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Supporting Information

Rapid Synthesis of Polysubstitued Phenanthridines from Simple Aliphatic/Aromatic Nitriles and Iodo Arenes *via* Pd(II) Catalyzed Domino C-C/C-C/C-N Bonds Formation

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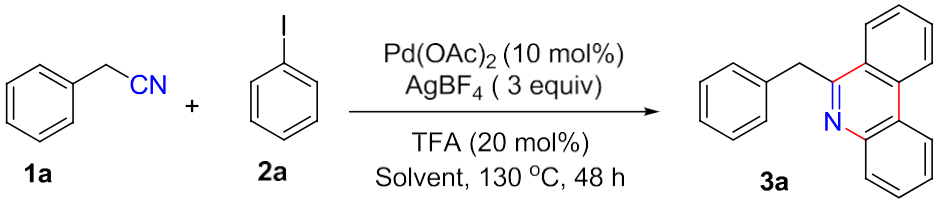
1. General Considerations:

Unless otherwise noted, all reagents were purchased from a commercial supplier and used without further purification. All the reactions were run under inert atmosphere in the pressure tubes and indicated temperature was that of oil bath. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C{^{1}H} NMR spectra were recorded at 100 MHz, $CDCl_3$ was used as solvent. Chemical shift are reported in δ ppm referenced to $CDCl_3$ (δ 7.26), for ^{1}H NMR and $CDCl_3$ (δ 77.0)for ^{13}C NMR. The following abbreviations were used to explain multiplicities: (s, singlet; d, doublet; t, triplet; q, quartet; m, multiple, br.s, broad singlet), coupling constant (Hertz). Infrared spectra were recorded by FT-IR apparatus. High-resolution mass spectra (HRMS) spectra were obtained on ESI-TOF (electron spray ionization-time of flight) spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was performed on silica gel (100-200) mesh using ethyl acetate/hexanes or DCM/hexanes as eluent in different ratio.

2. General procedure and data for reaction optimization:

Optimization of reaction conditions

Table S1. Optimization by varying solvents[a]

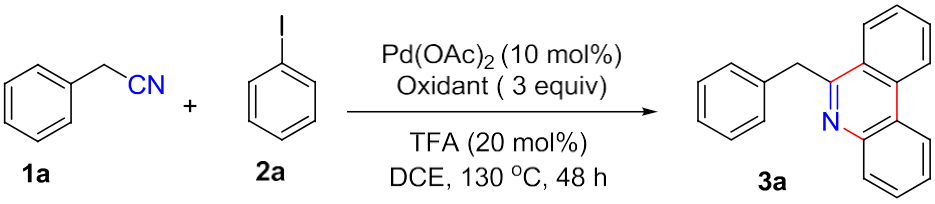


S. No.	Solvent	Yeild[b] of 3a (%)
1.	Toluene	17
2.	Chlorobenzene	10
3.	CH_3CN	n.r.
4.	HFIP	30
5.	DCE	70
[c]6.	DCE	42
7.	TFE	8

8.	Dioxane	n.r.
9.	THF	n.r.

[a]Reaction conditions: All reactions were performed with **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), $AgBF_4$ (3.0 equiv), TFA (20 mol%), in 2.0 mL of solvent for 48 h at 130 °C. [b]Isolated yield of **3a**.[c]2.0 equiv. of iodobenzene was used. n. r. = no reaction. DCE = Dichloroethane, TFE = 2,2,2-Trifluoroethanol, THF = Tetrahydrofuran.

Table S2. Optimization by varying oxidants[a]



S.No.	Oxidant	Yield[b] of 3a (%)
1.	Ag_2CO_3	n.r.
2.	Ag_2O	n.r.
3.	CH_3CO_2Ag	5
4.	$AgBF_4$	70
5.	AgOTf	n.r.
6.	$AgNO_3$	12
7.	$Cu(OAc)_2$	n.r.

[a]Reaction conditions: All reactions were performed with **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), oxidant (3.0 equiv), TFA (20 mol%), in 2.0 mL of DCE for 48 h at 130 °C. [b]Isolated yield of **3a**. n.r. = no reaction.

Table S3. Optimization by varying ligands[a]

S.No.	ligand	Yield[b] of 3a (%)
1.	TFA	70
2.	TfOH	55
3	AcOH	65
5.	SPhos	65
5.	XPhos	78

6.	XantPhos	77
7.	DavePhos	62
8.	JohnPhos	80
9.	JohnPhos	80[b]
10.	CyJohnPhos	77
11.	Rac. BINAP	n.r.

[a]Reaction conditions: All reactions were performed with **1a** (0.2 mmol), **2a** (0.6 mmol), $Pd(OAc)_2$ (10 mol %), $AgBF_4$ (3.0 equiv), ligand (20 mol%), in 2.0 mL of DCE for 48 h at 130 ^oC. [b]Isolated yield of **3a**. [b]4.0 equiv of iodobenzene was used. n. r. = no reaction.

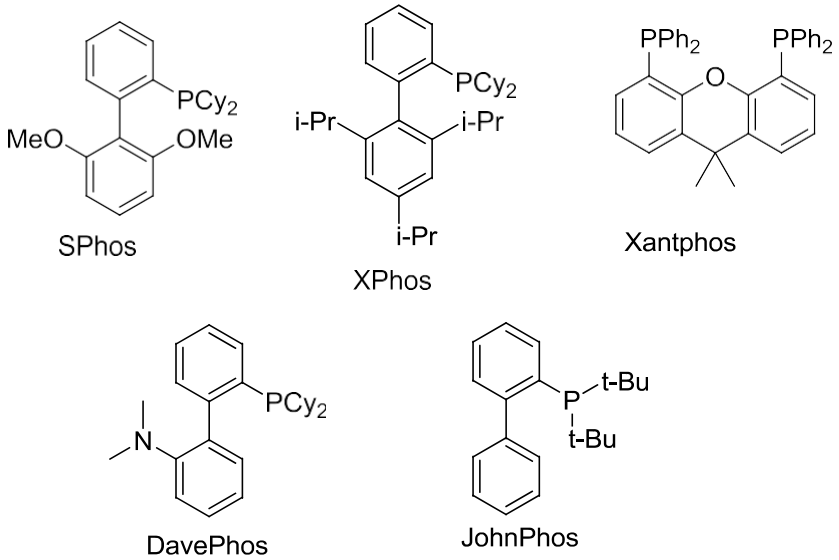
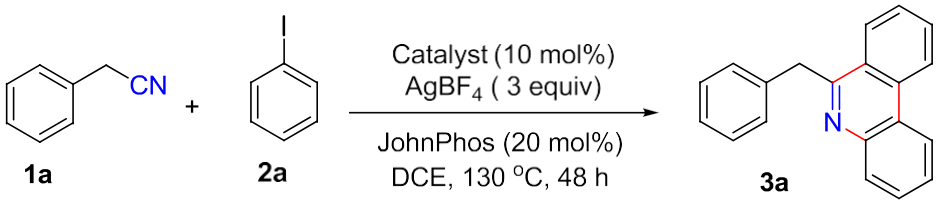


Table S4. Optimization by varying time and temperature[a]

S.No.	Time (h)	Temperature (^oC)	Yield[b] of 3a (%)
1	48	130	80
2	36	130	75
3	12	130	20
4	48	100	30

Table S5. Optimization by varying catalyst[a]



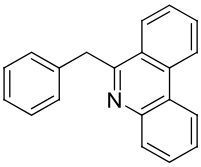
S. No.	Catalyst	Yield[b] of 3a (%)
1	$PdCl_2$	62
2	$PdBr_2$	58
3	$Pd(OCOCF_3)_2$	45
4	$Pd(PPh_3)_2Cl_2$	35
5	$Pd(CH_3CN)_4BF_4$	52
6	$Pd(OAc)_2$	80
7	$Pd(OAc)_2$	58[c]
8	$Pd(OAc)_2$	22[d]

[a]Reaction conditions: All reactions were performed with **1a** (0.2 mmol), **2a** (0.6 mmol), Catalyst (10 mol %), $AgBF_4$ (3.0 equiv), ligand (20 mol%), in 2.0 mL of DCE for 48 h at 130 °C. [b]Isolated yield of **3a**. [c]5 mol% of the metal catalyst was used. [d]Reaction was performed under oxygen atmosphere condition.

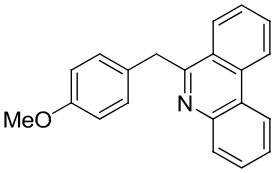
***General procedure for phenanthridines synthesis*:** To a clean oven-dried 15 mL pressure tube equipped with magnetic stir bar was sequentially added aryl nitriles (0.25mmol, 1 equiv.), $Pd(OAc)_2$(10 mol%, 5.6 mg), JohnPhos (0.05 mmol, 15.0 mg) in dry DCE (2.5 mL). The tube was carefully evacuated and backfilled with nitrogen for three cycles and subsequently aryl iodide (0.75 mmol, 3 equiv.) and silver tetrafluoroborate (0.75 mmol, 3.0 equiv, 145.5 mg) were added to the reaction mixture. The reaction mixture was placed in preheated oil bath of 130°C and vigorously stirred for 48 h. Upon completion as shown by TLC, the reaction mixture was cooled to room temperature and water was added to quench the reaction mixture. DCM (3 x15 mL) was used for extraction. Combined organic layers were passed through short pad of celite

and dried over Na_2SO_4. After evaporation of solvent, the crude reaction mixtures were purified by column chromatography using silica-gel (100-200 mess) with an eluent system ethyl acetate/hexanes (5:95) or DCM/hexanes (20:80) to afford the desired products.

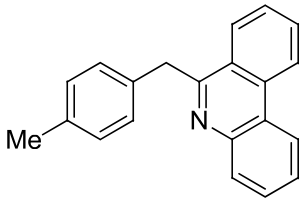
3. Characterization data for all products:



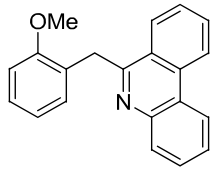
6-Benzyl-phenanthridine (3a):[1] Yellow solid (54 mg, 80%); Mp 100-102°C (Reported: 105-107 ^{o}C); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3073, 2925, 1448, 1248, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.22 (t, *J* = 8.0 Hz, 2H), 7.77 (q, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.27-7.23 (m, 2H), 7.19-7.16 (m, 1H), 4.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 143.5, 139.0, 133.3, 130.5, 129.7, 128.7, 128.5, 127.4, 127.1, 126.7, 126.3, 125.3, 123.9, 122.4, 121.9, 42.9.



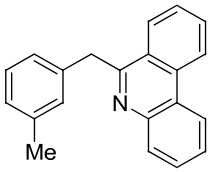
6-(4-Methoxy-benzyl)-phenanthridine (3b):[2] White solid (54 mg, 73%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 92-94 ^{o}C (Reported: 91-92 ^{o}C); IR(ATR): 2953, 1602, 1508, 1240, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.22-8.19 (m, 2H), 8.80-7.72 (m, 2H), 7.67-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.70 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 158.1, 143.7, 133.3, 131.2, 130.3, 129.8, 129.5, 127.3, 127.1, 126.6, 125.4, 123.9, 122.4, 121.9, 114.0, 55.2, 42.2.



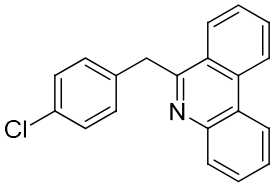
6-(4-Methyl-benzyl)-phenanthridine (3c):[2] White solid (55 mg, 78%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 68-70 ^oC (Reported: 69-70 ^oC); IR (ATR): 2920, 2860, 1513, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.61 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 7.79-7.73 (m, 2H), 7.67 – 7.63 (m, 1H), 7.60-7.56 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H). 4.73 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 143.7, 136.0, 135.8, 133.2, 130.3, 129.8, 129.2, 128.6, 128.4, 127.3, 127.0, 126.6, 125.3, 123.9, 122.3, 121.9, 42.6, 20.9.



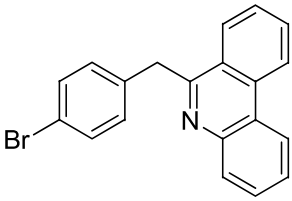
6-(2-Methoxy-benzyl)-phenanthridine (3d): White solid (40 mg, 53%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 105-107 ^oC; IR (ATR): 3066, 2923, 1456, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.63 (d, *J* = 8.1 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.20 (t, *J* = 8.8 Hz, 2H), 7.82 – 7.69 (m, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.94 (s, 2H), 6.72 (t, *J* = 7.1 Hz, 1H), 4.74 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 156.3, 133.1, 130.6, 129.6, 129.5, 128.7, 127.5, 127.4, 127.3, 126.6, 125.5, 123.9, 122.2, 121.9, 120.6, 110.3, 55.6, 35.6; HRMS (ESI-TOF) m/z Calcd for $C_{21}H_{18}NO$ [M + H]$^+$ 300.1383, found 300.1388.



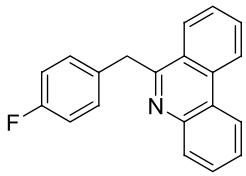
6-(3-Methyl-benzyl)-phenanthridine (3e):[2] Yellow sticky solid (46 mg, 65%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3066, 2923, 1483, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.21 (d, *J* = 8.2, 2H), 7.81 – 7.72 (m, 2H), 7.68-7.64 (m, 1H), 7.61 – 7.57 (m, 1H), 7.14-7.12 (m, 3H), 6.99 – 6.97 (m, 1H), 4.73 (s, 2H), 2.26 (s, 3H). δ = 160.2, 143.8, 139.0, 138.1, 133.3, 130.3, 129.9, 129.2, 128.6, 128.4, 127.3, 127.1, 127.0, 126.6, 125.6, 125.5, 123.9, 122.4, 121.9, 43.8, 21.4.



6-(4-Chloro-benzyl)-phenanthridine (3f) : White solid (46 mg, 60%); R_f (95:5 Hexanes/Ethyl acetate) = 0.4; Mp 135-137 ^oC; IR (ATR): 2926, 1483, 1086, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.82-7.74 (m, 2H), 7.67(t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.26-7.20 (m, 4H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 143.7, 137.6, 133.3, 132.1, 130.5, 129.9, 128.7, 128.6, 127.4, 126.8, 126.7, 125.2, 123.9, 122.5, 122.0, 42.3; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{15}ClN$ $[M+H]^+$ 304.0888, found 304.0892.

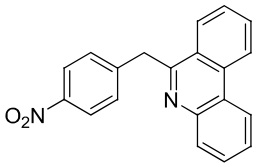


6-(4-Bromo-benzyl)-phenanthridine (3g): White solid (39 mg, 45%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 130-131 ^oC; IR (ATR) 2921, 1483, 1007, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.81-7.74 (m, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 143.6, 138.1, 133.3, 131.6, 130.5, 130.3, 129.8, 128.7, 127.4, 126.8, 126.7, 125.1, 123.9, 122.5, 122.0, 120.2, 42.4; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{15}BrN$ $[M + H]^+$ 348.0382, found 348.0392.

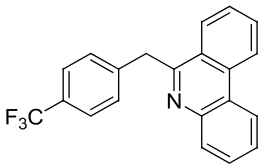


6-(4-Fluoro-benzyl)-phenanthridine (3h): White solid (45 mg, 63%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 115-117 ^oC; IR (ATR): 3060, 2923, 1500, 1206, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.82-7.74 (m, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.30- 7.27 (m, 2H), 6.93 (t, *J* = 8.0 Hz, 2H), 4.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (d, *J* = 243 Hz), 159.9, 143.4, 134.58 (d, *J* = 3.0 Hz), 133.34, 130.56, 129.9 (d, *J* = 8.0 Hz), 129.6, 128.8, 127.40,

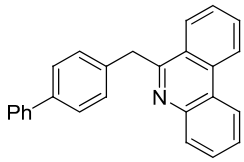
126.9, 126.8, 125.1, 123.9, 122.50, 121.97, 115.3 (d, *J* = 21.0 Hz), 41.9; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{15}FN$ $[M + H]^+$ 288.1183, found 288.1179.



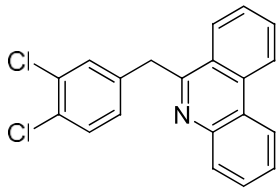
6-(4-Nitro-benzyl)-phenanthridine (3i): Yellow solid (51 mg, 65%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 158-160 ^oC; IR (ATR): 2829, 2850, 1505, 1336, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.09 (t, *J* = 7.6 Hz, 3H), 8.82 (t, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 12.0 Hz, 2H), 4.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 146.62, 146.60, 143.4, 133.4, 130.8, 129.7, 129.5, 128.9, 127.6, 127.1, 126.3, 125.0, 123.9, 123.6, 122.7, 122.0, 42.4; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{15}N_2O_2$ $[M + H]^+$ 315.1128, found 315.1133.



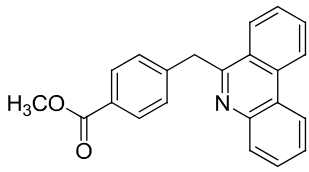
6-(4-Trifluoromethyl-benzyl)-phenanthridine (3j): White solid (51 mg, 61%); R_f (95:5 Hexanes/Ethyl acetate) = 0.4; Mp 120-122 ^oC; IR (ATR): 3070, 2923, 1323, 1110, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81-7.77 (m, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.52-7.45 (m, 4H), 4.82 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 143.5, 143.1, 133.3, 130.6, 129.8, 128.9, 128.8, 128.5, 127.5, 127.0, 126.6, 125.45 (q, *J* = 4.0 Hz), 125.1, 123.9, 122.8, 122.6, 122.0, 42.6; HRMS (ESI-TOF): m/z Calcd for $C_{21}H_{15}F_3N$ $[M + H]^+$ 338.1151, found 338.1162.



6-Biphenyl-4-ylmethyl-phenanthridine (3k): White solid (53 mg, 62%); R_f (8:2 Hexanes/DCM) = 0.5; Mp 159-161 ^oC; IR (ATR): 3066, 2930, 1483, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.24 (t, *J* = 7.6 Hz, 2H), 7.81-7.75 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61(d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.81 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 143.7, 140.8, 139.2, 138.2, 133.3, 130.4, 129.9, 128.9, 128.7, 127.4, 127.2, 127.1, 127.0, 126.9, 126.7, 125.4, 123.9, 122.4, 122.0, 42.7; HRMS (ESI-TOF): m/z Calcd for $C_{26}H_{20}N$ $[M + H]^+$ 346.1590, found 346.1597.

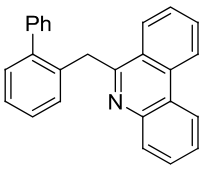


6-(3,4-Dichloro-benzyl)-phenanthridine (3l): White solid (55 mg, 64%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 86-88 ^oC; IR (ATR): 2923, 1466, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.69-7.64 (m, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 143.3, 130.1, 133.4, 132.5, 130.8, 130.5, 130.4, 129.7, 128.9, 128.0, 127.6, 127.1, 126.6, 125.0, 123.9, 122.7, 122.0, 41.7; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{14}Cl_2N$ $[M + H]^+$ 338.0498, found 338.0505.

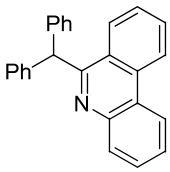


4-Phenanthridin-6-ylmethyl-benzoic acid methyl ester (3m): White solid (51 mg, 61%); R_f (95:5 Hexanes/Ethyl acetate) = 0.4; Mp 135-137 ^oC; IR(ATR): 2949, 1711, 1278, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.6 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.92(d, *J* = 8.0 Hz, 2H), 7.78(q, *J* = 8.0 Hz, 2H), 7.67

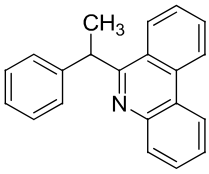
(t, J = 8.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 4.80 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 159.2, 144.5, 143.6, 133.3, 130.5, 129.8, 128.8, 128.6, 127.4, 126.8, 126.7. 125.2, 123.9, 122.5, 122.0, 52.0, 43.0; HRMS (ESI-TOF): m/z Calcd for $C_{22}H_{18}NO_2$[M + H]$^+$ 328.1332, found 328.1331.



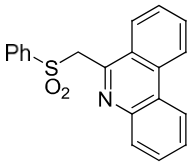
6-(Biphenyl-2-ylmethyl)-phenanthridine (3n): White solid (50 mg, 58%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 105-107 ^{o}C; IR (ATR): 3056, 2921, 1480, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60-8.54 (m, 2H), 8.18 (d, J = 8.0 Hz, 1H), 7.76-7.63 (m, 4H), 7.56-7.49 (m, 4H), 7.47-7.42 (m, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.13-7.09 (m, 2H), 4.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 143.7, 141.4, 136.6, 133.1, 130.0, 129.9, 129.5, 129.0, 128.6, 128.4, 127.5, 127.2, 127.1, 127.0, 126.6, 126.3, 125.2, 123.8, 122.2, 121.9, 40.6; HRMS (ESI-TOF): m/z Calcd for $C_{26}H_{20}N$ [M + H]$^+$ 346.1590, found 346.1598.



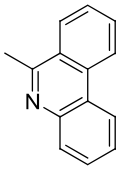
6-Benzhydryl-phenanthridine (3o): White solid (58 mg, 68%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp114-116 ^{o}C; IR(ATR): 3030, 2926, 1490, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, J = 8.0 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.69-7.58 (m, 3H), 7.6-7.29 (m, 8H), 7.24 (d, J = 8.0 Hz, 2H), 6.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 143.5, 142.6, 133.3, 130.6, 130.0, 129.7, 128.4, 128.2, 127.3, 126.7, 126.3, 125.5, 123.5, 122.5, 121.7, 55.6; HRMS (ESI-TOF): m/z Calcd for $C_{26}H_{20}N$ [M + H]$^+$ 346.1590, found 346.1599.



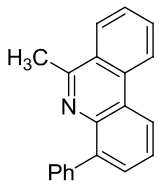
6-(1-Phenyl-ethyl)-phenanthridine (3p): Yellow sticky solid (46 mg, 65%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR(ATR): 2973, 2926, 1450, 1366, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.28-8.22 (m, 2H), 7.78-7.71 (m, 2H), 7.67– 7.63 (m, 1H), 7.58-7.53 (m, 1H), 7.38-7.36 (m, 2H), 7.27 – 7.23 (m, 2H), 7.18 – 7.13 (m, 1H), 5.12 (q, *J* = 6.9 Hz, 1H), 1.94 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 145.8, 143.6, 133.1, 130.3, 129.8, 128.5, 128.4, 127.6, 127.1, 126.5, 126.4, 126.2, 125.2, 123.7, 122.4, 121.8, 44.0, 22.0; HRMS (ESI-TOF): m/z Calcd for $C_{21}H_{18}N$ $[M + H]^+$ 284.1434, found 284.1441.



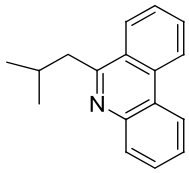
6-Benzenesulfonylmethyl-phenanthridine (3q):[3] Yellow solid (42 mg, 50%); R_f (8:2 Hexanes/Ethyl acetate) = 0.2; Mp 180-182 ^oC (Reported: 188-189 ^oC); IR (ATR): 2920, 2853, 1730, 1306, 1146, 740 (ATR) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.6 Hz, 1H), 8.55 (s, 1H), 8.36 (d, *J* = 7.6 Hz, 1H), 7.88 (s, 1H), 7.81 (s, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 7.68 (s, 4H), 7.56 (s, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 5.19 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 143.1, 138.3, 133.7, 133.2, 131.1, 129.8, 128.82, 128.77, 128.69, 127.7, 127.0, 125.5, 124.0, 122.3, 122.0, 62.4.



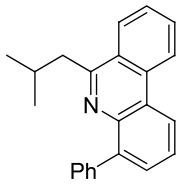
6-Methyl-phenanthridine (3r):[1] Yellow oil (22 mg, 45%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR(ATR): 3067, 2924, 1582, 1449, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 7.9 Hz, 1H), 8.57 (d, *J* = 7.7 Hz, 1H), 8.27 (d, *J* = 7.6 Hz, 2H), 7.91 (t, *J* = 7.1 Hz, 1H), 7.75 (t, *J* = 6.9 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 1H), 3.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 132.9, 131.3, 129.1, 129.1, 128.0, 127.7, 127.5, 126.9, 125.7, 123.8, 123.1, 122.5, 122.0, 29.7.



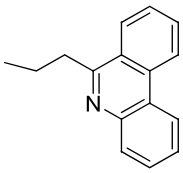
6-Methyl-4-phenyl-phenanthridine (3rr): Yellow oil (10 mg, 15%); R_f (95:5 Hexanes/Ethyl acetate) = 0.6; IR(ATR): 3059, 2922, 1573, 1442, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.46 (s, 3H), 7.39 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 143.9, 134.1, 131.1, 129.3, 128.9, 127.6, 124.4, 123.5, 122.3, 121.8, 22.6; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{16}N$ $[M + H]^+$ 270.1277, found 270.1281.



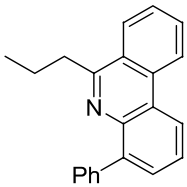
6-Isobutyl-phenanthridine (3s): Yellow oil (34 mg, 58%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3070, 2956, 1579, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.1 Hz, 1H), 8.56 (d, *J* = 7.7 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.74-7.67 (m, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 2H), 2.39 (m, 1H), 1.05 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 143.7, 132.9, 130.2, 129.6, 128.5, 127.1, 126.5, 126.2, 125.7, 123.6, 122.4, 121.9, 44.9, 29.2, 22.9; HRMS (ESI-TOF): m/z Calcd for $C_{17}H_{18}N$ $[M + H]^+$ 236.1434, found 236.1439.



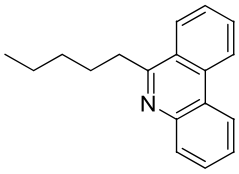
6-Isobutyl-4-phenyl-phenanthridine (3ss): White sticky solid (14 mg, 18%);R_f (95:5 Hexanes/Ethyl acetate) = 0.6; IR (ATR): 3064, 2953, 1570, 1448, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 6.9 Hz, 1H), 7.45 (s, 3H), 7.41 (s, 2H), 2.54 (d, *J* = 7.0 Hz, 2H), 1.81-1.65 (m, 1H), 0.44 (d, *J* = 6.4 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 143.7, 141.9, 134.3, 131.2, 129.4, 129.2, 128.9, 128.6, 128.3, 127.4, 126.2, 123.8, 123.3, 122.2, 121.7, 48.3, 28.8, 22.2; HRMS (ESI-TOF): m/z Calcd for $C_{23}H_{22}N$ $[M + H]^+$ 312.1747, found 312.1754.



6-Propyl-phenanthridine (3t):[1] Sticky solid (34 mg, 61%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR(ATR): 3073, 2960, 1580, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 3.35 (t, *J* = 7.6 Hz, 2H), 1.97 (dd, *J* = 15.2, 7.5 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 143.7, 132.9, 130.2, 129.5, 128.5, 127.2, 126.3, 126.2, 125.2, 123.6, 122.4, 121.9, 38.3, 22.9, 14.4.

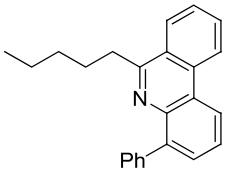


4-Phenyl-6-propyl-phenanthridine (3tt): Yellow sticky solid (15 mg, 20%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR(ATR): 3061, 2869, 1448, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 8.0 Hz, 1H), 8.58 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.45 (s, 3H), 7.40 (s, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.43 (dd, *J* = 14.9, 7.2 Hz, 2H), 0.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 143.9, 141.9, 134.4, 131.1, 129.11, 129.06, 128.9, 128.6, 128.2, 127.5, 126.2, 123.7, 123.3, 122.2, 121.8, 41.7, 23.1, 13.8; HRMS (ESI-TOF): m/z Calcd for $C_{22}H_{20}N$ $[M + H]^+$ 298.1590, found 298.1598.

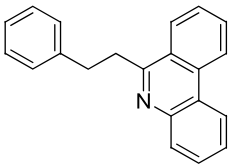


6-Pentyl-phenanthridine (3u):[4] Yellow oil (32 mg, 52%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR(ATR): 3070,. 2926, 1580, 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.0 Hz, 1H), 8.54 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 7.1 Hz, 1H), 7.70 (q, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 3.37 (t, *J* = 8.0 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.55 – 1.49 (m, 2H), 1.47- 1.40 (m, 2H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5, 143.8,

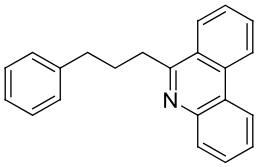
132.9, 130.2, 129.6, 128.5, 127.2, 126.3, 126.2, 125.2, 123.6, 122.5, 121.9, 36.5, 32.2, 29.4, 22.6, 14.1.



6-Pentyl-4-phenyl-phenanthridine (3uu): Yellow sticky solid (16 mg, 20%); R_f (95:5 = Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3061, 2926, 1448, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, *J* = 7.3 Hz, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 7.1 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (q, *J* = 3.0 Hz, 3H), 7.40 (dd, *J* = 6.9, 2.8 Hz, 2H), 2.62 – 2.56 (m, 2H), 1.46 – 1.36 (m, 2H), 1.09 (dd, *J* = 14.7, 7.3 Hz, 2H), 0.86 (dd, *J* = 15.2, 7.9 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.0, 143.9, 143.4, 141.9, 134.4, 131.2, 129.1, 129.1, 128.9, 128.6, 128.2, 127.5, 126.2, 123.7, 123.3, 122.2, 121.8, 39.9, 31.7, 29.4, 22.40, 13.9; HRMS (ESI-TOF): m/z Calcd for $C_{24}H_{24}N$ $[M + H]^+$326.1903, found 326.1907.

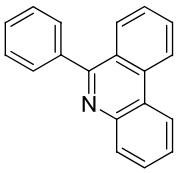


6-Phenethyl-phenanthridine (3v):[5] Sticky solid (48 mg, 68%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3066, 2923, 1580, 1366, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.1 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.40 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 7.3 Hz, 1H), 7.81-7.69 (m, 3H), 7.40 – 7.30 (m, 4H), 7.23 (t, *J* = 8.1 Hz, 1H), 3.82 (s, 2H), 3.33-3.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 142.0, 132.9, 130.4, 129.6, 128.9, 128.6, 128.50, 128.48, 128.2, 127.3, 127.1, 126.5, 126.1, 126.0, 125.2, 123.7, 122.5, 121.9, 37.8, 35.0.

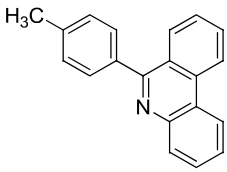


6-(3-Phenyl-propyl)-phenanthridine (3w): Yellow solid (52 mg, 70%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 70-75 ^oC; IR(ATR): 3066, 2930, 1580, 1453, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 8.1 Hz,

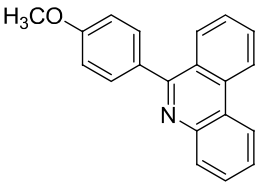
1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.16 (t, *J* = 8.7 Hz, 2H), 7.84 (t, *J* = 7.2 Hz, 1H), 7.75 (t, *J* = 7.0 Hz, 1H), 7.66 (dd, *J* = 15.8, 8.1 Hz, 2H), 7.36 - 7.31 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.44 (t, *J* = 7.6 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.36 – 2.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 143.7, 142.1, 132.9, 130.2, 129.6, 128.5, 128.3, 127.2, 126.3, 126.1, 125.8, 125.2, 123.6, 122.4, 121.9, 36.0, 35.6, 30.8; HRMS (ESI-TOF): m/z Calcd for $C_{22}H_{20}N$ $[M + H]^+$ 298.1590, found 298.1595.



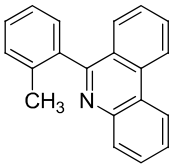
6-Phenyl-phenanthridine (5a):[1] Yellow solid (45 mg, 72%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 102-104 ^oC (Reported: 103-105 ^oC); IR (ATR): 2920, 1563, 1356, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.79-7.68 (m, 4H), 7.63-7.53 (m ,4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 143.7, 139.7, 133.4, 130.5, 129.7, 128.9, 128.8, 128.7, 128.4, 127.1, 126.9, 125.2, 123.7, 122.2, 121.9.



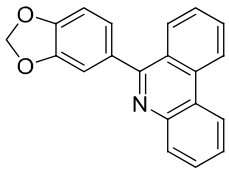
6-(*p*-Tolyl)-phenanthridine (5b):[6] Yellow solid (50 mg, 75%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 103-105^oC; IR (ATR): 2855, 2922, 1358, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.70-7.59 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 143.8, 138.5, 136.9, 133.4, 130.4, 130.3, 129.6, 129.1, 128.9, 128.7, 127.0, 126.7, 125.3, 123.6, 122.1, 121.9, 21.4.



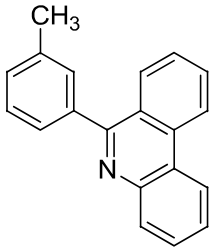
6-(4-Methoxy-phenyl)-phenanthridine (5c):[6] White solid (44 mg, 62%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 125-127 ^oC; IR(ATR): 3066, 2933, 1606, 1243, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 7.77-7.60 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 160.1, 143.9, 133.5, 132.3, 131.2, 130.4, 130.2, 128.9, 128.8, 127.0, 126.7, 125.3, 123.6, 122.2, 121.9, 113. 9, 55.4.



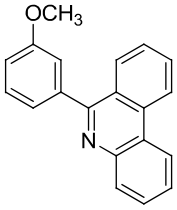
6-(*o*-Tolyl)-phenanthridine (5d):[7] Yellow sticky solid (47 mg, 70%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3063, 2923, 1566, 1356, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 8.1 Hz, 1H), 8.65 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.0 Hz, 1H), 7.78 (t, *J* = 6.9 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.36 (m, 4H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 143.8, 139.2, 136.4, 133.0, 130.6, 130.3, 130.3, 129.3, 128.8, 128.6, 128.5, 127.3, 126.9, 125.8, 123.8, 122.1, 122.0, 19.8.



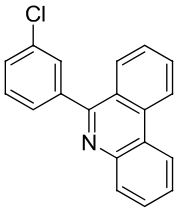
6-Benzo[1,3]dioxol-5-yl-phenanthridine (5e): Yellow sticky solid (49 mg, 65%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; IR (ATR): 3070, 2893, 1736, 1490, 1240, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 7.7 Hz, 1H), 8.59 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 7.2 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.26-7.22 (m, 2H), 7.0 (d, *J* = 8.0 Hz, 1H) 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 148.2, 147.7, 143.5, 133.7, 133.5, 130.5, 130.2, 128.79, 128.78, 127.1, 126.8, 125.2, 123.9, 123.6, 122.2, 121.9, 110.4, 108.3, 101.3; HRMS (ESI-TOF): m/z Calcd for $C_{20}H_{13}O_2N$ $[M + H]^+$ 300.1019, found 300.0997.



6-(*m*-Tolyl)-phenanthridine (5f):[6] White solid (46 mg, 68%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 92-94 ^oC; IR 3063, 2920, 1566, 1360, 723 (ATR) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 11.1 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 143.8, 139.7, 138.2, 133.4, 130.5, 130.3, 130.2, 129.4, 129.0, 128.8, 128.1, 127.0, 126.8, 125.3, 123.7, 122.1, 121.9.

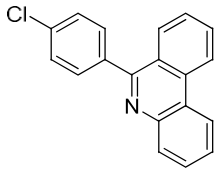


6-(3-Methoxy-phenyl)-phenanthridine (5g):[1] White solid (51 mg, 72%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 112-114 ^oC (Reported: 115-116 ^oC); IR (ATR): 3053, 2996, 1586, 1253, 1033, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.1 Hz, 1H), 8.62 (d, *J* = 7.7 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.86 (t, *J* = 7.2 Hz, 1H), 7.77 (t, *J* = 6.9 Hz, 1H), 7.69 (t, *J* = 7.0 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 6.5 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 159.6, 143.7, 141.1, 133.4, 130.6, 130.3, 129.4, 128.9, 128.8, 127.1, 126.9, 125.2, 123.8, 122.2, 122.1, 121.9, 115.0, 114.7, 55.4.

