Supporting Information

An umpolung strategy for rapid access to thermally activated delayed fluorescent (TADF) materials based on phenazine†

Huaxing Zhang,[a] Qiang Guo,[b] Hu Cheng,[a] Chunhao Ran,[a] Di Wu*[a] and Jingbo Lan*[a]

[a]Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P.R. China

[b]College of Optoelectronic Engineering, Chengdu University of Information Technology, 24 Xuefu Road, Chengdu 610225, P.R. China

Table of contents

I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz or a Varian Inova 400 MHz spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, DMSO-d_6 or $CDCl_2CDCl_2$ as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm; $CDCl_2CDCl_2$: δ = 6.00 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-ITTOF (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini plus or an Oxford Xcalibur E single crystal diffraction. Melting points were determined with XRC-1 and are uncorrected. UV/Vis spectra were measured on a HITACHI U-2910. Fluorescence spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. To reduce the fluctuation in the excitation intensity, the xenon lamp was kept on for 1 hour prior to the experiment. Transient PL decay spectra were obtained with Horiba Single Photon Counting Controller: FluoroHub and Horiba TBX Picosecond Photon Detection.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Arylboronic acids[1] and 2-aryl diazaboroles[2] were prepared according to the literature.

II. Preliminary regioselectivity investigation

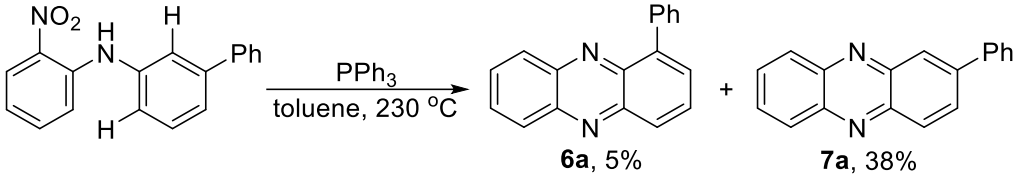
i) Reductive cyclization of 2-nitro-3'-phenyl-diphenylamine

1) Cadogan reaction of 2-nitro-3'-phenyl-diphenylamine[3]

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-nitro-3'-phenyl-diphenylamine (100 mg, 0.34 mmol), PPh_3 (267.5 mg, 1.02 mmol, 3.0 equiv). Next, the solvent toluene (3 mL) was added *via* a syringe and the rubber septum was replaced with a stopper. Then the reaction mixture was stirred at the 230 ^{o}C for 4 h under an air atmosphere in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was

dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Scheme S1. Cadogan reaction of 2-nitro-3'-phenyl-diphenylamine

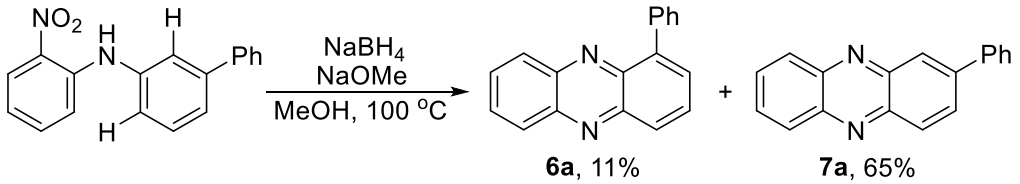


Reaction conditions: 2-nitro-3'-phenyl-diphenylamine (0.34 mmol), PPh_3 (3.0 equiv), and toluene (3.0 mL) at 230 ºC for 4 h under Air.

2) Reductive cyclization of 2-nitro-3'-phenyl-diphenylamine in the presence of $NaBH_4$[4]

A flame-dried Schlenk bottle with a magnetic stir bar was charged with 2-nitro-3'-phenyl-diphenylamine (192 mg, 0.66 mmol), $NaBH_4$ (99.8 mg, 2.64 mmol, 4.0 equiv). Next, 5 M NaOMe in MeOH (35 mL) was added *via* a syringe and the rubber septum was replaced with a stopper, then the reaction mixture was stirred at the 100 ºC for 4 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Scheme S2. Reductive cyclization reaction of 2-nitro-3'-phenyl-diphenylamine in the presence of $NaBH_4$



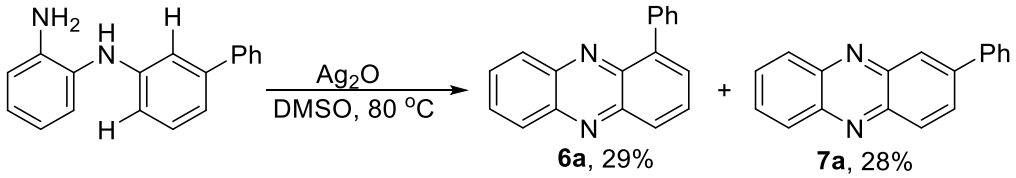
Reaction conditions: 2-nitro-3'-phenyl-diphenylamine (0.66 mmol), $NaBH_4$ (4.0 equiv) and 5 M NaOMe in MeOH (35 mL) at 100 ºC for 4 h under Air.

ii) Oxidative cyclization of 2-amino-3'-phenyl-diphenylamine

1) Oxidative cyclization of 2-amino-3'-phenyl-diphenylamine in the presence of Ag_2O

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-amino-3'-phenyl-diphenylamine (52.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at 80 °C for 24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Scheme S3. Oxidative cyclization of 2-amino-3'-phenyl-diphenylamine in the presence of Ag_2O



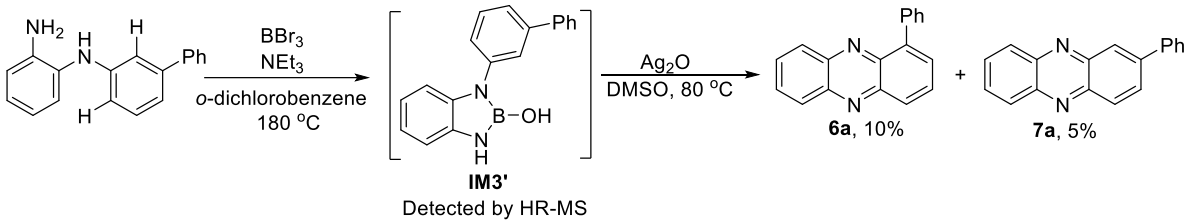
Reaction conditions: 2-amino-3'-phenyl-diphenylamine (0.2 mmol), Ag_2O (4.0 equiv) and DMSO (2.0 mL) at 80 °C for 24 h under N_2.

2) Oxidative cyclization of 2-amino-3'-phenyl-diphenylamine treated by BBr_3[5]

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-amino-3'-phenyl-diphenylamine (130 mg, 0.5 mmol). Next, the solvent *o*-dichlorobenzene (10 mL) was added *via* a syringe and the rubber septum was replaced with a stopper. Then the NEt_3 (139 μL, 2.0 equiv) was added to the reaction at 0 °C. After stir for 5 minutes, the BBr_3 (72 μL) was added. Then the reaction mixture was stirred at the 180 °C for 8 h under an N_2 atmosphere in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was purified *via* flash column chromatography on silica gel (100-200 mesh) with DCM to provide the crude products. The crude was detected by high resolution mass (HRMS (ESI^+): calcd for $C_{18}H_{16}BN_2O^+$ [**IM3'** + H]$^+$ 287.1350, found 287.1343). Next, the crude

product was treated by AgO_2 to get 1-phenyl phenazine and 2-phenyl phenazine.

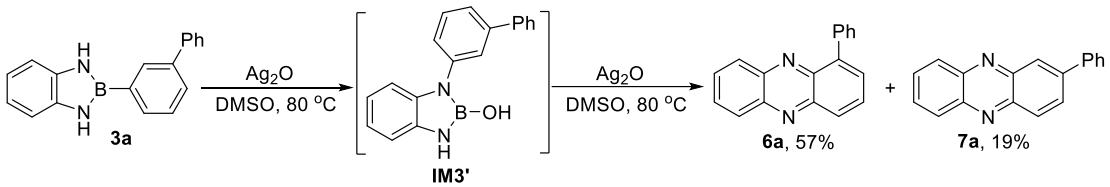
Scheme S4. Oxidative cyclization reaction after treated by BBr_3



3) Oxidative cyclization reaction of 2-phenyl diazaborole

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-([1,1'-biphenyl]-3-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**3a**, 0.2 mmol), Ag_2O (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO (2 mL) was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at the 80 ºC for 24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

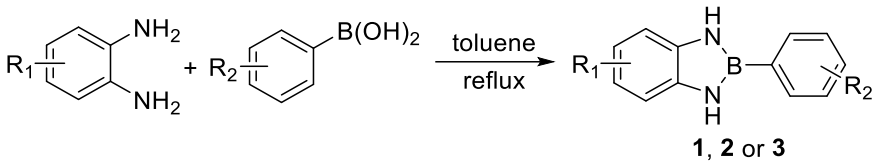
Scheme S5. Oxidative cyclization reaction of 2-aryl diazaborole



Reaction conditions: **3a** (0.2 mmol), Ag_2O (4.0 equiv) and DMSO (2.0 mL) at 80 ºC for 24 h under N_2.

III. Synthesis and compounds characterization

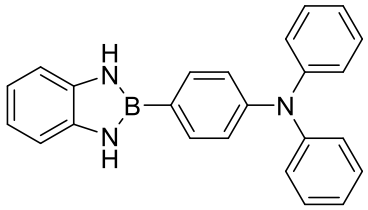
i) Synthesis of 2-aryl diazaborole substrates



1, **2** or **3**

2-Aryl diazaboroles were prepared according to the literature.[2]

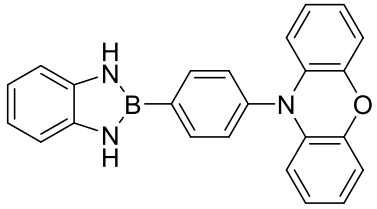
To a solution of *o*-phenylenediamine in toluene (5 mmol in 50 mL) was added aryl boronic acid (5 mmol) in one portion. The round-bottomed flask was equipped with a Dean and Stark trap, and the solution was stirred and heated to reflux at 120 °C for 4 h. The precipitate was isolated and recrystallization. 2-Aryl diazaborole substrates were obtained without further purification because of their poor stability in the process of separation and purification by column chromatography.



4-(1,3-Dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline (**1k)**

Following the general procedure, 4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline was prepared (90%, white solid).

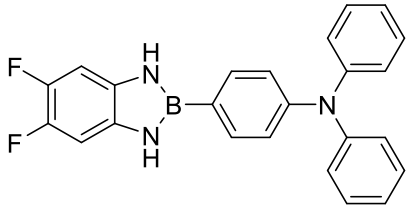
^{1}H NMR (400 MHz,$CDCl_3$) δ = 6.71 (s, 2H), 6.96 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 7.05-7.16 (m, 10H), 7.27-7.31 (m, 4H), 7.59 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.1, 119.3, 122.6, 123.4, 124.3, 125.0, 129.5, 134.1, 136.6, 147.6, 149.4. HRMS (ESI^+): calcd for $C_{24}H_{21}BN_3^+$ $[M+H]^+$ 362.1823, found 362.1818.



10-(4-(1,3-Dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-10*H*-phenoxazine (1n)

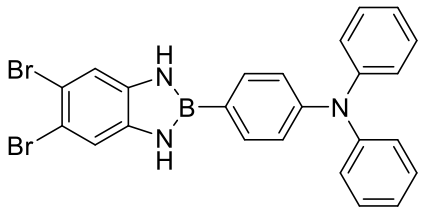
Following the general procedure, 10-(4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-10*H*-phenoxazine was prepared (43%, white solid). ^{1}H NMR (400 MHz,

DMSO-d_6) δ = 5.91-5.93 (m, 2H), 6.65-6.68 (m, 4H), 6.73-6.76 (m, 2H), 6.85 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 7.09 (dd, J = 6.0 Hz, 3.6 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 9.28 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 111.0, 113.3, 115.3, 118.5, 121.5, 123.8, 129.9, 133.9, 136.3, 137.1, 139.2, 143.1. HRMS (ESI$^+$): calcd for $C_{24}H_{19}BN_3O^+$ $[M+H]^+$ 376.1616, found 376.1612.



4-(5,6-Difluoro-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline (2a)

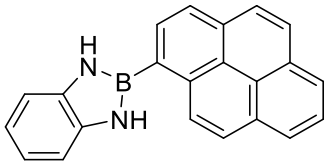
Following the general procedure, 4-(5,6-difluoro-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline was prepared (63%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.62 (s, 2H), 6.87 (t, J = 8.8 Hz, 2H), 7.05-7.14 (m, 9H), 7.28-7.30 (m, 3H), 7.53 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 99.61 (dd, J_{C-F} = 13.4 Hz, 8.7 Hz), 122.4, 122.8, 123.6, 124.2, 125.1, 129.42 (d, J_{C-F} = 17.7 Hz), 131.8 (t, J_{C-F} = 5.3 Hz), 134.0, 147.4, 149.7. HRMS (ESI$^+$): calcd for $C_{24}H_{19}BF_2N_3^+$ $[M+H]^+$ 398.1635, found 398.1637.



4-(5,6-Dibromo-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline (2c)

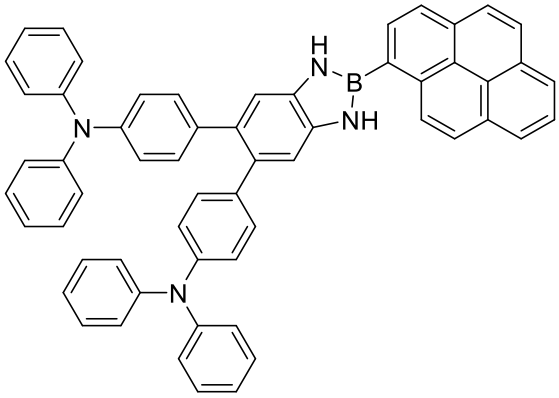
Following the general procedure, 4-(5,6-dibromo-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline was prepared (72%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.53 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.8 Hz, 5H), 7.13 (d, J = 8.0 Hz, 4H), 7.05-7.10 (m, 5H), 6.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.9, 147.4, 137.2, 134.2, 129.5, 125.2, 124.3, 123.7, 122.2, 115.3, 113.5. HRMS (ESI$^+$): calcd for $C_{24}H_{19}BBr_2N_3^+$ $[M+H]^+$ 518,0034, 520.0013, 521.9993, found

518.0037, 520.0017, 521.9995.



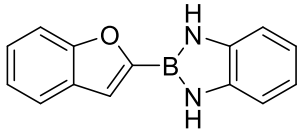
2-(Pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (2i)

Following the general procedure, 2-(pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (81%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.04-7.10 (m, 4H), 7.27-7.28 (m, 2H), 8.05 (t, *J* = 7.2 Hz, 1H), 8.10-8.16 (m, 3H), 8.23 (d, *J* = 7.2 Hz, 3H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.4, 119.7, 124.5, 124.7, 125.0, 125.2, 125.3, 126.0, 127.6, 127.8, 127.9, 128.1, 131.0, 131.5, 132.0, 132.1, 134.6, 136.4. HRMS (ESI^+): calcd for $C_{22}H_{16}BN_2^+$ $[M+H]^+$ 319.1402, found 319.1401.



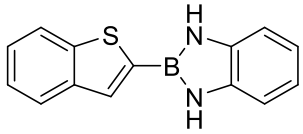
4,4'-(2-(Pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) (2j)

Following the general procedure, 4,4'-(2-(pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) was prepared (66%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 6.98-7.05 (m, 10H), 7.10-7.12 (m, 12H), 7.22-7.24 (m, 7H), 7.261-7.262 (m, 1H), 7.30 (s, 2H), 8.02-8.05 (m, 1H), 8.12-8.15 (m, 3H), 8.21-8.24 (m, 3H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.55 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 113.0, 122.7, 123.6, 124.2, 124.5, 124.68, 124.73, 125.0, 125.3, 125.4, 126.1, 127.7, 127.8, 128.2, 129.3, 129.4, 131.0, 131.3, 131.5, 132.0, 132.2, 132.7, 134.7, 135.9, 137.3, 145.8, 148.0. HRMS (ESI^+): calcd for $C_{58}H_{41}BN_4Na^+$ $[M+H]^+$ 827.3316, found 827.3315.



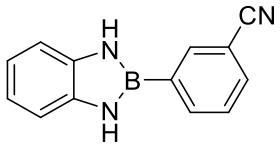
2-(Benzofuran-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (2l)

Following the general procedure, 2-(benzofuran-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (80%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 6.74 (s, 2H), 6.98-7.02 (m, 4H), 7.165-7.17 (m, 2H), 7.33-7.37 (m, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.5, 111.6, 115.5, 117.1, 119.9, 120.7, 121.6, 122.8, 125.3, 135.9. HRMS (ESI^+): calcd for $C_{14}H_{12}BN_2O^+$ $[M+H]^+$ 235.1037, found 235.1031.



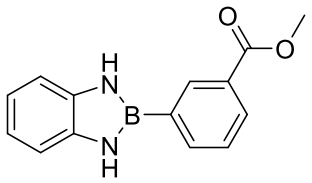
2-(Benzo[*b*]thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (2m)

Following the general procedure, 2-(benzo[*b*]thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (36%, pink solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.92-7.94 (m, 1H), 7.87-7.89 (m, 1H), 7.75 (s, 1H), 7.37-7.39 (m, 2H), 7.14-7.16 (m, 2H), 6.99-7.01 (m, 2H), 6.87 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.5, 119.9, 122.6, 124.0, 124.5, 125.0, 128.8, 130.7, 135.3, 138.2. HRMS (ESI^+): calcd for $C_{14}H_{12}BN_2S^+$ $[M+H]^+$ 251.0809, found 251.0813.



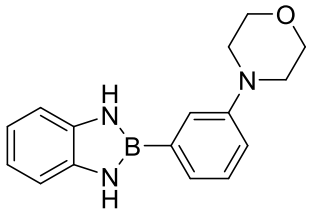
3-(1,3-Dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile (**3b)**

Following the general procedure, 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile was prepared (95%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 6.87 (s, 2H), 6.99-7.03 (m, 2H), 7.15-7.17 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.71 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.93-7.95 (m, 1H), 8.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.6, 111.7, 119.1, 120.0, 129.0, 133.1, 136.0, 136.7, 137.2. HRMS (ESI^+): calcd for $C_{13}H_{11}BN_3^+$ $[M+H]^+$ 220.1041, found 220.1040.



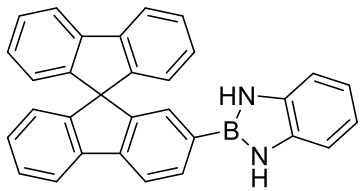
Methyl 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzoate (3c)

Following the general procedure, methyl 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzoate was prepared (90%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 3.95 (s, 3H), 6.89 (s, 2H), 6.99-7.02 (m, 2H), 7.14-7.16 (m, 2H), 7.81 (d, J = 7.6 Hz, 2H), 8.08-8.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 52.3, 111.5, 119.80, 119.83, 129.2, 131.06, 131.09, 136.2, 167.3. HRMS (ESI^+): calcd for $C_{14}H_{14}BN_2O_2^+$ $[M+H]^+$ 253.1143, found 253.1148.



4-(3-(1,3-Dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)morpholine (3e)

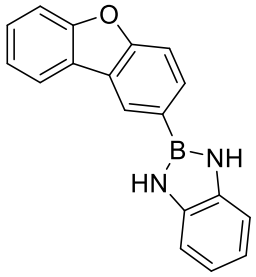
Following the general procedure, 4-(3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)morpholine was prepared (89%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 3.23 (t, J = 4.8 Hz, 4H), 3.91 (t, J = 4.8 Hz, 4H), 6.79 (s, 2H), 6.97-7.03 (m, 3H), 7.12-7.14 (m, 2H), 7.26-7.30 (m, 2H), 7.37 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.7, 67.1, 111.2, 117.5, 119.5, 120.4, 125.1, 129.2, 136.4, 151.2. HRMS (ESI^+): calcd for $C_{16}H_{19}BN_3O^+$ $[M+H]^+$ 280.1616, found 280.1616.



2-(9,9'-Spirobi[fluoren]-2-yl)-2,3-dihydro-1H-benzo[d][1,3,2]diazaborole (3f)

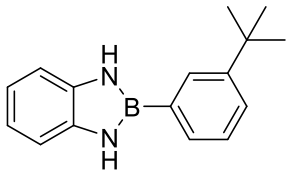
Following the general procedure, 2-(9,9'-spirobi[fluoren]-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (50%, gray solid). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.58 (d, J = 7.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 2H), 6.74 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 6.93 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 7.13 (t, J = 7.2 Hz, 3H), 7.22 (s, 1H),

7.38-7.43 (m, 3H), 7.99-8.10 (m, 5H), 9.05 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 65.5, 110.7, 114.5, 117.3, 118.2, 120.2, 120.6, 120.7, 123.4, 123.6, 127.9, 128.0, 128.2, 128.3, 133.3, 137.1, 141.2, 141.4, 142.5, 147.7, 148.4, 148.8. HRMS (ESI$^+$): calcd for $C_{31}H_{22}BN_2^+$ $[M+H]^+$ 433.1871, found 433.1869.



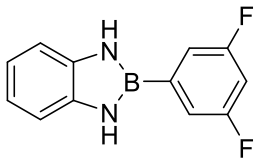
2-(Dibenzo[*b*,*d*]furan-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3h)

Following the general procedure, 2-(dibenzo[*b*,*d*]furan-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (77%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 6.88 (s, 2H), 6.99 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 7.16 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.4 Hz, 1H), 7.62 (dd, J = 15.2 Hz, 8.4 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 8.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.3, 111.8, 111.9, 119.5, 120.8, 123.1, 124.1, 124.5, 125.6, 127.4, 132.2, 136.5, 156.4, 157.5. HRMS (ESI$^+$): calcd for $C_{18}H_{14}BN_2O^+$ $[M+H]^+$ 285.1194, found 285.1195.



2-(3-(*tert*-Butyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3l)

Following the general procedure, 2-(3-(*tert*-butyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (72%, white solid). ^{1}H NMR (400 MHz,$CDCl_3$) δ = 1.43 (s, 9H), 6.83 (s, 2H), 7.00-7.04 (m, 2H), 7.14-7.19 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.6, 34.8, 111.2, 119.4, 127.0, 128.1, 129.9, 130.4, 136.5, 150.8. HRMS (ESI$^+$): calcd for $C_{16}H_{20}BN_2^+$ $[M+H]^+$ 251.1714, found 251.1708.



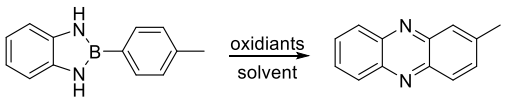
2-(2,4-Difluorophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (3m)

Following the general procedure, 2-(2,4-difluorophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole was prepared (63%, white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (td, J = 9.6 Hz, 2.4 Hz, 1H), 6.94-7.01 (m, 5H), 7.15 (dd, J = 5.6 Hz, 3.2 Hz, 2H), 7.65 (dd, J = 15.2 Hz, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 104.01 (dd, $J_{C\text{-}F}$ = 27.8 Hz, 24.3 Hz), 111.4, 111.82 (dd, $J_{C\text{-}F}$ = 20.2 Hz, 3.3 Hz), 119.7, 135.73 (dd, $J_{C\text{-}F}$ = 10.9 Hz, 9.6 Hz), 163.3, 164.6 (dd, $J_{C\text{-}F}$ = 250.1 Hz, 13.0 Hz). HRMS (ESI^+): calcd for $C_{12}H_9BF_2N_2Na^+$ $[M+H]^+$ 253.0719, found 253.0722.

ii) Optimization of the oxidative cyclization reaction of 2-(4-tolyl)diazaborole

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-(*p*-tolyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**1a**, 0.2 mmol) and additive. The system was evacuated thrice and back filled with N_2. Next, the solvent was added *via* a syringe and the rubber septum was replaced with a glass stopper under N_2. Then the reaction mixture was stirred at the indicated temperature for 2-24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired product **4a**.

Table S1. Optimization of the oxidative cyclization reaction of 2-(4-tolyl)diazaborole[a]



1a **4a**

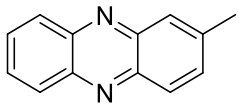
Entry	Oxidants	Solvent	Temperature (^{o}C)	Time (h)	Yield[b] (%)
1	AgOAc	DMSO	80	12	30
2	AgOAc	DCE	80	12	trace
3	AgOAc	DMF	80	12	24

4	AgOAc	MeCN	80	12	trace
5	AgOAc	Toluene	80	12	trace
6	AgOAc	THF	80	12	30
7	AgOAc	Dioxane	80	12	20
8	AgOAc	*tert*-Amyl alcohol	80	12	N.D.
9	MnO_2	DMSO	80	12	10
10	BQ	DMSO	80	12	N.D.
11	Ag_2O	DMSO	80	12	72
12	$Cu(OAc)_2$	DMSO	80	12	N.D.
13	$K_2S_2O_8$	DMSO	80	12	N.D.
14	Ag_2CO_3	DMSO	80	12	33
15	$PhI(OAc)_2$	DMSO	80	12	trace
16	AgTFA	DMSO	80	12	N.D.
19[c]	Ag_2O	DMSO	80	12	55
20[d]	Ag_2O	DMSO	80	12	38
21	Ag_2O	DMSO	60	12	20
22	Ag_2O	DMSO	120	12	60
23	Ag_2O	DMSO	80	24	87
17[e]	Ag_2O	DMSO	80	24	57
18[f]	AgOAc	DMSO	80	24	53

[a]Reaction conditions: 2-(4-tolyl)diazaborole (**1a**, 0.2 mmol), oxidant (4.0 equiv) and solvent (2.0 mL) at 80 ºC for 12 h under N_2. [b]isolated yields. [c]O_2 1 atm. [d]Air. [e]Ag_2O (3.0 equiv). [f]AgOAc (8.0 equiv). BQ = 1,4-benzoquinone, DMSO = dimethylsulfoxide, DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, N.D. = no detection.

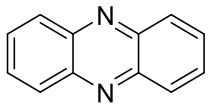
iii) General procedure for the oxidative cyclization reaction of 2-aryl diazaboroles

A dried Schlenk tube with a magnetic stir bar was charged with several of 2-aryl diazaboroles (0.2 mmol), Ag_2O (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO (2 mL) was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at the 80 °C for 24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.



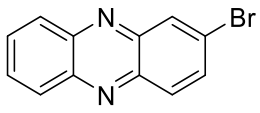
2-Methylphenazine (4a)

Following the general procedure, the mixture of 2-(*p*-tolyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1a** (41.6 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4a** (34.1 mg) in 88% yield as a yellow solid. M.p.: 112-114 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 2.65 (s, 3H), 7.66-7.69 (m, 1H), 7.80-7.83 (m, 2H), 7.99 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.21-8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.4, 127.8, 129.2, 129.6, 129.8, 130.1, 130.5, 133.7, 141.4, 142.5, 143.1, 143.6, 143.8. HRMS (ESI^+): calcd for $C_{13}H_{11}N_2^+$ $[M+H]^+$ 195.0917, found 195.0926.



Phenazine (4b)

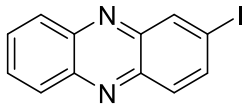
Following the general procedure, the mixture of 2-phenyl-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1b** (38.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4b** (24.5 mg) in 68% yield as a yellow solid. M.p.: 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (dd, J = 6.8 Hz, 3.6 Hz, 4H), 8.26 (dd, J = 6.8 Hz, 3.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.8, 130.6, 143.6. HRMS (ESI^+): calcd for $C_{12}H_9N_2^+$ $[M+H]^+$ 181.0760, found 181.0762.



2-Bromophenazine (4c)

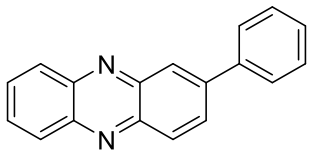
Following the general procedure, the mixture of 2-(4-bromophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1c** (54.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography

on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4c** (45.4 mg) in 88% yield as a yellow solid. M.p.: 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86-7.91 (m, 3H), 8.12 (d, J = 9.6 Hz, 1H), 8.22-8.25 (m, 2H), 8.46 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 125.1, 129.8, 129.9, 131.0, 131.1, 131.3, 131.8, 134.4, 142.2, 143.7, 143.8, 143.9. HRMS (ESI^+): calcd for $C_{12}H_8BrN_2^+$ $[M+H]^+$ 258.9865, 260.9845, found 258.9862, 260.9839.



2-Iodophenazine (4d)

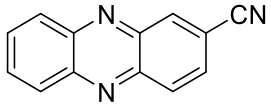
Following the general procedure, the mixture of 2-(4-iodophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1d** (64.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4d** (37.4 mg) in 61% yield as a yellow solid. M.p.: 172-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84-7.87 (m, 2H), 7.94 (d, J = 9.2 Hz, 1H), 8.02-8.04 (m, 1H), 8.20-8.23 (m, 2H), 8.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 97.3, 129.86, 129.91, 130.8, 131.1, 131.3, 138.9, 139.2, 142.5, 143.7, 143.8, 144.0. HRMS (ESI^+): calcd for $C_{12}H_8IN_2^+$ $[M+H]^+$ 306.9727, found 306.9729.



2-Phenylphenazine (4e)

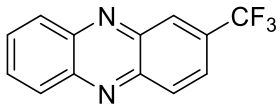
Following the general procedure, the mixture of 2-([1,1'-biphenyl]-4-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1e** (54.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4e** (41.5 mg) in 81% yield as a yellow solid. M.p.: 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.48 (m, 1H), 7.53-7.57 (m, 2H), 7.83-7.86 (m, 4H), 8.15 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.24-8.27 (m, 2H), 8.32 (dd, J = 9.6 Hz, 0.8 Hz, 1H), 8.46 (dd, J = 2.4 Hz,

0.4Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 126.6, 127.5, 127.7, 128.7, 129.3, 129.7, 129.8, 130.1, 130.5, 130.7, 130.9, 139.6, 143.1, 143.6, 143.8, 144.0. HRMS (ESI^+): calcd for $C_{18}H_{13}N_2^+$ $[M+H]^+$ 257.1073, found 257.1072.



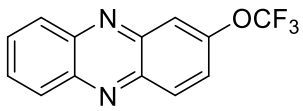
Phenazine-2-carbonitrile (4f)

Following the general procedure, the mixture of 4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile **1f** (43.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4f** (40.6 mg) in 99% yield as a yellow solid. M.p.: 215-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91-7.96 (m, 3H), 8.26-8.29 (m, 2H), 8.35 (dd, J = 9.2 Hz, 0.8 Hz, 1H), 8.68 (dd, J = 2.0 Hz, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 114.0, 118.2, 129.8, 130.0, 130.2, 131.7, 132.0, 132.6, 136.8, 142.1, 144.0, 144.7, 144.8. HRMS (ESI^+): calcd for $C_{13}H_8N_3^+$ $[M+H]^+$ 206.0713, found 206.0713.



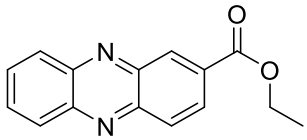
2-(Trifluoromethyl)phenazine (4g)

Following the general procedure, the mixture of 2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1g** (52.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4g** (44.6 mg) in 90% yield as a yellow solid. M.p.: 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88-7.94 (m, 2H), 7.97 (dd, J = 9.2 Hz, 2.0 Hz, 1H), 8.26-8.28 (m, 2H), 8.37 (d, J = 9.2 Hz, 1H), 8.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 123.7 (d, J_{CF} = 271 Hz), 125.7 (q, J_{CF} = 3 Hz), 128.2 (q, J_{CF} = 5 Hz), 129.9, 130.0, 131.4, 131.5, 132.0 (d, J_{CF} = 33 Hz), 132.1, 142.1, 143.9, 144.3, 144.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.28 (s). HRMS (ESI^+): calcd for $C_{13}H_8F_3N_2^+$ $[M+H]^+$ 249.0634, found 249.0635.



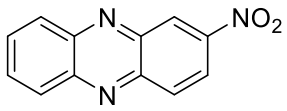
2-(Trifluoromethoxy)phenazine (4h)

Following the general procedure, the mixture of 2-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1h** (55.6 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4h** (45.0 mg) in 85% yield as a yellow solid. M.p.: 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (dd, J = 9.6 Hz, 2.8 Hz, 1H), 7.85-7.91 (m, 2H), 8.07 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 8.22-8.26 (m, 2H), 8.30 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =117.7, 120.6 (d, J_{CF} = 258 Hz), 125.3, 129.6, 129.9, 131.0, 131.5, 132.0, 141.7, 143.4, 143.6, 144.0, 150.1. ^{19}F NMR (376 MHz,$CDCl_3$) δ = -57.83 (s). HRMS (ESI^+): calcd for $C_{13}H_8F_3ON_2^+$ $[M+H]^+$ 265.0583, found 265.0581.



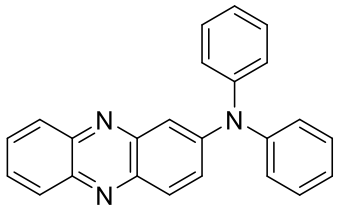
Ethyl phenazine-2-carboxylate (4i)

Following the general procedure, the mixture of ethyl 4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzoate **1i** (53.2 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4i** (38.0 mg) in 75% yield as a yellow solid. M.p.: 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.48 (t, J = 7.2 Hz, 3H), 4.50 (q, J = 7.2 Hz, 2H), 7.86-7.92 (m, 2H), 8.24-8.30 (m, 3H), 8.40 (dd, J = 9.2 Hz, 2.0 Hz, 1H), 9.01 (dd, J = 1.6 Hz, 0.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.5, 61.9, 129.5, 129.9, 130.0, 130.1, 131.1, 131.8, 132.1, 133.0, 142.7, 144.3, 144.5, 144.8, 165.9. HRMS (ESI^+): calcd for $C_{15}H_{13}N_2O_2^+$ $[M+H]^+$ 253.0972, found 253.0979.



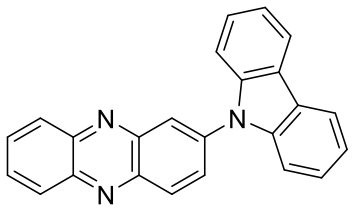
2-Nitrophenazine (4j)

Following the general procedure, the mixture of 2-(4-nitrophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1j** (47.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 ℃ for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 10/1/1, v/v) afforded the product **4j** (14.9 mg) in 33% yield as a yellow solid. M.p.: 212-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93-8.00 (m, 2H), 8.28-8.33 (m, 2H), 8.41 (d, *J* = 9.6 Hz, 1H), 8.58 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 9.22 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 123.4, 126.9, 130.1, 130.2, 131.8, 132.1, 132.9, 141.8, 142.4, 144.8, 144.97, 145.05. HRMS (ESI^+): calcd for $C_{12}H_8N_3O_2^+$ $[M+H]^+$ 226.0611, found 226.0609.



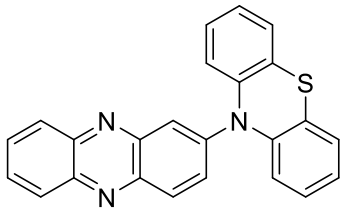
***N*,*N*-Diphenylphenazin-2-amine (4k)**

Following the general procedure, the mixture of 4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline **1k** (72.2 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 ℃ for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4k** (55.6 mg) in 80% yield as an orange solid. M.p.: 155-157 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.14 (d, *J* = 2.4 Hz, 1H), 7.26-7.30 (m, 6H), 7.45-7.49 (m, 4H), 7.58 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 7.77-7.87 (m, 2H), 8.01-8.08 (m, 2H), 8.15 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 111.8, 125.6, 126.2, 127.6, 128.5, 129.1, 129.3, 130.0, 130.1, 130.8, 140.3, 141.3, 143.2, 144.4, 145.7, 149.3. HRMS (ESI^+): calcd for $C_{24}H_{18}N_3^+$ $[M+H]^+$ 348.1495, found 348.1498.



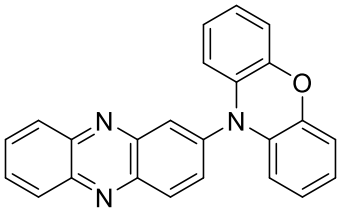
2-(9*H*-Carbazol-9-yl)phenazine (4l)

Following the general procedure, the mixture of 9-(4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-9*H*-carbazole **1l** (71.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 ℃ for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4l** (44.2 mg) in 64% yield as an orange solid. M.p.: 191-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.38 (m, 2H), 7.45-7.49 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.89-7.92 (m, 2H), 8.15 (dd, *J* = 9.2 Hz, 2.4 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 2H), 8.27-8.33 (m, 2H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.50 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.1, 120.7, 121.1, 124.2, 125.1, 126.5, 129.7, 129.9, 130.0, 130.8, 131.3, 131.6, 139.7, 140.3, 142.5, 143.7, 144.06, 144.09. HRMS (ESI^+): calcd for $C_{24}H_{16}N_3^+$ $[M+H]^+$ 346.1339, found 346.1334.



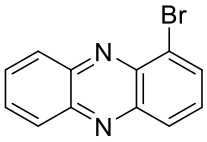
10-(Phenazin-2-yl)-10*H*-phenothiazine (4m)

Following the general procedure, the mixture of 10-(4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-10*H*-phenothiazine **1m** (78.2 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 ℃ for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4m** (40.0 mg) in 53% yield as an orange solid. M.p.: 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (td, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.33 (td, *J* = 7.6 Hz, 1.6 Hz, 2H), 7.41-7.46 (m, 4H), 7.71-7.80 (m, 4H), 8.09-8.12 (m, 2H), 8.16-8.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.7, 125.4, 125.8, 126.2, 127.7, 128.9, 129.0, 129.2, 129.7, 130.7, 130.8, 132.8, 141.1, 141.6, 142.3, 144.0, 144.9, 146.6. HRMS (ESI^+): calcd for $C_{24}H_{16}N_3S^+$ $[M+H]^+$ 378.1059, found 378.1056.



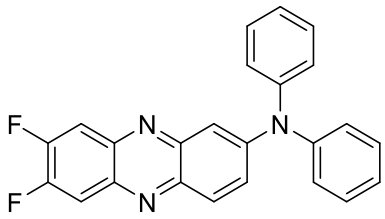
10-(Phenazin-2-yl)-10*H*-phenoxazine (4n)

Following the general procedure, the mixture of 10-(4-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-10*H*-phenoxazine **1n** (75.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4n** (45.0 mg) in 62% yield as a carmine solid. M.p.: 200-202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.17 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 6.62 (td, *J* = 8.0 Hz, 1.6 Hz, 2H), 6.70-6.79 (m, 4H), 7.79 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 7.88-7.92 (m, 2H), 8.26-8.33 (m, 3H), 8.45 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 113.9, 116.0, 122.4, 123.5, 129.8, 129.9, 131.1, 131.3, 131.6, 132.9, 133.1, 133.4, 140.7, 143.0, 143.7, 143.9, 144.2, 144.4. HRMS (ESI$^+$): calcd for $C_{24}H_{16}N_3O^+$ $[M+H]^+$ 362.1288, found 362.1286.



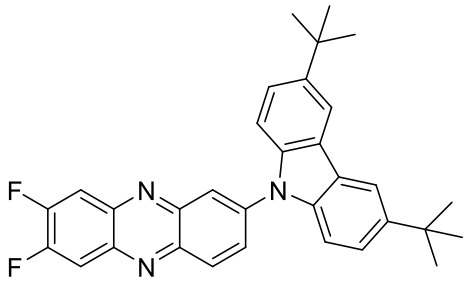
1-Bromophenazine (4o)

Following the general procedure, the mixture of 2-(2-bromophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **1o** (54.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **4o** (34.1 mg) in 66% yield as a yellow solid. M.p.: 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68-7.72 (m, 1H), 7.87-7.91 (m, 2H), 8.18-8.28 (m, 3H), 8.38-8.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 124.5, 129.5, 129.8, 130.2, 130.5, 131.2, 131.5, 133.7, 141.0, 143.8, 143.9, 144.0. HRMS (ESI$^+$): calcd for $C_{12}H_8BrN_2^+$ $[M+H]^+$ 258.9865, 260.9845, found 258.9862, 260.9839



7,8-Difluoro-*N*,*N*-diphenylphenazin-2-amine (5a)

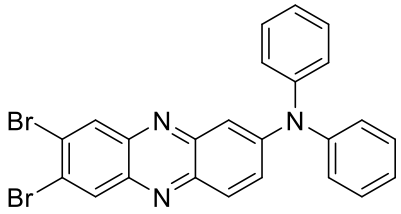
Following the general procedure, the mixture of 4-(5,6-difluoro-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline **2a** (79.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5a** (59.1 mg) in 77% yield as a red-orange solid. M.p.: 170-172 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.08 (d, J = 2.8 Hz, 1H), 7.27-7.31 (m, 6H), 7.45-7.49 (m, 4H), 7.57 (dd, J = 9.6 Hz, 2.8 Hz, 1H), 7.96-8.04 (m, 2H), 8.15 (dd, J = 11.2 Hz, 8.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 111.0, 113.5, 114.2, 114.3, 125.8, 126.3 127.7, 129.7, 130.1, 140.08, 140.09, 140.82, 140.84, 144.2, 145.5, 149.6. HRMS (ESI$^+$): calcd for $C_{24}H_{16}F_2N_3^+$ $[M+H]^+$ 384.1307, found 384.1307.



7-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)-2,3-difluorophenazine (5b)

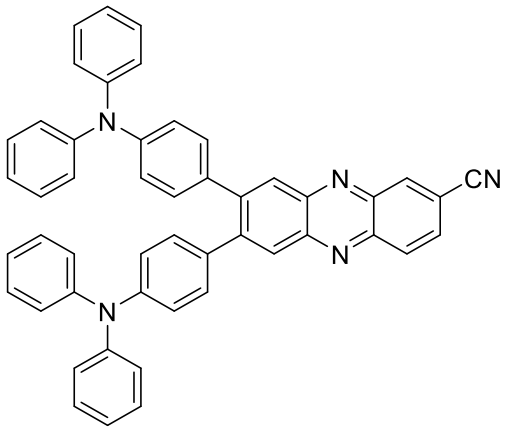
Following the general procedure, the mixture of 3,6-di-*tert*-butyl-9-(4-(5,6-difluoro-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)-9*H*-carbazole **2b** (101.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5b** (49.3 mg) in 50% yield as a orange solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.49 (s, 18H), 7.51 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.93-8.02 (m, 2H), 8.18 (s, 3H), 8.37-8.41 (m, 2H). ^{13}C NMR (100

MHz, $CDCl_3$) δ = 32.1, 35.0, 109.5, 114.2 ($J_{C\text{-}F}$ = 30 Hz, 17 Hz) , 116.7, 123.7, 124.2, 124.3, 130.3, 131.1, 138.5, 140.6, 140.9, 141.0, 141.6, 141.7, 142.1 ($J_{C\text{-}F}$ = 2 Hz), 144.0 ($J_{C\text{-}F}$ = 3 Hz), 144.3. HRMS (ESI^+): calcd for $C_{32}H_{30}F_2N_3^+$ $[M+H]^+$ 494.2402, found 494.2401.



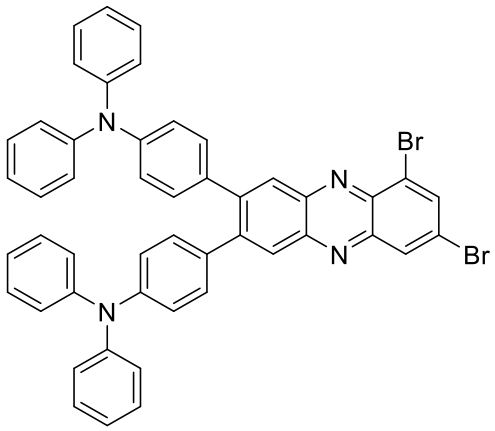
7,8-Dibromo-*N*,*N*-diphenylphenazin-2-amine (5c)

Following the general procedure, the mixture of 4-(5,6-dibromo-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-*N*,*N*-diphenylaniline **3c** (103.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5c** (81.5 mg) in 81% yield as a red-orange solid. M.p.: 197-199 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.20-7.24 (m, 5H), 7.35-7.40 (m, 6H), 7.66 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 7.93 (d, J = 9.6 Hz, 1H), 8.35 (s, 1H), 8.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 112.6, 124.9, 125.7, 126.5, 127.2, 129.1, 130.0, 130.1, 132.6, 133.4, 140.8, 141.8, 142.9, 145.7, 146.0, 150.5. HRMS (ESI^+): calcd for $C_{24}H_{16}Br_2N_3^+$ $[M+H]^+$ 503.9705, 505.9685, 507.9665, found 503.9702, 505.9685, 507.9655.



7,8-Bis(4-(diphenylamino)phenyl)phenazine-2-carbonitrile (5d)

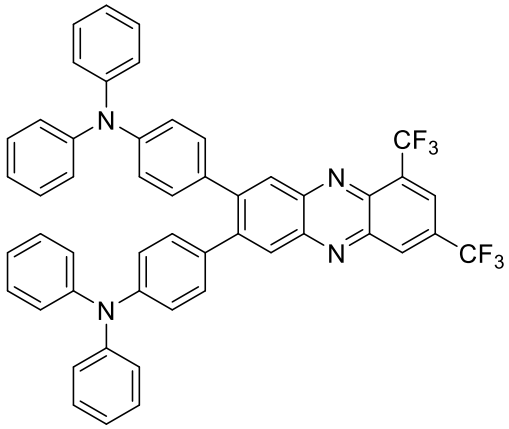
Following the general procedure, the mixture of 4-(5,6-bis(4-(diphenylamino)phenyl)-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile **4d** (141.1 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/DCM = 3/1, v/v) afforded the product **5d** (70.5 mg) in 51% yield as a deepred solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01-7.09 (m, 8H), 7.13-7.18 (m, 12H), 7.26-7.30 (m, 8H), 7.89 (dd, *J* = 9.2 Hz, 2.0 Hz, 1H), 8.26 (*d*, *J* = 2.0 Hz, 2H), 8.31-8.33 (m, 1H), 8.65-8.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 113.4, 118.4, 122.2, 122.3, 123.5, 123.6, 124.99, 125.04, 129.4, 129.5, 129.6, 129.7, 130.76, 130.78, 131.5, 133.1, 133.2, 136.6, 142.2, 144.22, 144.25, 144.4, 146.0, 146.6, 147.43, 147.45, 147.79, 147.84. HRMS (ESI^+): calcd for $C_{49}H_{34}N_5^+$ $[M+H]^+$ 692.2809, found 692.2809.



4,4'-(6,8-Dibromophenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) (5e)

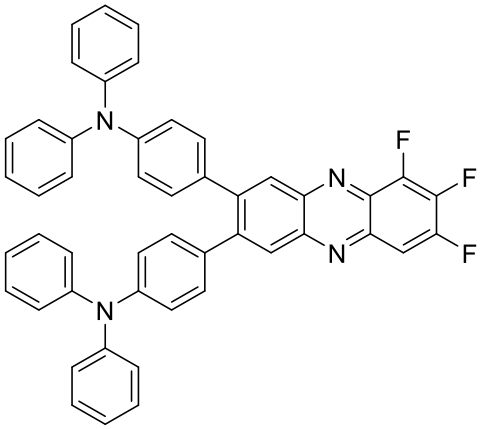
Following the general procedure, the mixture of 4,4'-(2-(3,5-dibromophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) **2e** (167.2 mg mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5e** (120.0 mg) in 73% yield as a red solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01-7.08 (m, 9H), 7.12-7.18 (m, 13H), 7.28-7.30 (m, 6H), 8.22-8.23 (m, 2H), 8.368-8.370 (m, 1H), 8.395-8.404 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.3, 122.4, 123.4, 123.5, 123.6, 124.9, 125.0, 125.3, 129.0, 129.50, 129.51, 130.0, 130.79, 130.82, 131.6, 133.4, 133.5, 136.3, 139.9, 143.3,

143.7, 144.0, 145.5, 146.0, 147.49, 147.52, 147.6, 147.7. HRMS (ESI^+): calcd for $C_{48}H_{33}Br_2N_4^+$ $[M+H]^+$ 825.1046, 826.1080, 823.1066, found 825.1046, 826.1080, 823.1063.



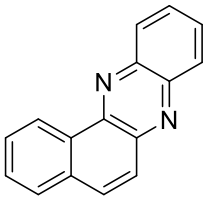
4,4'-(6,8-Bis(trifluoromethyl)phenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) (5f)

Following the general procedure, the mixture of 4,4'-(2-(3,5-bis(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) **2f** (163.3 mg mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/DCM = 3/1, v/v) afforded the product **5f** (130.0 mg) in 81% yield as a deepred solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02-7.09 (m, 8H), 7.13-7.16 (m, 8H), 7.20 (d, J = 8.4 Hz, 4H), 7.27-7.31 (m, 8H), 8.28-8.30 (m, 2H), 8.39 (s, 1H), 8.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.2, 122.4, 123.5, 123.6, 124.2, 124.6, 124.9, 125.0, 129.3, 129.52, 129.54, 129.7, 130.0, 130.2, 130.8, 132.3, 133.0, 133.2, 140.7, 142.0, 143.9, 144.0, 146.6, 147.0, 147.4, 147.5, 147.8, 147.9. ^{19}F NMR (376 MHz,$CDCl_3$) δ = -63.17 (s), -60.57 (s). HRMS (ESI^+): calcd for $C_{50}H_{33}F_6N_4^+$ $[M+H]^+$ 803.2604, found 803.2609.



4,4'-(6,7,8-Trifluorophenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) (5g)

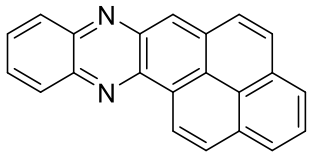
Following the general procedure, the mixture of 4,4'-(2-(3,4,5-trifluorophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) **2g** (146.9 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/DCM = 3/1, v/v) afforded the product **5g** (103.7 mg) in 72% yield as a red solid. M.p.: 248-250 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.94 (d, J = 8.4 Hz, 4H), 7.04-7.07 (m, 11H), 7.18 (dd, J = 8.8 Hz, 2.0 Hz, 4H), 7.26-7.30 (m, 8H), 8.12-8.17(m, 1H), 8.19 (s, 1H), 8.25 (d, J = 4.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.3, 122.27, 122.32, 123.5, 124.97, 124.99, 129.2, 129.4, 129.5, 130.8, 133.2, 133.3, 138.0, 139.3, 139.4, 142.4, 143.6, 145.6, 145.9, 147.5, 147.69, 147.70. HRMS (ESI$^+$): calcd for $C_{48}H_{32}F_3N_4^+$ $[M+H]^+$ 721.2574, found 721.2576.



Benzo[a]phenazine (5h)

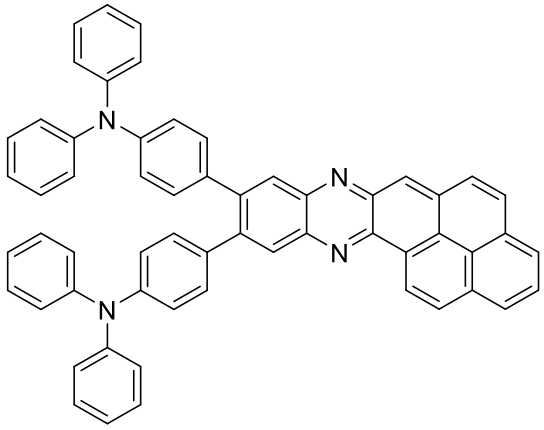
Following the general procedure, the mixture of 2-(naphthalen-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **2h** (48.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded the product **5h**(40.9 mg) in 89% yield as a yellow solid. M.p.: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ =

7.78-7.81 (m, 2H), 7.86-7.92 (m, 3H), 7.95-8.03 (m, 2H), 8.27-8.30 (m, 1H), 8.36-8.39 (m, 1H), 9.41-9.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 125.5, 127.3, 128.1, 128.4, 129.3, 129.87, 129.95, 130.0, 130.2, 131.3, 133.39, 133.42, 142.1, 142.8, 142.9, 143.8. HRMS (ESI$^+$): calcd for $C_{16}H_{11}N_2^+$ $[M+H]^+$ 231.0917, found 231.0915.



Phenaleno[1,9-*ab*]phenazine (5i)

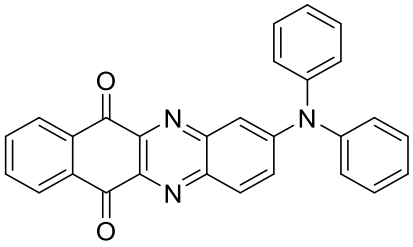
Following the general procedure, the mixture of 2-(pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **2i** (64.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/THF/DCM = 10/1/1, v/v) afforded the product **5i** (52.0 mg) in 85% yield as a red solid. M.p.: 241-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 9.2 Hz, 1H), 7.86-7.94 (m, 4H), 7.98 (d, *J* = 6.4 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 1H), 8.35-8.39 (m, 2H), 8.45-8.48 (m, 1H), 8.55 (s, 1H), 9.69 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 123.69, 123.71, 124.9, 125.8, 126.0, 127.1, 127.3, 128.0, 128.6, 129.1, 129.4, 129.8, 130.1, 130.3, 130.4, 131.2, 132.8, 134.9, 139.3, 141.3, 142.0, 143.5. HRMS (ESI$^+$): calcd for $C_{22}H_{13}N_2^+$ $[M+H]^+$ 305.1073, found 305.1070.



4,4'-(Phenaleno[1,9-*ab*]phenazine-9,10-diyl)bis(*N*,*N*-diphenylaniline) (5j)

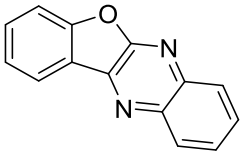
Following the general procedure, the mixture of 4,4'-(2-(pyren-1-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) **2j** (160.9 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification

via column chromatography on silica gel (petroleum ether/THF/DCM = 10/1/1, v/v) afforded the product **5j** (99.6 mg) in 63% yield as a red solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04-7.08 (m, 8H), 7.16 (d, *J* = 8.0 Hz, 8H), 7.23 (dd, *J* = 8.4 Hz, 2.4 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 8H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.90-7.95 (m, 2H), 8.00 (d, *J* = 7.2 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.40 (d, *J* = 10.0 Hz, 2H), 8.49 (s, 1H), 8.57 (s, 1H), 9.70 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.6, 122.7, 123.25, 123.29, 123.7, 123.8, 124.76, 124.83, 125.0, 125.7, 126.0, 127.0, 127.2, 128.0, 128.5, 129.1, 129.2, 129.5, 129.6, 130.0, 130.2, 131.0, 131.2, 132.8, 134.2, 134.4, 134.6, 139.5, 141.51, 141.52, 143.0, 143.5, 144.1, 147.2, 147.3, 147.62, 147.65. HRMS (ESI^+): calcd for $C_{58}H_{39}N_4^+$ $[M+H]^+$ 791.3169, found 791.3170.



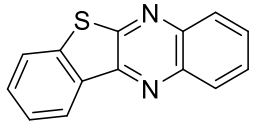
2-(Diphenylamino)benzo[b]phenazine-6,11-dione (5k)

Following the general procedure, the mixture of 2-(4-(diphenylamino)phenyl)-2,3-dihydro-1*H*-naphtho[2,3-*d*][1,3,2]diazaborole-4,9-dione **2k** (88.2 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 5/1/1, v/v) afforded the product **5k** (51.3 mg) in 60% yield as a red solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ = 7.32-7.34 (m, 6H), 7.44-7.48(m, 4H), 7.55 (d, *J* = 2.8 Hz, 1H), 7.76 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H), 7.87-7.93 (m, 2H), 8.17 (d, *J* = 9.6 Hz, 1H), 8.39-8.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 113.6, 126.6, 126.9, 128.17, 128.20, 128.7, 130.3, 131.6, 133.7, 134.1, 134.8, 135.1, 140.8, 141.4, 145.0, 145.3, 146.2, 152.8, 181.3, 182.0. HRMS (ESI^+): calcd for $C_{28}H_{18}N_3O_2^+$ $[M+H]^+$ 428.1394, found 428.1394.



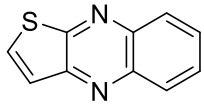
Benzofuro[2,3-*b*]quinoxaline (5l)

Following the general procedure, the mixture of 2-(benzofuran-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **2l** (46.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5l** (14.0 mg) in 32% yield as a white solid. M.p.: 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.54 (m, 1H), 7.68-7.74 (m, 2H), 7.77-7.84 (m, 2H), 8.16-8.18 (m, 1H), 8.29-8.31 (m, 1H), 8.35 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 112.9, 121.4, 123.0, 124.6, 128.4, 128.8, 129.3, 129.9, 132.5, 139.9, 140.7, 141.4, 156.0, 158.6. HRMS (ESI^+): calcd for $C_{14}H_9N_2O^+$ $[M+H]^+$ 221.0709, found 221.0705.



Benzo[4,5]thieno[2,3-*b*]quinoxaline (5m)

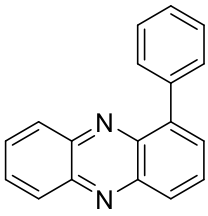
Following the general procedure, the mixture of 2-(benzo[*b*]thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **2m** (50.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5m** (14.7 mg) in 31% yield as a white solid. M.p.: 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (td, J = 8.0 Hz, 1.2 Hz, 1H), 7.68 (td, J = 8.0 Hz, 1.6 Hz, 1H), 7.81-7.84 (m, 2H), 7.88 (dt, J = 8.0 Hz, 0.8 Hz, 1H), 8.16-8.18 (m, 1H), 8.28-8.31 (m, 1H), 8.58-8.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 123.7, 124.5, 125.9, 128.5, 129.2, 129.7, 129.9, 131.1, 131.5, 140.1, 140.6, 141.5, 148.0, 157.5. HRMS (ESI^+): calcd for $C_{14}H_8N_2S^+$ $[M+H]^+$ 237.0481, found 237.0482.



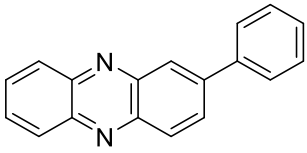
Thieno[2,3-*b*]quinoxaline (5n)

Following the general procedure, the mixture of 2-(thiophen-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **2n** (40.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography

on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **5n** (15.2 mg) in 41% yield as a white solid. M.p.: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, J = 6.0 Hz, 1H), 7.81-7.83 (m, 2H), 8.07 (d, J = 6.4 Hz, 1H), 8.18-8.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.7, 128.8, 129.56, 129.58, 129.7, 135.9, 140.4, 141.1, 150.4, 156.1. HRMS (ESI^+): calcd for $C_{10}H_7N_2S^+$ $[M+H]^+$ 187.0324, found 187.0325.



(**6a**)



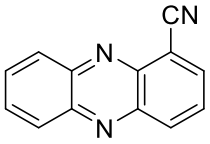
(**7a**)

1-Phenylphenazine (**6a**) **2-Phenylphenazine** (**7a**)

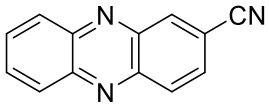
Following the general procedure, the mixture of 2-([1,1'-biphenyl]-3-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3a** (54.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/DCM= 20/1/10, v/v) afforded the product **6a** (29.2 mg) in 57% yield and **7a** (9.7 mg) in 19% yield as a yellow solid.

6a M.p.: 151-153 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.47-7.51 (m, 1H), 7.54-7.58 (m, 2H), 7.77-7.82 (m, 1H), 7.83-7.87 (m, 3H), 7.88-7.93 (m, 2H), 8.21-8.23 (m, 1H), 8.24-8.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 128.0, 128.2, 129.2, 129.5, 130.2, 130.46, 130.52, 130.6, 130.8, 131.1, 138.5, 141.2, 141.9, 143.1, 143.4, 143.7. HRMS (ESI^+): calcd for $C_{18}H_{13}N_2^+$ $[M+H]^+$ 257.1073, found 257.1075.

7a M.p.: 157-159 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.44-7.48 (m, 1H), 7.53-7.57 (m, 2H), 7.83-7.86 (m, 4H), 8.15 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.24-8.27 (m, 2H), 8.32 (dd, J = 9.2 Hz, 0.8 Hz, 1H), 8.46 (dd, J = 2.0 Hz, 0.4Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 126.6, 127.5, 127.7, 128.7, 129.3, 129.7, 129.8, 130.1, 130.5, 130.7, 130.9, 139.6, 143.1, 143.6, 143.8, 144.0. HRMS (ESI^+): calcd for $C_{18}H_{13}N_2^+$ $[M+H]^+$ 257.1073, found 257.1072.



(**6b**)



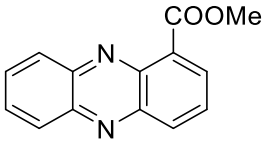
(**7b**)

Phenazine-1-carbonitrile (**6b**) **Phenazine-2-carbonitrile** (**7b**)

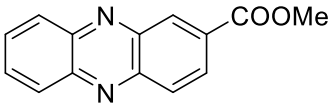
Following the general procedure, the mixture of 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzonitrile **3b** (43.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/DCM = 3/1, v/v) afforded the product **6b** (13.5 mg) in 33% yield and **7b** (9.8 mg) in 24% yield as a yellow solid.

6b M.p.: 180-182 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.88-7.97 (m, 3H), 8.25-8.31 (m, 2H), 8.39-8.42 (m, 1H), 8.48-8.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 113.7, 116.5, 129.1, 129.8, 130.3, 132.1, 132.2, 135.2, 137.3, 142.1, 142.4, 144.2, 144.5. HRMS (ESI$^+$): calcd for $C_{13}H_8N_3^+$ $[M+H]^+$ 206.0713, found 206.0715.

7b M.p.: 215-217 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 7.91-7.96 (m, 3H), 8.26-8.29 (m, 2H), 8.35 (dd, *J* = 9.2 Hz, 0.8 Hz, 1H), 8.68 (dd, *J* = 2.0 Hz, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 114.0, 118.2, 129.8, 130.0, 130.2, 131.7, 132.0, 132.6, 136.8, 142.1, 144.0, 144.7, 144.8. HRMS (ESI$^+$): calcd for $C_{13}H_8N_3^+$ $[M+H]^+$ 206.0713, found 206.0713.



(**6c**)



(**7c**)

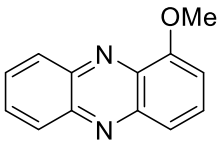
Methyl phenazine-1-carboxylate (**6c**) **Methyl phenazine-2-carboxylate** (**7c**)

Following the general procedure, the mixture of methyl 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)benzoate **3c** (50.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ ethyl acetate = 5/1, v/v) afforded the product **6c** (17.8 mg) in 37% yield and **7c** (12.0 mg) in 25% yield as a yellow solid.

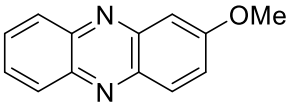
6c M.p.: 135-137 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 4.11 (s, 3H), 7.84-7.88 (m, 3H), 8.22-8.25 (m, 2H), 8.32-8.35 (m, 1H), 8.39 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 52.9, 129.2, 129.6, 130.6, 131.1, 131.4, 131.6, 132.2, 133.6, 141.2,

142.9, 143.5, 143.9, 167.3. HRMS (ESI$^+$): calcd for $C_{14}H_{11}N_2O_2^+$ $[M+H]^+$ 239.0815, found 239.0819.

7c M.p.: 125-127 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 4.04 (s, 3H), 7.85-7.92 (m, 2H), 8.24-8.29 (m, 3H), 8.39 (dd, J = 9.2 Hz, 2.0 Hz, 1H), 8.99-9.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 52.9, 129.4, 129.9, 130.11, 130.14, 131.1, 131.7, 131.8, 133.1, 142.7, 144.3, 144.5, 144.8, 166.4. HRMS (ESI$^+$): calcd for $C_{14}H_{11}N_2O_2^+$ $[M+H]^+$ 239.0815, found 239.0819.



(**6d**)



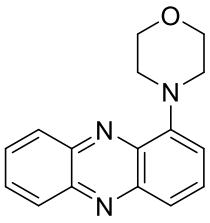
(**7d**)

1-Methoxyphenazine (**6d**) **2-Methoxyphenazine** (**7d**)

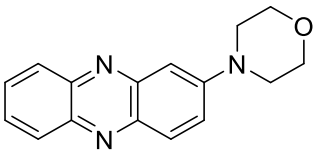
Following the general procedure, the mixture of 2-(3-methoxyphenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3d** (44.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ ethyl acetate = 5/1, v/v) afforded the product **6d** (16.7 mg) in 40% yield and **7c** (9.1 mg) in 21% yield as a yellow solid.

6d M.p.: 121-123 °C.^{1}H NMR (400 MHz,$CDCl_3$) δ = 4.17 (s, 3H), 7.06 (d, J = 7.2 Hz, 1H), 7.72-7.76 (m, 1H), 7.80-7.86 (m, 3H), 8.21-8.23 (m, 1H), 8.38-8.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.6, 106.6, 121.6, 129.4, 130.30, 130.33, 130.7, 131.0, 137.0, 142.3, 143.6, 144.4, 155.2. HRMS (ESI$^+$): calcd for $C_{13}H_{11}N_2O^+$ $[M+H]^+$ 211.0866, found 211.0869.

7d M.p.: 165-167 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 4.02 (s, 3H), 7.40 (d, J = 2.4 Hz, 1H), 7.51 (dd, J = 9.6 Hz, 2.8 Hz, 1H), 7.74-7.83 (m, 2H), 8.09 (d, J = 9.6 Hz, 1H), 8.15-8.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 56.1, 104.6, 126.6, 129.0, 129.2, 129.8, 130.6, 130.8, 140.9, 142.0, 143.4, 145.2, 161.4. HRMS (ESI$^+$): calcd for $C_{13}H_{11}N_2O^+$ $[M+H]^+$ 211.0866, found 211.0866.



(**6e**)



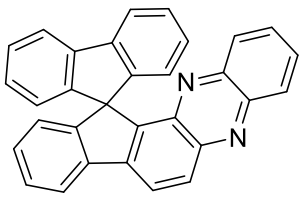
(**7e**)

4-(Phenazin-1-yl)morpholine (**6e**) **4-(Phenazin-2-yl)morpholine** (**7e**)

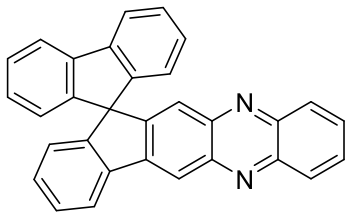
Following the general procedure, the mixture of 4-(3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)phenyl)morpholine **3e** (55.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 ℃ for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ ethyl acetate = 5/1, v/v) afforded the product **6e** (28.0 mg) in 53% yield as a red solid and **7e** (12.0 mg) in 23% yield as an orange solid.

