22 x 0.24 x 0.3mm^3
Radiation	MoKα (λ = 0.710)
2Θ range for data collection/°	3.558 to 49.994
Index ranges	$-10 \leq h \leq 10$, $-22 \leq k \leq 19$, $-10 \leq l \leq 17$
Reflections collected	16180
Independent reflections	4327 [R_{int} = 0.0218, R_{sigma} = 0.0237]
Data/restraints/parameters	4327/0/285
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0285, wR_2 = 0.0704
Final R indexes [all data]	R_1 = 0.0352, wR_2 = 0.0740
Largest diff. peak/hole / e Å^{-3}	0.64/-0.30

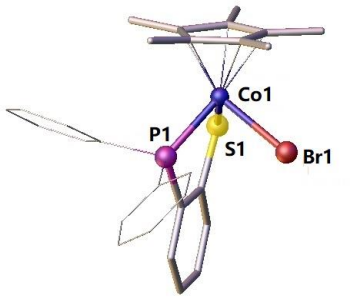


Figure S87. X-ray structure of **1-Br** showing 50% probability ellipsoids.

Table S3. Crystal data and structure refinement for **1-Br**.

Identification code	1-Br
Empirical formula	$C_{28}H_{29}BrCoPS$
Formula weight	567.38
Temperature/K	172.99(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	16.6717(15)
b/Å	10.051(2)
c/Å	14.516(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2432.4(11)
Z	4
ρ_{calc}g/cm^3	1.549
μ/mm^{-1}	2.515
F(000)	1160.0
Crystal size/mm^3	0.31 x 0.28 x 0.42mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.944 to 50.67
Index ranges	$-18 \leq h \leq 20$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections collected	10560
Independent reflections	3956 [R_{int} = 0.0649, R_{sigma} = 0.0790]
Data/restraints/parameters	3956/1/295
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0480, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0588, wR_2 = 0.1016
Largest diff. peak/hole / e Å^{-3}	0.54/-0.45
Flack parameter	0.024(19)

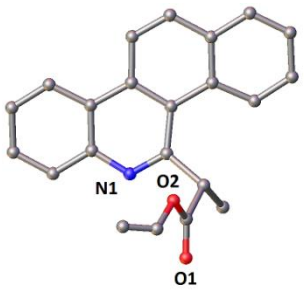


Figure S88. X-ray structure of **6a** showing 50% probability ellipsoids.

Table S4. Crystal data and structure refinement for **6a**.

Identification code	6a
Empirical formula	$C_{22}H_{18}NO_2$
Formula weight	328.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7660(3)
b/Å	7.3952(2)
c/Å	18.2702(4)
α/°	90
β/°	103.067(2)
γ/°	90
Volume/Å^3	1680.16(7)
Z	4
ρ_{calc}g/cm^3	1.298
μ/mm^{-1}	0.660
F(000)	692.0
Crystal size/mm^3	0.3 x 0.24 x 0.3mm^3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.698 to 134.134
Index ranges	$-15 \le h \le 15$, $-8 \le k \le 8$, $-21 \le l \le 17$
Reflections collected	8706
Independent reflections	2978 [R_{int} = 0.0396, R_{sigma} = 0.0325]
Data/restraints/parameters	2978/20/238
Goodness-of-fit on F^2	1.187
Final R indexes [I>=2σ (I)]	R_1 = 0.0707, wR_2 = 0.1844
Final R indexes [all data]	R_1 = 0.0807, wR_2 = 0.1974
Largest diff. peak/hole / e Å^{-3}	0.36/-0.71

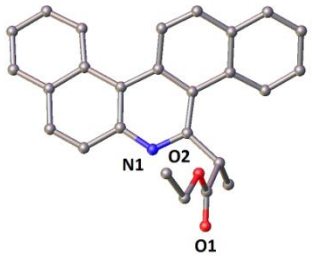


Figure S89. X-ray structure of **6c** showing 50% probability ellipsoids.

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Table S5. Crystal data and structure refinement for **6c**.

Identification code	6c
Empirical formula	$C_{26}H_{21}NO_2$
Formula weight	379.44
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.4718(9)
b/Å	10.1700(13)
c/Å	13.6849(15)
α/°	80.313(10)
β/°	76.092(10)
γ/°	74.405(11)
Volume/Å^3	966.3(2)
Z	2
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.082
F(000)	400.0
Crystal size/mm^3	0.36 x 0.21 x 0.32mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.064 to 49.992
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected	10401
Independent reflections	3378 [R_{int} = 0.0453, R_{sigma} = 0.0481]
Data/restraints/parameters	3378/0/264
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0523, wR_2 = 0.1325
Final R indexes [all data]	R_1 = 0.0706, wR_2 = 0.1454
Largest diff. peak/hole / e Å^{-3}	0.36/-0.27

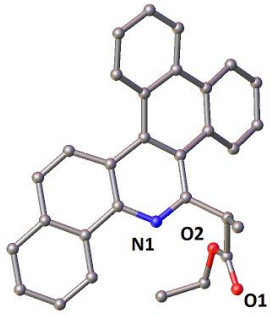

Figure S90. X-ray structure of **6e** showing 50% probability ellipsoids.

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Table S6. Crystal data and structure refinement for **6e**.

Identification code	6e
Empirical formula	$C_{30}H_{23}NO_2$
Formula weight	429.49
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.3192(6)
b/Å	11.4476(7)
c/Å	14.2878(11)
α/°	109.541(6)
β/°	103.435(7)
γ/°	90.850(6)
Volume/Å^3	1091.70(15)
Z	2
ρ_{calc}g/cm^3	1.307
μ/mm^{-1}	0.640
F(000)	452.0
Crystal size/mm^3	0.35 x 0.28 x 0.43mm^3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.238 to 134.138
Index ranges	$-8 \leq h \leq 7$, $-13 \leq k \leq 13$, $-17 \leq l \leq 15$
Reflections collected	9483
Independent reflections	3840 [R_{int} = 0.0422, R_{sigma} = 0.0519]
Data/restraints/parameters	3840/0/300
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1343
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1468
Largest diff. peak/hole / e Å^{-3}	0.26/-0.29

6. References

1. E. E. Bunel, L. Valle and J. M. Manriquez, *Organometallics*, 1985, **4**, 1680.
2. H. Jiang, Y. Cheng, R. Wang, M. Zheng, Y. Zhang and S. Yu, *Angew. Chem. Int. Ed.*, 2013, **52**, 13289.