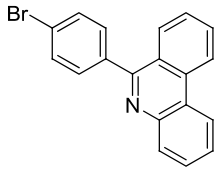


6-(3-Chloro-phenyl)-phenanthridine (5h):[8] White solid (46 mg, 63%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 131-133 ^oC (Reported: 122-123 ^oC); IR(ATR): 2930, 1566, 1356, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, *J* = 8.0 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H),

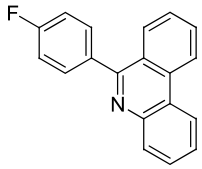
7.87 (t, *J* = 7.2 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.51-7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 143.6, 141.5, 134.5, 133.4, 130.7, 130.3, 129.8, 129.6, 129.0, 128.8, 128.4, 127.9, 127.3, 127.2, 124.9, 123.8, 122.3, 122.0.



6-(4-Chloro-phenyl)-phenanthridine (5i):[6] White solid (42 mg, 58%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 145-147 ^{o}C; IR(ATR): 3046, 2923, 1483, 1086, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 8.0 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.71-7.69 (m, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.9, 143.7, 138.2, 134.9, 133.5, 131.1, 130.7, 130.3, 128.9, 128.6, 128.4, 127.2, 127.1, 124.9, 123.7, 122.3, 121.9.

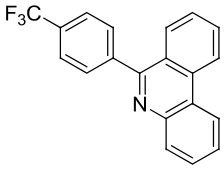


6-(4-Bromo-phenyl)-phenanthridine (5j):[1] White solid (55 mg, 66%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 163-165 ^{o}C (Reported: 152-154 ^{o}C); IR(ATR): 2920, 1481, 821, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.71-7.69 (m, 3H), 7.64-7.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 143.7, 138.7, 133.5, 131.6, 131.4, 130.7, 130.4, 129.0, 128.5, 127.3, 127.2, 125.0, 123.8, 123.1,122.3, 122.0.

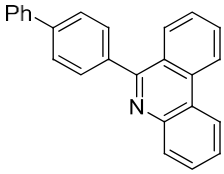


6-(4-Fluoro-phenyl)-phenanthridine (5k):[9] White solid (45 mg, 66%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 122-124 ^{o}C; IR(ATR): 3066, 2926, 1596, 1216, 826 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91 (d, *J* = 8.0 Hz, 1H), 8.82 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.07 (t, *J* = 8.0 Hz, 1H), 7.99-7.88 (m, 4H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100

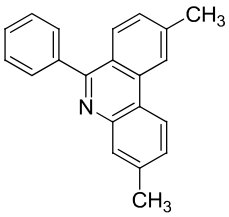
MHz, $CDCl_3$); δ = 163.1 (d, *J* = 247 Hz), 160.1, 143.7, 135.8 (d, *J* = 4.0 Hz), 133.5, 131.6 (d, *J* = 8.0 Hz), 130.6, 130.3, 128.9, 128.6, 127.2, 127.0, 125.1, 123.7, 122.3, 121.9, 115.4 (d, *J* = 21.0 Hz).



6-(4-Trifluoromethyl-phenyl)-phenanthridine (5l):[10] White solid (60 mg, 75%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 162-164 ^oC (Reported: 171 ^oC); IR(ATR): 3066, 1316, 1106, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.96 (d, *J* = 12.0 Hz, 1H), 8.88 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.15-8.10 (m, 5H), 8.03 (t, *J* = 7.6 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 159.7, 143.6, 143.3, 133.4, 130.8, 130.4, 130.1, 129.0, 128.6, 127.3, 125.4 (q, *J* = 4.0 Hz), 124.8, 123.8, 122.4, 122.0.

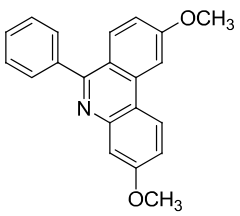


6-Biphenyl-4-yl-phenanthridine (5m):[11] White solid (51 mg, 62%); R_f (8:2 Hexanes/DCM) = 0.5; Mp 190-192 ^oC (Reported: 200-201 ^oC); IR(ATR): 2920, 1482, 692, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.89-7.77 (m, 6H), 7.72 (d, *J* = 8.0 Hz, 3H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 143.8, 141.6, 140.8, 138.7, 133.5, 130.5, 130.3, 130.2, 128.84, 128.82, 127.5, 127.20, 127.18, 127.1, 126.9, 125.2, 123.7, 122.2, 121.9.

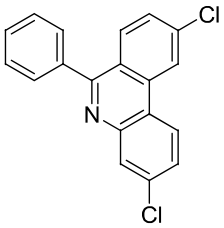


3,9-Dimethyl-6-phenyl-phenanthridine (5n): White solid (52 mg, 73%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 112-114 ^oC; IR(ATR): 2963, 1256, 1020, 790 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.0 Hz, 1H), 8.43 (s,1H), 8.04 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.56-7.48 (m, 4H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.64 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz,

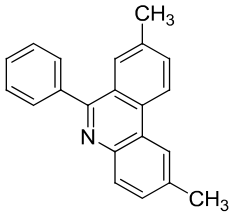
$CDCl_3$): δ = 161.0, 144.1, 140.8, 140.0, 138.8, 129.7, 128.5, 128.4, 128.3, 123.0, 121.7, 121.6, 121.2, 22.2, 21.5; HRMS (ESI-TOF): m/z Calcd for $C_{21}H_{18}N$ [M + H]$^+$ 284.1434, found 284.1433.



3,9-Dimethoxy-6-phenyl-phenanthridine (5o): White solid (47 mg, 60%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 85-87 ^oC; IR (ATR): 2922, 1611, 1374, 966 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 9.2 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.70 (d, *J* = 6.4 Hz, 2H), 7.62 (s, 1H), 7.54 (q, *J* = 7.2 Hz, 3H), 7.30-7.26 (m, 1H), 7.14-7.12 (m, 1H), 4.0 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 161.2, 160.3, 145.8, 140.0, 135.6, 130.9, 129.6, 128.5, 128.4, 123.2, 119.4, 117.7, 116.6, 116.4, 109.8, 102.1, 55.6. 55.5; HRMS (ESI-TOF): m/z Calcd for $C_{21}H_{18}NO_2$ [M + H]$^+$ 316.1332, found 316.1329.

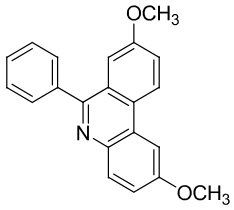


3,9-Dichloro-6-phenyl-phenanthridine (5p): White solid (26 mg, 32%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 175-177 ^oC; IR (ATR): 3053, 1599, 1077, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.57-7.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.9, 144.9, 139.0, 137.6, 135.3, 134.9, 130.7, 129.6, 129.2, 128.6, 128.0, 127.8, 123.41, 123.36, 121.9, 121.2; HRMS (ESI-TOF): m/z Calcd for $C_{19}H_{12}Cl_2N$ [M + H]$^+$ 324.0341, found 324.0343.

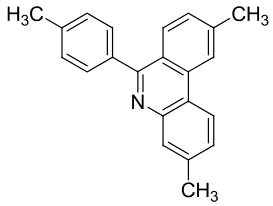


2,8-Dimethyl-6-phenyl-phenanthridine (5q):[12] White solid (45 mg, 63%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 178-180 ^oC; IR(ATR) 2913, 1360, 823, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 8.0 Hz, 1H), 8.36 (s. 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.73 (d, *J* = 6.4 Hz, 2H),

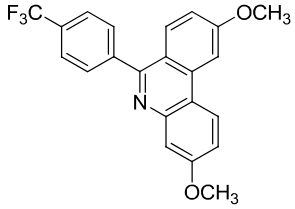
7.66 (d, J = 8.0 Hz, 1H), 7.57-7.54 (m, 4H), 2.64 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 141.8, 140.0, 136.9, 136.7, 132.0, 131.0, 130.1, 129.9, 128.5, 128.4, 128.1, 125.4, 123.6, 122.0, 121.3, 22.0, 21.7.



2,8-Dimethoxy-6-phenyl-phenanthridine (5r): White solid (39 mg, 50%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 89-91 ^{o}C; IR (ATR): 2953, 2833, 1606, 1210, 826 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.86 (s. 1H), 7.73 (d, J = 6.4 Hz, 2H), 7.57-7.45 (m, 5H), 7.34-7.32 (m, 1H), 4.03 (s, 3H), 4.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 158.48, 157.9, 140.0, 138.4, 131.7, 129.6, 128.5, 128.47, 127.3, 126.7, 124.9, 123.9, 120.6, 117.8, 108.8, 102.3, 55.6, 55.4; HRMS (ESI-TOF): m/z Calcd for $C_{21}H_{18}NO_2$ [M + H]$^+$ 316.1332, found 316.1340.

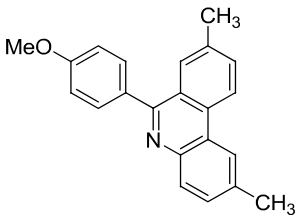


3,9-Dimethyl-6-p-tolyl-phenanthridine (5s):[13] White solid (52 mg, 70%); R_f (95:5 Hexanes/Ethyl acetate) = 0.5; Mp 88-90 ^{o}C; IR(ATR): 2919, 1616, 1359, 778 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 8.4 Hz, 1H), 8.42 (s, 1H), 8.02 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.48 (dd, J = 8.3, 1.6 Hz, 1H), 7.40 – 7.35 (m, 3H), 2.64 (s, 3H), 2.59 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (10 MHz, $CDCl_3$): δ = 161.1, 144.1, 140.7, 138.7, 138.4, 137.2, 133.6, 129.8, 129.6, 129.0, 128.8, 128.3, 123.1, 121.7, 121.6, 121.2, 22.2, 21.5, 21.4.

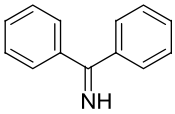


3,9-Dimethoxy-6-(4-trifluoromethyl-phenyl)-phenanthridine (5t): White solid (65 mg, 68%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 138-140 ^{o}C; IR (ATR): 2919, 1613, 1314, 1103 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 8.3 Hz, 1H), 7.89 – 7.78 (m, 6H), 7.61 (s, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 8.7 Hz, 1H), 4.06 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$): δ = 161.5, 160.4, 159.6, 145.7, 143.6, 135.9, 130.6 (q, *J* = 32 Hz), 130.0, 124.2 (q, *J* = 271 Hz), 125.4 (q, *J* = 4.0 Hz), 123.2, 119.0, 118.1, 117.7, 116.8, 109.8, 102.2, 55.6, 55.5; HRMS (ESI-TOF): m/z Calcd for $C_{22}H_{17}F_3NO_2$ $[M + H]^+$ 384.1206, found384.1200.



6-(4-Methoxy-phenyl)-2,9-dimethyl-phenanthridine (5u): White solid (43 mg, 55%); R_f (95:5 Hexanes/Ethyl acetate) = 0.3; Mp 134-136 ^oC; IR (ATR): 2919, 1607, 1245, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 7.6 Hz, 1H), 8.34 (s, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.90 (s, 1H), 7.70-7.65 (m, 3H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 6.5 Hz, 2H), 3.92 (s, 3H), 2.63 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 159.7, 141.9, 136.8, 136.5, 132.6, 132.0, 131.1, 130.0, 129.9, 128.2, 125.5, 123.5, 122.1, 121.3, 113.8, 55.4, 22.0, 21.7; HRMS (ESI-TOF): m/z Calcd for $C_{22}H_{20}NO$ $[M + H]^+$ 314.1539, found 314.1538.

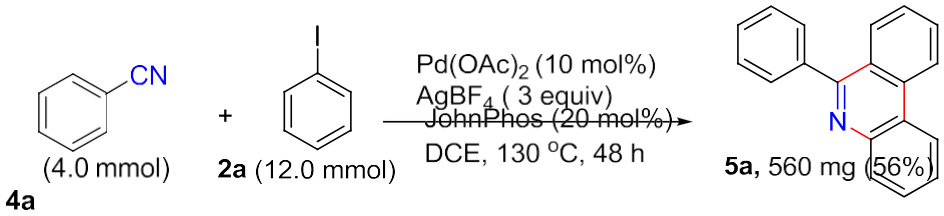


Benzhydrylideneamine (6): ^1H NMR (400 MHz, $CDCl_3$): δ = 9.70 (brs, 1H), 9.57-9.55 (m, 4H), 7.47-7.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 139.3, 130.3, 128.4, 128.3.

5. Procedure for preparative scale synthesis

To a clean oven-dried 120 mL pressure tube equipped with magnetic stir bar was sequentially added aryl nitrile (4.0 mmol, 1 equiv), $Pd(OAc)_2$ (10 mol%, 89.6 mg), JohnPhos (0.8mmol, 238.0 mg). Then iodobenzene (12.0 mmol, 1.3 mL) and silvertetrafluoroborate (12.0 mmol, 2.3 g) in dry DCE (40 mL) under nitrogen atmosphere was added. The reaction mixture was placed in preheated oil bath of 130^oC and vigorously stirred for 48 h.The reaction was monitored by TLC, after completion, the reaction mixture was cooled to room temperature and water was added to quench the reaction mixture. DCM (3 x 100 mL) was used for extraction. Combined organic

layers were passed through short pad of celite and dried over Na_2SO_4. After evaporation of solvent, the crude mixture was purified by column chromatography on silica gel using ethyl acetate/hexanes (5:95) as eluent to give the yellow solid.



6. X-Ray Crystallographic Information for product 5c (CCDC 1817112)

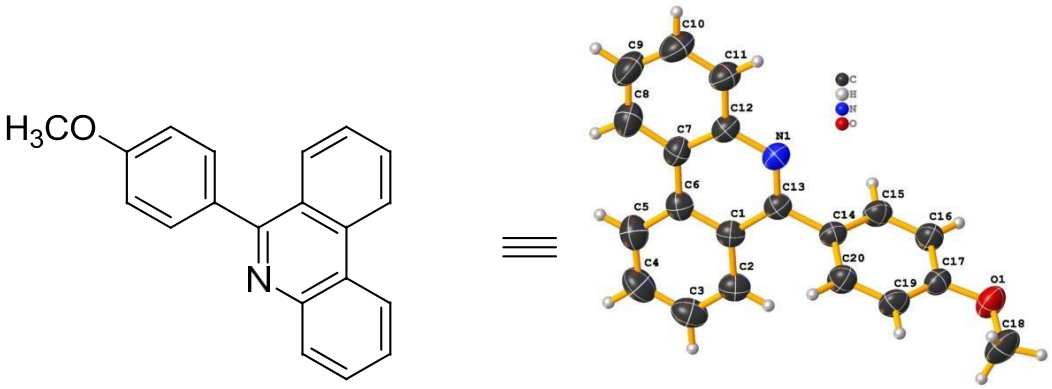


Figure S1. Ortep diagram of 5c with 50% ellipsoidal probability.

Chemical formula	$C_{20}H_{15}NO$
Formula weight	285.33 g/mol
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal size	0.100 x 0.100 x 0.200 mm
Crystal system	monoclinic
Space group	P 1 21/n 1

Unit cell dimensions	a = 13.107(3) Å	α = 90°
	b = 5.8099(12) Å	β = 102.575(7)°
	c = 19.648(4) Å	γ = 90°
Volume	1460.3(5) $Å^3$	
Z	4	
Density (calculated)	1.298 g/cm^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	600	
Theta range for data collection	3.19 to 27.52°	
Index ranges	-16<=h<=15, -7<=k<=7, -25<=l<=25	
Reflections collected	29074	
Independent reflections	2948 [R(int) = 0.0655]	
Max. and min. transmission	0.9920 and 0.9840	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	2948 / 0 / 201	
Goodness-of-fit on F2	0.996	
Final R indices	1629 data; I>2σ(I)	R1 = 0.0543, wR2 = 0.1112
	all data	R1 = 0.1355, wR2 = 0.1396
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0597P)^2+0.3631P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0107(18)	
Largest diff. peak and hole	0.150 and -0.137 $eÅ^{-3}$	
R.M.S. deviation from mean	0.034 $eÅ^{-3}$	

8. References:

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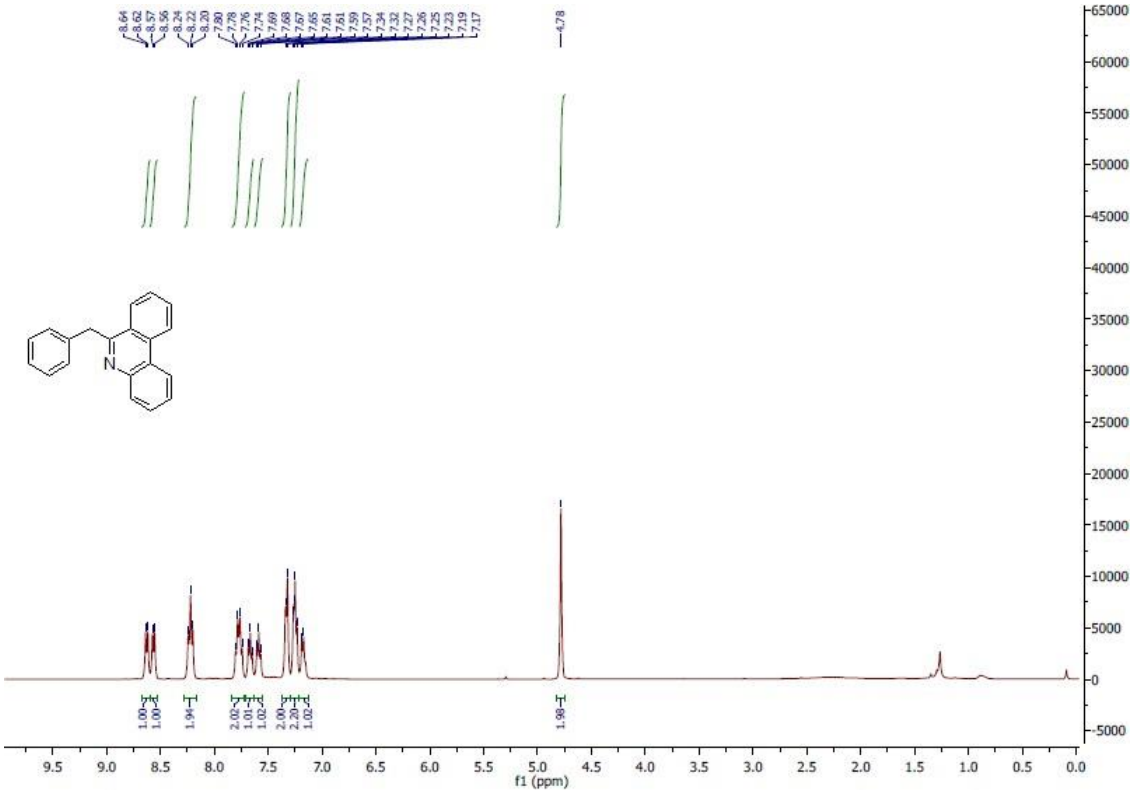
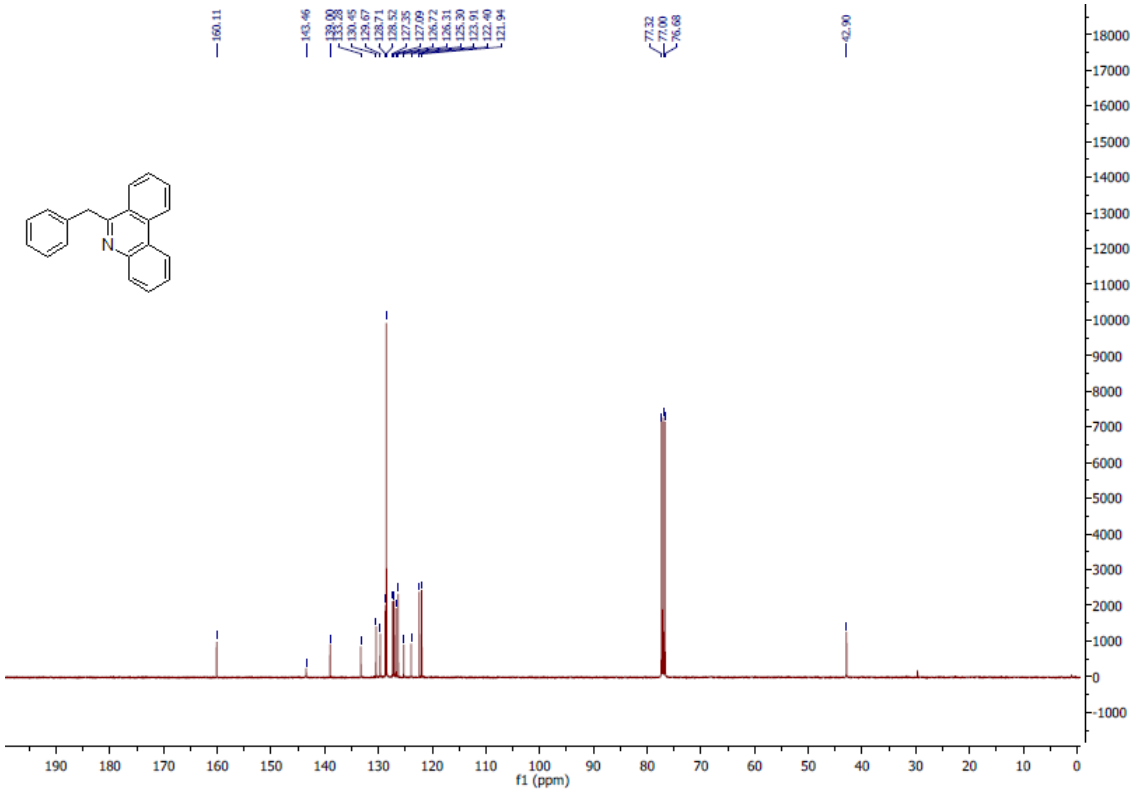
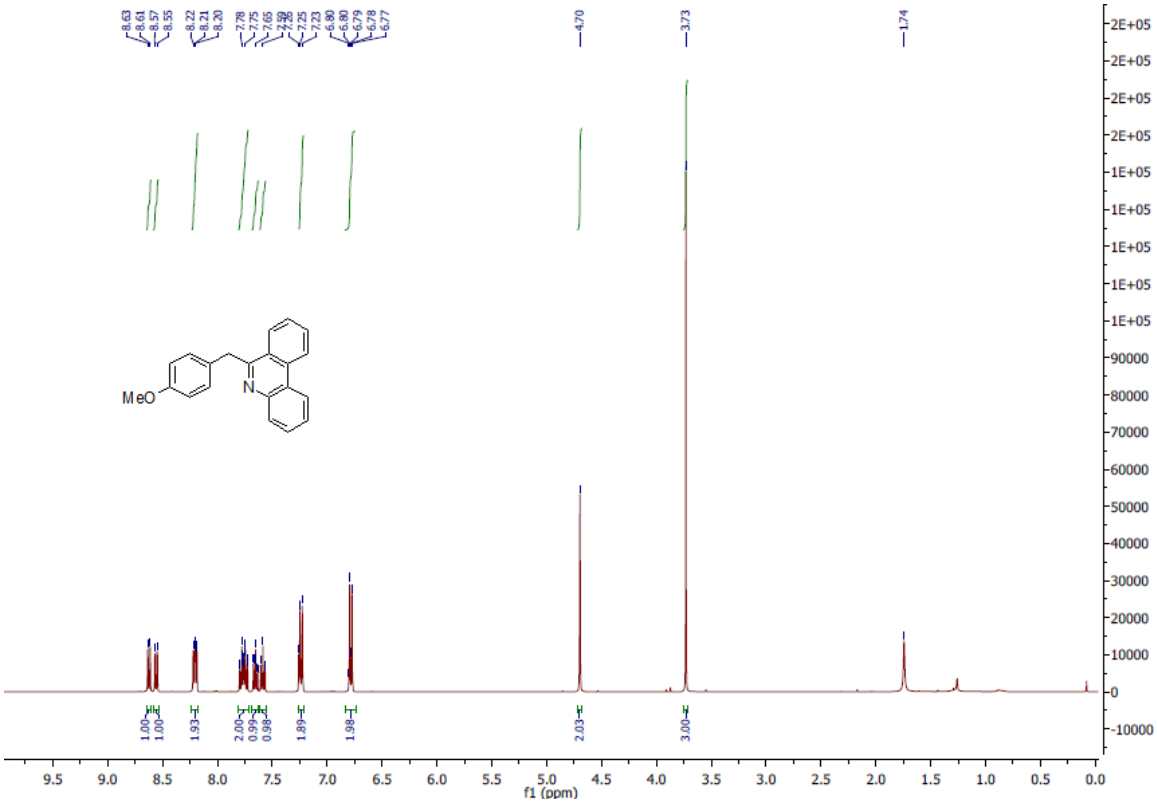
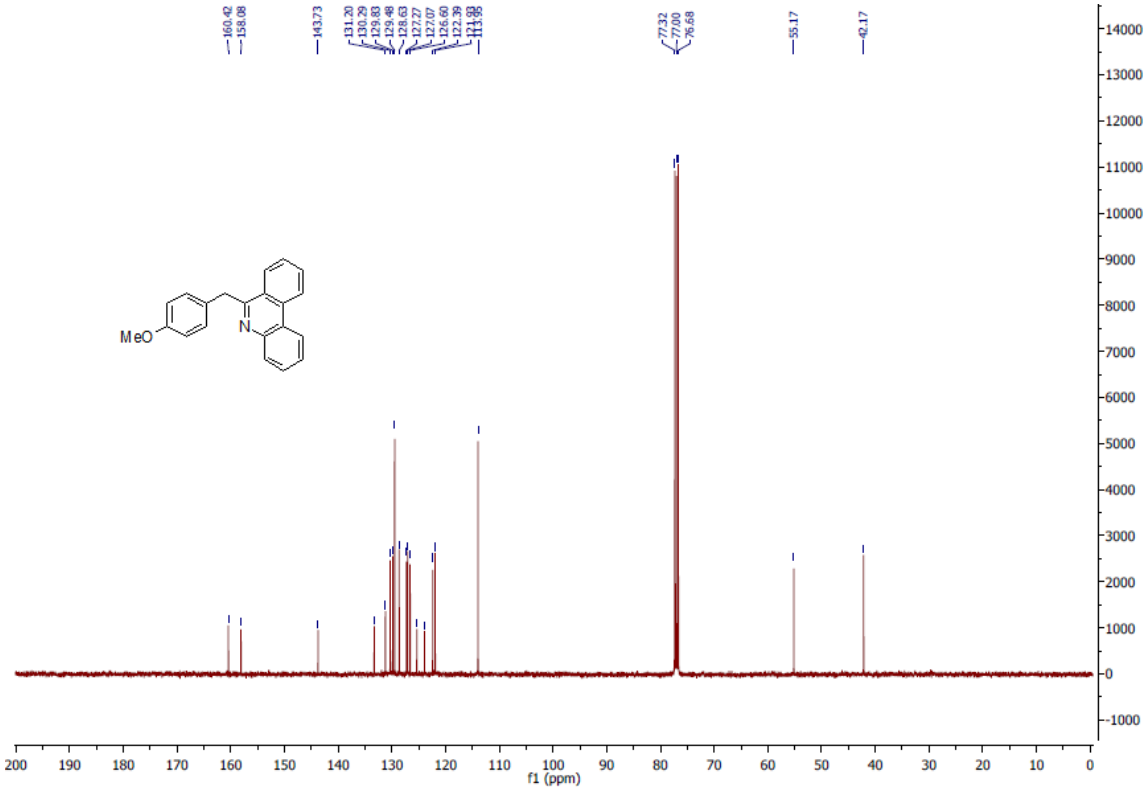
9.^{1}H and ^{13}{C} spectra of **3a**