6e M.p.: 169-171 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 3.54 (t, *J* = 4.8 Hz, 4H), 4.11 (t, *J* = 4.4 Hz, 4H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.72-7.76 (m, 1H), 7.78-7.84 (m, 2H), 7.86-7.88 (m, 1H), 8.19-8.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 52.8, 67.2, 115.0, 123.3, 129.3, 130.0, 130.3, 130.7, 131.0, 138.9, 141.3, 143.0, 144.9, 149.2. HRMS (ESI^+): calcd for $C_{16}H_{16}N_3O^+$ $[M+H]^+$ 266.1288, found 266.1286.

7e M.p.: 150-152 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 3.44 (t, *J* = 4.8 Hz, 4H), 3.93 (t, *J* = 4.8 Hz, 4H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.65 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 7.69-7.72 (m, 1H), 7.75-7.79 (m, 1H), 8.07 (d, *J* = 10.0 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 48.6, 66.7, 107.3, 124.7, 128.7, 128.9, 129.7, 130.4, 130.5, 140.5, 141.9, 143.9, 145.3, 152.1. HRMS (ESI^+): calcd for $C_{16}H_{16}N_3O^+$ $[M+H]^+$ 266.1288, found 266.1286.



Spiro[fluorene-9,12'-indeno[2,1-*a*]phenazine] (6f)

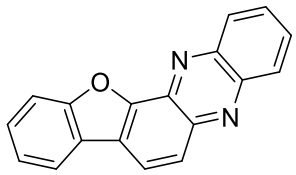


Spiro[fluorene-9,11'-indeno[1,2-*b*]phenazine] (7f)

Following the general procedure, the mixture of 2-(9,9'-spirobi[fluoren]-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3f** (86.4 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/DCM = 5/1, v/v) afforded the product **6f** (28.6 mg) in 34% yield and the product **7f** (21.7 mg) in 26% as a yellow solid.

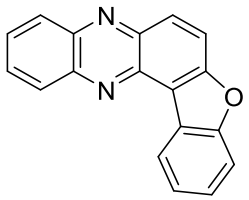
6f M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.65 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 3.6 Hz, 2H), 7.60-7.64 (m, 1H), 7.98-8.02 (m, 3H), 8.05 (d, *J* = 8.8 Hz, 1H), 8.32-8.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 66.3, 120.2, 120.6, 123.2, 123.9, 124.2, 127.3, 127.6, 127.9, 128.7, 129.3, 129.8, 130.0, 130.5, 131.0, 140.1, 141.2, 142.5, 143.2, 143.5, 143.8, 143.86, 143.95, 148.0, 151.5. HRMS (ESI^+): calcd for $C_{31}H_{19}N_2^+$ $[M+H]^+$ 419.1543, found 419.1540.

7f M.p.: 253-255 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82 (d, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 7.12 (td, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.29 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.40 (td, *J* = 7.6 Hz, 0.8 Hz, 2H), 7.48-7.53 (m, 2H), 7.73-7.82 (m, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 8.06 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.23 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 8.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 65.4, 118.4, 120.3, 122.1, 124.1, 124.4, 125.0, 128.2, 128.3, 128.7, 129.5, 129.6, 130.1, 130.4, 130.7, 139.9, 141.6, 142.9, 143.4, 144.0, 144.2, 145.3, 149.5, 149.9, 153.3. HRMS (ESI^+): calcd for $C_{31}H_{19}N_2^+$ $[M+H]^+$ 419.1543, found 419.1540.



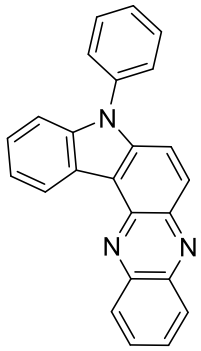
Benzofuro[2,3-*a*]phenazine (6g)

Following the general procedure, the mixture of 2-(dibenzo[*b*,*d*]furan-3-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3g** (56.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded the product **6g** (37.8 mg) in 70% yield as a yellow solid. M.p.: 234-236 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.49 (m, 1H), 7.55-7.59 (m, 1H), 7.85-7.92 (m, 3H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 9.2 Hz, 1H), 8.27-8.30 (m, 1H), 8.34 (d, *J* = 8.8 Hz, 1H), 8.44-8.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 112.9, 120.8, 123.0, 123.7, 123.9, 124.4, 125.4, 127.8, 129.86, 129.88, 130.6, 131.1, 133.6, 142.8, 143.1, 143.8, 149.6, 157.1. HRMS (ESI^+): calcd for $C_{18}H_{11}N_2O^+$ $[M+H]^+$ 271.0866, found 271.0867.



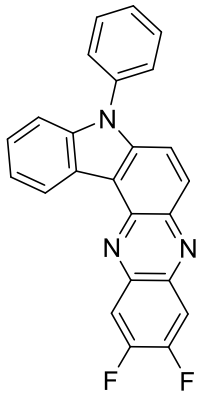
Benzofuro[3,2-*a*]phenazine (6h)

Following the general procedure, the mixture of 2-(dibenzo[*b*,*d*]furan-2-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3h** (56.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded the product **6h** (32.5 mg) in 60% yield as a yellow solid. M.p.: 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.54 (m, 2H), 7.67-7.70 (m, 1H), 7.80-7.88 (m, 2H), 8.05 (d, *J* = 9.2 Hz, 1H), 8.18 (d, *J* = 9.6 Hz, 1H), 8.24-8.26 (m, 1H), 8.32-8.34 (m, 1H), 8.84-8.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.8, 118.0, 119.2, 123.8, 124.1, 124.6, 126.7, 129.3, 129.7, 129.9, 130.6, 140.5, 141.8, 142.2, 143.0, 156.1, 156.3. HRMS (ESI^+): calcd for $C_{18}H_{11}N_2O^+$ $[M+H]^+$ 271.0866, found 271.0867.



8-Phenyl-8*H*-indolo[3,2-*a*]phenazine (6i)

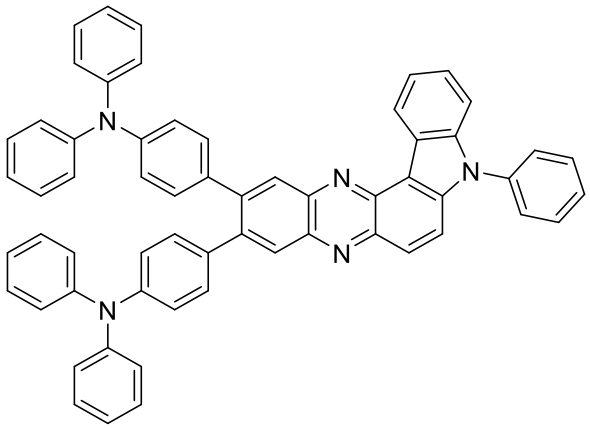
Following the general procedure, the mixture of 3-(1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-9-phenyl-9*H*-carbazole **3i** (71.8 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 10/1/1, v/v) afforded the product **6i** (60.0 mg) in 87% yield as a red solid. M.p.: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50-7.60 (m, 4H), 7.63-7.70 (m, 4H), 7.80-7.84 (m, 1H), 7.87-7.93 (m, 2H), 8.12 (d, J = 9.2 Hz, 1H), 8.28-8.30 (m, 1H), 8.44-8.47 (m, 1H), 9.31 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.8, 115.2, 119.0, 122.2, 123.9, 124.4, 125.4, 127.7, 128.0, 128.6, 128.8, 129.66, 129.71, 130.1, 130.2, 136.8, 139.7, 140.1, 141.3, 141.8, 142.0, 143.2. HRMS (ESI^+): calcd for $C_{24}H_{16}N_3^+$ $[M+H]^+$ 346.1339, found 346.1334.



2,3-Difluoro-8-phenyl-8*H*-indolo[3,2-*a*]phenazine (6j)

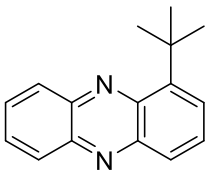
Following the general procedure, the mixture of 3-(5,6-difluoro-1,3-dihydro-2*H*-benzo[*d*][1,3,2]diazaborol-2-yl)-9-phenyl-9*H*-carbazole **3j** (79.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded

the product **6j** (51.0 mg) in 67% yield as a yellow solid. M.p.: 162-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49-7.64 (m, 6H), 7.68-7.71 (m, 2H), 7.91-7.98 (m, 2H), 8.04 (d, *J* = 9.6 Hz, 1H), 8.12 (dd, *J* = 10.8 Hz, 8.8 Hz, 1H), 9.20 (*d*, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.9, 114.07, 114.08, 114.21, 114.23, 114.25, 114.38, 114.40, 119.3, 122.3, 123.7, 124.2, 125.6, 127.6, 127.7, 128.7, 130.3, 136.6, 138.3, 139.8, 140.1, 141.5. HRMS (ESI^+): calcd for $C_{24}H_{14}F_2N_3^+$ $[M+H]^+$ 382.1150, found 382.1148.

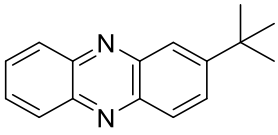


4,4'-(8-Phenyl-8*H*-indolo[3,2-a]phenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) (6k)

Following the general procedure, the mixture of 4,4'-(2-(9-phenyl-9*H*-carbazol-3-yl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole-5,6-diyl)bis(*N*,*N*-diphenylaniline) **3k** (84.5 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded the product **6k** (73.6 mg) in 88% yield as an orange solid. M.p.: > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.03-7.08 (m, 8H), 7.13-7.16 (m, 8H), 7.21-7.25 (m, 5H), 7.27-7.30 (m, 7H), 7.51-7.60 (m, 4H), 7.64-7.71 (m, 4H), 7.91 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 9.2 Hz, 1H), 8.33 (s, 1H), 8.50 (s, 1H), 9.30-9.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 110.8, 115.3, 118.6, 122.2, 122.8, 123.0, 123.1, 123.2, 123.9, 124.5, 124.6, 124.7, 125.3, 127.7, 128.0, 128.6, 129.5, 129.7, 129.9, 130.2, 131.0, 134.6, 134.9, 136.8, 139.7, 140.1, 140.8, 142.0, 142.1, 142.3, 142.6, 143.7, 147.06, 147.14, 147.72, 147.75. HRMS (ESI^+): calcd for $C_{60}H_{42}N_5^+$ $[M+H]^+$ 832.3435, found 832.3429.



(**6l**)



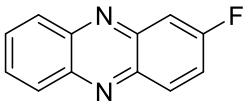
(**7l**)

1-(*tert*-Butyl)phenazine (**6l**) **2-(*tert*-Butyl)phenazine** (**7l**)

Following the general procedure, the mixture of 2-(3-(*tert*-butyl)phenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3l** (50.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ ethyl acetate = 5/1, v/v) afforded the product **6l** (16.1 mg) in 34% yield and **7l** (19.2 mg) in 41% yield as a yellow solid.

6l M.p.: 90-92 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 1.76 (s, 9H), 7.73-7.75 (m, 2H), 7.79-7.84 (m, 2H), 8.09 (dd, J = 6.8 Hz, 3.2 Hz, 1H), 8.19-8.22 (m, 1H), 8.26-8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.3, 37.1, 126.4, 128.4, 129.2, 129.8, 130.35, 130.42, 141.4, 142.1, 143.3, 144.4, 149.0. HRMS (ESI^+): calcd for $C_{16}H_{17}N_2^+$ $[M+H]^+$ 237.1386, found 237.1383.

7l M.p.: 138-140 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ = 1.49 (s, 9H), 7.80-7.85 (m, 2H), 7.95-7.97 (m, 1H), 8.15-8.20 (m, 2H), 8.22-8.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 30.9, 35.7, 124.1, 129.1, 129.6, 129.8, 130.1, 130.4, 130.6, 142.5, 143.3, 143.6, 143.8, 154.1. HRMS (ESI^+): calcd for $C_{16}H_{17}N_2^+$ $[M+H]^+$ 237.1386, found 237.1383.



2-Fluorophenazine (6m)

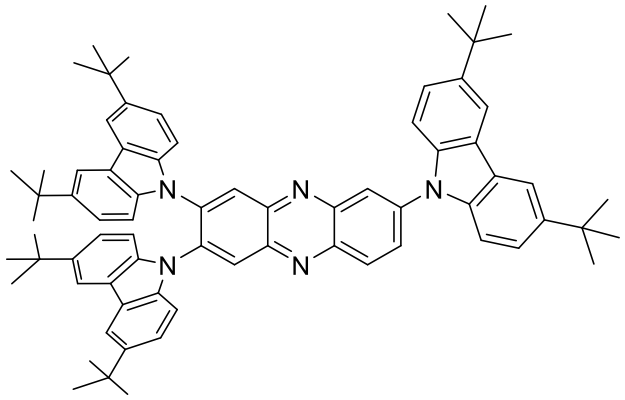
Following the general procedure, the mixture of 2-(2,4-difluorophenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole **3m** (46.0 mg, 0.2 mmol), Ag_2O (185.4 mg, 4.0 equiv), DMSO (2 mL) was stirred at 80 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ ethyl acetate = 10/1, v/v) afforded the product **6m** (20.0 mg) in 50% yield as a yellow solid. M.p.: 198-200 °C. ^{1}H NMR (400 MHz, DMSO-*d6*) δ = 7.91-7.94 (m, 1H), 7.95-8.01 (m, 3H), 8.21-8.26 (m, 2H), 8.32-8.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.8 (d, J_{CF} = 21 Hz), 122.7 (d, J_{CF} = 28 Hz), 129.4, 129.9 (d, J_{CF} = 1 Hz), 130.5(d, J_{CF} = 1 Hz), 131.3, 132.2 (d, J_{CF} = 10 Hz), 141.1, 143.1

(d, J_{CF} = 2 Hz), 143.8, 144.0 (d, J_{CF} = 13 Hz), 163.2 (d, J_{CF} = 254 Hz). HRMS (ESI^+): calcd for $C_{12}H_8FN_2^+$ $[M+H]^+$ 199.0666, found 199.0663.

iv) General procedure for the nucleophilic aromatic substitution reaction and suziki reaction.

1) General procedure for nucleophilic aromatic substitution reaction

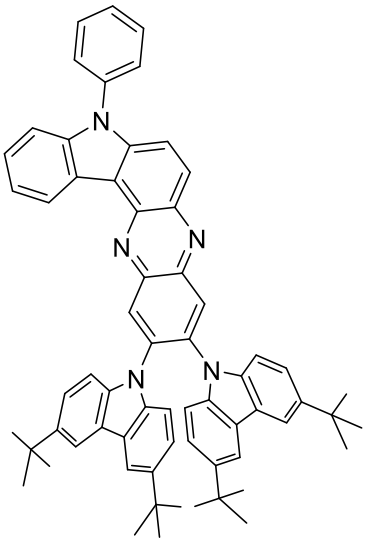
A dried Schlenk tube with a magnetic stir bar was charged with several of 3,6-bis(*tert*-butyl)carbazole (2.5 equiv), *t*-BuOk (2.5 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMF (2 mL) was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred 30 min at room temperature, followed the fluoro-substituted phenazines (0.2 mmol) were added, the reaction was stirred at 80 °C for 8 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.



2,3,7-Tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenazine (8a)

Following the general procedure, the mixture of 7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-2,3-difluorophenazine **5b** (98.6 mg, 0.2 mmol), 3,6-bis(*tert*-butyl)carbazole (139.71mg, 2.5 equiv), *t*-BuOk (56.1 mg, 2.5equiv), DMF (3 mL) was stirred at 80 °C for 8 h. Purification *via* column chromatography on silica gel (petroleum ether/ DCM = 3/1, v/v) afforded the product **8a** (161.8 mg) in 80% yield as a salmon solid. M.p.: 232-234 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ =1.36 (d, J = 2.4 Hz, 36H), 1.51 (s, 18H), 6.91

(d, *J* = 8.4 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 7.57 (dd, *J* = 8.8 Hz, 2.0 Hz, 2H), 7.63 (s, 4H), 7.71 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 5.2 Hz, 2H), 8.25 (dd, *J* = 9.2 Hz, 2.0 Hz, 1H), 8.49-8.53 (m, 2H), 8.72 (s, 1H), 8.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 32.0, 32.1, 34.6, 35.0, 109.01, 109.03, 109.7, 115.5, 116.7, 123.0, 123.8, 123.9, 124.2, 124.4, 129.6, 130.0, 130.4, 131.4, 137.9, 138.1, 138.2, 138.6, 140.7, 142.7, 142.9, 143.3, 143.4, 144.3. HRMS (ESI+): calcd for $C_{72}H_{78}N_5^+$ $[M+H]^+$ 1012.6252, found 1012.6255.



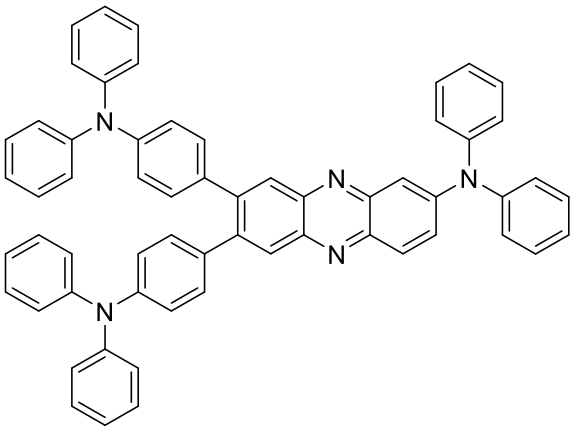
2,3-Bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-8-phenyl-8*H*-indolo[3,2-*a*]phenazine (8b)

Following the general procedure, the mixture of 2,3-difluoro-8-phenyl-8*H*-indolo[3,2-*a*]phenazine **6j** (76.2 mg, 0.2 mmol), 3,6-bis(*tert*-butyl)carbazole (139.71mg, 2.5 equiv), *t*-BuOK (56.1 mg, 2.5equiv), DMF (3 mL) was stirred at 80 °C for 8 h. Purification *via* column chromatography on silica gel (petroleum ether/ DCM = 3/1, v/v) afforded the product **8b** (134.9 mg) in 75% yield as a yellow solid. M.p.: 225-227 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ =1.36 (d, *J* = 4.4 Hz, 36H), 6.89-6.95 (m, 4H), 6.97-7.02 (m, 4H), 7.51-7.59 (m, 3H), 7.62-7.65 (m, 5H), 7.69-7.74 (m, 4H), 8.01 (d, *J* = 9.6 Hz, 1H), 8.19 (d, *J* = 9.2 Hz, 1H), 8.75 (s, 1H), 8.89 (s, 1H), 9.33 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 32.0, 34.63, 34.64, 109.16, 109.18, 110.9, 115.4, 115.4, 119.7, 122.5, 122.90, 122.94, 123.81, 123.84, 124.0, 125.6, 127.7, 128.0, 128.7, 129.9, 130.1, 130.3, 135.5, 136.7, 136.9, 138.4, 138.5, 140.0, 140.4, 142.3, 142.3, 142.5,

143.0, 143.1. HRMS (ESI$^+$): calcd for $C_{64}H_{62}N_5^+$ $[M+H]^+$ 900.5000, found 900.4991.

2) General procedure for suzuki reaction

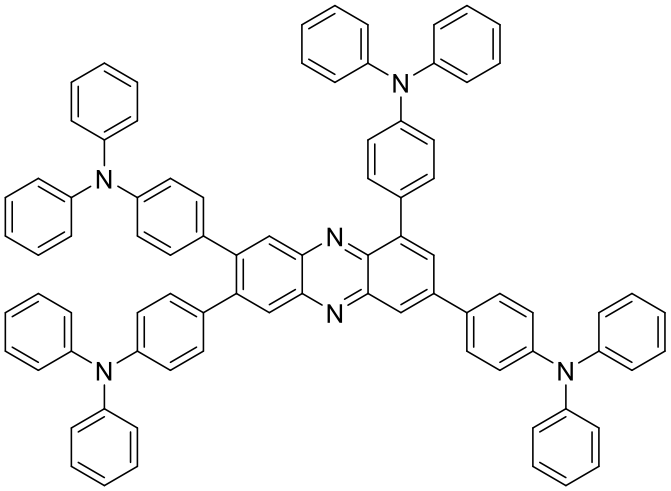
A dried Schlenk tube with a magnetic stir bar was charged with several of bromo-substituted phenazines (0.2 mmol), 4-(diphenylamino)phenylboronic acid (2.25 equiv), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent dioxane and H_2O (3.3 mL, V/V = 10:1) was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at 90 °C for 24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.



4,4'-(7-(Diphenylamino)phenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) (8c)

Following the general procedure, the mixture of 7,8-dibromo-*N*,*N*-diphenylphenazin-2-amine **5c** (100.6 mg, 0.2 mmol), 4-(diphenylamino)phenylboronic acid (130.1 mg, 2.25 equiv), $Pd(PPh_3)_4$ (11.6 mg, 5 mol%), K_2CO_3 (110 mg, 4.0 equiv). dioxane/H_2O (3 mL, 10/1) was stirred at 90 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ DCM = 3/1, v/v) afforded the product **8c** (143.3 mg) in 86% yield as a red solid. M.p.: 236-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00-7.07 (m, 8H), 7.13-7.23 (m, 14H), 7.26-7.29 (m, 12H), 7.39 (t, J = 8.0 Hz, 4H), 7.49 (d, J = 2.4 Hz, 1H), 7.66 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 8.01 (d, J = 9.6 Hz, 1H), 8.09 (s, 1H), 8.19

(s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 114.0, 122.5, 122.7, 123.19, 123.23, 124.7, 124.8, 125.2, 126.3, 128.1, 128.9, 129.4, 129.7, 129.8, 129.9, 130.8, 134.2, 134.4, 141.4, 141.6, 142.4, 143.4, 144.1, 145.4, 146.5, 147.1, 147.2, 147.6, 147.7, 149.6. HRMS (ESI^+): calcd for $C_{60}H_{44}N_5^+$ $[M+H]^+$： 834.3591, found 834.3590.

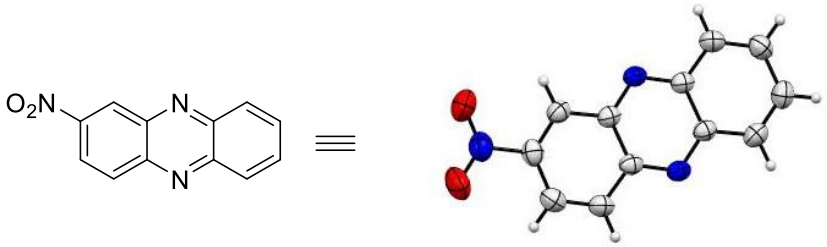


4,4',4'',4'''-(Phenazine-1,3,7,8-tetrayl)tetrakis(*N*,*N*-diphenylaniline) (8d)

Following the general procedure, the mixture of 4,4'-(6,8-dibromophenazine-2,3-diyl)bis(*N*,*N*-diphenylaniline) **5e** (164.4 mg, 0.2 mmol), 4-(diphenylamino)phenylboronic acid (130.1 mg, 2.25 equiv), $Pd(PPh_3)_4$ (11.6 mg, 5 mol%), K_2CO_3 (110 mg, 4.0 equiv). dioxane/H_2O (3 mL, 10/1) was stirred at 90 °C for 24 h. Purification *via* column chromatography on silica gel (petroleum ether/ DCM = 3/1, v/v) afforded the product **8d** (209.7 mg) in 91% yield as a red solid. M.p.: 245-247 °C. ^{1}H NMR (400 MHz, $CDCl_2CDCl_2$) δ = 7.66-8.02 (m, 52H), 8.47 (d, J = 8.4 Hz, 4H), 8.83-8.90 (m, 3H), 9.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.5, 122.79, 122.82, 123.18, 123.24, 123.3, 123.4, 123.6, 124.1, 124.7, 124.8, 124.9, 124.9, 124.96, 125.04, 128.3, 129.1, 129.5, 129.6, 129.8, 130.5, 130.8, 130.9, 131.9, 132.2, 132.9, 134.1, 134.4, 140.5, 141.6, 141.9, 143.5, 144.46, 144.55, 147.2, 147.3, 147.5, 147.6, 147.7, 147.8, 148.4. HRMS (ESI^+): calcd for $C_{84}H_{61}N_6^+$ $[M+H]^+$： 1153.4952, found 1153.4951.

IV. Single crystal X-ray structures of 4j, 4m, 5a, 6f, 6h, 6i, 6j, 6k.

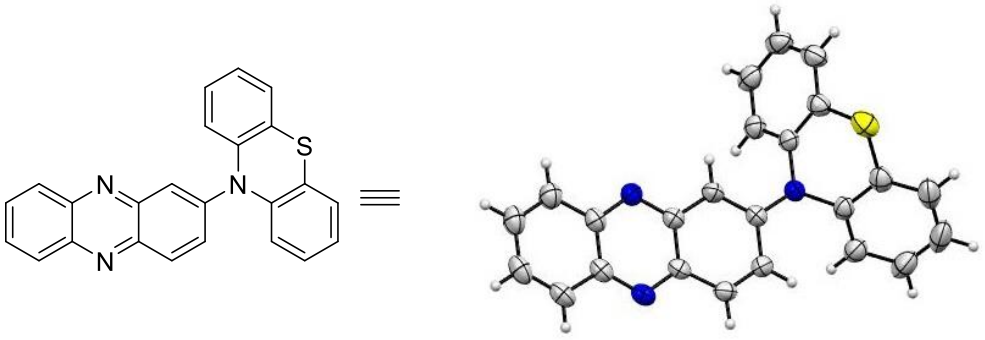
Table S2. Crystal data and structure refinement for 4j



(CCDC:2041452)

Identification code	**4j**
Empirical formula	$C_{12}H_7N_3O_2$
Formula weight	225.21
Temperature/K	296.4(8)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.8370(4)
b/Å	22.4145(11)
c/Å	7.1605(4)
α/°	90
β/°	114.235(7)
γ/°	90
Volume/Å^3	1000.63(10)
Z	4
ρ_{calc}g/cm^3	1.495
μ/mm^{-1}	0.884
F(000)	464
Crystal size/mm^3	0.5 × 0.3 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.888 to 142.538
Index ranges	$-6 \le h \le 8$, $-27 \le k \le 27$, $-8 \le l \le 8$
Reflections collected	5414
Independent reflections	1917 [R_{int} = 0.0327, R_{sigma} = 0.0253]
Data/restraints/parameters	1917/0/154
Goodness-of-fit on F^2	1.1
Final R indexes [I>=2σ (I)]	R_1 = 0.0702, wR_2 = 0.2204
Final R indexes [all data]	R_1 = 0.0785, wR_2 = 0.2332
Largest diff. peak/hole / e Å^{-3}	0.32/-0.30

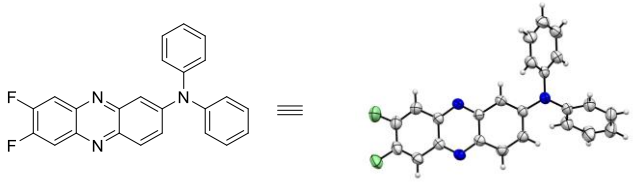
Table S3. Crystal data and structure refinement for 4m



(CCDC: 2041804)

Identification code	**4m**
Empirical formula	C24H15N3S
Formula weight	377.45
Temperature/K	295.7(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	10.2292(3)
b/Å	16.3951(5)
c/Å	11.6492(3)
α/°	90
β/°	113.281(4)
γ/°	90
Volume/Å3	1794.60(10)
Z	4
ρcalcg/cm3	1.397
μ/mm-1	1.707
F(000)	784
Crystal size/mm3	0.6 × 0.4 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.412 to 143.122
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -11 ≤ l ≤ 14
Reflections collected	8706
Independent reflections	3377 [Rint = 0.0367, Rsigma = 0.0353]
Data/restraints/parameters	3377/0/253
Goodness-of-fit on F2	1.035
Final R indexes [I>=2σ (I)]	R1 = 0.0628, wR2 = 0.1660
Final R indexes [all data]	R1 = 0.0680, wR2 = 0.1770
Largest diff. peak/hole / e Å-3	0.27/-0.42

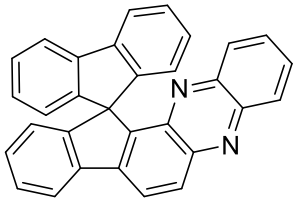
Table S4. Crystal data and structure refinement for 5a



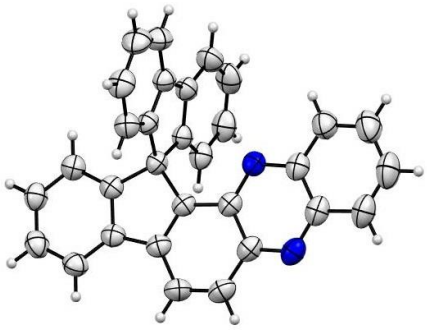
CCDC: 2071049

Identification code	**5a**
Empirical formula	$C_{24}H_{15}F_2N_3$
Formula weight	383.39
Temperature/K	296.75(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.16800(11)
b/Å	22.8606(4)
c/Å	23.0265(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3773.23(13)
Z	8
ρ_{calc}g/cm^3	1.35
μ/mm^{-1}	0.781
F(000)	1584
Crystal size/mm^3	0.5 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.678 to 142.892
Index ranges	-8≤ h ≤5, -27 ≤ k ≤28, -27 ≤ l ≤ 24
Reflections collected	11013
Independent reflections	3607 [R_{int} = 0.0431, R_{sigma} = 0.0335]
Data/restraints/parameters	3607/0/262
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0662, wR_2 = 0.1695
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.1818
Largest diff. peak/hole / e Å^{-3}	0.33/-0.46

Table S5. Crystal data and structure refinement for 6f



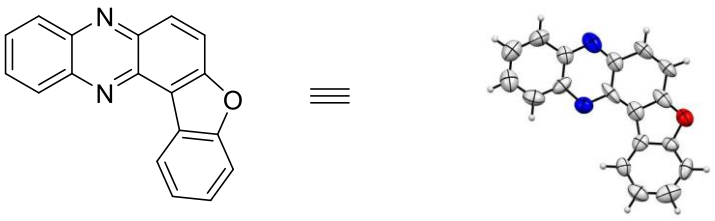
≡



(CCDC: 2041453)

Identification code	**6f**
Empirical formula	$C_{31}H_{18}N_2$
Formula weight	418.47
Temperature/K	292.8(8)
Crystal system	triclinic
Space group	P-1
a/Å	8.2871(4)
b/Å	9.5533(5)
c/Å	14.9700(8)
α/°	73.340(5)
β/°	87.044(4)
γ/°	72.220(5)
Volume/Å^3	1080.34(10)
Z	2
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	0.582
F(000)	436
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.144 to 143.088
Index ranges	-10 ≤ h ≤ 7, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	9414
Independent reflections	4092 [R_{int} = 0.0352, R_{sigma} = 0.0390]
Data/restraints/parameters	4092/0/298
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0644, wR_2 = 0.1739
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1916
Largest diff. peak/hole / e Å^{-3}	0.21/-0.30

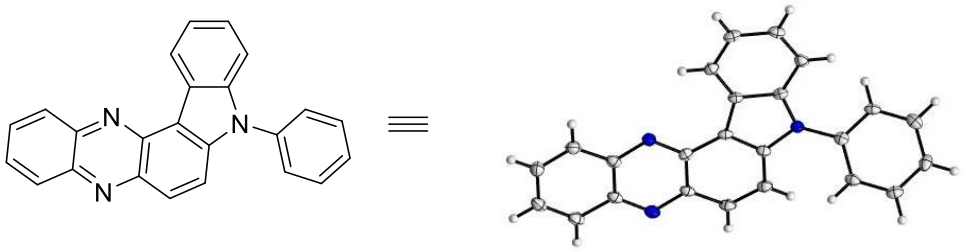
Table S6. Crystal data and structure refinement for 6h



(CCDC: 2110954)

Identification code	**6h**
Empirical formula	$C_{18}H_{10}N_2O$
Formula weight	270.28
Temperature/K	302.0
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	25.483(3)
b/Å	3.8577(3)
c/Å	25.757(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2532.1(4)
Z	8
ρ_{calc}g/cm^3	1.418
μ/mm^{-1}	0.090
F(000)	1120.0
Crystal size/mm^3	0.43 × 0.08 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.496 to 55.08
Index ranges	-33 ≤ h ≤ 33, -4 ≤ k ≤ 5, -33 ≤ l ≤ 33
Reflections collected	34196
Independent reflections	5773 [R_{int} = 0.1241, R_{sigma} = 0.0767]
Data/restraints/parameters	5773/18/379
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0810, wR_2 = 0.2076
Final R indexes [all data]	R_1 = 0.1727, wR_2 = 0.2710
Largest diff. peak/hole / e Å^{-3}	0.80/-0.30

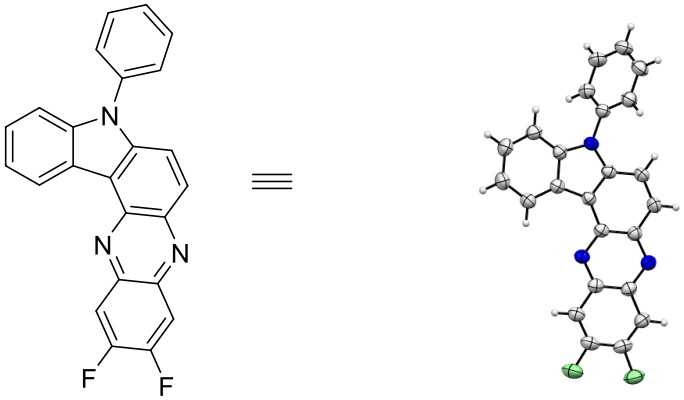
Table S7. Crystal data and structure refinement for 6i



(CCDC: 2041455)

Identification code	**6i**
Empirical formula	$C_{24}H_{15}N_3$
Formula weight	345.39
Temperature/K	150.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	3.91044(13)
b/Å	19.7705(8)
c/Å	21.0267(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1625.60(10)
Z	4
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.661
F(000)	720
Crystal size/mm^3	0.5 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.41 to 142.858
Index ranges	$-4 \le h \le 2$, $-23 \le k \le 14$, $-25 \le l \le 25$
Reflections collected	5486
Independent reflections	2839 [R_{int} = 0.0365, R_{sigma} = 0.0529]
Data/restraints/parameters	2839/0/244
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0602, wR_2 = 0.1569
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.1639
Largest diff. peak/hole / e Å^{-3}	0.26/-0.42
Flack parameter	-0.4(7)

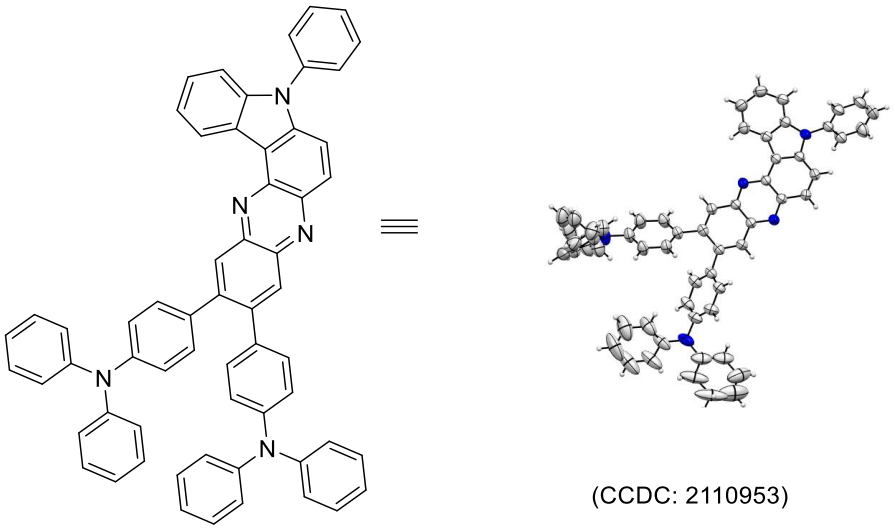
Table S8. Crystal data and structure refinement for 6j



(CCDC: 2110952)

Identification code	**6j**
Empirical formula	$C_{24}H_{13}F_2N_3$
Formula weight	381.37
Temperature/K	298.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.9727(12)
b/Å	21.106(2)
c/Å	13.7772(18)
α/°	90
β/°	120.245(3)
γ/°	90
Volume/Å^3	1751.6(4)
Z	4
ρ_{calc}g/cm^3	1.446
μ/mm^{-1}	0.102
F(000)	784.0
Crystal size/mm^3	0.43 × 0.19 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.86 to 55.008
Index ranges	$-9 \le h \le 9$, $-27 \le k \le 27$, $-17 \le l \le 17$
Reflections collected	20872
Independent reflections	4010 [R_{int} = 0.0744, R_{sigma} = 0.0581]
Data/restraints/parameters	4010/0/263
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1071
Final R indexes [all data]	R_1 = 0.1016, wR_2 = 0.1310
Largest diff. peak/hole / e Å^{-3}	0.19/-0.16

Table S9. Crystal data and structure refinement for 6k



(CCDC: 2110953)

Identification code	**6k**
Empirical formula	$C_{60}H_{42}N_5$
Formula weight	832.98
Temperature/K	298.0
Crystal system	monoclinic
Space group	P2/n
a/Å	9.5511(3)
b/Å	13.5323(3)
c/Å	37.4313(9)
α/°	90
β/°	93.885(2)
γ/°	90
Volume/Å^3	4826.8(2)
Z	4
ρ_{calc}g/cm^3	1.146
μ/mm^{-1}	0.521
F(000)	1748.0
Crystal size/mm^3	0.34 × 0.04 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.732 to 136.76
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -44 ≤ l ≤ 42
Reflections collected	39694
Independent reflections	8794 [R_{int} = 0.0744, R_{sigma} = 0.0563]
Data/restraints/parameters	8794/7/580
Goodness-of-fit on F^2	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0684, wR_2 = 0.1955
Final R indexes [all data]	R_1 = 0.1030, wR_2 = 0.2159
Largest diff. peak/hole / e Å^{-3}	0.40/-0.40

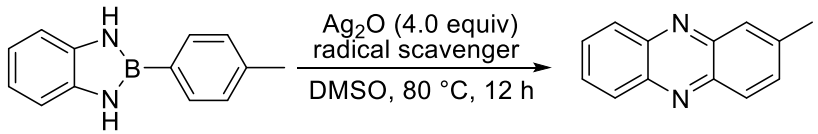
V. Mechanistic study

i) Radical inhibition experiments

General procedure for the oxidative cyclization reaction of 2-aryl diazaboroles in the presence of radical scavenger

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-(*p*-tolyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**1a**, 0.2 mmol), Ag_2O (4.0 equiv) and the radical scavenger. The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at 80 ºC for 24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Table S10. Oxidative cyclization reaction of 2-aryl diazaborole in the presence of radical scavenger[a,b]



1a **4a**

Entry	Radical Scavenger	Equivalent	Yield (%)[b]
1	TEMPO	0.5	70
2	TEMPO	1.0	64
3	TEMPO	2.0	57
4	TEMPO	3.0	54
5	ascorbic acid	0.5	50
6	ascorbic acid	1.0	23
7	ascorbic acid	2.0	0
8	ascorbic acid	3.0	0
9	BHT	0.5	50
10	BHT	1.0	0
11	BHT	2.0	0
12	BHT	3.0	0

[a]Reaction conditions: 2-aryl diazaborole (**1a**, 0.2 mmol), Ag_2O (4.0 equiv) and DMSO (2.0 mL) at

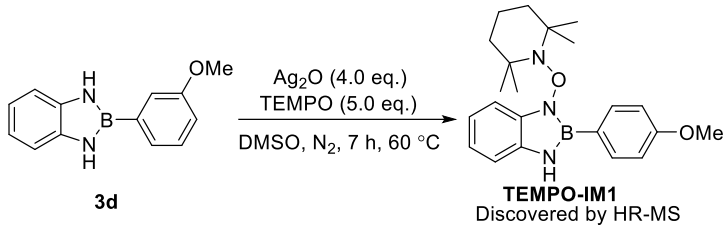
80 ºC for 24 h under N_2. [b]isolated yields. TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy; BHT: 2,6-*di-tert*-butyl-4-methylphenol.

ii) Radical trapping experiment

General procedure for the oxidative cyclization reaction of 2-aryl diazaborole in the presence of radical scavenger TEMPO

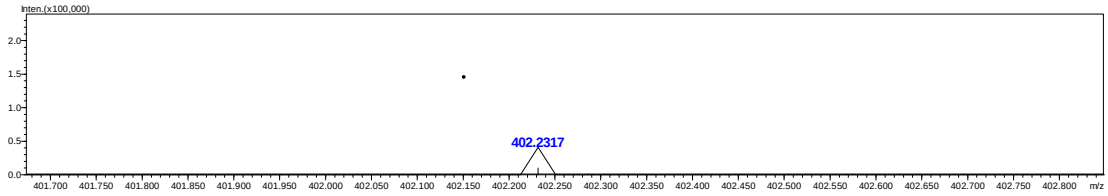
A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-(3-methoxyphenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**3d**, 0.2 mmol), Ag_2O (4.0 equiv) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 5.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at the 60 ºC for 7 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the reaction system was filtered through a celite pad, and then was detected by high resolution mass spectra.

Scheme S6. Oxidative cyclization reaction of 2-aryl diazaborole in the presence of TEMPO[a]



3d **TEMPO-IM1** Discovered by HR-MS

HRMS (ESI$^+$): calcd for $C_{22}H_{30}BN_3NaO_2^+$ [TEMPO-**IM1** + Na]$^+$ 402.2323, found 402.2317.



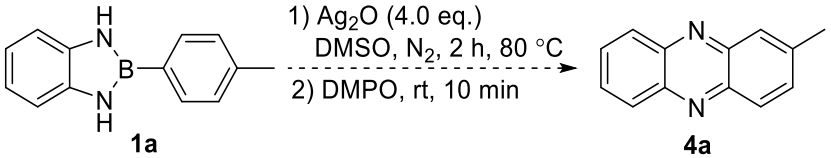
[a]Reaction conditions: 2-aryl diazaborole (**3d**, 0.2 mmol), Ag_2O (4.0 equiv), TEMPO (5.0 equiv) and DMSO (2.0 mL) at 60 ºC for 7 h under N_2. TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy.

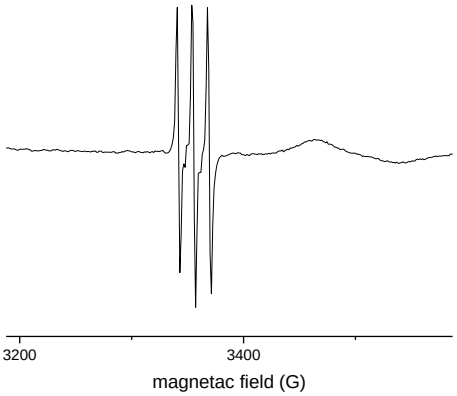
iii) Electron paramagnetic resonance (EPR) experiment

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-(*p*-tolyl)-2,3-

dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**1a**, 0.2 mmol), Ag_2O (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at the 80 ºC for 2 h in an oil bath. Followed by the addition of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 23 μL). The reaction mixture was stirred at room temperature for 10 minutes. Detected by a Bruker A300 spectrometer at room temperature. For the experimental EPR spectrum of the reaction system, instrument setting were modulation frequency: 100.00 KHz; S22 modulation amplitude: 2.00 G; sweep width: 80.0000 G; time constant: 40.960 ms; conversion: 80.000 ms; sweep time: 81.92 s; receiver gain: 1.00 × 103. The microwave power was 18.92 mW, and the frequency was 9.439633 GHz.

Scheme S7. EPR experiment of oxidative cyclization reaction[a]





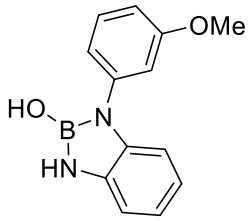
[a]Reaction conditions: 2-aryl diazaborole (**1a**, 0.2 mmol), Ag_2O (4.0 equiv), DMPO (23 μL) and DMSO (2.0 mL) at 80 ºC for 2 h under N_2. DMPO: 5,5-dimethyl-1-pyrroline N-oxide.

iv) Reaction intermediate monitoring experiment

A flame-dried Schlenk tube with a magnetic stir bar was charged with 2-(3-methoxyphenyl)-2,3-dihydro-1*H*-benzo[*d*][1,3,2]diazaborole (**3d** 0.2 mmol), Ag_2O (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent

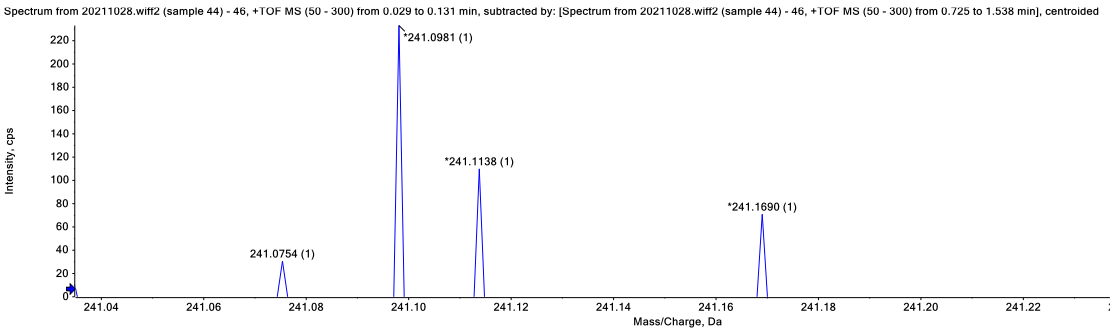
DMSO was added *via* a syringe and the rubber septum was replaced with a stopper under N_2. Then the reaction mixture was stirred at 80 ºC for 1 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the reaction system was filtered through a celite pad under N_2 atmosphere, and then was detected by High resolution mass spectra.

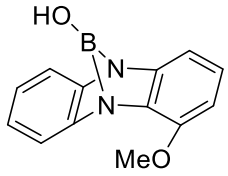
Scheme S8. Detection of intermediate with high resolution mass

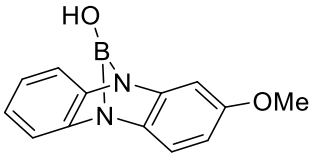


Intermediate **IM3**

HRMS (ESI$^+$): calcd for $C_{13}H_{14}BN_2O_2^+$ [**IM3** + H]$^+$ 241.1143, found 241.1138.

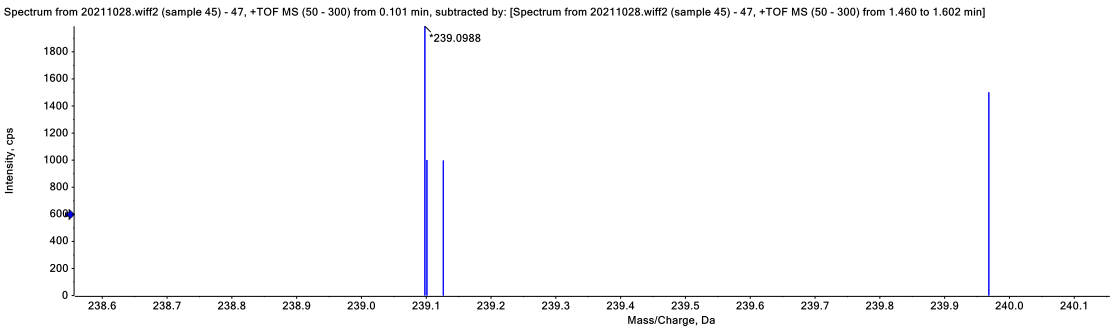


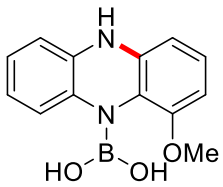


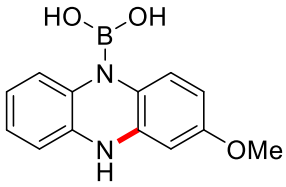


Intermediate **IM7** Intermediate **IM9**

HRMS (ESI$^+$): calcd for $C_{13}H_{12}BN_2O_2^+$ [**IM7** + H]$^+$ or [**IM9** + H] $^+$ 239.0986, found 239.0988.

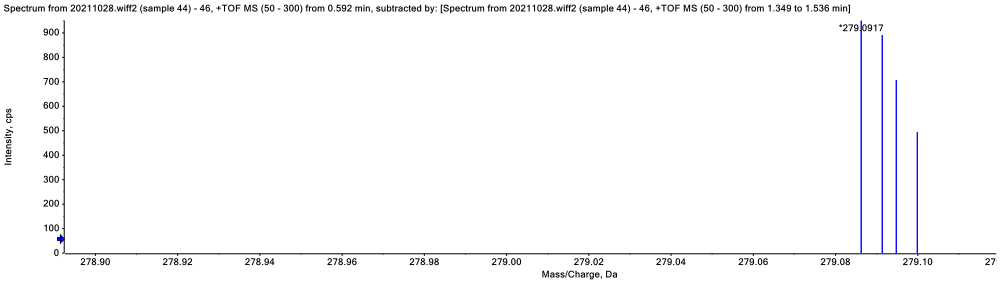






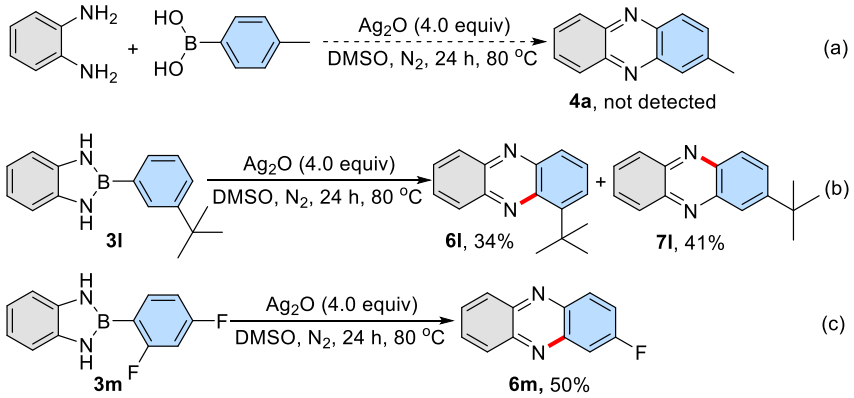
Intermediate **IM8** Intermediate **IM10**

HRMS (ESI$^+$): calcd for $C_{13}H_{13}BN_2NaO_3^+$ [**IM8** + H]$^+$ or [**IM10** + H]$^+$ 279.0911, found 279.0917.

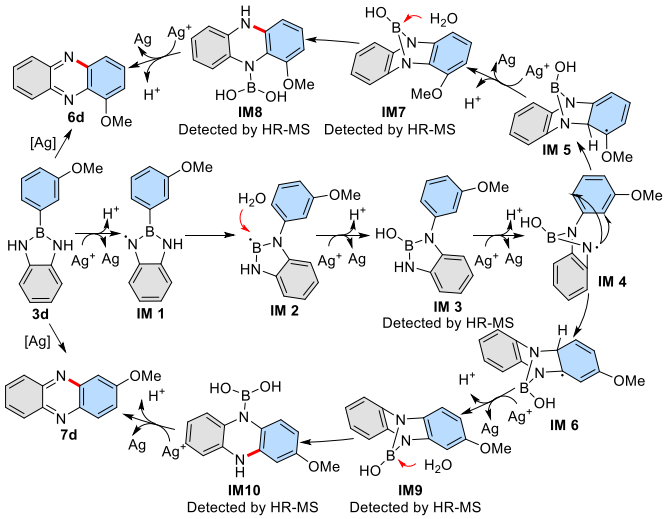


v) Plausible mechanistic pathway

Scheme S9. Comparative experiments



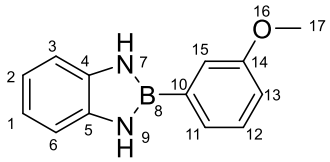
Scheme S10. Plausible mechanistic pathway



VI. DFT calculations of local electrophilicity/nucleophilicity

The Fukui functions for electrophilic and nucleophilic attacks were calculated based on the molecular geometries optimized at the density functional theory (DFT) wB97XD/6-31G (d, p) level with solvation model based on density (SMD) in DMSO.

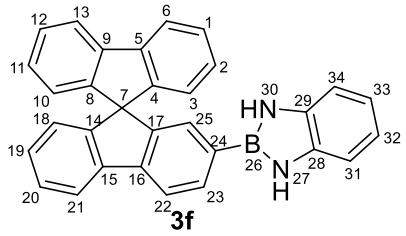
Table S11. Fukui functions (f_k^+, f_k^-), local softness (s_k^+, s_k^-), and local electrophilicity indices (ω_k) and local nucleophilicity indices (N_k) for selected atomic sites of 3d, using Mulliken population analysis at wB97XD/6-31 G (d, p) level



3d

Atom (k)	q(N)	q(N+1)	q(N-1)	f_k^-	f_k^+	s_k^-	s_k^+	N_k	ω_k
1(C)	0.0121	-0.0854	0.0907	0.0786	0.0974	1.3839	1.7164	0.07778	1.0294
2(C)	0.0118	-0.0852	0.0903	0.0786	0.0969	1.3841	1.7072	0.07778	1.02392
3(C)	-0.0312	-0.0806	0.0092	0.0404	0.0494	0.7107	0.8707	0.03994	0.5222
4(C)	0.1127	0.0148	0.2004	0.0877	0.0979	1.5452	1.724	0.08684	1.03396
5(C)	0.1125	0.0146	0.2	0.0875	0.0979	1.5418	1.7236	0.08665	1.03372
6(C)	-0.0315	-0.0806	0.0088	0.0403	0.0491	0.7103	0.8646	0.03992	0.51852
7(N)	-0.0789	-0.1404	-0.0039	0.075	0.0614	1.3218	1.0822	0.07428	0.64907
8(B)	0.2134	0.1253	0.2765	0.0631	0.0881	1.1117	1.552	0.06247	0.93079
9(N)	-0.0794	-0.1404	-0.0041	0.0753	0.061	1.3263	1.074	0.07454	0.64414
10(C)	-0.0824	-0.0872	-0.0628	0.0196	0.0048	0.3449	0.0844	0.01938	0.05063
11(C)	-0.0485	-0.065	-0.0179	0.0306	0.0165	0.5397	0.2903	0.03033	0.17411
12(C)	-0.0441	-0.0534	-0.028	0.0161	0.0094	0.2834	0.1652	0.01593	0.09906
13(C)	-0.056	-0.0754	-0.0177	0.0383	0.0194	0.6743	0.341	0.03789	0.2045
14(C)	0.0721	0.0654	0.0839	0.0118	0.0067	0.2085	0.1187	0.01172	0.07121
15(C)	-0.0509	-0.0678	-0.0268	0.024	0.0169	0.4231	0.2979	0.02377	0.17869
16(O)	-0.1477	-0.1507	-0.142	0.0057	0.003	0.1007	0.0525	0.00566	0.03148
17(C)	0.0077	0.0061	0.0103	0.0026	0.0016	0.0455	0.0287	0.00256	0.01722

Table S12. Fukui functions (f_k^+, f_k^-), local softness (s_k^+, s_k^-), and local electrophilicity indices (ω_k) and local nucleophilicity indices (N_k) for selected atomic sites of 3f, using Mulliken population analysis at wB97XD/6-31 G (d, p) level

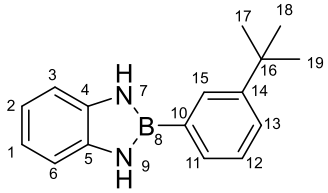


3f

Atom (k)	q(N)	q(N+1)	q(N-1)	f_k^-	f_k^+	s_k^-	s_k^+	N_k	ω_k
1(C)	-0.0436	-0.051	-0.0388	0.0048	0.0075	0.0335	0.0524	0.01662	0.01257
2(C)	-0.0435	-0.0491	-0.0399	0.0036	0.0056	0.0256	0.039	0.01271	0.00935
3(C)	-0.0445	-0.0488	-0.0422	0.0024	0.0043	0.0166	0.0301	0.00822	0.00723
4(C)	-0.0022	-0.0006	-0.0021	0.0001	-0.0016	0.0008	-0.0113	0.0004	-0.00272
5(C)	-0.0121	-0.0163	-0.0091	0.003	0.0042	0.021	0.0293	0.01042	0.00703
6(C)	-0.044	-0.0495	-0.0409	0.0031	0.0055	0.0219	0.0386	0.01088	0.00925
7(C)	0.0188	0.0146	0.0211	0.0023	0.0041	0.0163	0.0289	0.00811	0.00693
8(C)	-0.0023	-0.0006	-0.0021	0.0002	-0.0016	0.0012	-0.0113	0.00058	-0.00271
9(C)	-0.0122	-0.0163	-0.0091	0.003	0.0042	0.0214	0.0293	0.01061	0.00701
10(C)	-0.0446	-0.049	-0.0422	0.0024	0.0043	0.017	0.0303	0.00845	0.00728
11(C)	-0.0437	-0.0492	-0.04	0.0037	0.0055	0.0257	0.0389	0.01275	0.00933
12(C)	-0.0437	-0.0511	-0.0388	0.0048	0.0074	0.034	0.0523	0.01689	0.01253
13(C)	-0.0441	-0.0496	-0.041	0.0031	0.0055	0.022	0.0385	0.0109	0.00923
14(C)	-0.0013	-0.0281	0.0131	0.0144	0.0267	0.1013	0.1878	0.05028	0.04502
15(C)	-0.012	-0.0516	0.0004	0.0124	0.0396	0.087	0.2783	0.04317	0.06672
16(C)	-0.0089	-0.0692	0.0236	0.0324	0.0603	0.2278	0.4238	0.11304	0.10161
17(C)	-0.0032	-0.0339	0.0129	0.016	0.0307	0.1124	0.2158	0.05579	0.05175
18(C)	-0.0443	-0.0801	-0.0339	0.0104	0.0358	0.0731	0.2516	0.03629	0.06031
19(C)	-0.0425	-0.1085	-0.0177	0.0248	0.066	0.1743	0.4636	0.08648	0.11114
20(C)	-0.0431	-0.0751	-0.0291	0.0141	0.032	0.0988	0.2246	0.04903	0.05384
21(C)	-0.0431	-0.0958	-0.0262	0.0169	0.0527	0.1186	0.3702	0.05885	0.08875
22(C)	-0.0447	-0.1004	-0.024	0.0207	0.0557	0.1456	0.3909	0.07226	0.09371
23(C)	-0.0385	-0.0799	-0.0102	0.0283	0.0414	0.1984	0.2907	0.09847	0.06969
24(C)	-0.0763	-0.1481	-0.0515	0.0248	0.0719	0.1741	0.5047	0.08642	0.12099
25(C)	-0.0402	-0.0884	-0.0203	0.0199	0.0482	0.1399	0.3384	0.06942	0.08114
26(B)	0.1179	0.0682	0.1682	0.0504	0.0496	0.3538	0.3486	0.17558	0.08359
27(N)	-0.1332	-0.1472	-0.0845	0.0486	0.0141	0.3416	0.0987	0.16953	0.02366

28(C)	0.0226	0.0164	0.0844	0.0618	0.0062	0.4339	0.0437	0.21532	0.01047
29(C)	0.0226	0.0165	0.0845	0.0618	0.0062	0.4343	0.0435	0.2155	0.01043
30(N)	-0.1332	-0.1469	-0.0851	0.0481	0.0138	0.3379	0.0966	0.16766	0.02317
31(C)	-0.0684	-0.0837	-0.0292	0.0392	0.0154	0.2751	0.1078	0.13652	0.02586
32(C)	-0.0681	-0.0812	0.0019	0.0699	0.0131	0.4912	0.092	0.24375	0.02206
33(C)	-0.068	-0.0812	0.0022	0.0702	0.0132	0.4931	0.093	0.2447	0.02229
34(C)	-0.0683	-0.0836	-0.0294	0.039	0.0153	0.2737	0.1071	0.13584	0.02568

Table S13. Fukui functions (f_k^+, f_k^-), local softness (s_k^+, s_k^-), and local electrophilicity indices (ω_k) and local nucleophilicity indices (N_k) for selected atomic sites of 3l, using Mulliken population analysis at wB97XD/6-31 G (d, p) level



3l

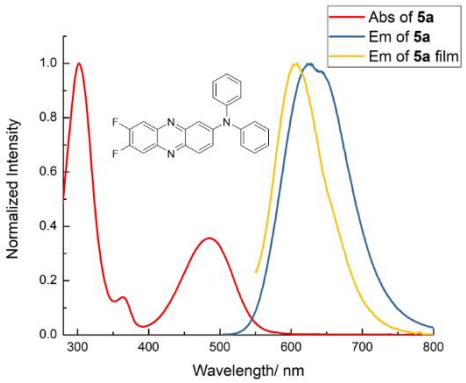
Atom (k)	q(N)	q(N+1)	q(N-1)	f_k^-	f_k^+	s_k^-	s_k^+	N_k	ω_k
1(C)	0.0112	-0.0856	0.089	0.0778	0.0968	1.3815	1.7193	0.0652	1.02259
2(C)	0.0111	-0.0856	0.0889	0.0778	0.0967	1.3812	1.7165	0.06519	1.0209
3(C)	-0.0318	-0.081	0.0084	0.0401	0.0493	0.7126	0.8749	0.03363	0.52037
4(C)	0.1116	0.0143	0.1983	0.0867	0.0972	1.54	1.7266	0.07269	1.02689
5(C)	0.1116	0.0143	0.1985	0.0868	0.0974	1.5416	1.7287	0.07276	1.02818
6(C)	-0.0318	-0.0809	0.0084	0.0402	0.0492	0.713	0.8734	0.03365	0.51947
7(N)	-0.0793	-0.141	-0.0039	0.0754	0.0616	1.3386	1.0946	0.06318	0.65103
8(B)	0.2108	0.1241	0.2713	0.0606	0.0866	1.0756	1.5385	0.05077	0.91504
9(N)	-0.0796	-0.1411	-0.0041	0.0755	0.0615	1.3406	1.092	0.06327	0.64949
10(C)	-0.0863	-0.0912	-0.0647	0.0216	0.0049	0.3838	0.0873	0.01812	0.05195
11(C)	-0.0356	-0.0522	-0.0077	0.028	0.0166	0.4963	0.295	0.02342	0.17544
12(C)	-0.0492	-0.0586	-0.0325	0.0167	0.0094	0.2966	0.167	0.014	0.0993
13(C)	-0.0349	-0.0546	0.0028	0.0377	0.0197	0.6686	0.3497	0.03156	0.20799
14(C)	0.0029	-0.0036	0.0146	0.0117	0.0065	0.2074	0.1163	0.00979	0.06916
15(C)	-0.03	-0.0465	-0.0031	0.0269	0.0166	0.4773	0.2945	0.02253	0.17514
16(C)	0.0223	0.0214	0.0239	0.0016	0.001	0.0282	0.0171	0.00133	0.01016
17(C)	-0.0911	-0.0921	-0.0895	0.0016	0.001	0.0279	0.0182	0.00132	0.01085
18(C)	-0.0928	-0.0937	-0.0913	0.0015	0.0009	0.0266	0.0154	0.00125	0.00915
19(C)	-0.0928	-0.0937	-0.0913	0.0015	0.0009	0.0266	0.0154	0.00125	0.00915

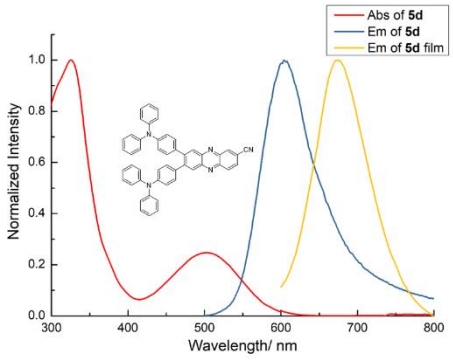
VII. Photophysical data

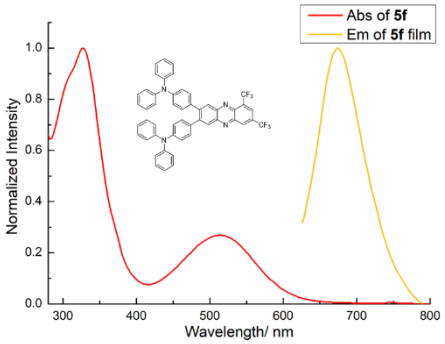
Table S14: Absorption maxima, emission maxima, stokes shifts, fluorescence quantum yields and transient decay data.

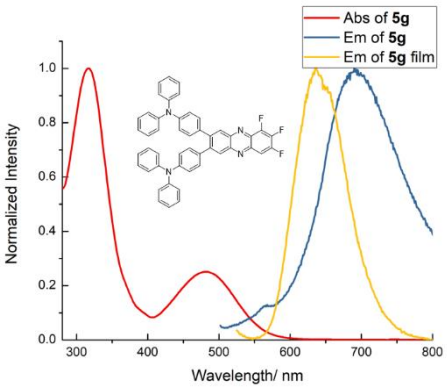
Compd.	λ_{abs} (nm)[a] in CH_2Cl_2	λ_{em} (nm)[b] in CH_2Cl_2	λ_{em} (nm)[c] in film	(Φ_f)[d] in film	τ[e] (μs)
5a	302, 486	624	607	0.19	6.6
5d	326, 502	607	674	0.16	2.5
5f	328, 515	-	674	0.17	2.5
5g	317, 480	690	635	0.12	4.5
5j	346, 525	668	668	0.02	0.0062
5k	287, 479	666	630	0.07	11
8a	297, 340, 507	651	610	0.16	1.8
8b	288, 303, 409	527	533	0.08	2.5
8c	316, 503	611	607	0.06	0.036
8d	326, 489	661	616	0.20	8.5

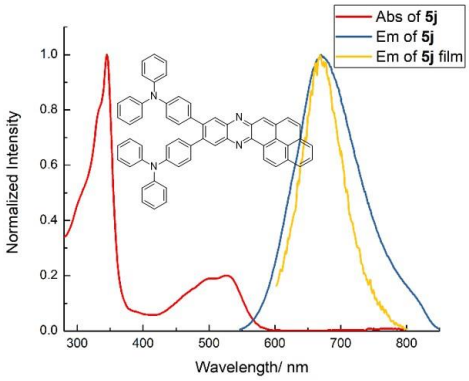
[a]Absorption maximum in CH_2Cl_2 at 1×10^{-5} mol/L. [b]Emission maximum in CH_2Cl_2 at 1×10^{-5} mol/L. [c]Emission maximum in film. [d]Absolute quantum yield determined in mCBP films (10 wt%) at room temperature. [e]Photoluminescence transient decay curves in neat film.

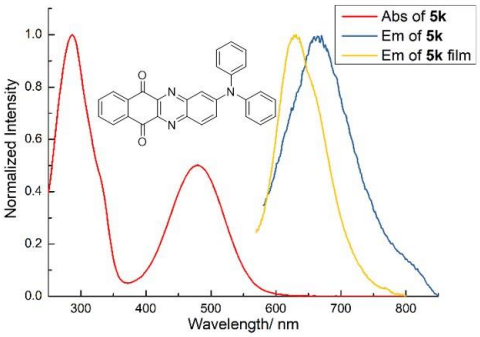


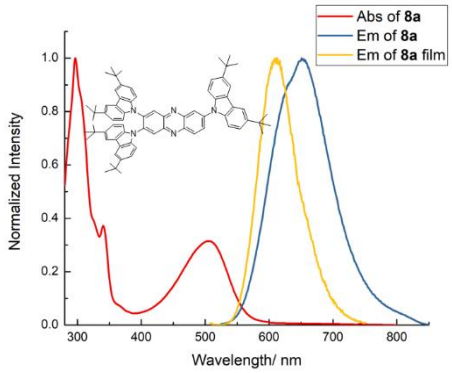


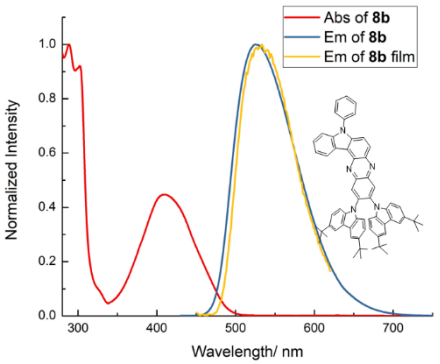


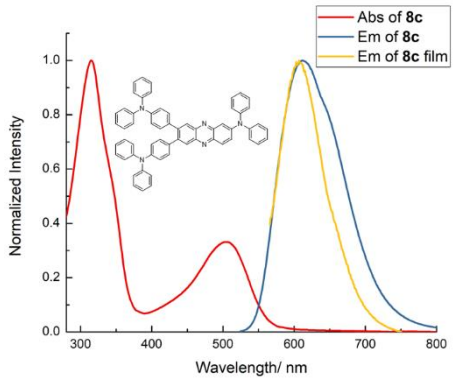


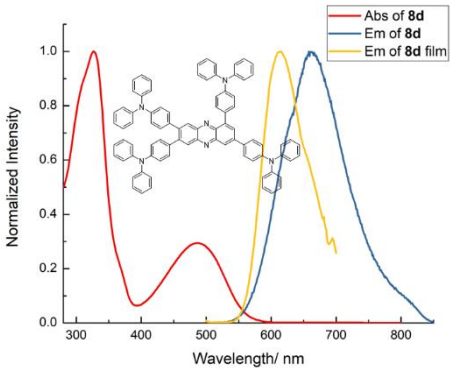

Abs of 5j
Em of 5j
Em of 5j film
Normalized Intensity
Wavelength/ nm

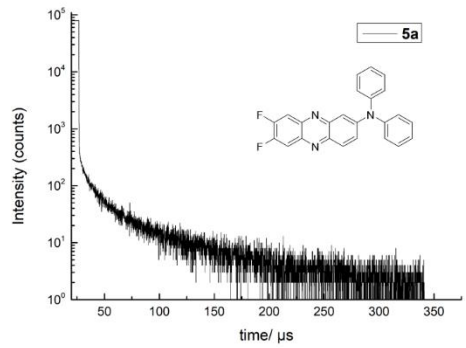

Abs of 5k
Em of 5k
Em of 5k film
Normalized Intensity
Wavelength/ nm

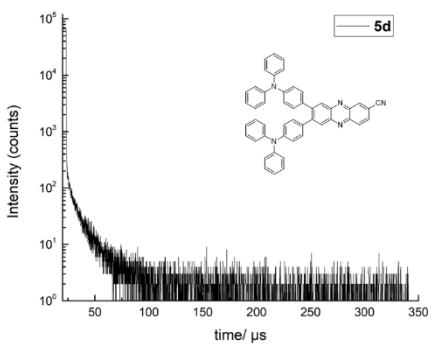

Abs of 8a
Em of 8a
Em of 8a film
Normalized Intensity
Wavelength/ nm

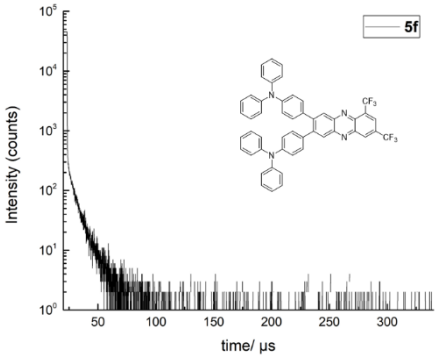

Abs of 8b
Em of 8b
Em of 8b film
Normalized Intensity
Wavelength/ nm

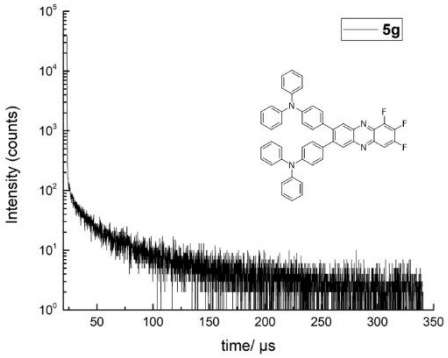

Abs of 8c
Em of 8c
Em of 8c film
Normalized Intensity
Wavelength/ nm

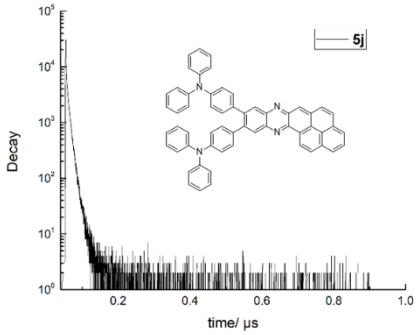

Abs of 8d
Em of 8d
Em of 8d film
Normalized Intensity
Wavelength/ nm

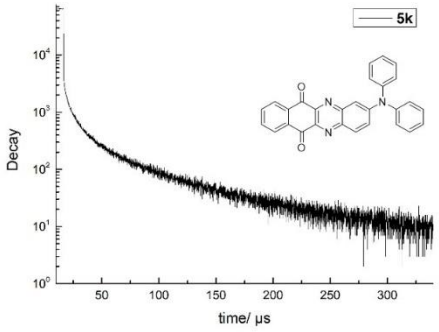

5a
Intensity (counts)
time/ μs

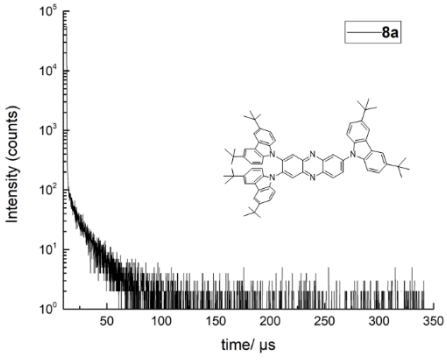

5d
Intensity (counts)
time/ μs

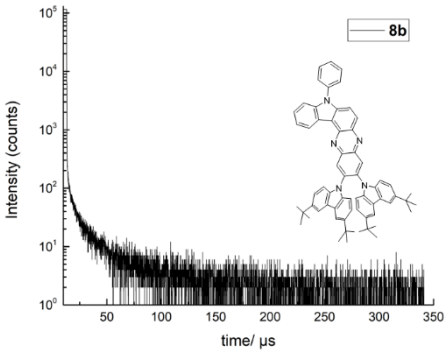

5f
Intensity (counts)
time/ μs

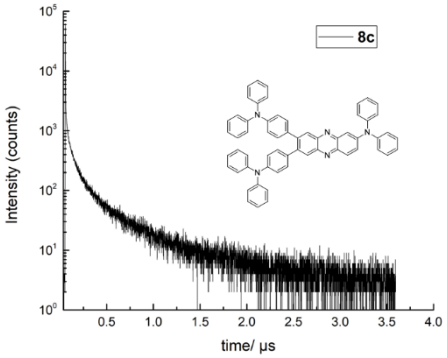

5g
Intensity (counts)
time/ μs

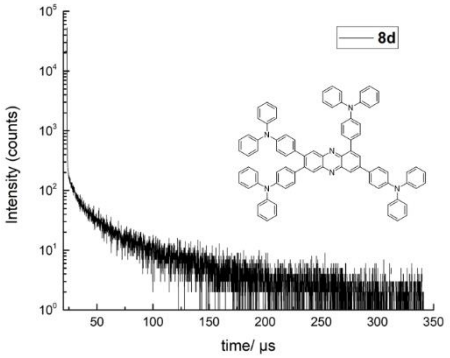

5j
Decay
time/ μs


5k
Decay
time/ μs


8a
Intensity (counts)
time/ μs


8b
Intensity (counts)
time/ μs


8c
Intensity (counts)
time/ μs


8d
Intensity (counts)
time/ μs

VII. References

1. (a) S. Ha, Y. Lee, Y. Kwak, A. Mishra, E. Yu, B. Ryou and C.-M. Park, *Nat. Commun.*, 2020, **11**, 2509. (b) C. Liu, P. Zhao and W. Huang, *Open Chem.*, 2007, ***5***, 303-315. (c) J. A. Christensen, B. T. Phelan, S. Chaudhuri, A. Acharya, V. S. Batista and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2018, **140**, 5290-5299.

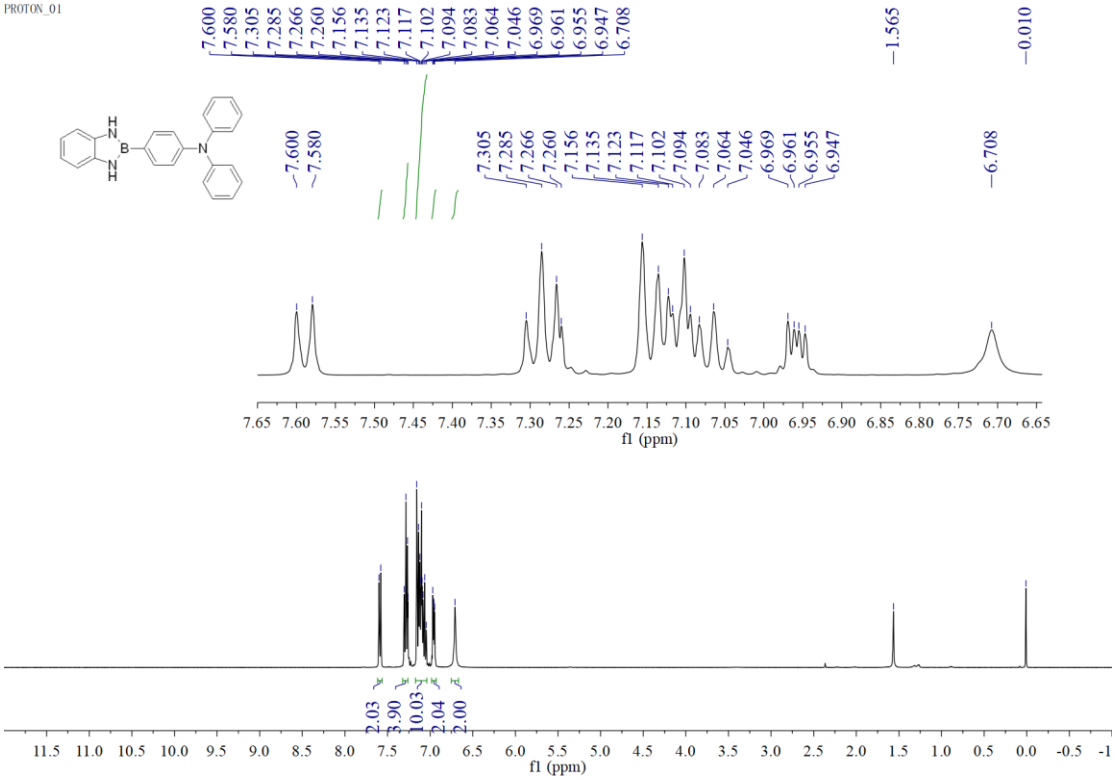
2. (a) W.-M. Wan, D. Tian, Y.-N. Jing, X.-Y. Zhang, W. Wu, H. Ren and H.-L. Bao, *Angew. Chem., Int. Ed.*, 2018, **57**, 15510-15516. (b) C.-W. Ju, B. Li, L. Li, W. Yan, C. Cui, X. Ma and D. Zhao, *J. Am. Chem. Soc.*, 2021, **143**, 5903-5916. (c) A. R. Goldberg and B. H. Northrop, *J. Org. Chem.*, 2016, **81**, 969-980.

3. (a) F. B. Mortzfeld, J. Pietruszka and I. R. Baxendale, *Eur. J. Org. Chem.*, 2019, 5424-5433. (b) C. Chen, K. C. Chong, Y. Pan, G. Qi, S. Xu and B. Liu, *ACS Mater. Lett.*, 2021, **3**, 1081-1087.

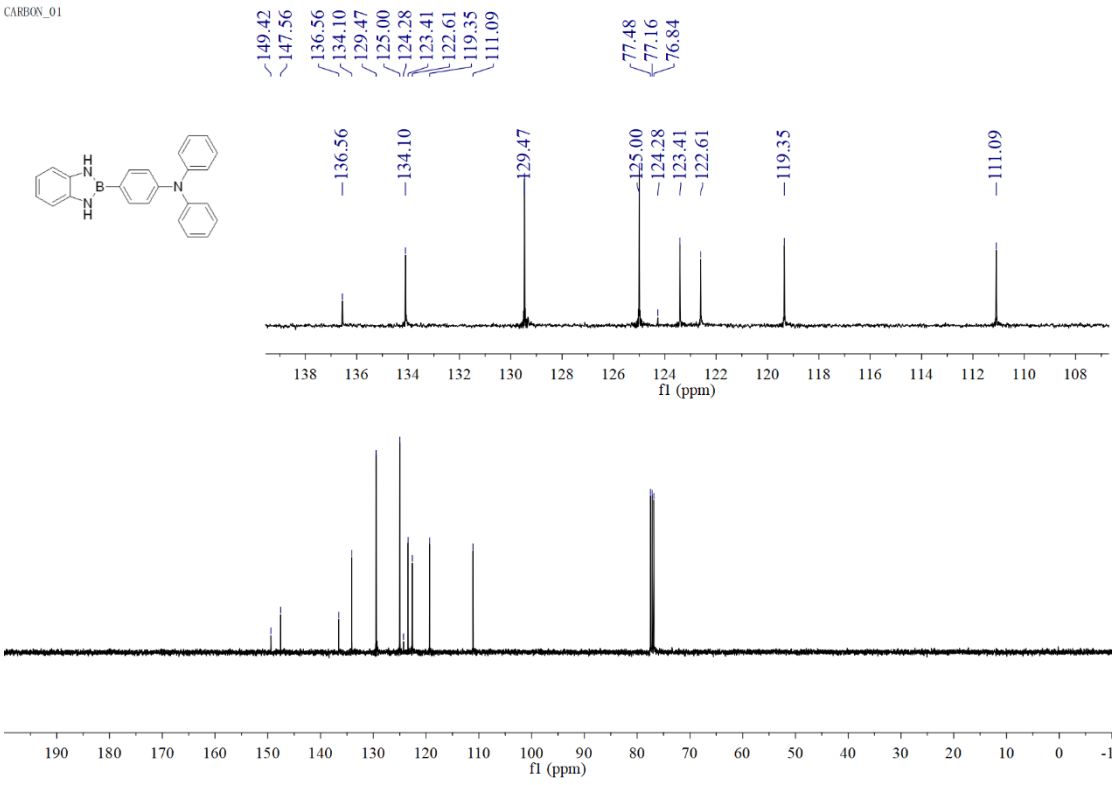
4. (a) M. Tietze, A. Iglesias, E. Merisor, J. Conrad, I. Klaiber and U. Beifuss, *Org. Lett.*, 2005, **7**, 1549-1552. (b)) N. V. Borrero, F. Bai, C. Perez, B. Q. Duong, J. R. Rocca, S. Jin and R. W. Huigens, *Org. Biomol. Chem.*, 2014, **12**, 881-886.

5. (a) X.-Y. Wang, H.-R. Lin, T. Lei, D.-C. Yang, F.-D. Zhuang, J.-Y. Wang, S. C. Yuan and J. Pei, *Angew. Chem., Int. Ed.*, 2013, **52**, 3117-3120. (b) C.-J. Sun, G. Meng, Y. Li, N. Wang, P. Chen, S. Wang and X. Yin, *Inorg. Chem.*, 2021, **60**, 1099-1106.

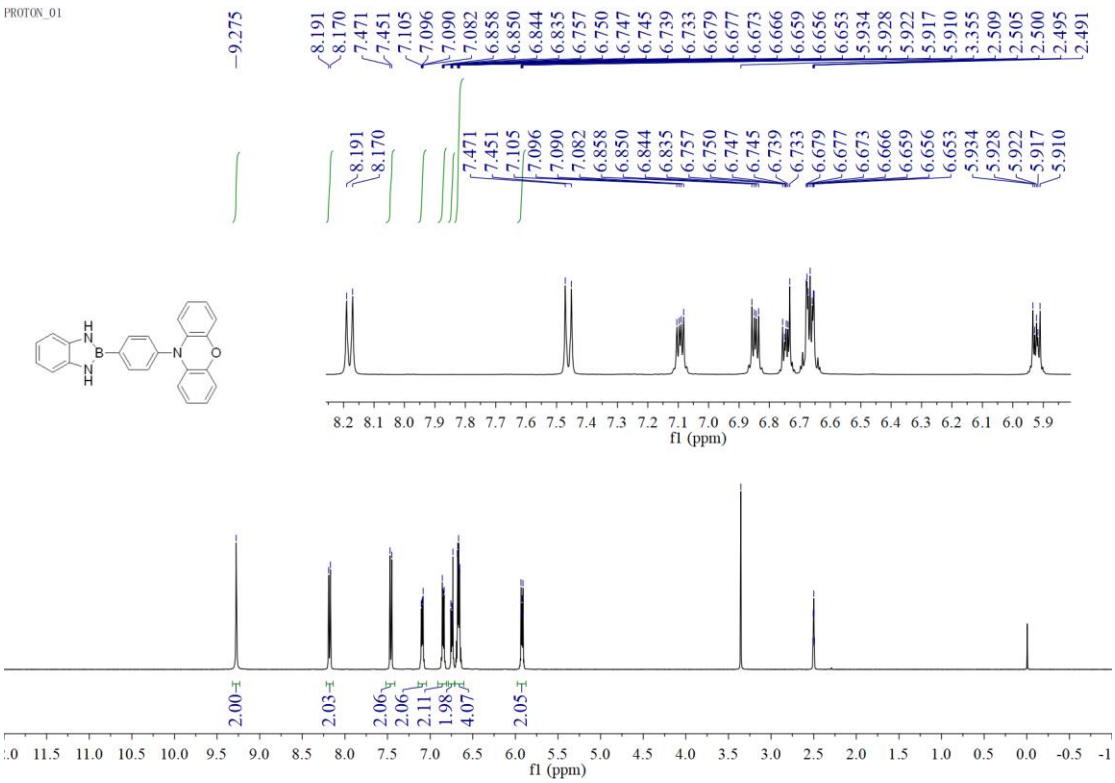
VIII. Copies of NMR spectra



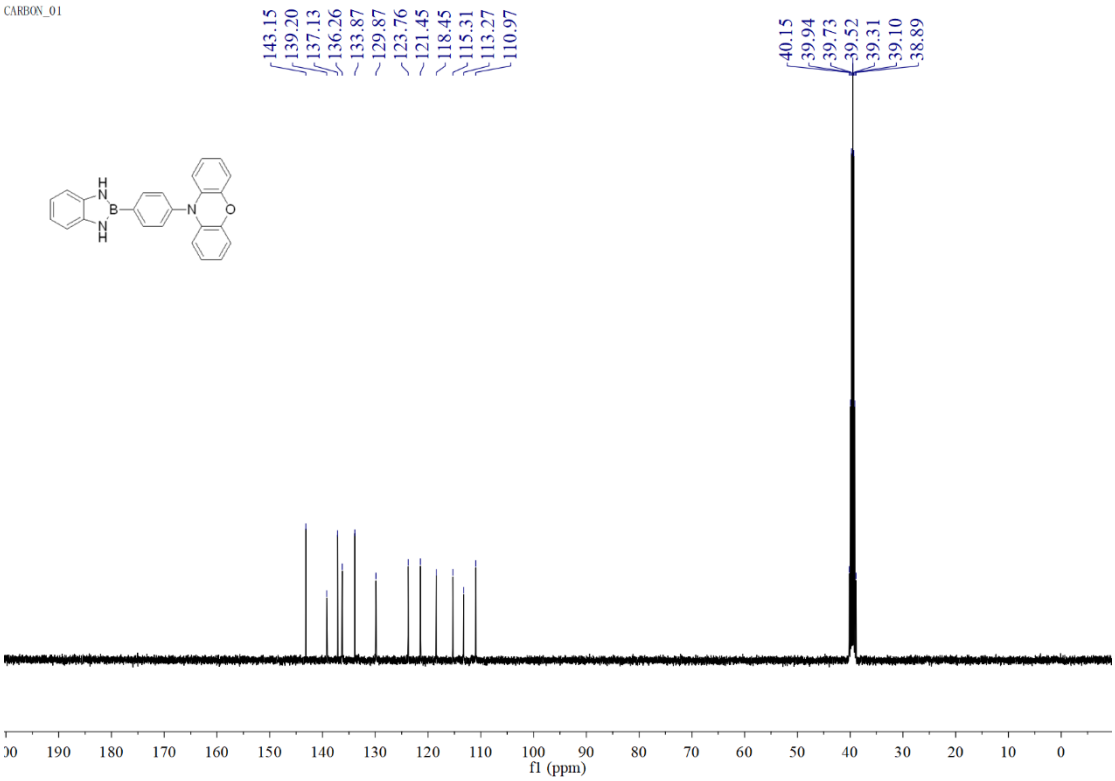
^{1}H NMR spectrum of **1k** in $CDCl_3$



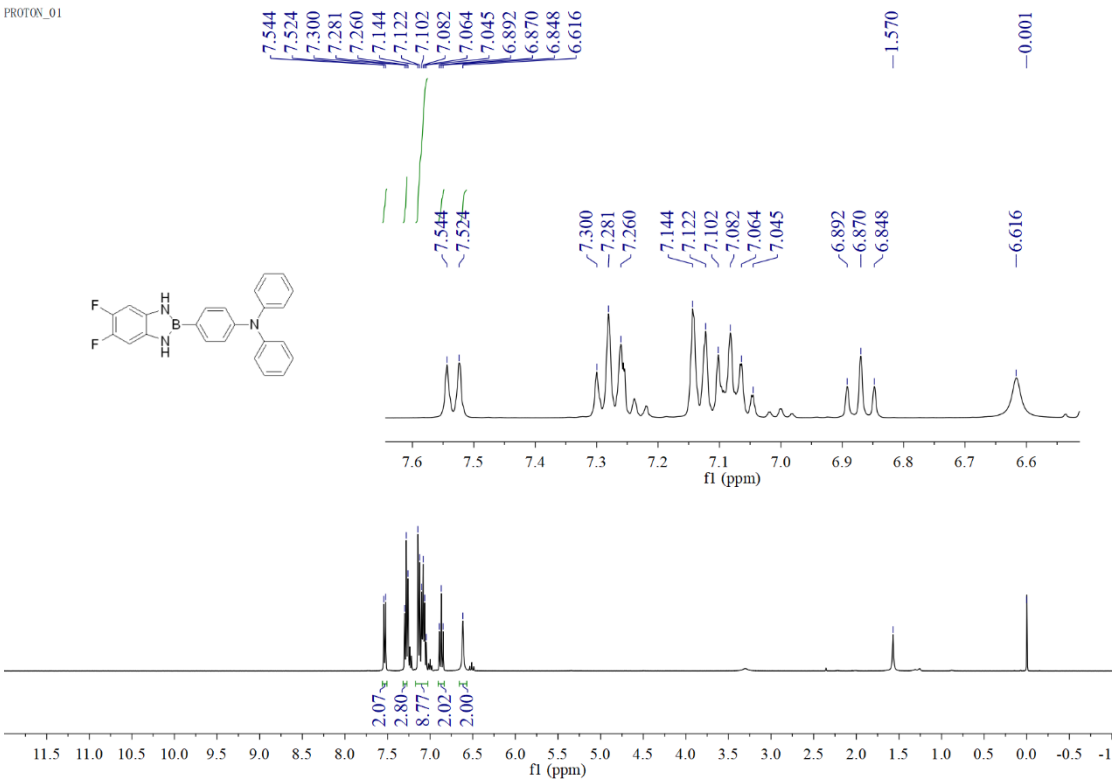
^{13}C NMR spectrum of **1k** in $CDCl_3$



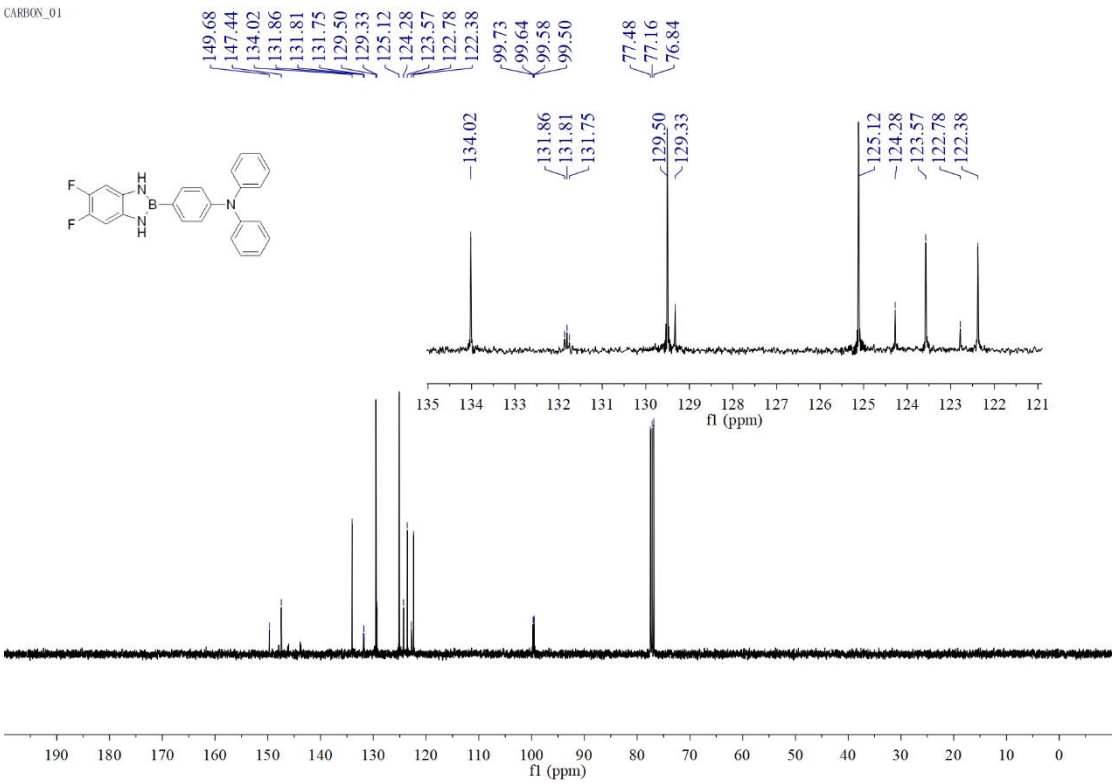
^{1}H NMR spectrum of **1n** in $CDCl_3$



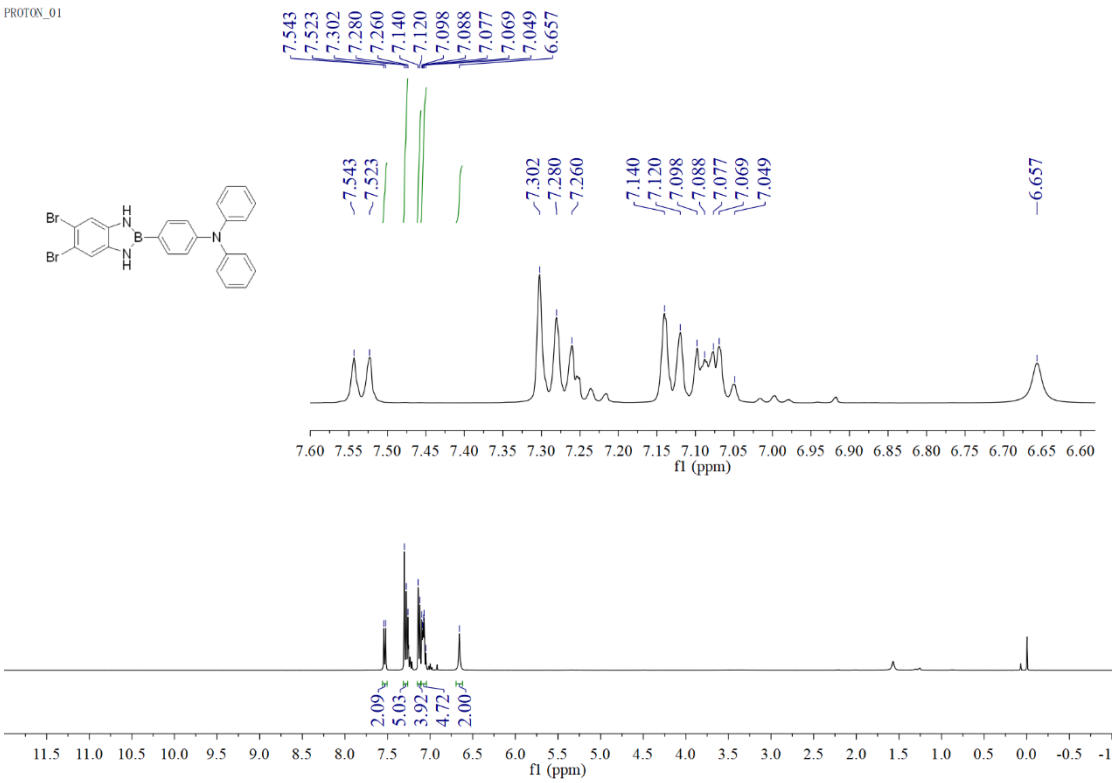
^{13}C NMR spectrum of **1n** in $CDCl_3$



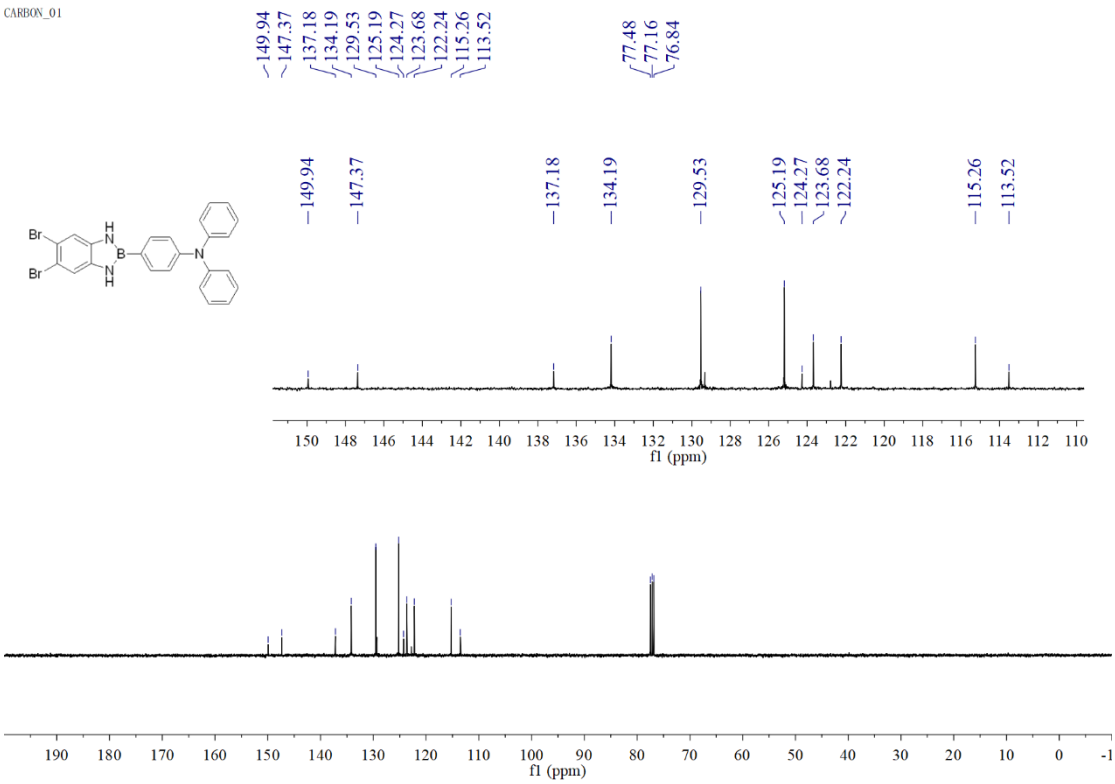
^{1}H NMR spectrum of **2a** in $CDCl_3$



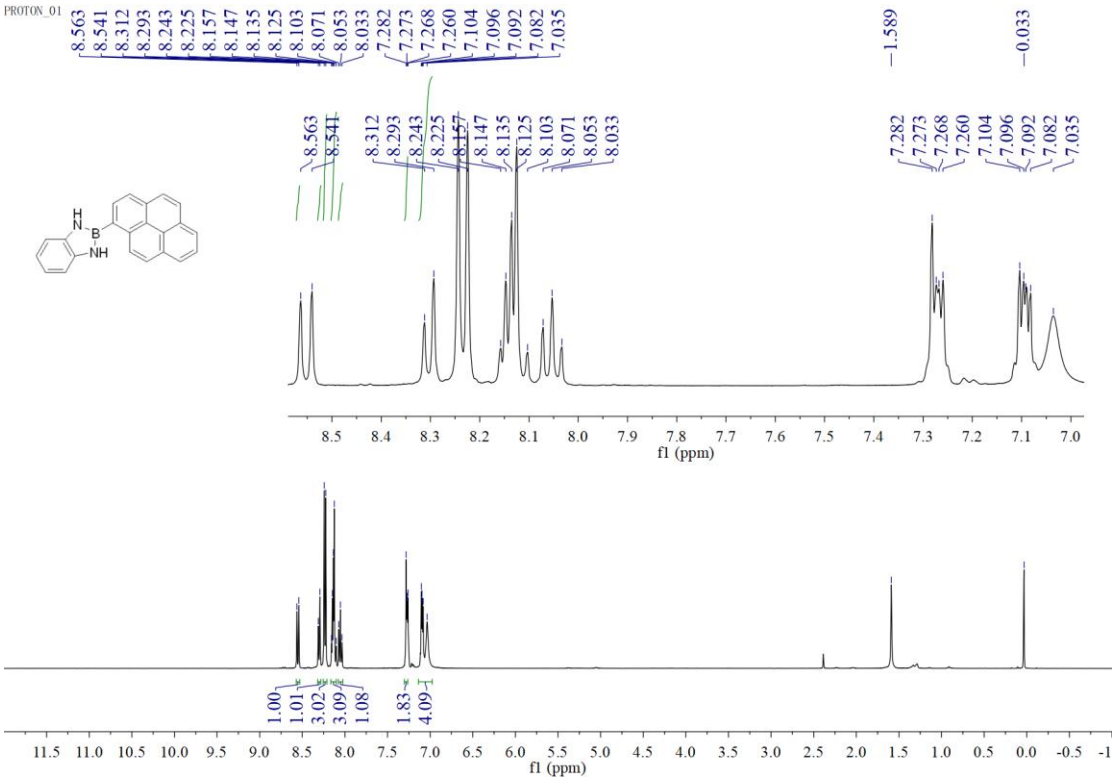
^{13}C NMR spectrum of **2a** in $CDCl_3$



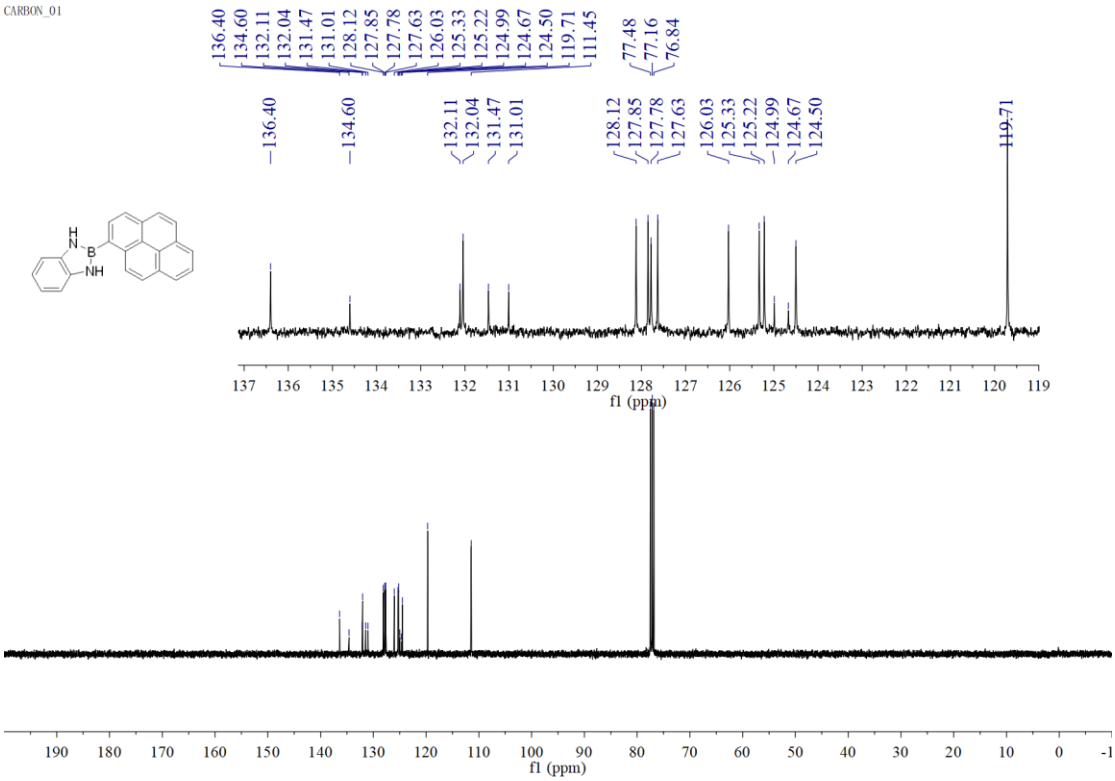
^{1}H NMR spectrum of **2c** in $CDCl_3$



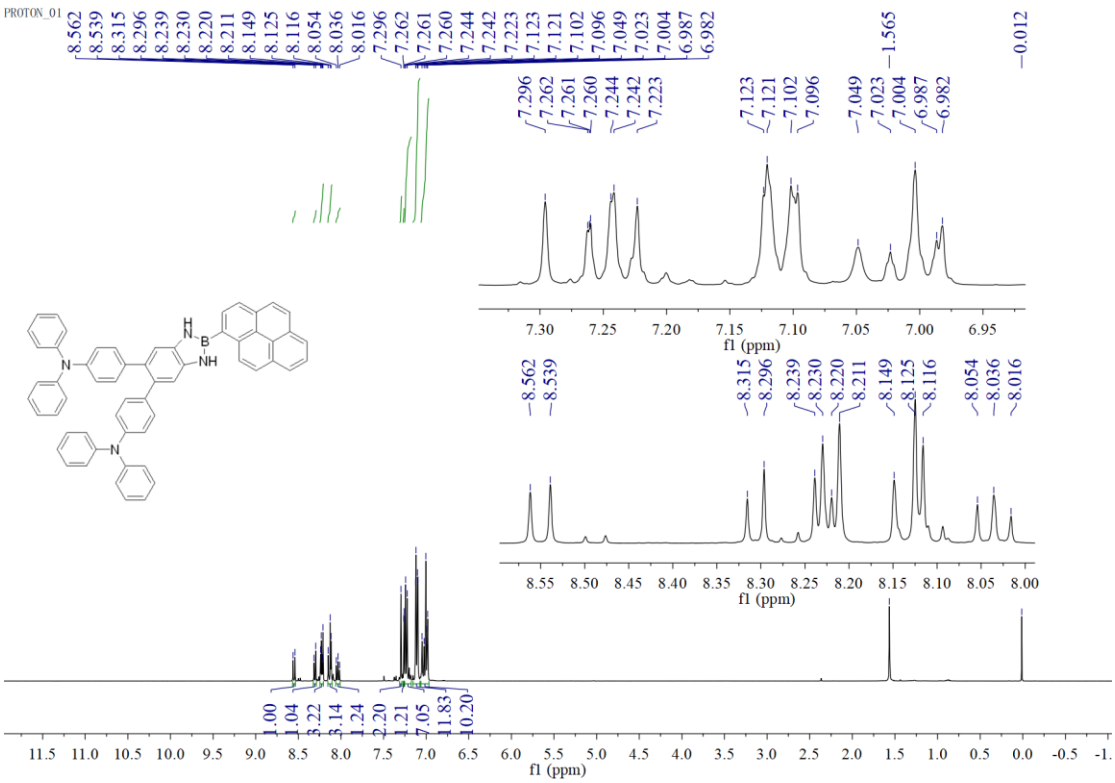
^{13}C NMR spectrum of **2c** in $CDCl_3$



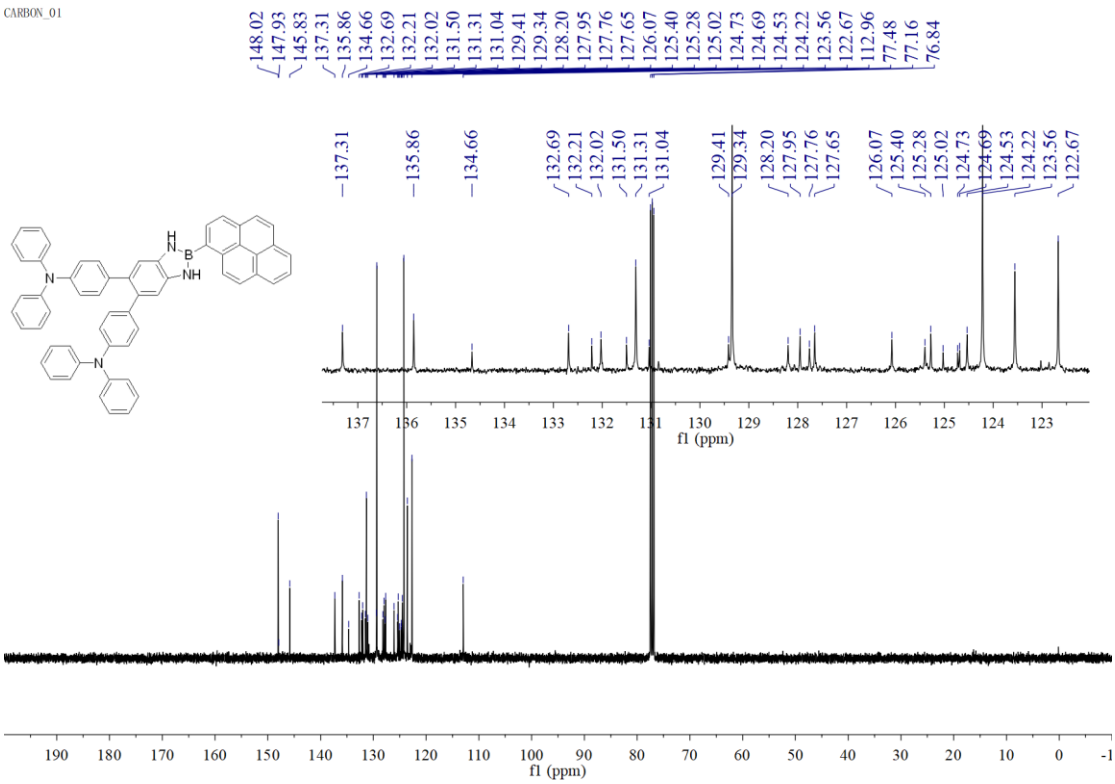
^{1}H NMR spectrum of **2i** in $CDCl_3$



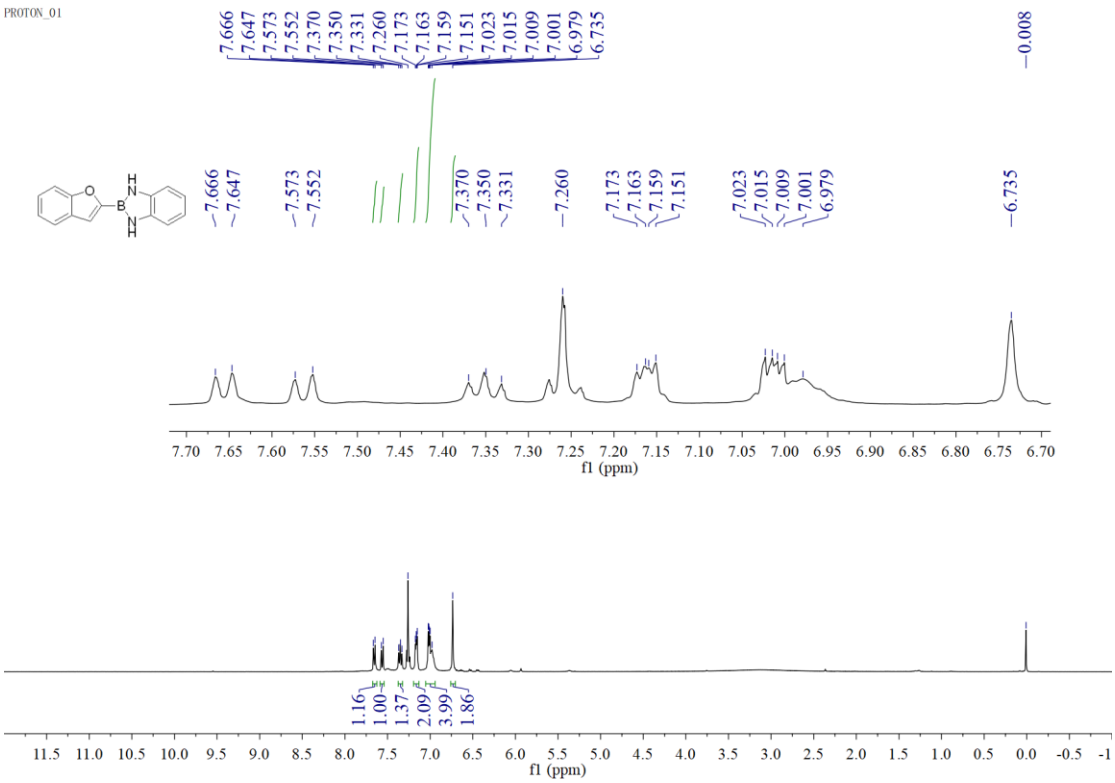
^{13}C NMR spectrum of **2i** in $CDCl_3$



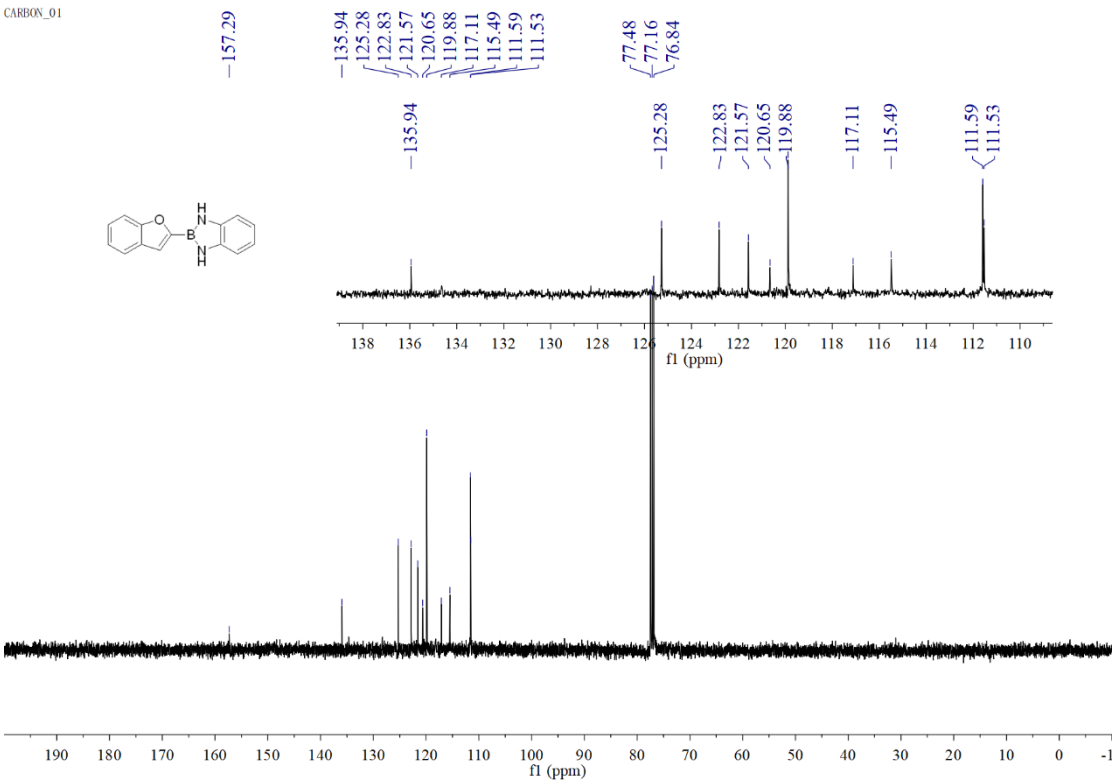
^{1}H NMR spectrum of **2j** in $CDCl_3$



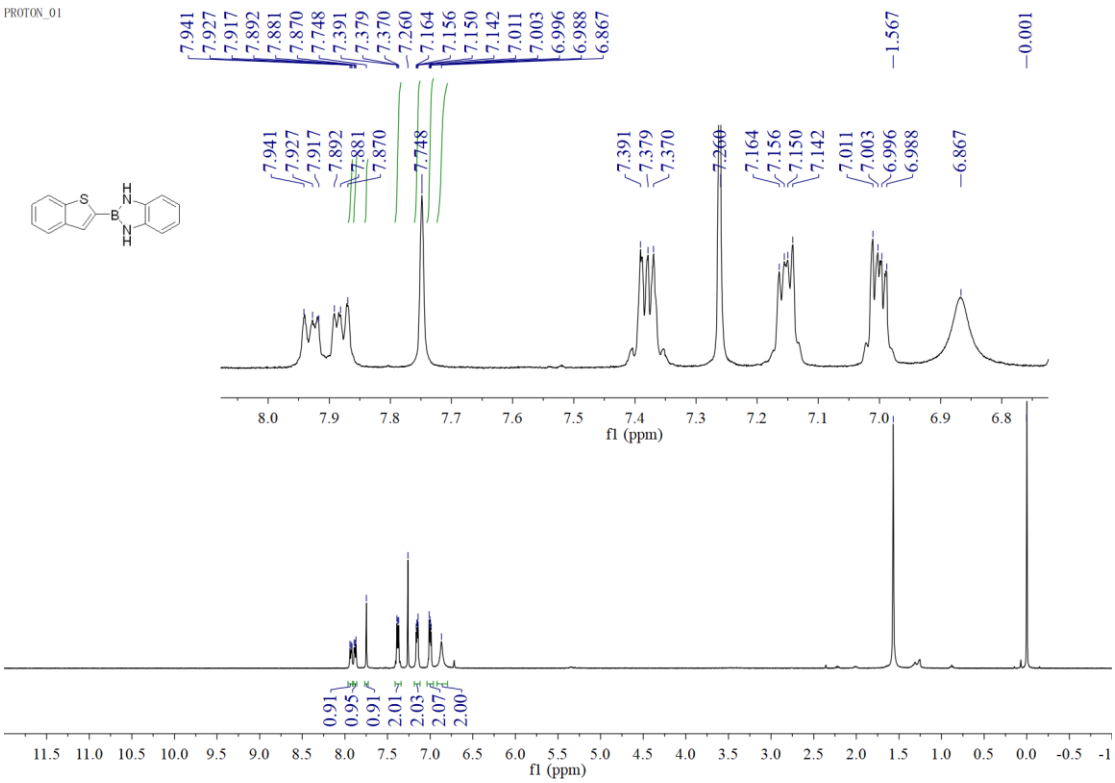
^{13}C NMR spectrum of **2j** in $CDCl_3$



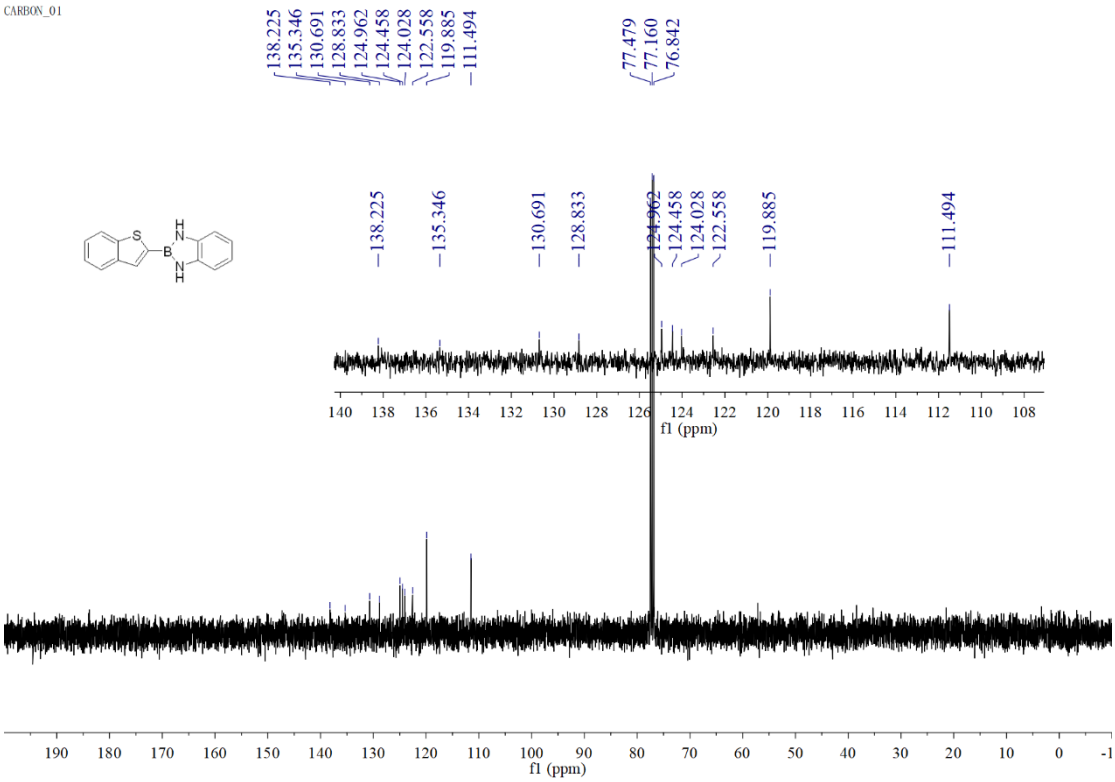
^{1}H NMR spectrum of **2l** in $CDCl_3$



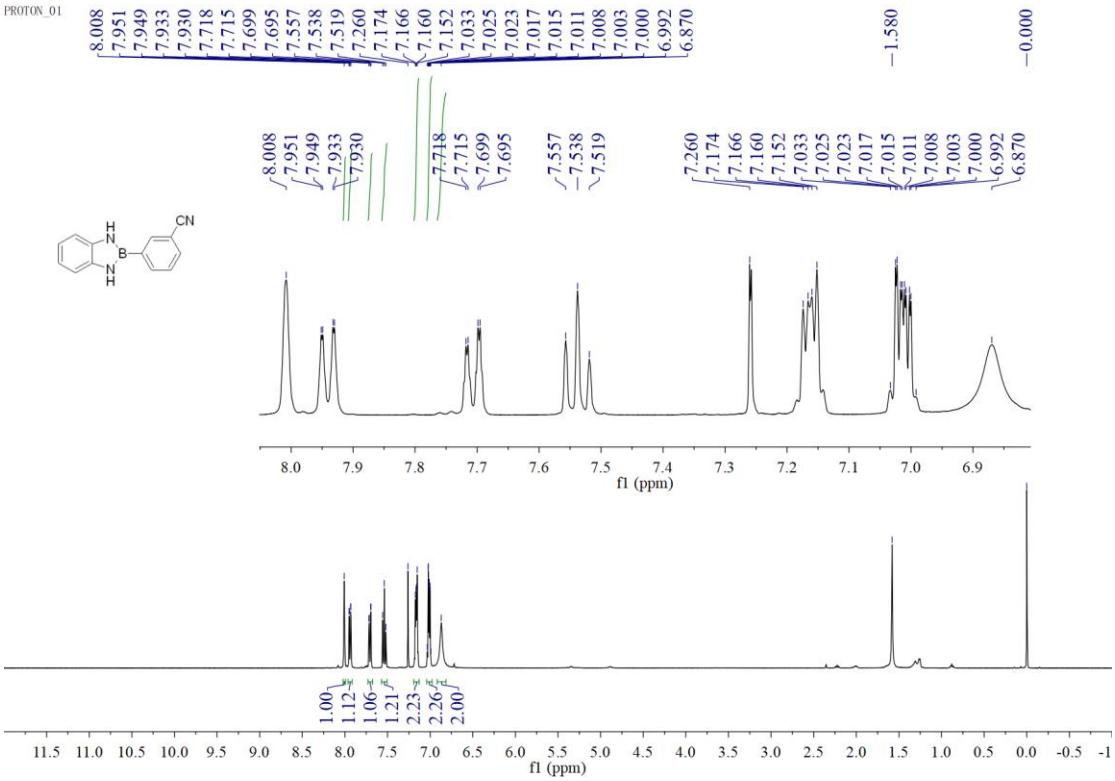
^{13}C NMR spectrum of **2l** in $CDCl_3$



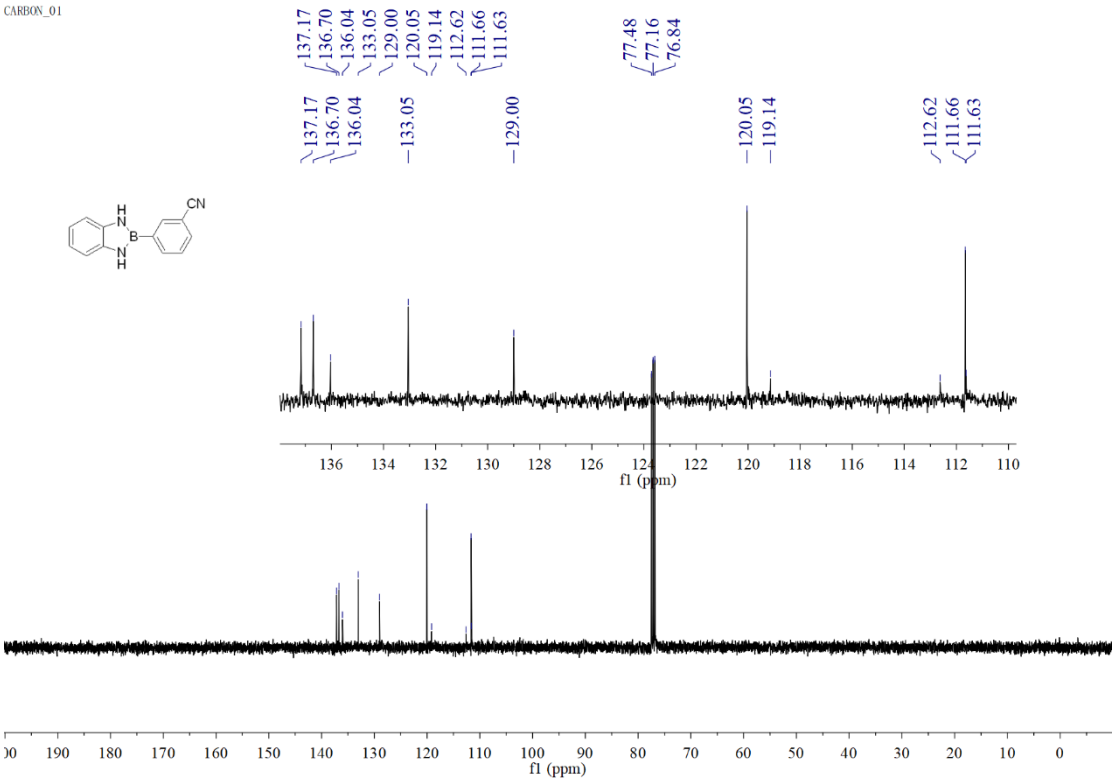
^{1}H NMR spectrum of **2m** in $CDCl_3$



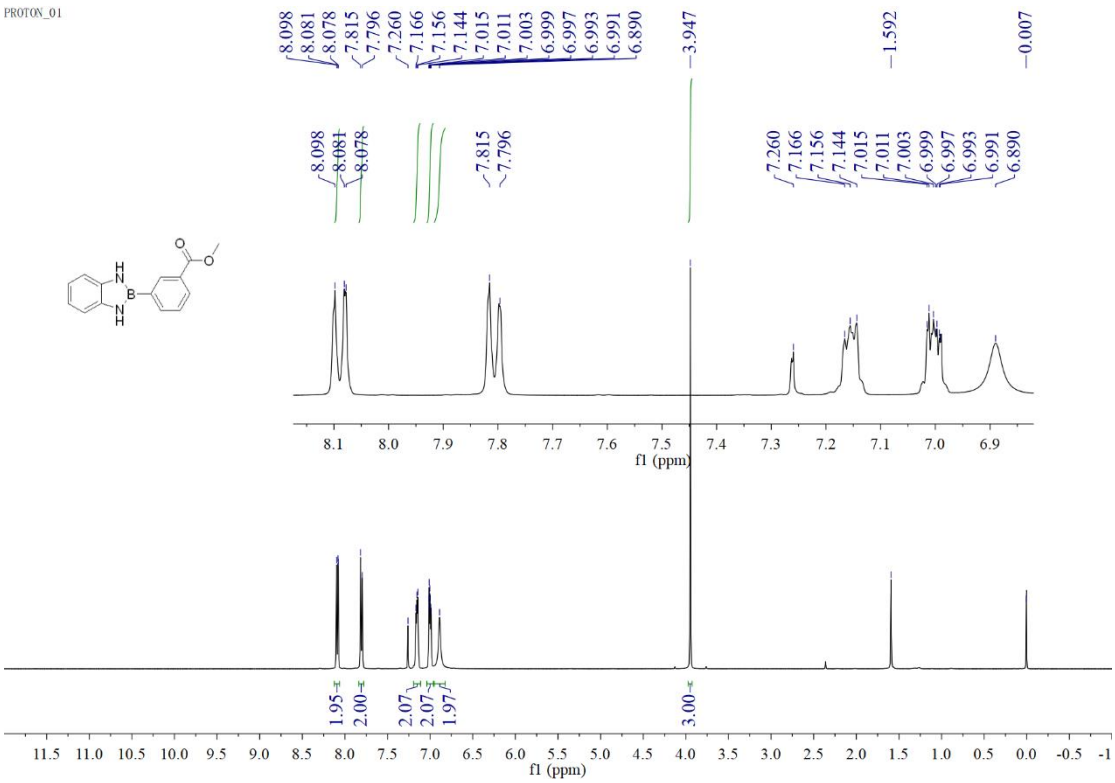
^{13}C NMR spectrum of **2m** in $CDCl_3$



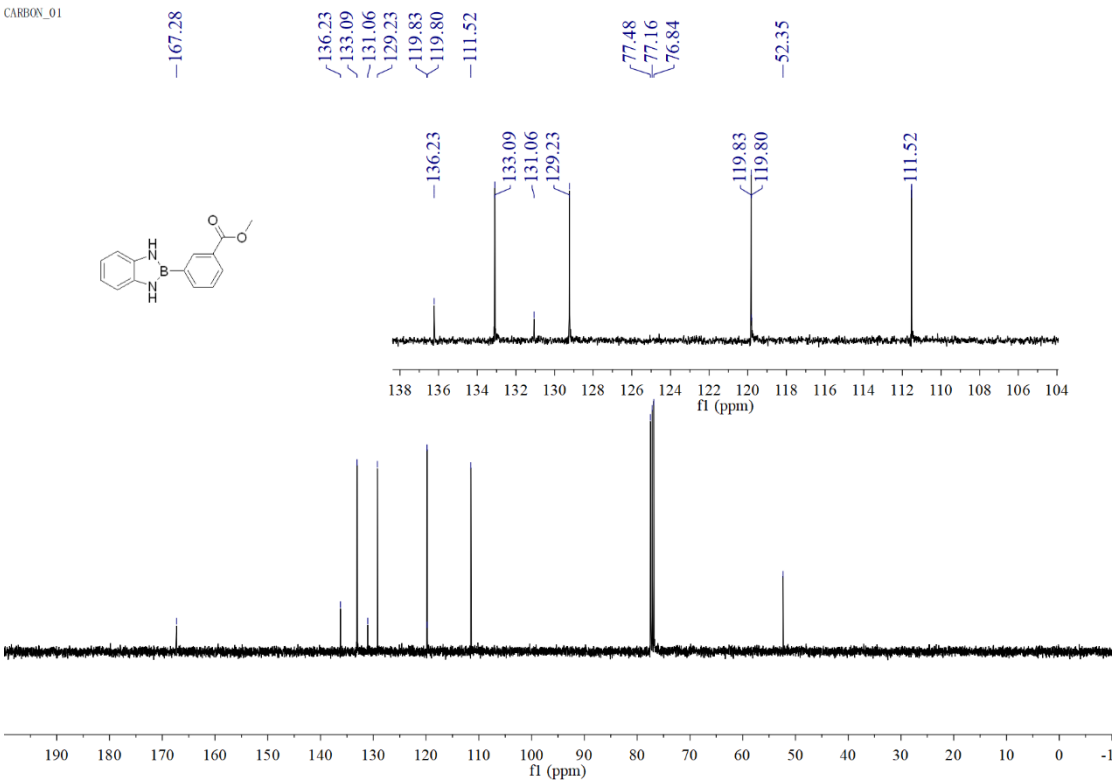
^{1}H NMR spectrum of **3b** in $CDCl_3$