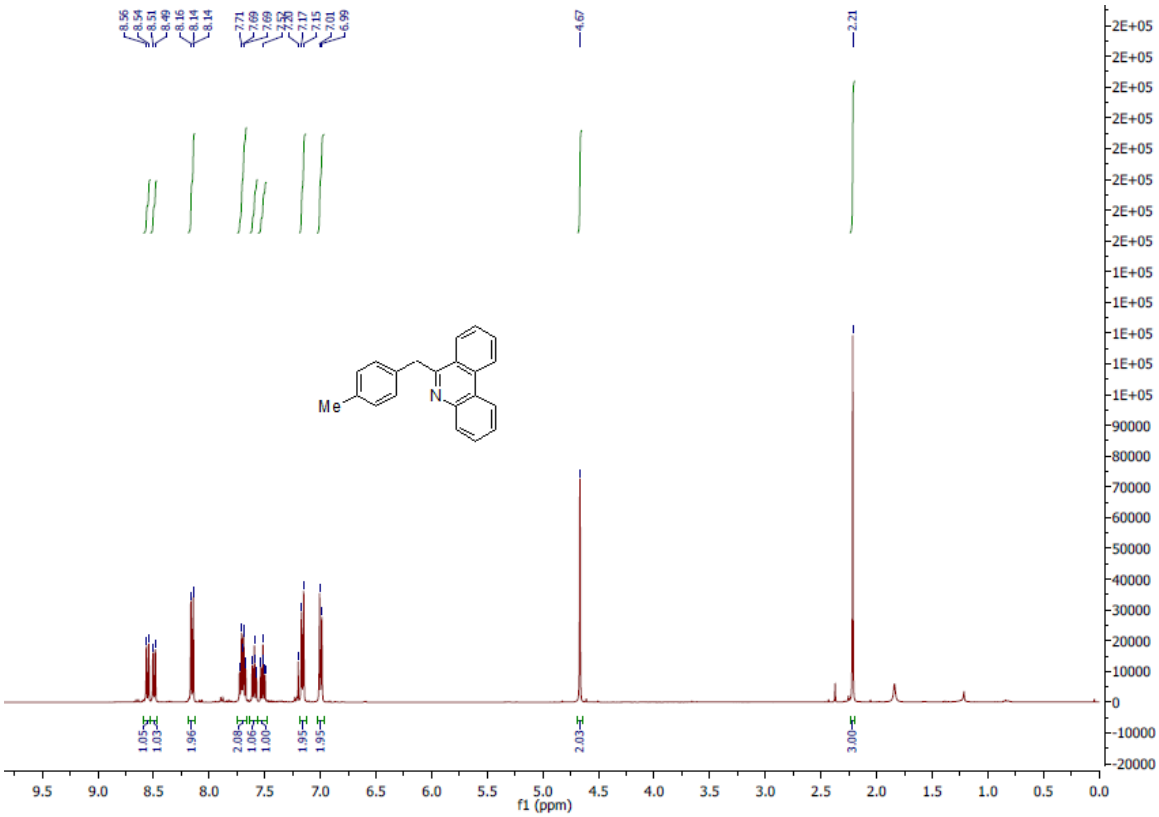


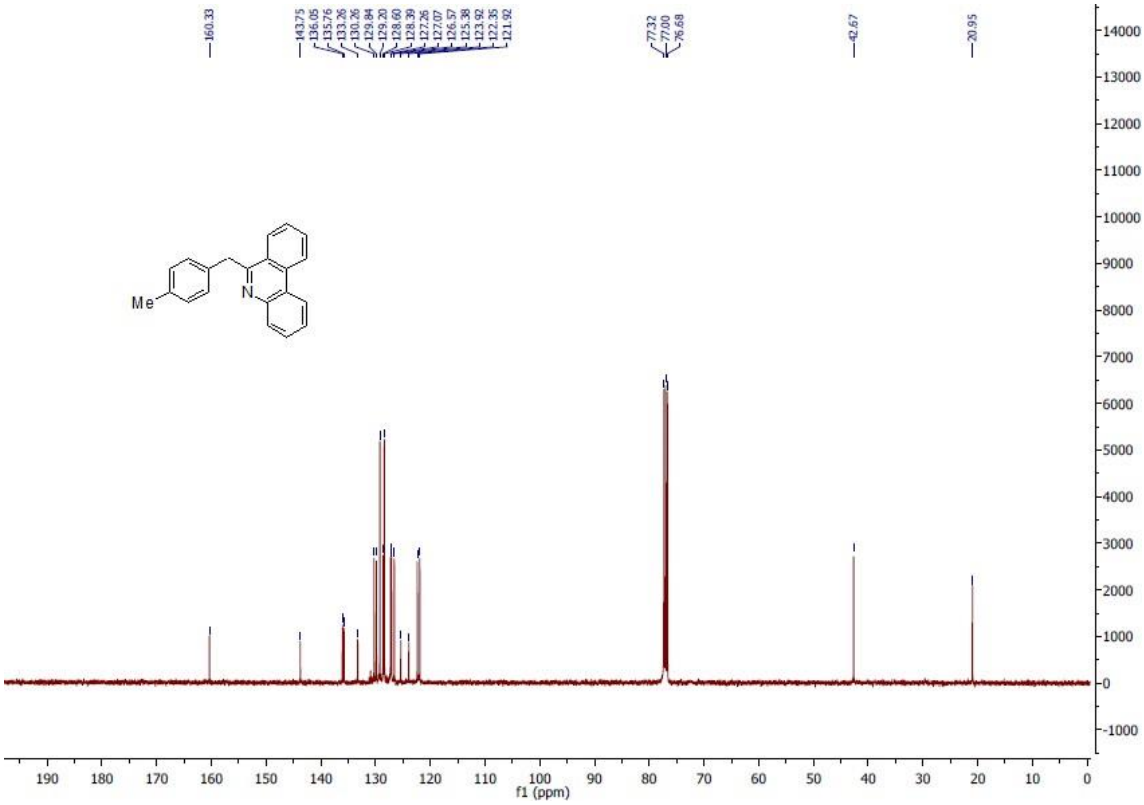
^{1}H and ^{13}{C} spectra of **3b**





^{1}H and ^{13}{C} spectra of **3c**





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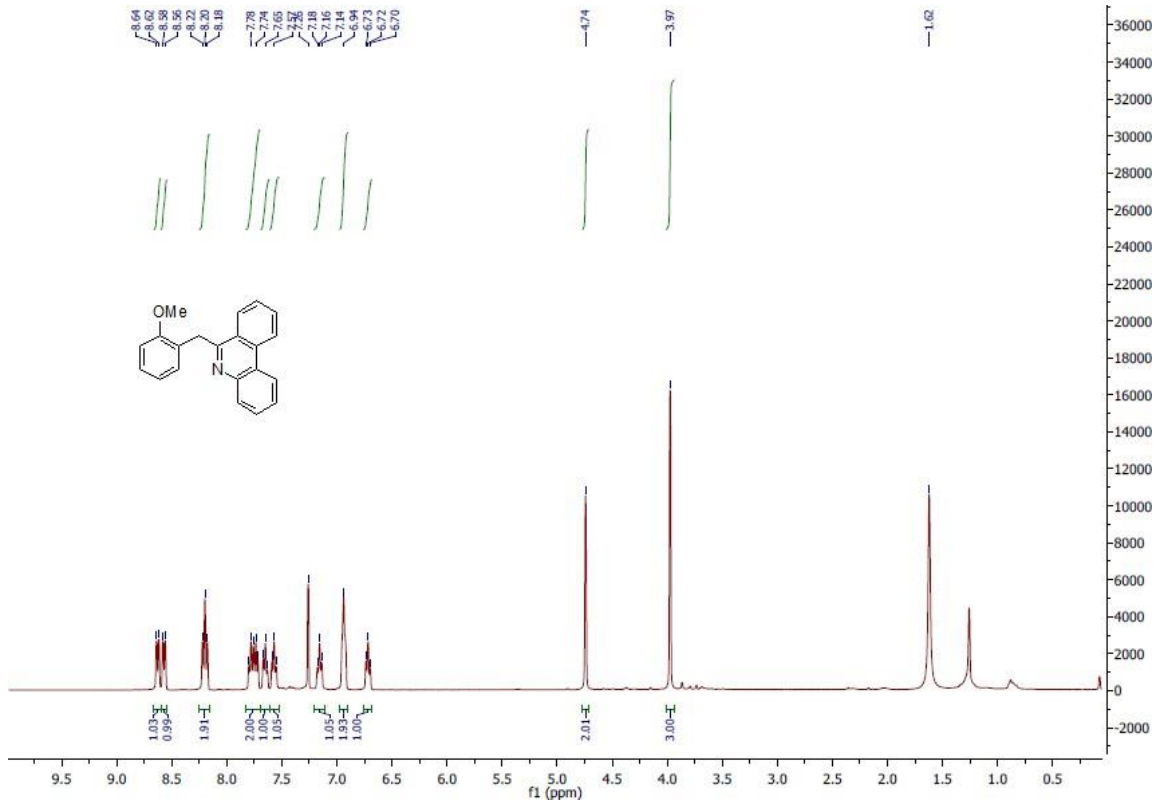
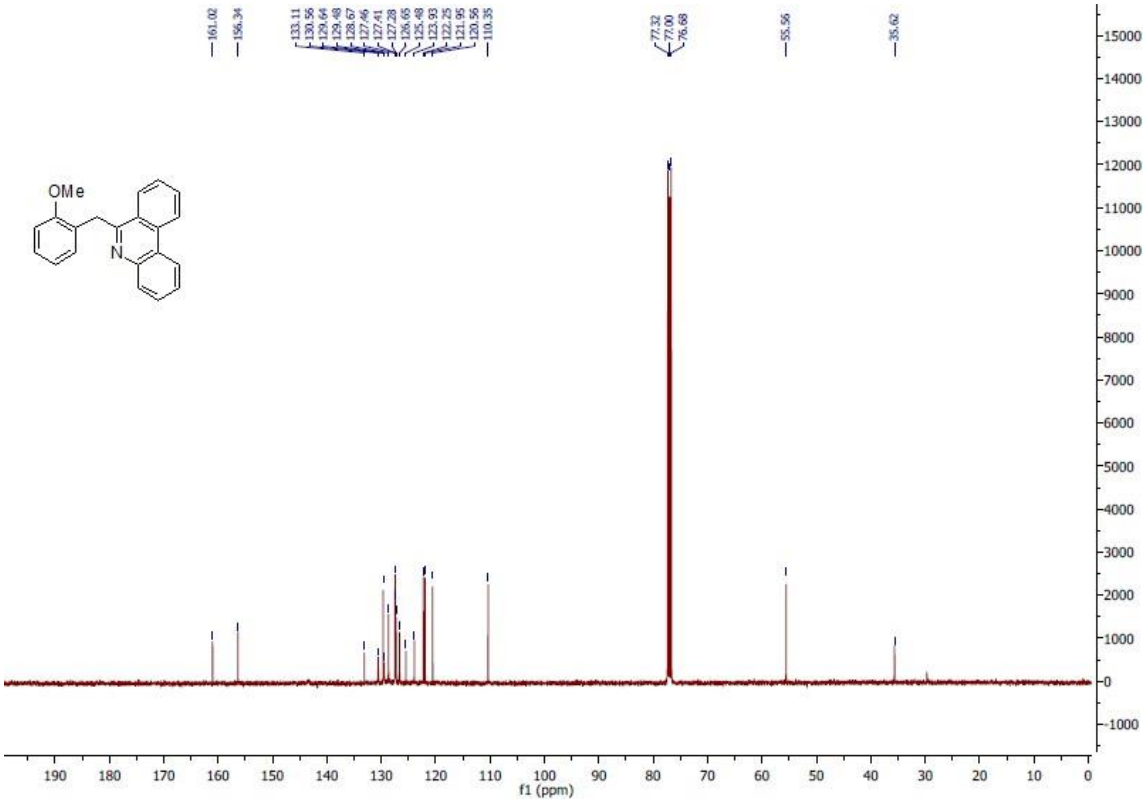
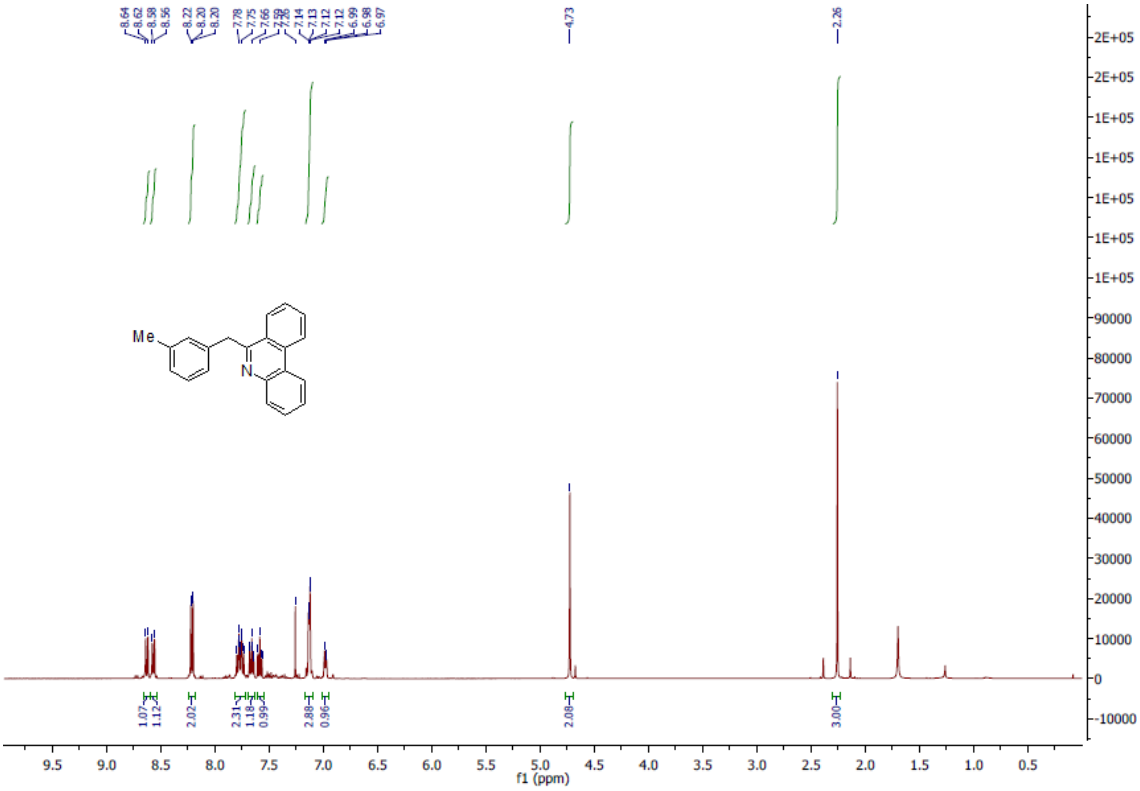
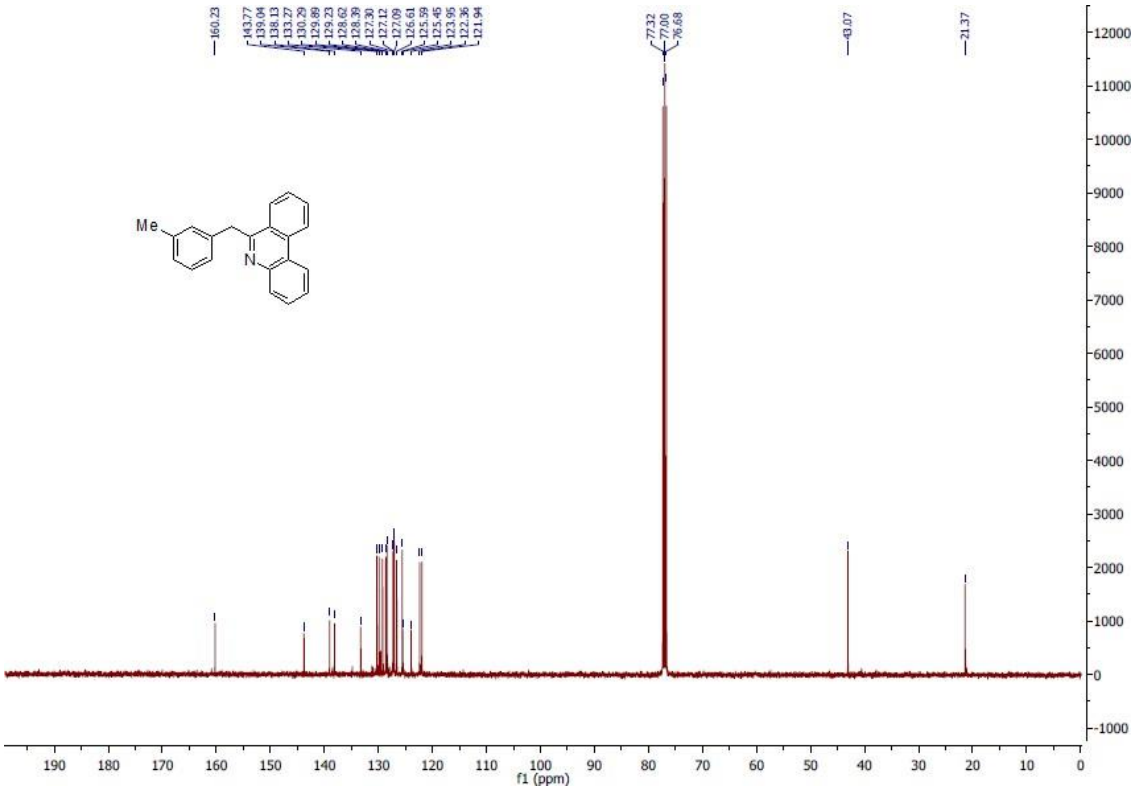