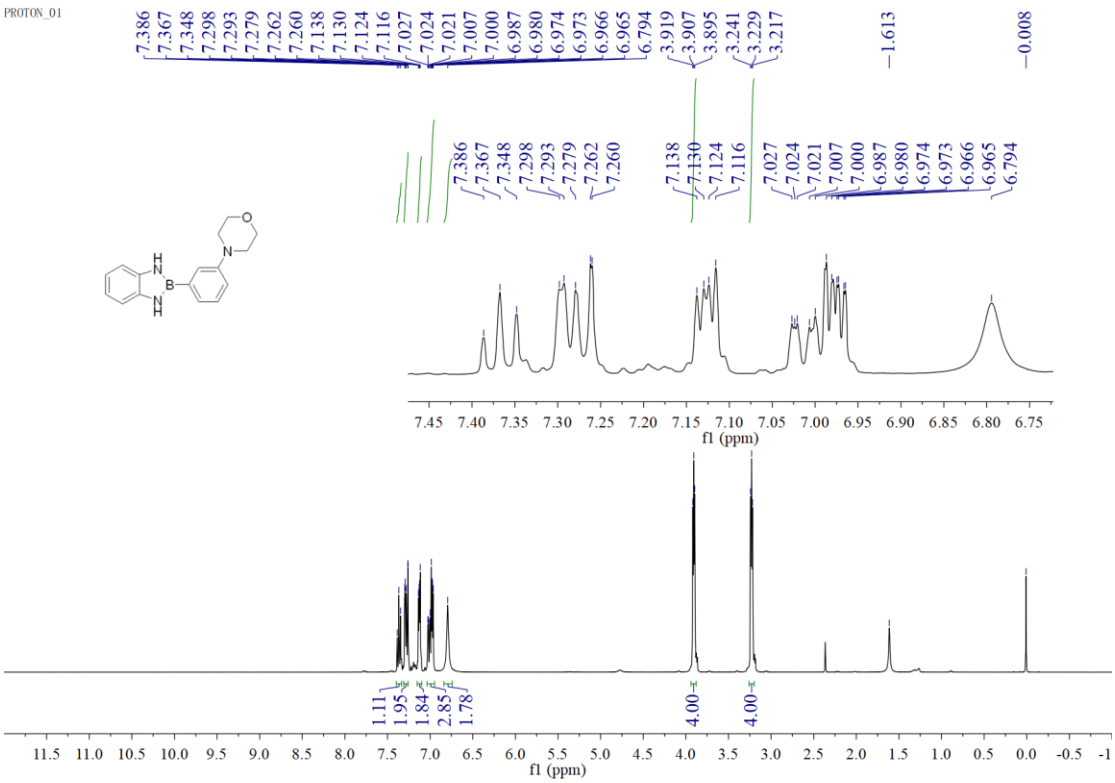
^{13}C NMR spectrum of **3b** in $CDCl_3$



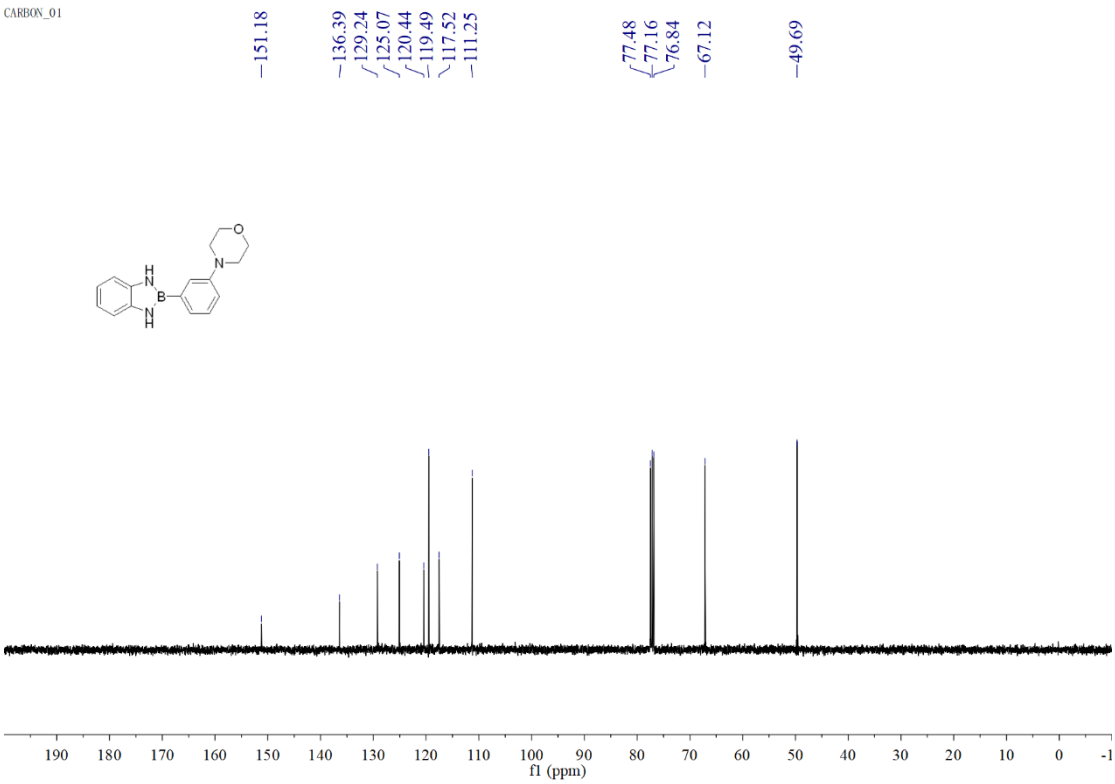
^{1}H NMR spectrum of **3c** in $CDCl_3$



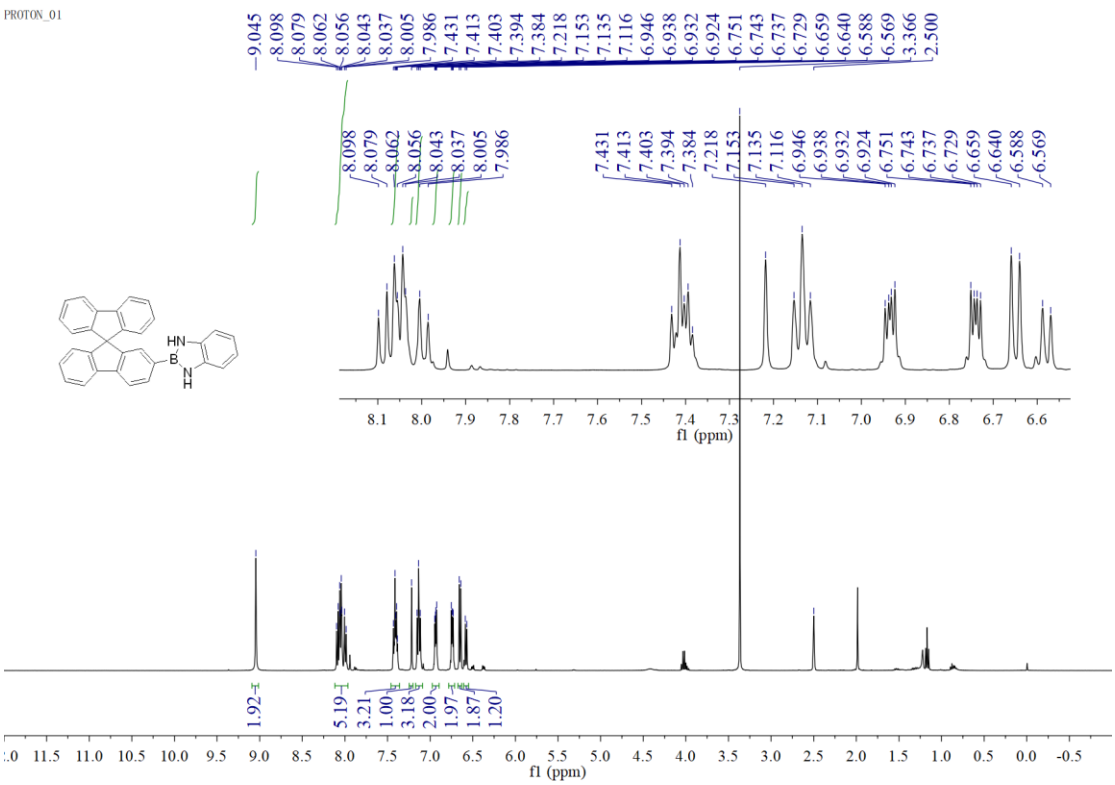
^{13}C NMR spectrum of **3c** in $CDCl_3$



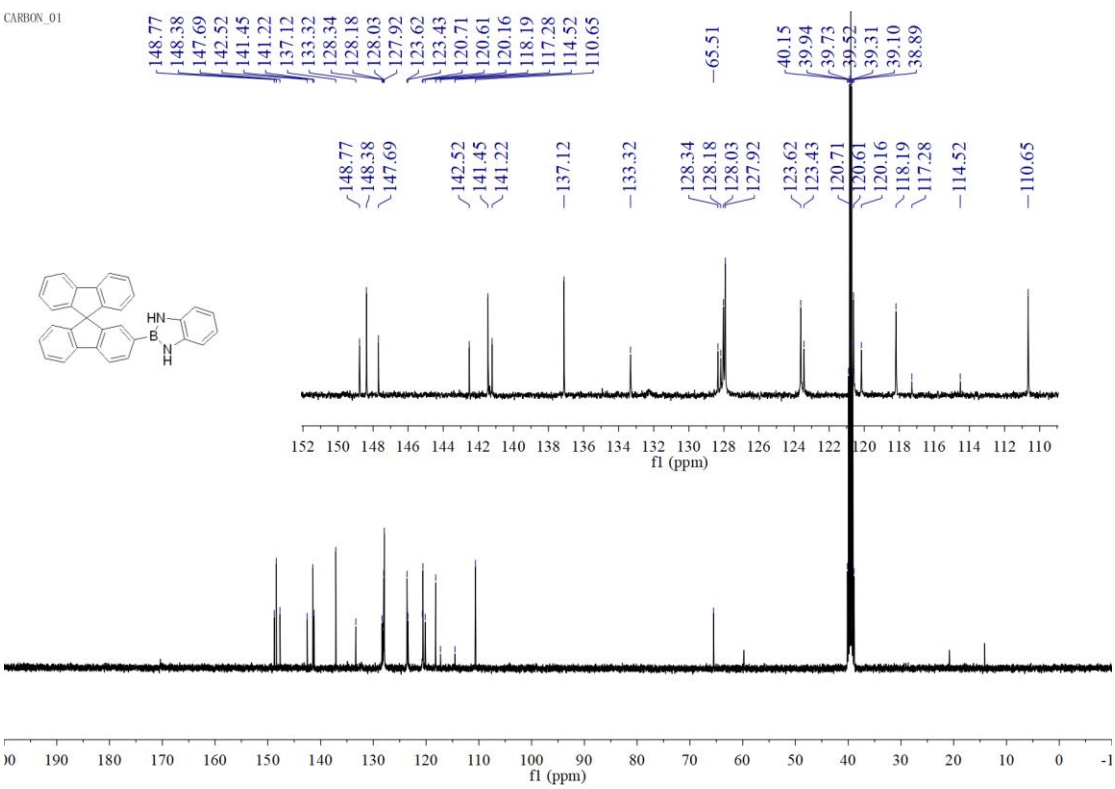
^{1}H NMR spectrum of **3e** in $CDCl_3$



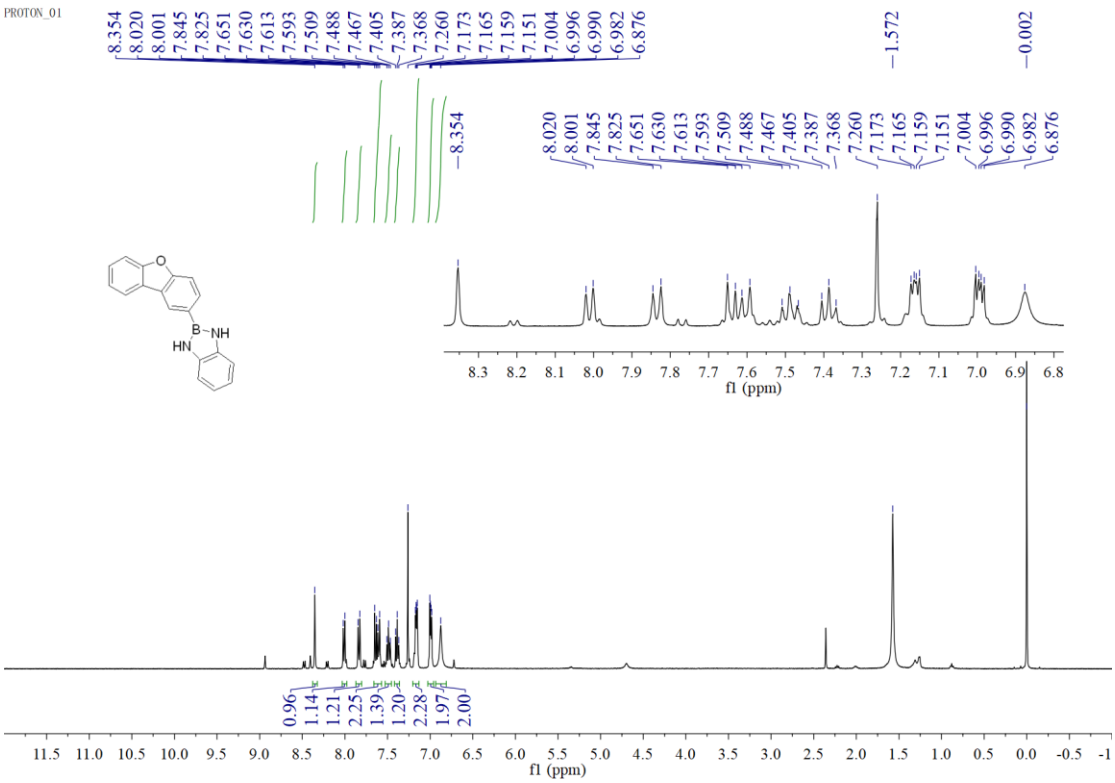
^{13}C NMR spectrum of **3e** in $CDCl_3$



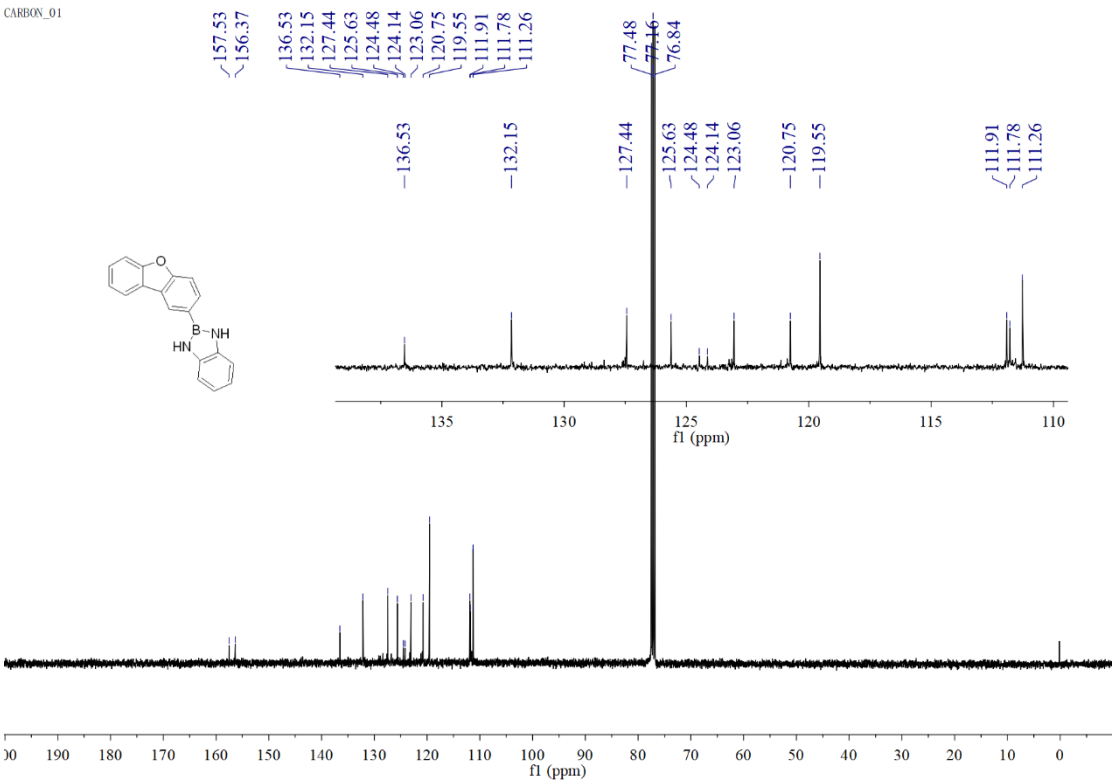
^{1}H NMR spectrum of **3f** in $CDCl_3$



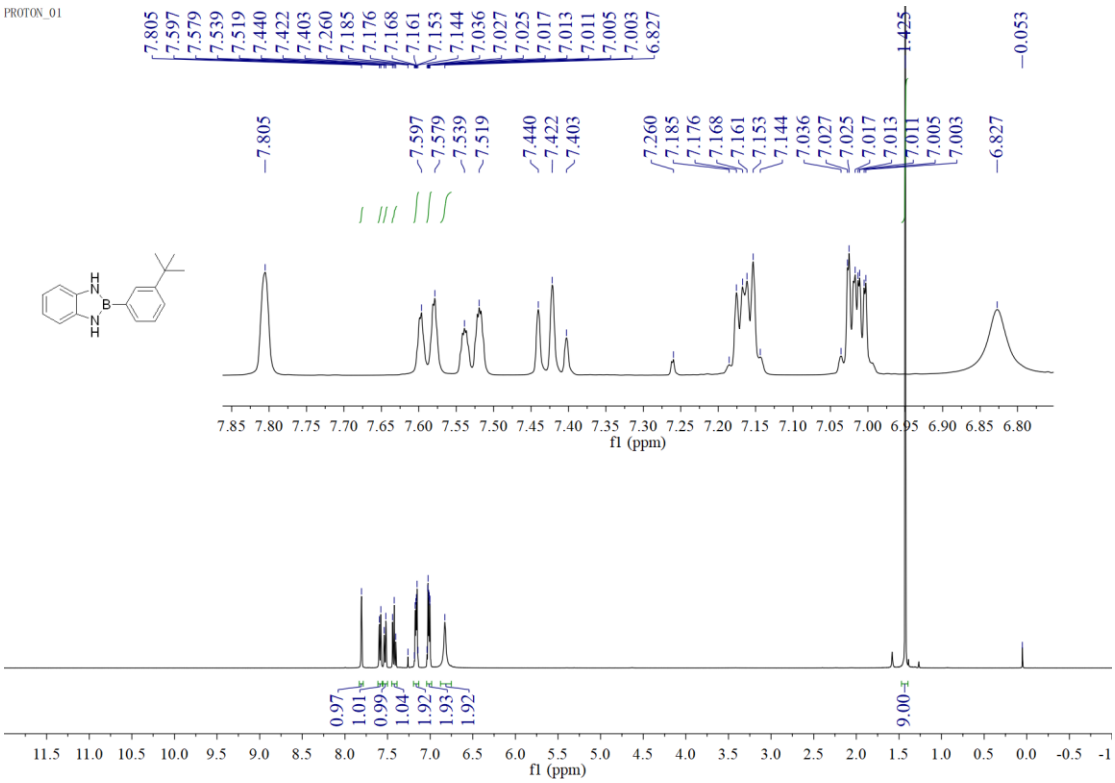
^{13}C NMR spectrum of **3f** in $CDCl_3$



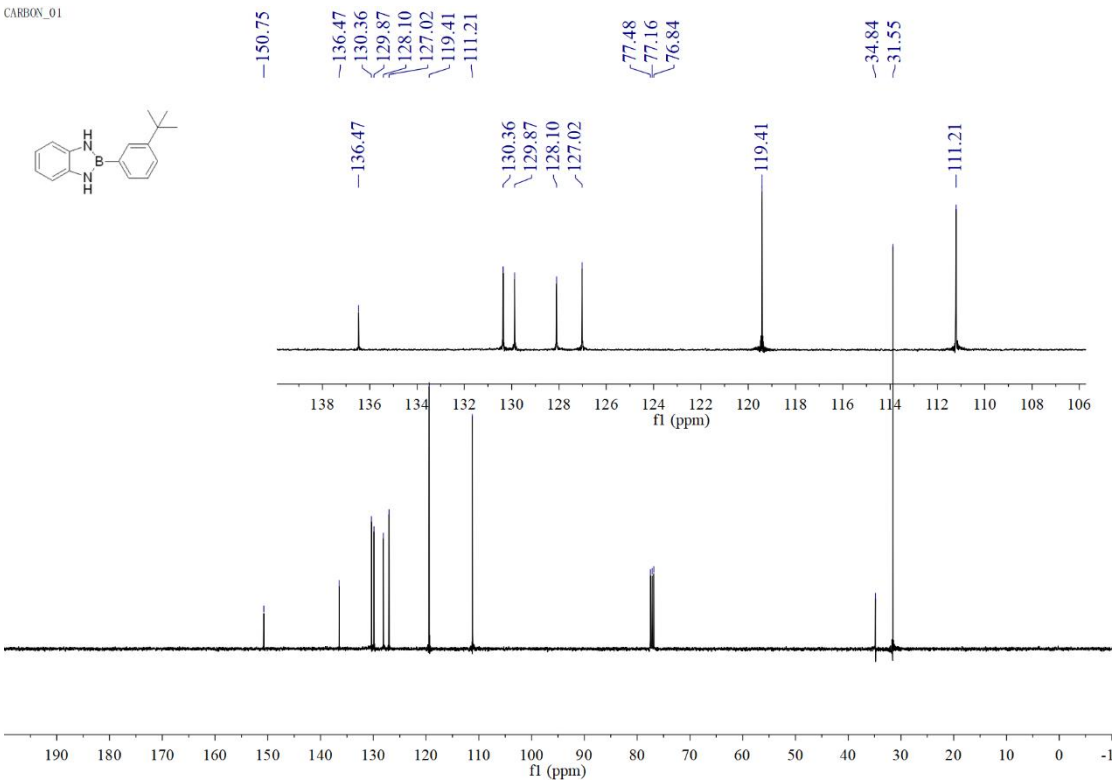
^{1}H NMR spectrum of **3h** in $CDCl_3$



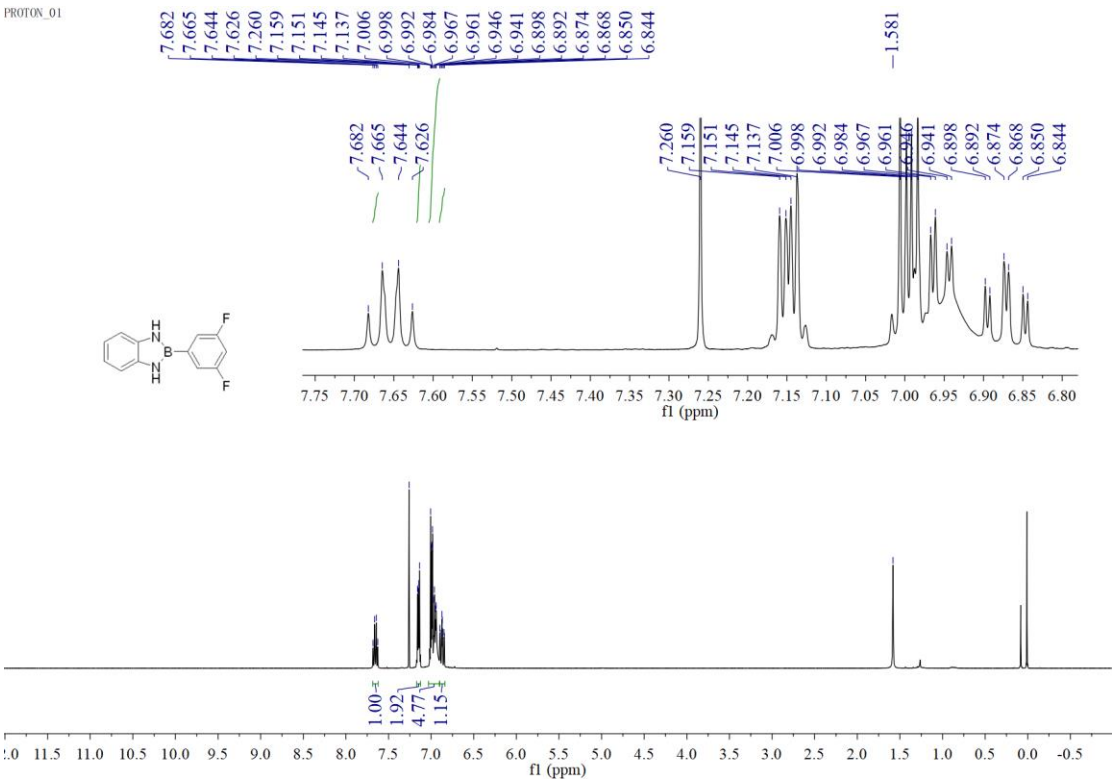
^{13}C NMR spectrum of **3h** in $CDCl_3$



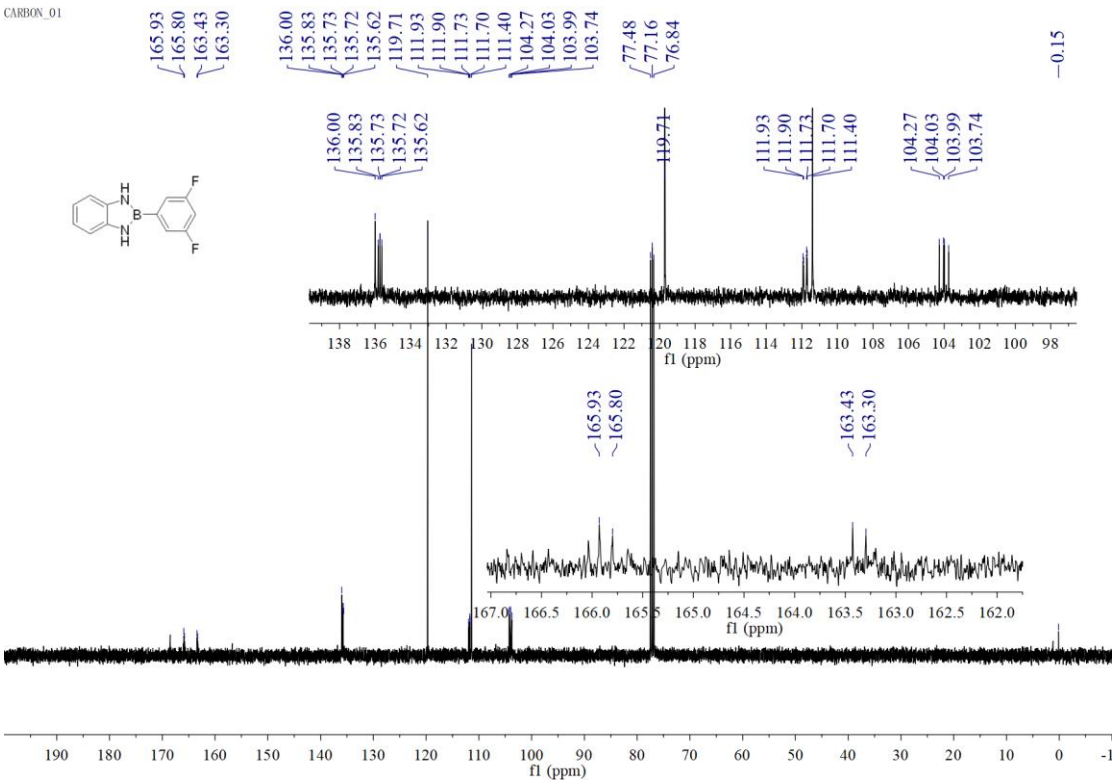
^{1}H NMR spectrum of **3l** in $CDCl_3$



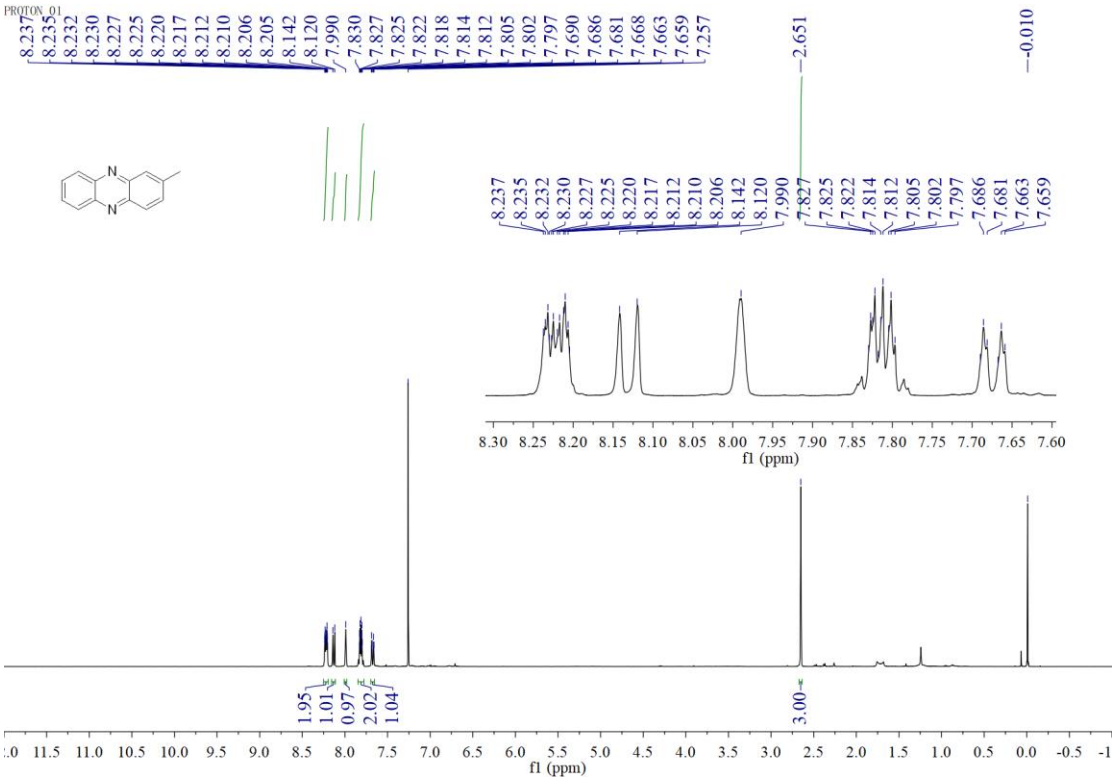
^{13}C NMR spectrum of **3l** in $CDCl_3$



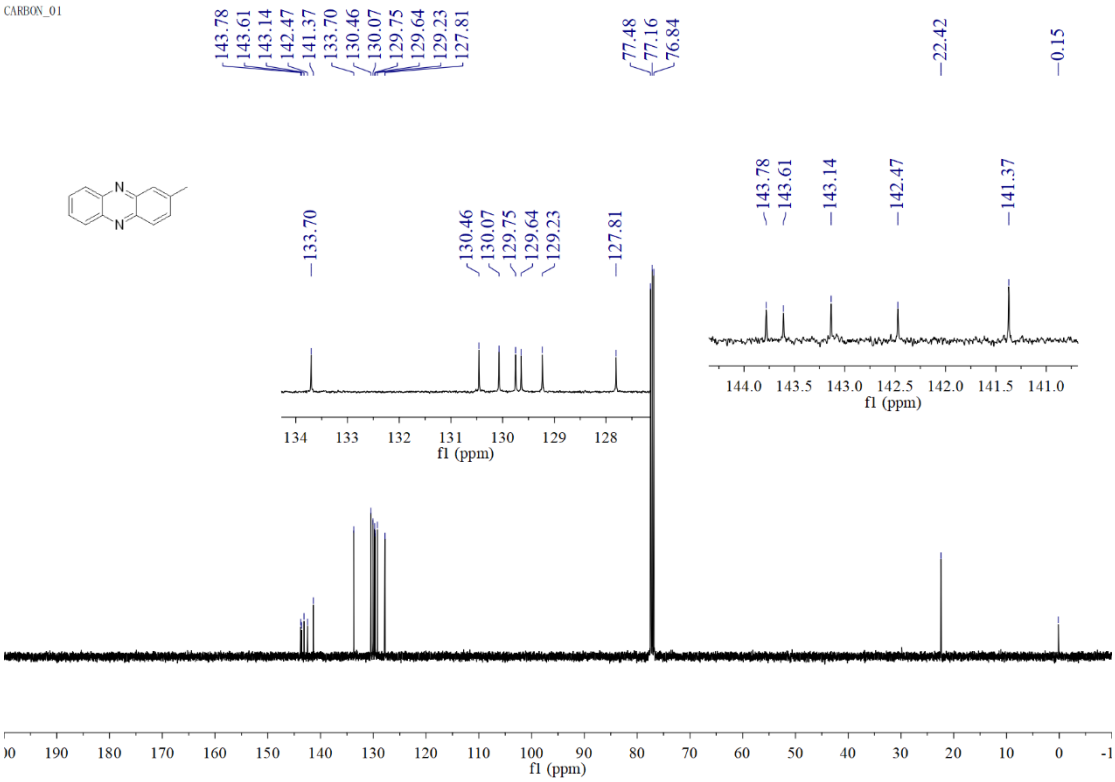
^{1}H NMR spectrum of **3m** in $CDCl_3$



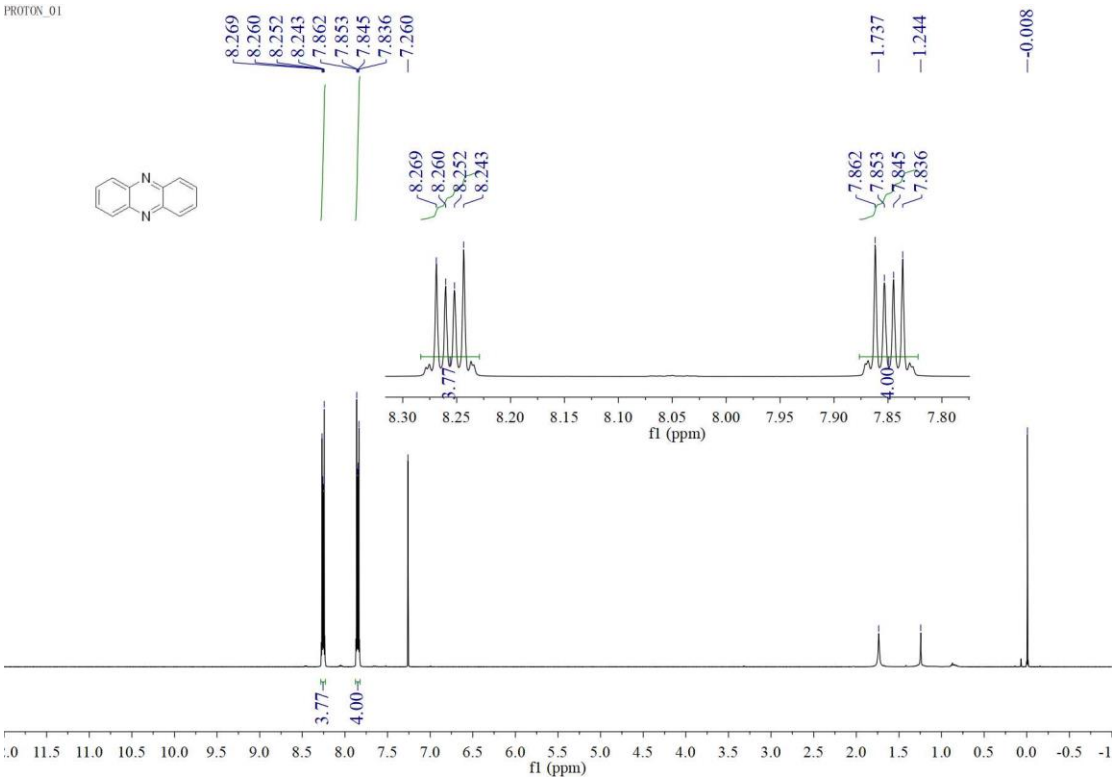
^{13}C NMR spectrum of **3m** in $CDCl_3$



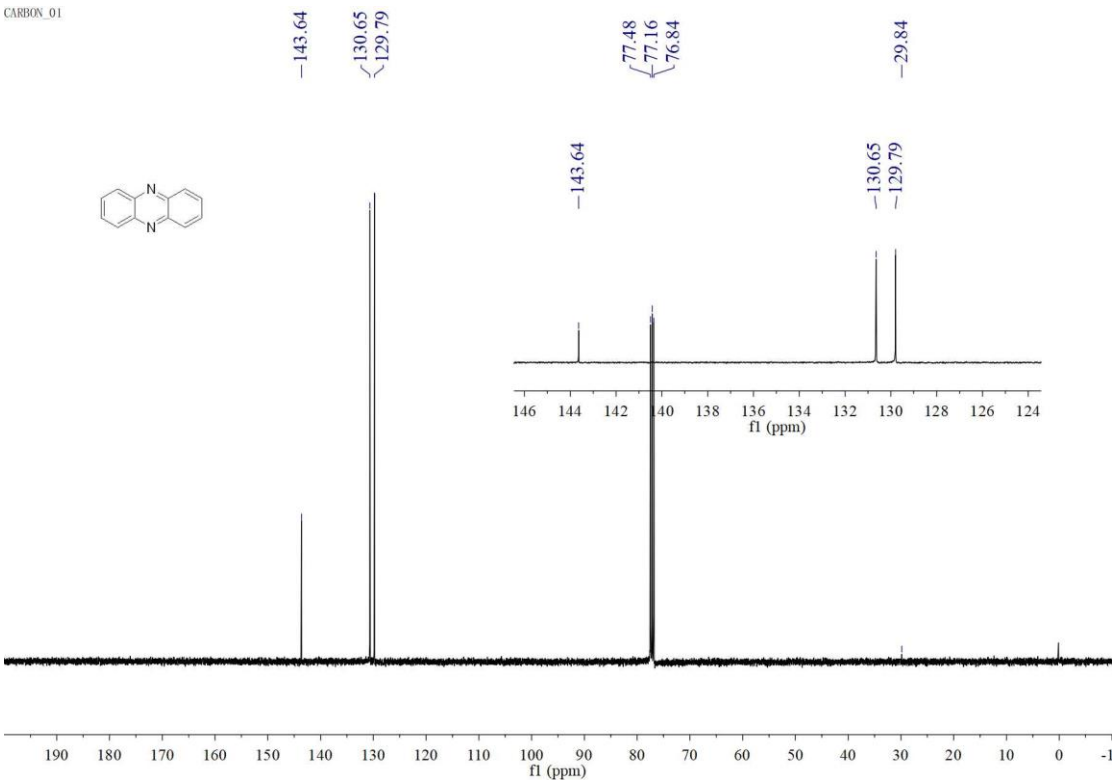
^{1}H NMR spectrum of **4a** in $CDCl_3$



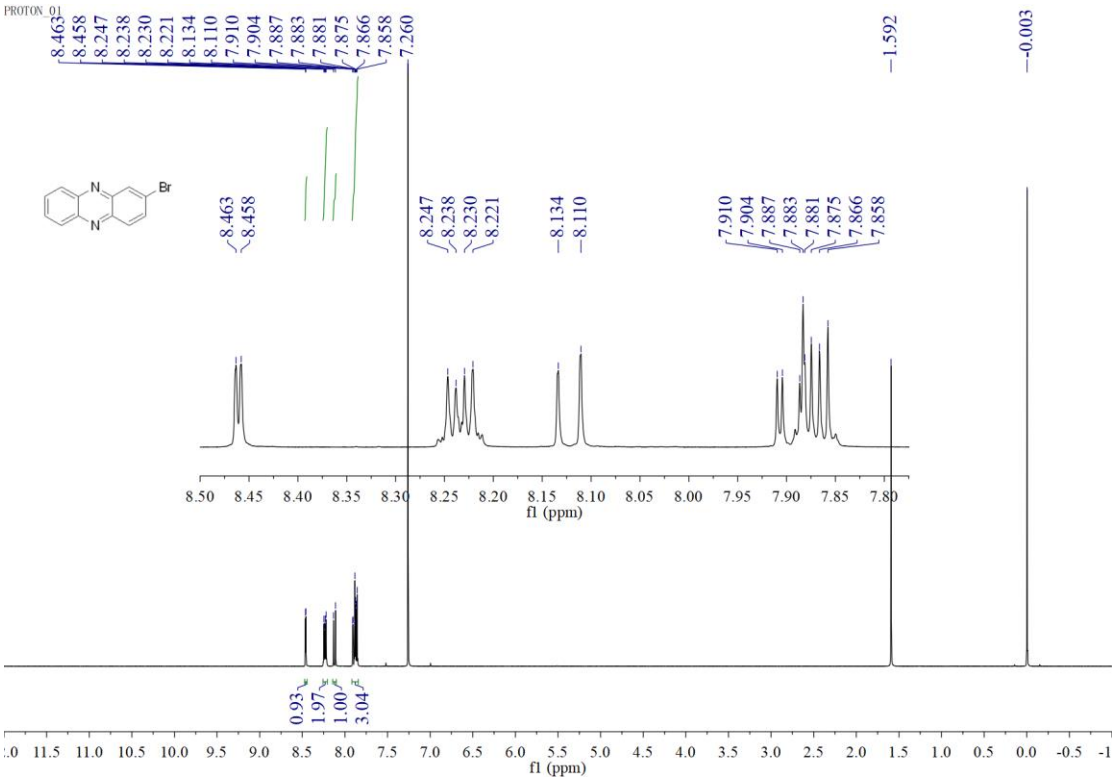
^{13}C NMR spectrum of **4a** in $CDCl_3$



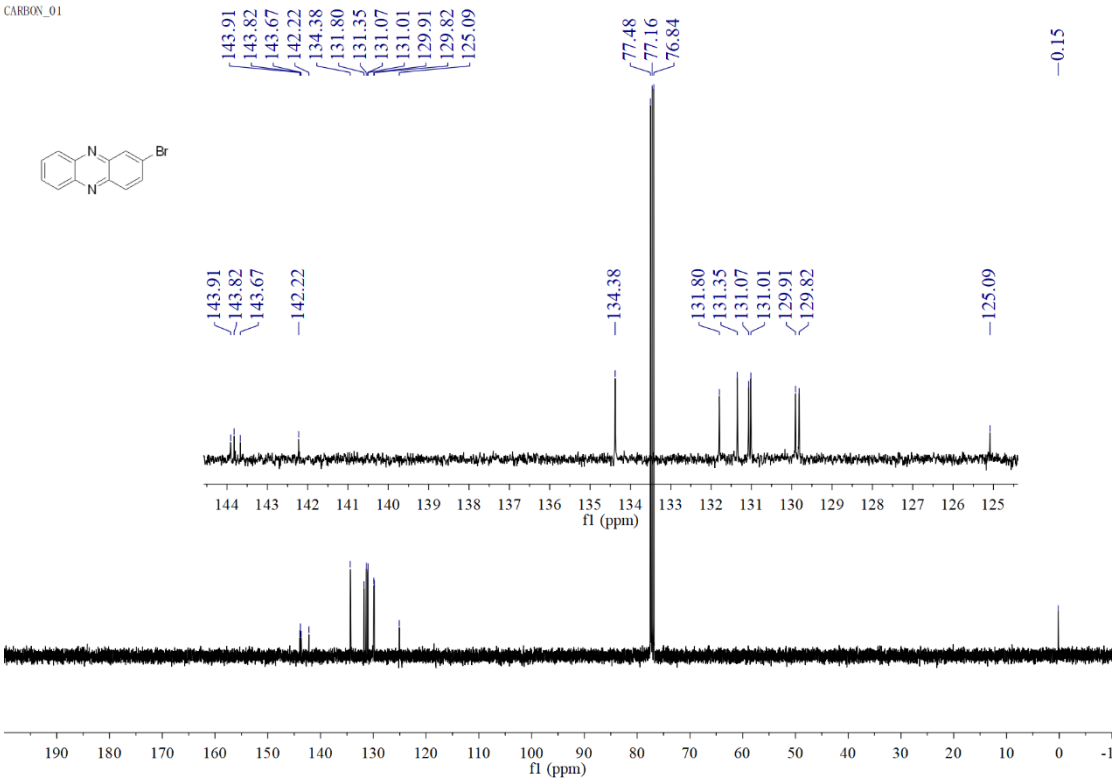
^{1}H NMR spectrum of **4b** in $CDCl_3$



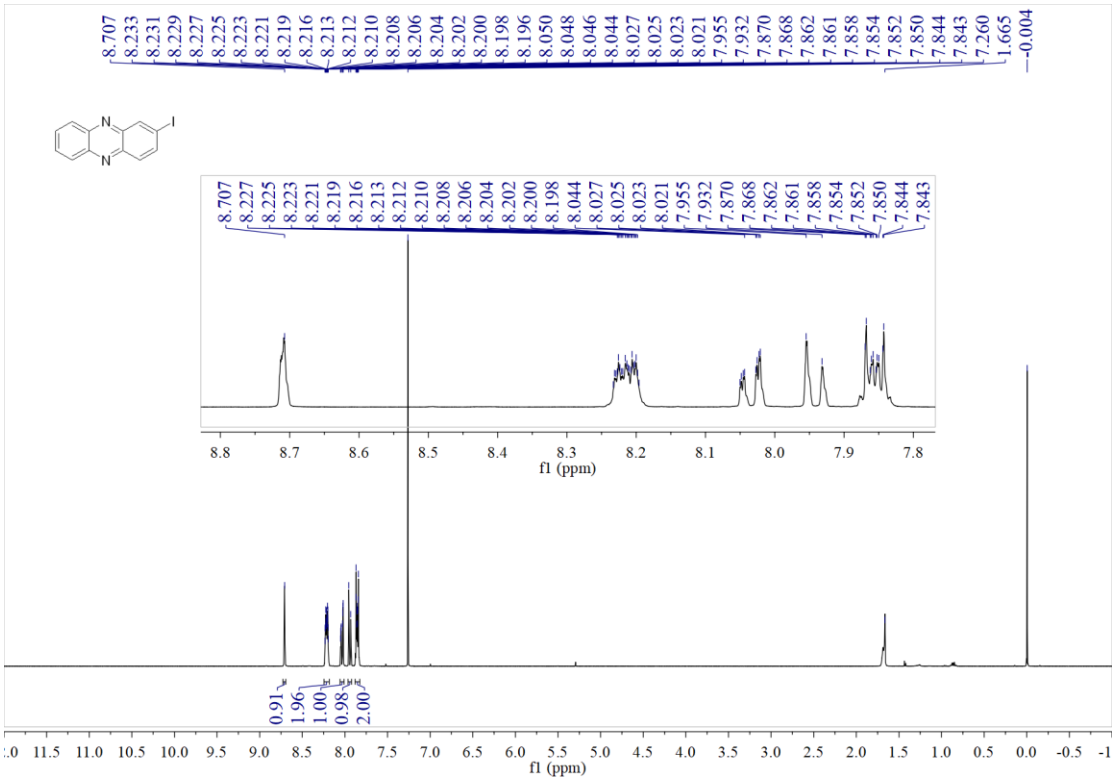
^{13}C NMR spectrum of **4b** in $CDCl_3$



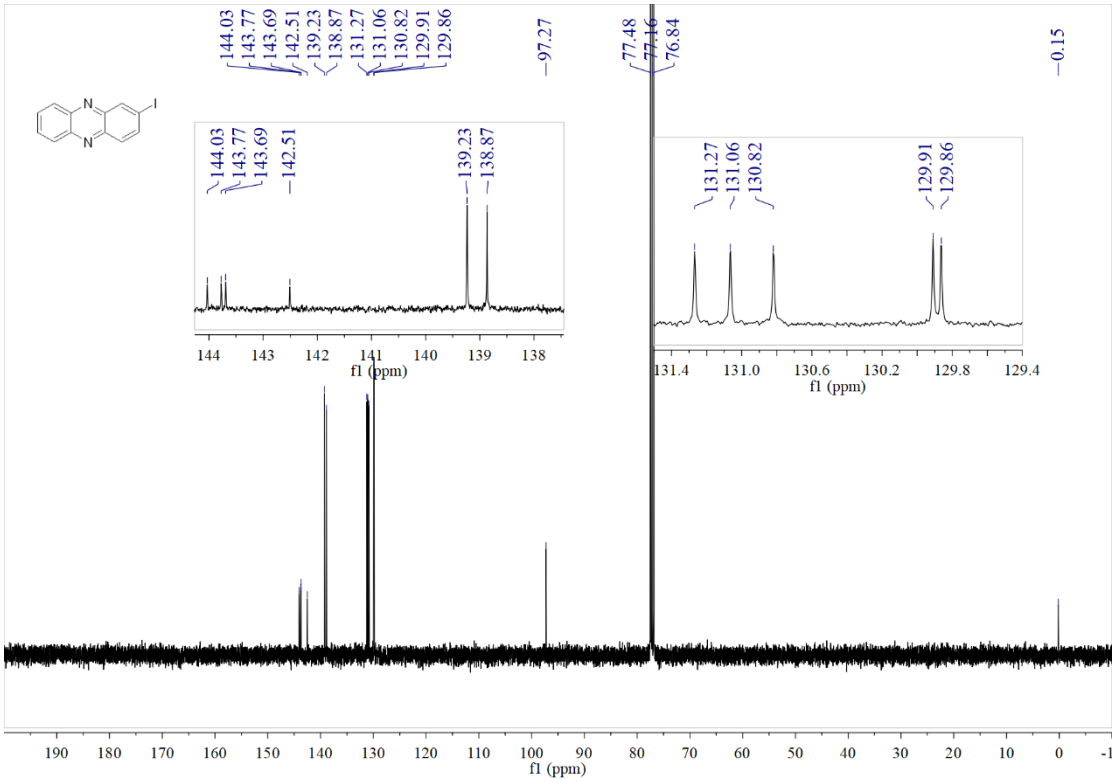
^{1}H NMR spectrum of **4c** in $CDCl_3$



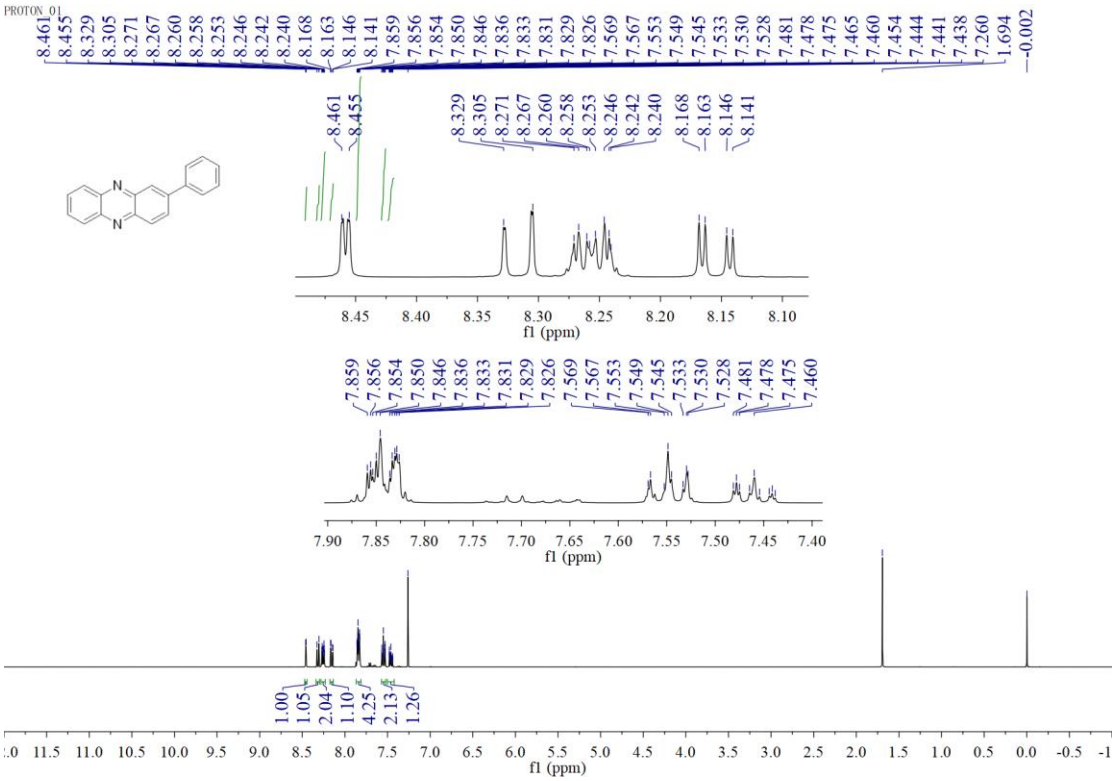
^{13}C NMR spectrum of **4c** in $CDCl_3$



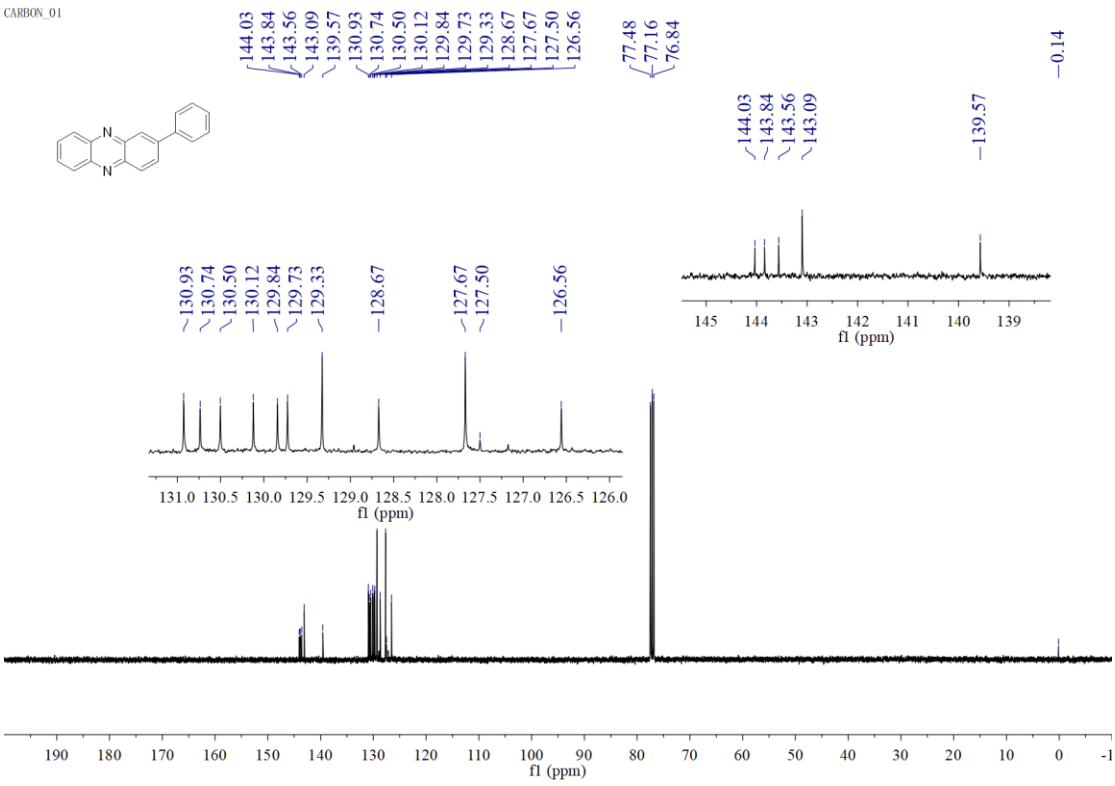
^{1}H NMR spectrum of **4d** in $CDCl_3$



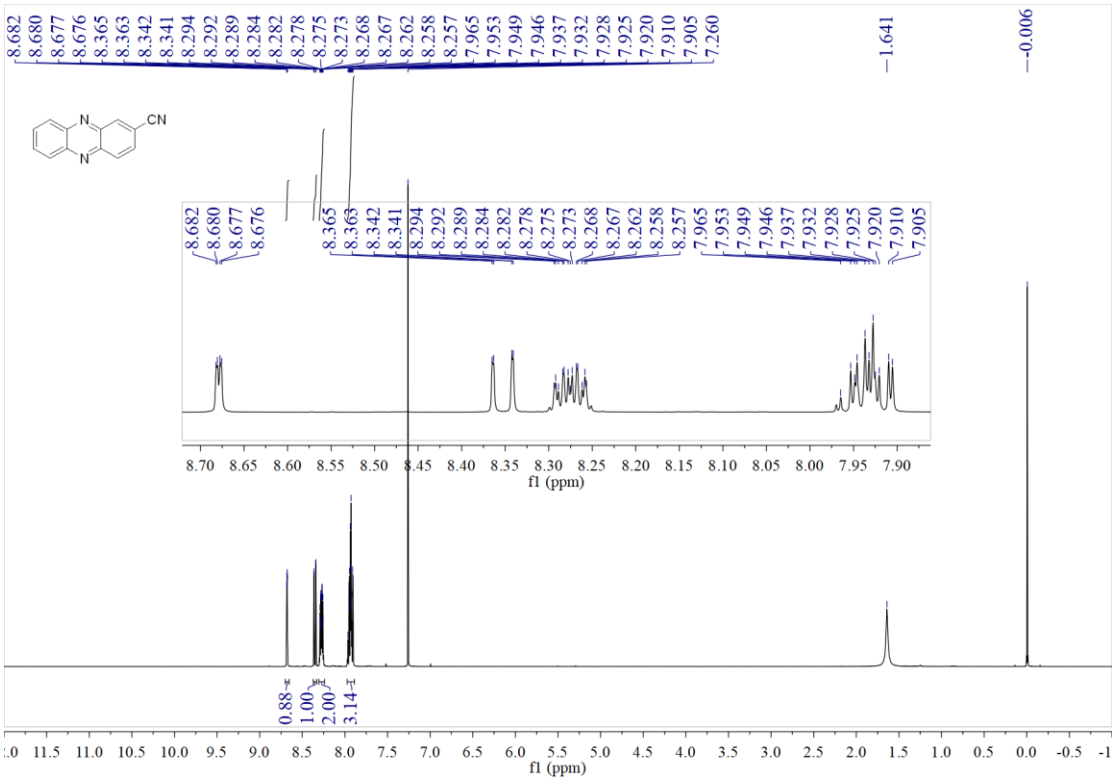
^{13}C NMR spectrum of **4d** in $CDCl_3$



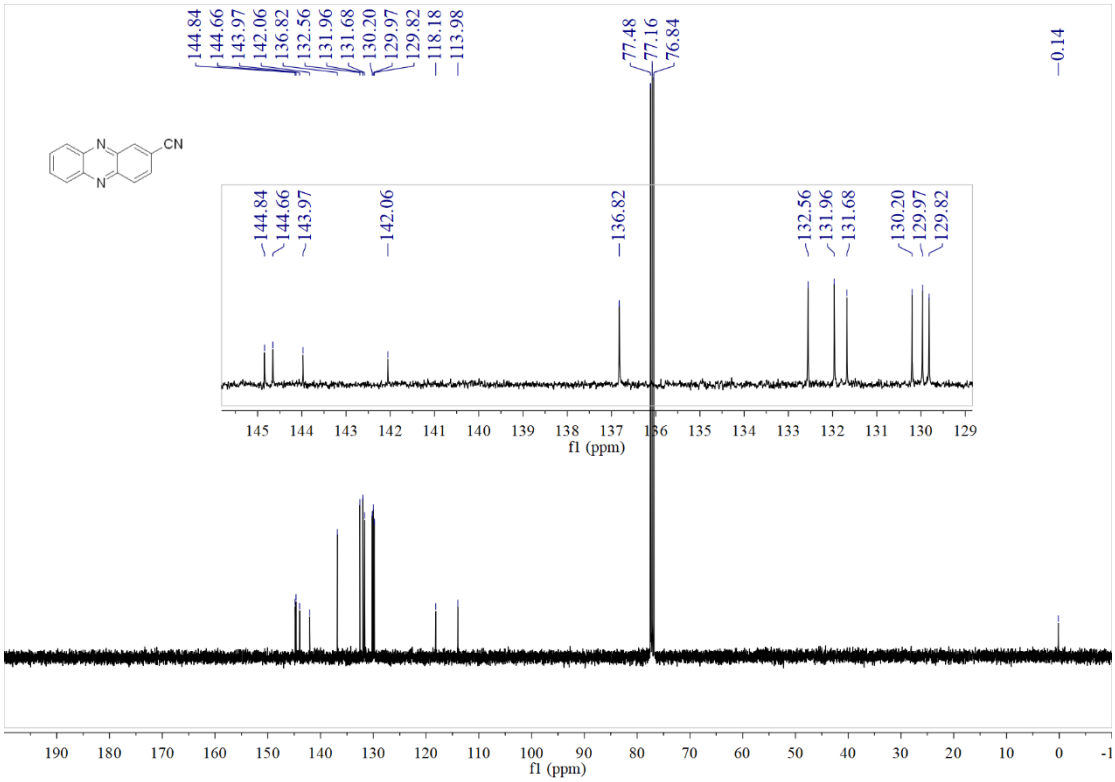
^{1}H NMR spectrum of **4e** in $CDCl_3$



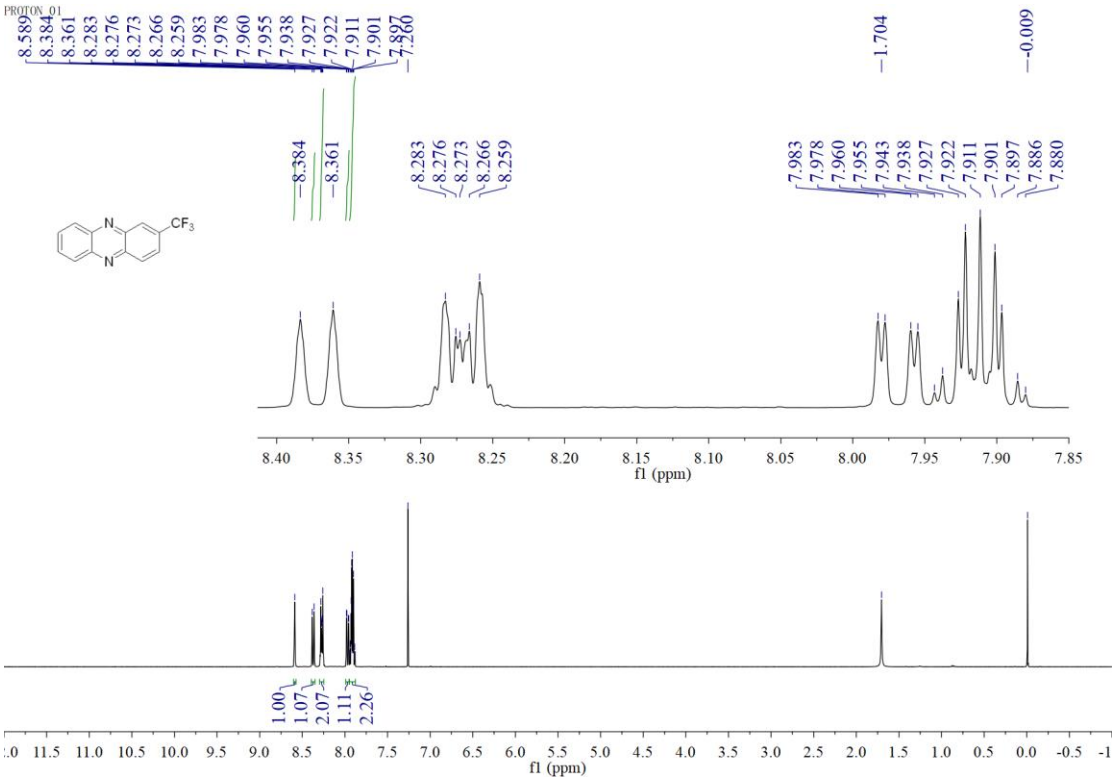
^{13}C NMR spectrum of **4e** in $CDCl_3$



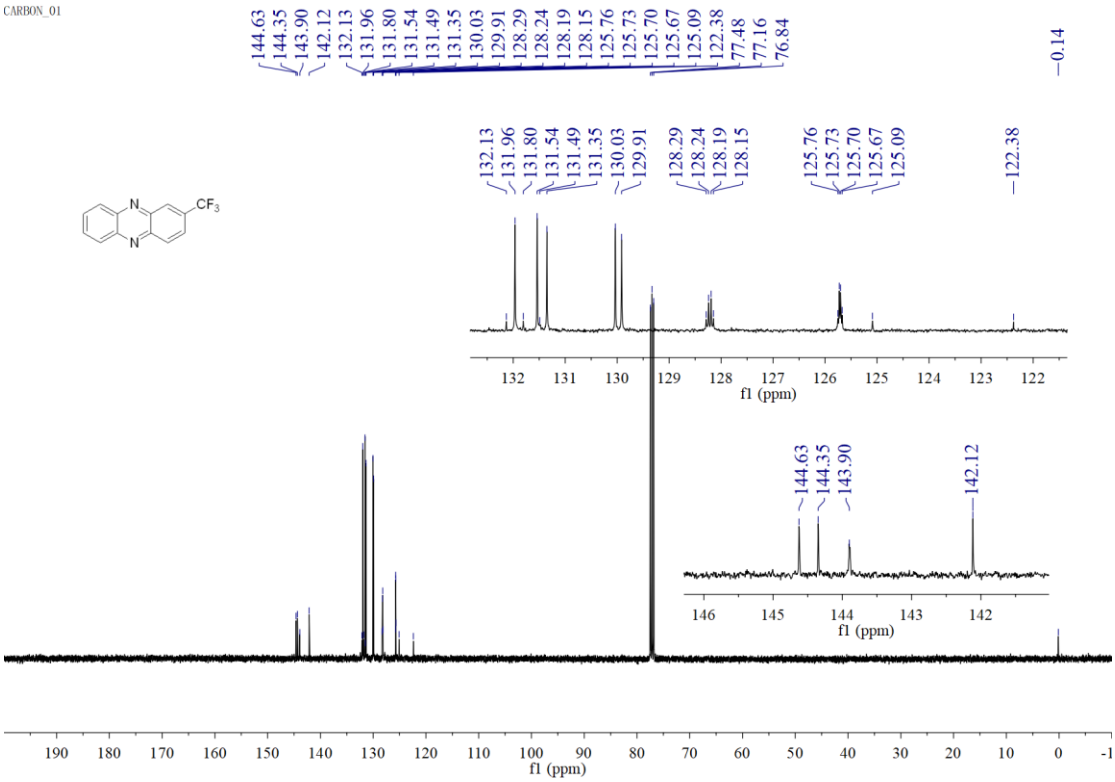
^{1}H NMR spectrum of **4f** in $CDCl_3$