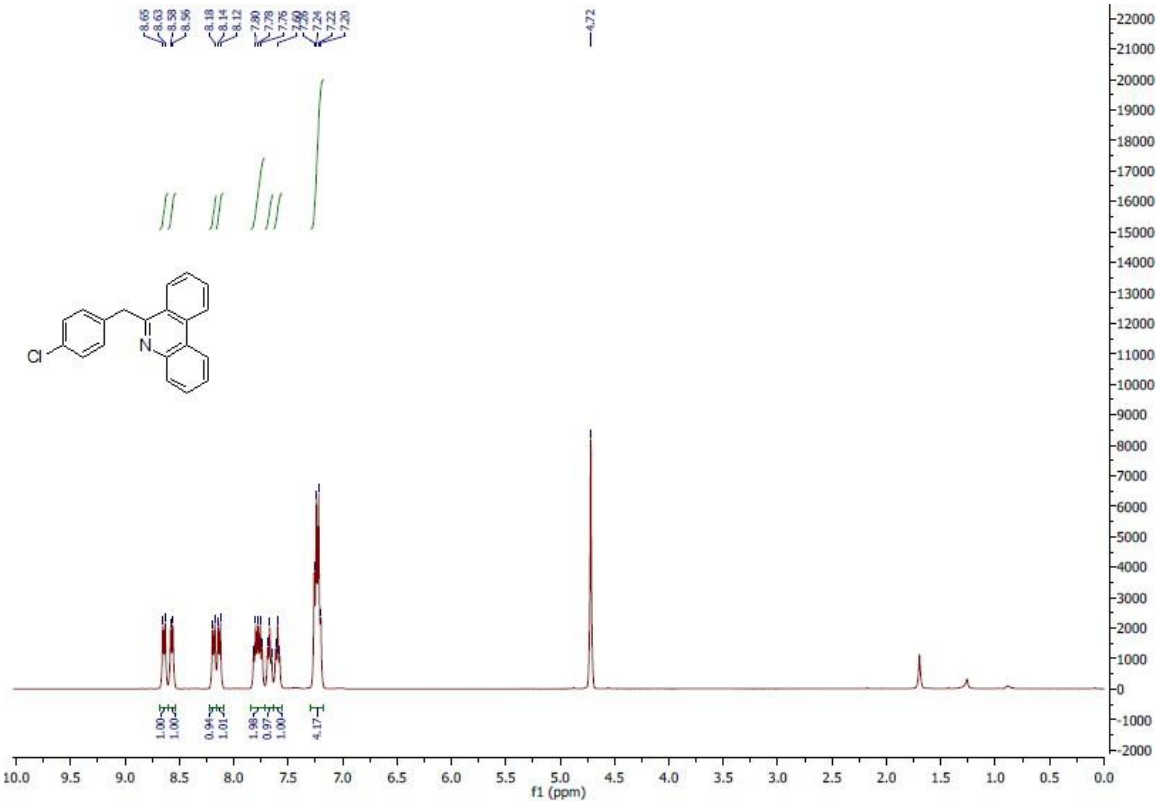


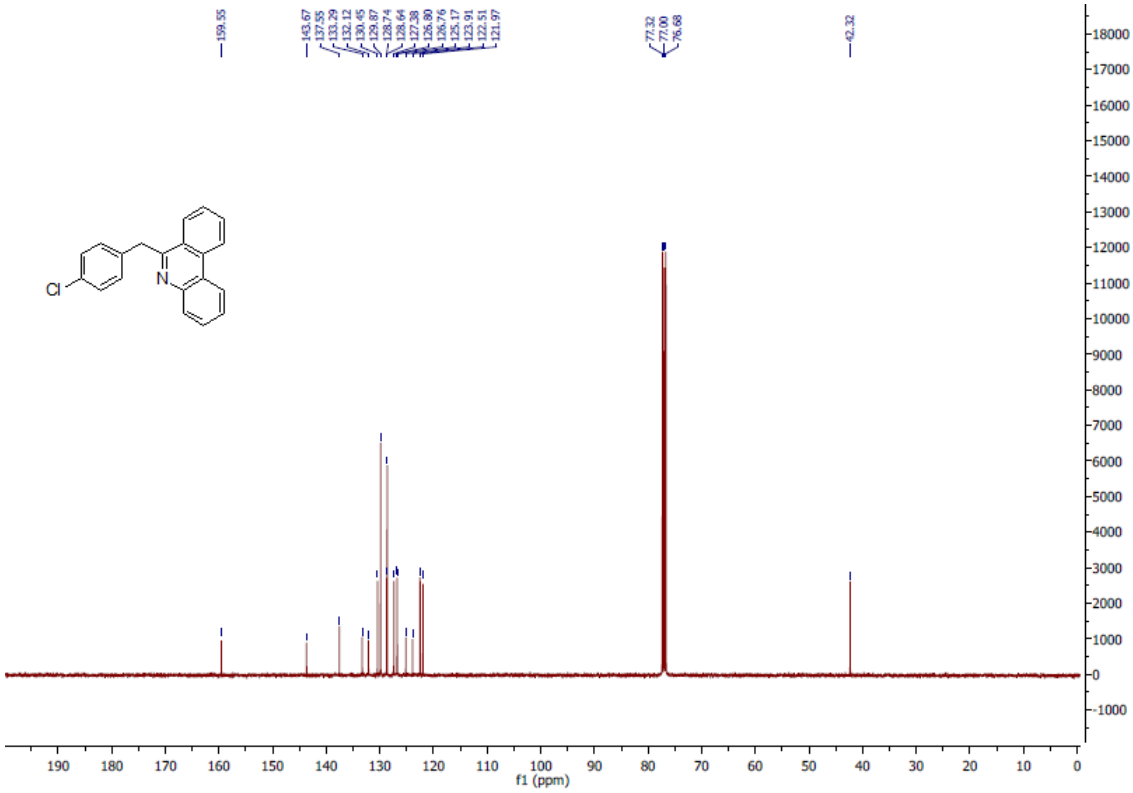
^{1}H and ^{13}{C} spectra of **3e**



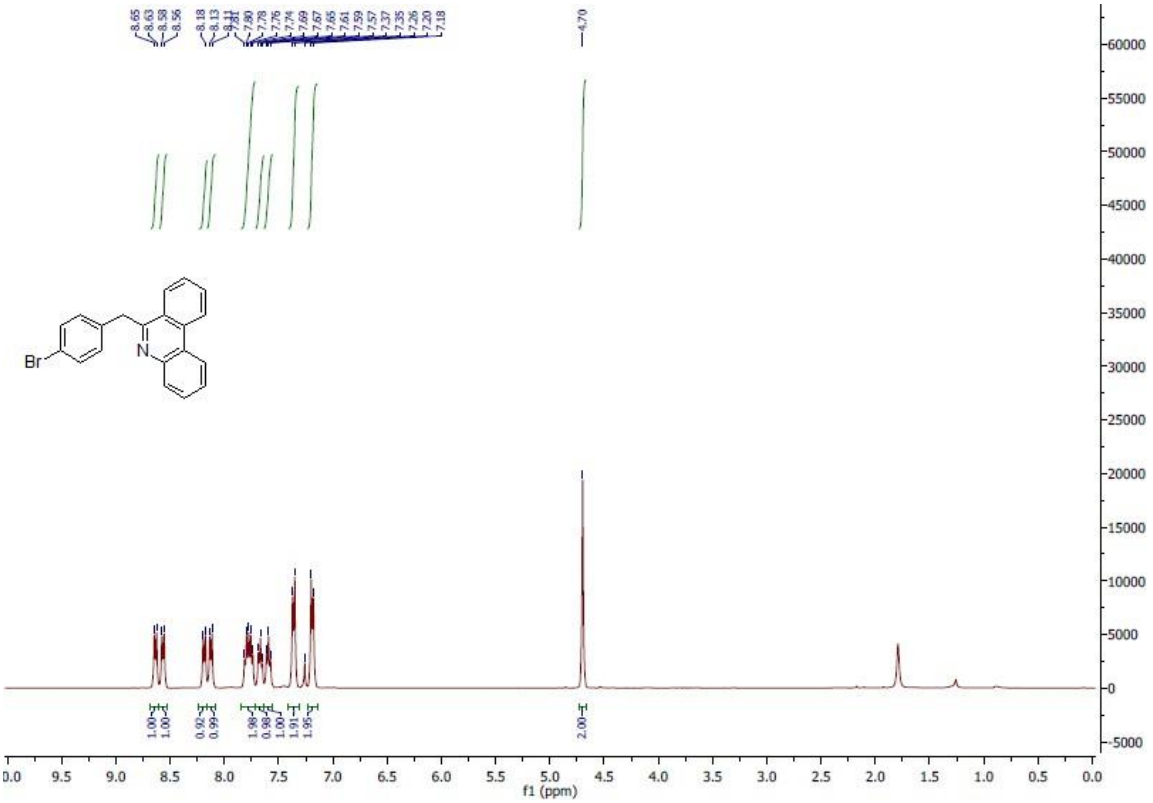


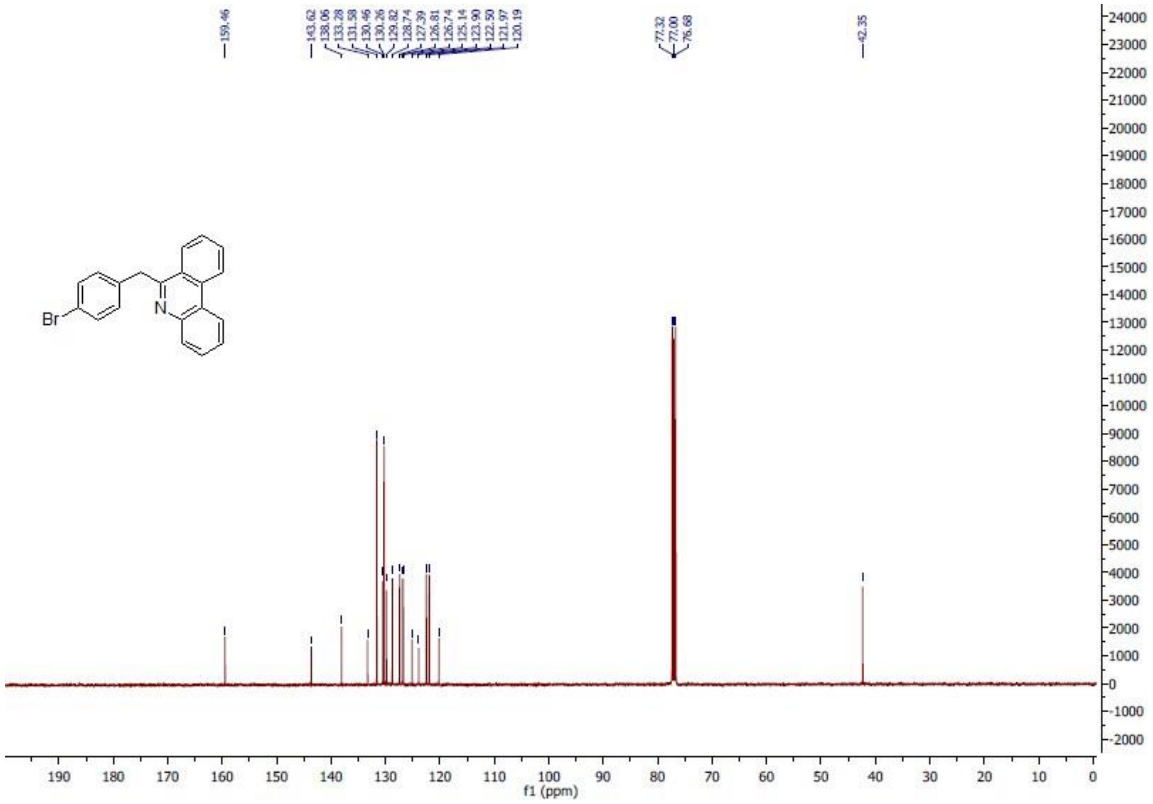
^{1}H and ^{13}{C} spectra of **3f**



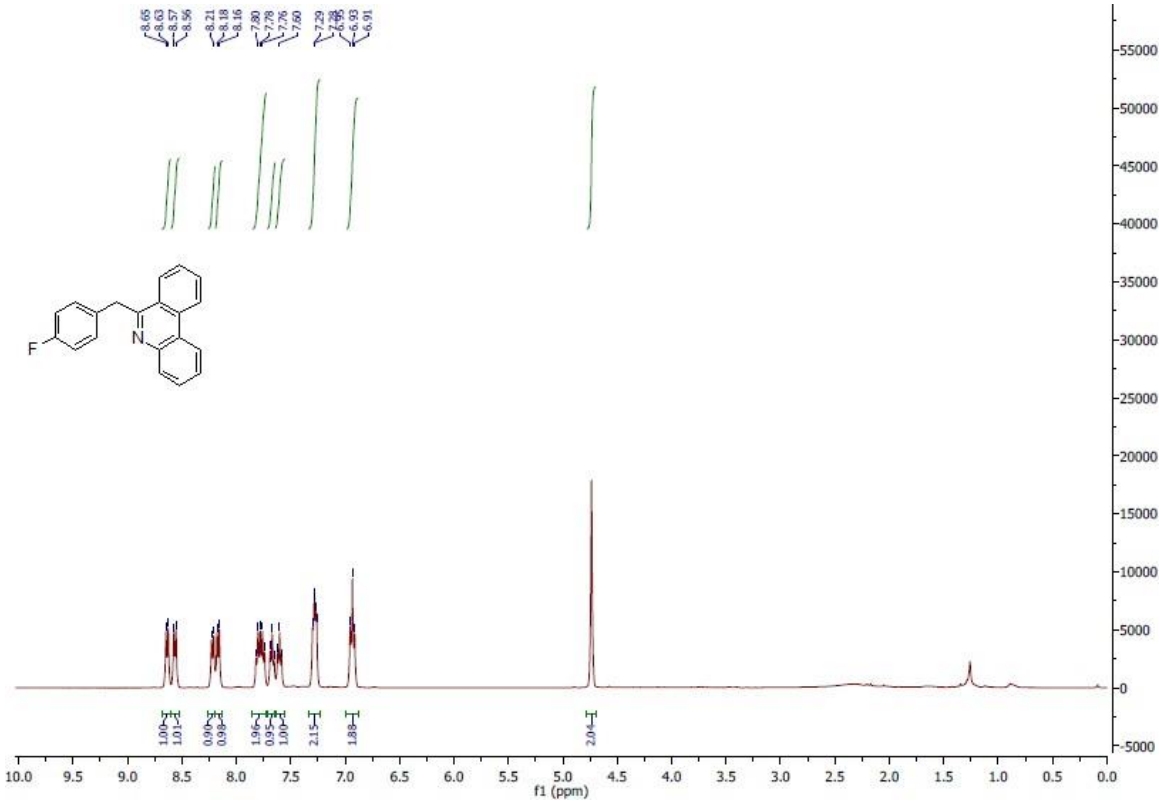


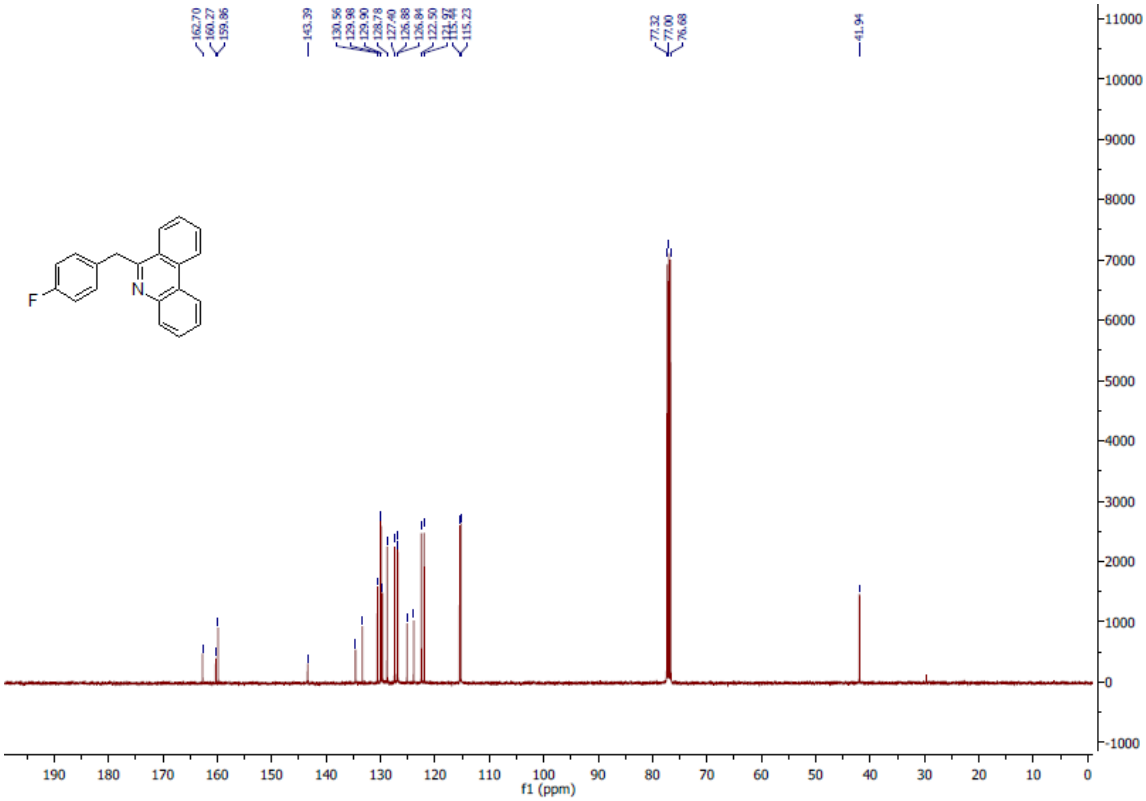
^{1}H and ^{13}{C} spectra of **3g**



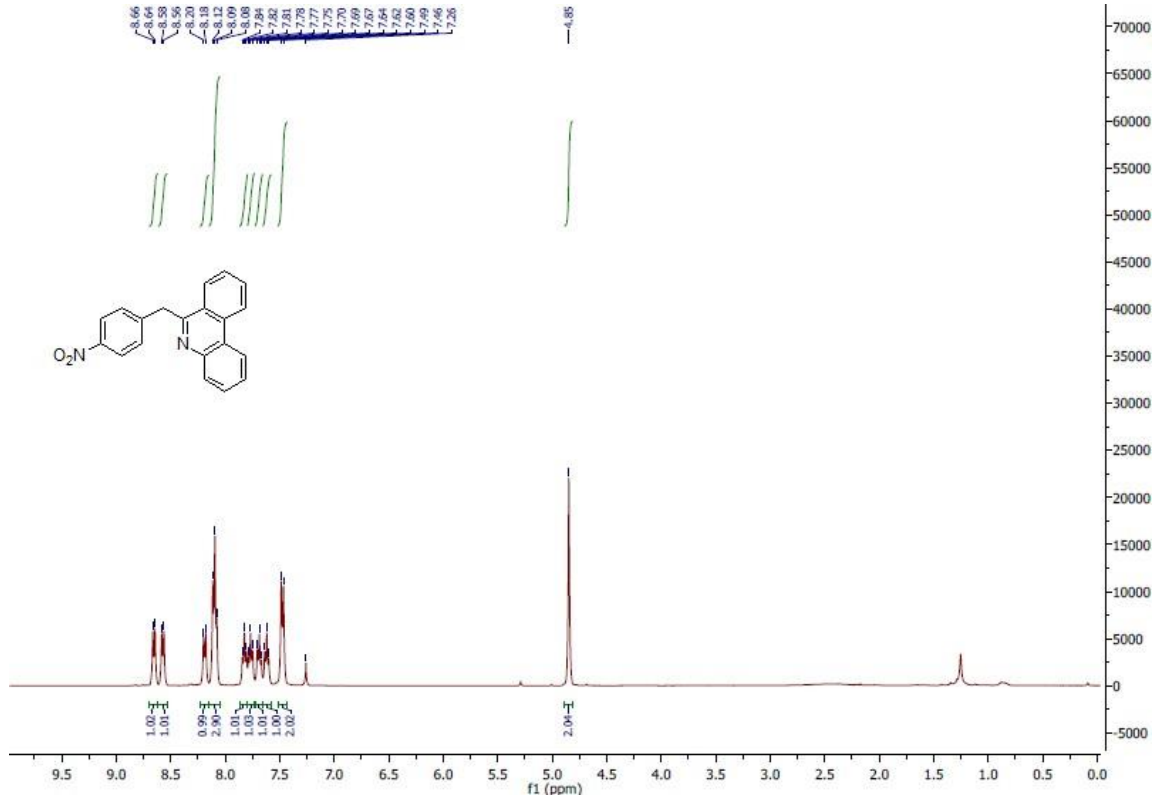


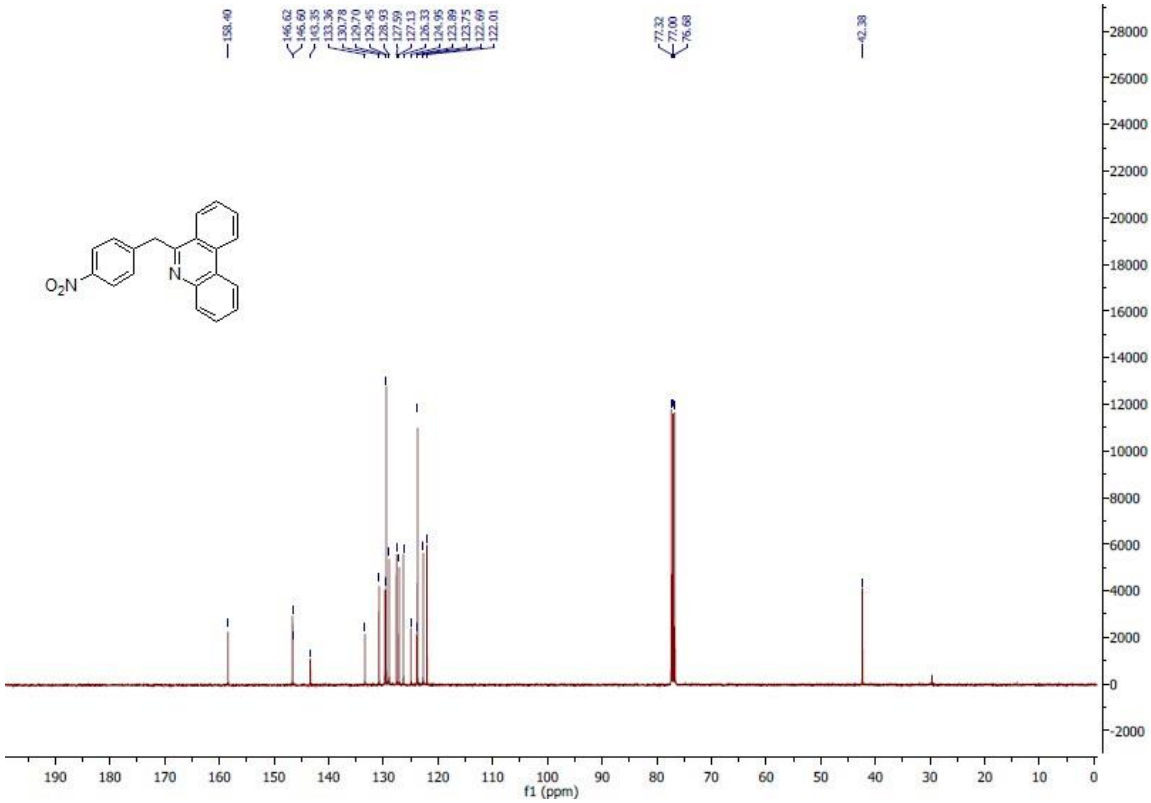
^{1}H and ^{13}{C} spectra of **3h**



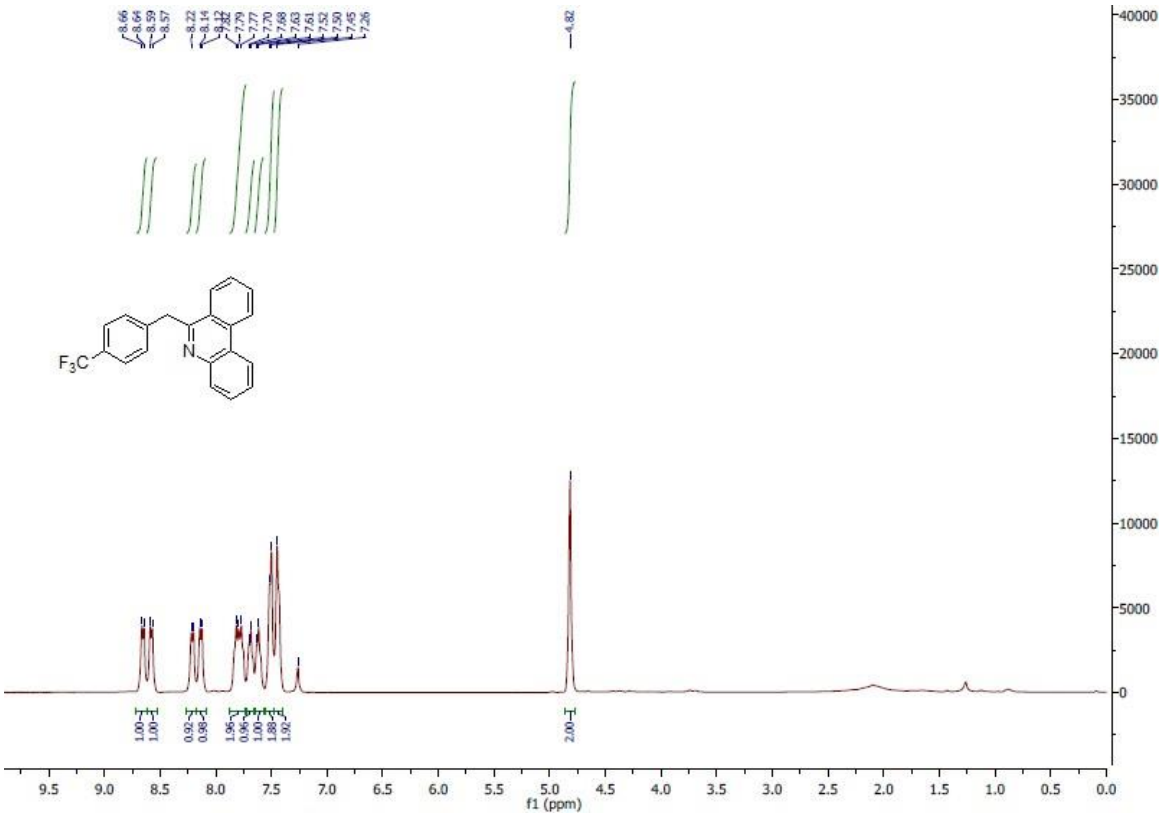


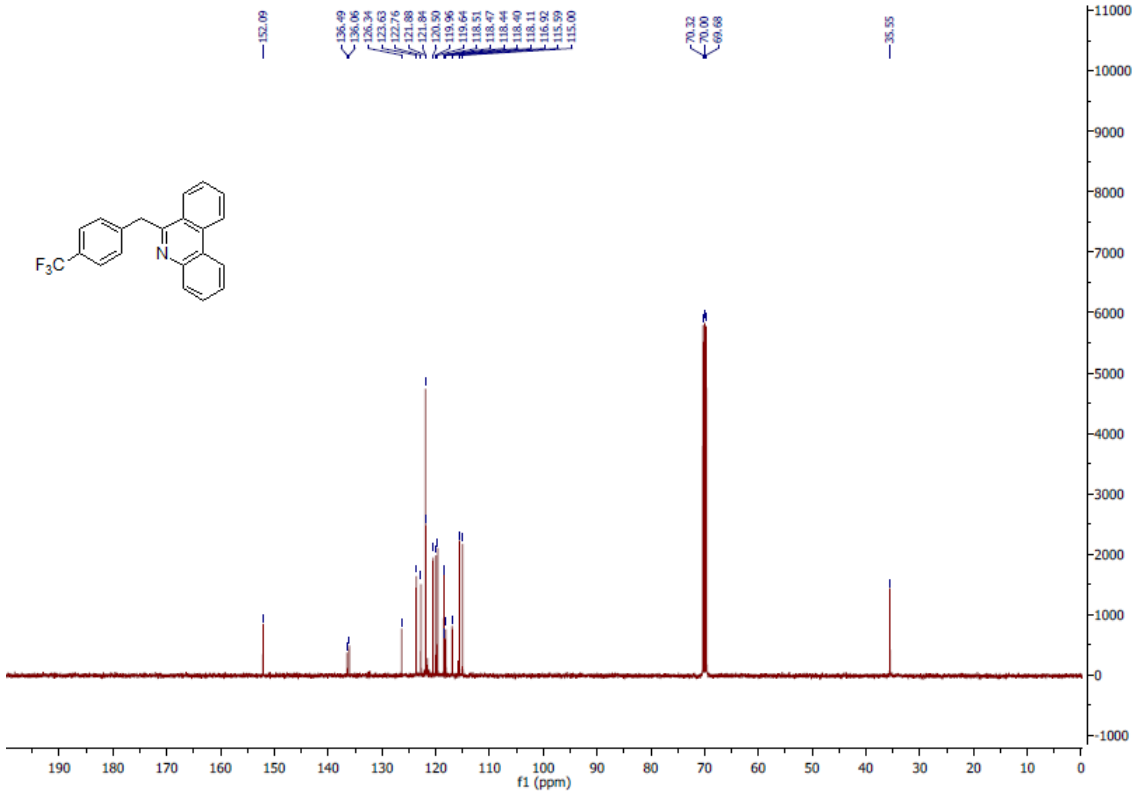
^{1}H and ^{13}\{C\} spectra of **3i**



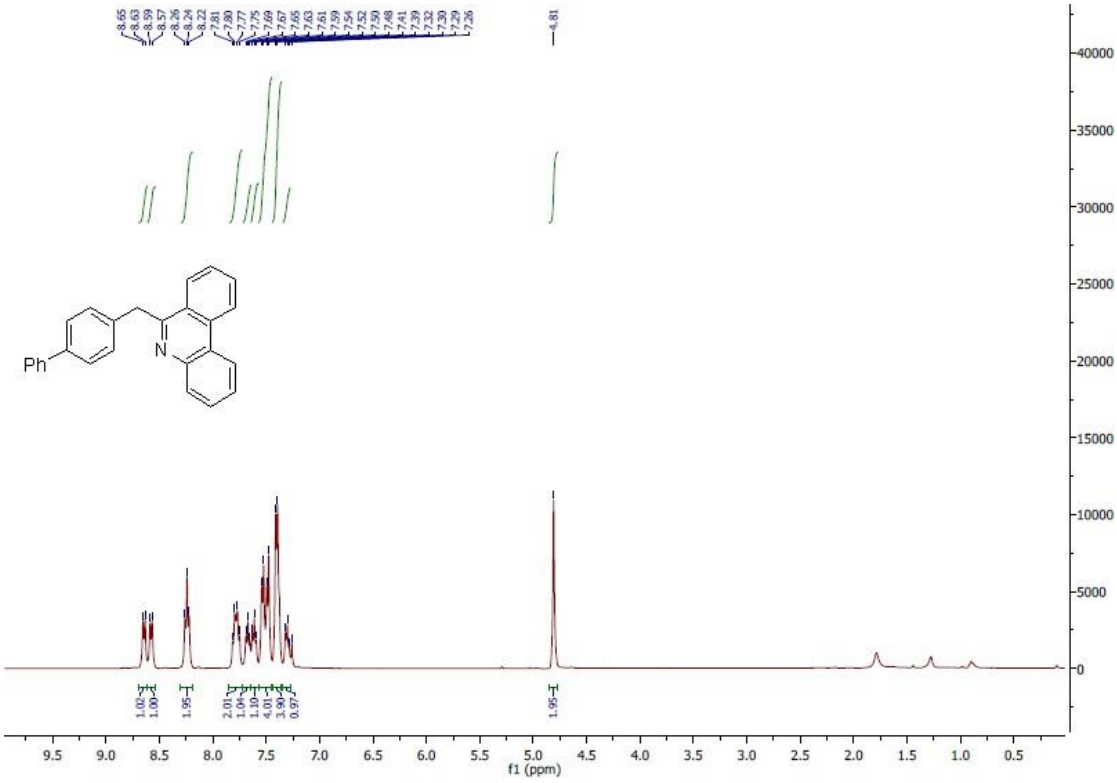


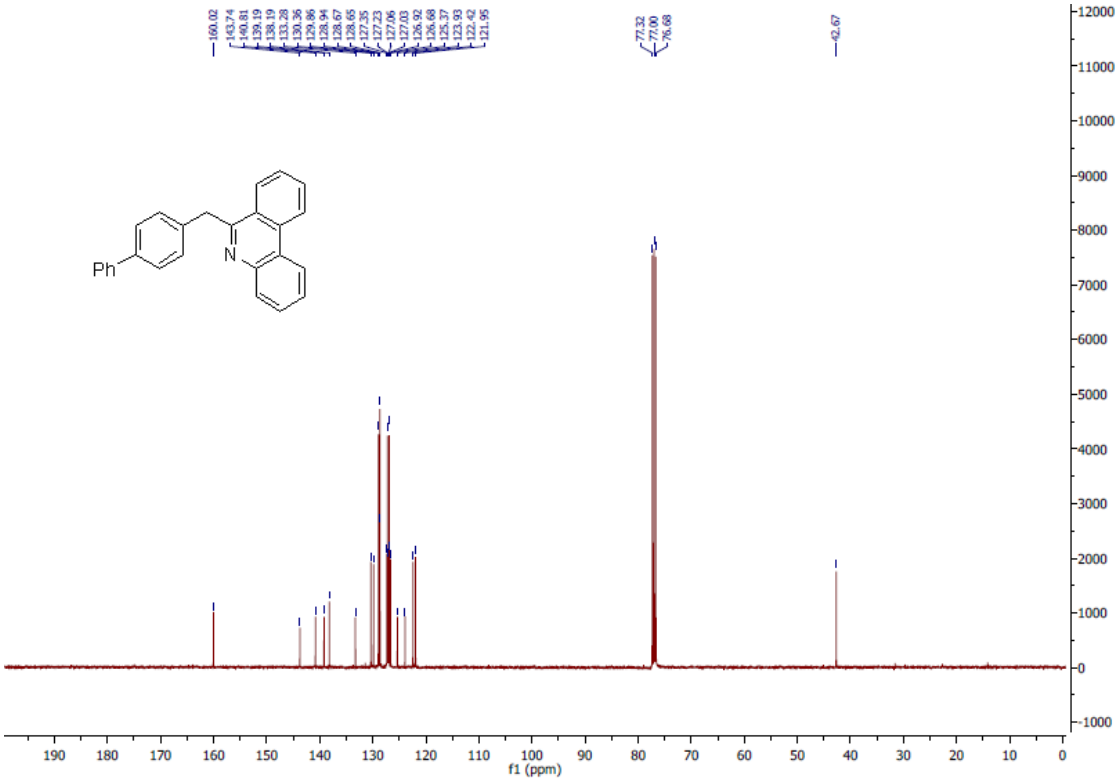
^{1}H and ^{13}{C} spectra of **3j**



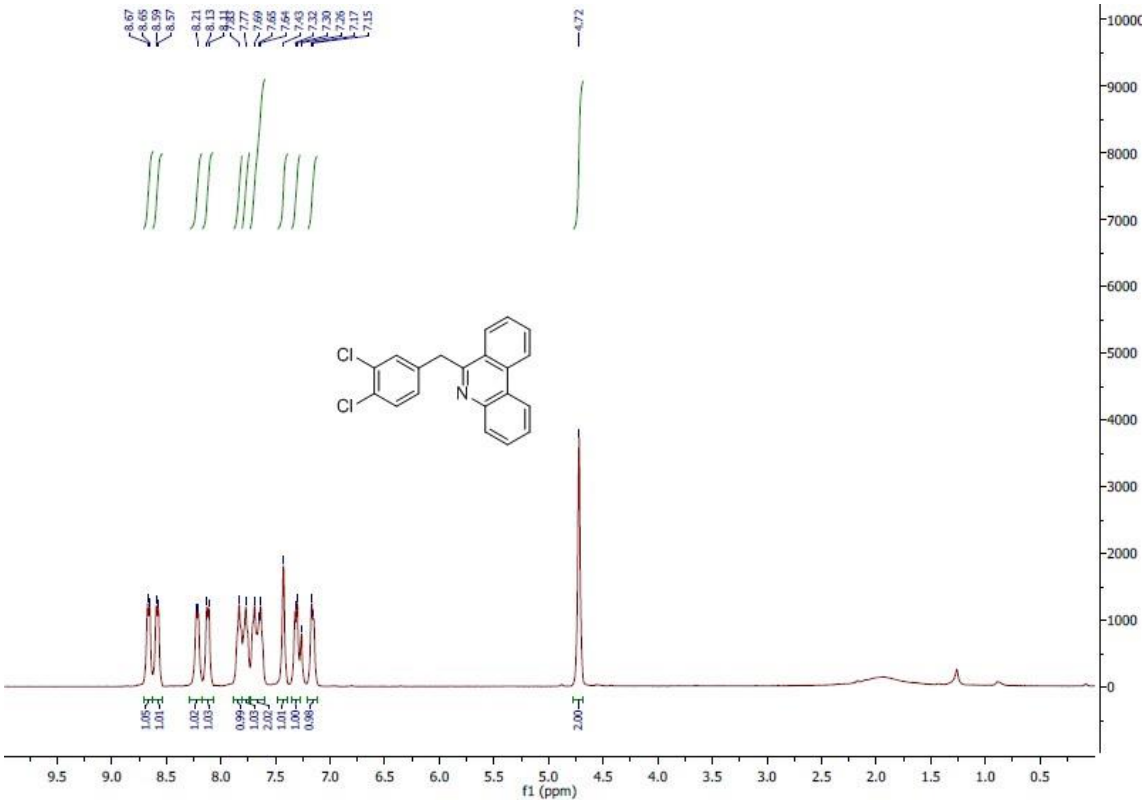


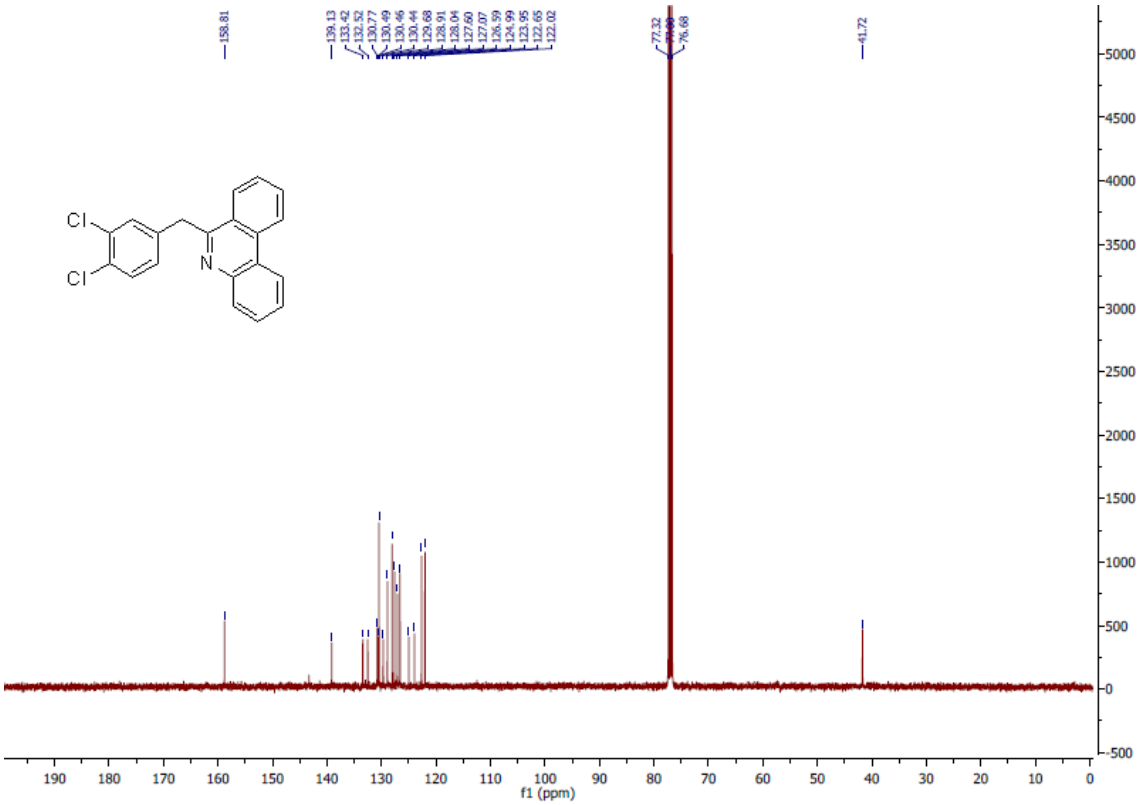
^{1}H and ^{13}{C} spectra of **3k**



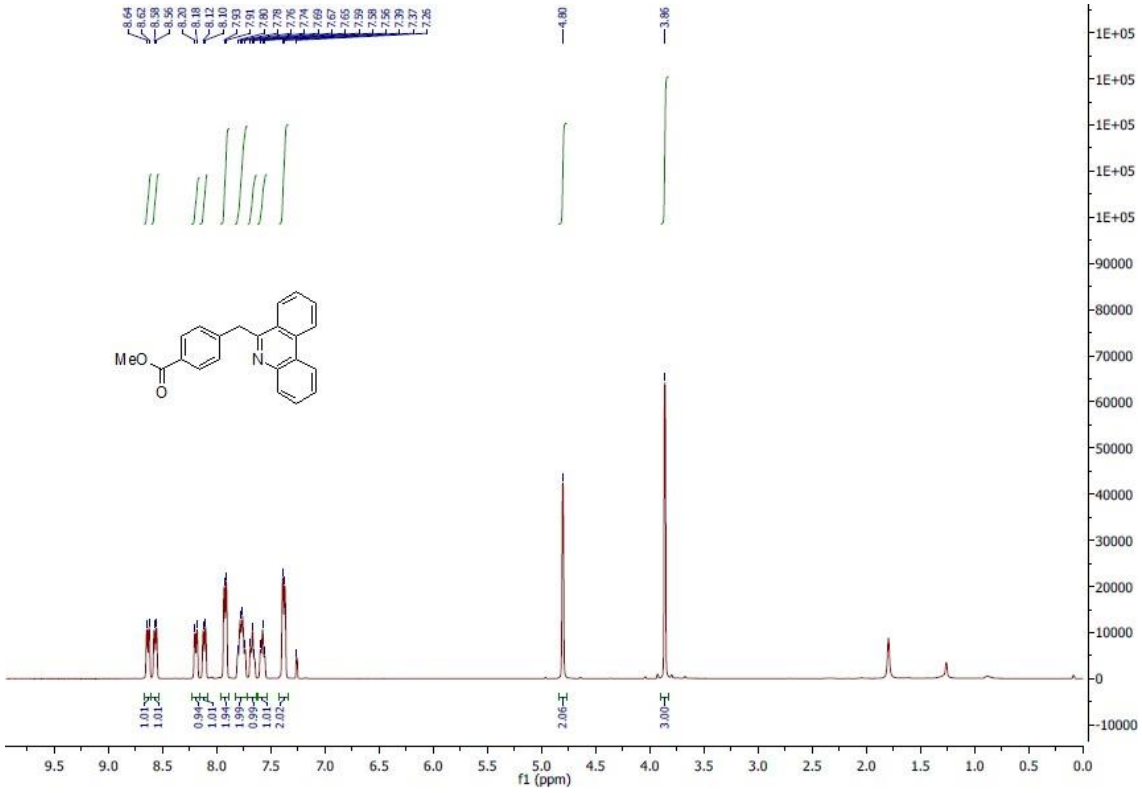


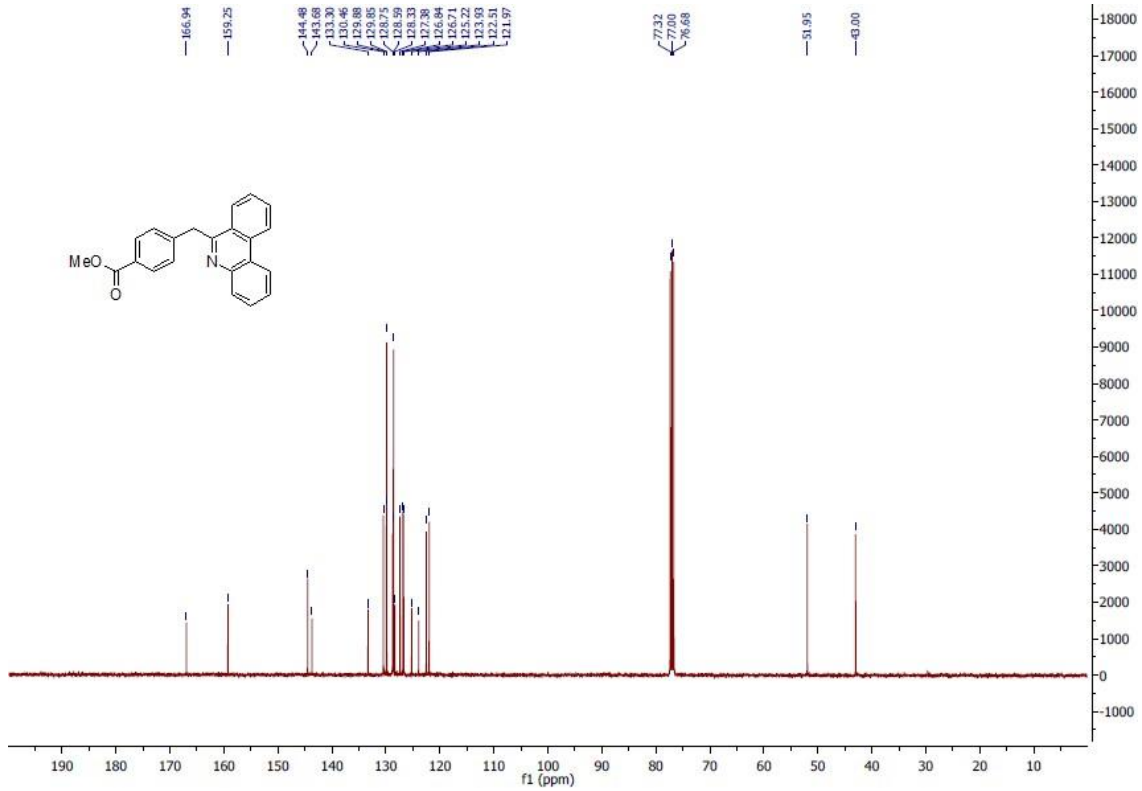
^{1}H and ^{13}{C} spectra of **3l**



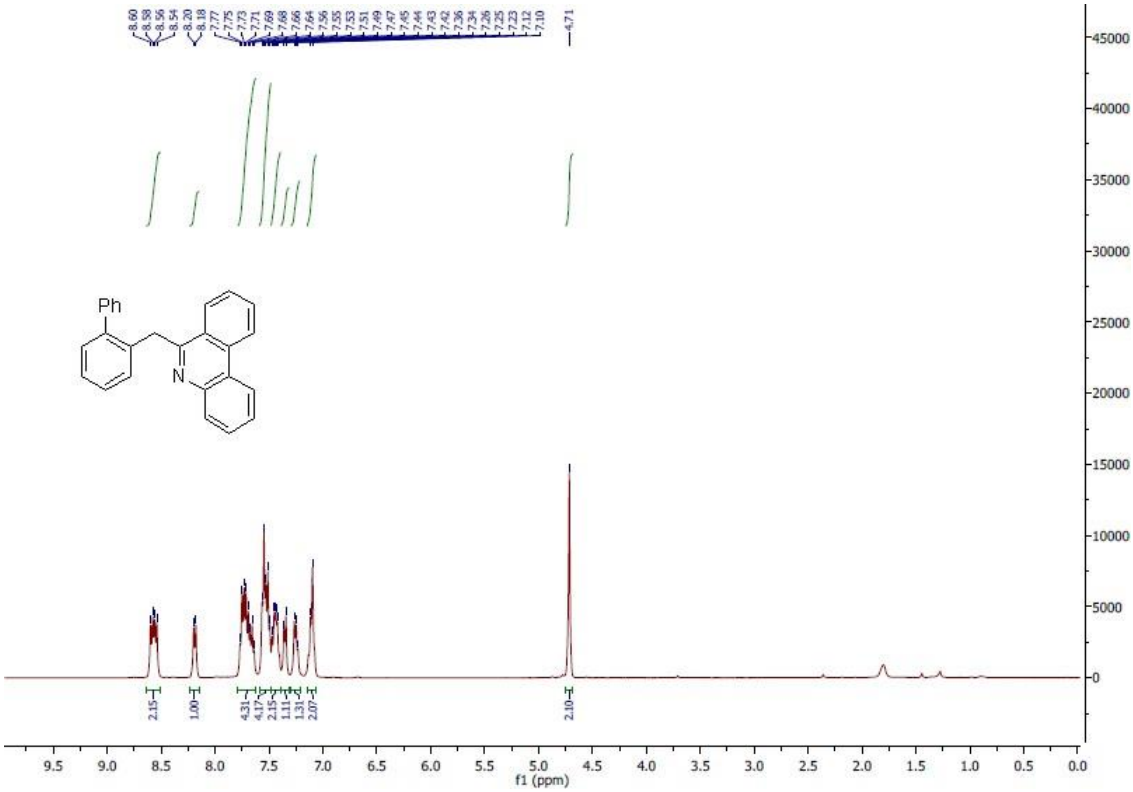


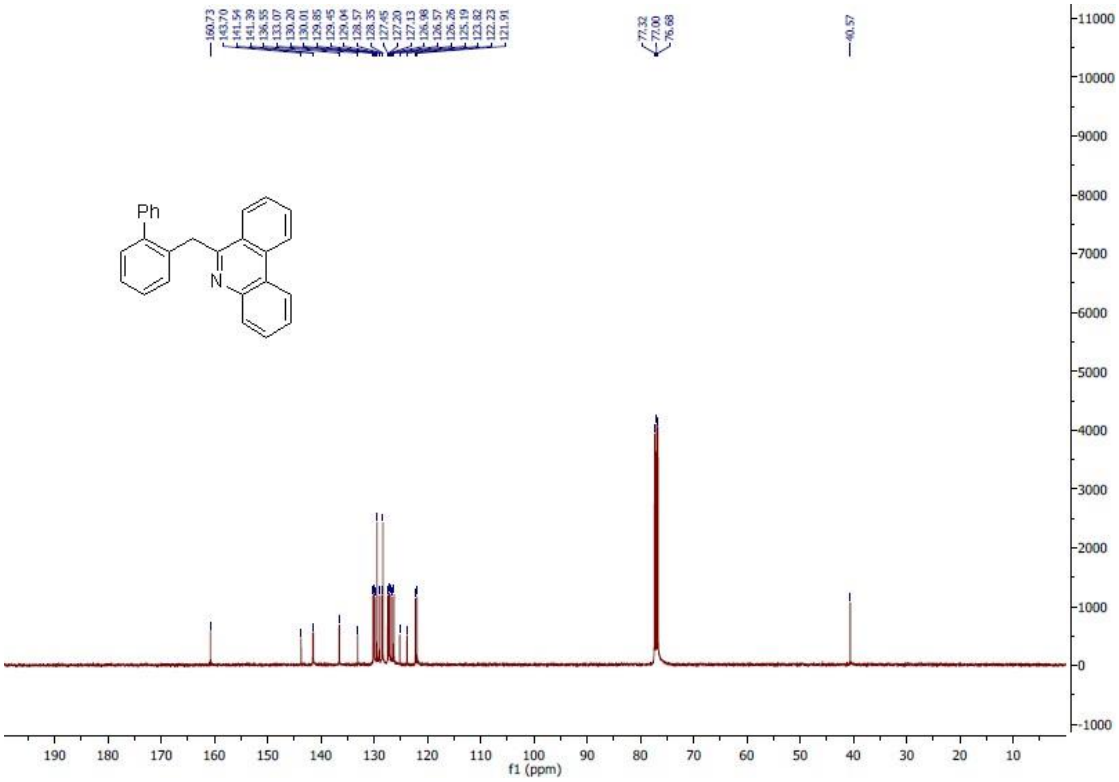
^{1}H and ^{13}{C} spectra of **3m**



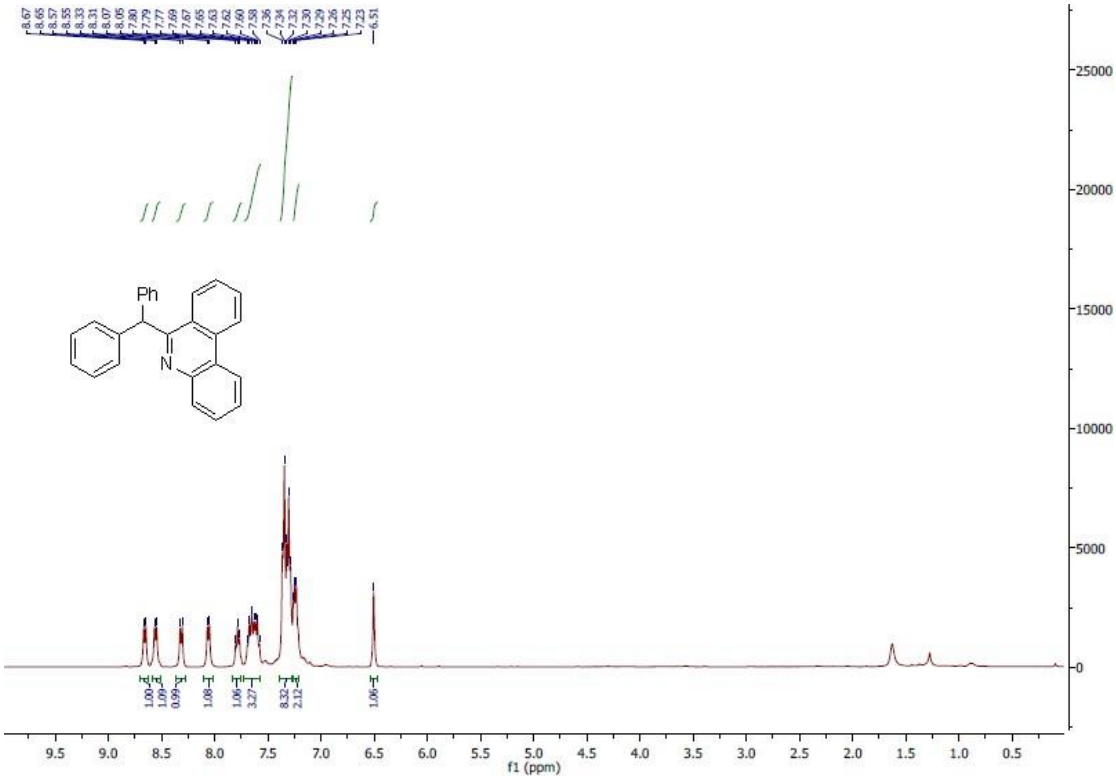


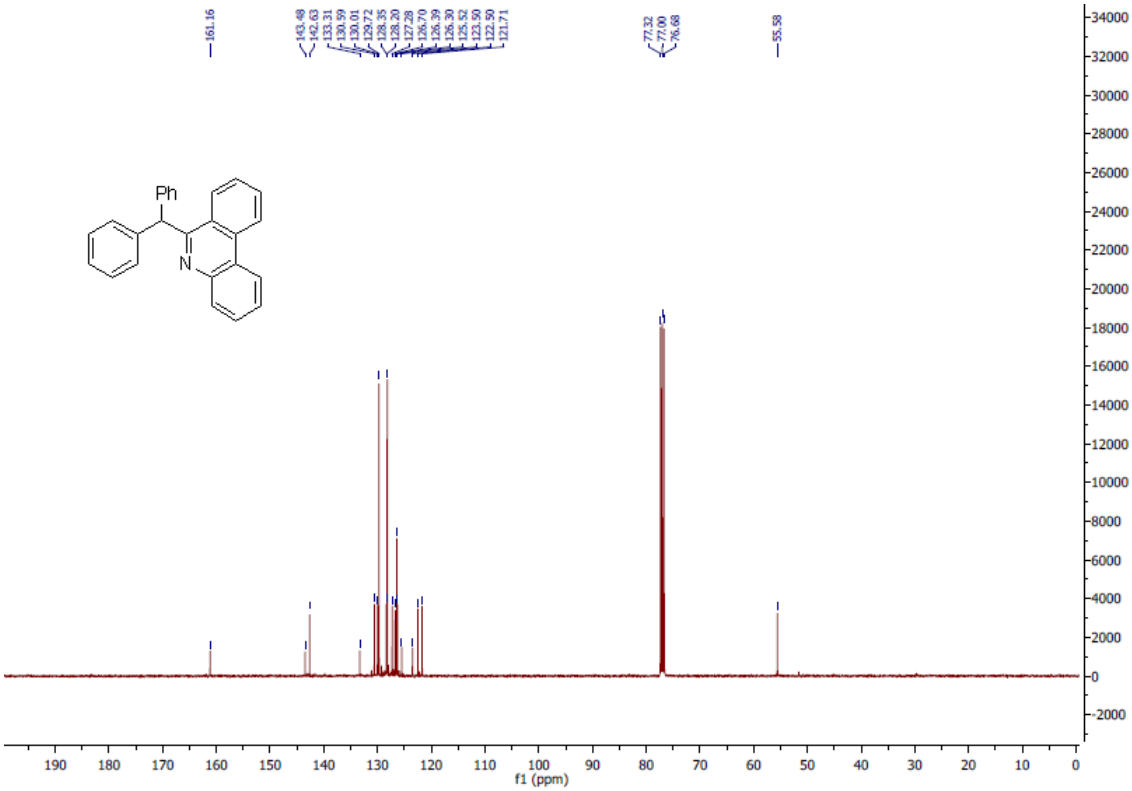
^{1}H and ^{13}{C} spectra of **3n**



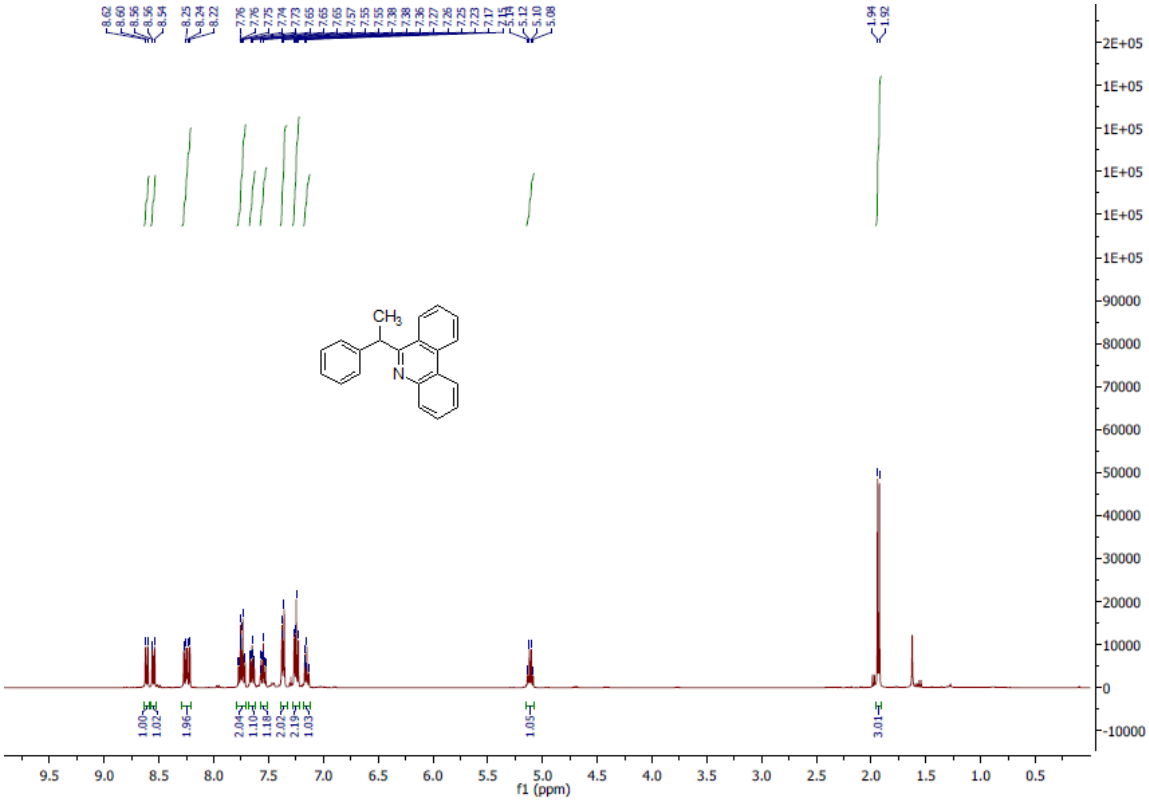


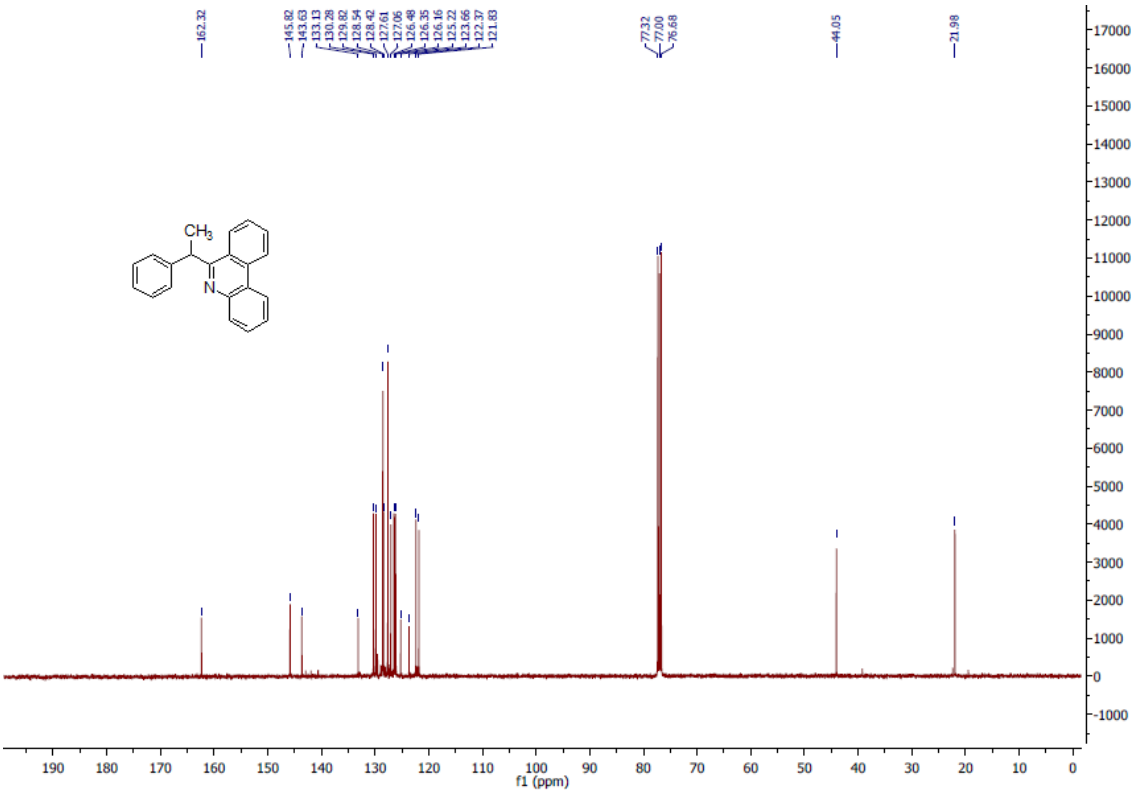
^{1}H and ^{13}{C} spectra of **3o**



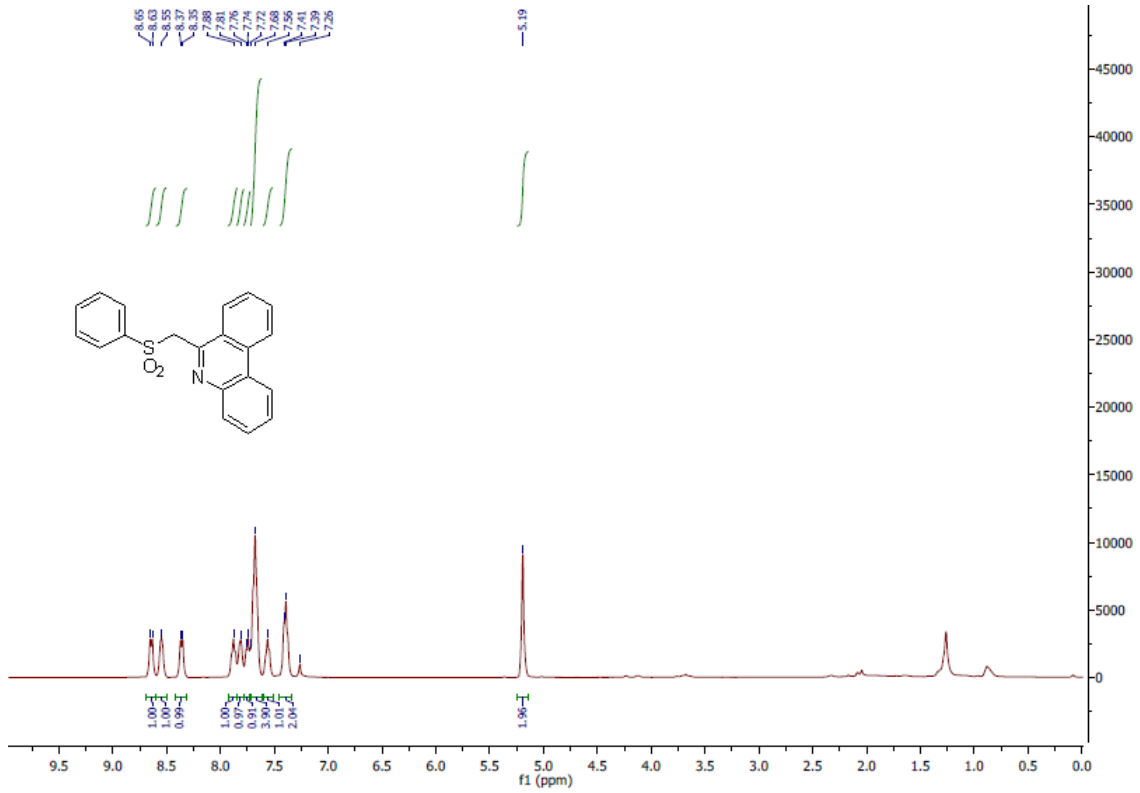


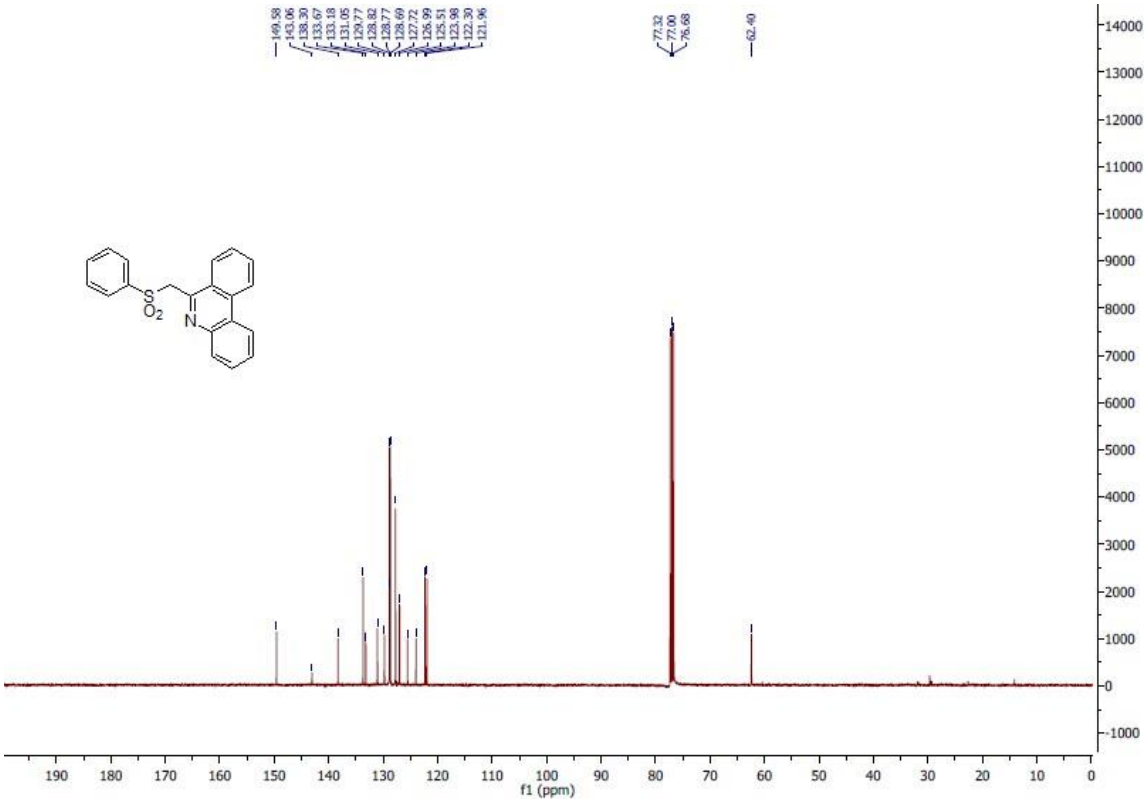
^{1}H and ^{13}\{C\} spectra of **3p**



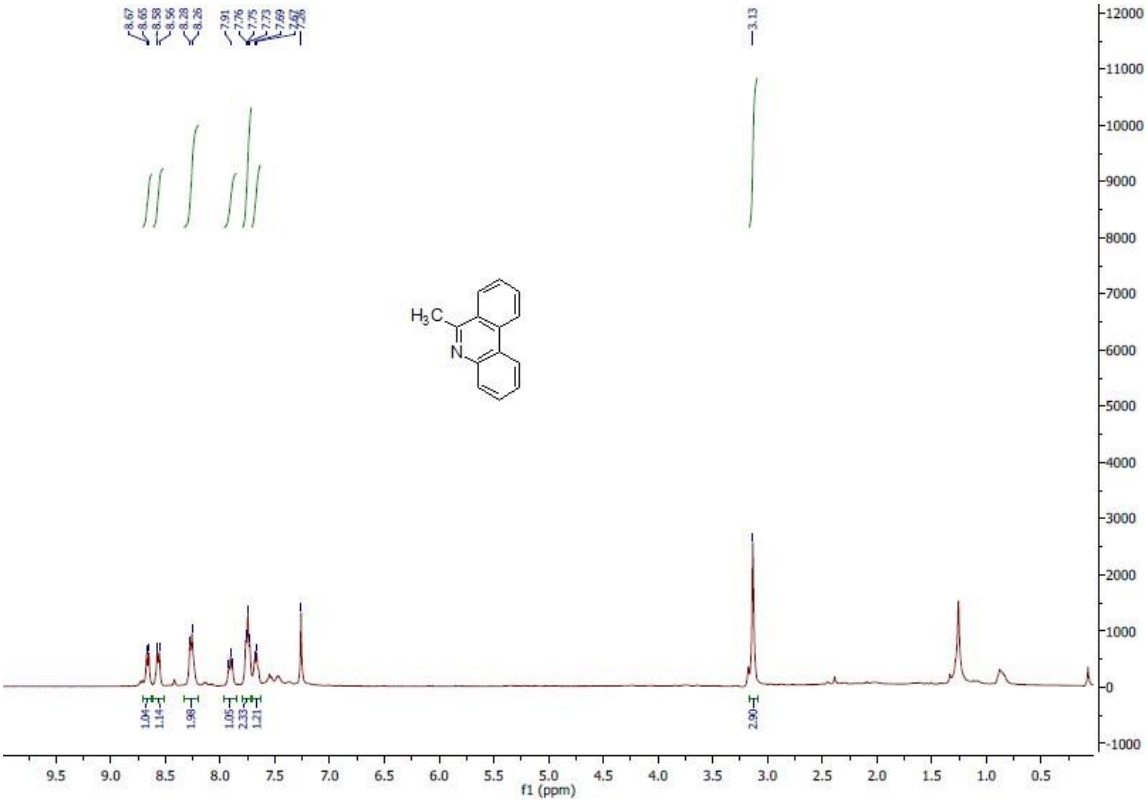


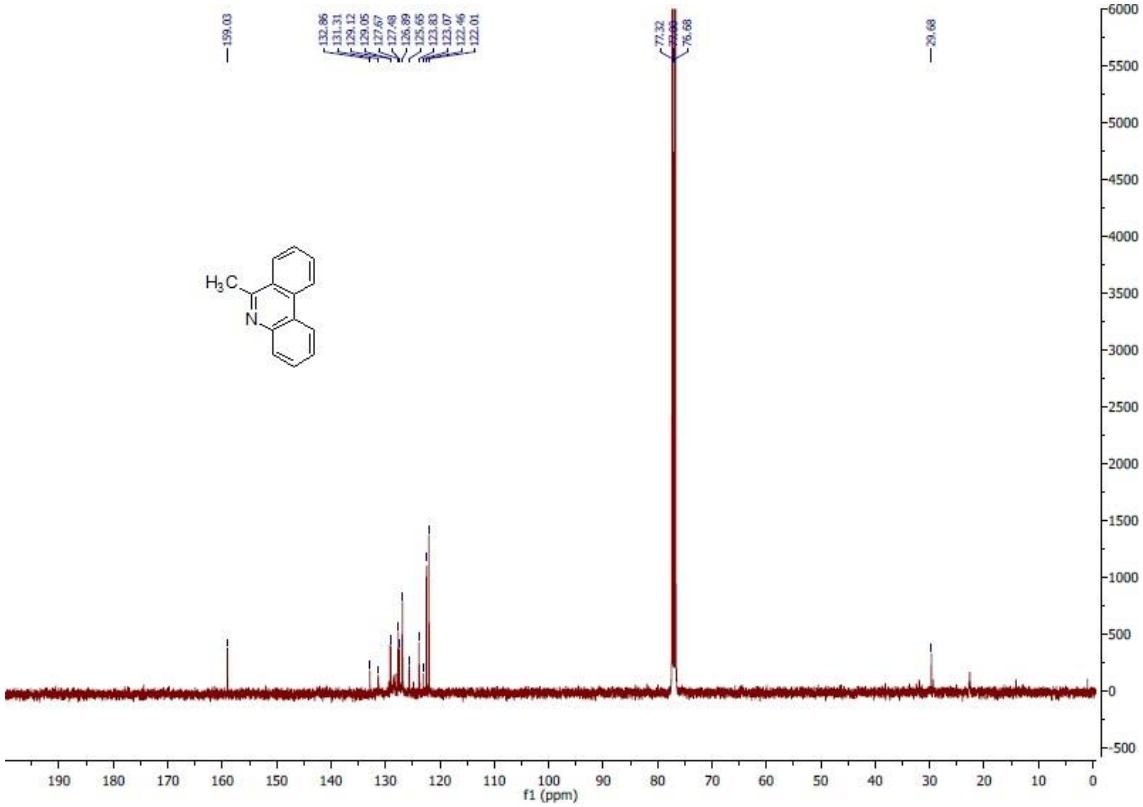
^{1}H and ^{13}{C} spectra of **3q**



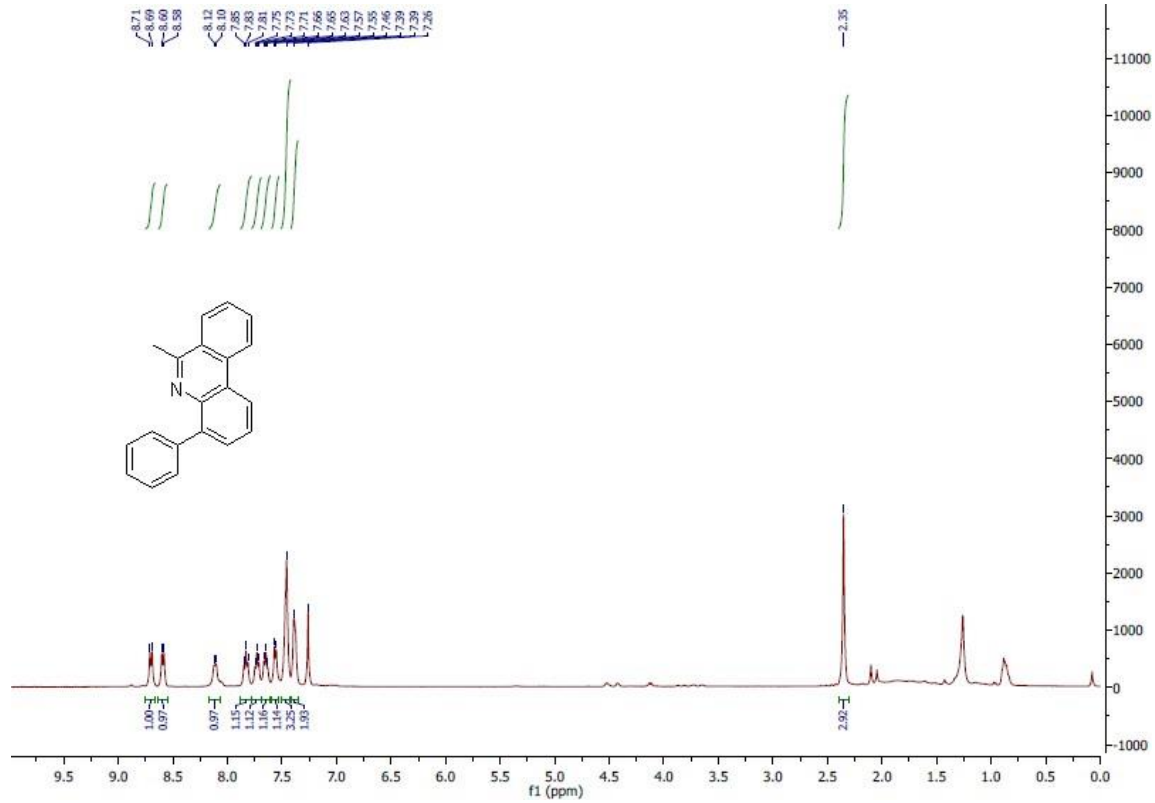


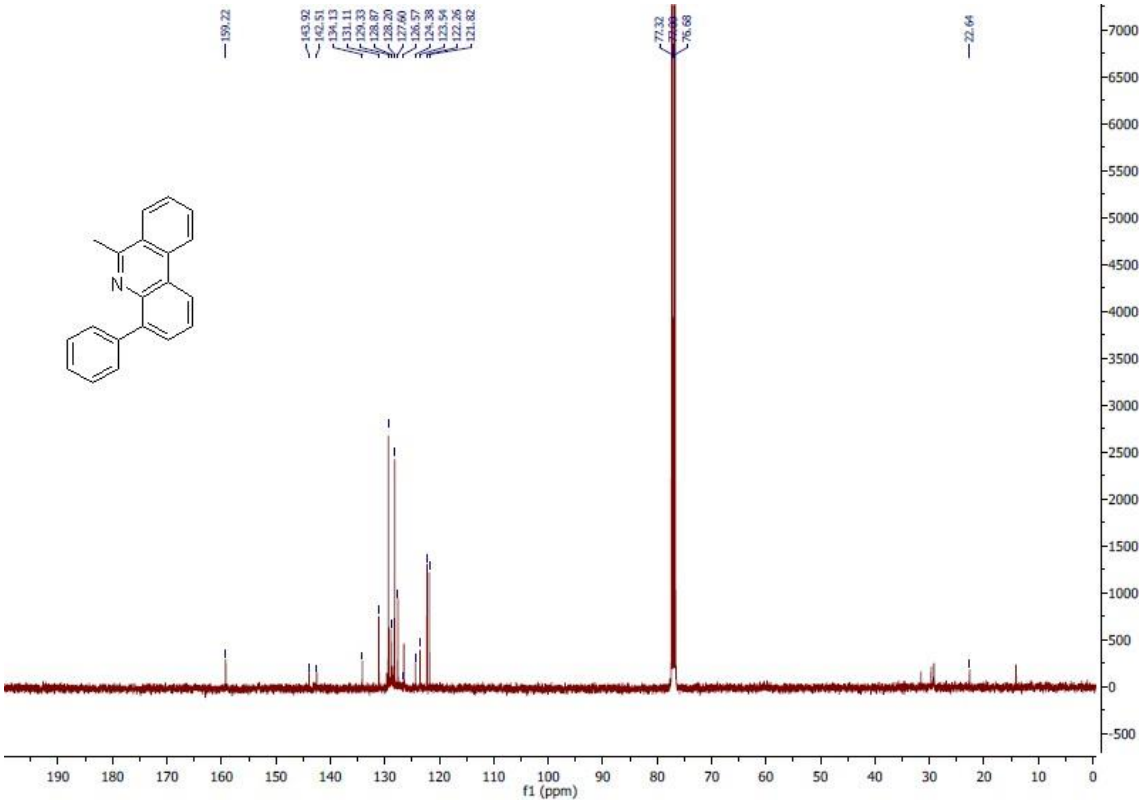
^{1}H and ^{13}\{C\} spectra of **3r**



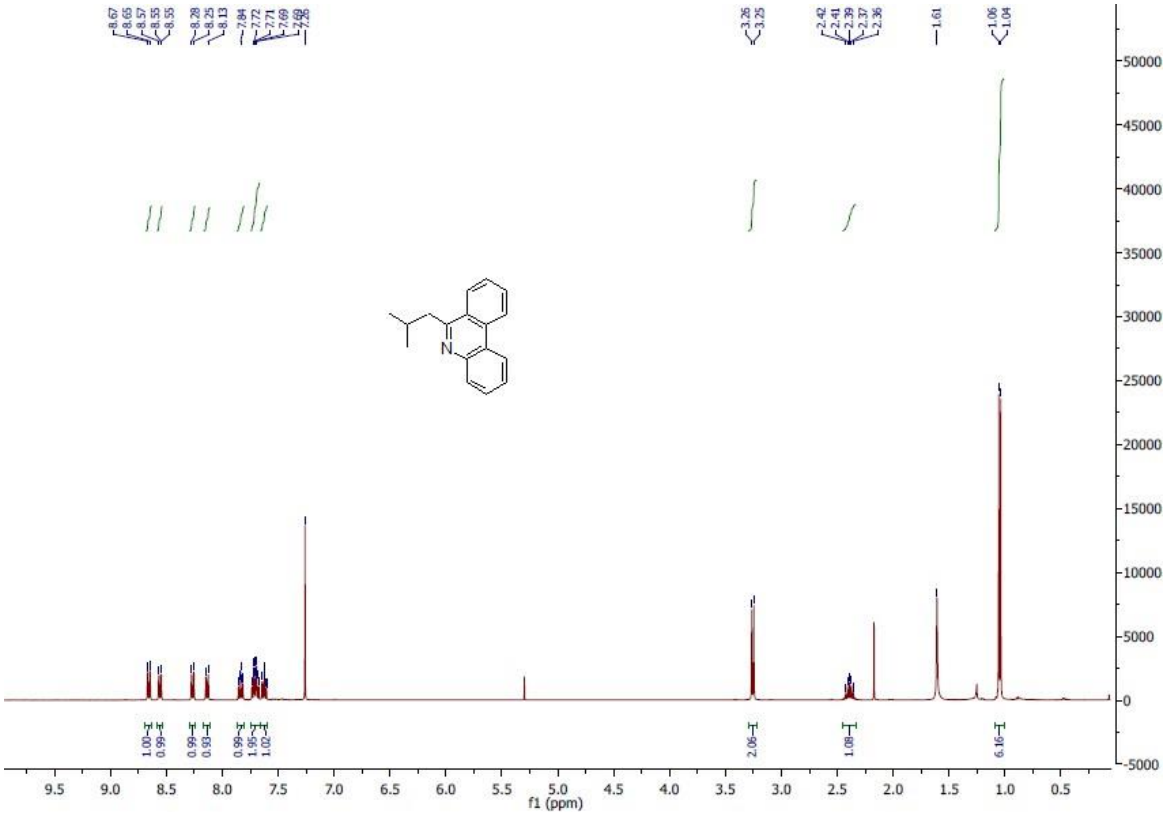