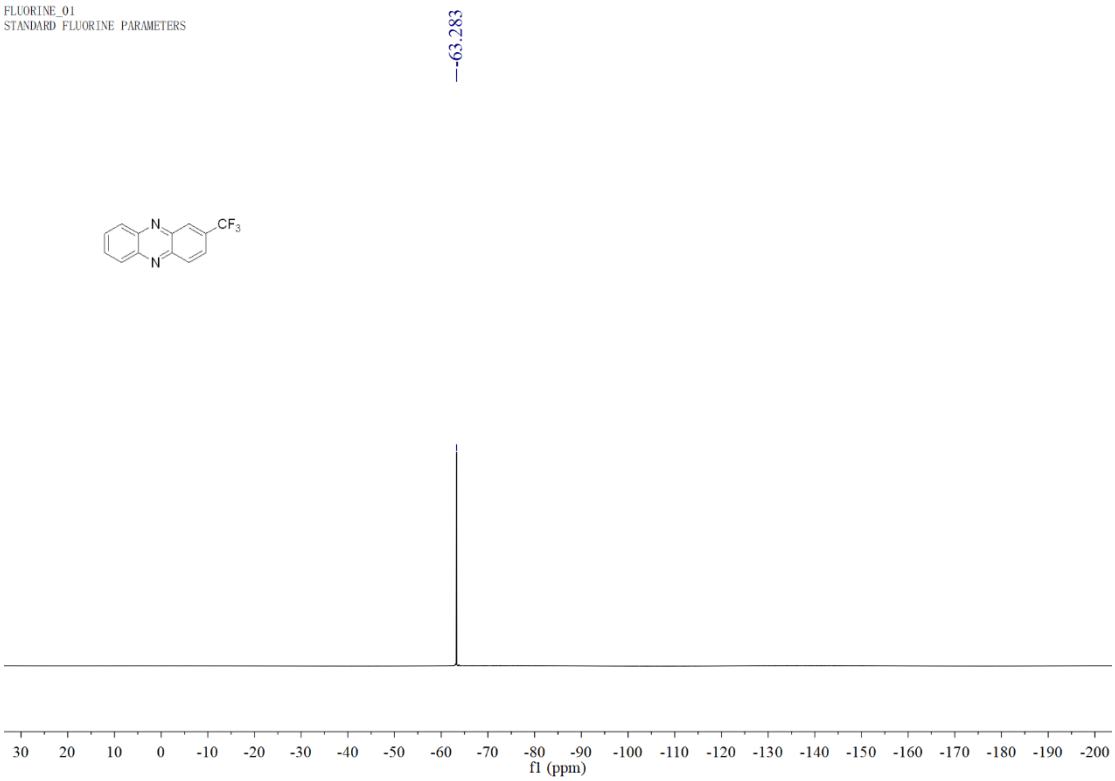
^{13}C NMR spectrum of **4f** in $CDCl_3$



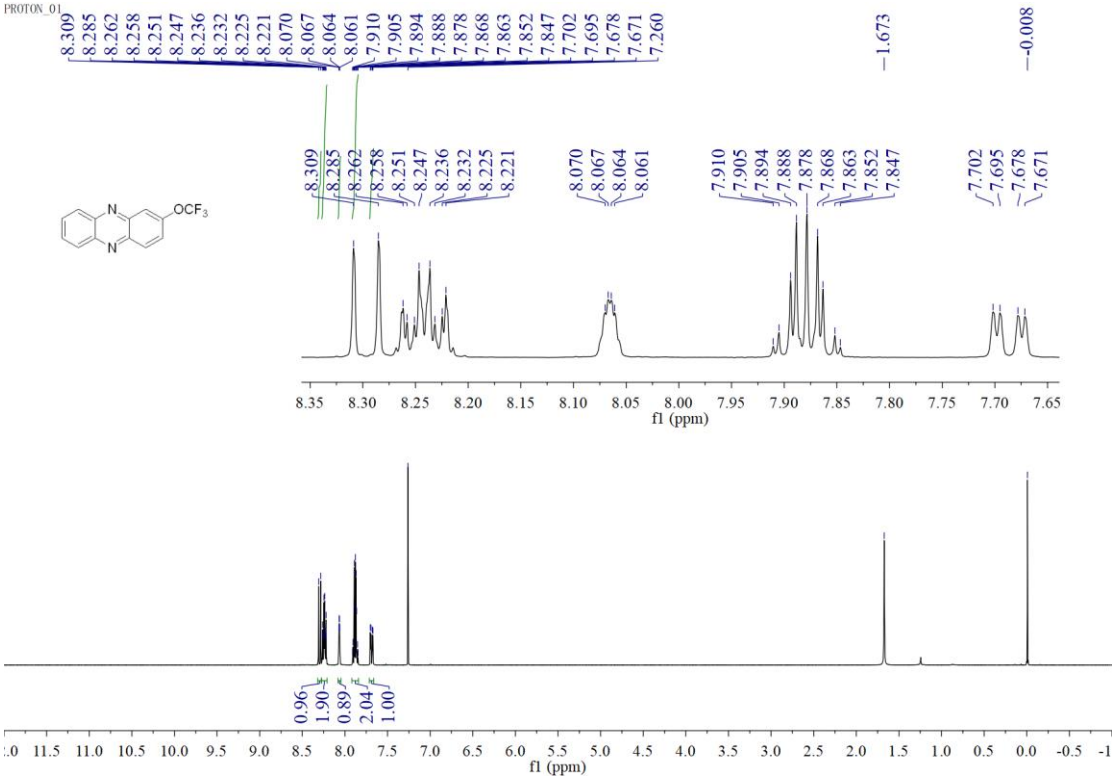
^{1}H NMR spectrum of **4g** in $CDCl_3$



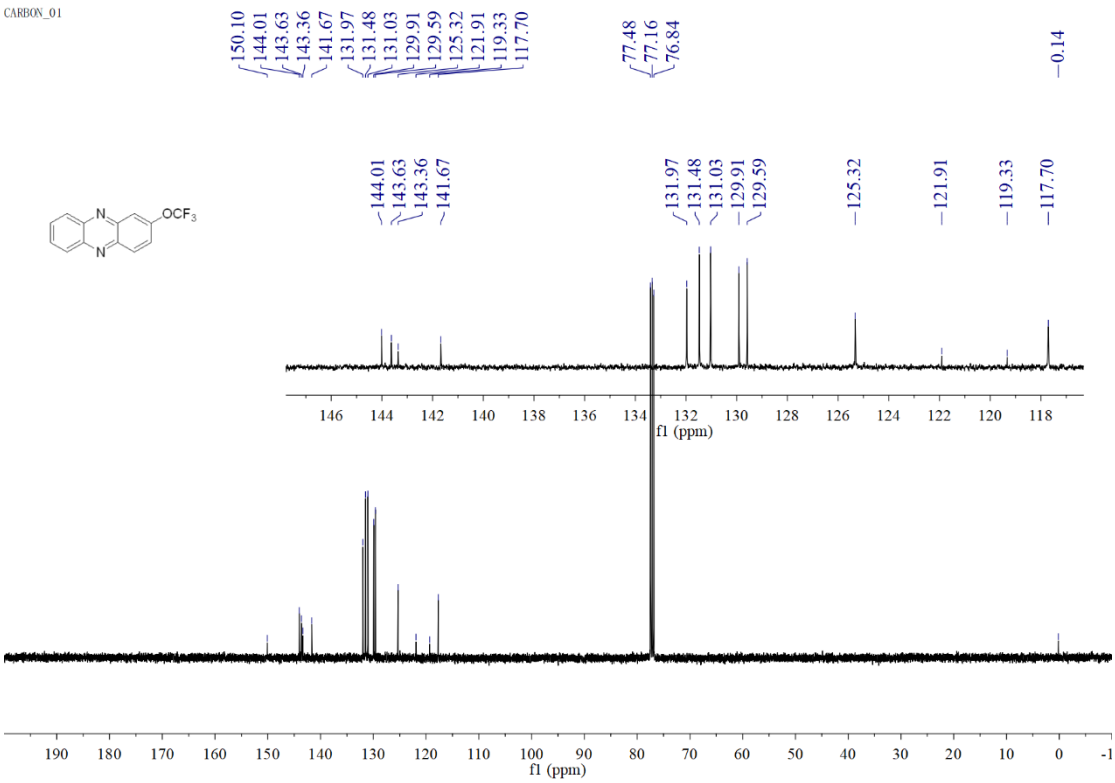
^{13}C NMR spectrum of **4g** in $CDCl_3$



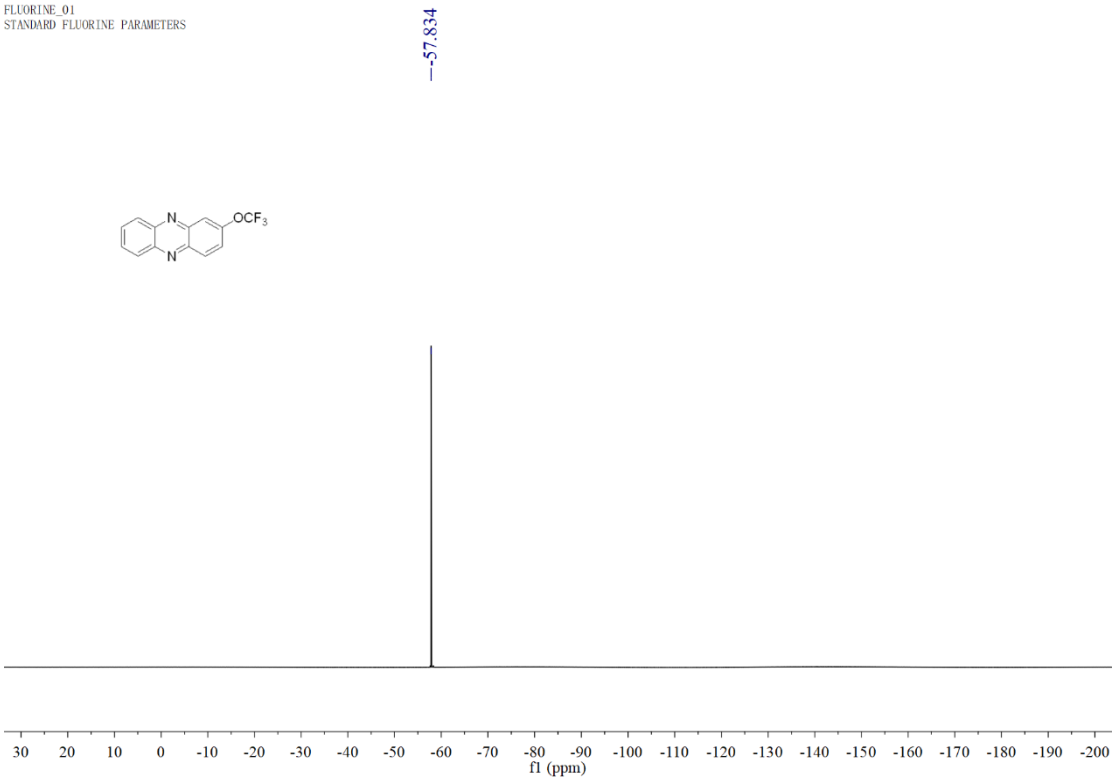
^{19}F NMR spectrum of **4g** in $CDCl_3$



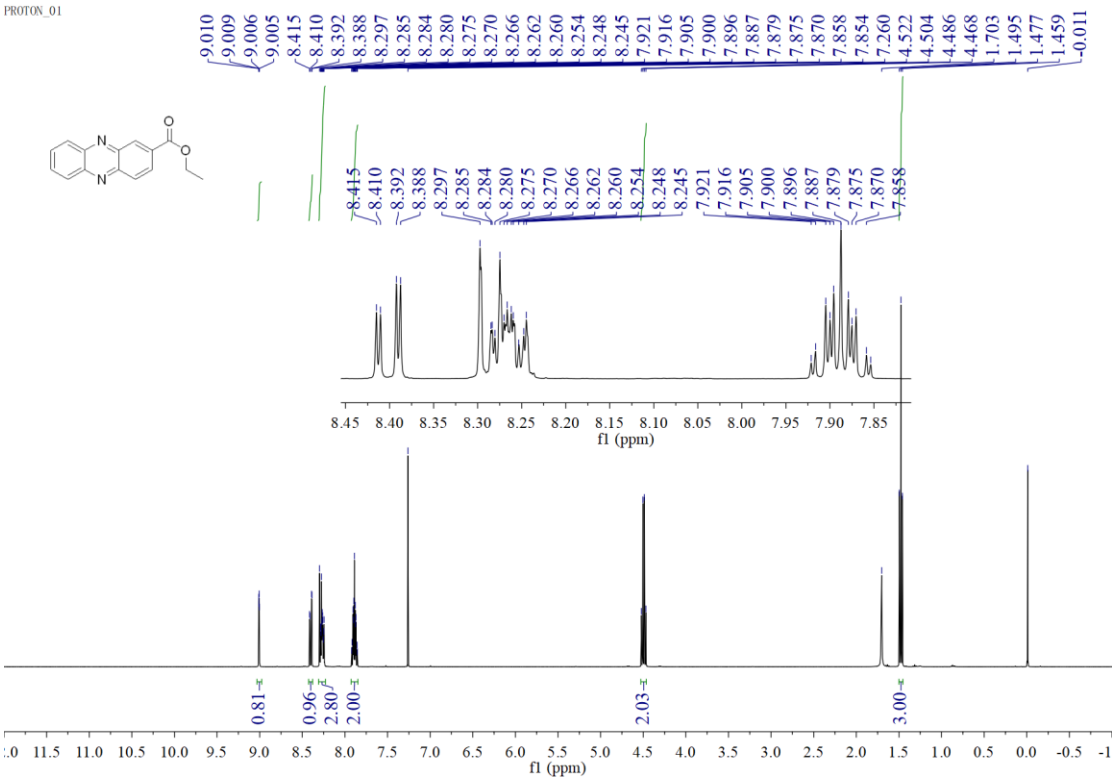
^{1}H NMR spectrum of **4h** in $CDCl_3$



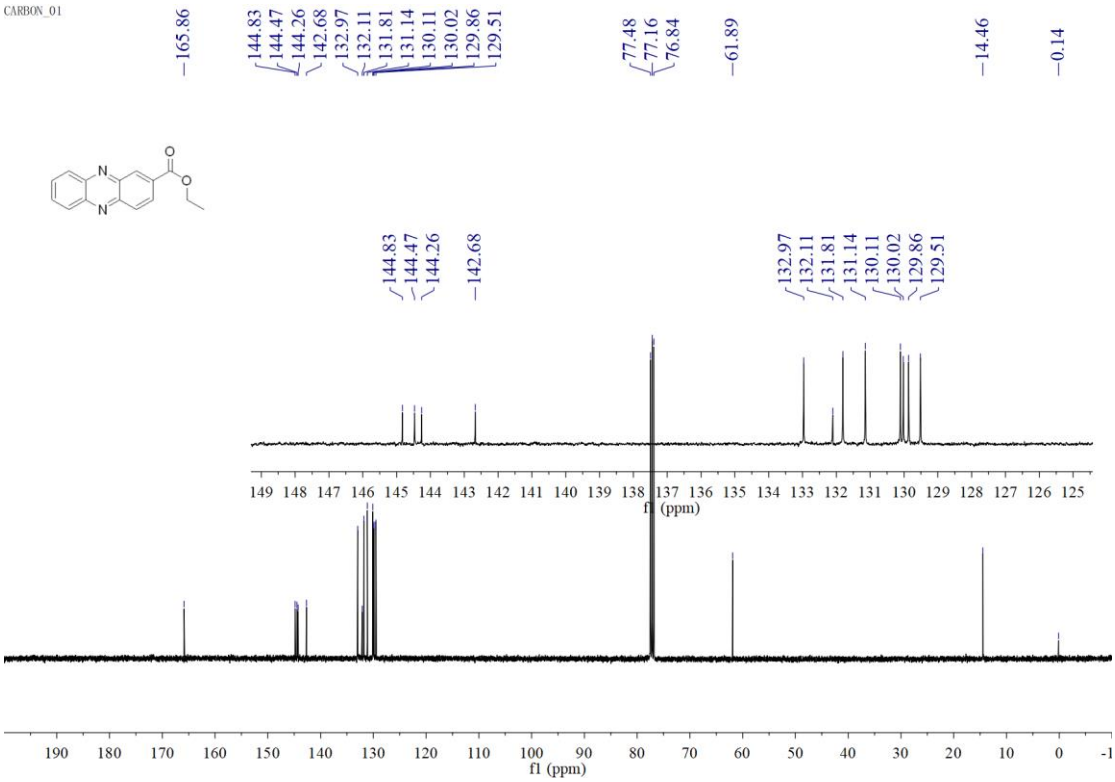
^{13}C NMR spectrum of **4h** in $CDCl_3$



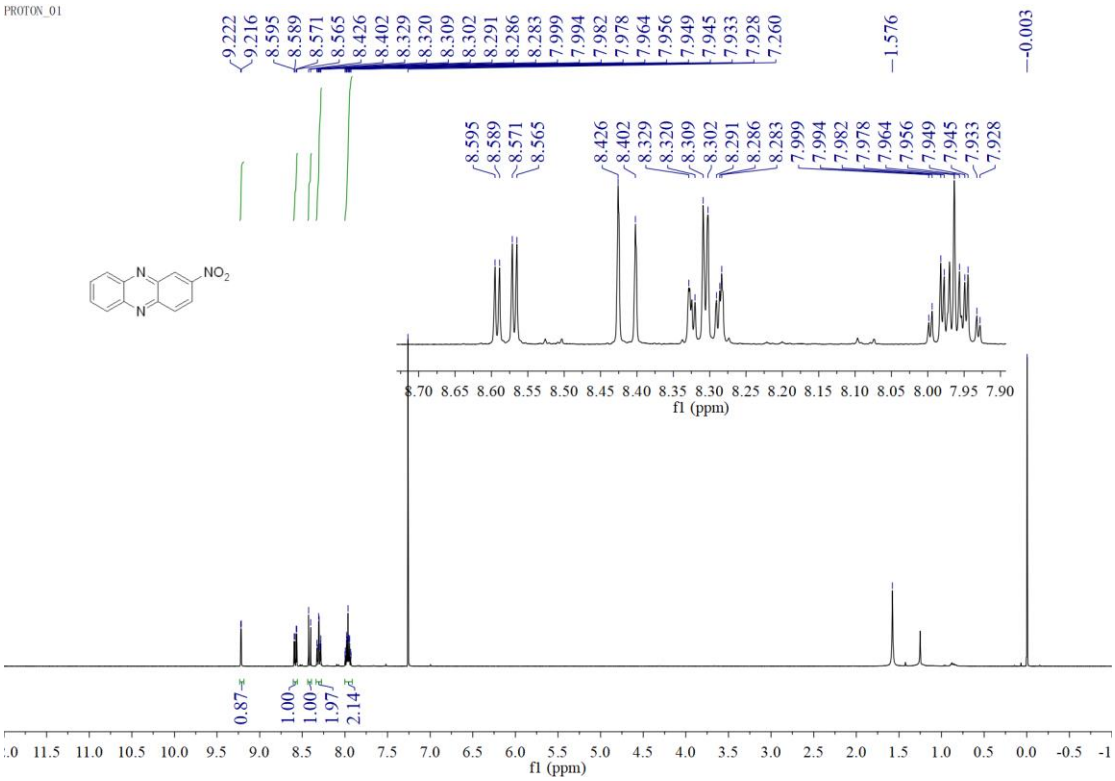
^{19}F NMR spectrum of **4h** in $CDCl_3$



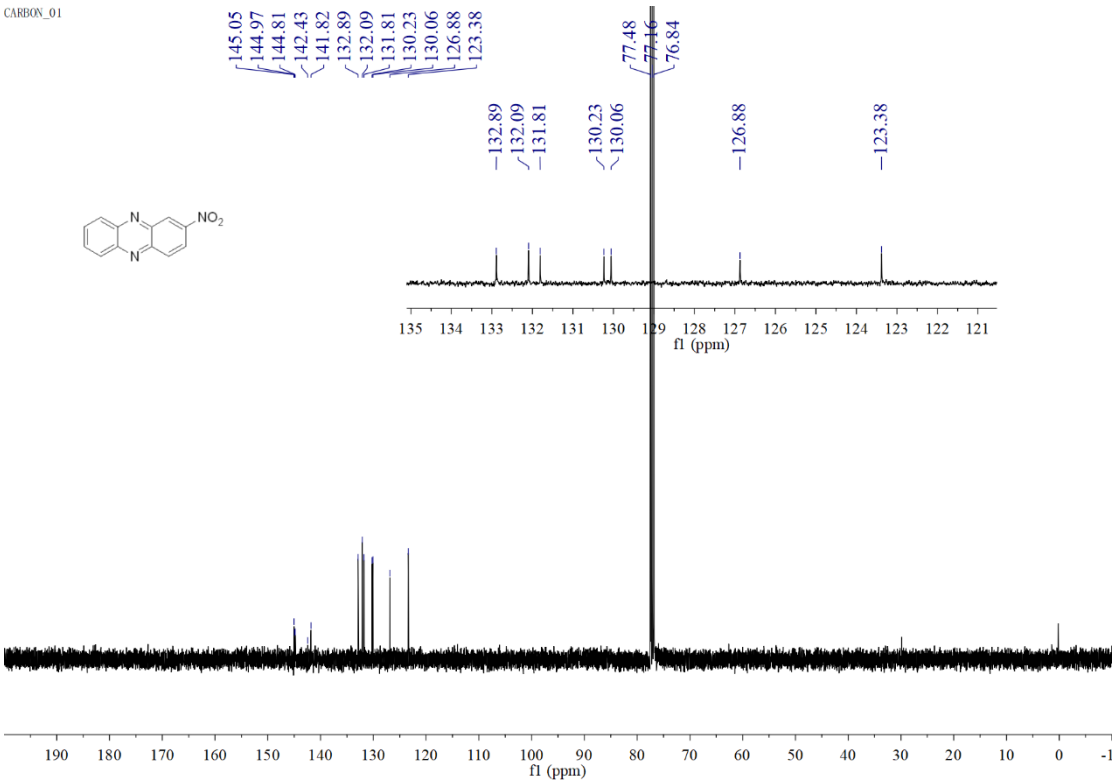
^{1}H NMR spectrum of **4i** in $CDCl_3$



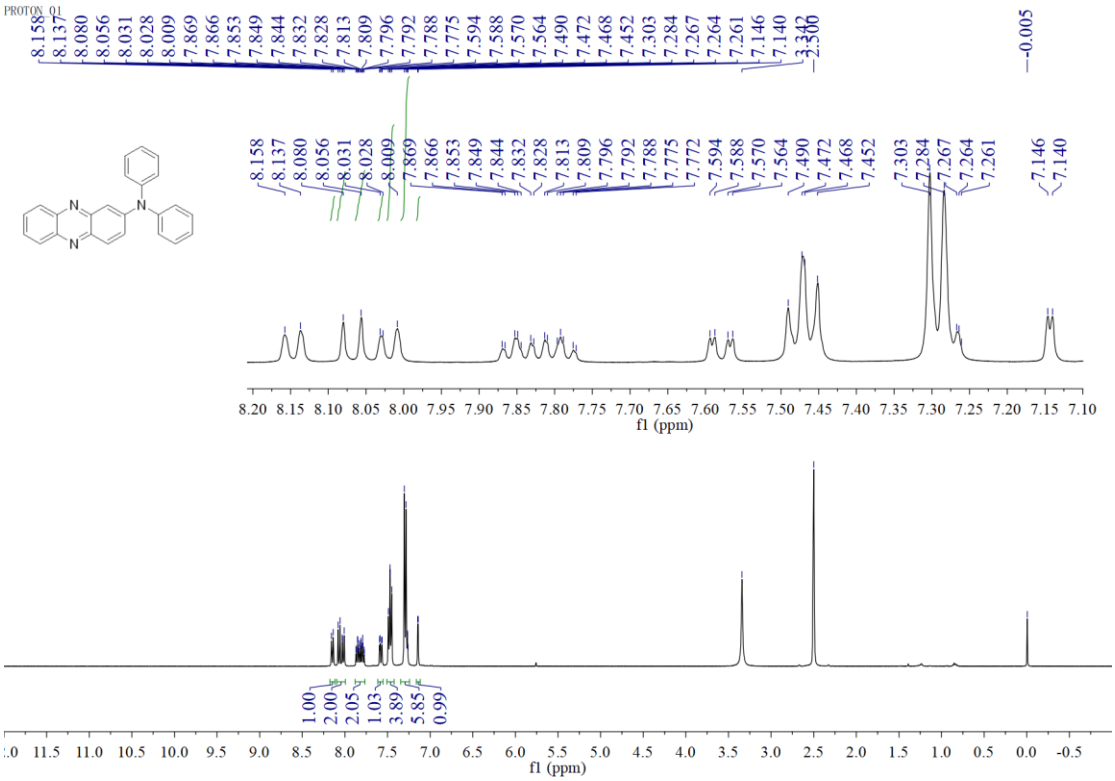
^{13}C NMR spectrum of **4i** in $CDCl_3$



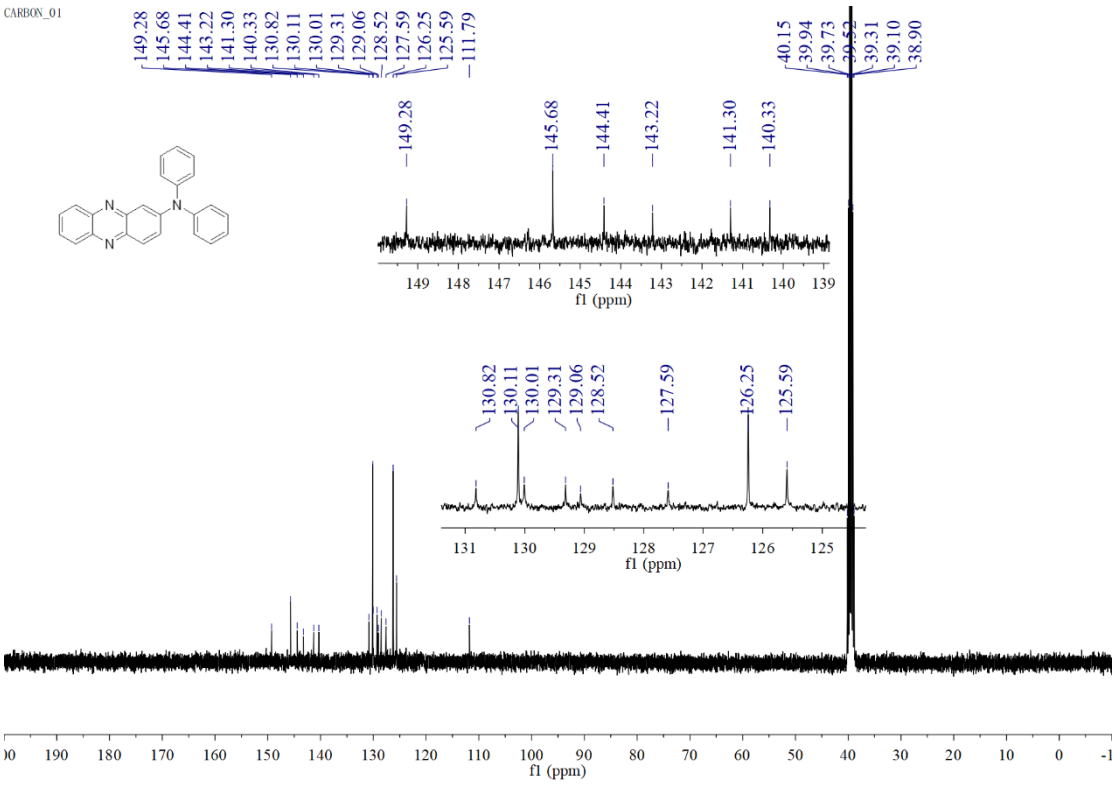
^{1}H NMR spectrum of **4j** in $CDCl_3$



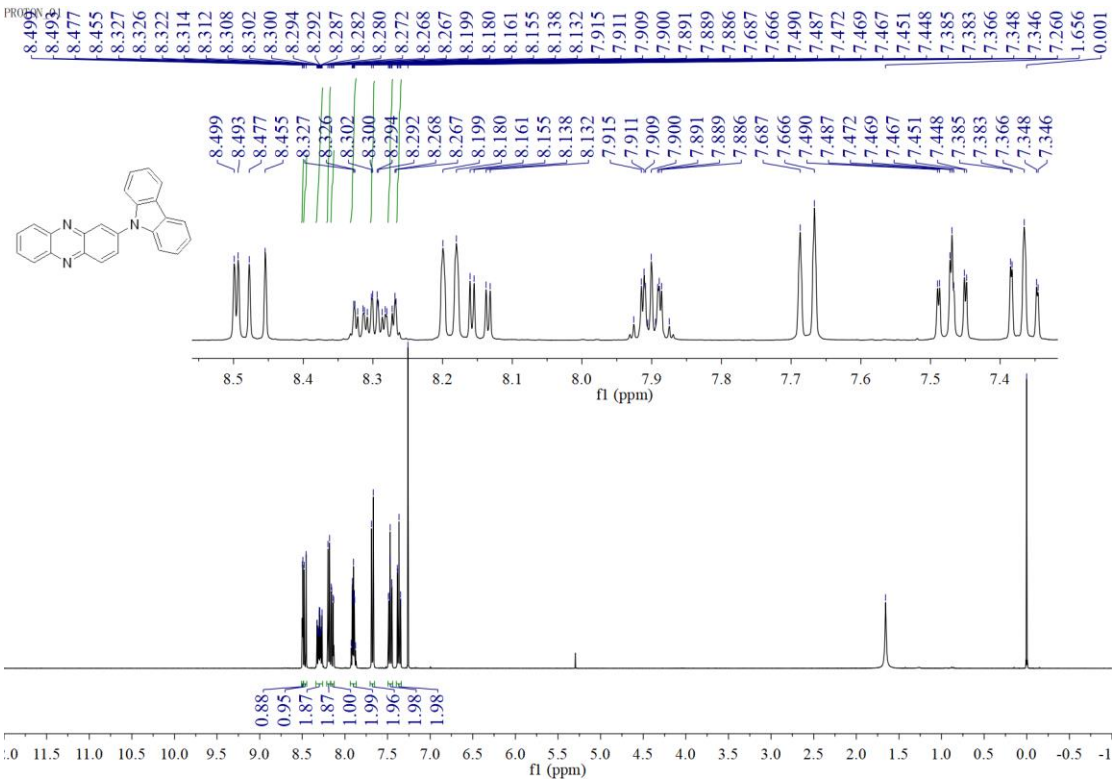
^{13}C NMR spectrum of **4j** in $CDCl_3$



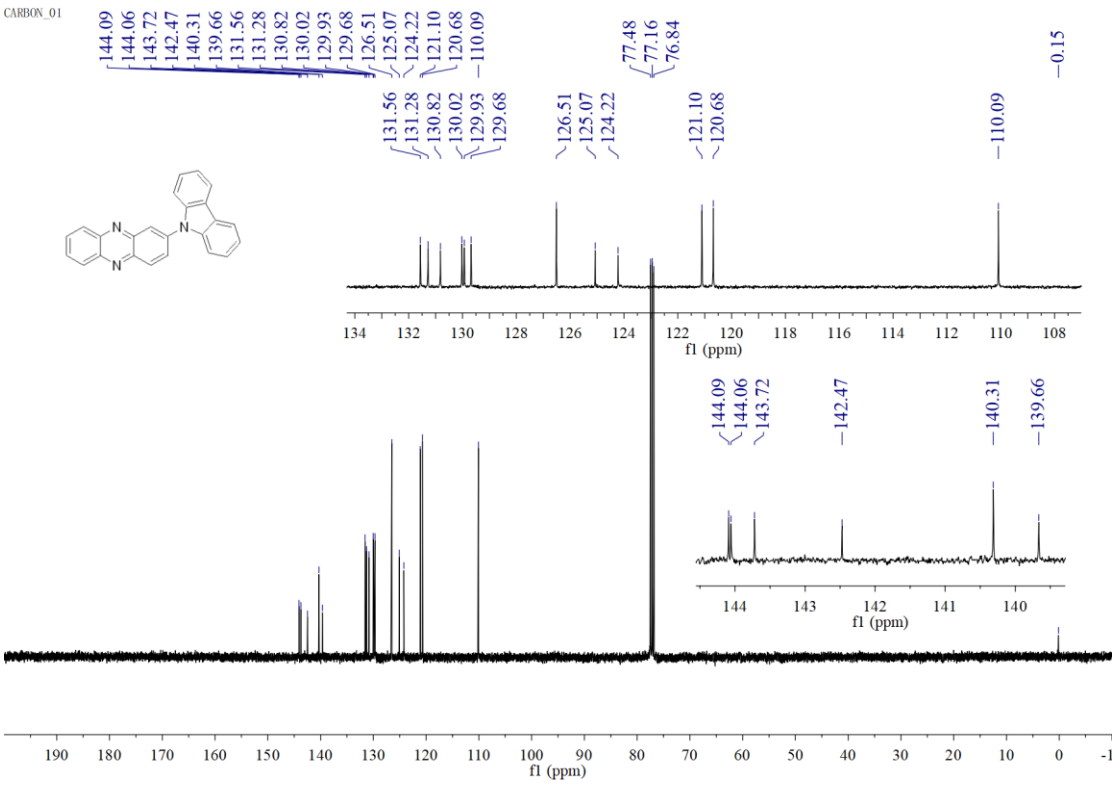
^{1}H NMR spectrum of **4k** in DMSO-*d6*



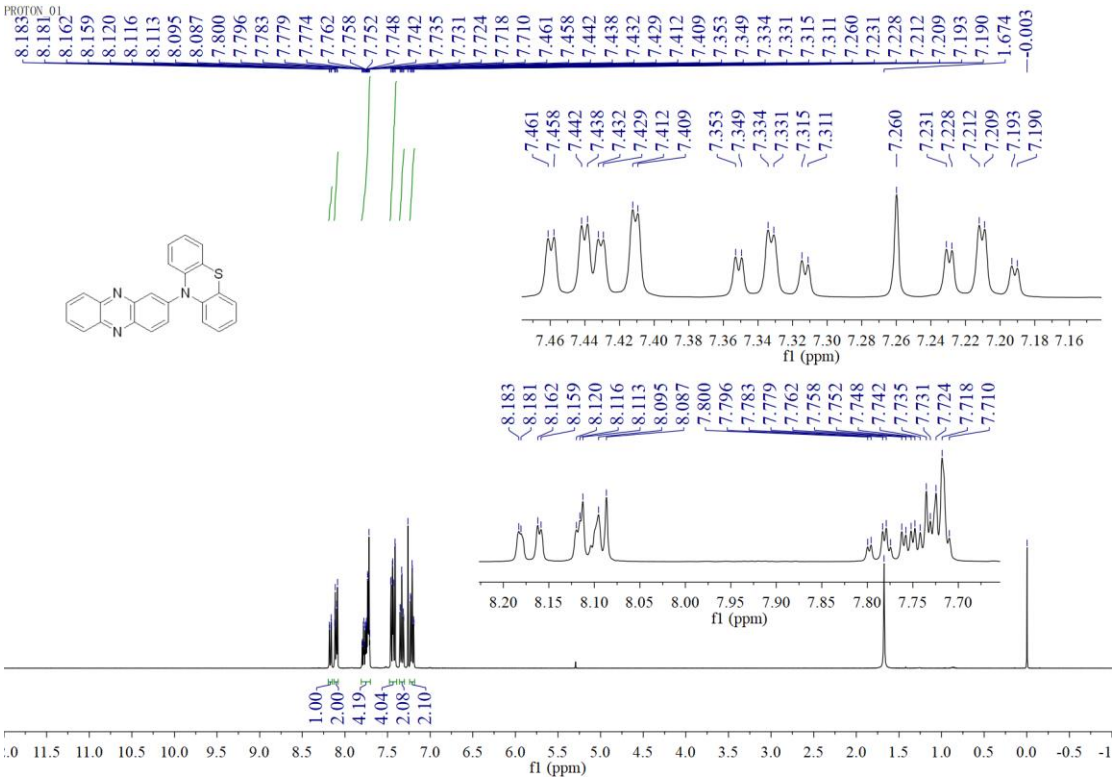
^{13}C NMR spectrum of **4k** in DMSO-*d6*



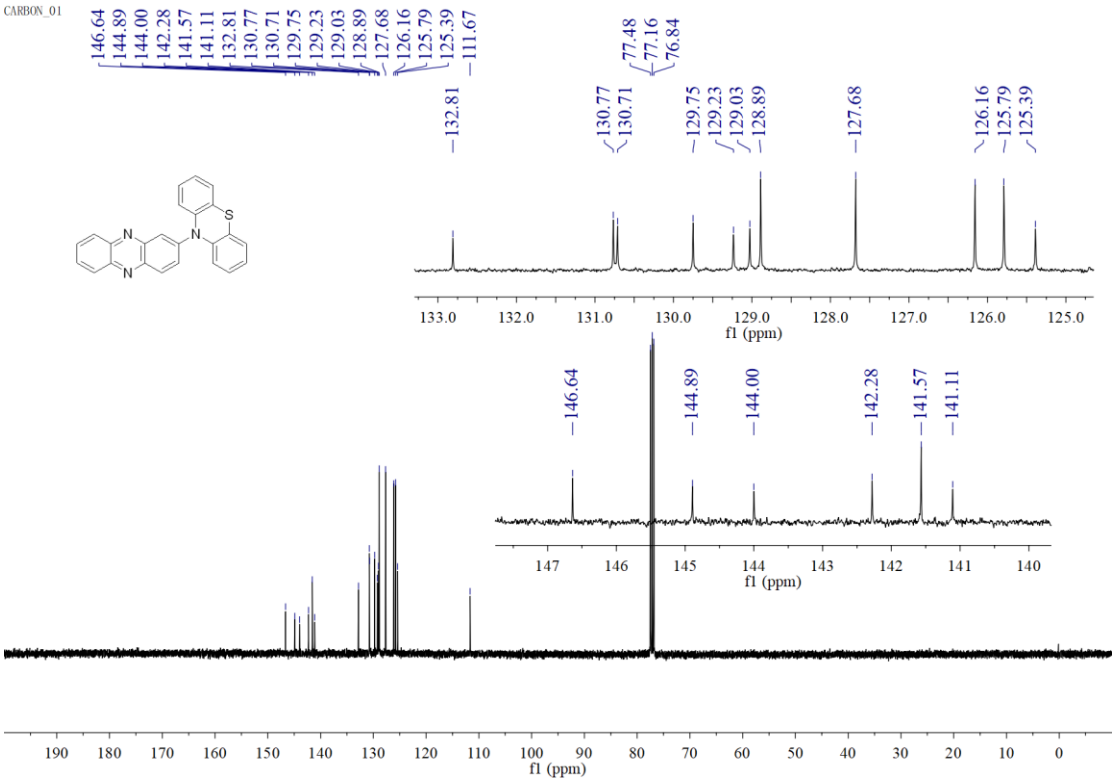
^{1}H NMR spectrum of **4l** in $CDCl_3$



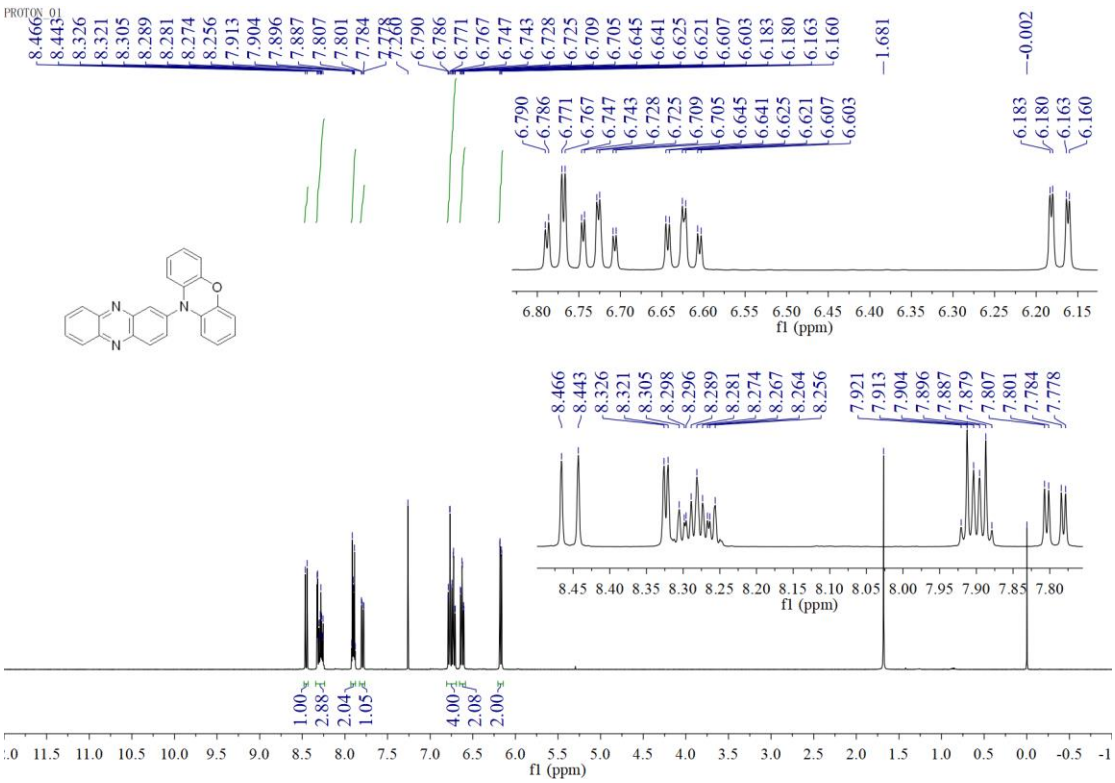
^{13}C NMR spectrum of **4l** in $CDCl_3$



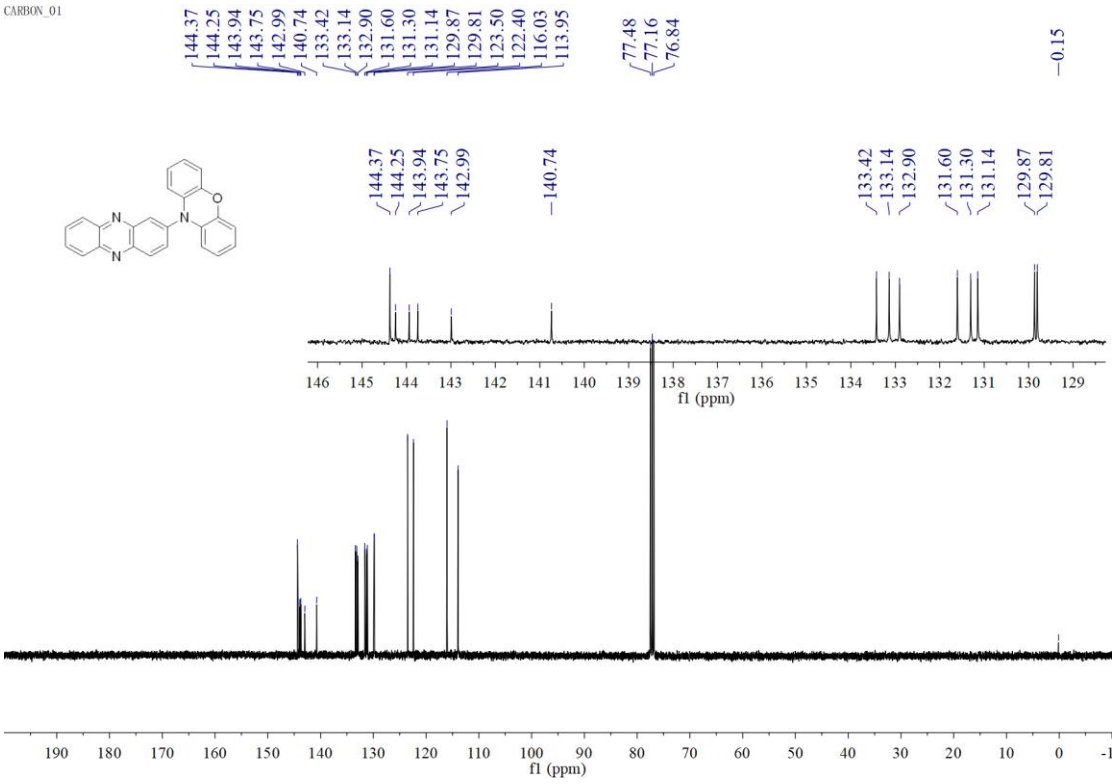
^{1}H NMR spectrum of **4m** in $CDCl_3$



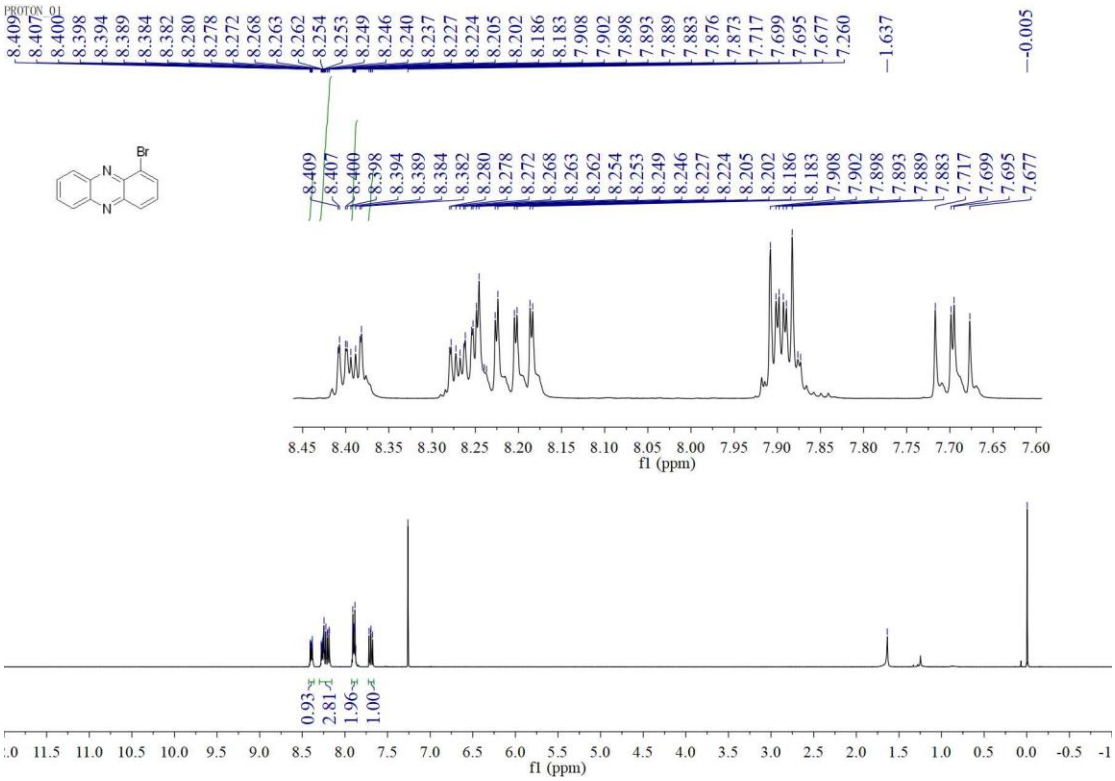
^{13}C NMR spectrum of **4m** in $CDCl_3$



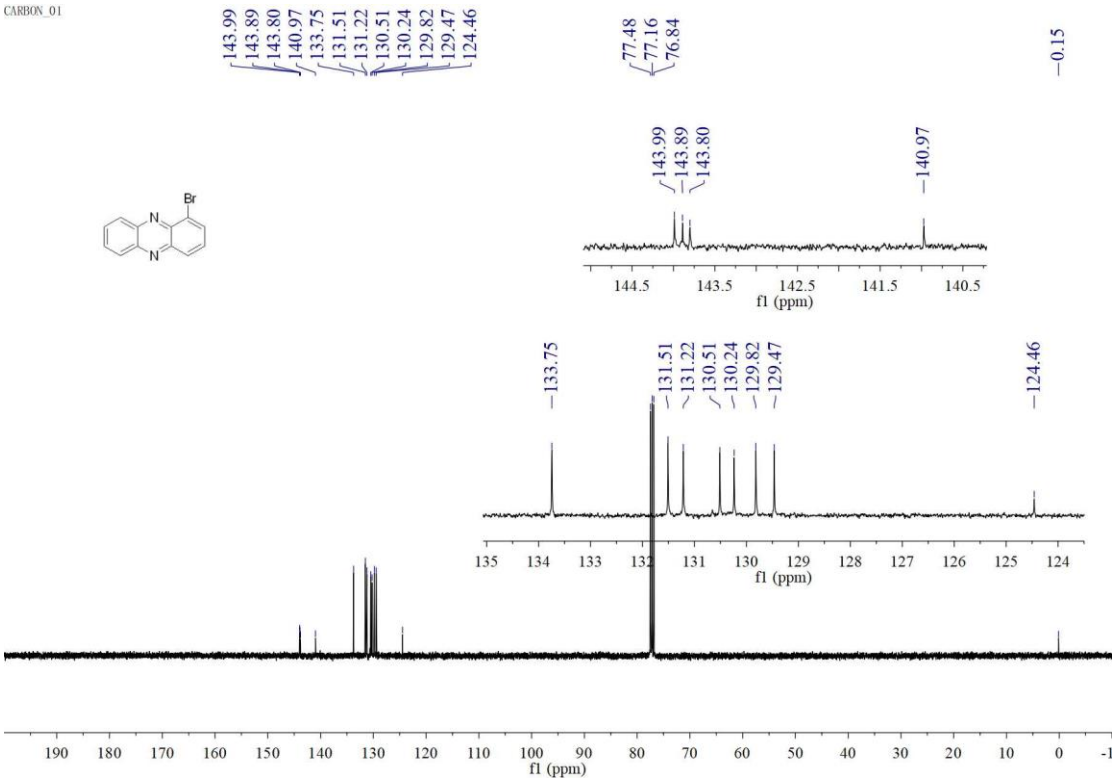
^{1}H NMR spectrum of **4n** in $CDCl_3$



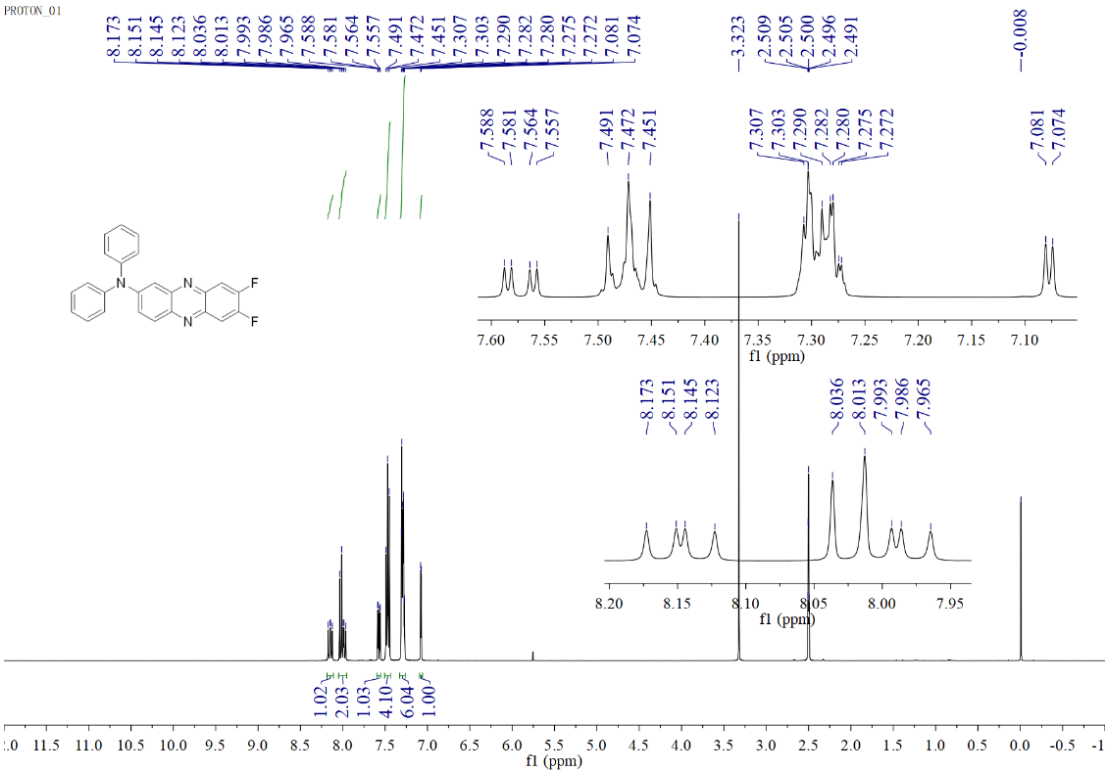
^{13}C NMR spectrum of **4n** in $CDCl_3$



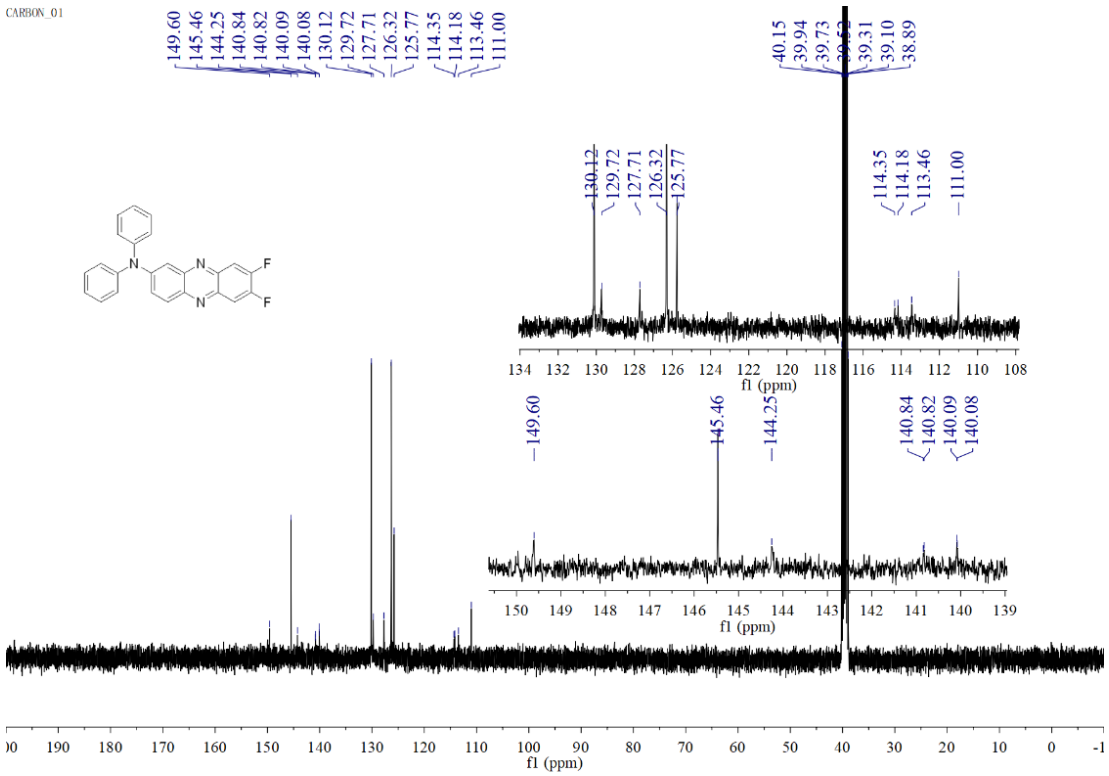
^{1}H NMR spectrum of **4o** in $CDCl_3$



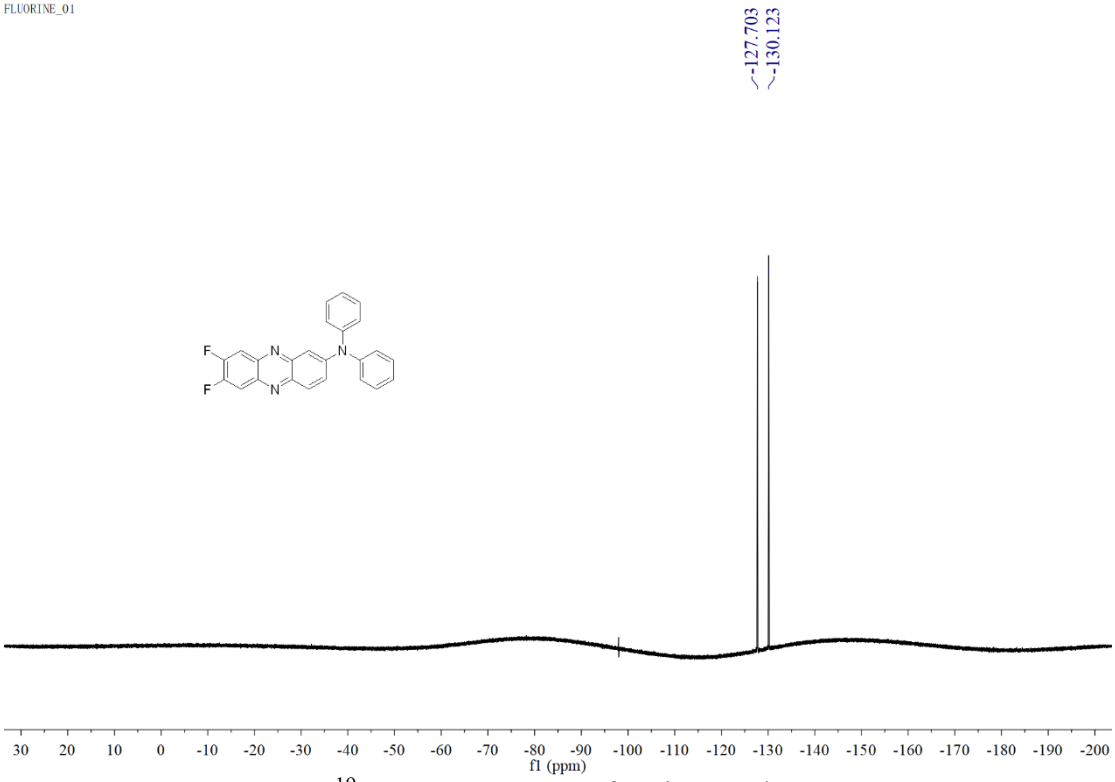
^{13}C NMR spectrum of **4o** in $CDCl_3$



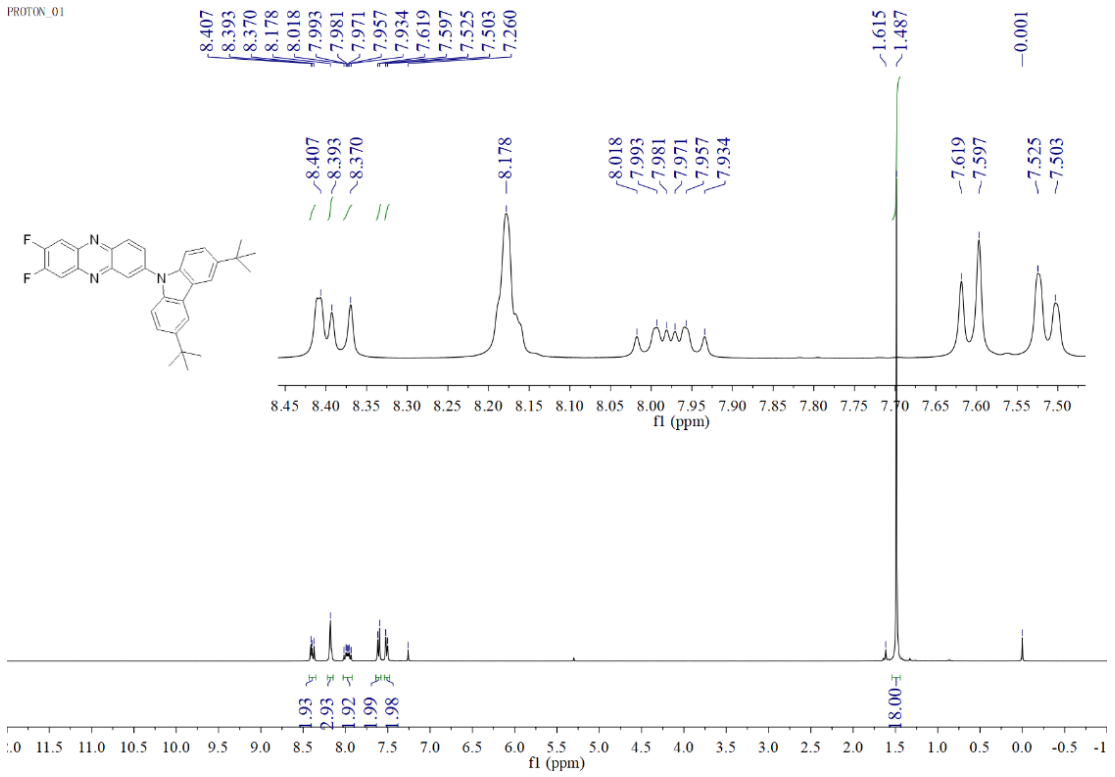
^{1}H NMR spectrum of **5a** in DMSO-*d6*



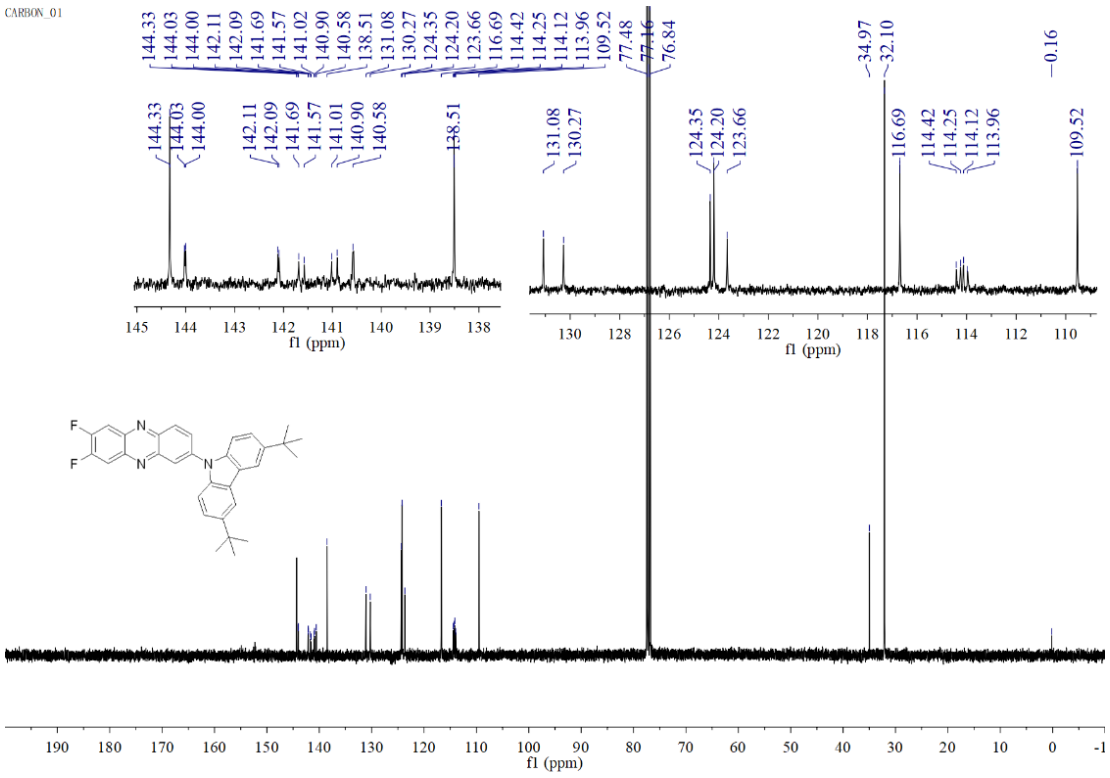
^{13}C NMR spectrum of **5a** in DMSO-*d6*



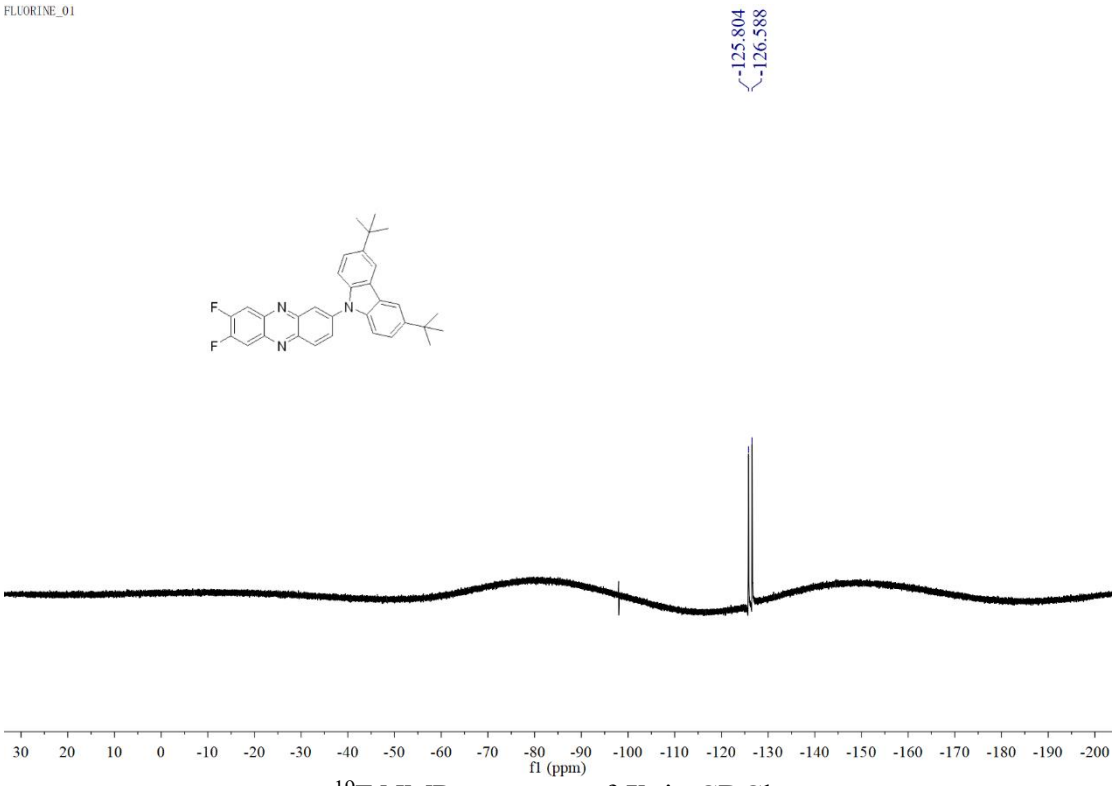
^{19}F NMR spectrum of **5a** in $CDCl_3$