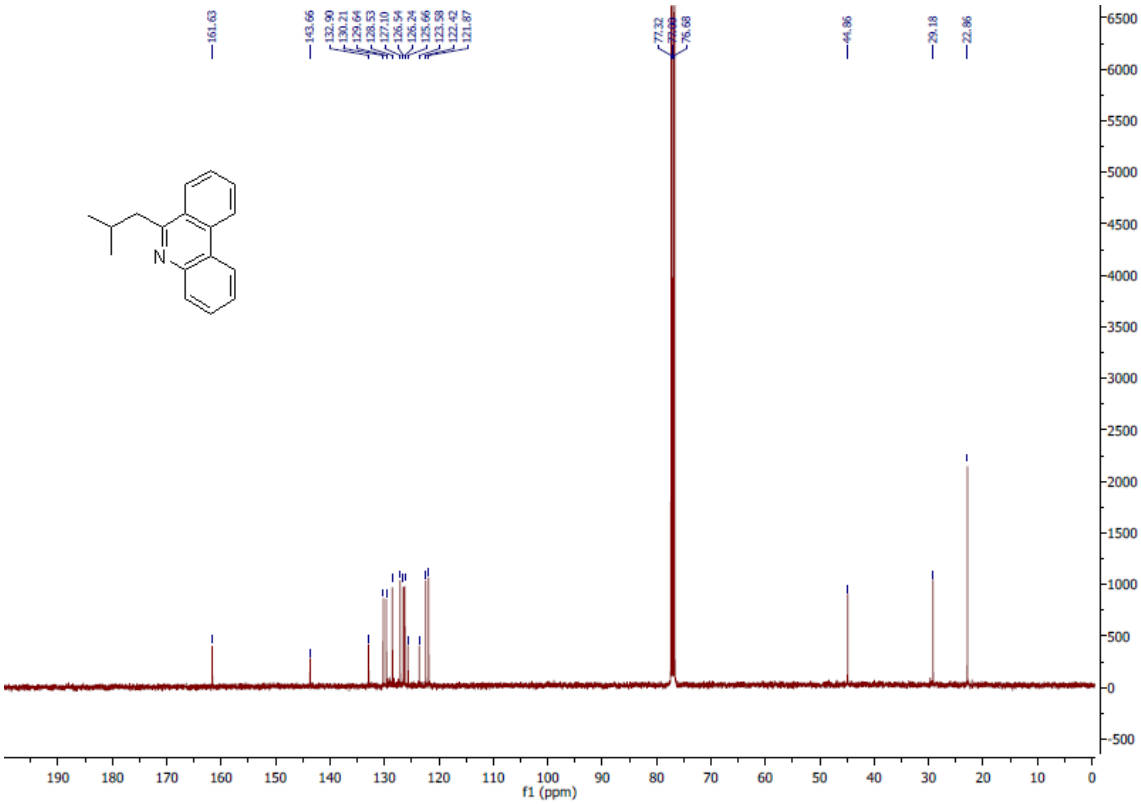
^{1}H and ^{13}{C} spectra of **3rr**



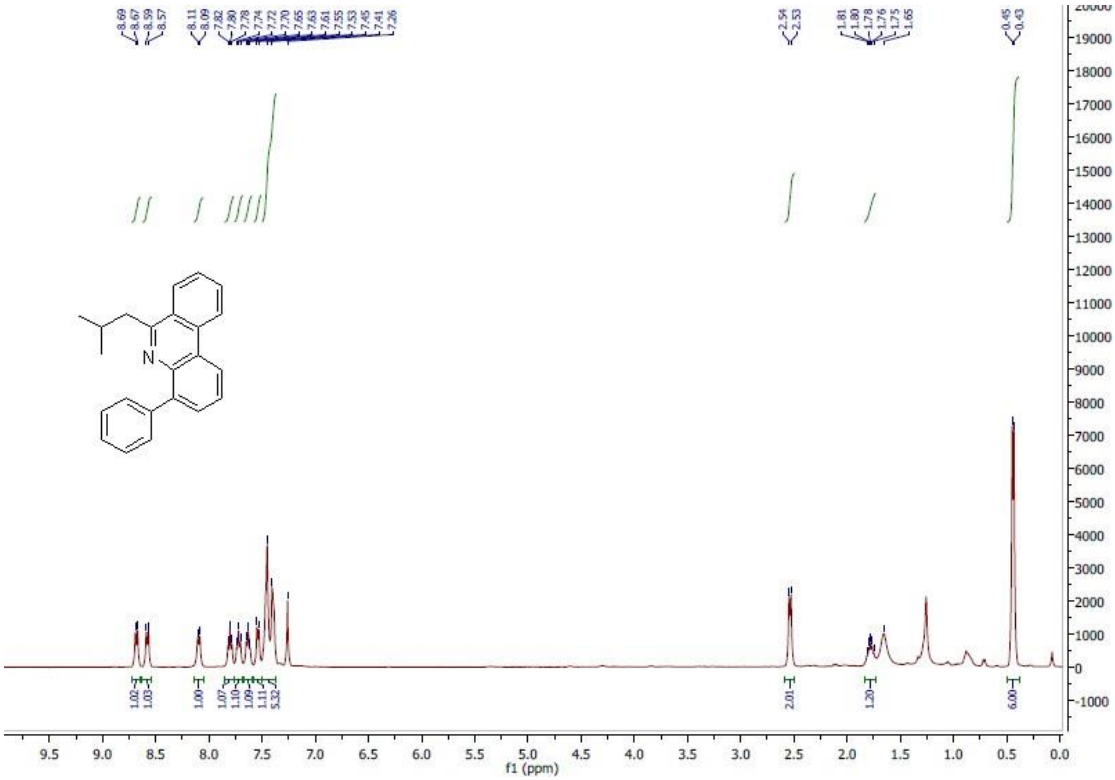


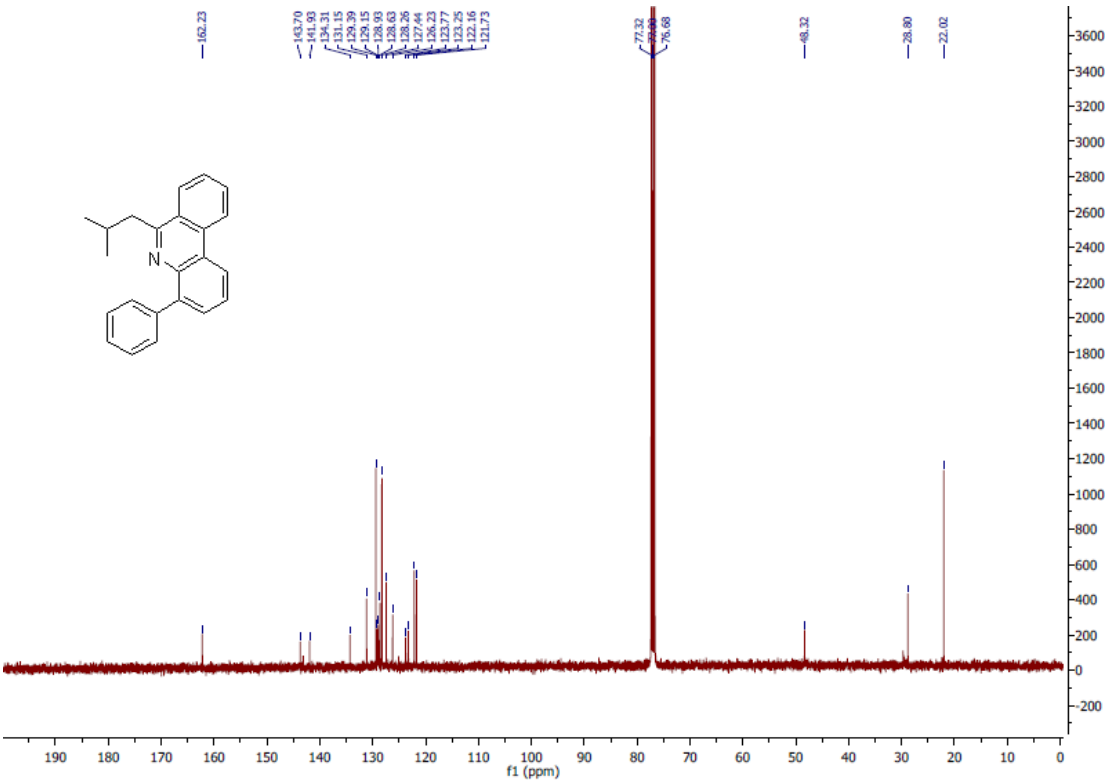
^{1}H and ^{13}{C} spectra of **3s**



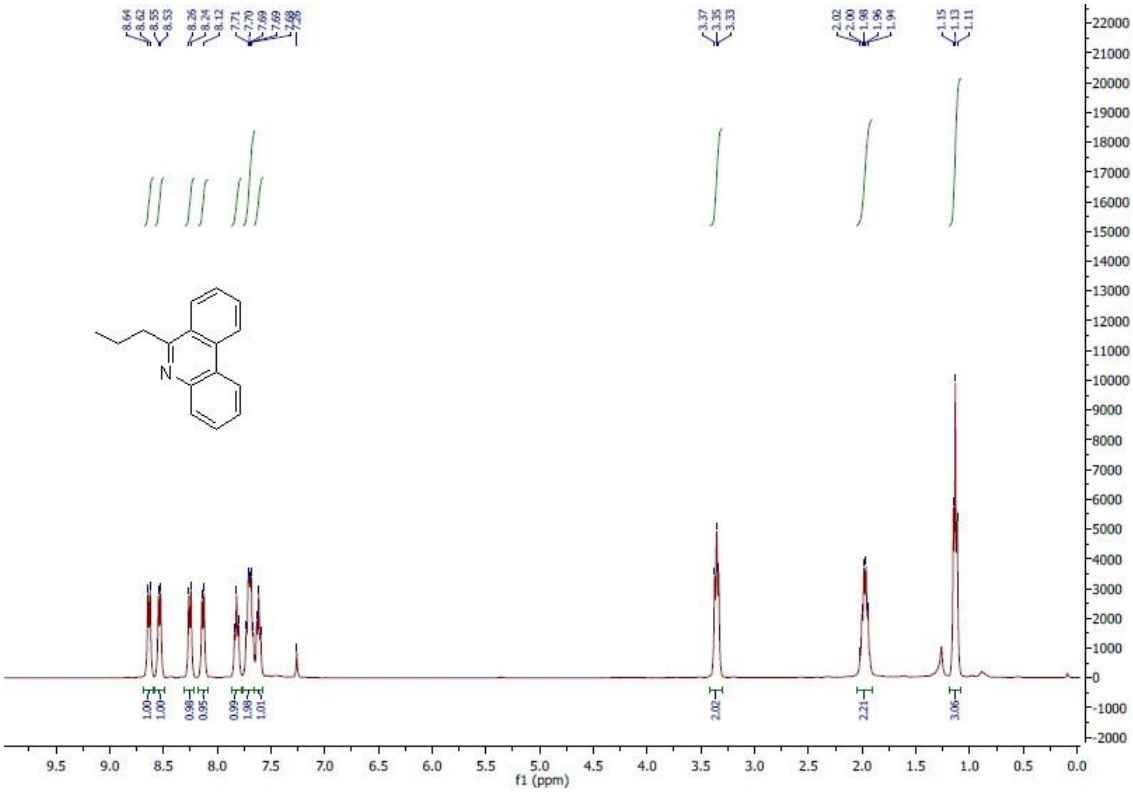


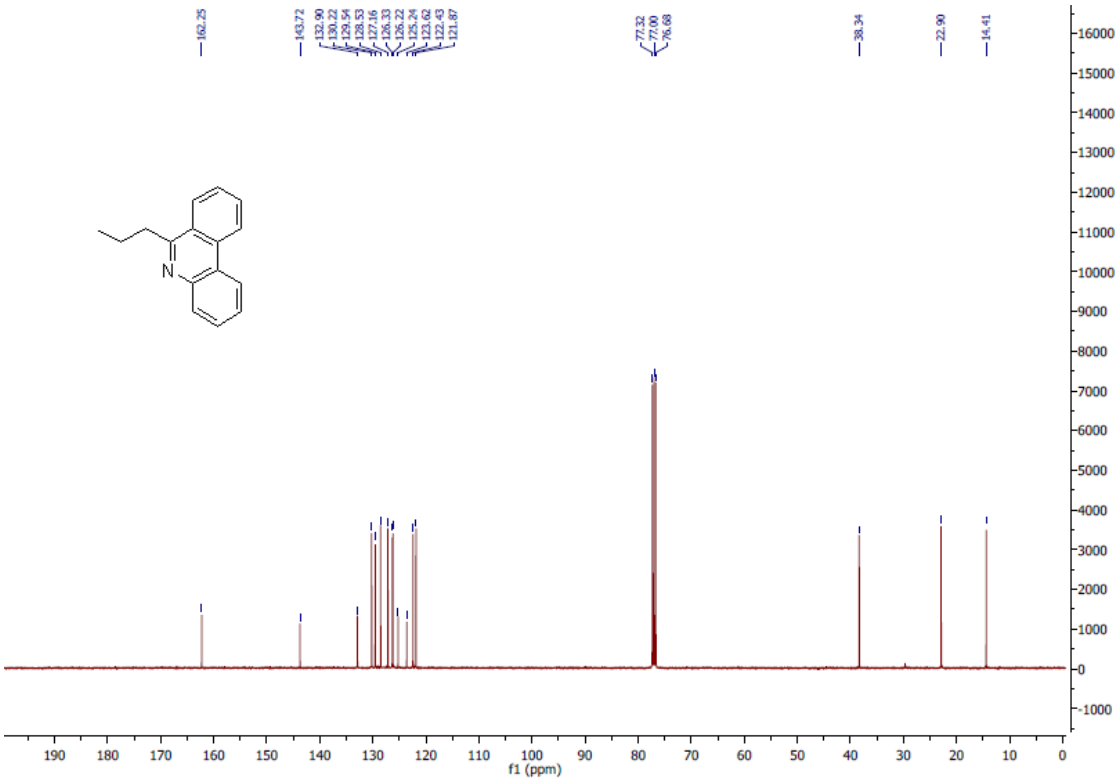
^{1}H and ^{13}{C} spectra of **3ss**



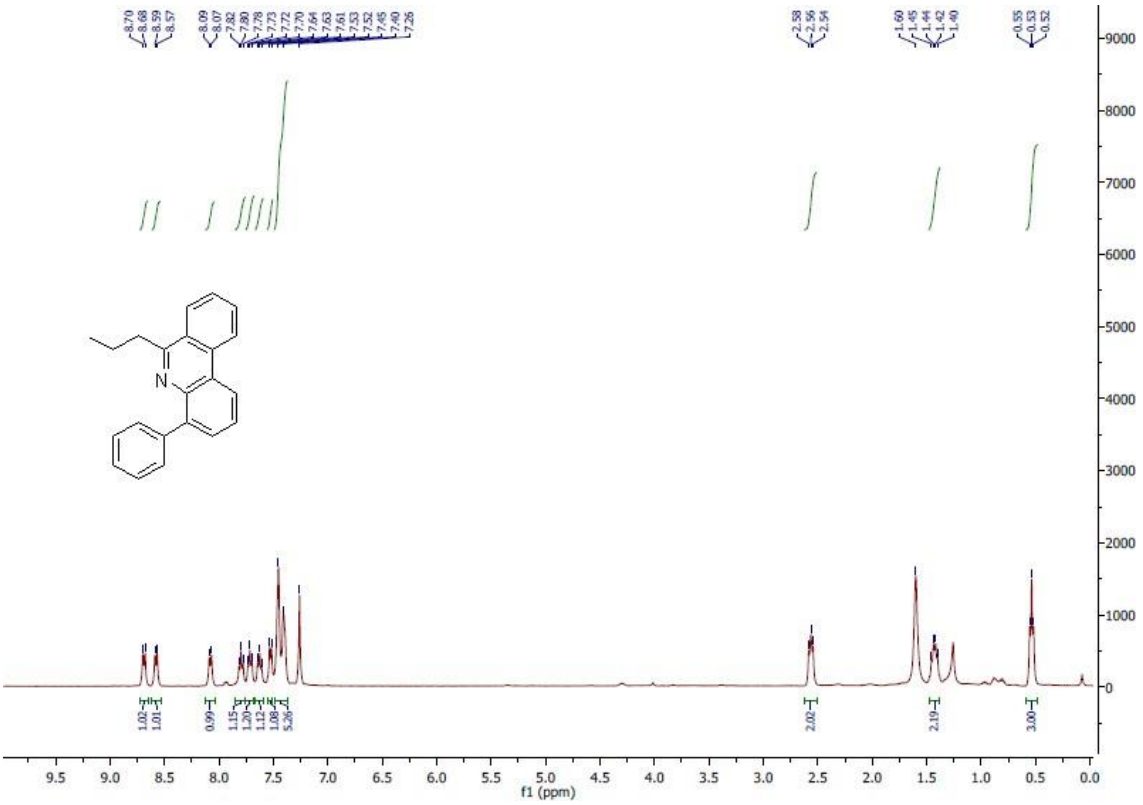


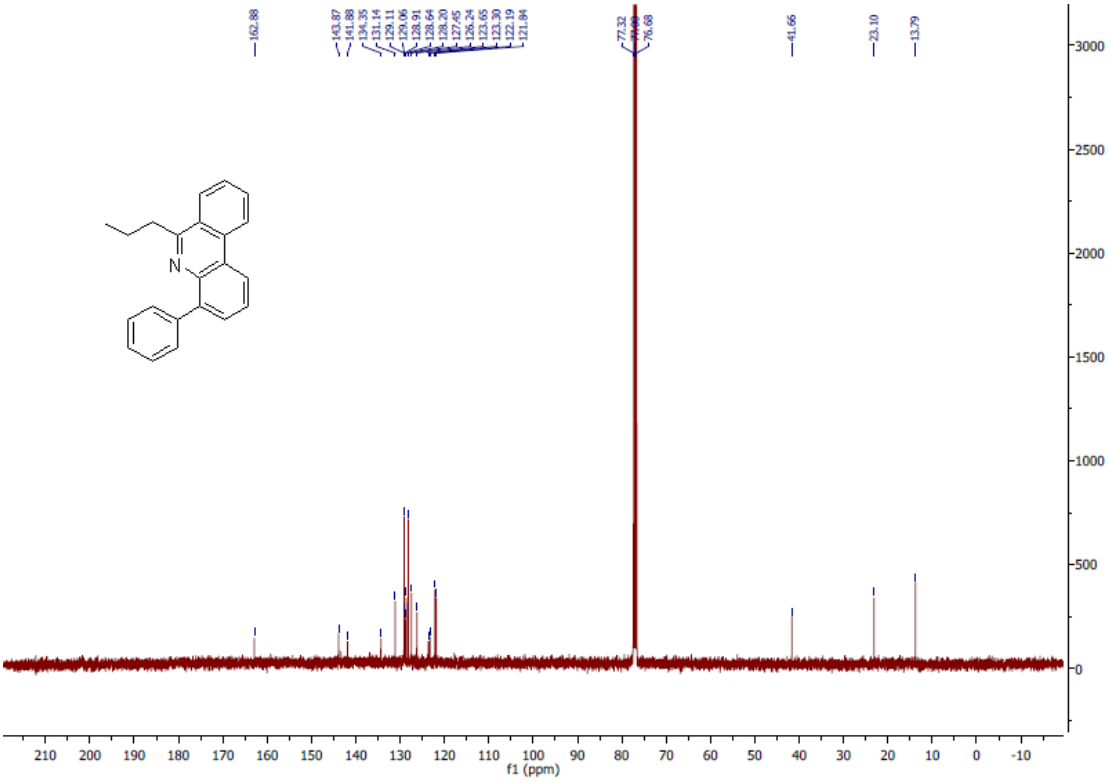
^{1}H and ^{13}{C} spectra of **3t**



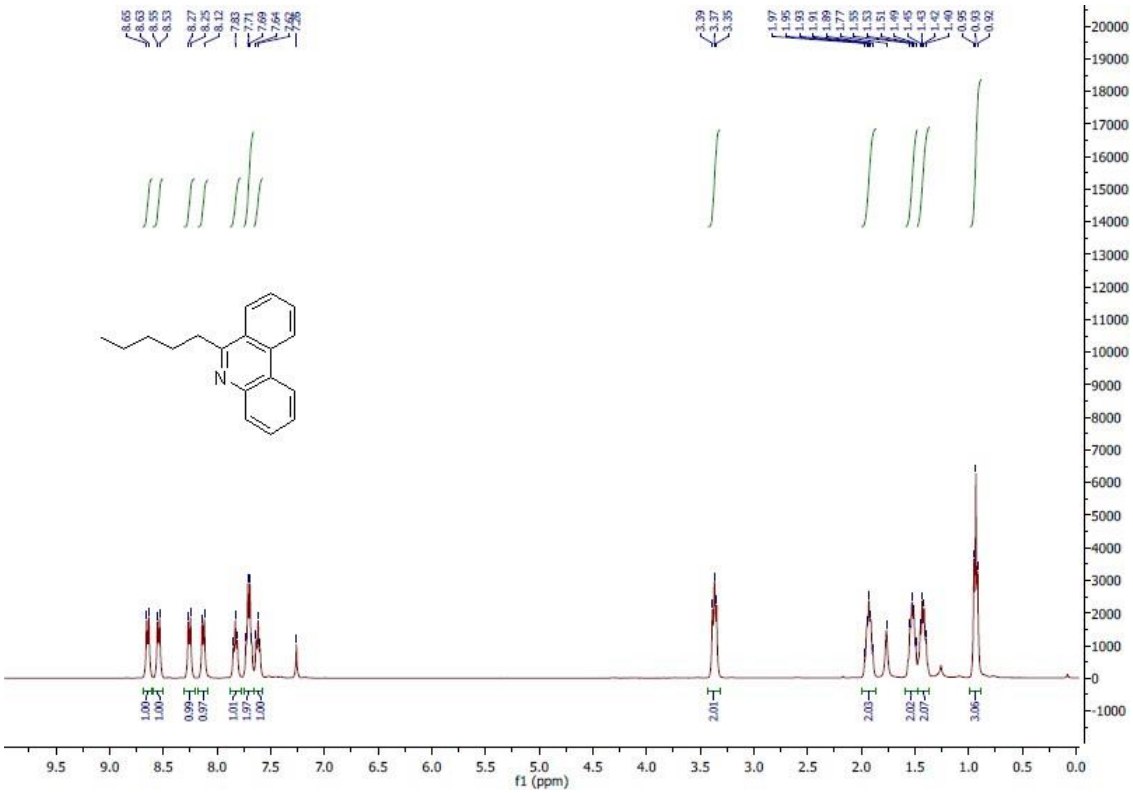


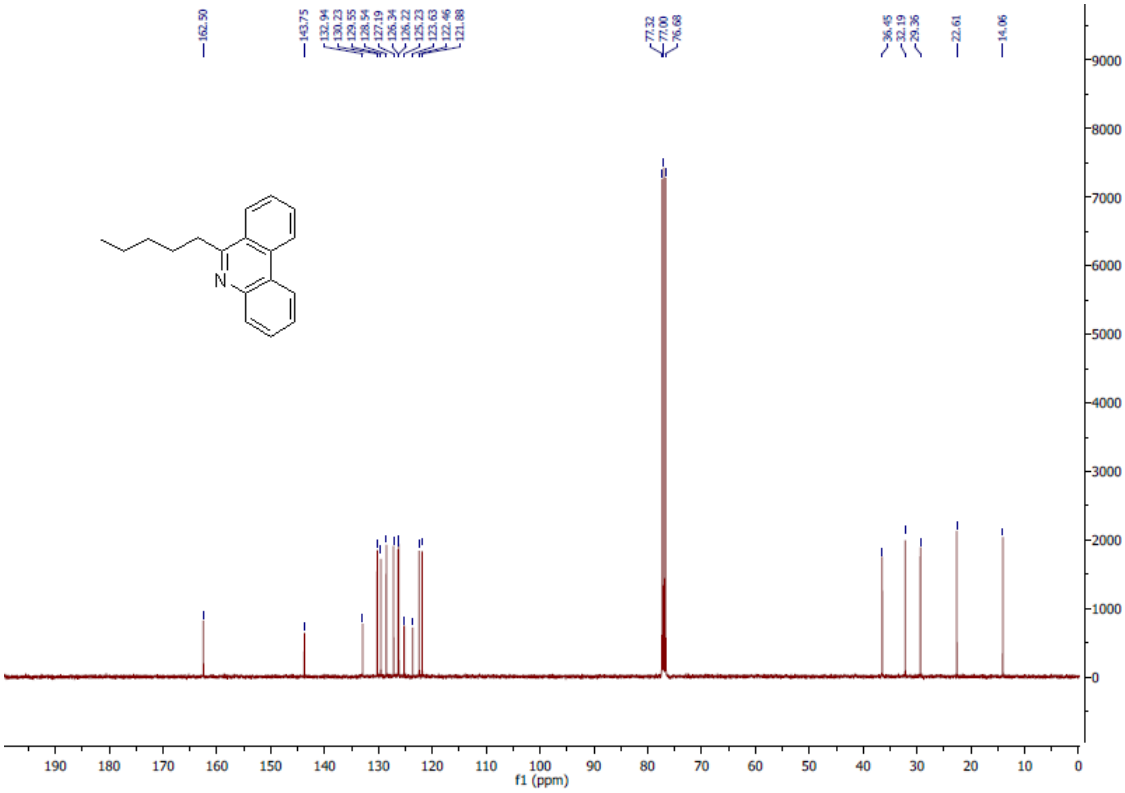
^{1}H and ^{13}\{C\} spectra of **3tt**



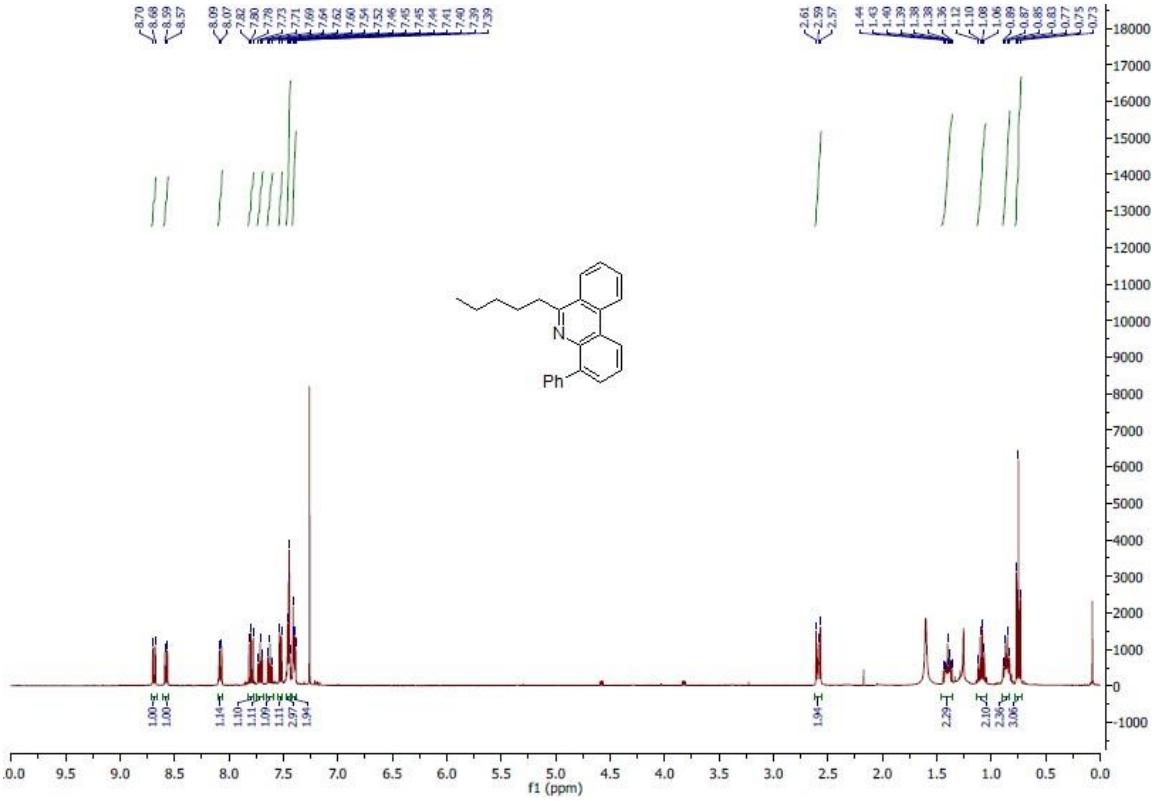


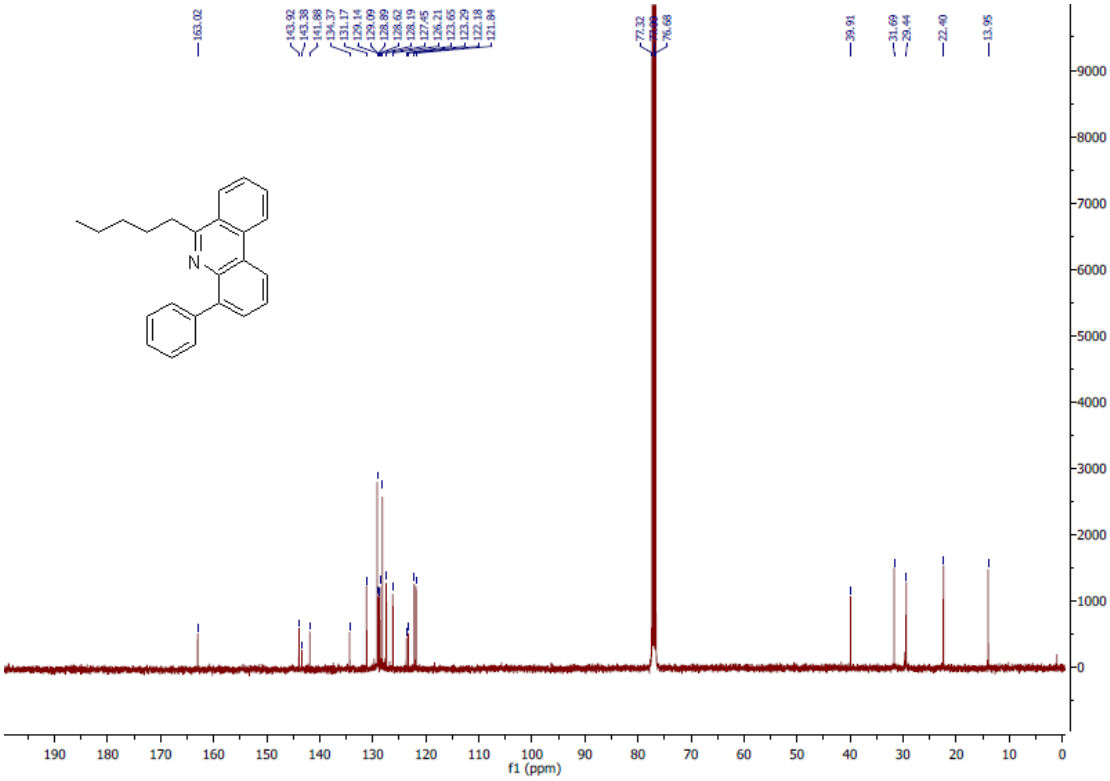
^{1}H and ^{13}{C} spectra of **3u**



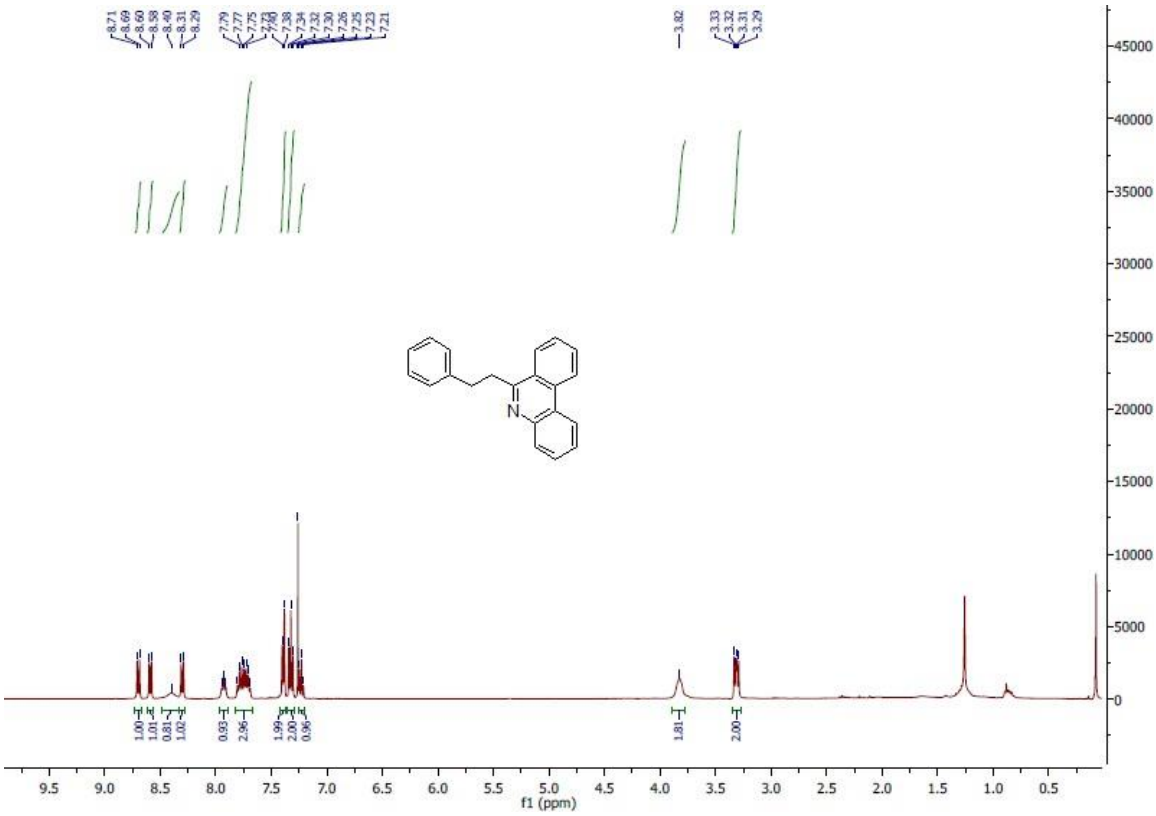


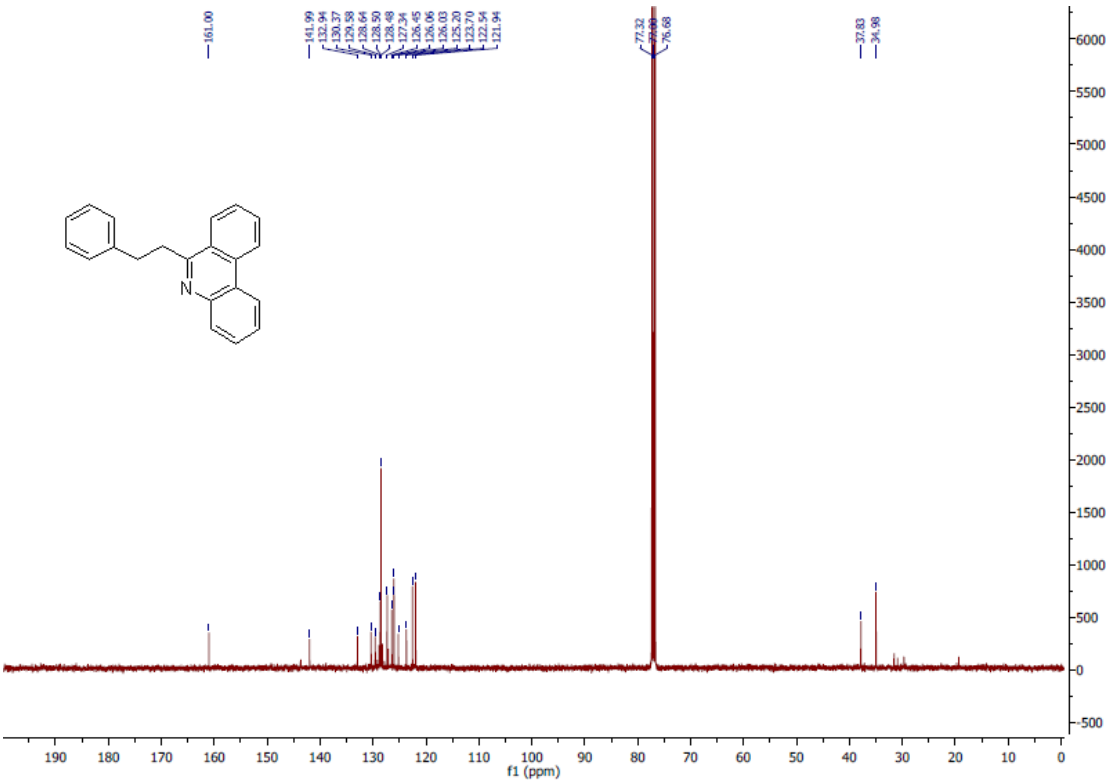
^{1}H and ^{13}\{C\} spectra of **3uu**



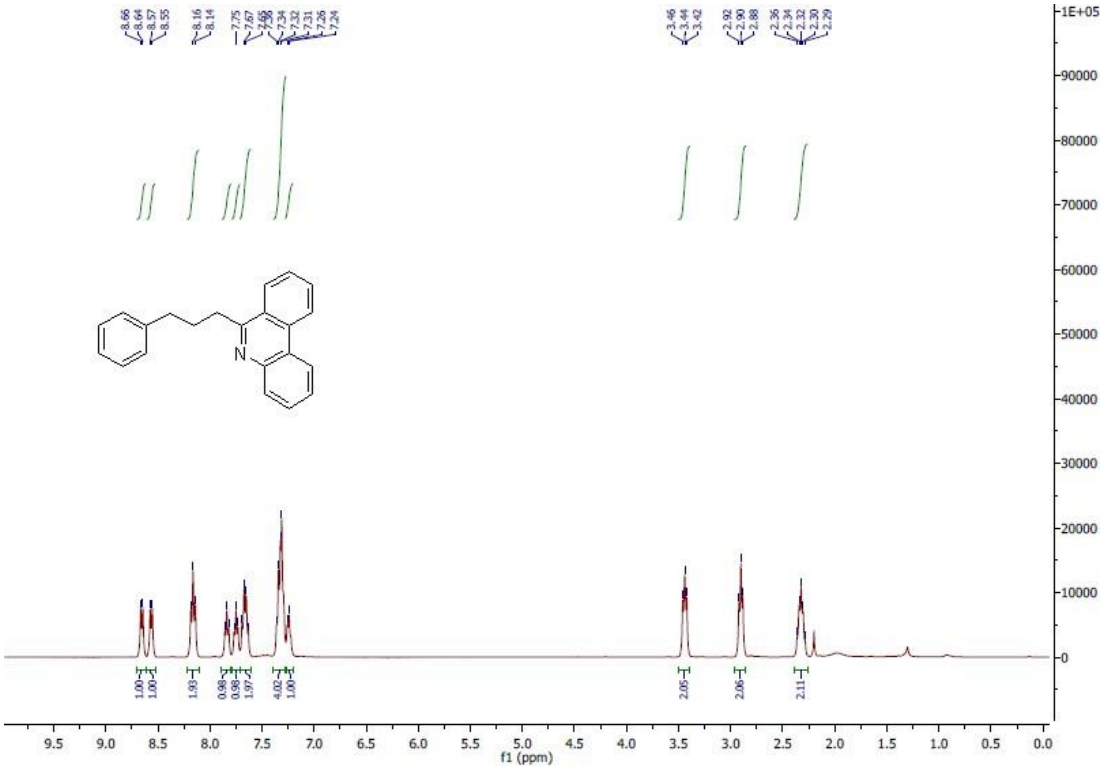


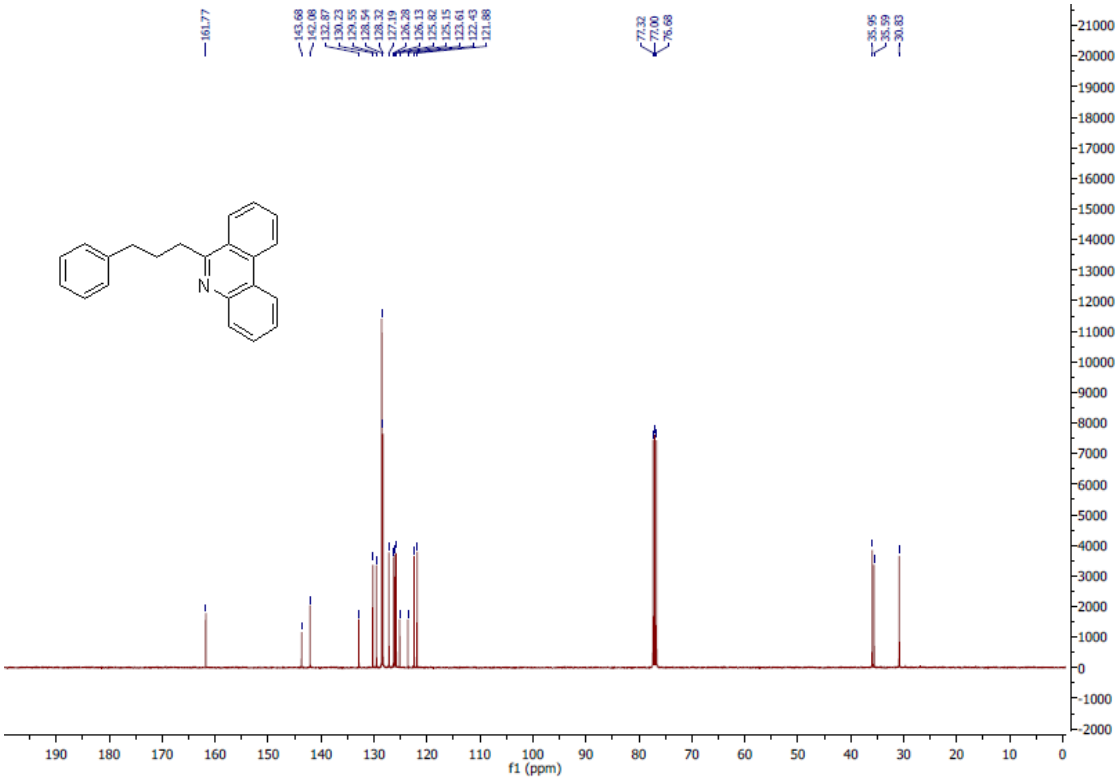