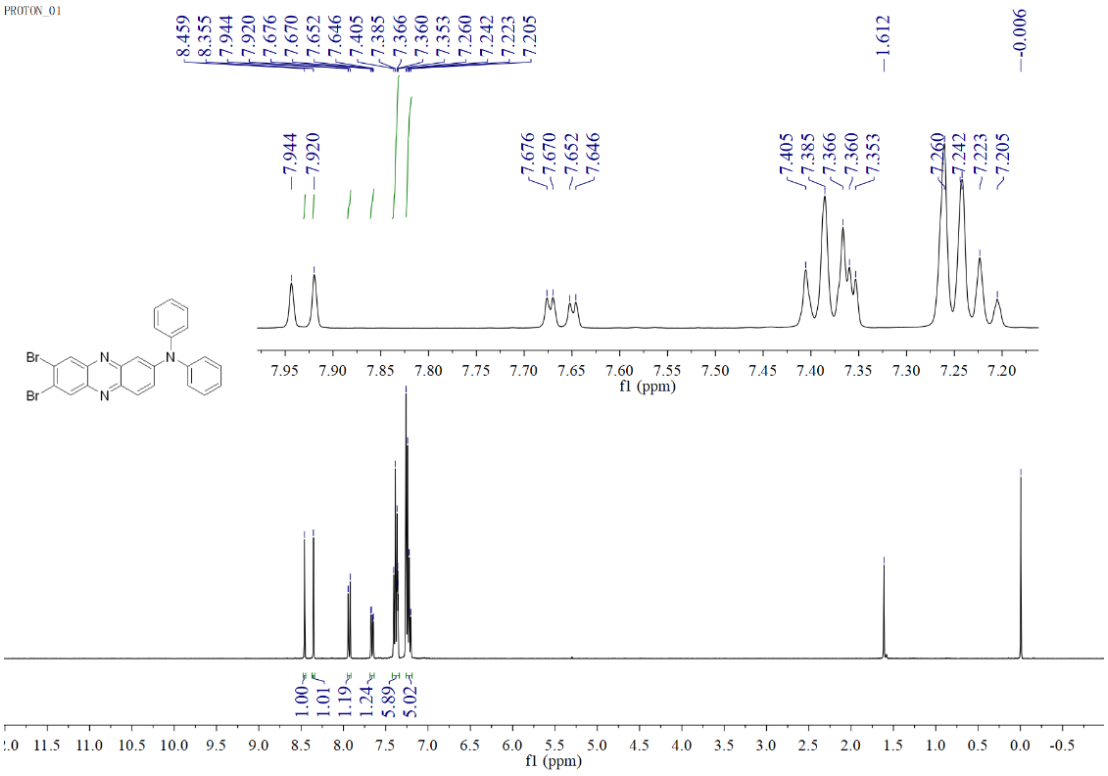
^{1}H NMR spectrum of **5b** in $CDCl_3$



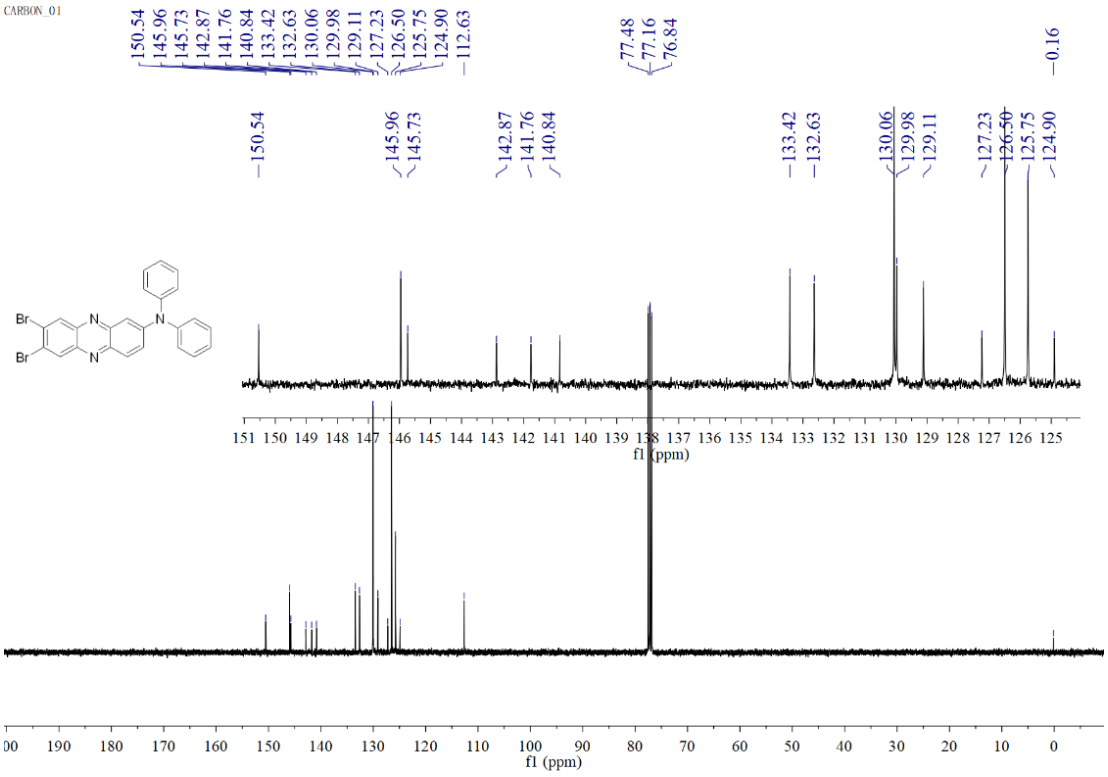
^{13}C NMR spectrum of **5b** in $CDCl_3$



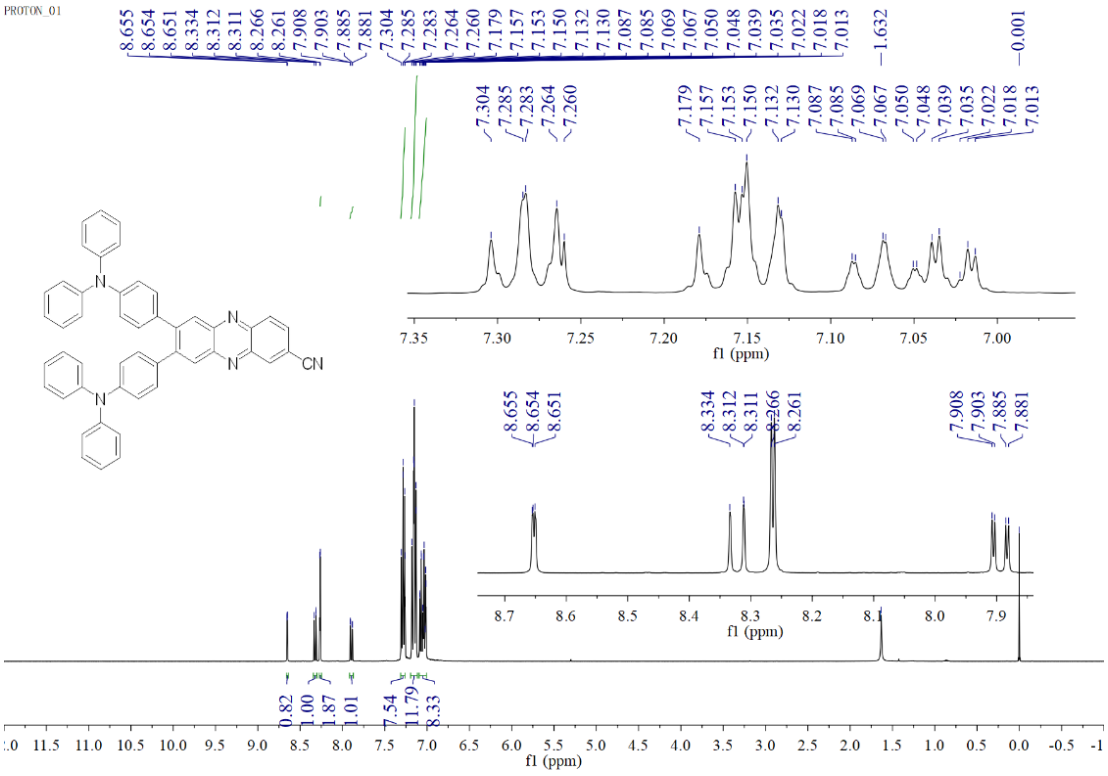
^{19}F NMR spectrum of **5b** in $CDCl_3$



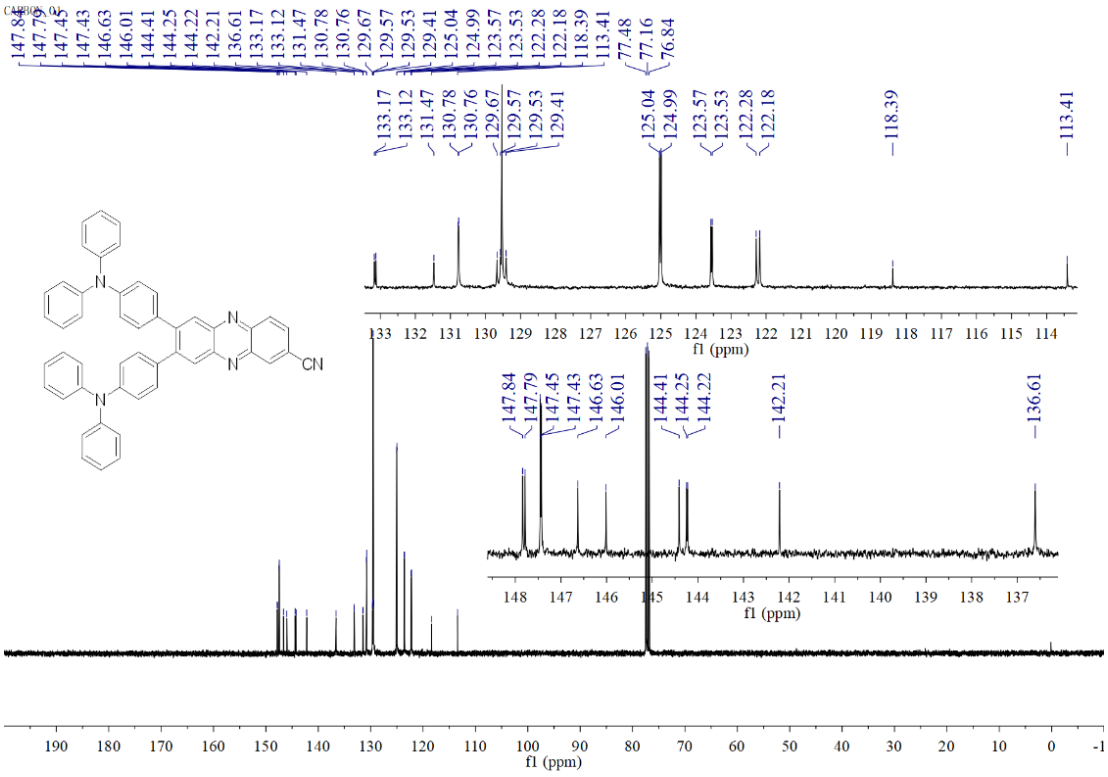
^{1}H NMR spectrum of **5c** in $CDCl_3$



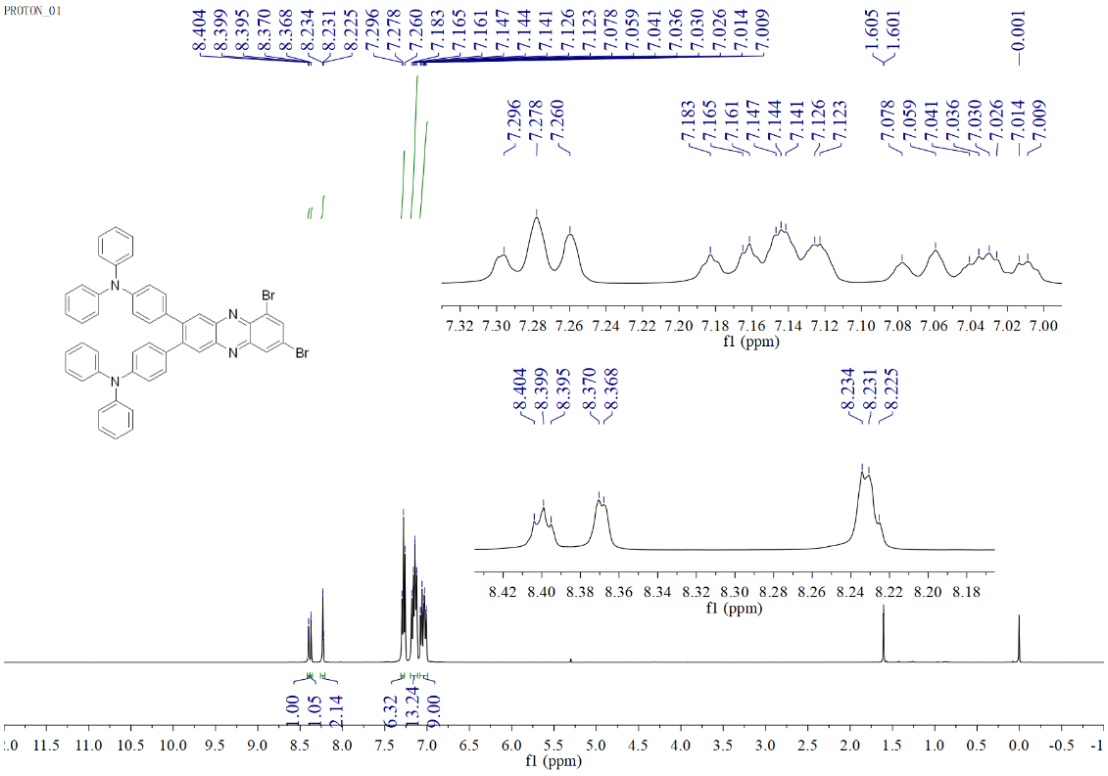
^{13}C NMR spectrum of **5c** in $CDCl_3$



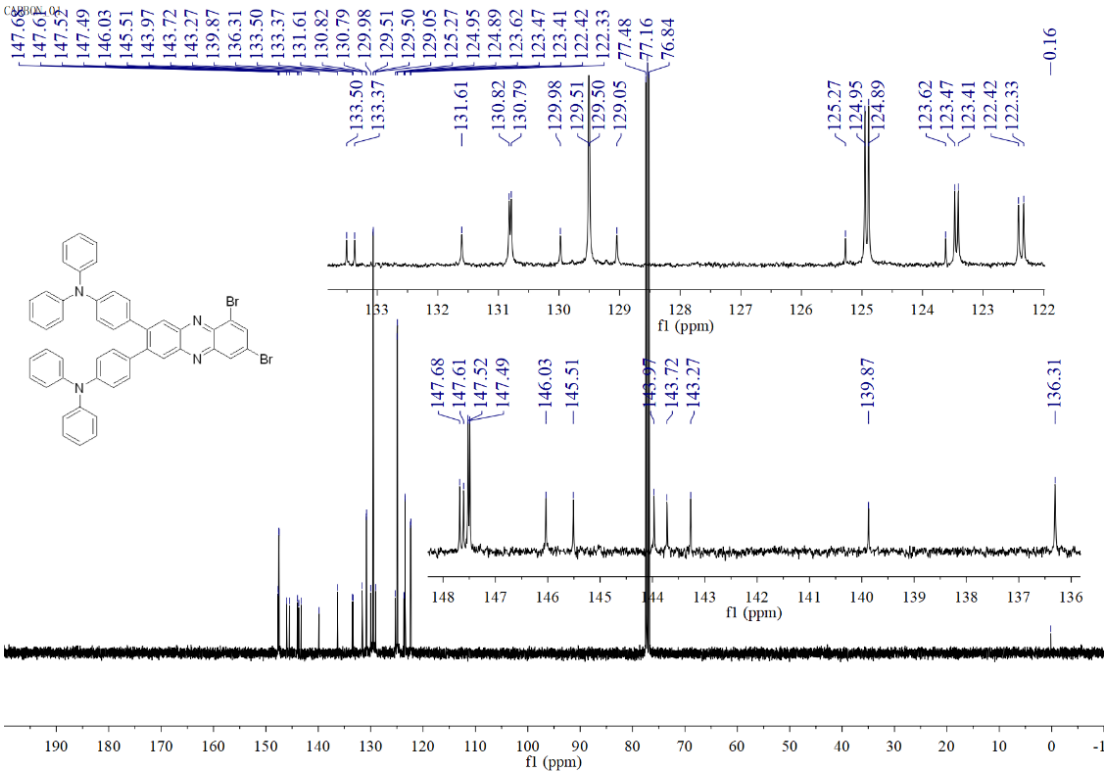
^{1}H NMR spectrum of **5d** in $CDCl_3$



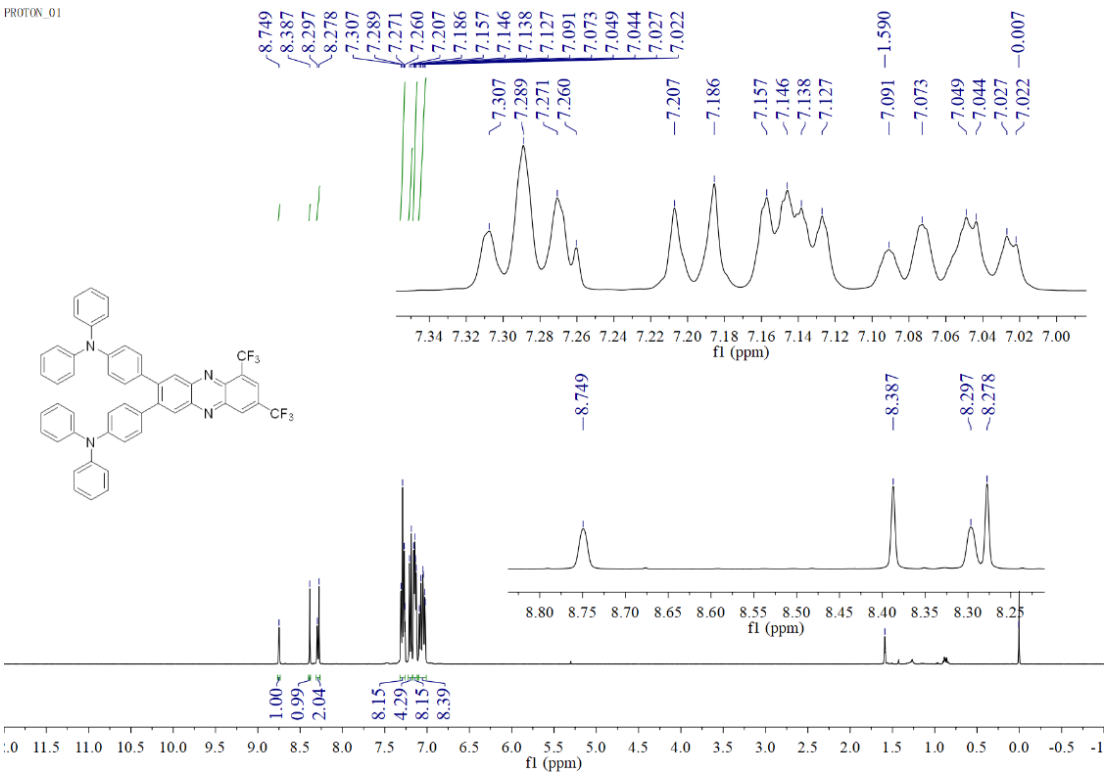
^{13}C NMR spectrum of **5d** in $CDCl_3$



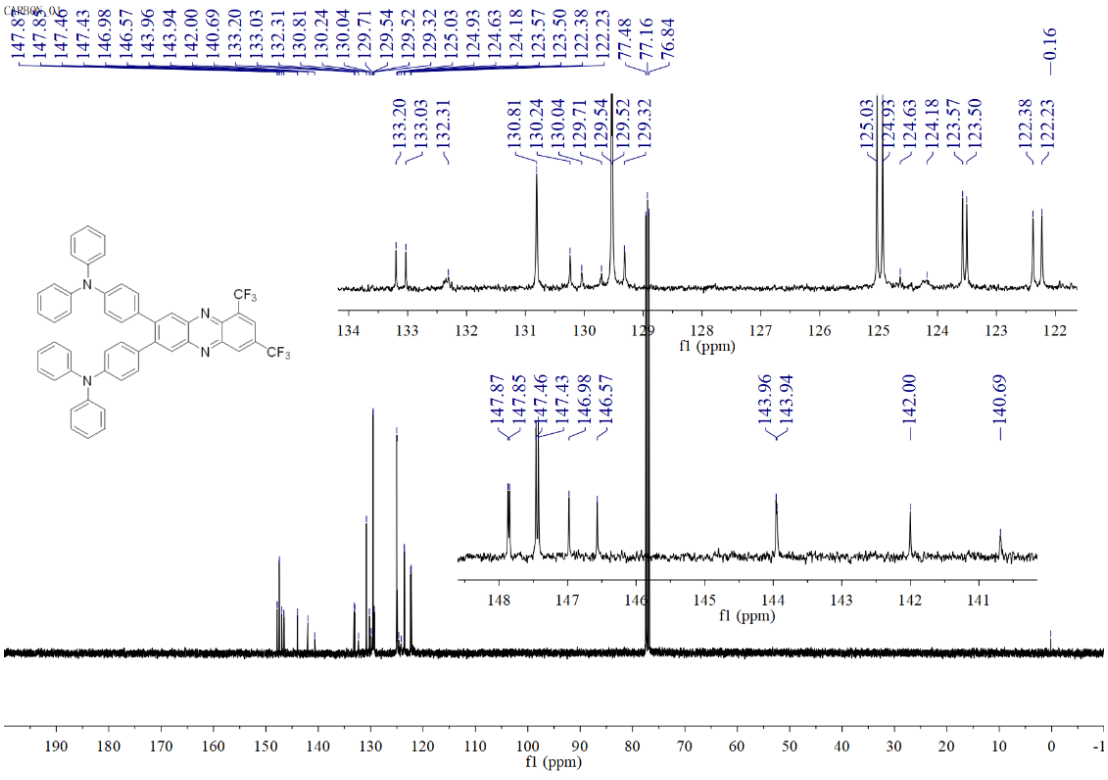
^{1}H NMR spectrum of **5e** in $CDCl_3$



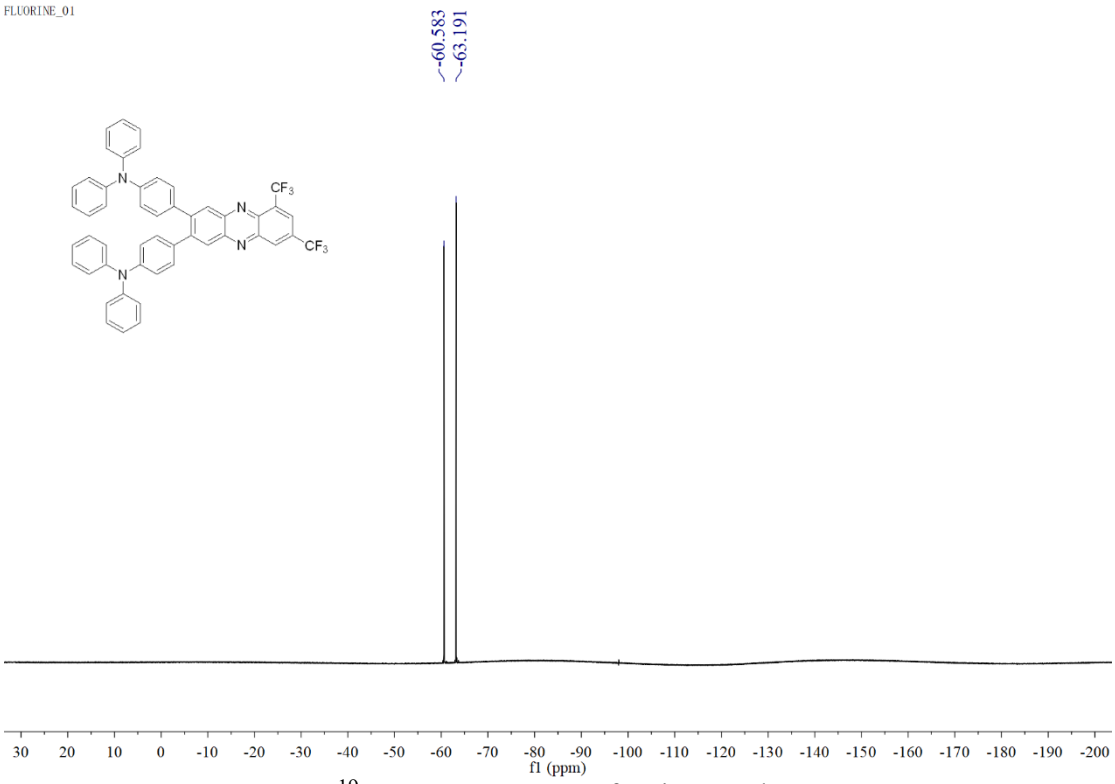
^{13}C NMR spectrum of **5e** in $CDCl_3$



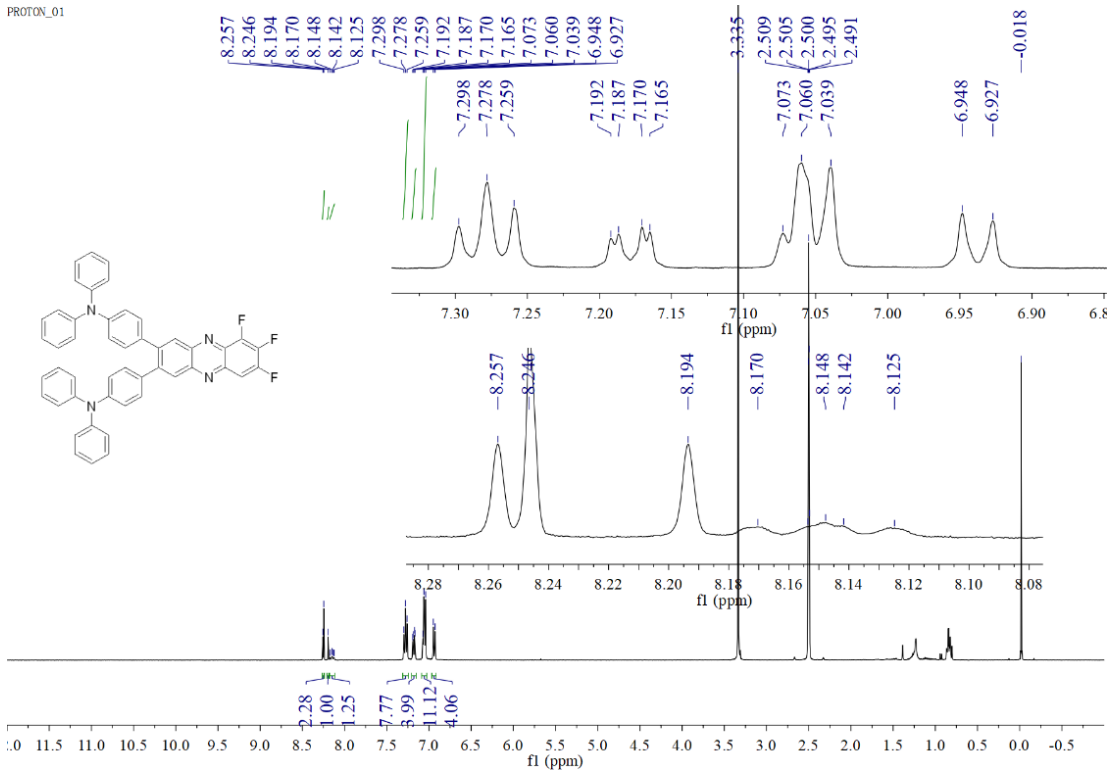
^{1}H NMR spectrum of **5f** in $CDCl_3$



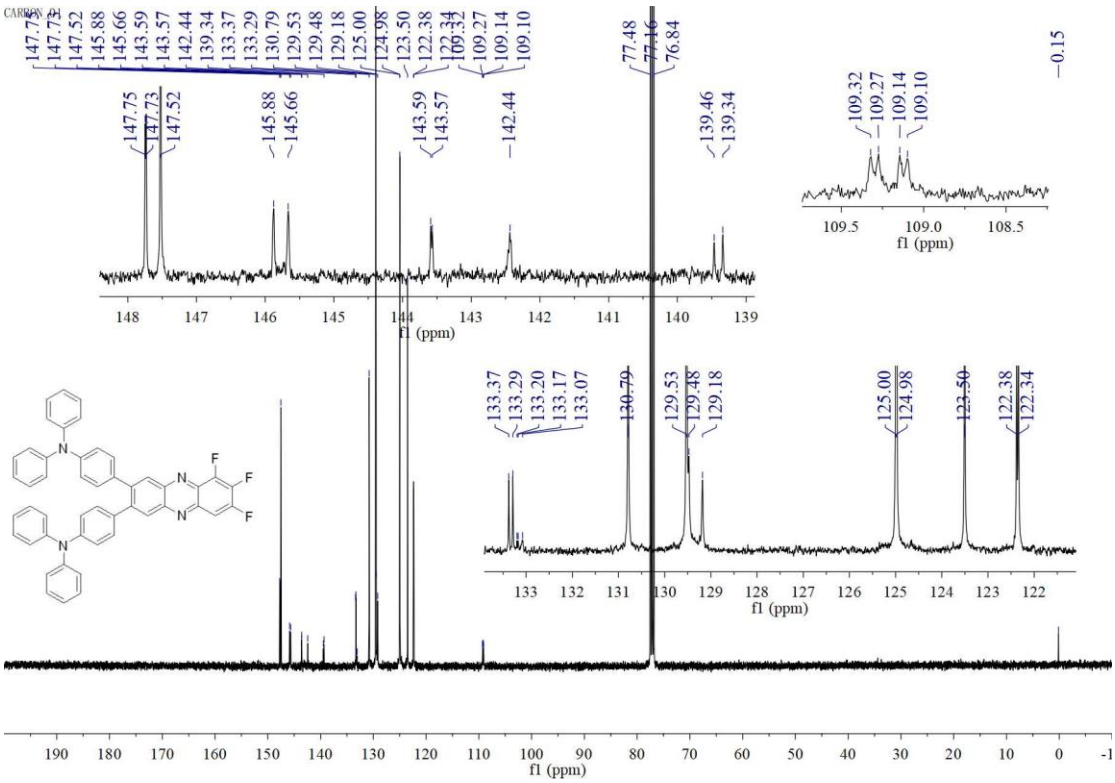
^{13}C NMR spectrum of **5f** in $CDCl_3$



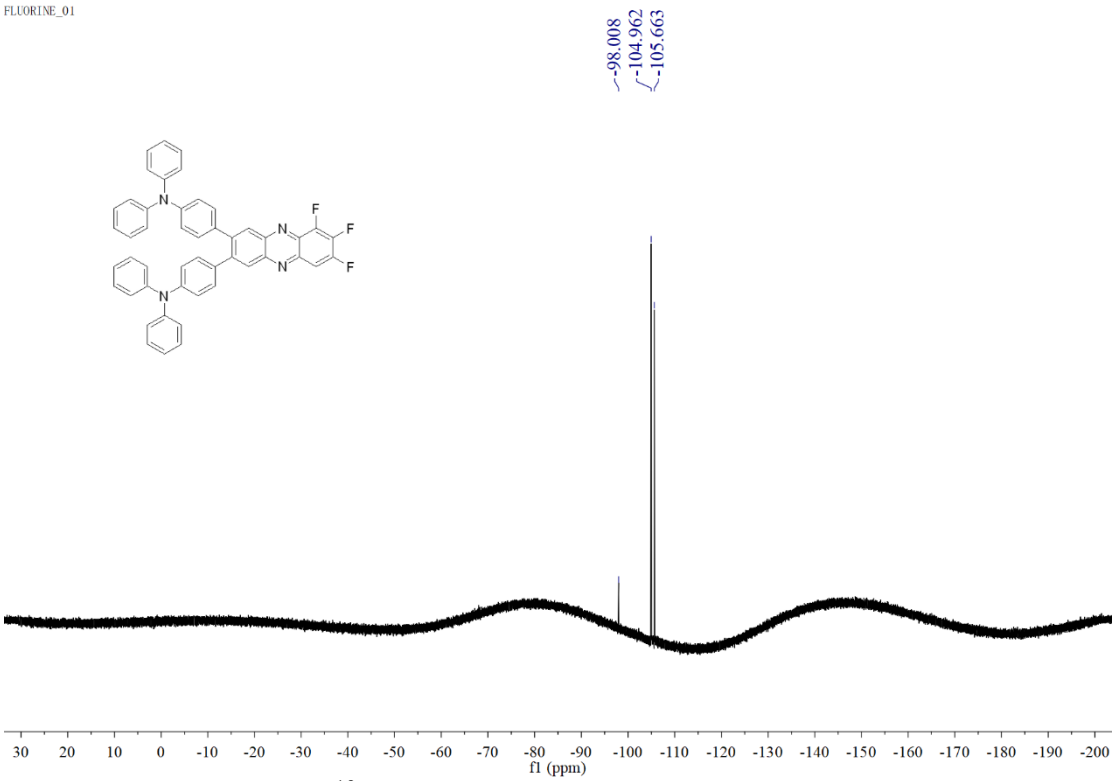
^{19}F NMR spectrum of **5f** in $CDCl_3$



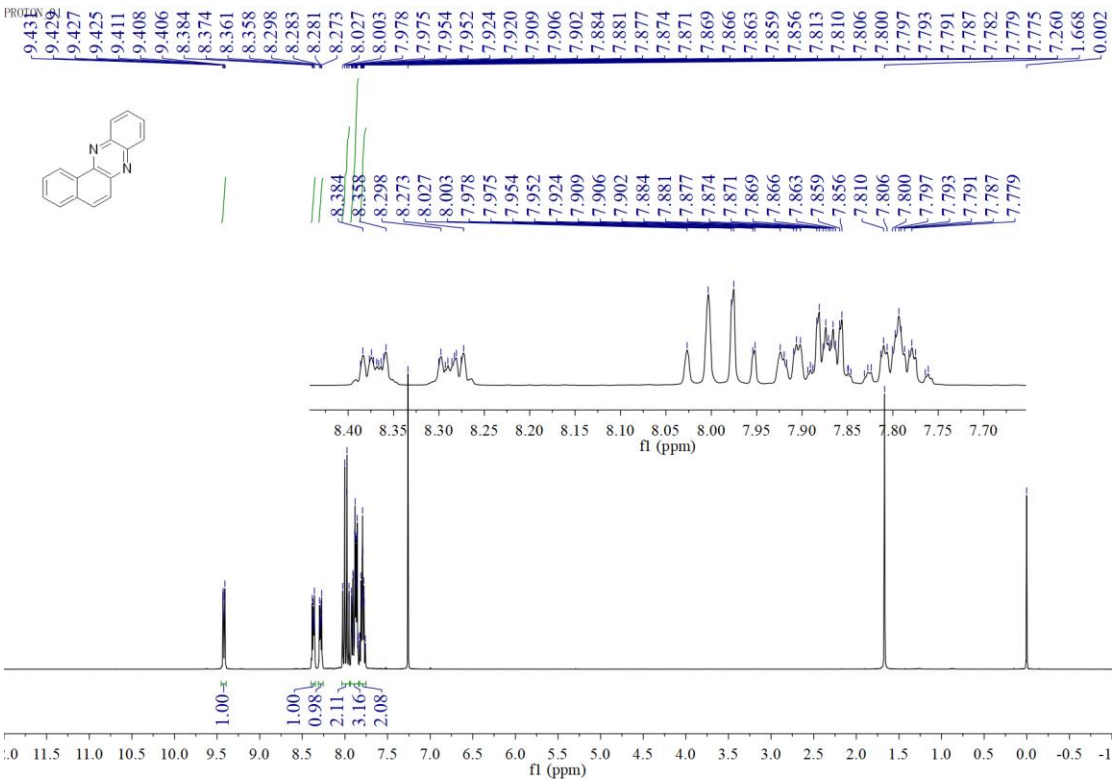
^{1}H NMR spectrum of **5g** in DMSO-d_6



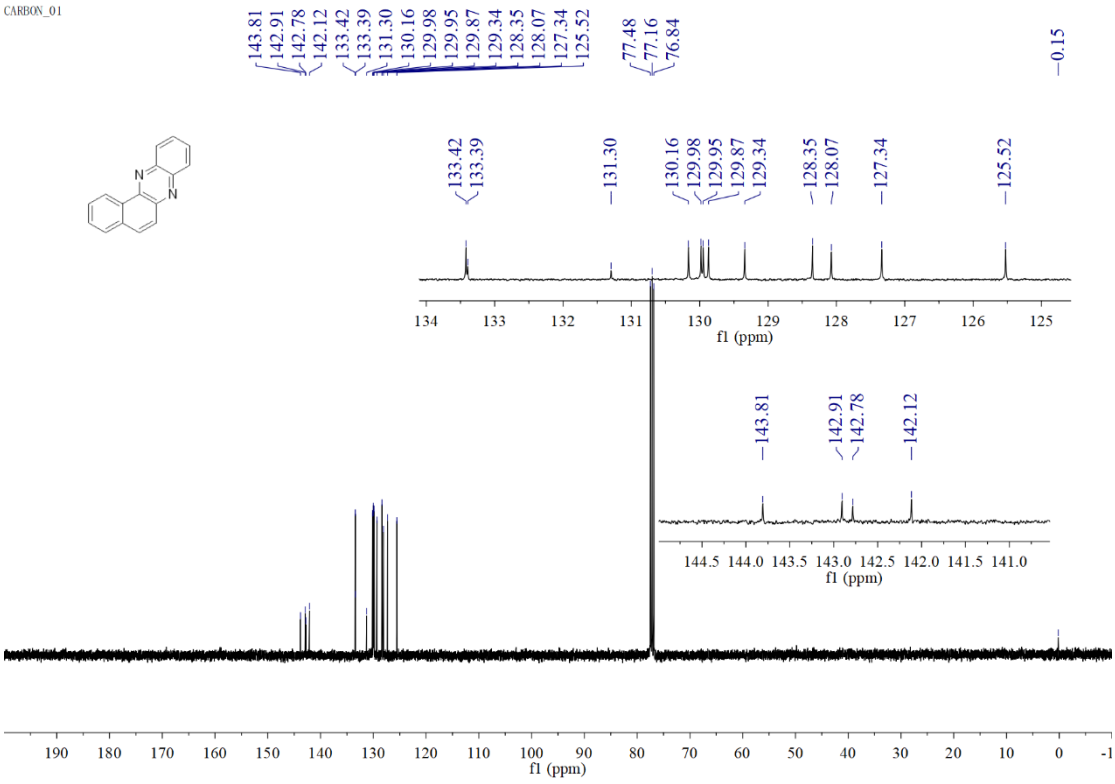
^{13}C NMR spectrum of **5g** in $CDCl_3$



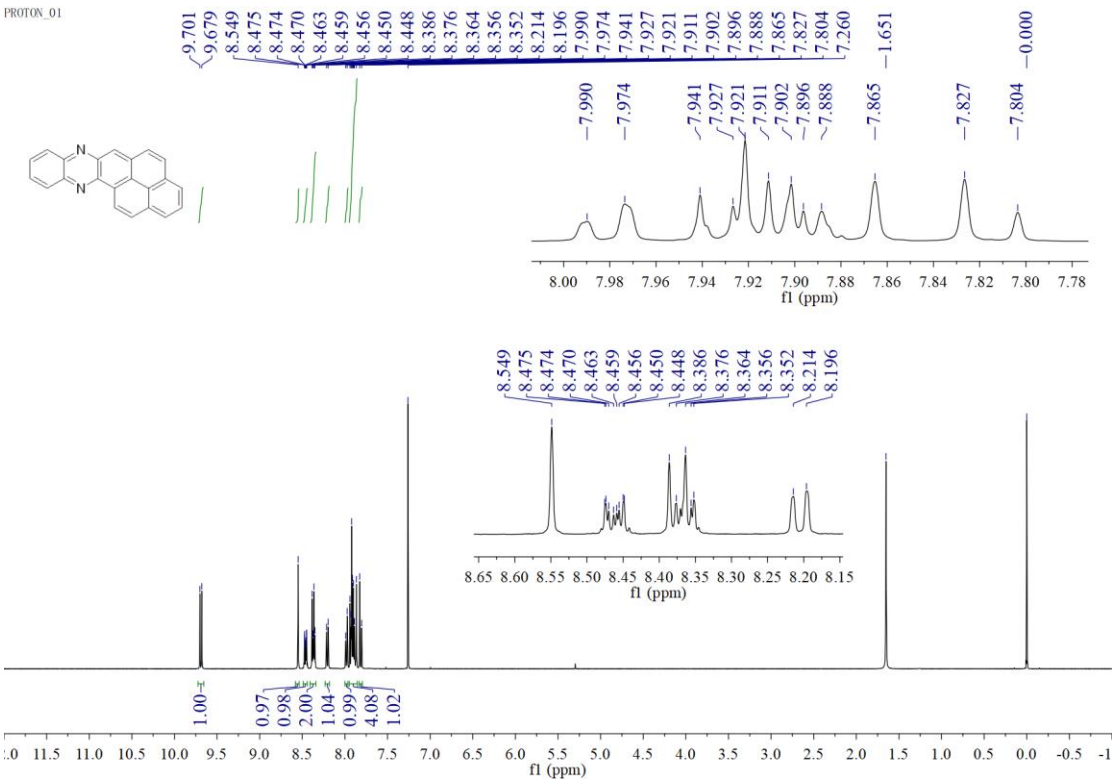
^{19}F NMR spectrum of **5g** in $CDCl_3$



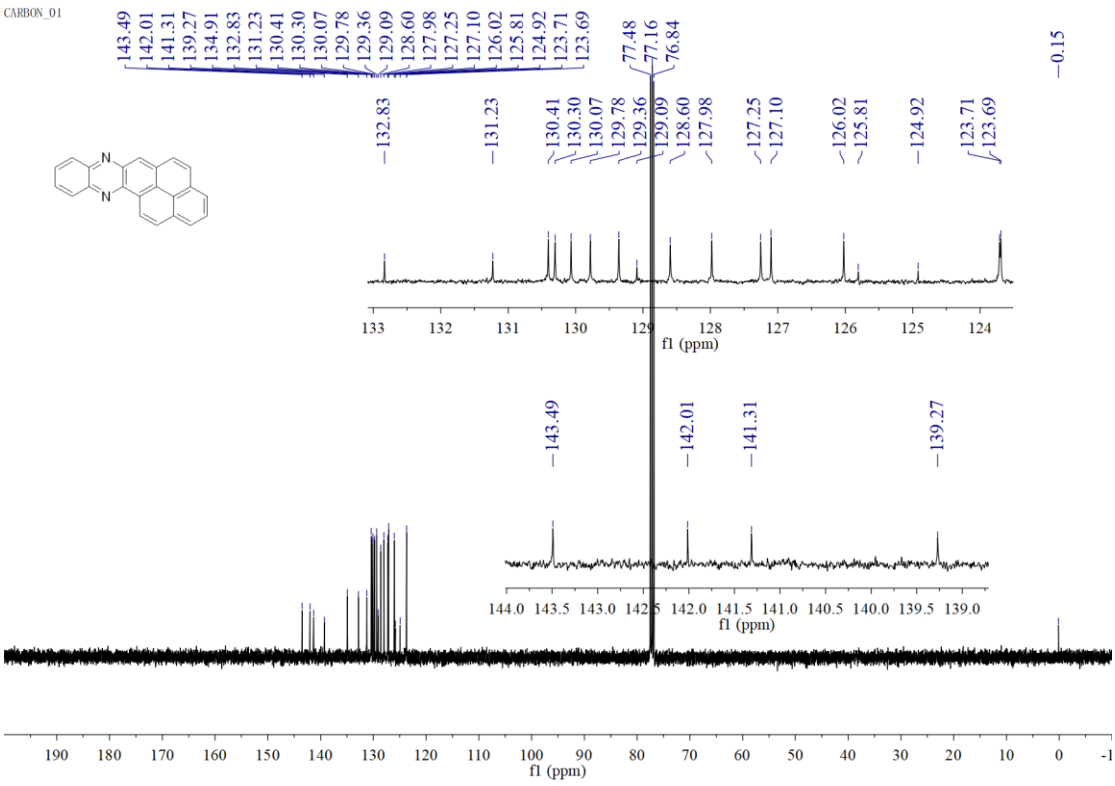
^{1}H NMR spectrum of **5h** in $CDCl_3$



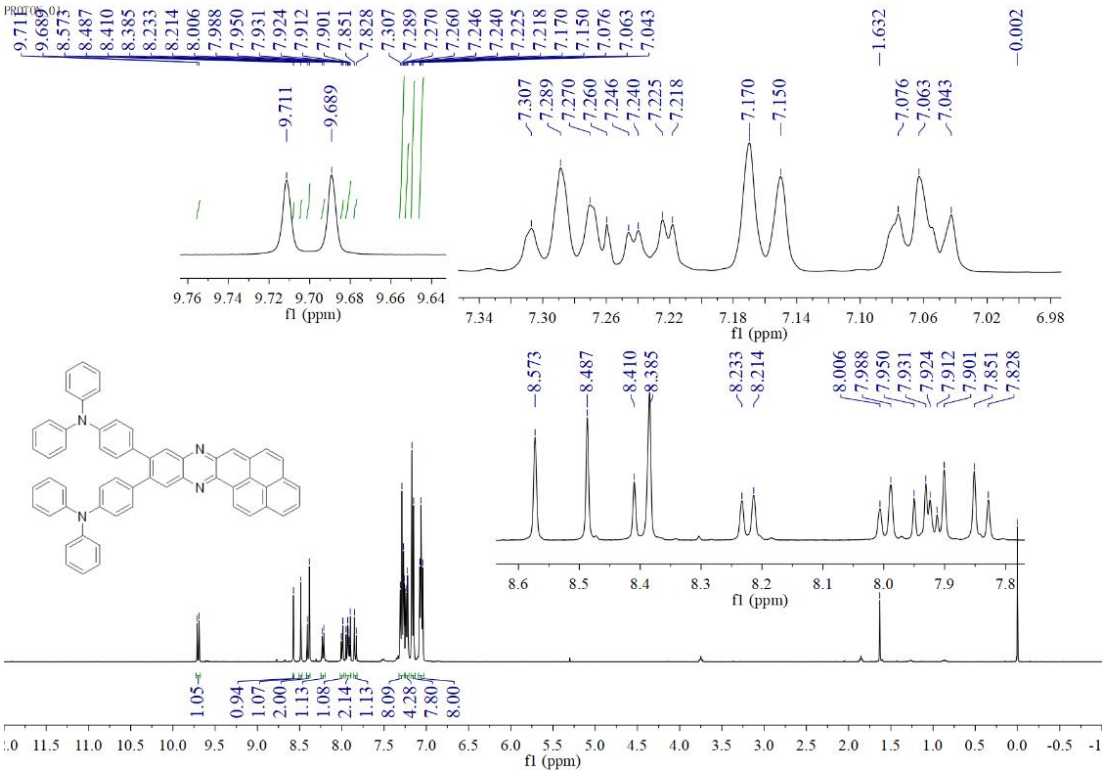
^{13}C NMR spectrum of **5h** in $CDCl_3$



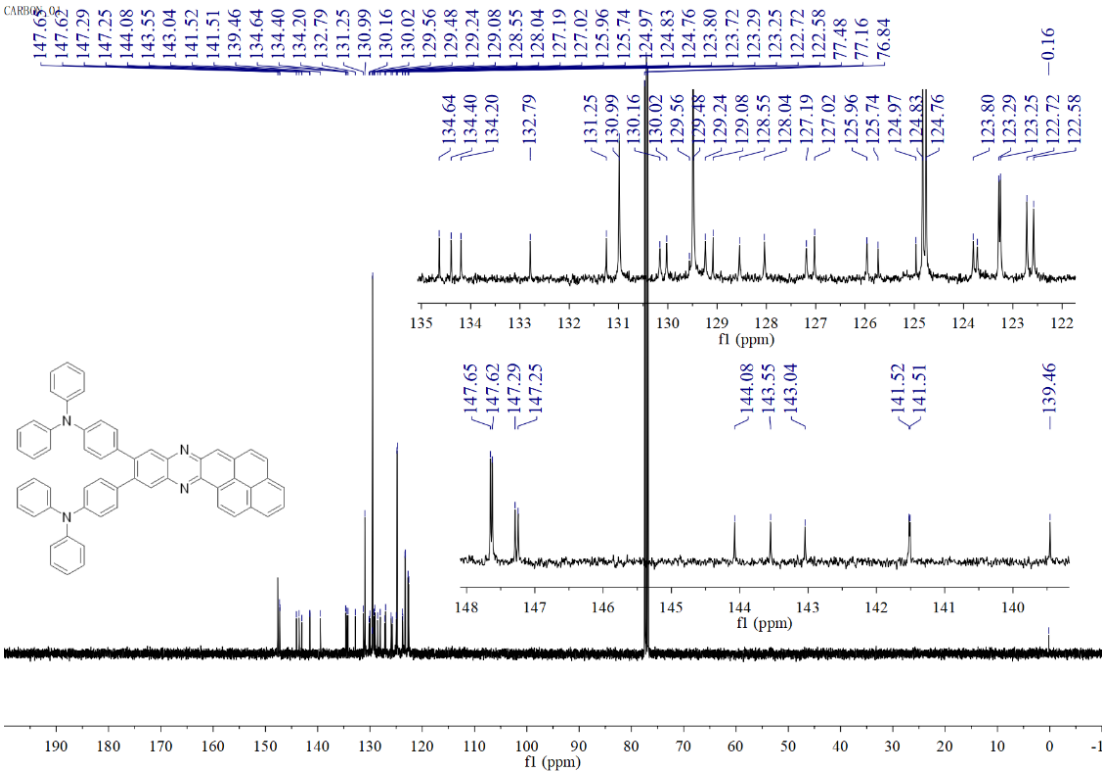
^{1}H NMR spectrum of **5i** in $CDCl_3$



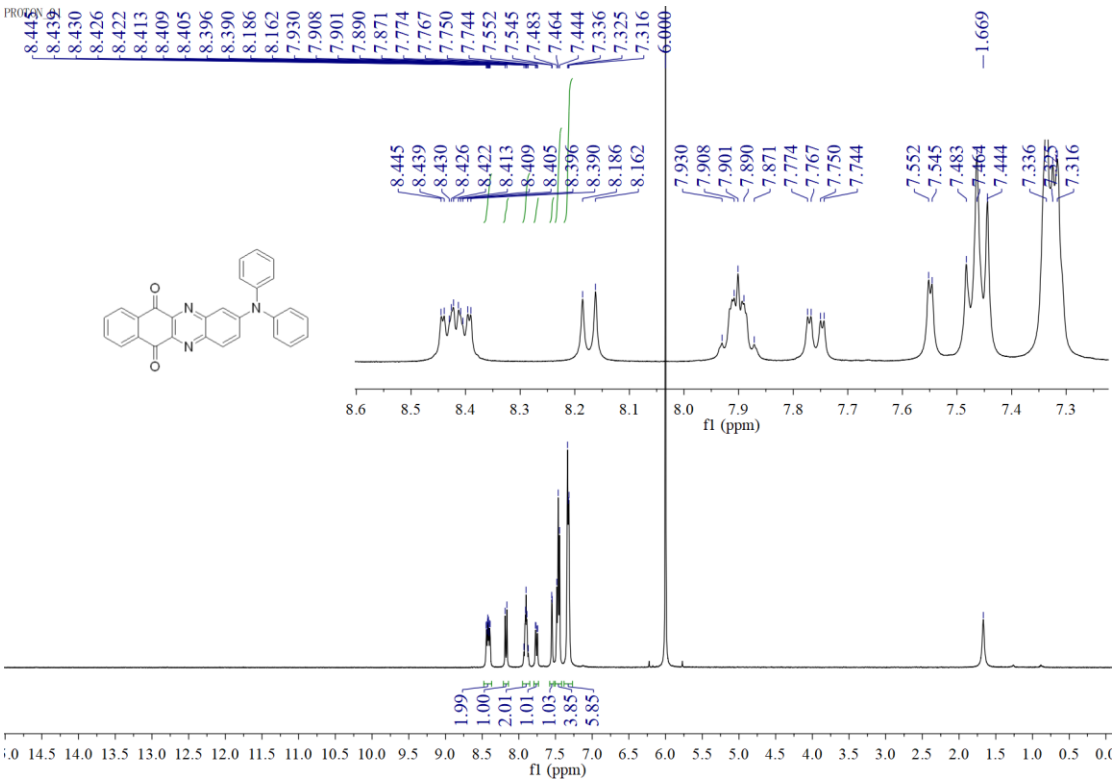
^{13}C NMR spectrum of **5i** in $CDCl_3$



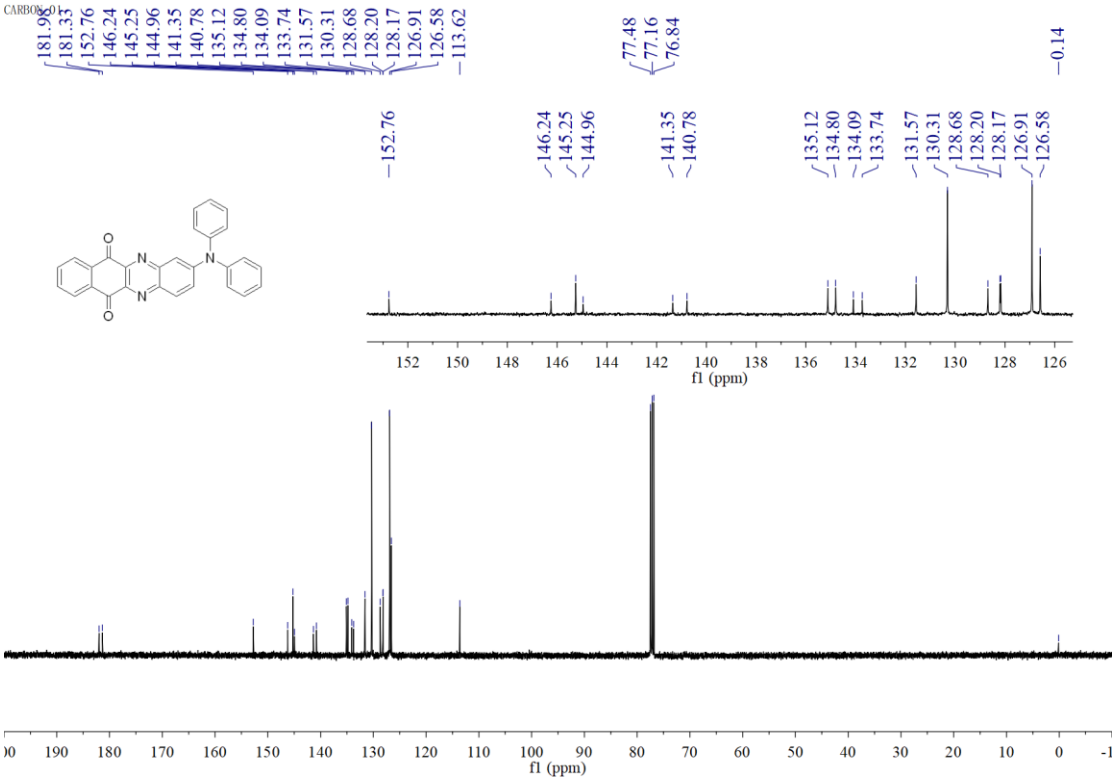
^{1}H NMR spectrum of **5j** in $CDCl_3$



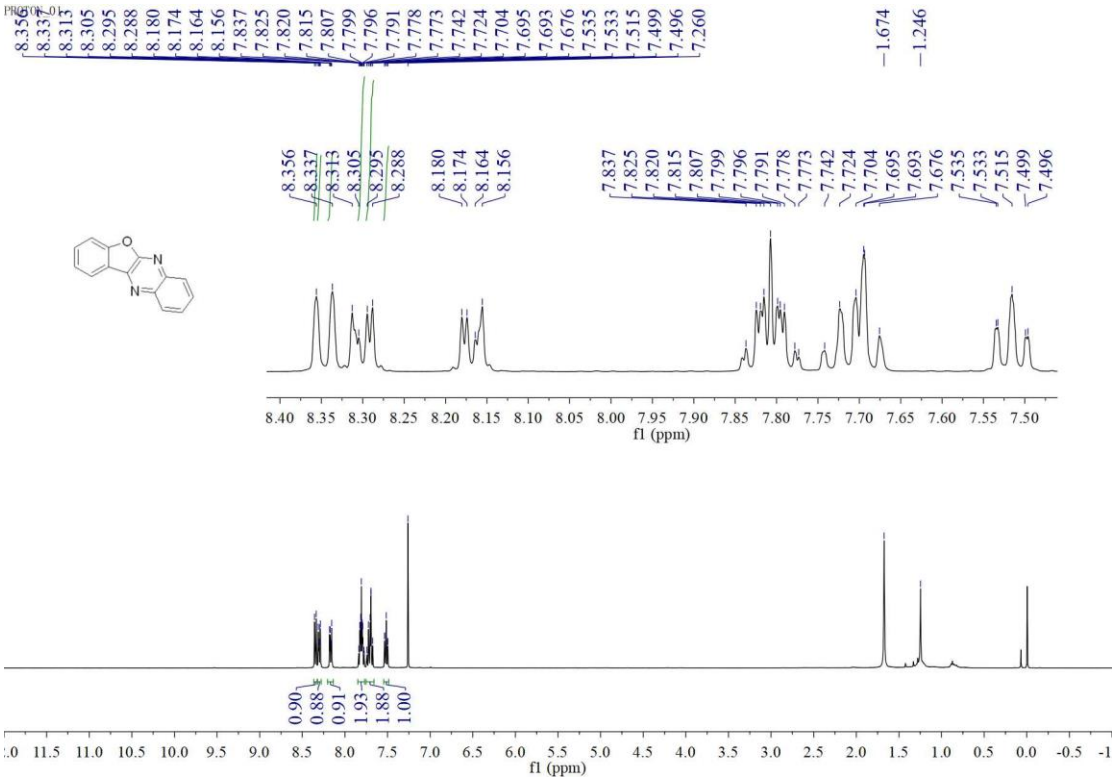
^{13}C NMR spectrum of **5j** in $CDCl_3$



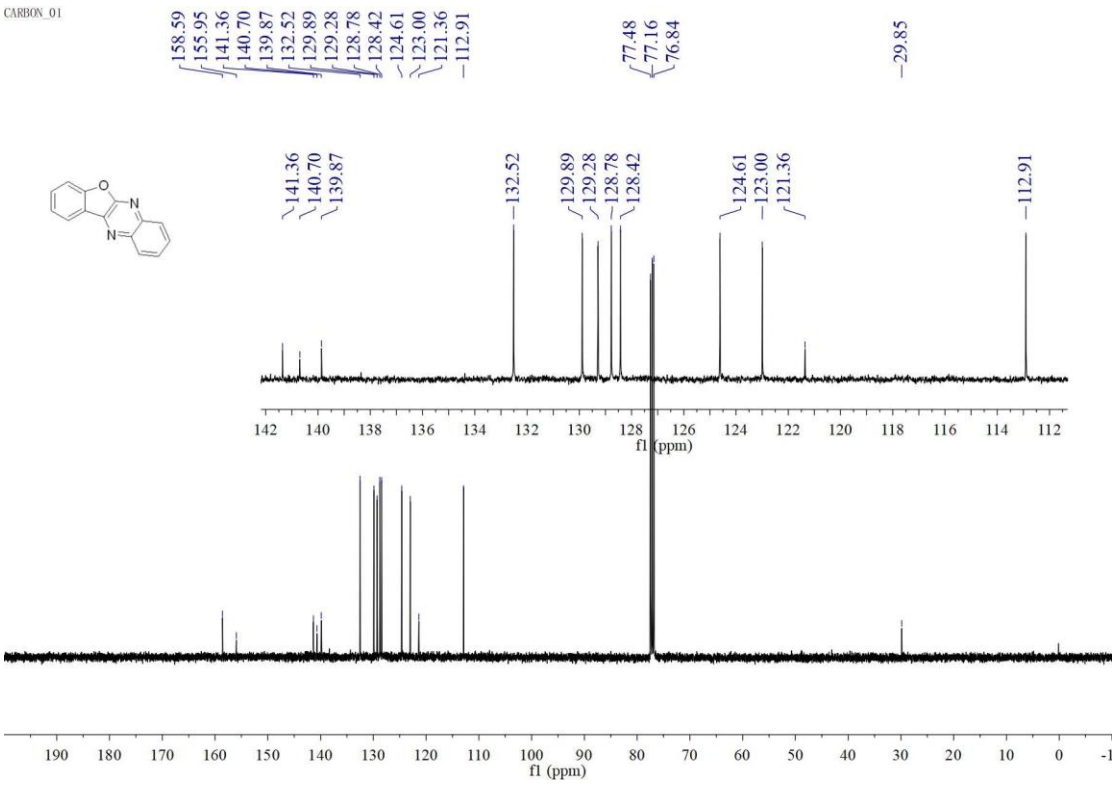
^{1}H NMR spectrum of **5k** in $CDCl_2CDCl_2$



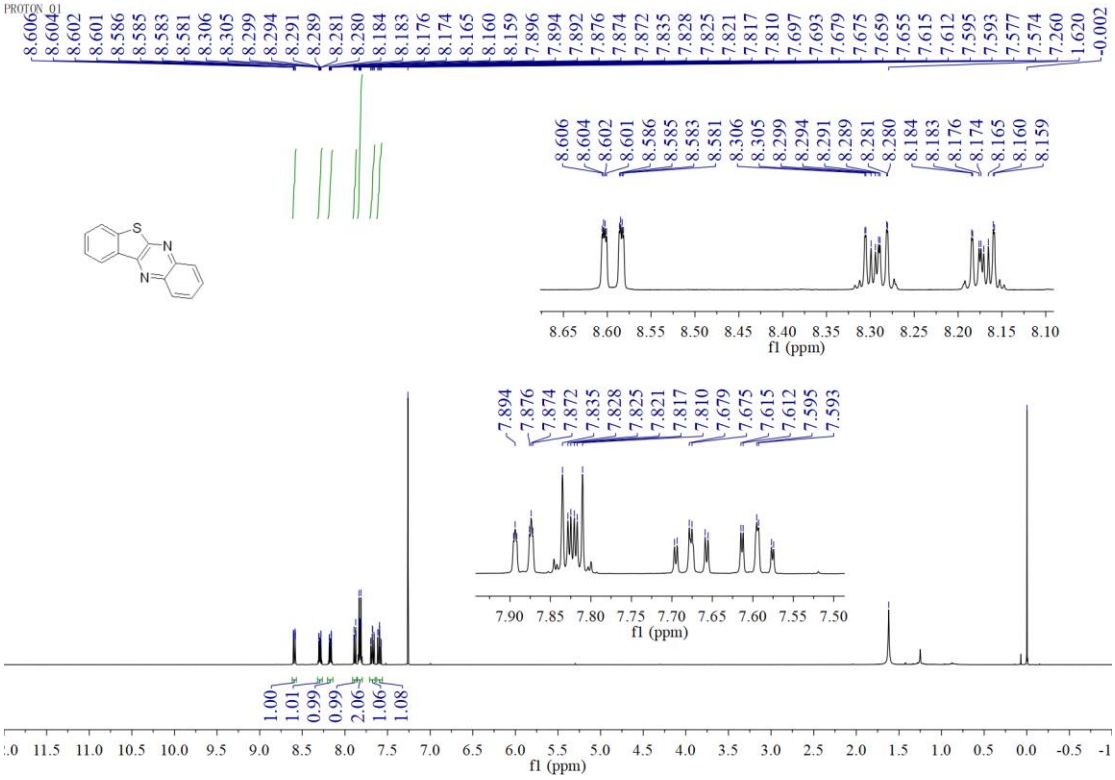
^{13}C NMR spectrum of **5k** in $CDCl_3$



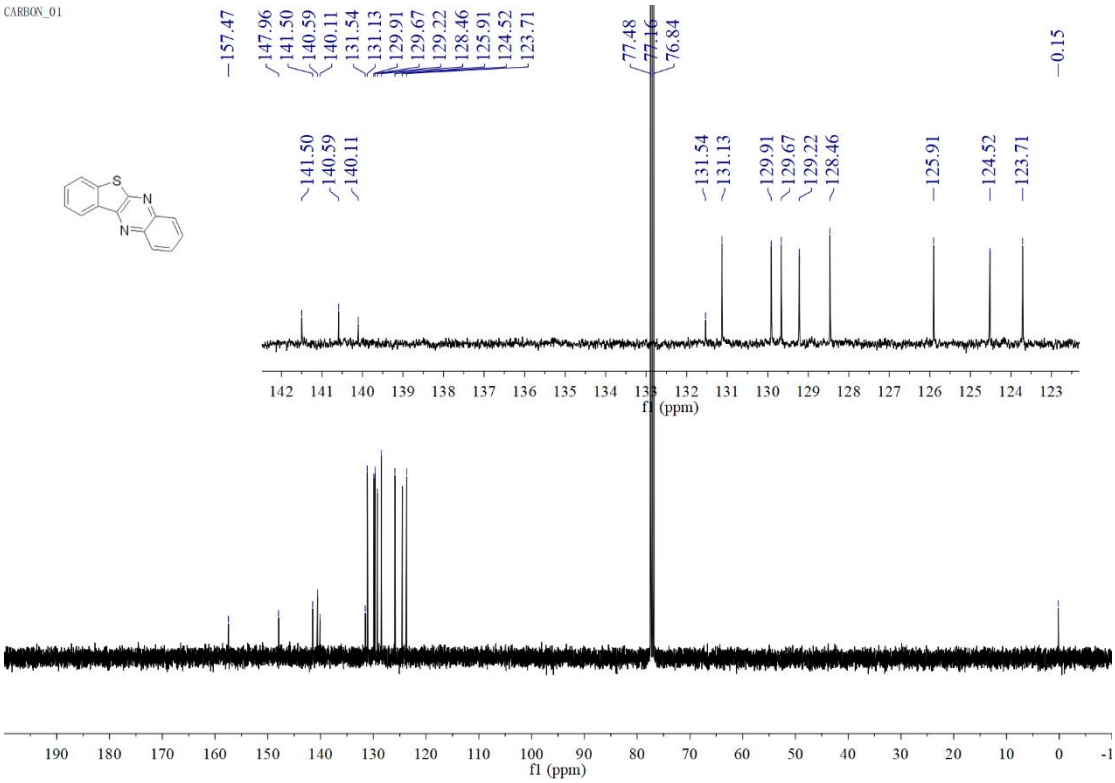
^{1}H NMR spectrum of **5l** in $CDCl_3$