^{1}H and ^{13}{C} spectra of **3v**



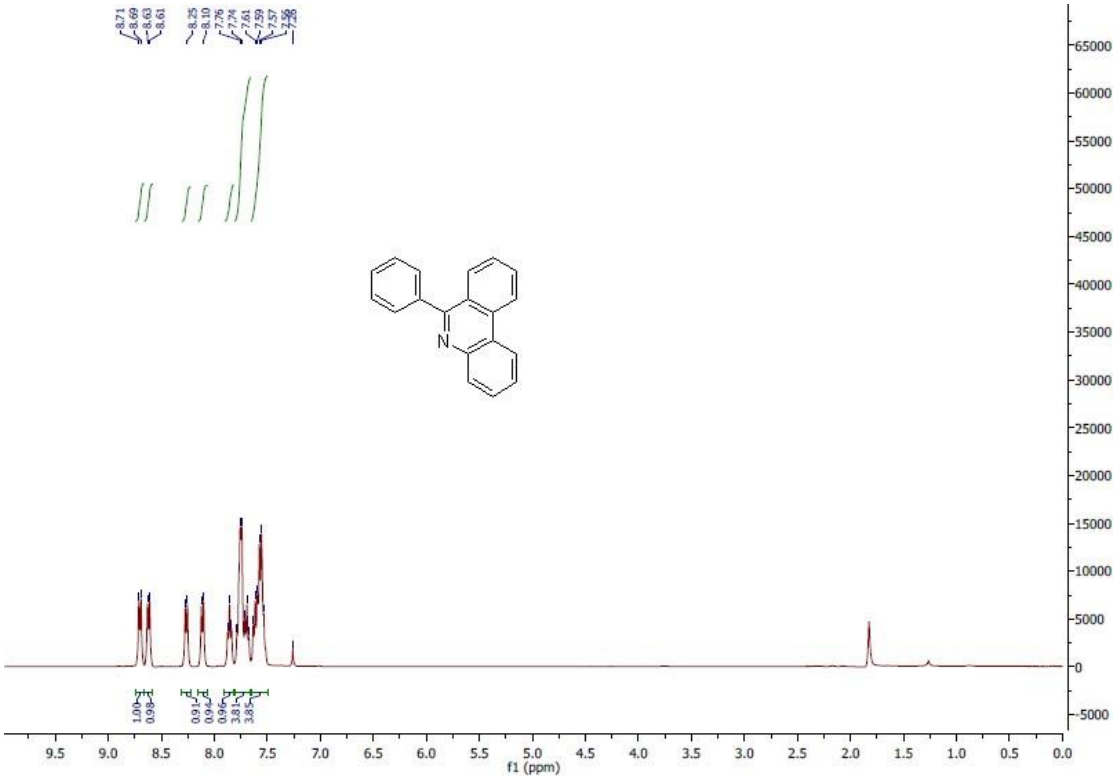


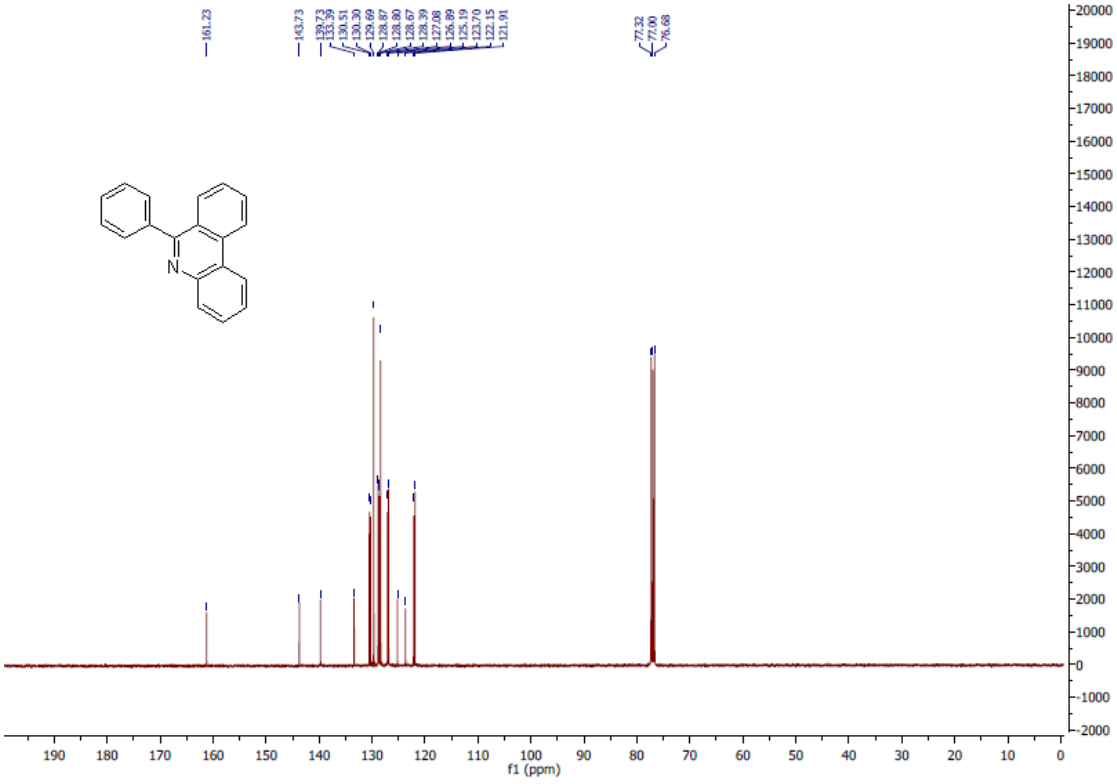
^{1}H and ^{13}\{C\} spectra of **3w**



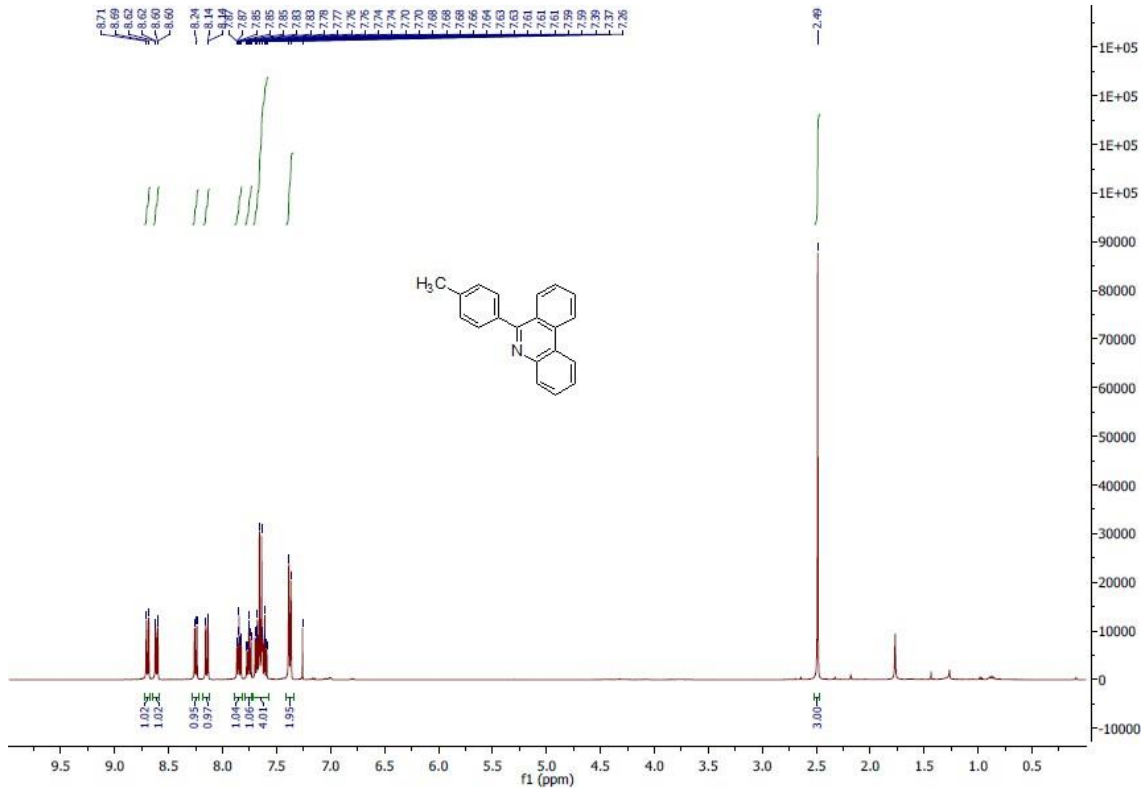


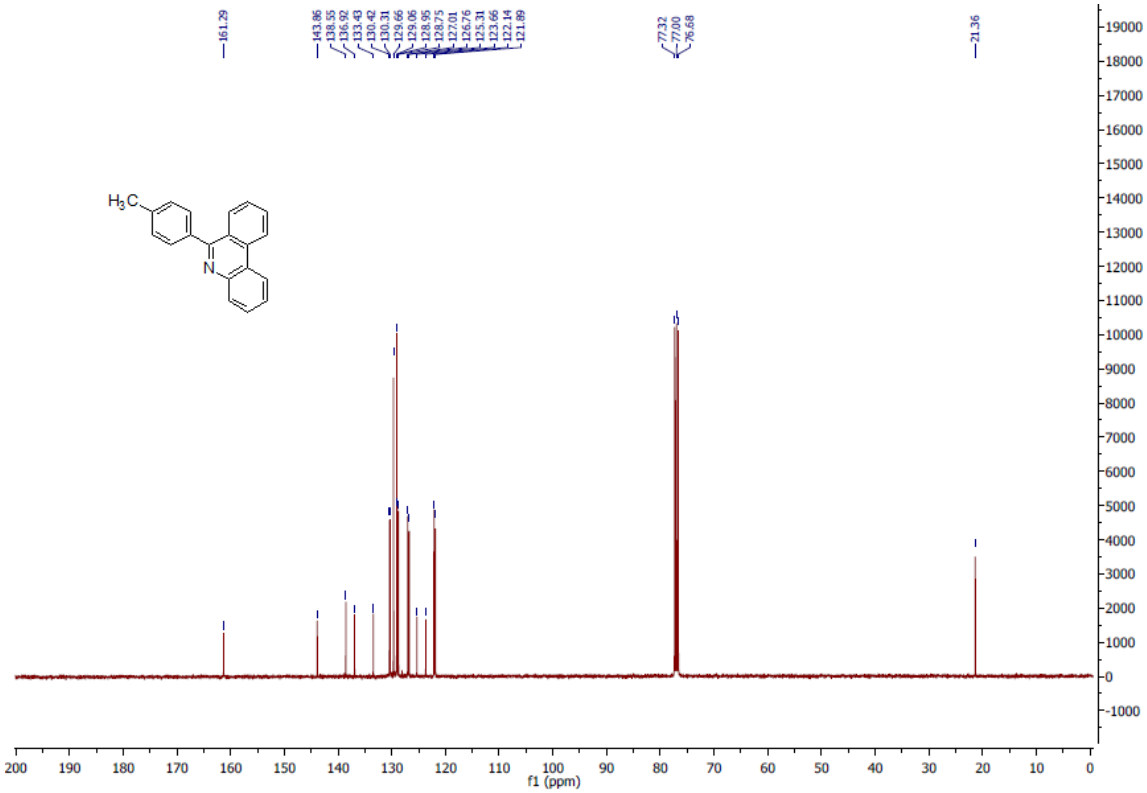
^{1}H and ^{13}{C} spectra of **5a**



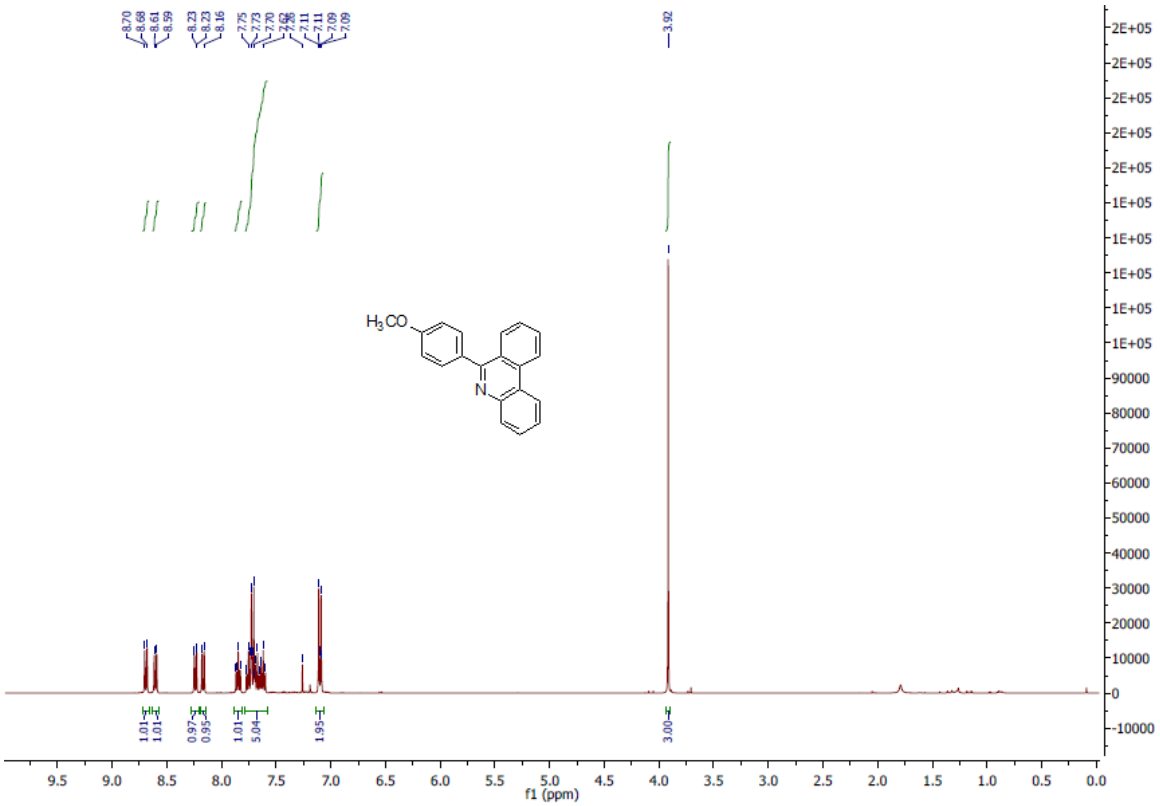


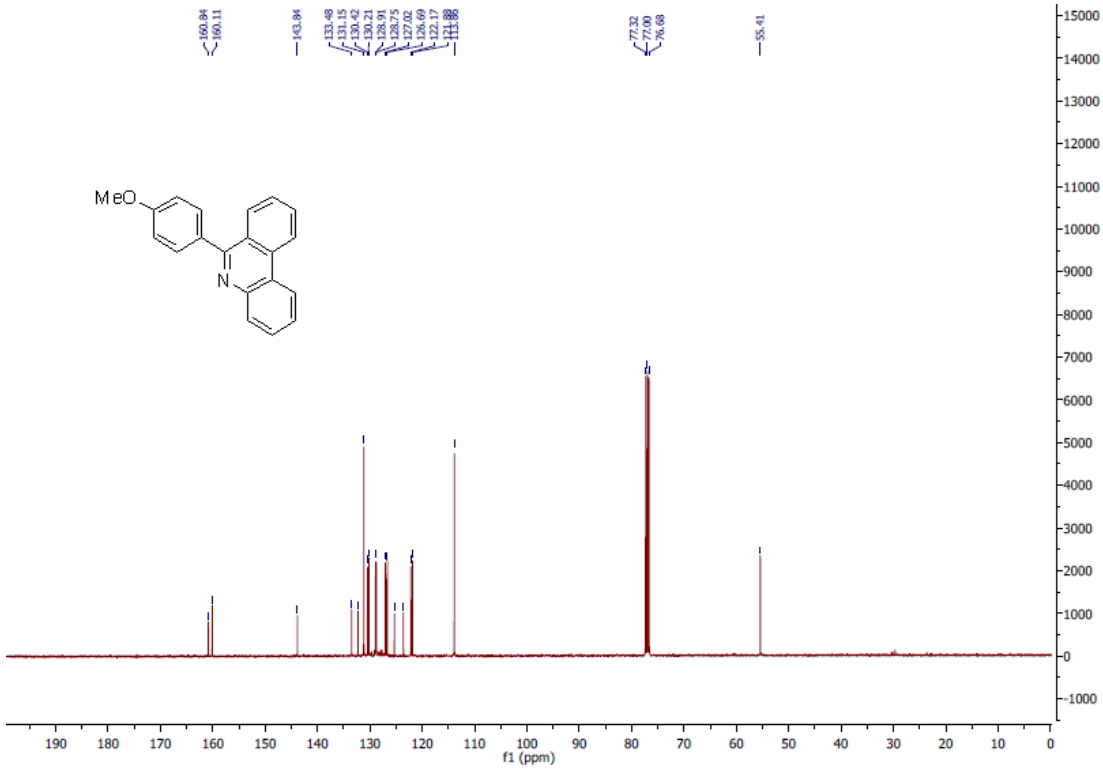
^{1}H and ^{13}\{C\} spectra of **5b**



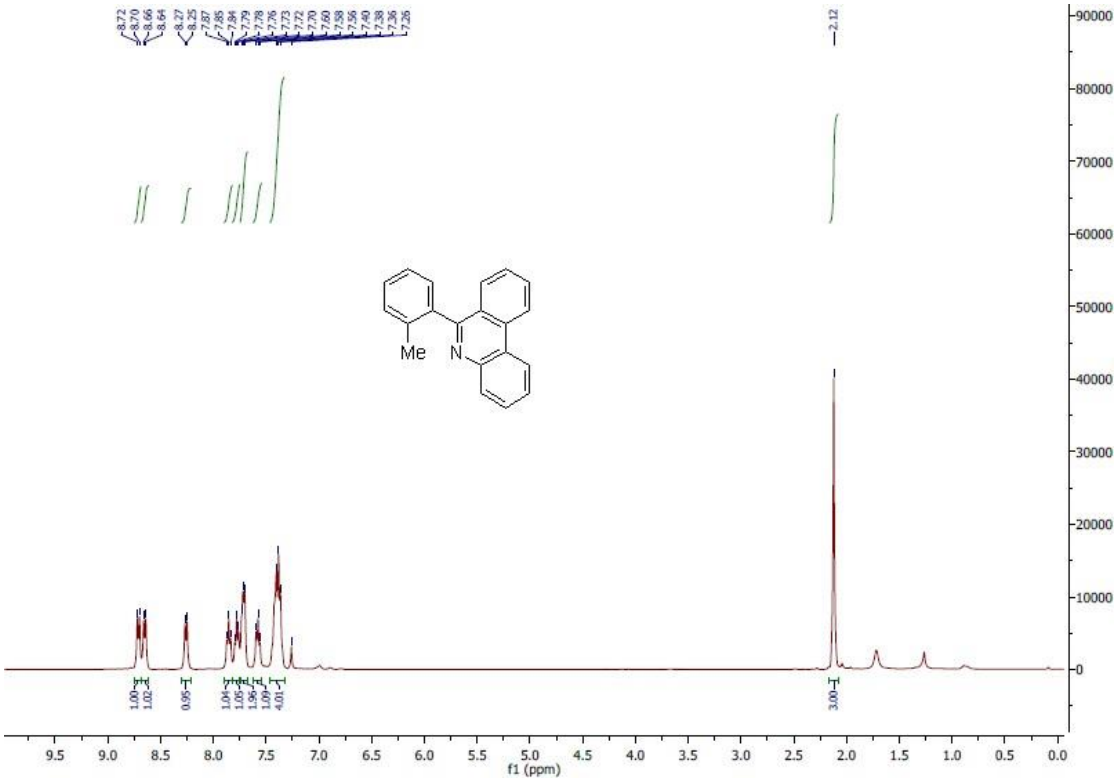


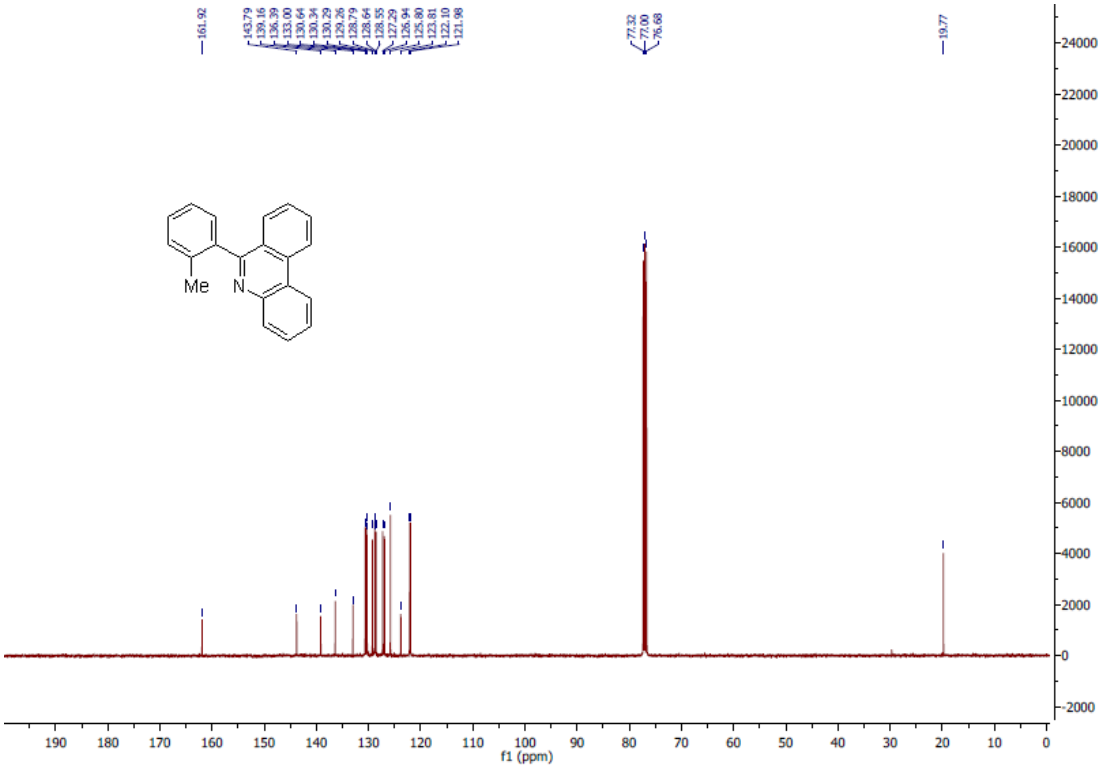
^{1}H and ^{13}{C} spectra of **5c**



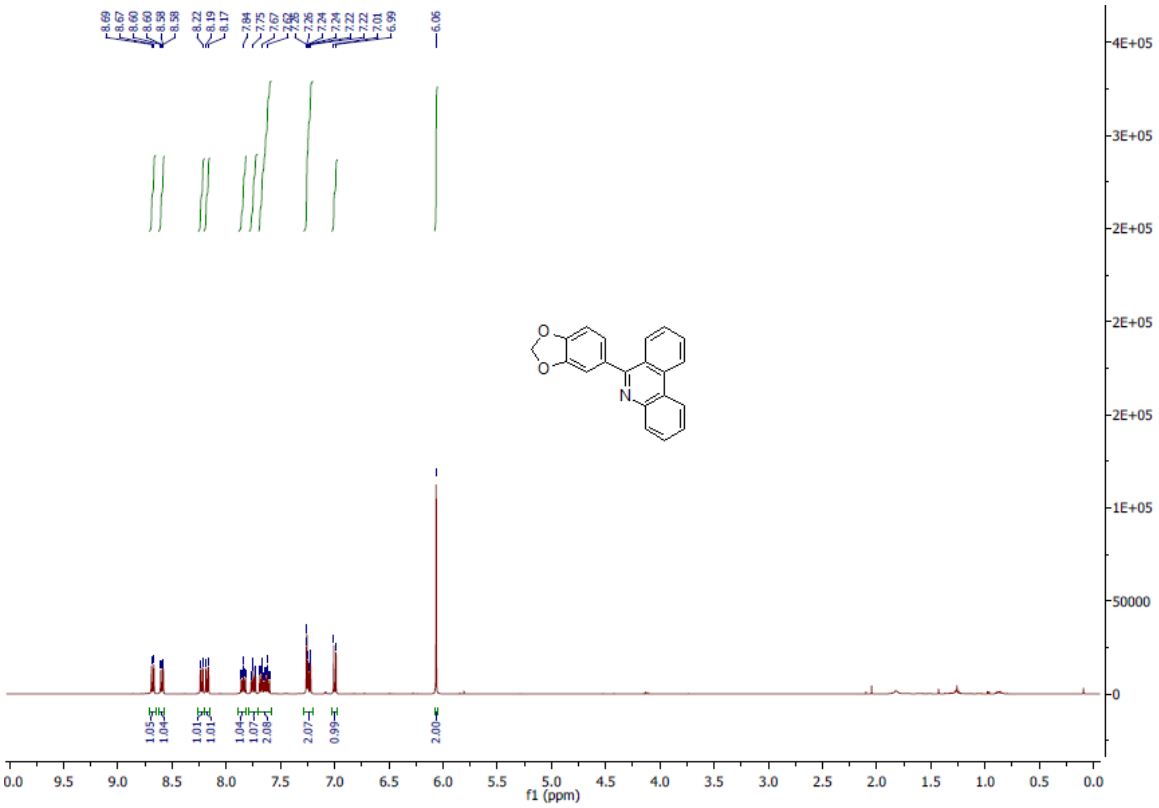


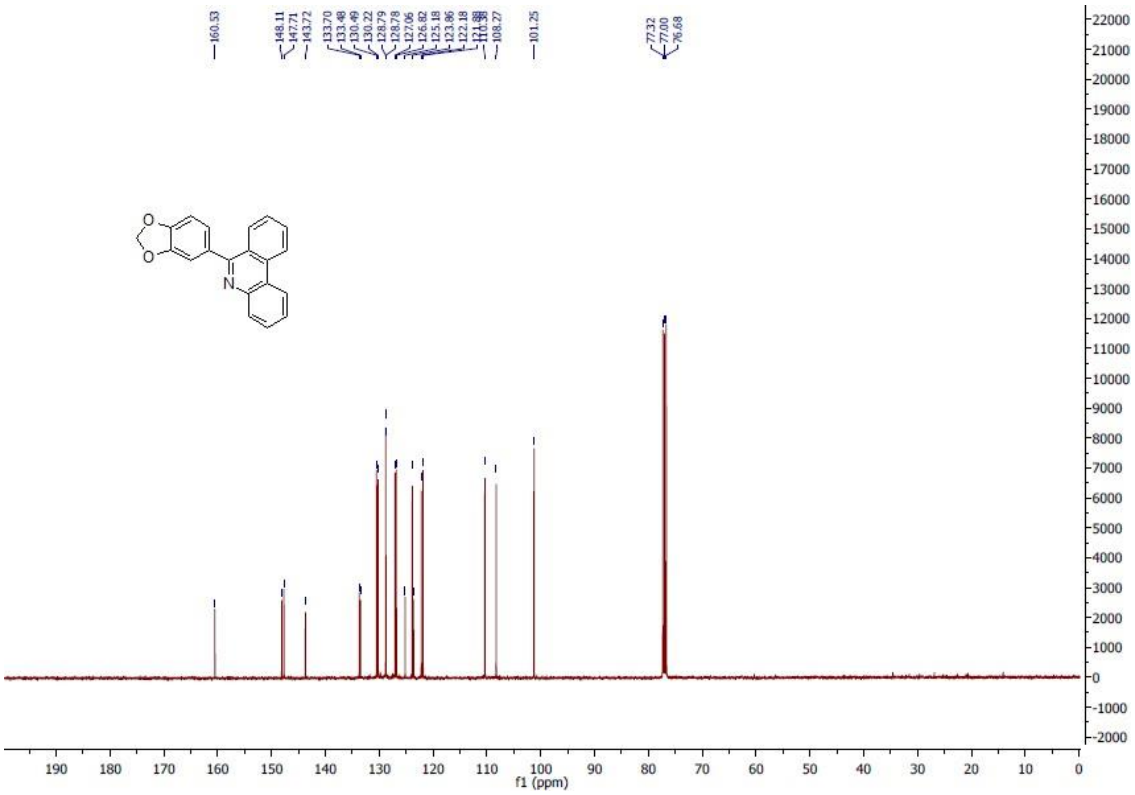
^{1}H and ^{13}{C} spectra of **5d**



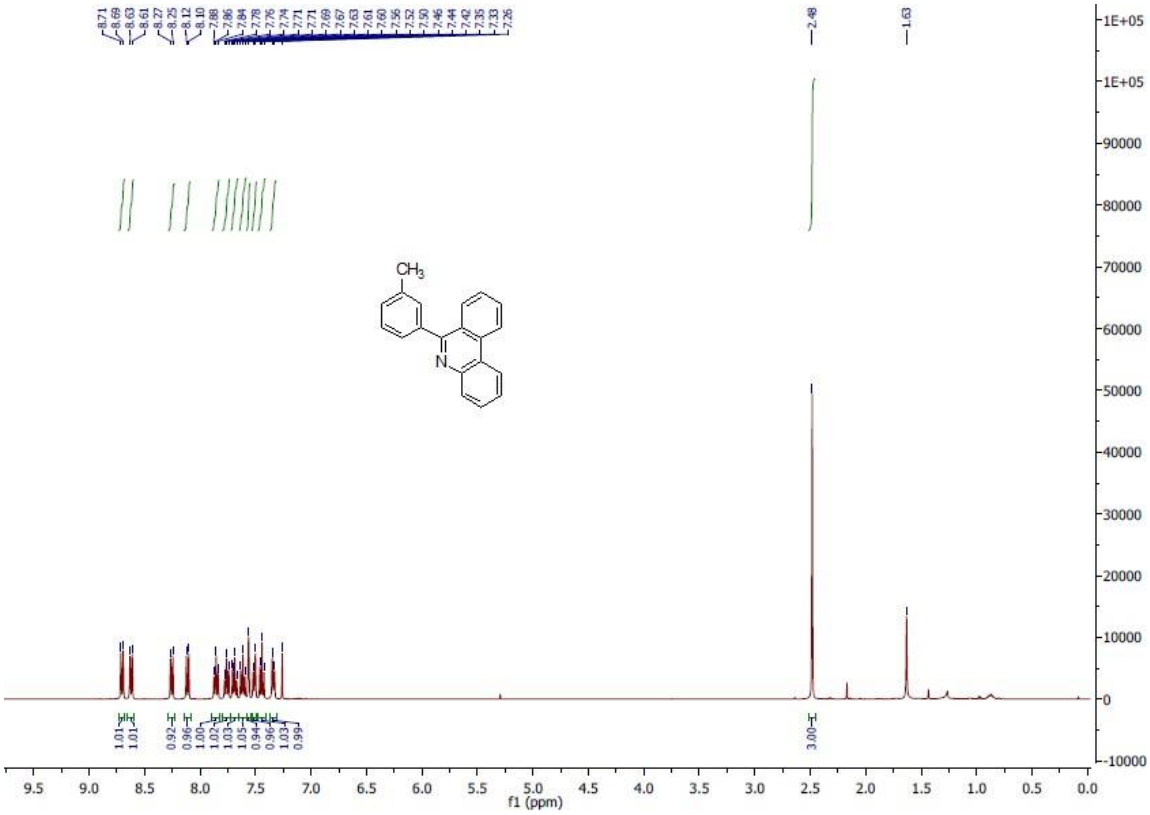


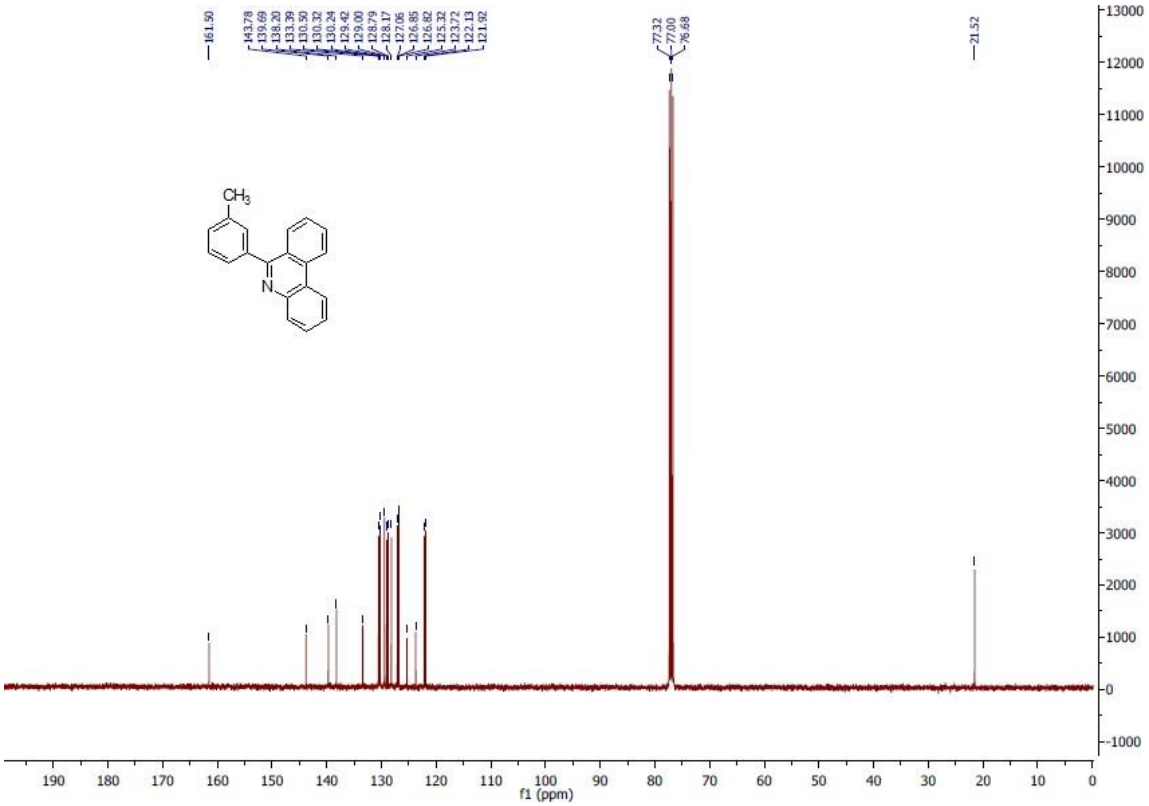
^{1}H and ^{13}{C} spectra of **5e**



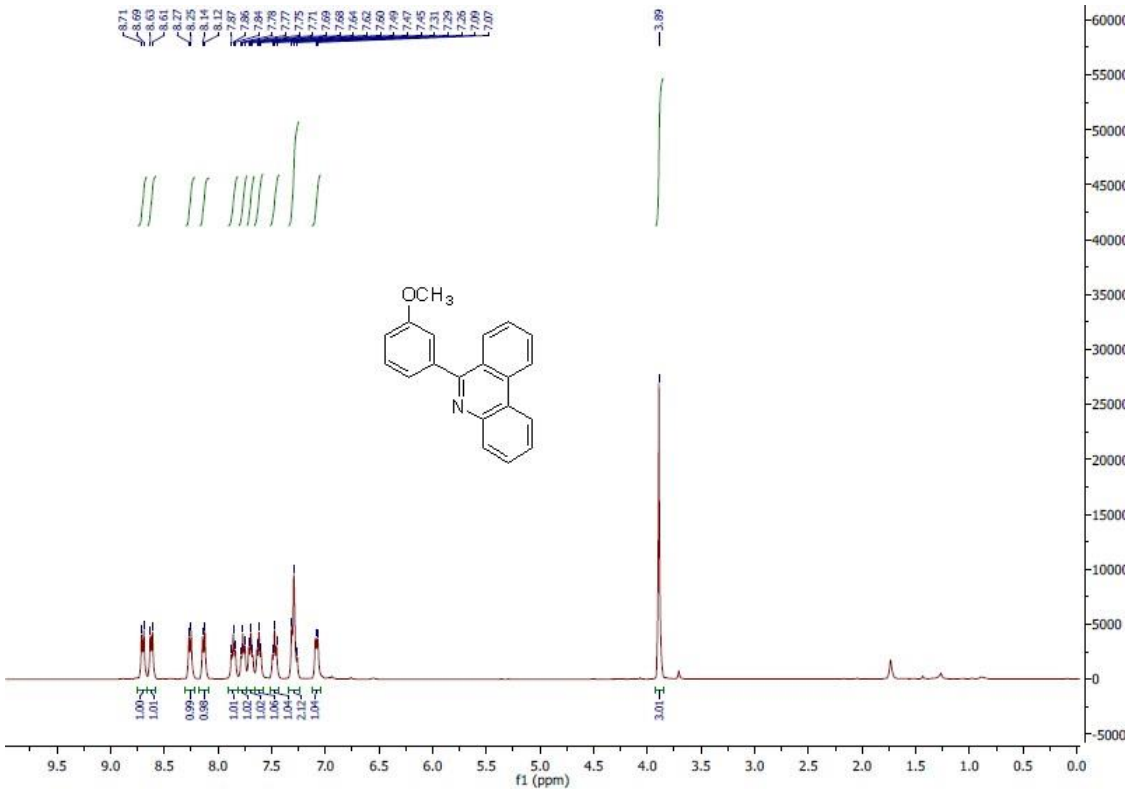


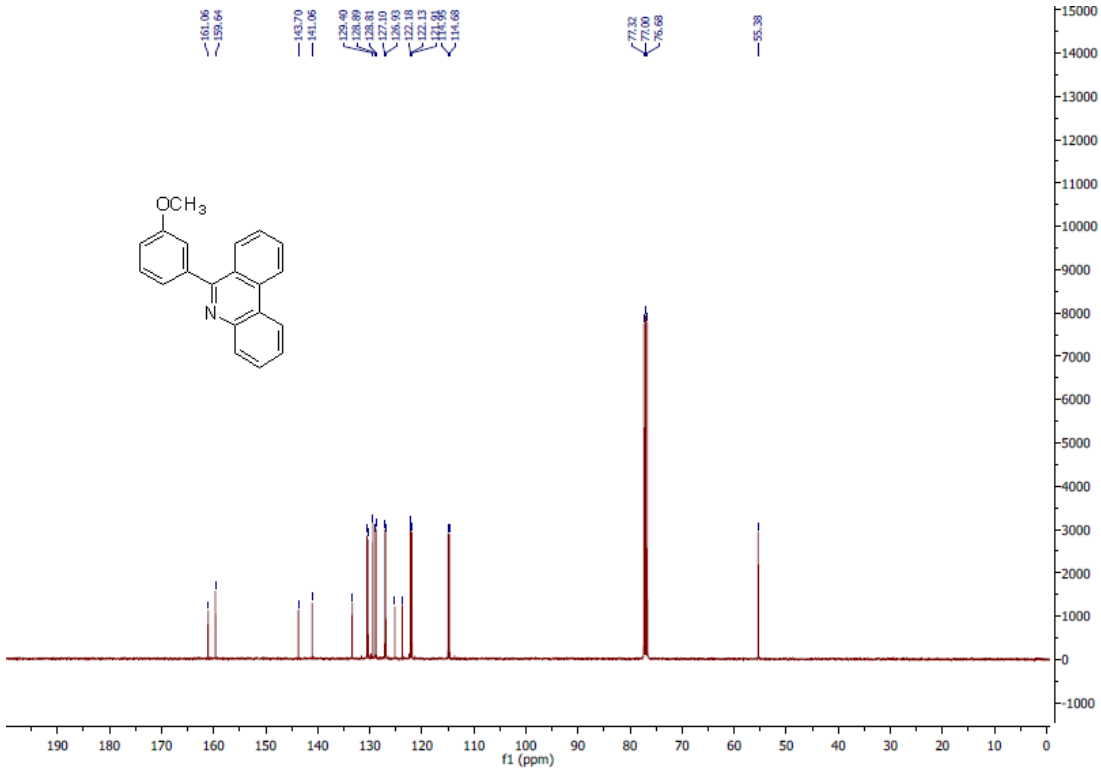