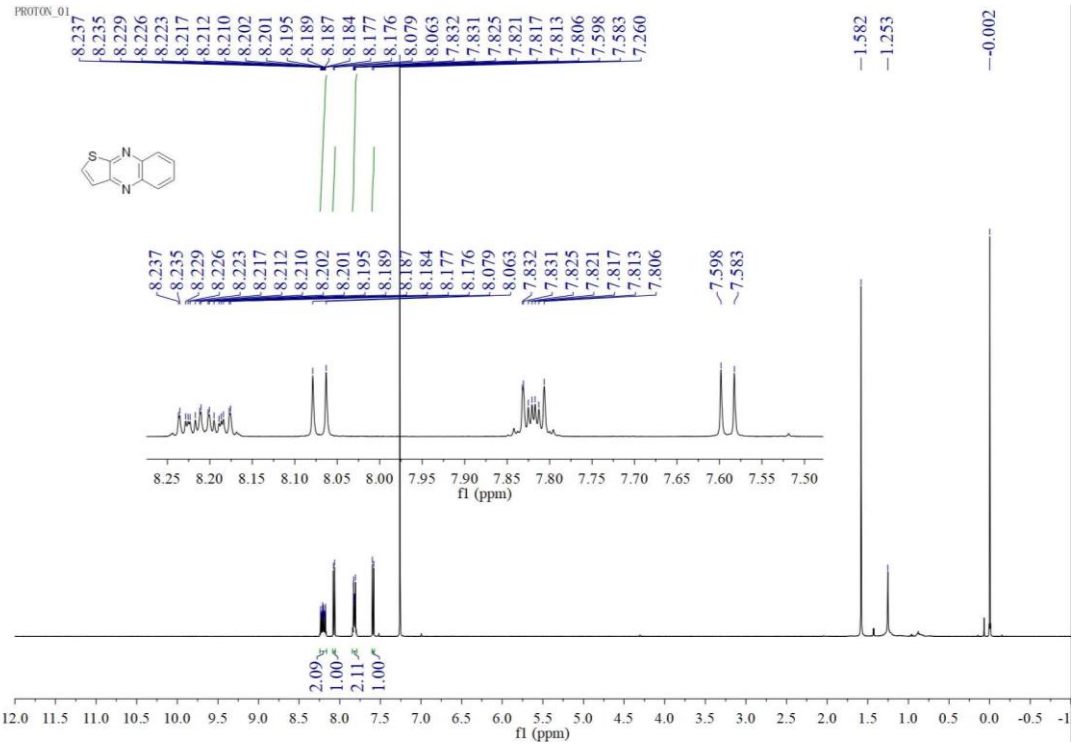
^{13}C NMR spectrum of **5l** in $CDCl_3$



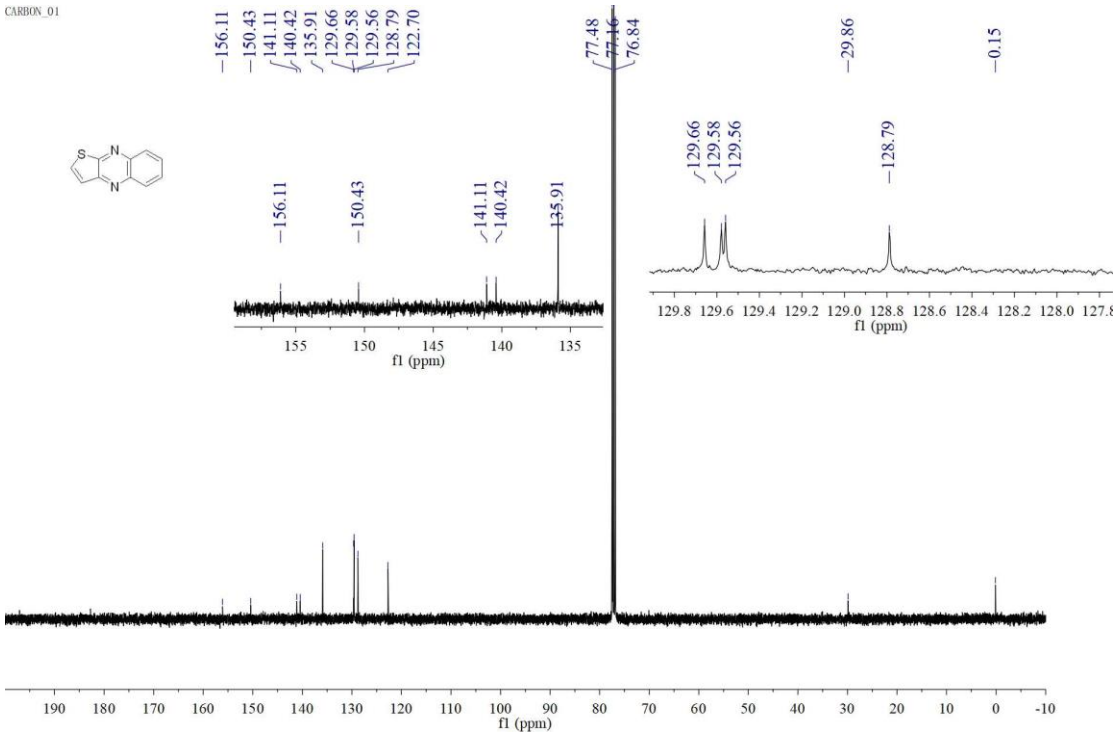
^{1}H NMR spectrum of **5m** in $CDCl_3$



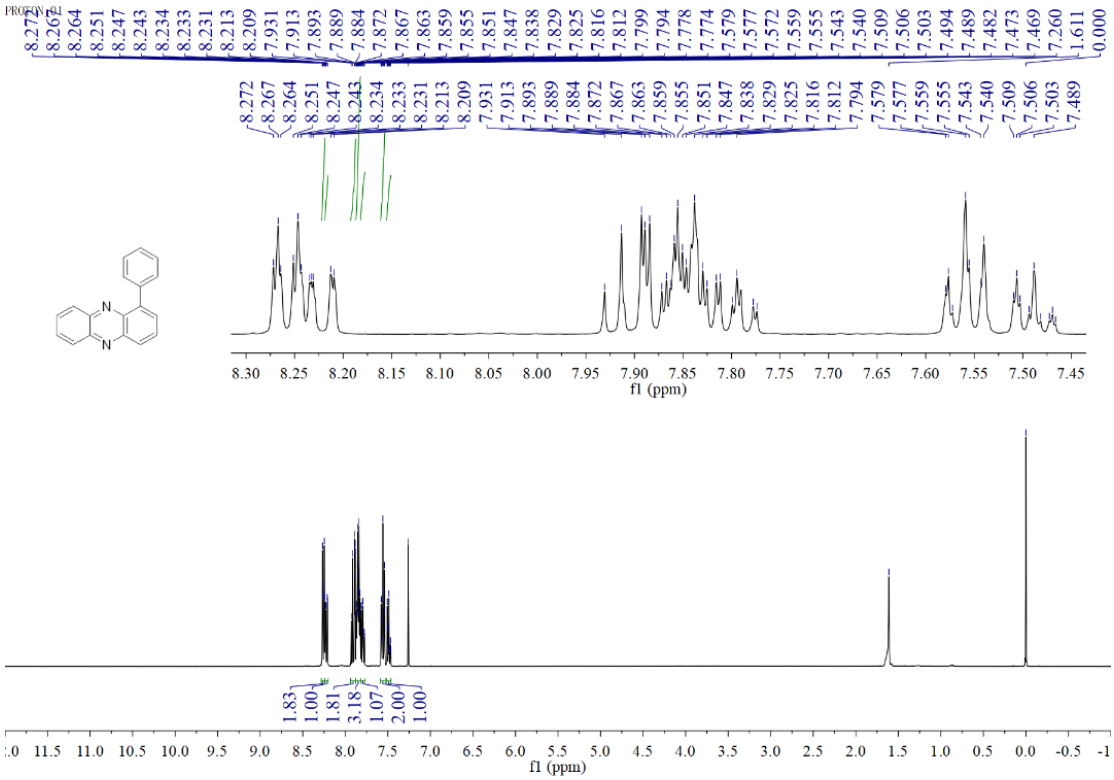
^{13}C NMR spectrum of **5m** in $CDCl_3$



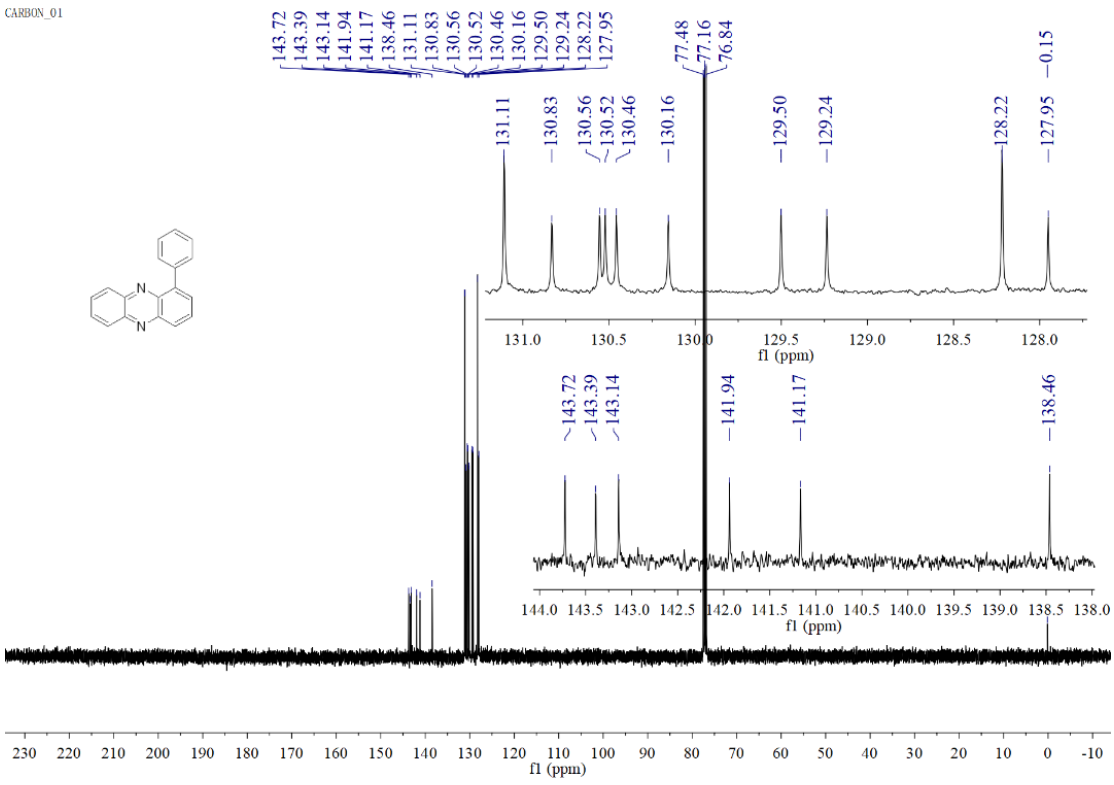
^{1}H NMR spectrum of **5n** in $CDCl_3$



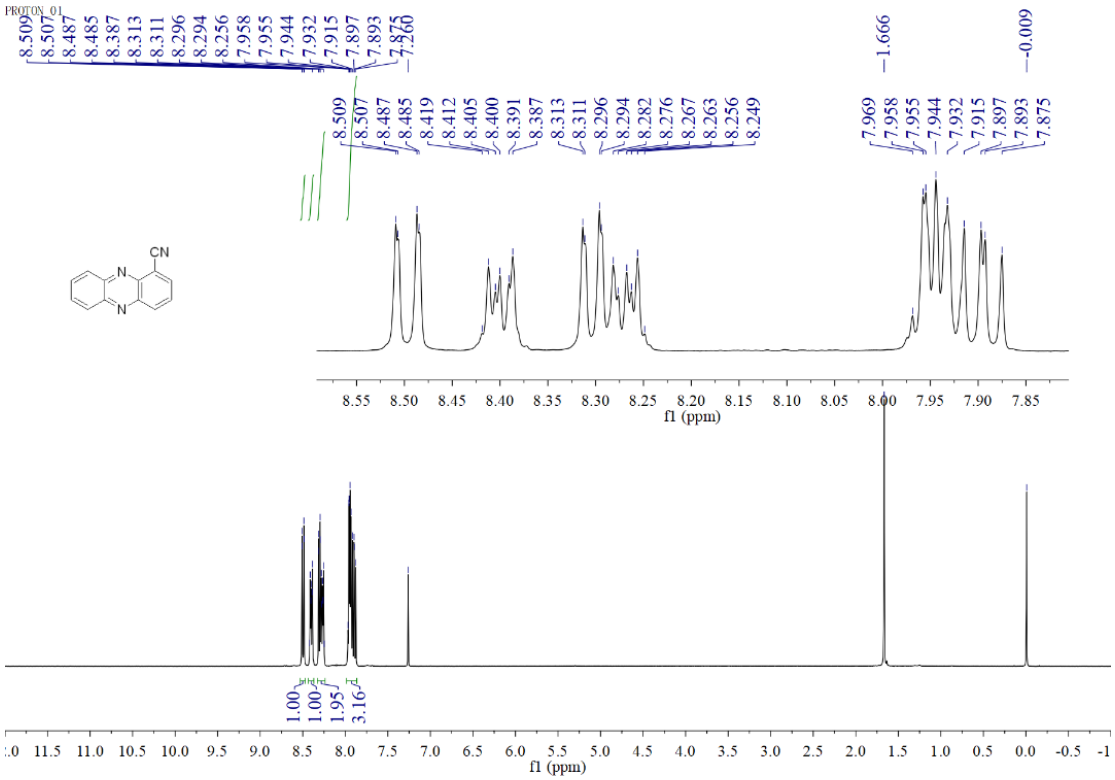
^{13}C NMR spectrum of **5n** in $CDCl_3$



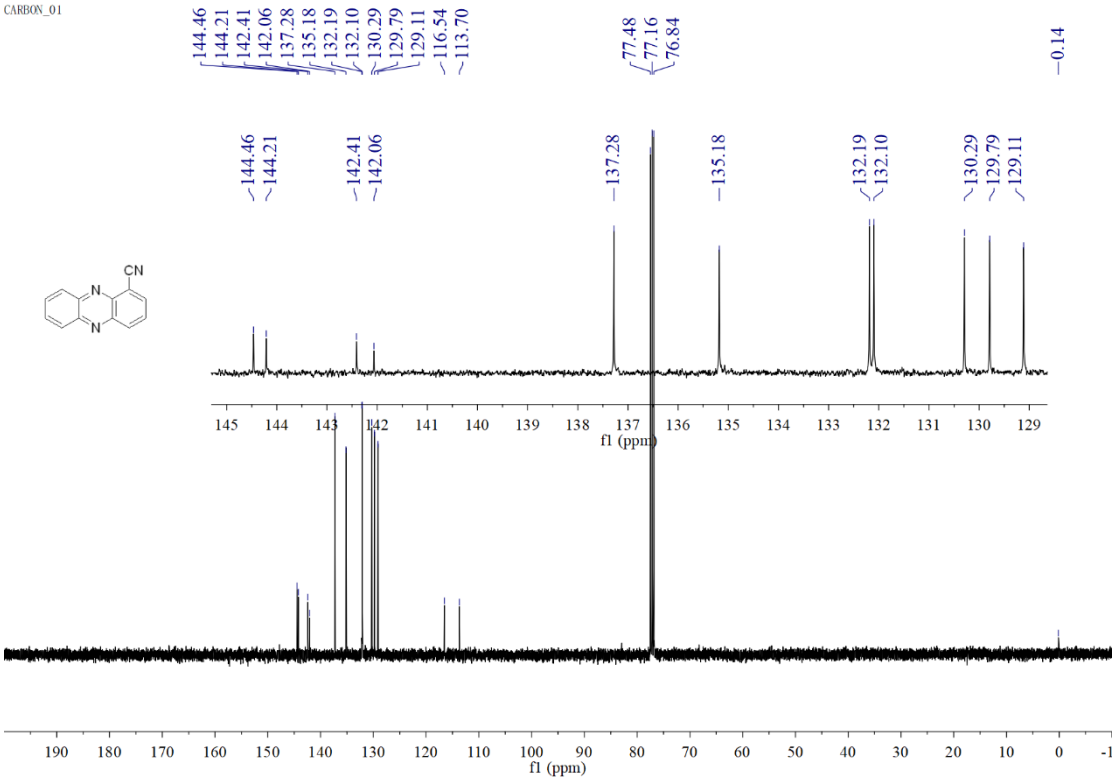
^{1}H NMR spectrum of **6a** in $CDCl_3$



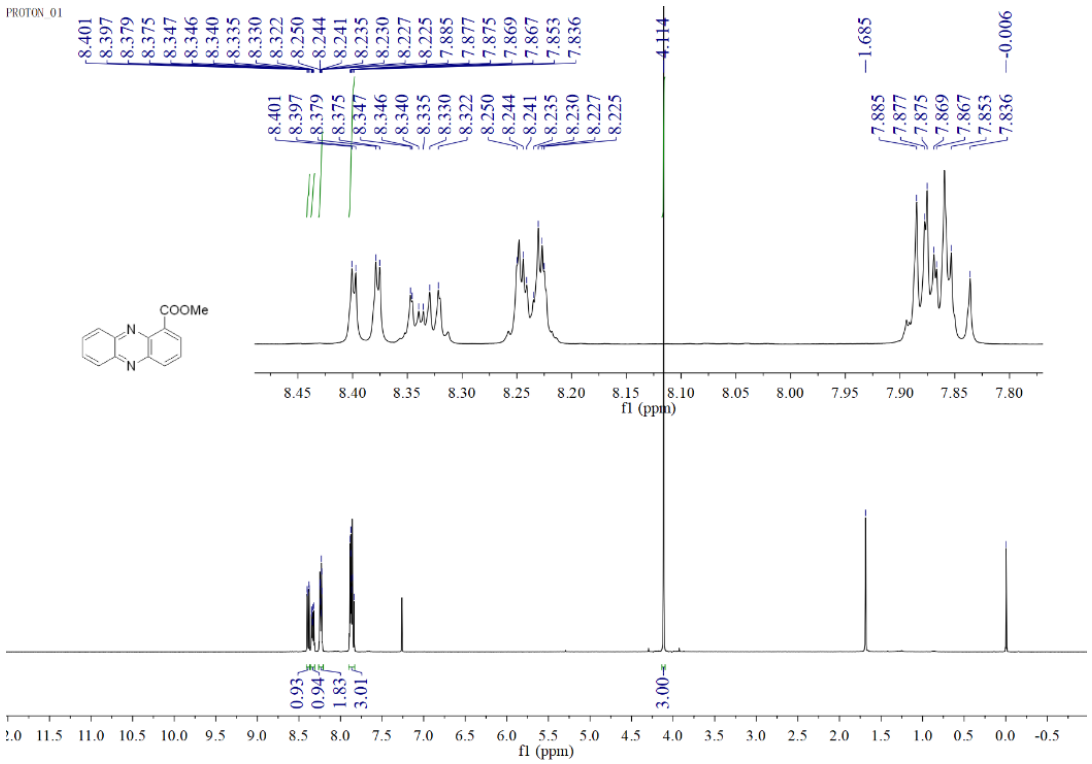
^{13}C NMR spectrum of **6a** in $CDCl_3$



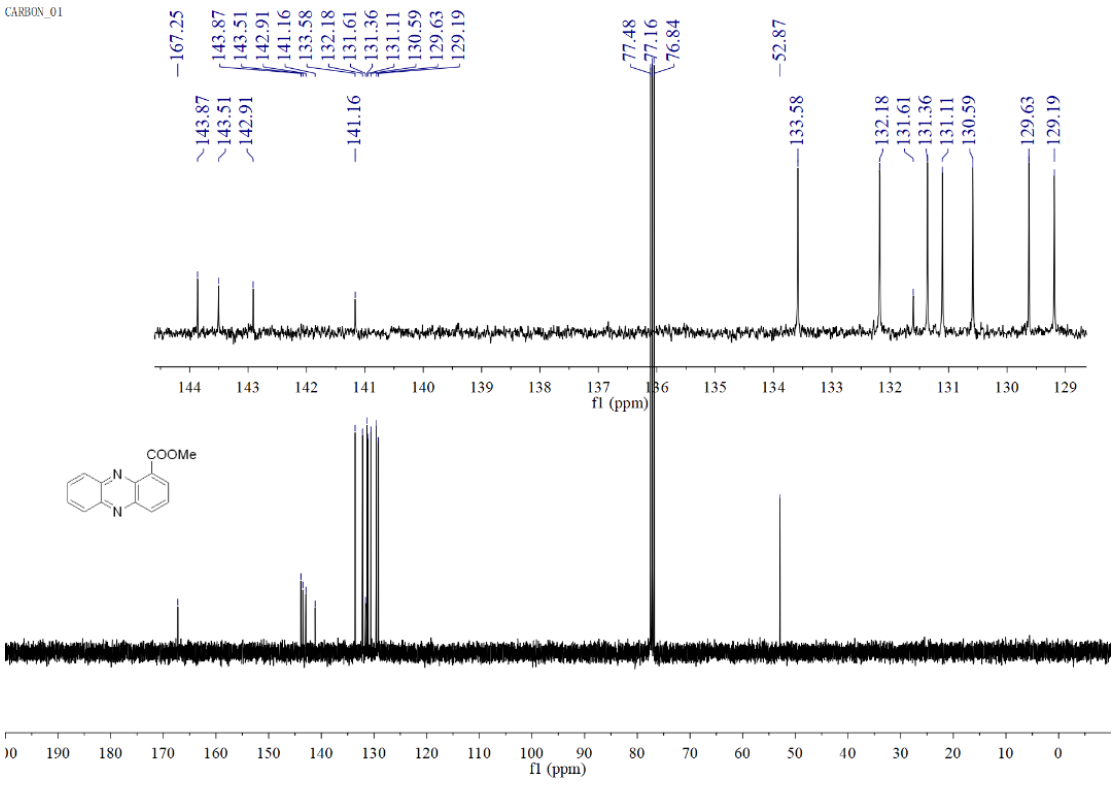
^{1}H NMR spectrum of **6b** in $CDCl_3$



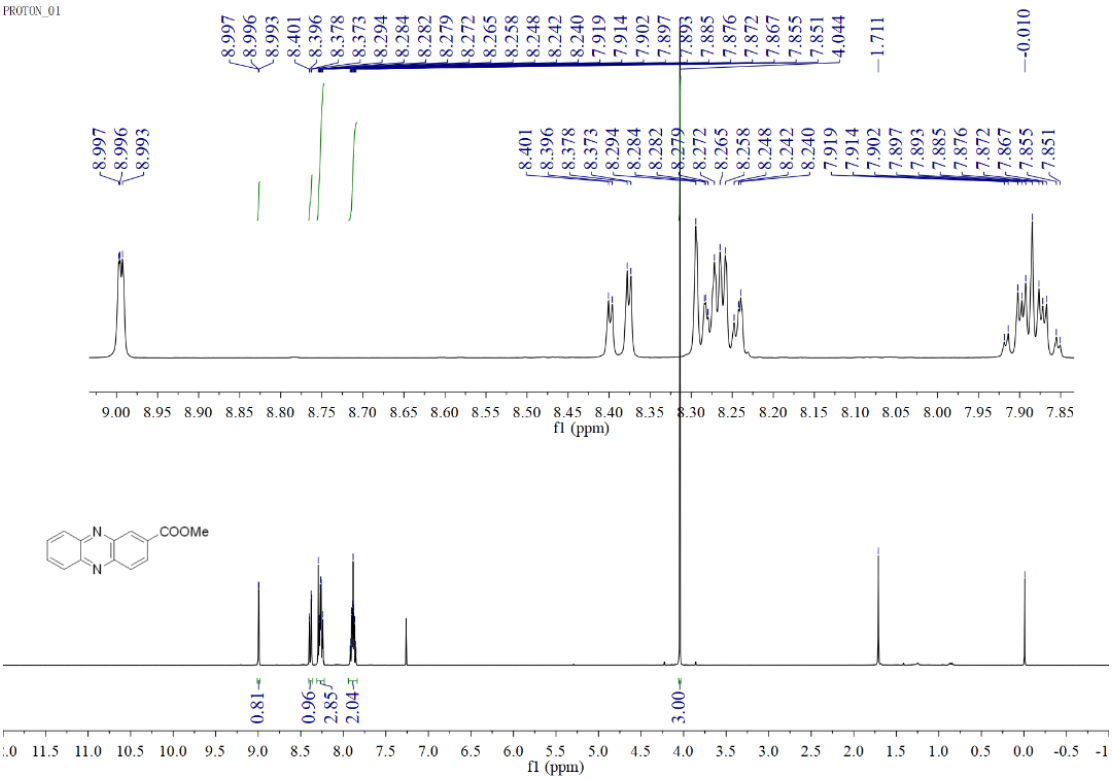
^{13}C NMR spectrum of **6b** in $CDCl_3$



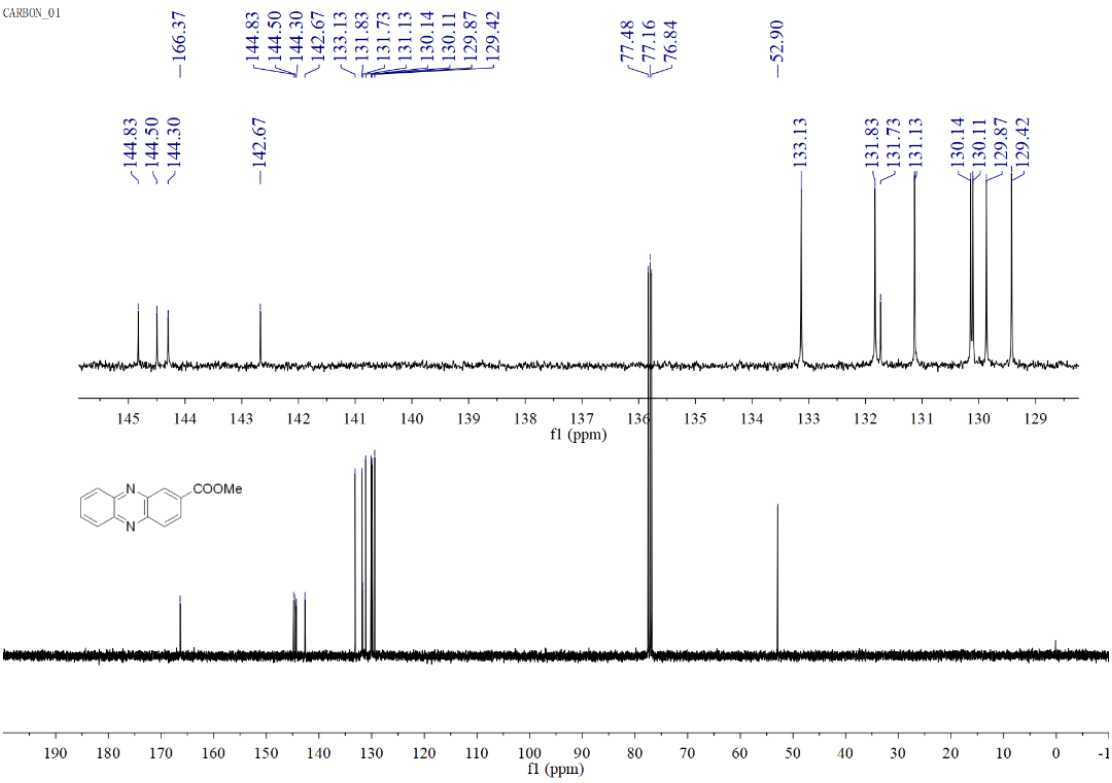
^{1}H NMR spectrum of **6c** in $CDCl_3$



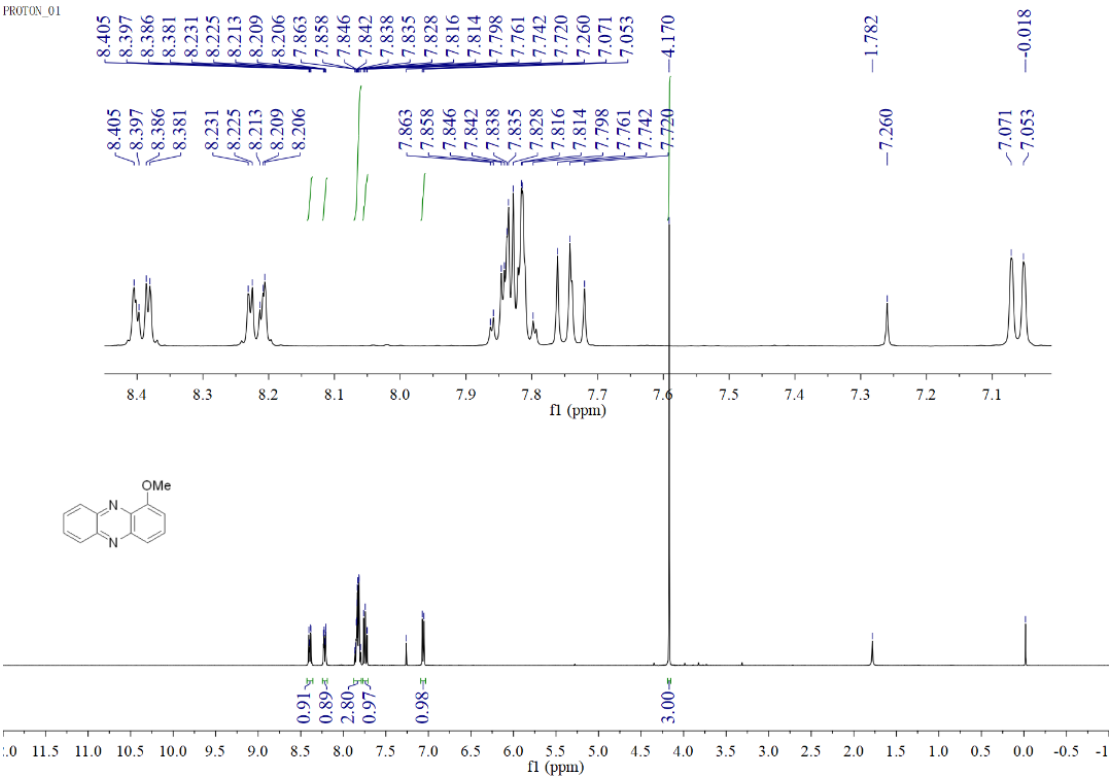
^{13}C NMR spectrum of **6c** in $CDCl_3$



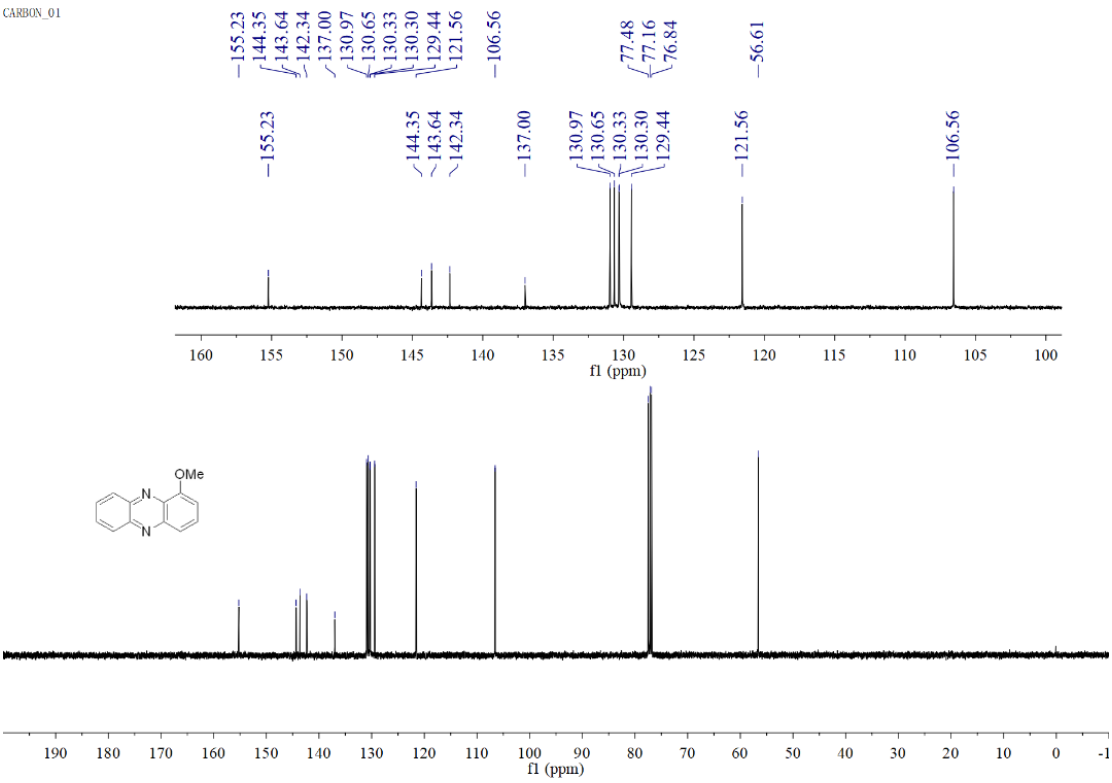
^{1}H NMR spectrum of **7c** in $CDCl_3$



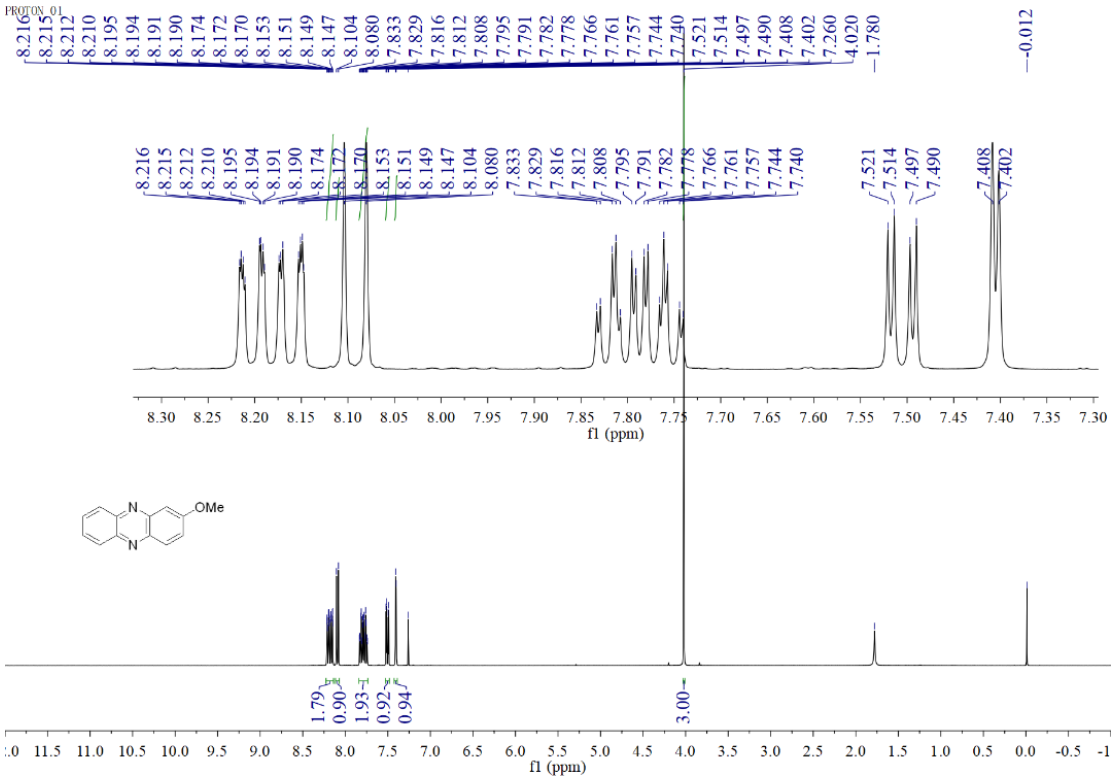
^{13}C NMR spectrum of **7c** in $CDCl_3$



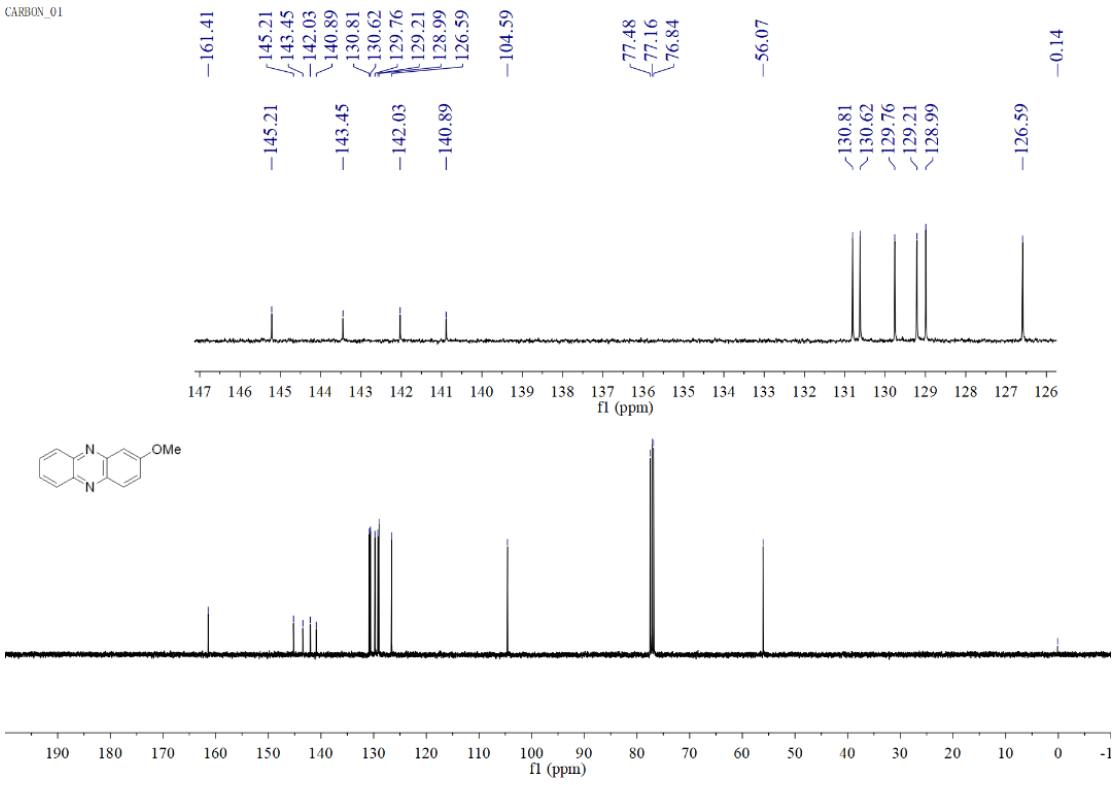
^{1}H NMR spectrum of **6d** in $CDCl_3$



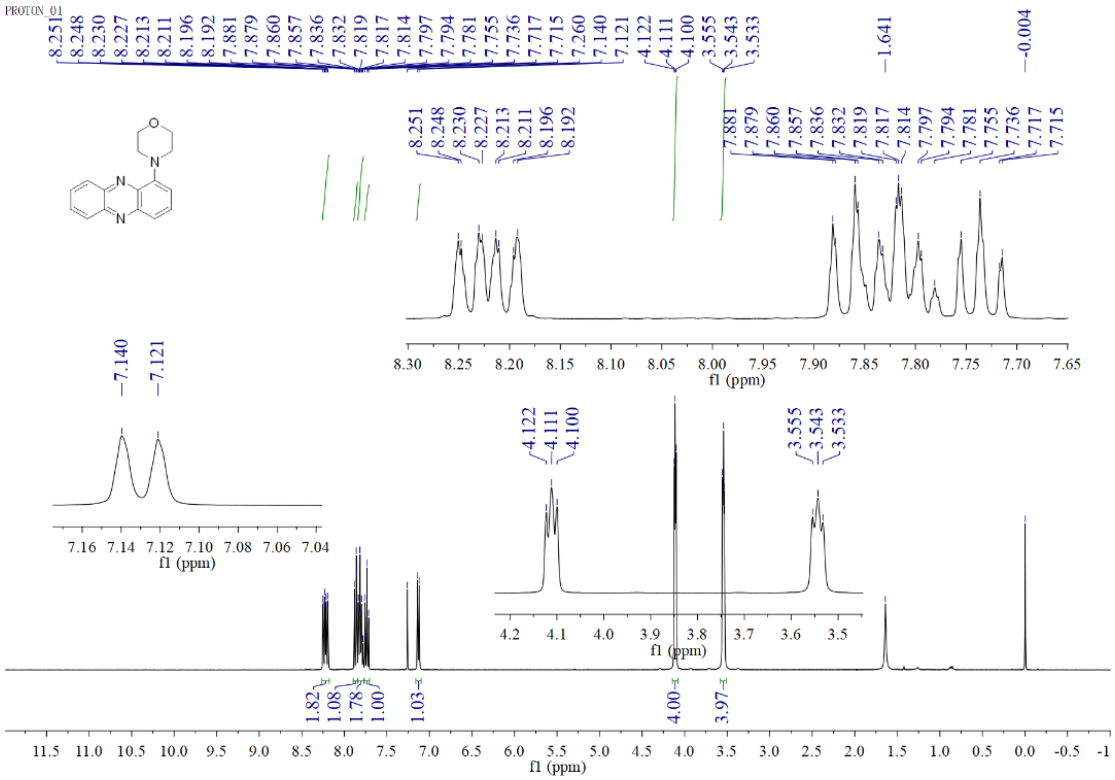
^{13}C NMR spectrum of **6d** in $CDCl_3$



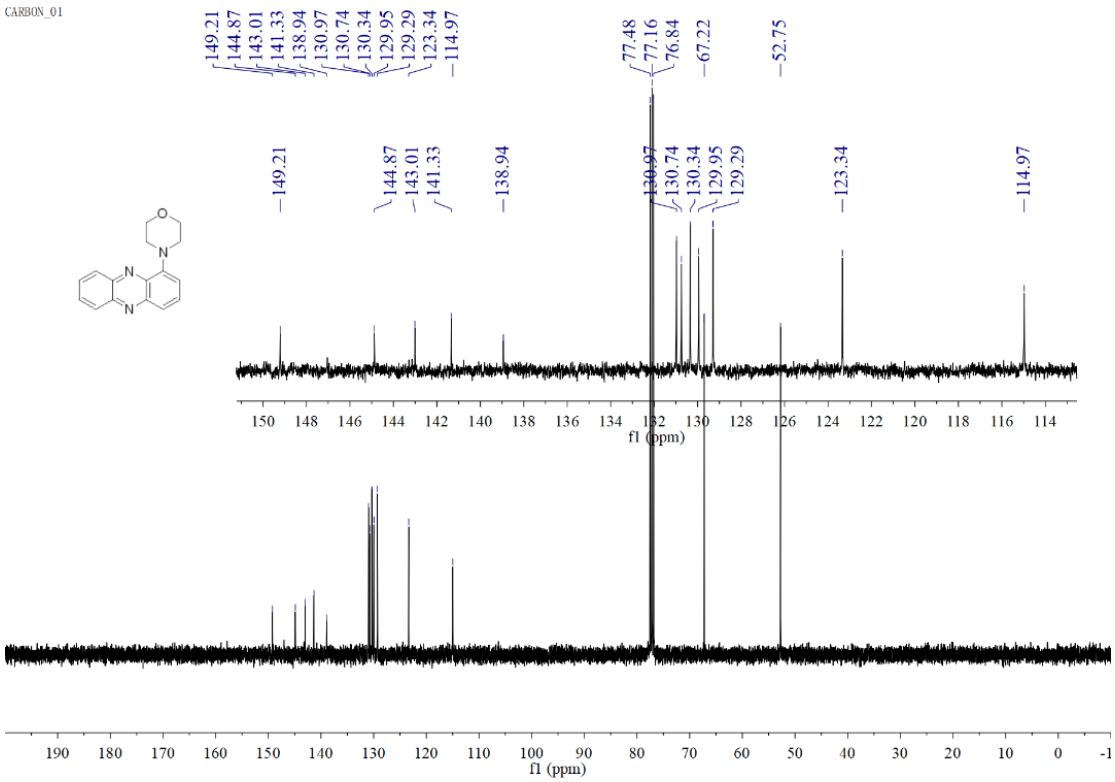
^{1}H NMR spectrum of **7d** in $CDCl_3$



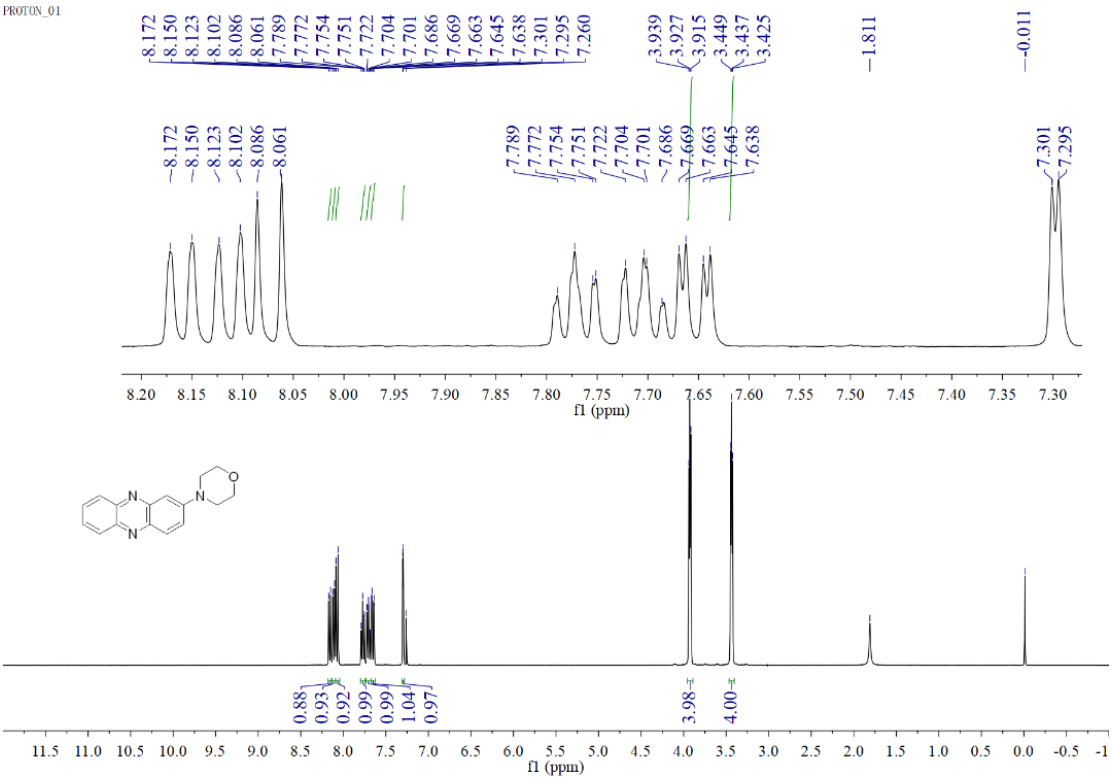
^{13}C NMR spectrum of **7d** in $CDCl_3$



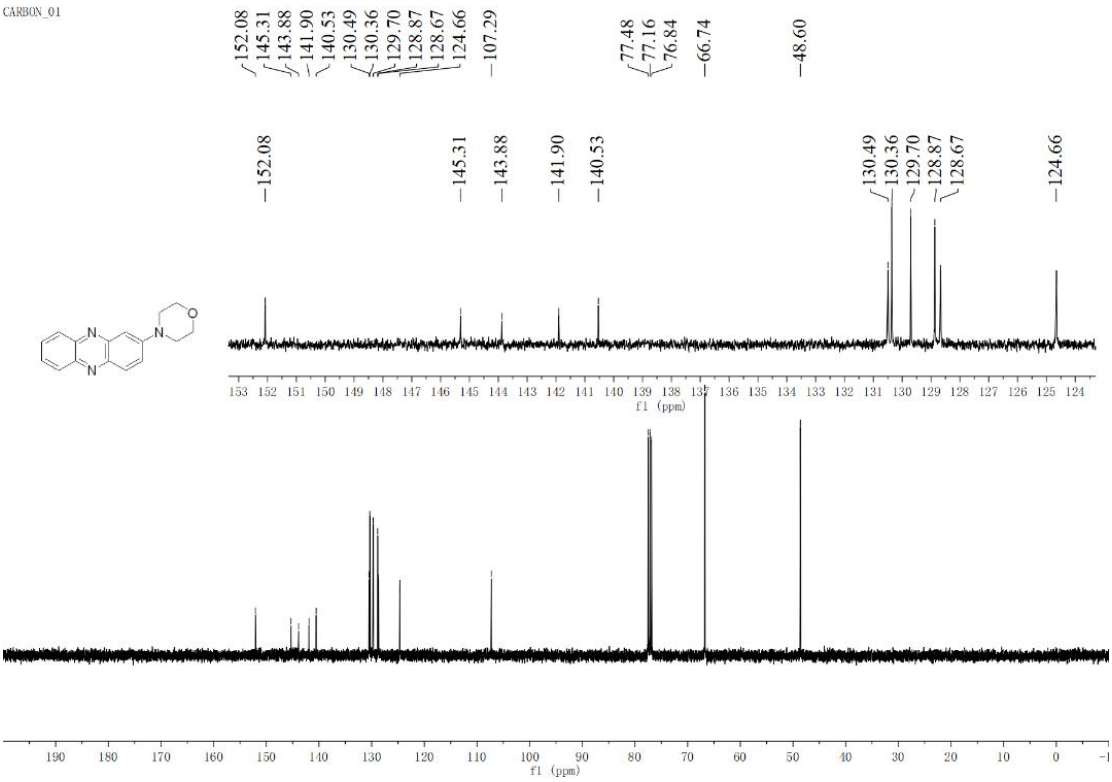
^{1}H NMR spectrum of **6e** in $CDCl_3$



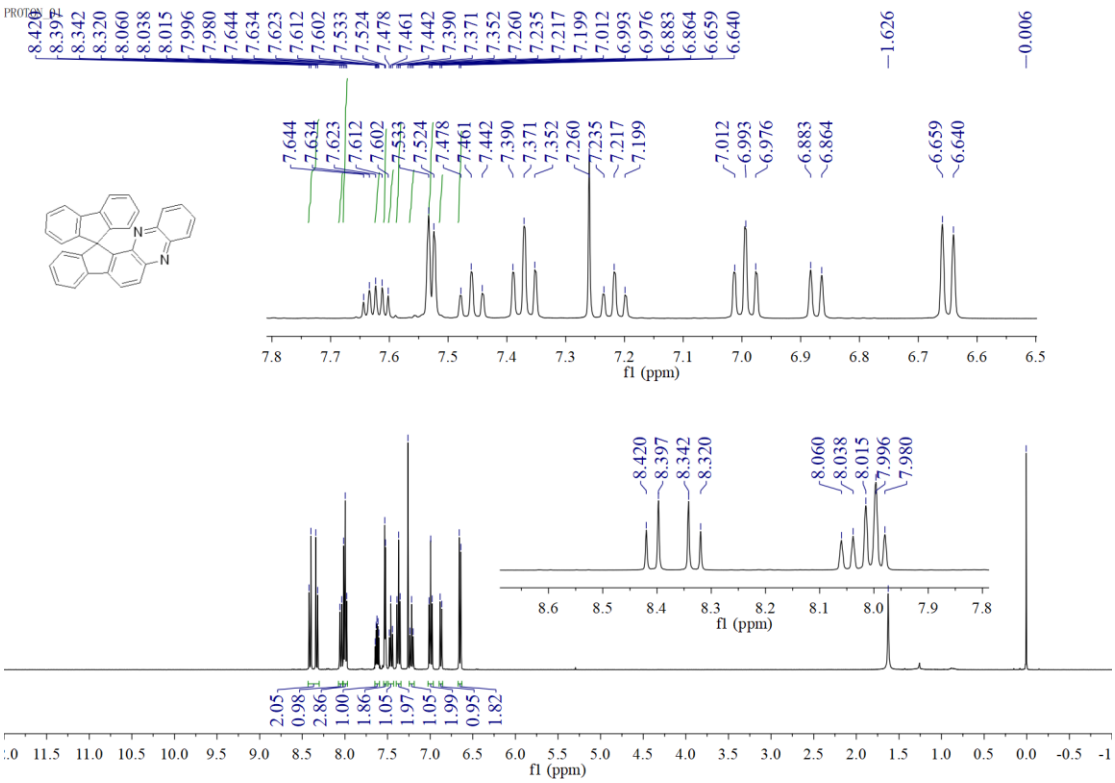
^{13}C NMR spectrum of **6e** in $CDCl_3$



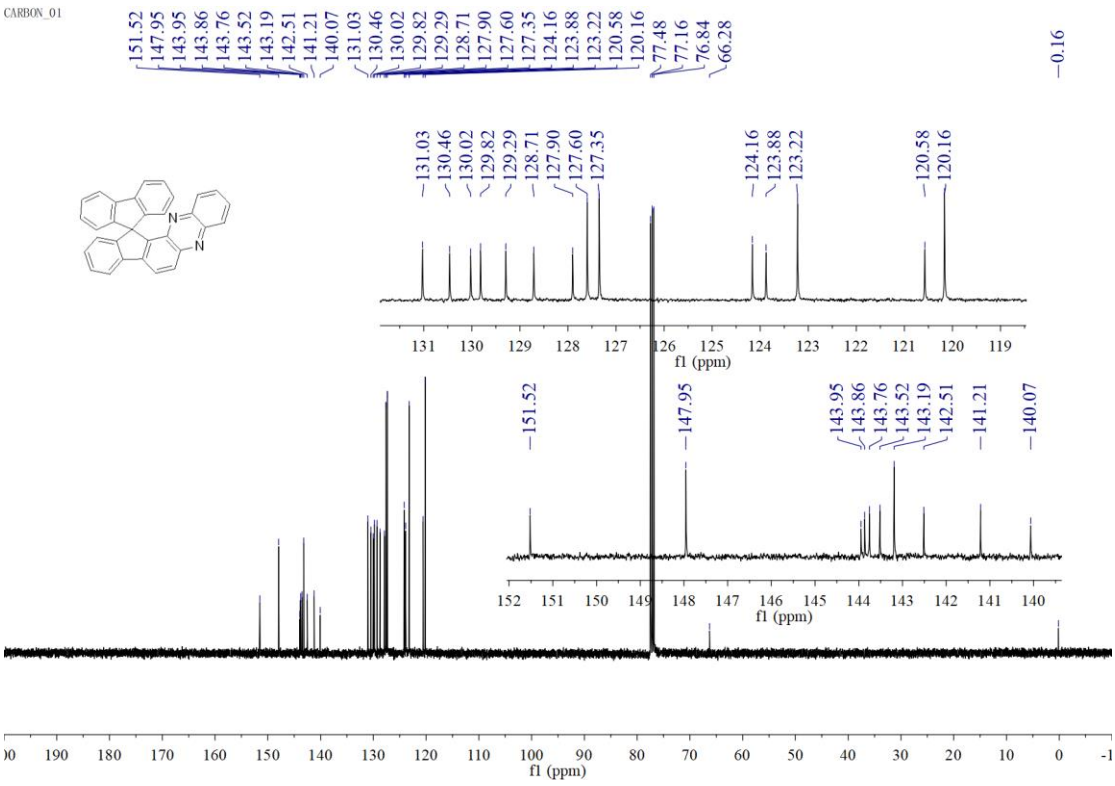
^{1}H NMR spectrum of **7e** in $CDCl_3$



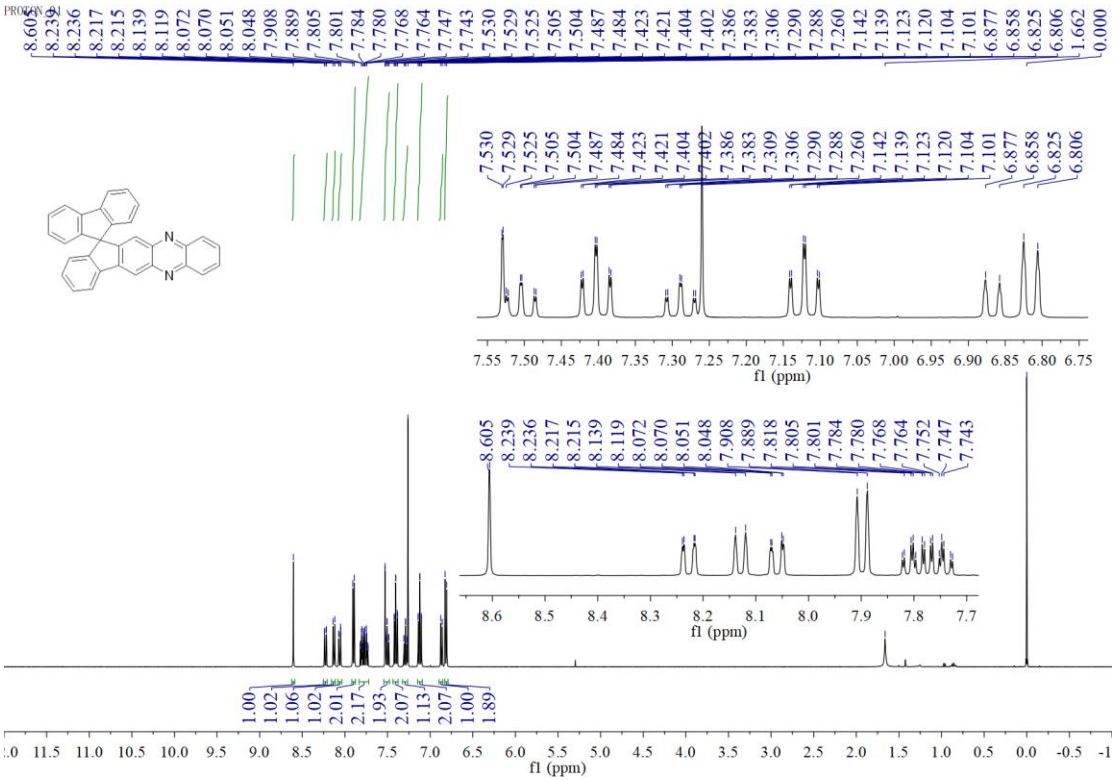
^{13}C NMR spectrum of **7e** in $CDCl_3$



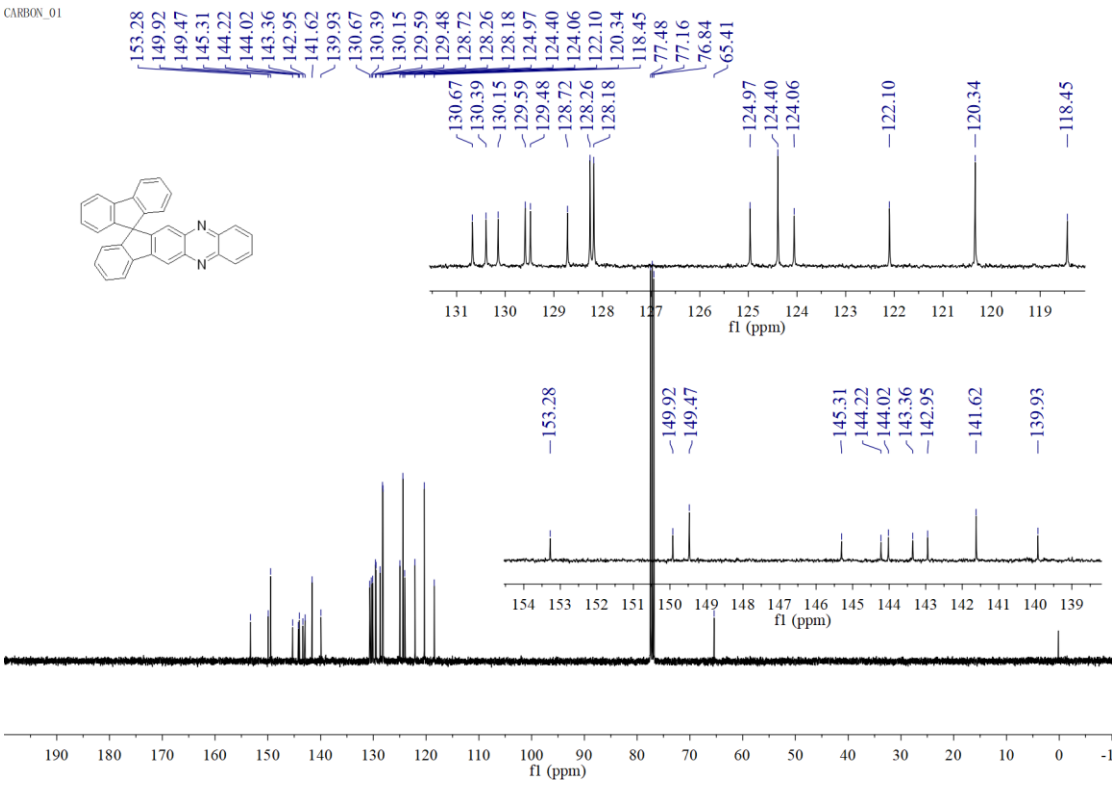
^{1}H NMR spectrum of **6f** in $CDCl_3$



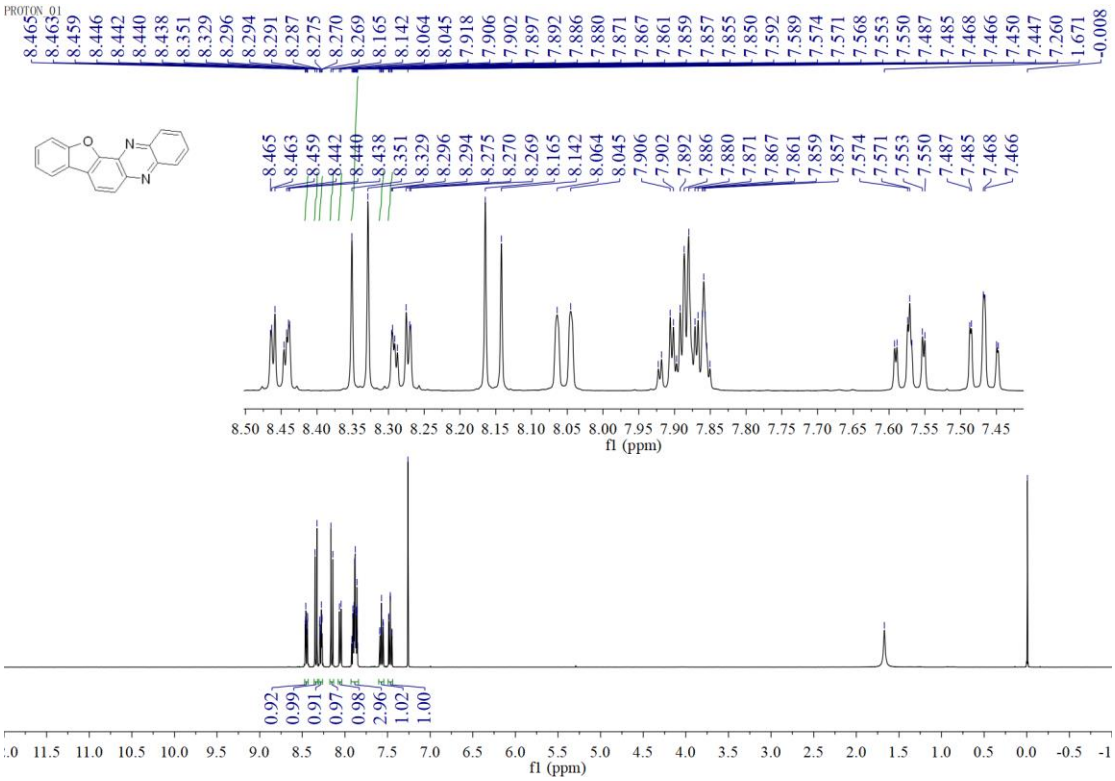
^{13}C NMR spectrum of **6f** in $CDCl_3$



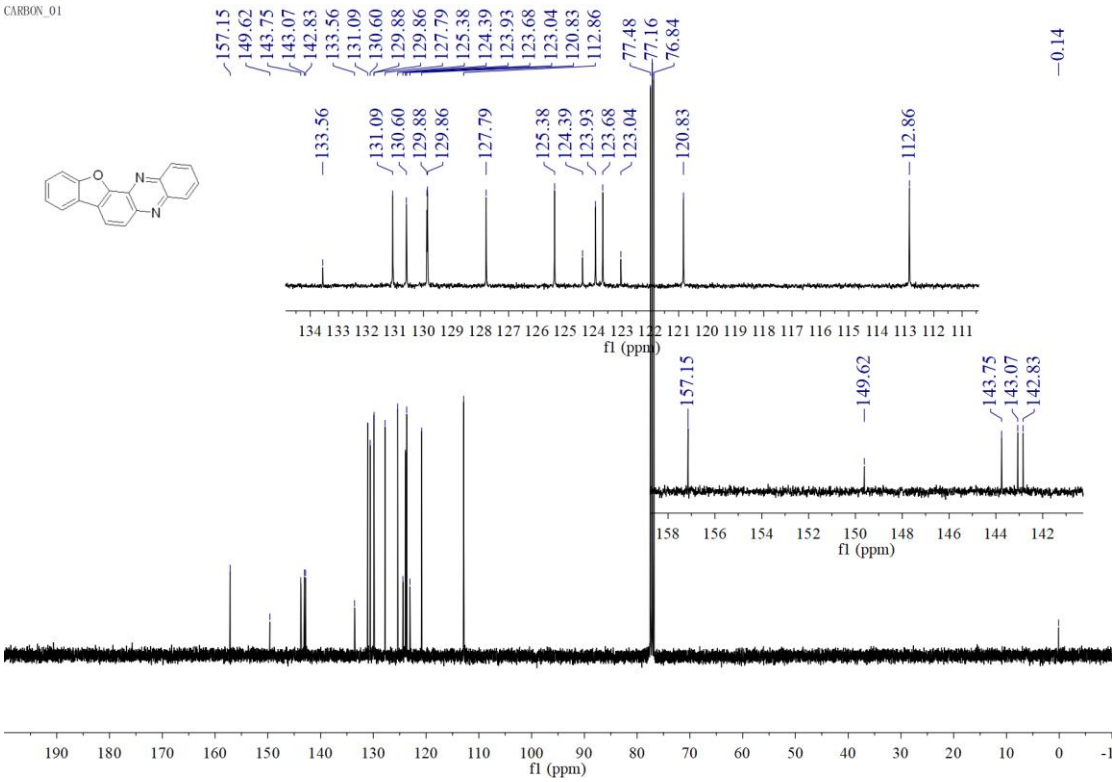
^{1}H NMR spectrum of **7f** in $CDCl_3$



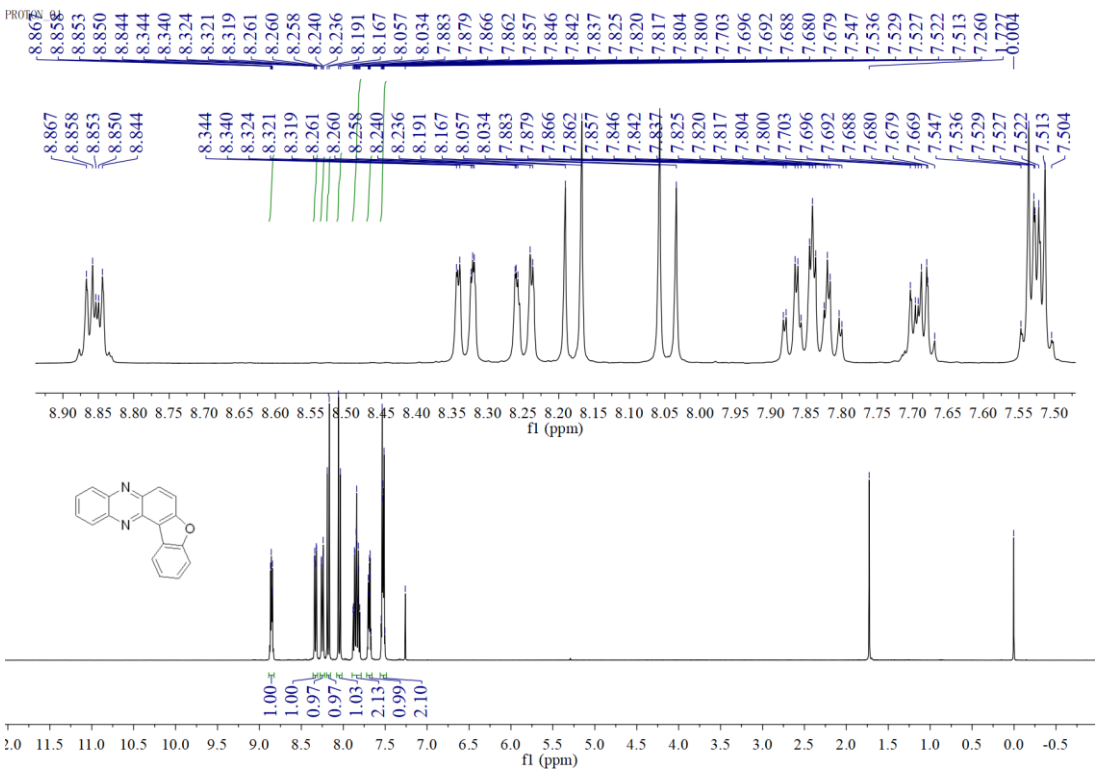
^{13}C NMR spectrum of **7f** in $CDCl_3$



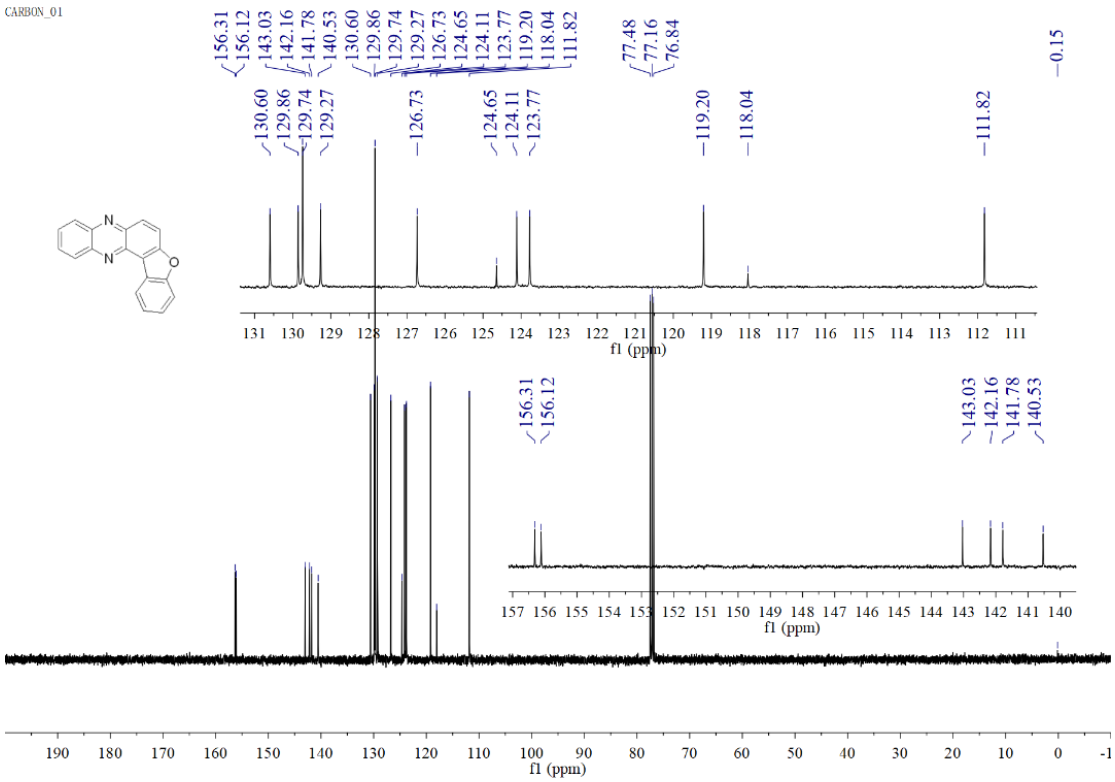
^{1}H NMR spectrum of **6g** in $CDCl_3$



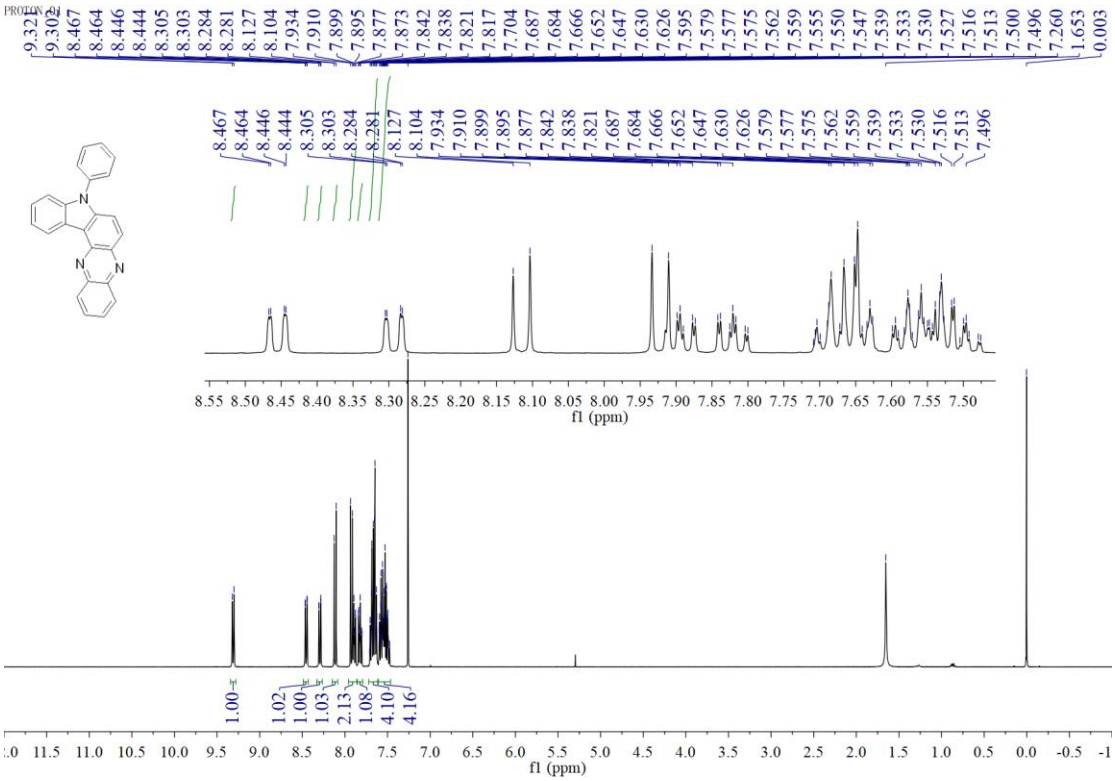
^{13}C NMR spectrum of **6g** in $CDCl_3$



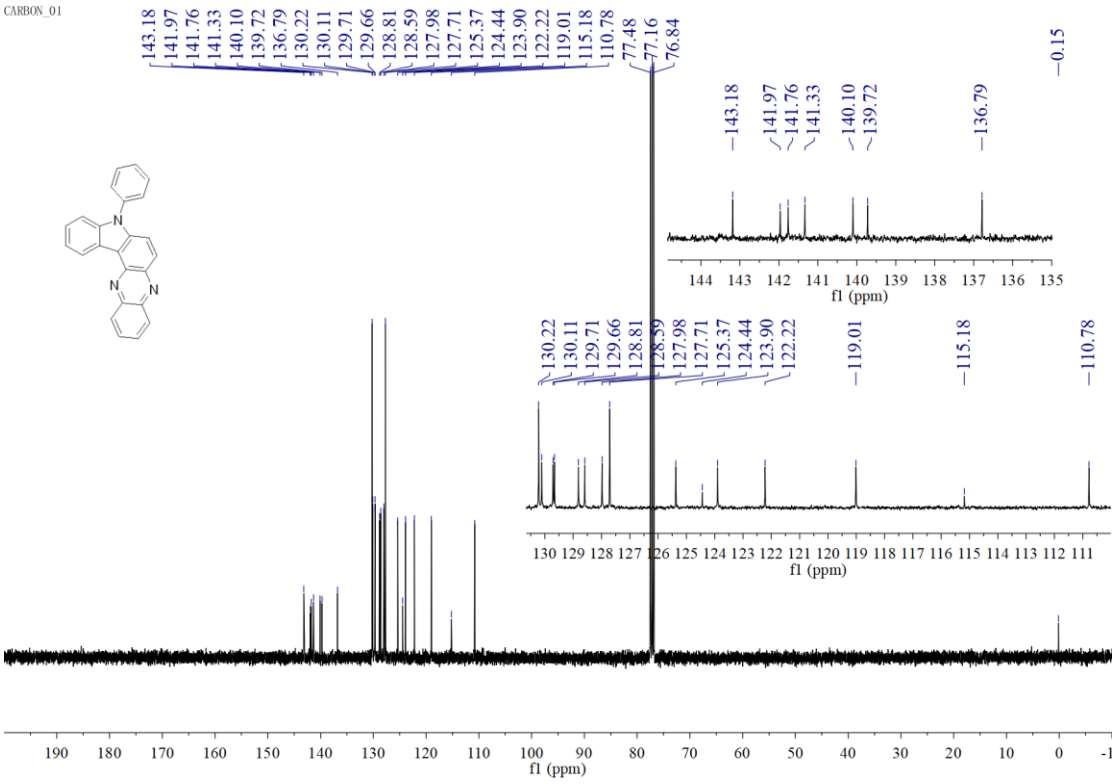
^{1}H NMR spectrum of **6h** in $CDCl_3$



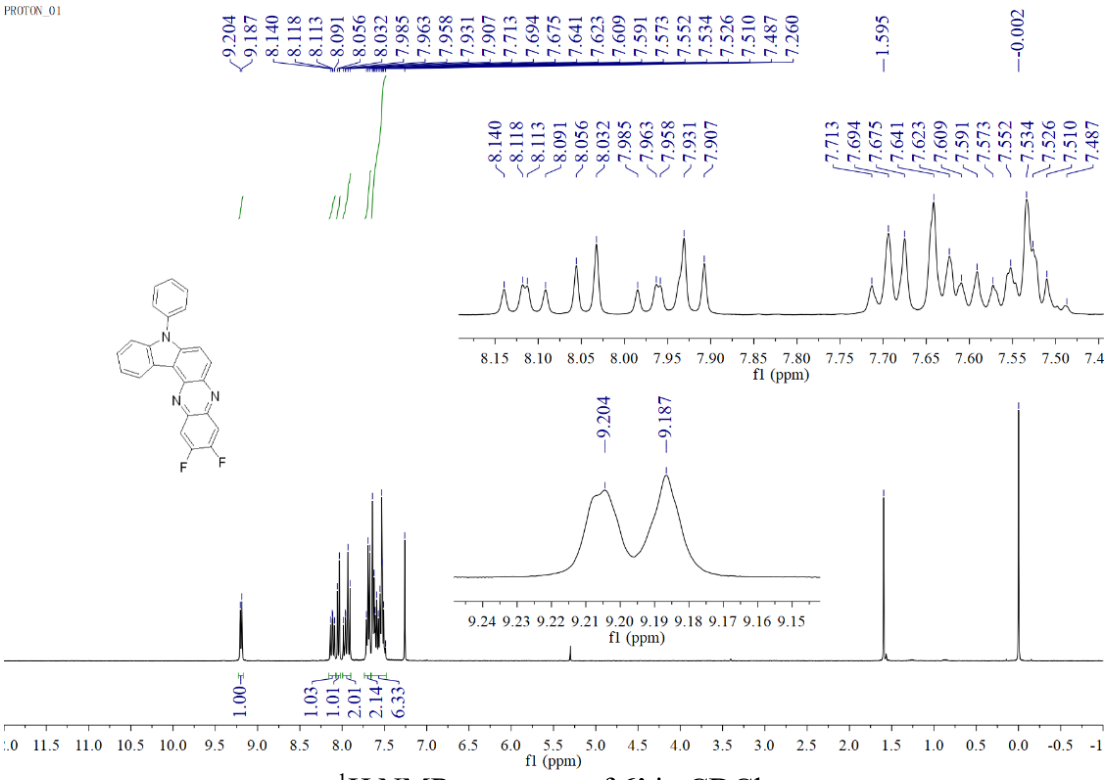
^{13}C NMR spectrum of **6h** in $CDCl_3$



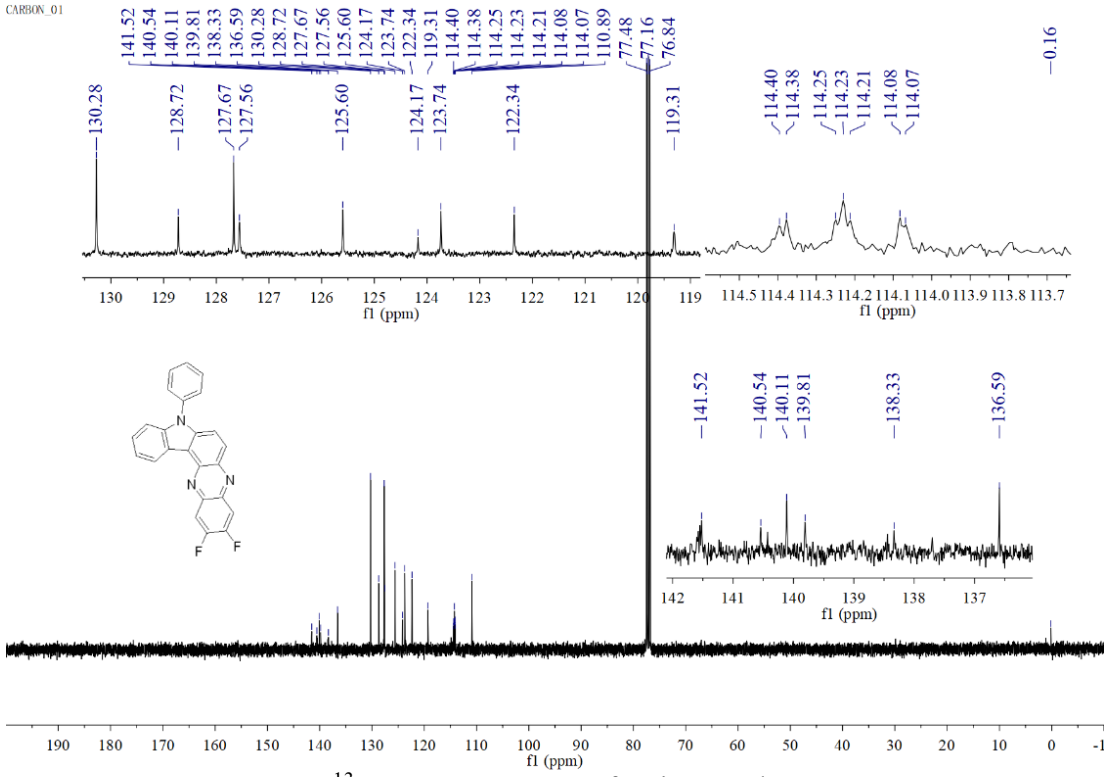
^{1}H NMR spectrum of **6i** in $CDCl_3$



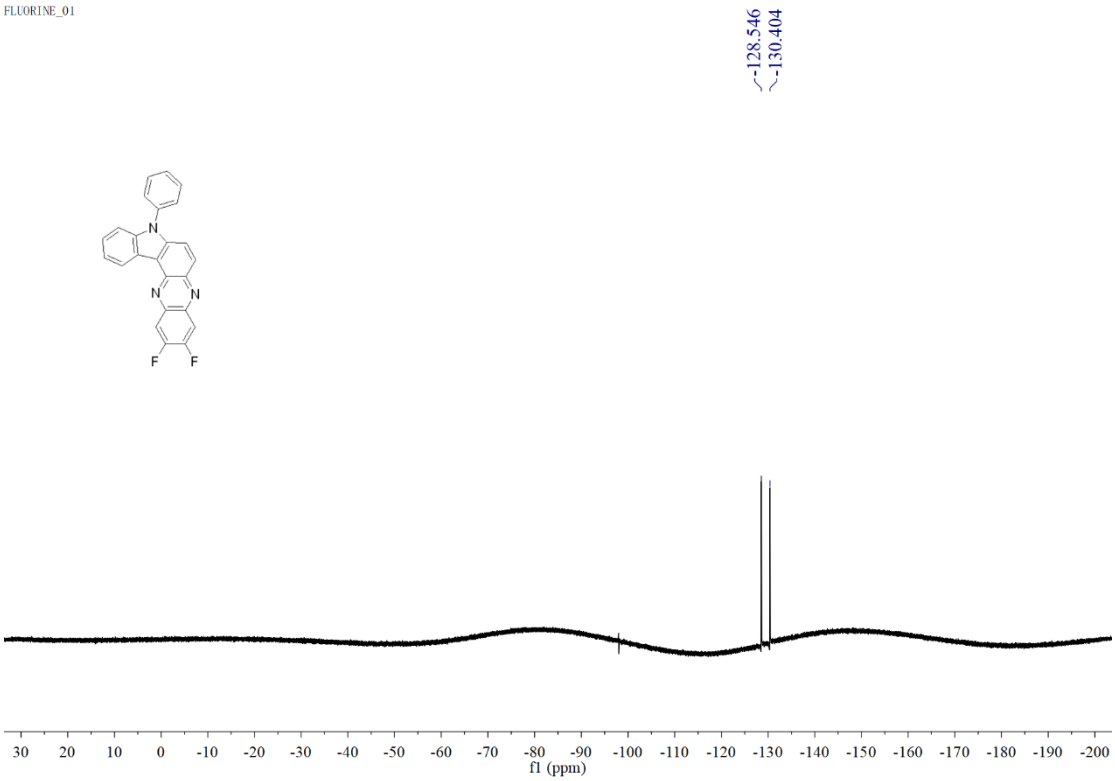
^{13}C NMR spectrum of **6i** in $CDCl_3$



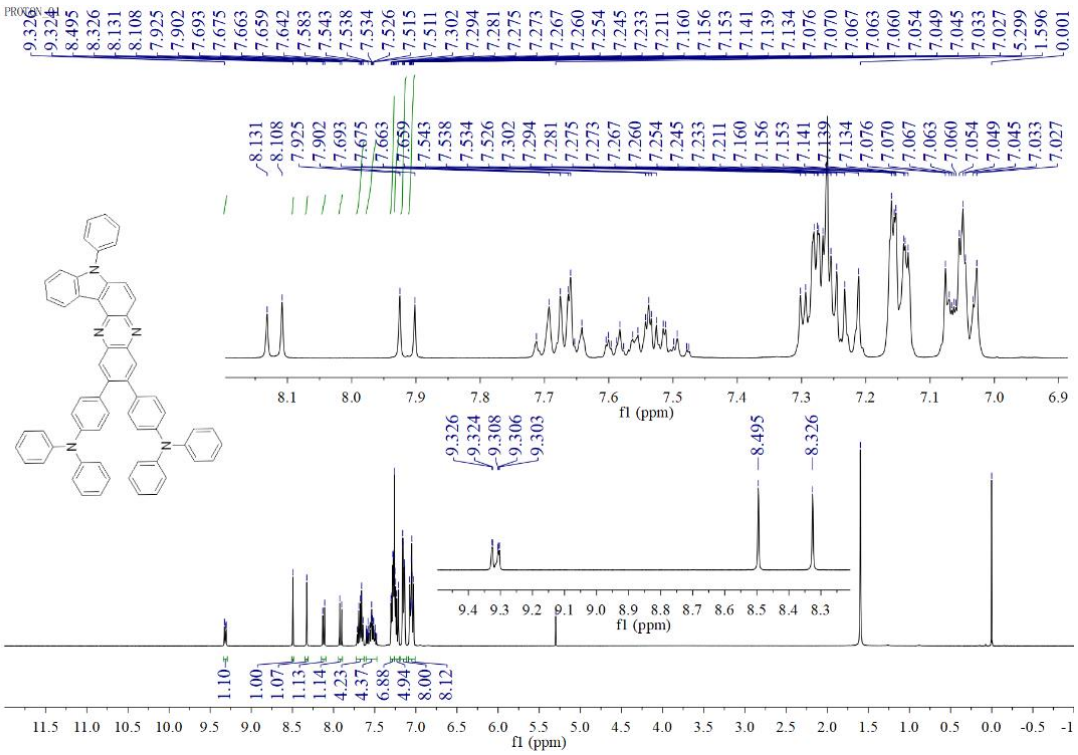
^{1}H NMR spectrum of **6j** in $CDCl_3$



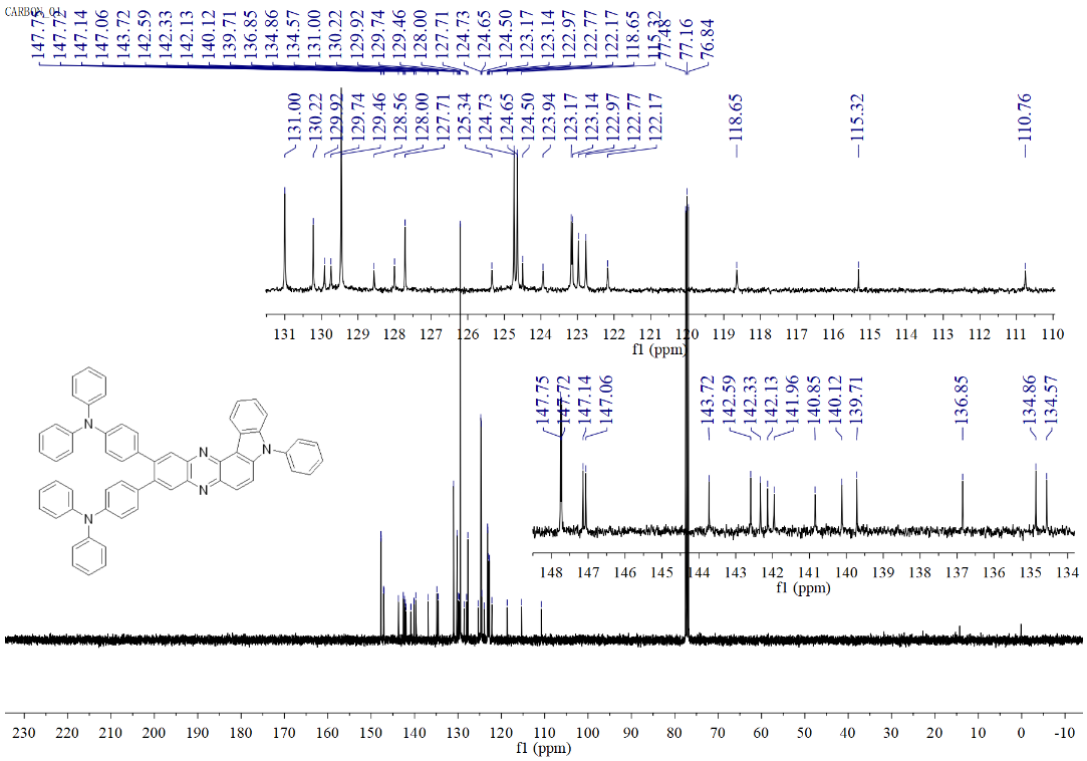
^{13}C NMR spectrum of **6j** in $CDCl_3$



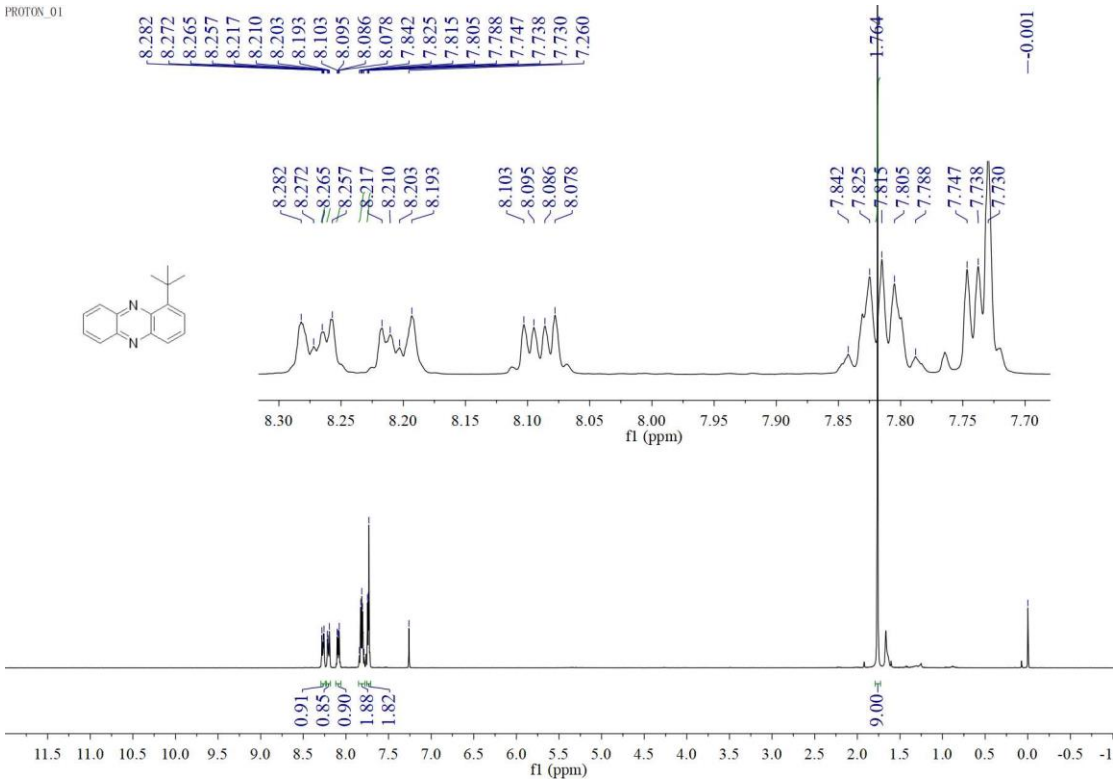
^{19}F NMR spectrum of **6j** in $CDCl_3$



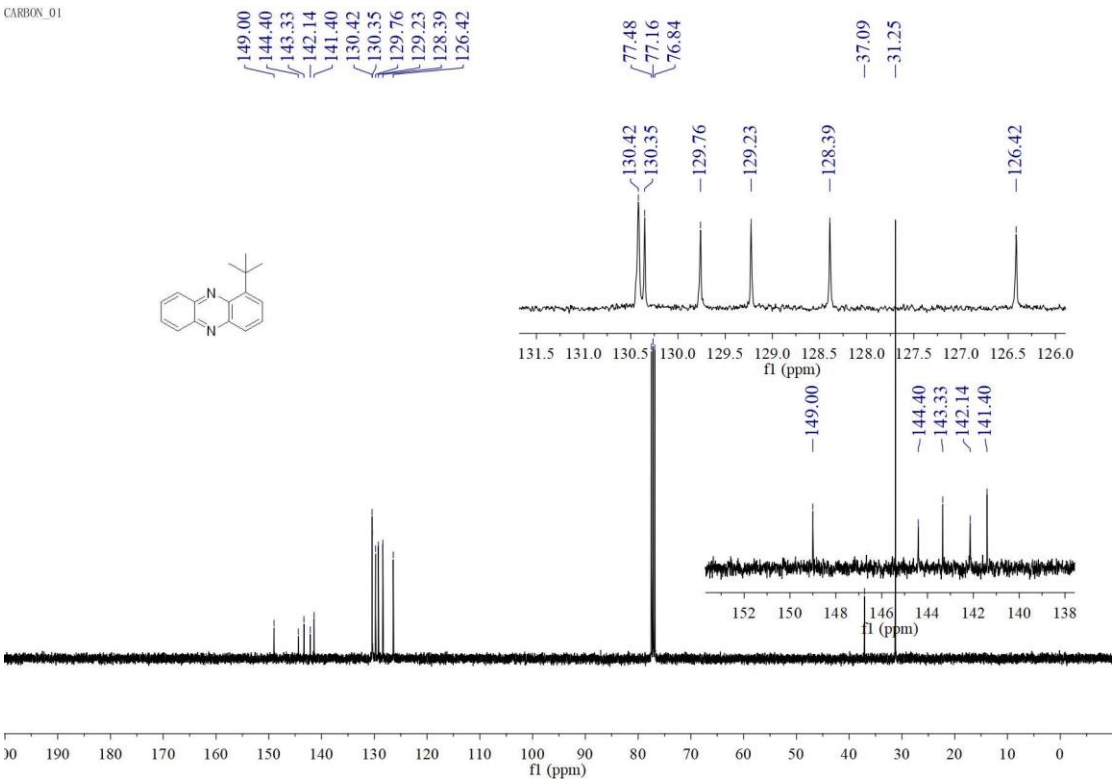
^{1}H NMR spectrum of **6k** in $CDCl_3$



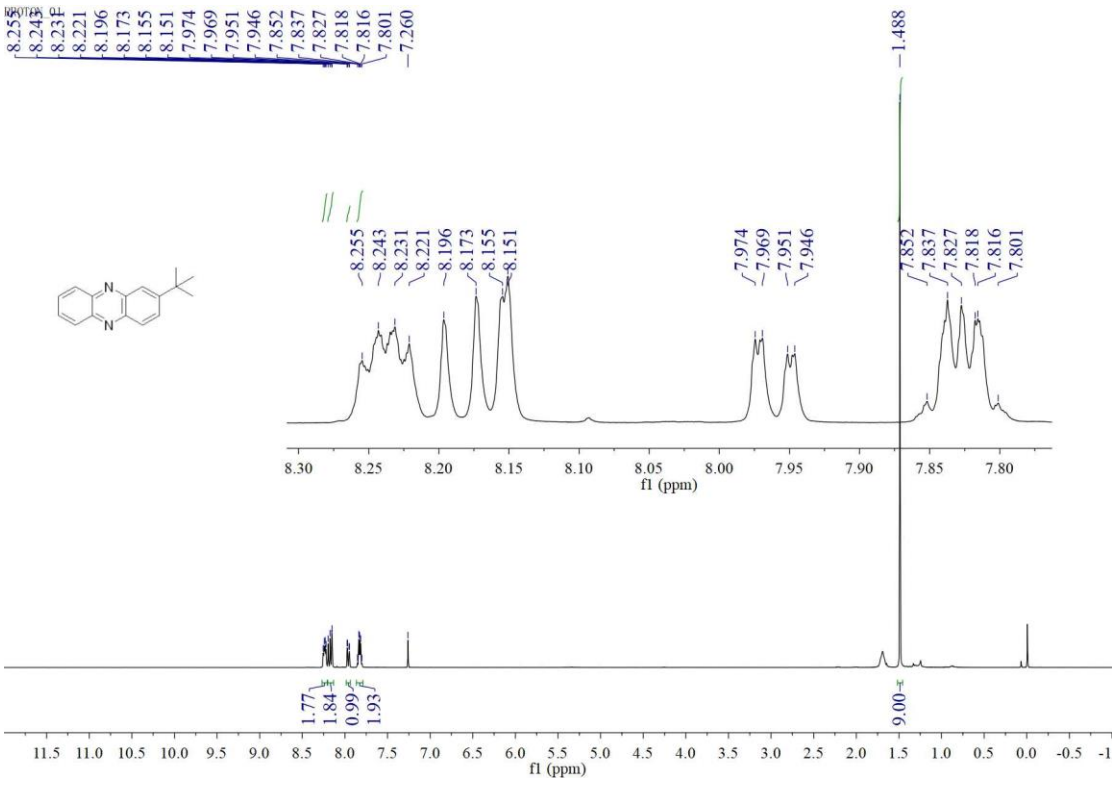
^{13}C NMR spectrum of **6k** in $CDCl_3$



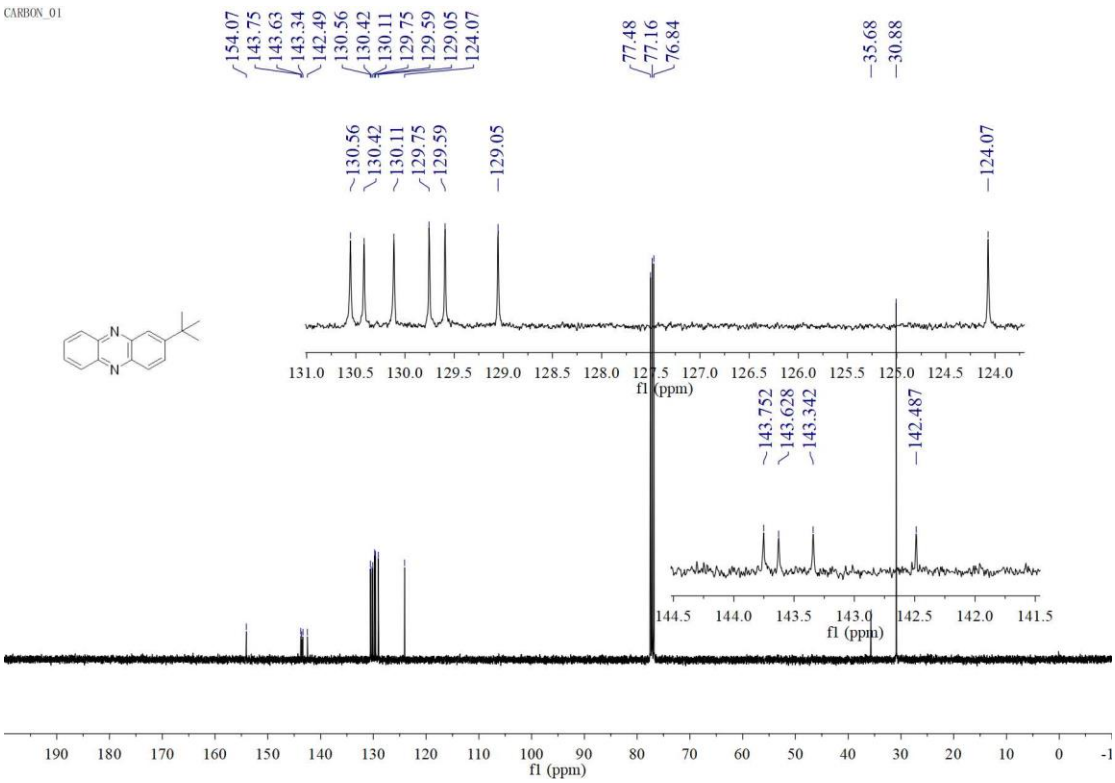
^{1}H NMR spectrum of **6l** in $CDCl_3$



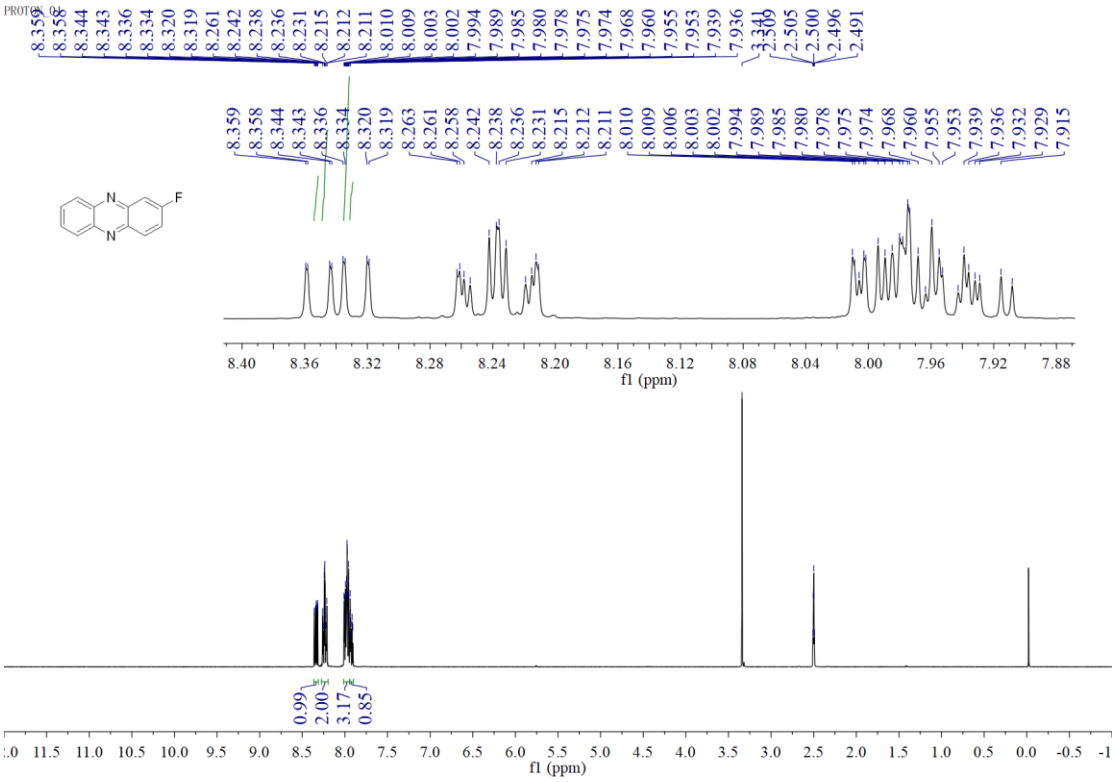
^{13}C NMR spectrum of **6l** in $CDCl_3$



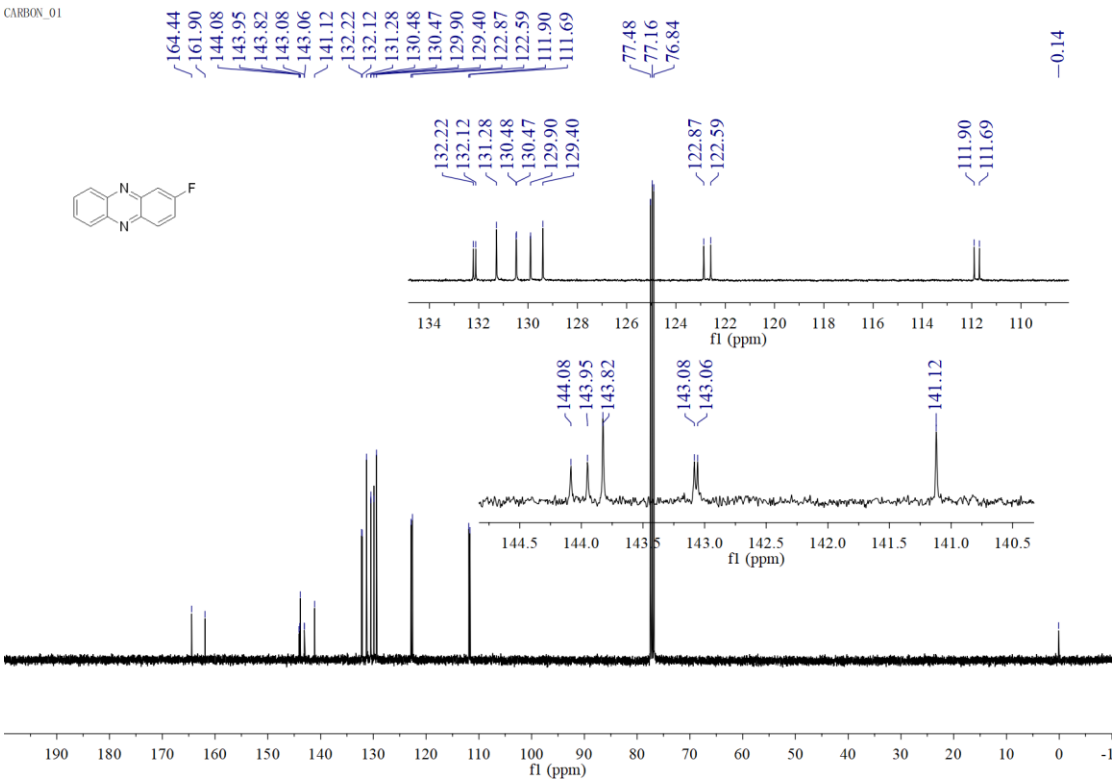
^{1}H NMR spectrum of **7l** in $CDCl_3$



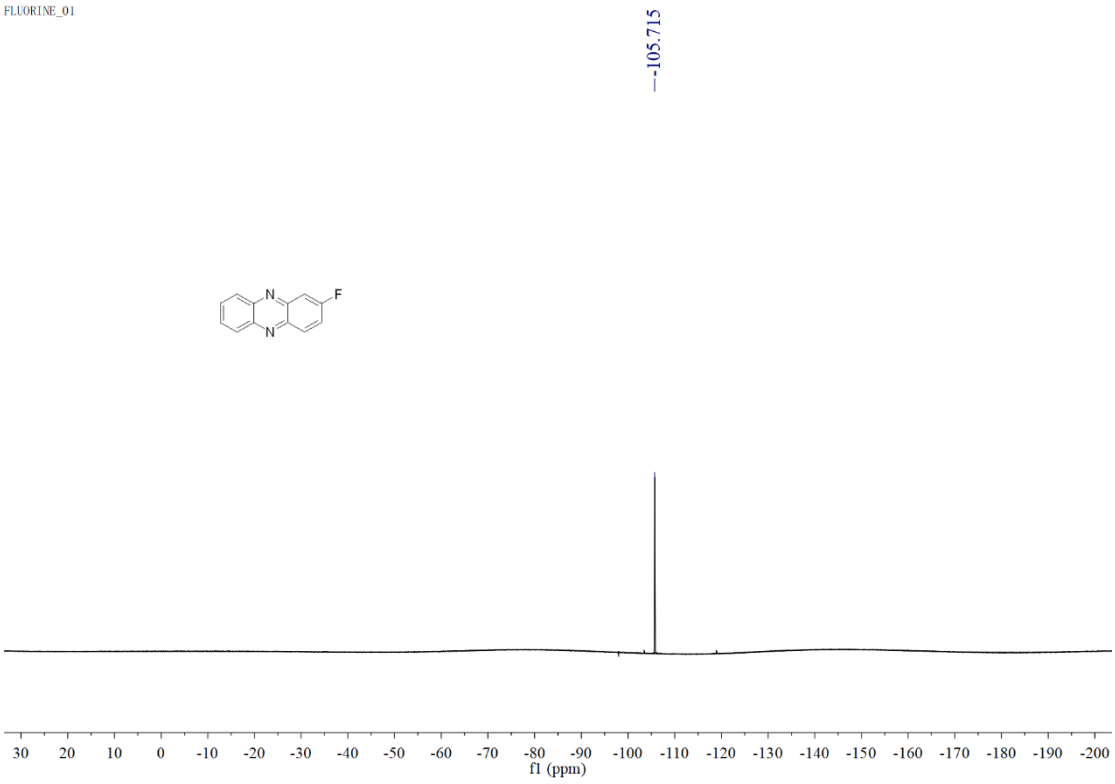
^{13}C NMR spectrum of **7l** in $CDCl_3$



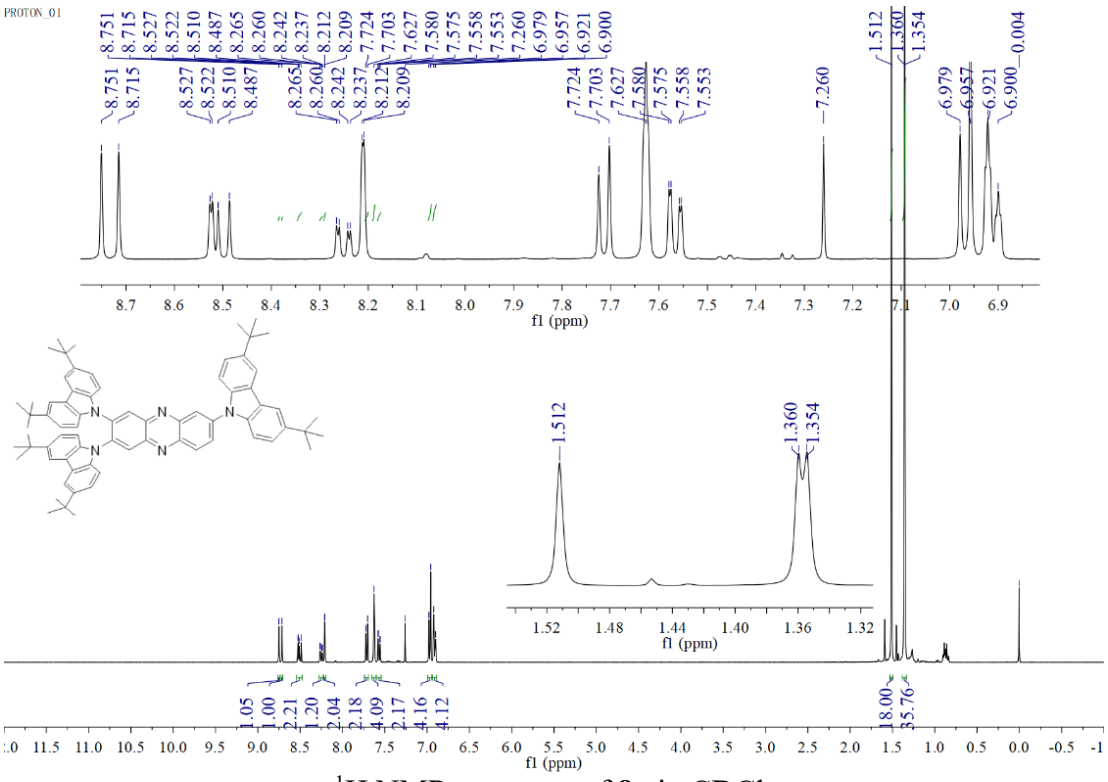
^{1}H NMR spectrum of **6m** in DMSO-*d6*



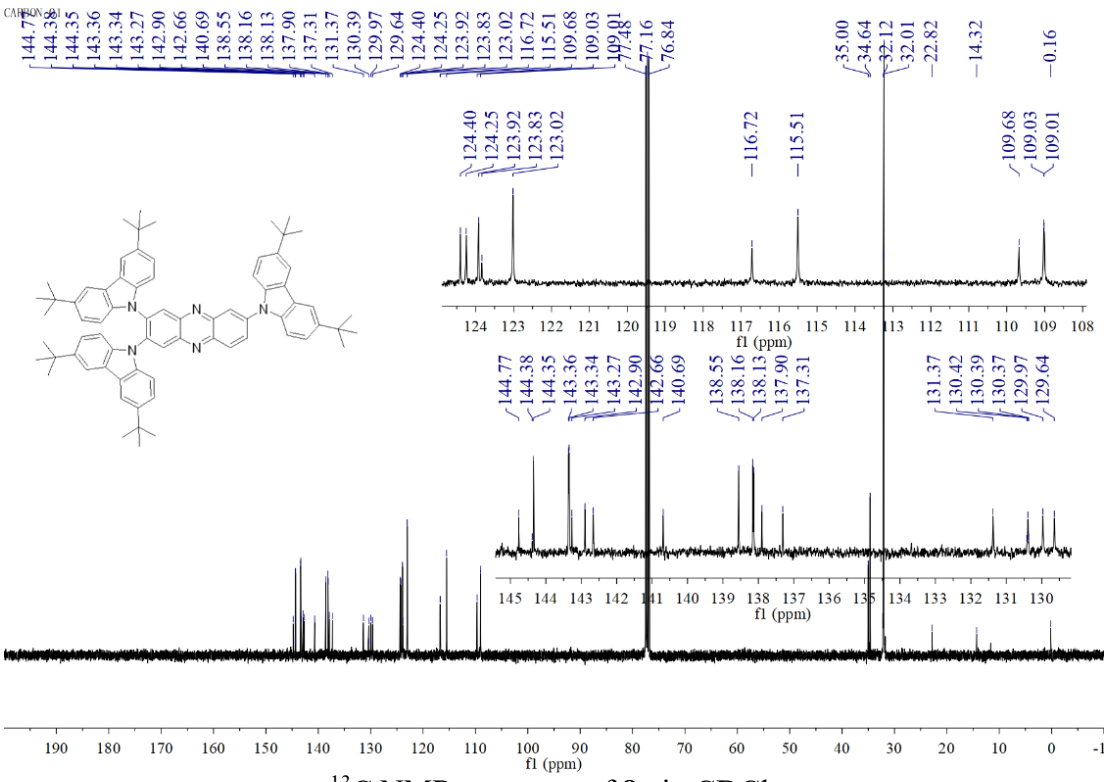
^{13}C NMR spectrum of **6m** in $CDCl_3$



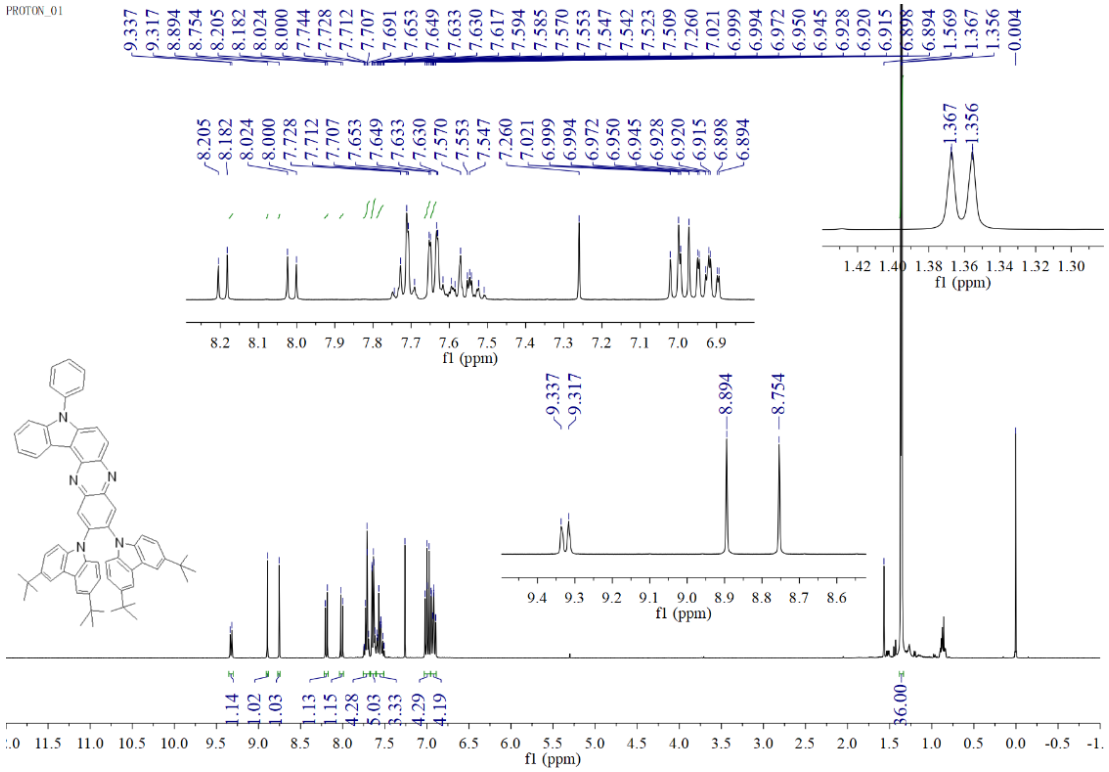
^{19}F NMR spectrum of **6m** in $CDCl_3$



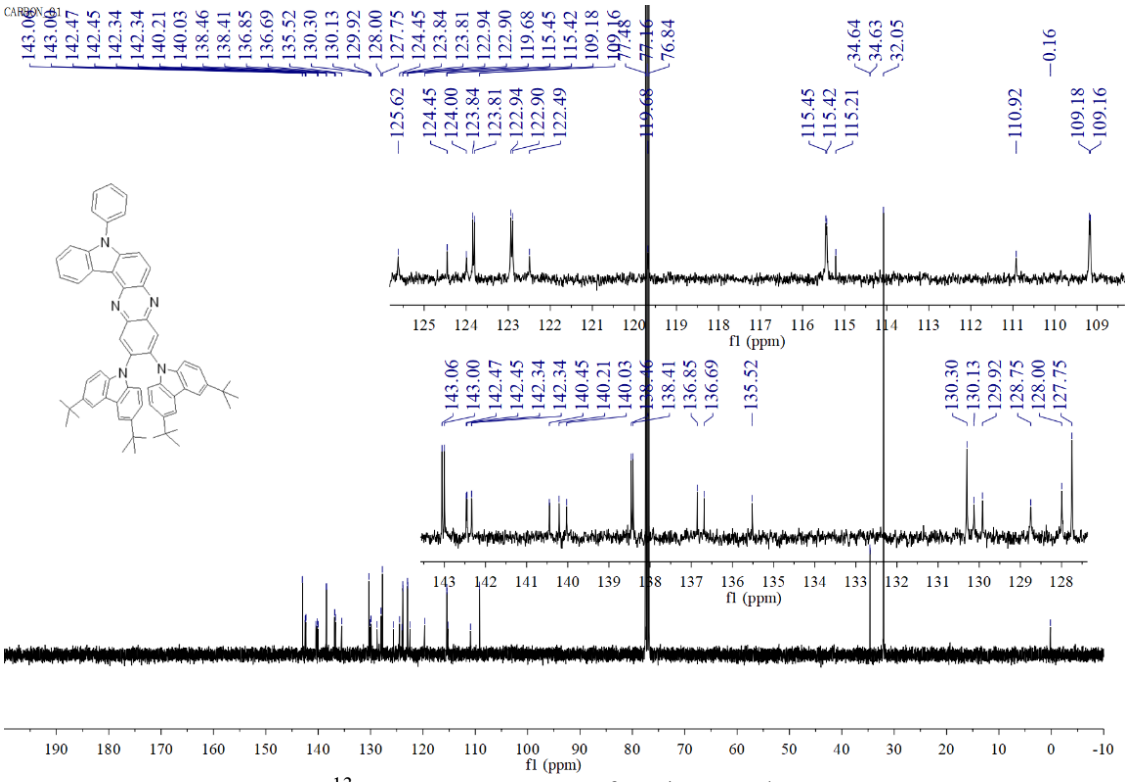
^{1}H NMR spectrum of **8a** in $CDCl_3$



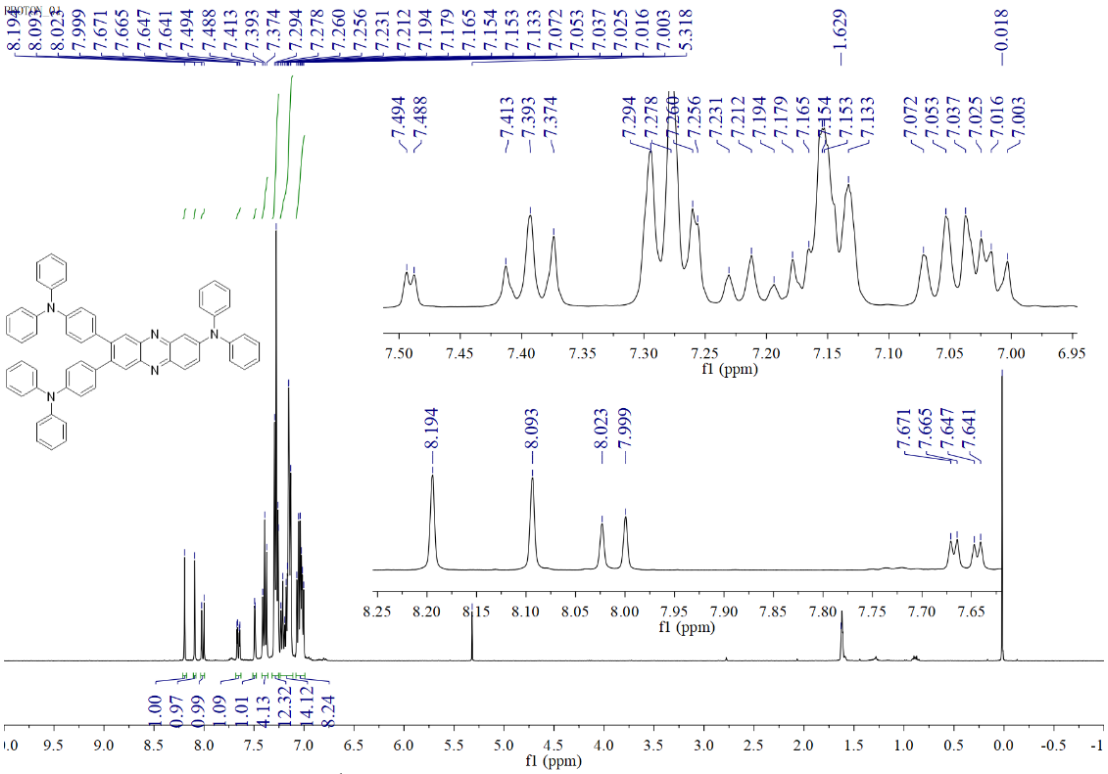
^{13}C NMR spectrum of **8a** in $CDCl_3$



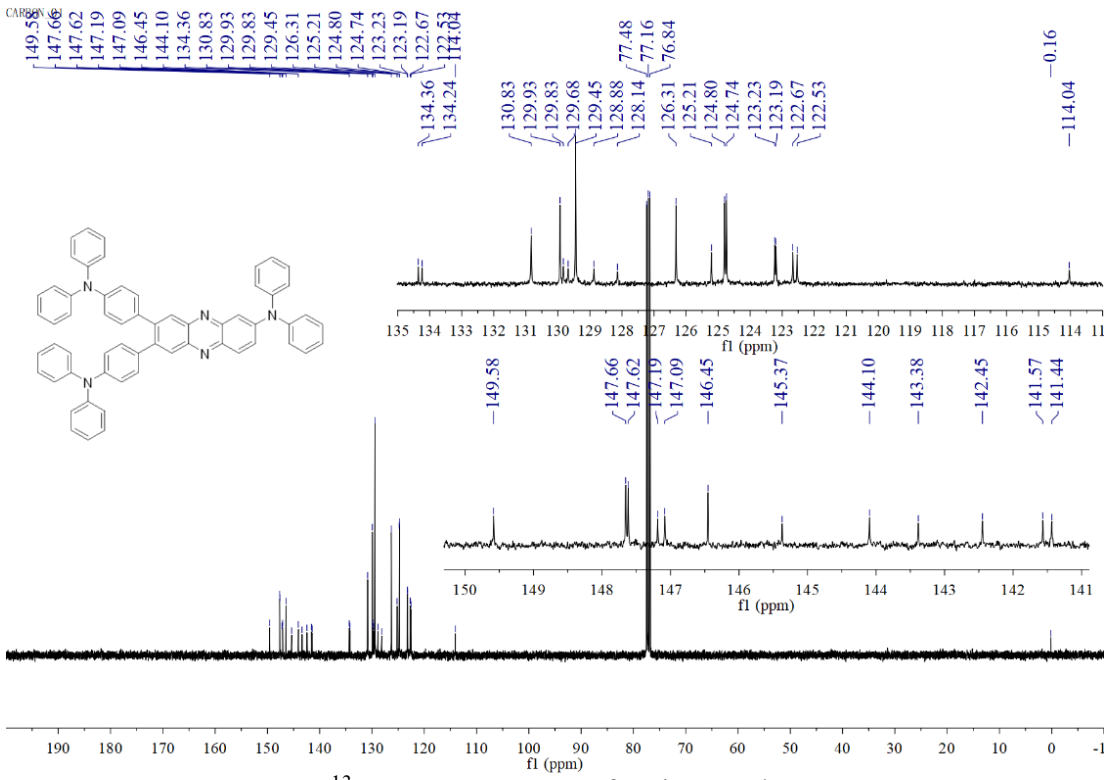
^{1}H NMR spectrum of **8b** in $CDCl_3$



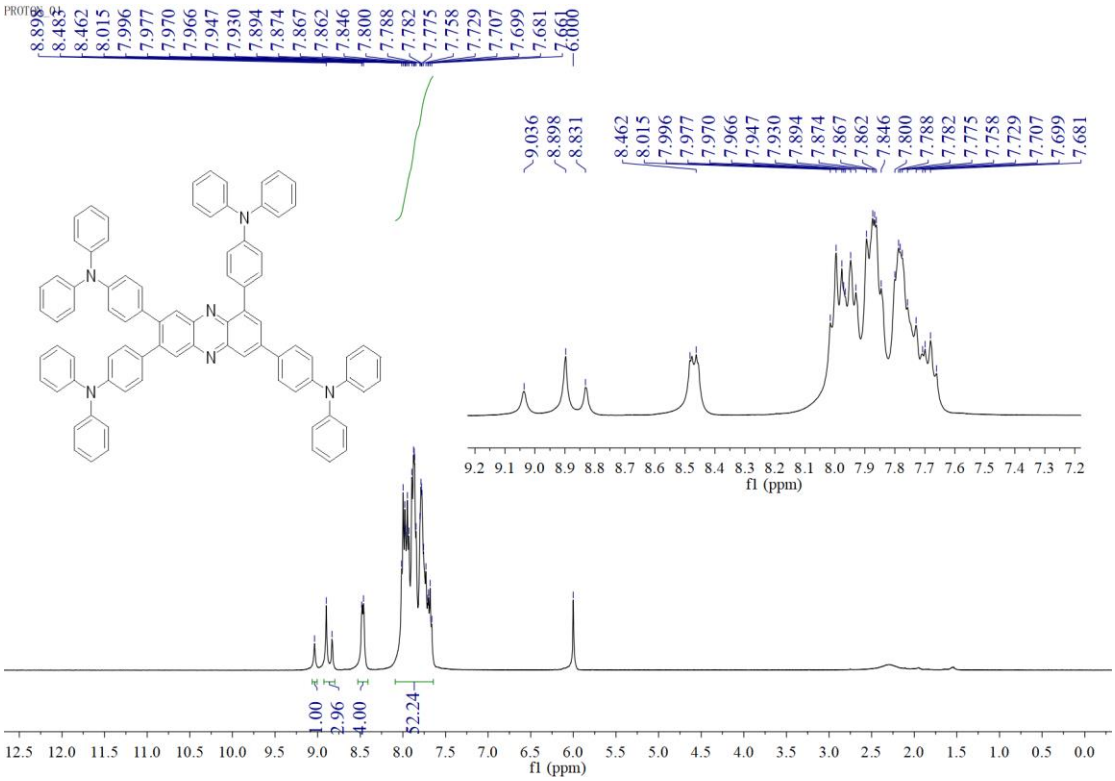
^{13}C NMR spectrum of **8b** in $CDCl_3$



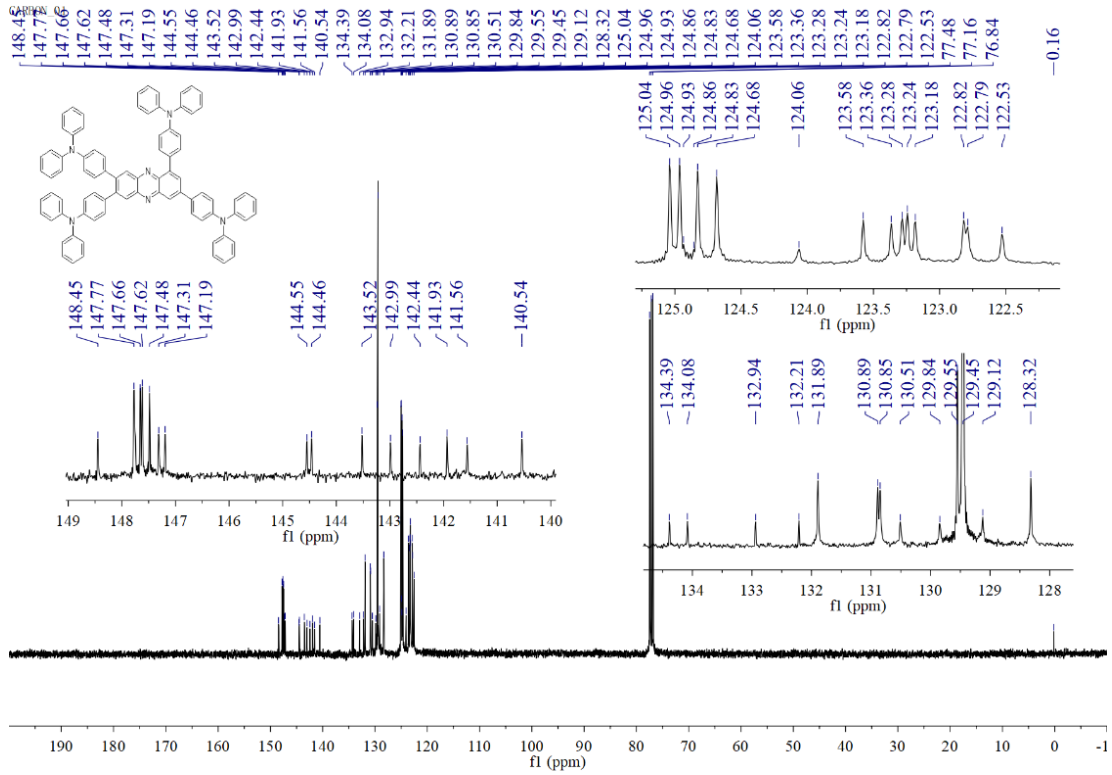
^{1}H NMR spectrum of **8c** in $CDCl_3$



^{13}C NMR spectrum of **8c** in $CDCl_3$



^{1}H NMR spectrum of **8d** in $CDCl_2CDCl_2$



^{13}C NMR spectrum of **8d** in $CDCl_3$