^{1}H and ^{13}\{C\} spectra of **5f**



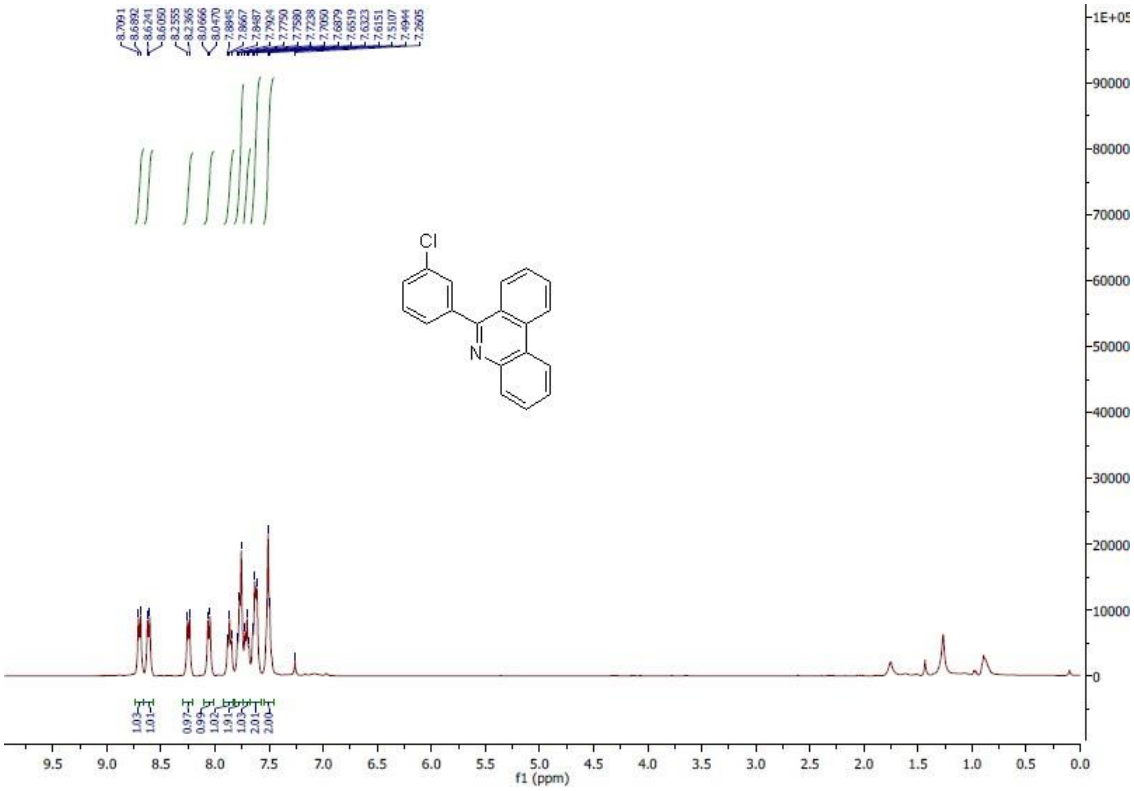


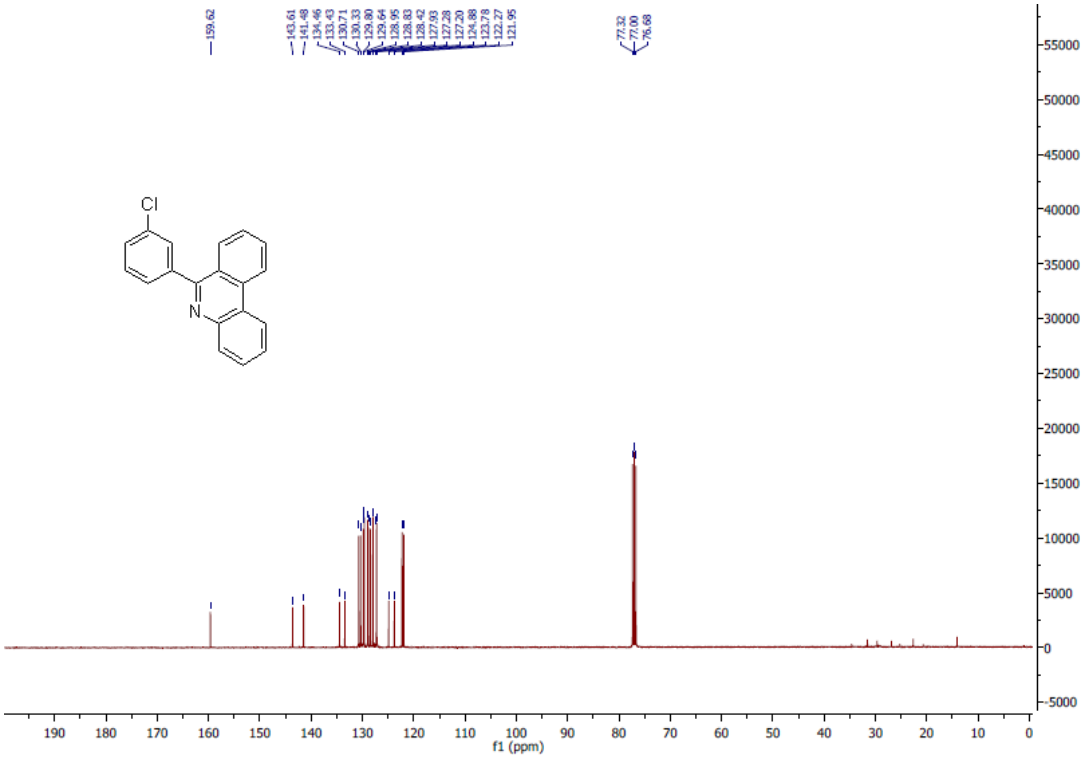
^{1}H and ^{13}{C} spectra of **5g**



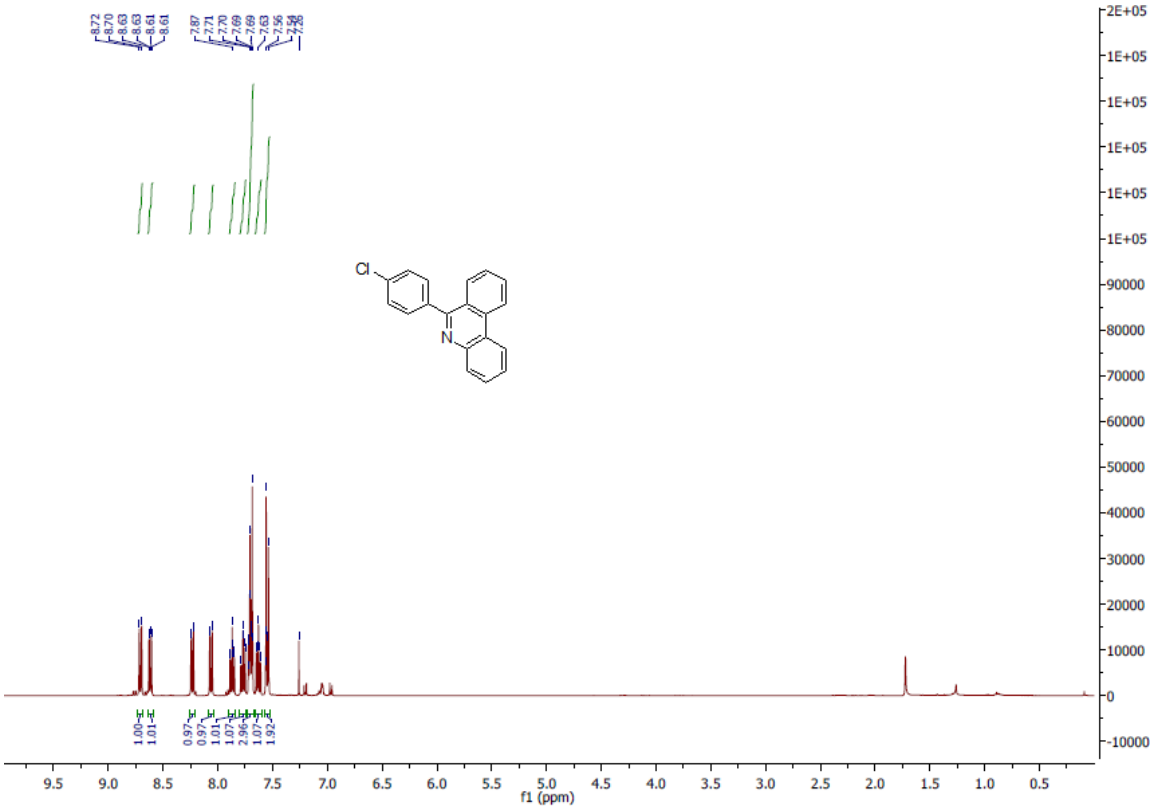


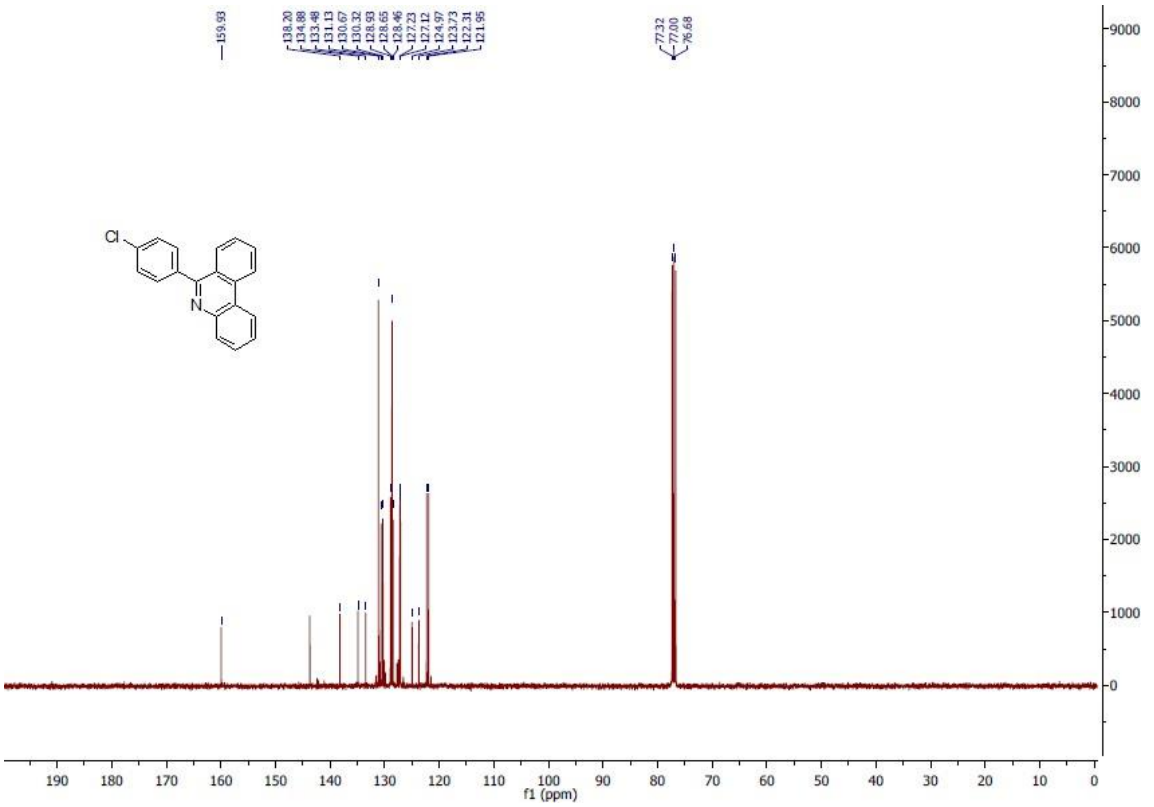
^{1}H and ^{13}{C} spectra of **5h**



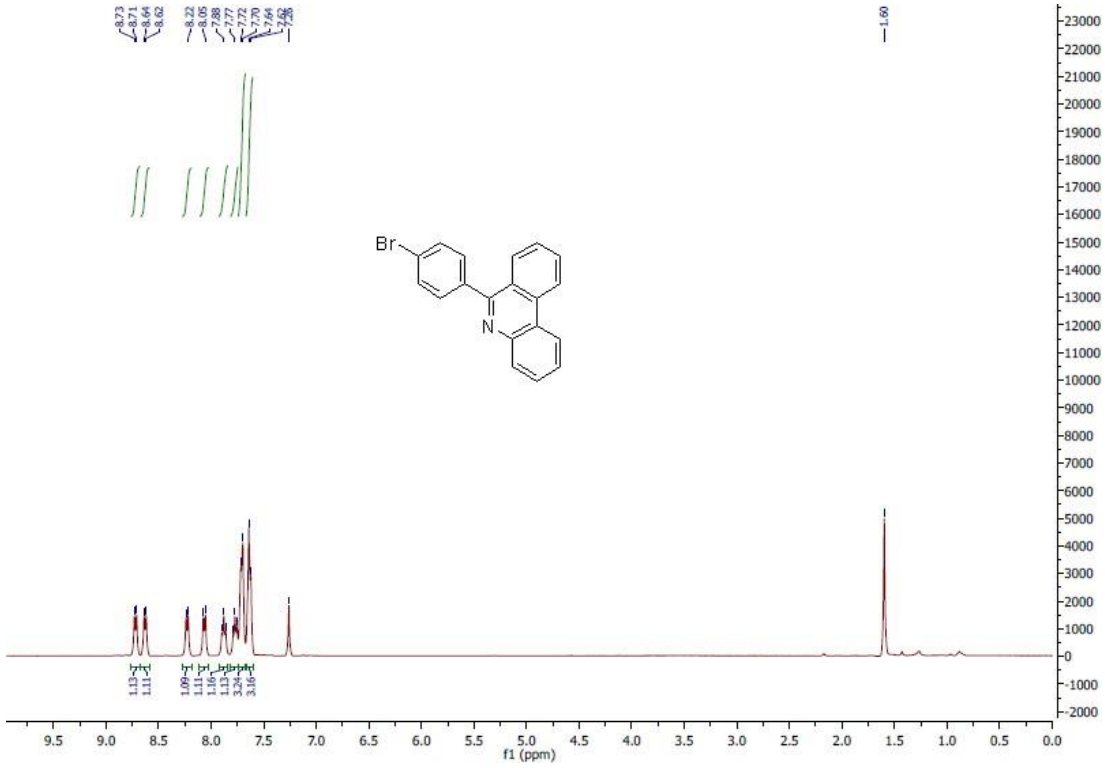


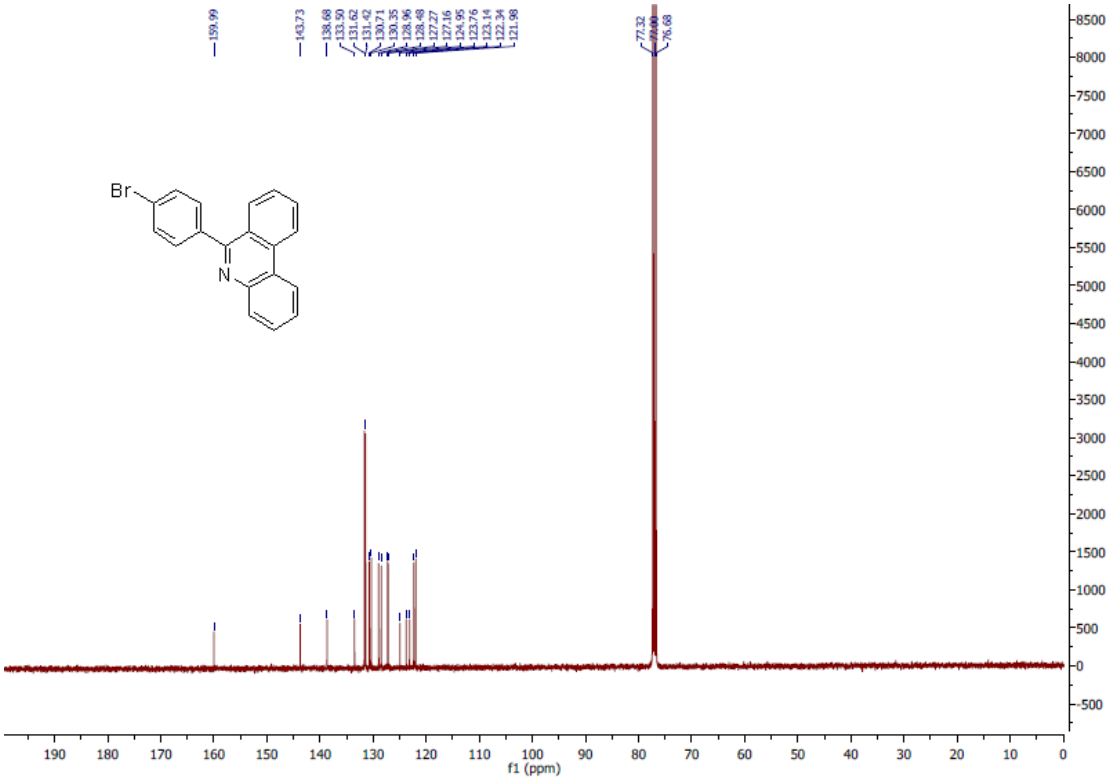
^{1}H and ^{13}{C} spectra of **5i**



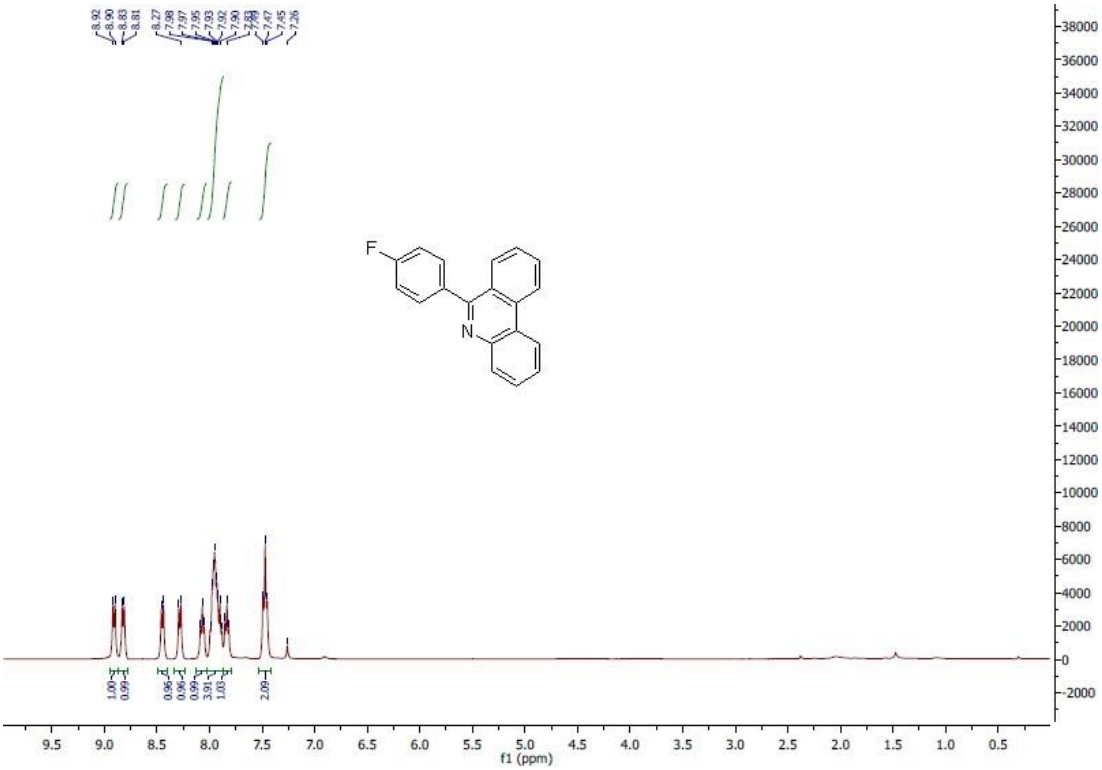


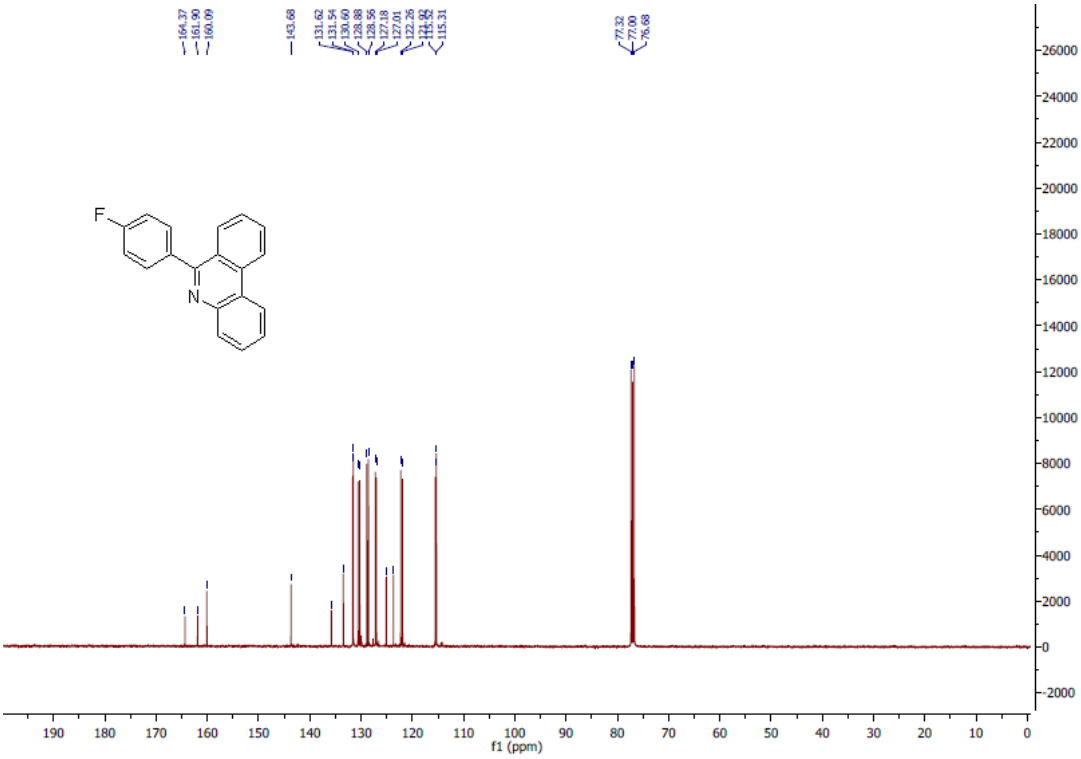
^{1}H and ^{13}\{C\} spectra of **5j**



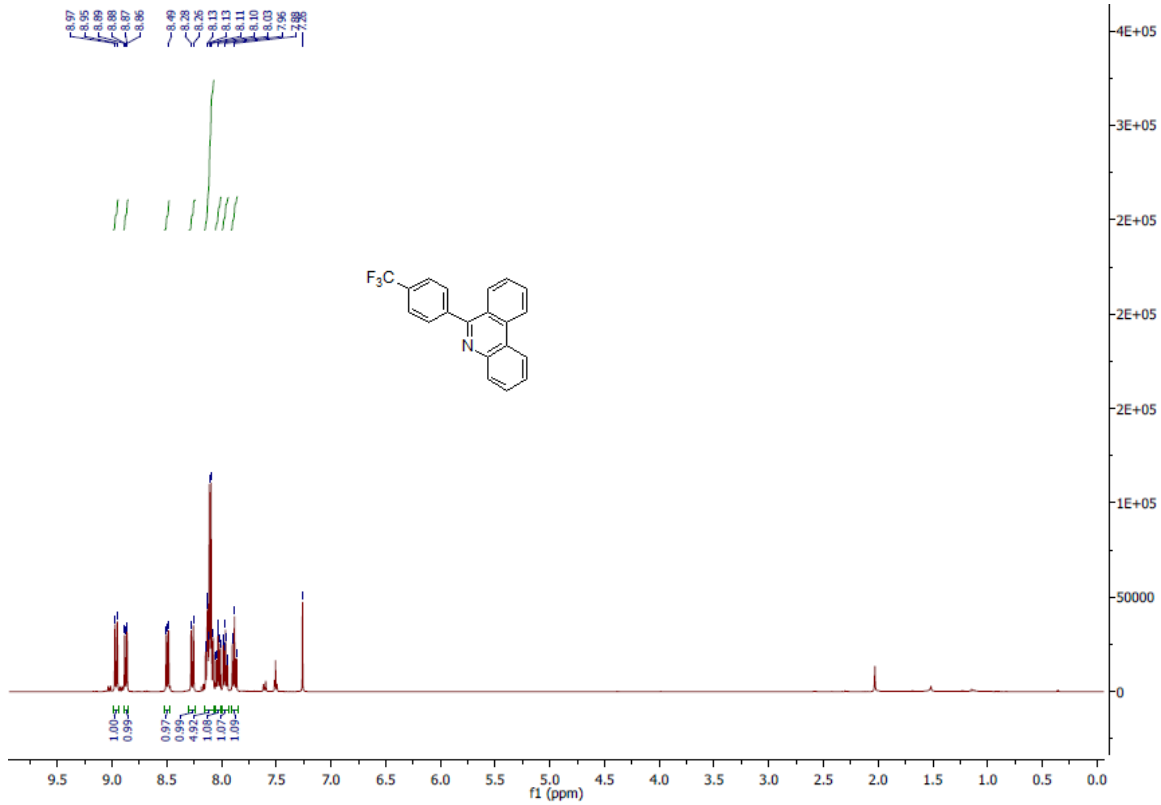


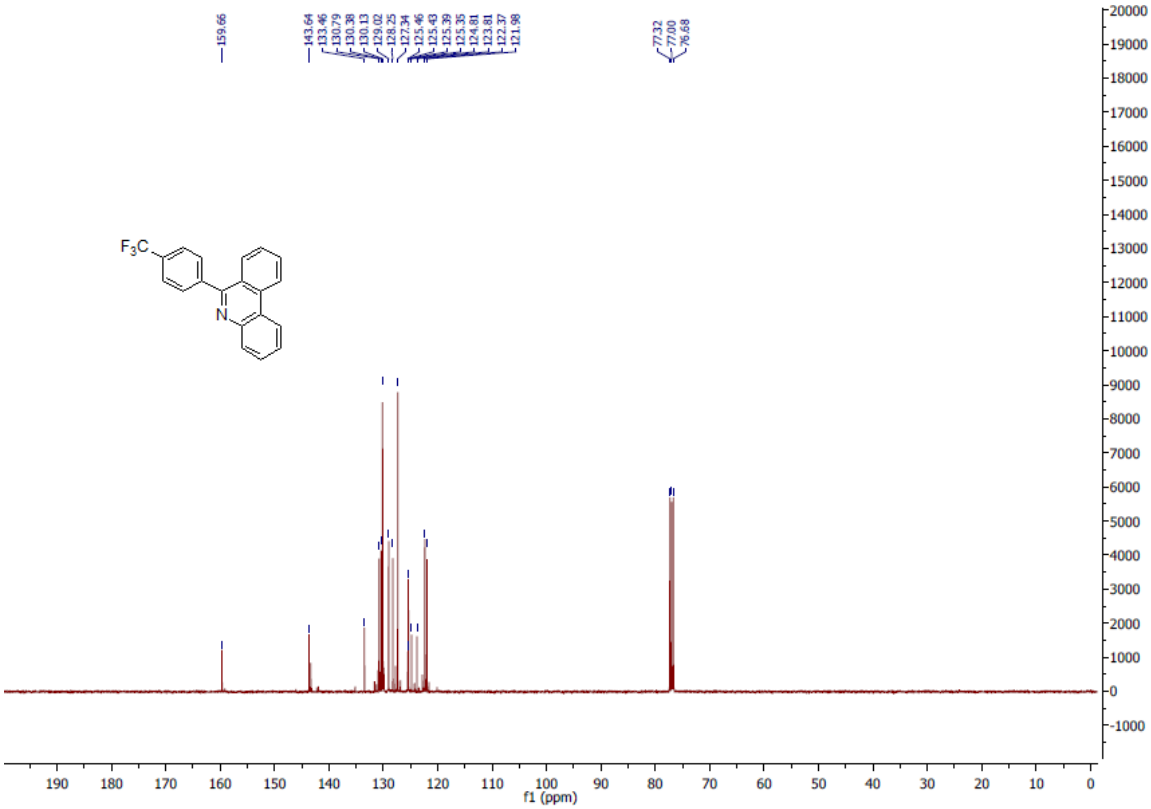
^{1}H and ^{13}{C} spectra of **5k**



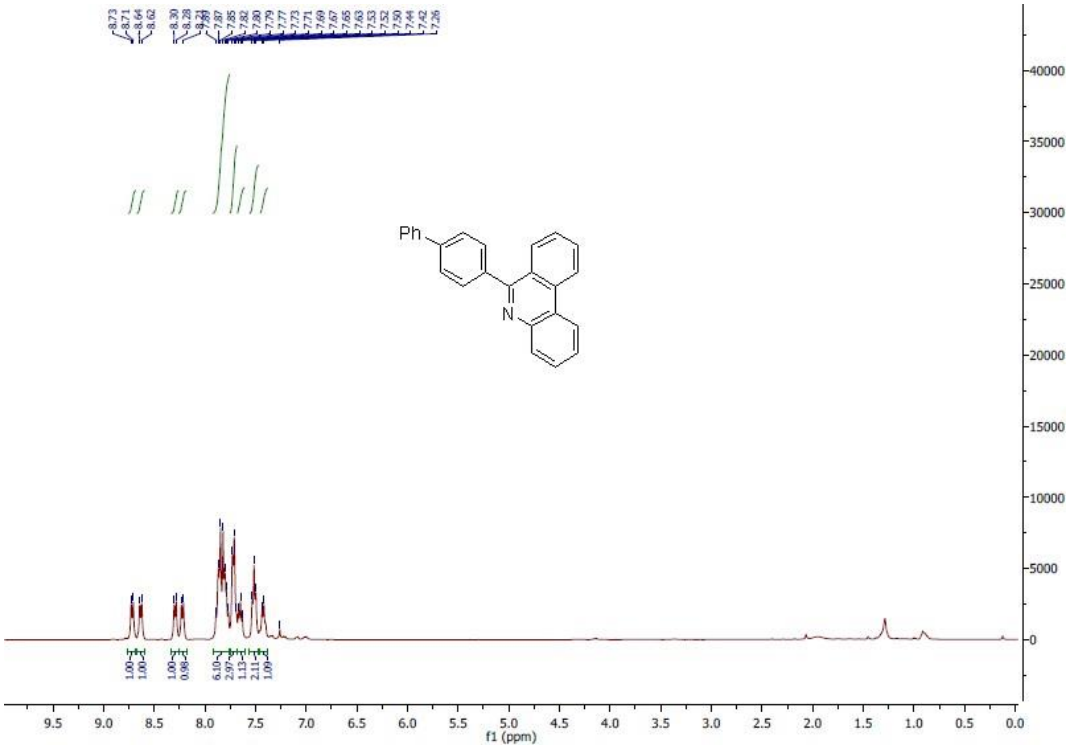


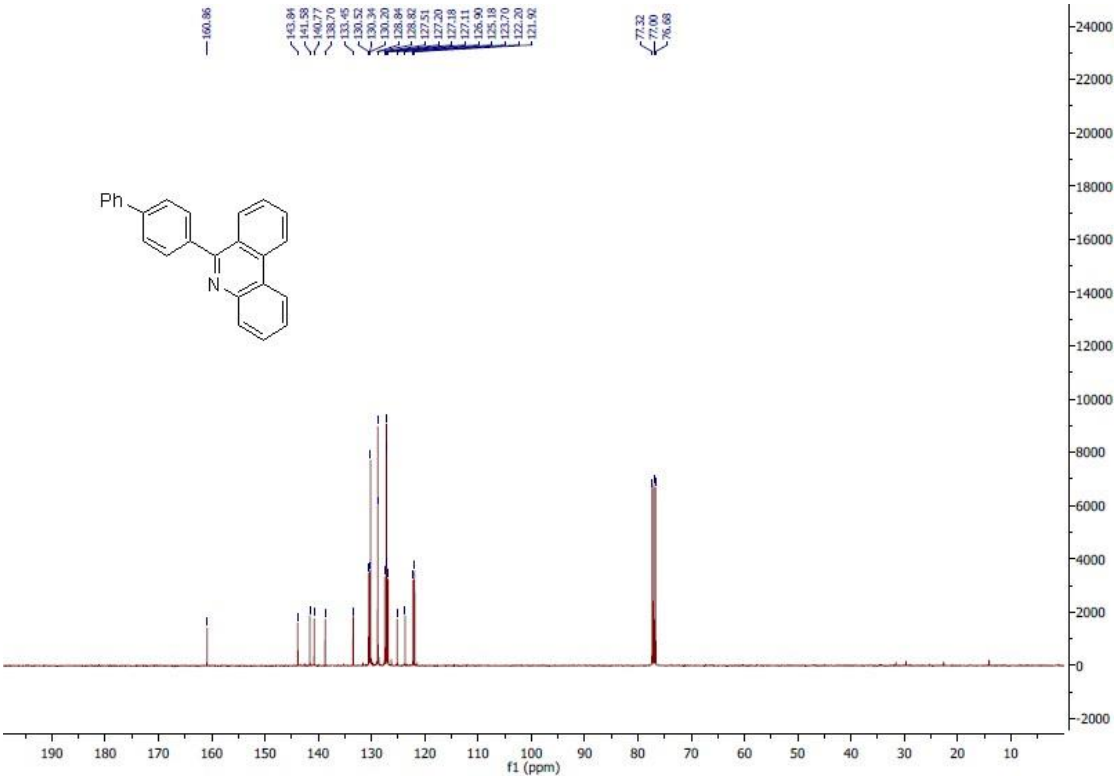
^{1}H and ^{13}{C} spectra of **5l**



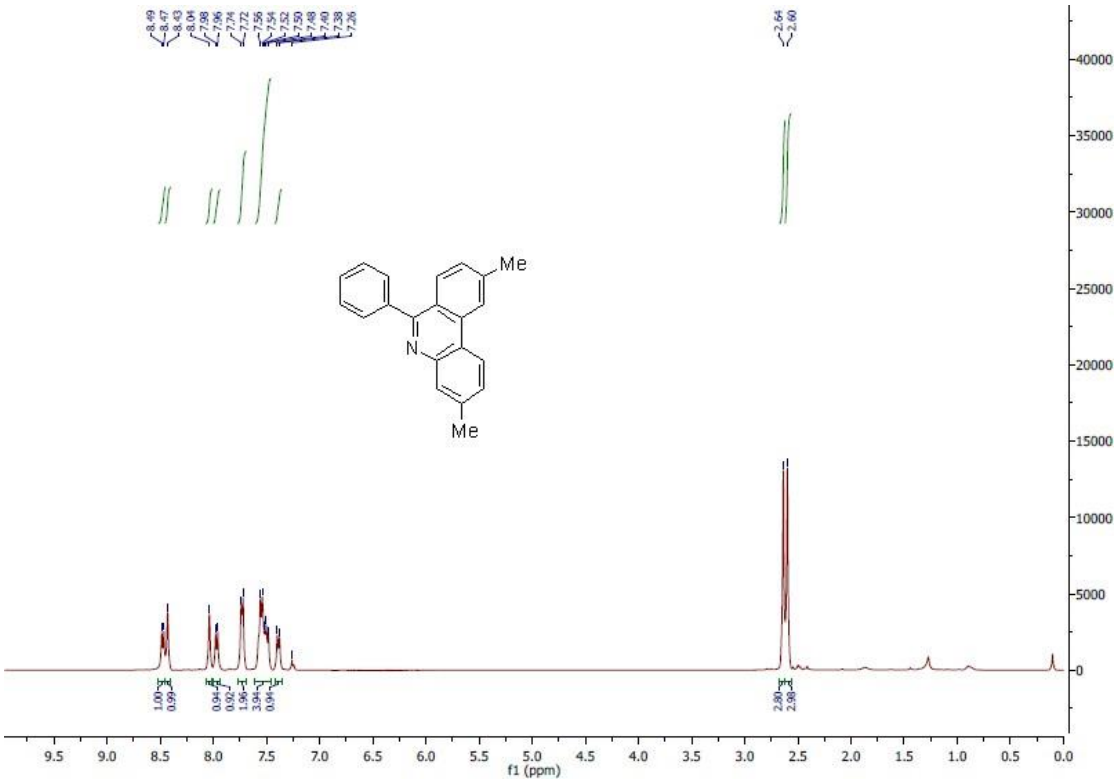


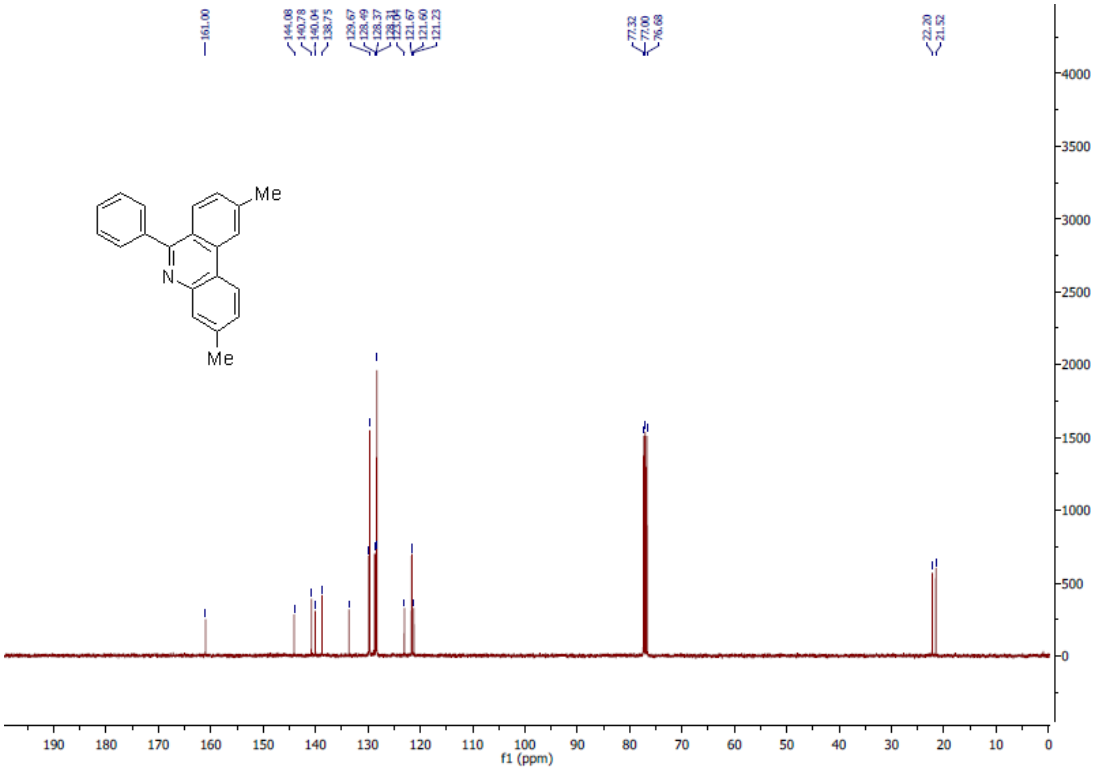
^{1}H and ^{13}{C} spectra of **5m**



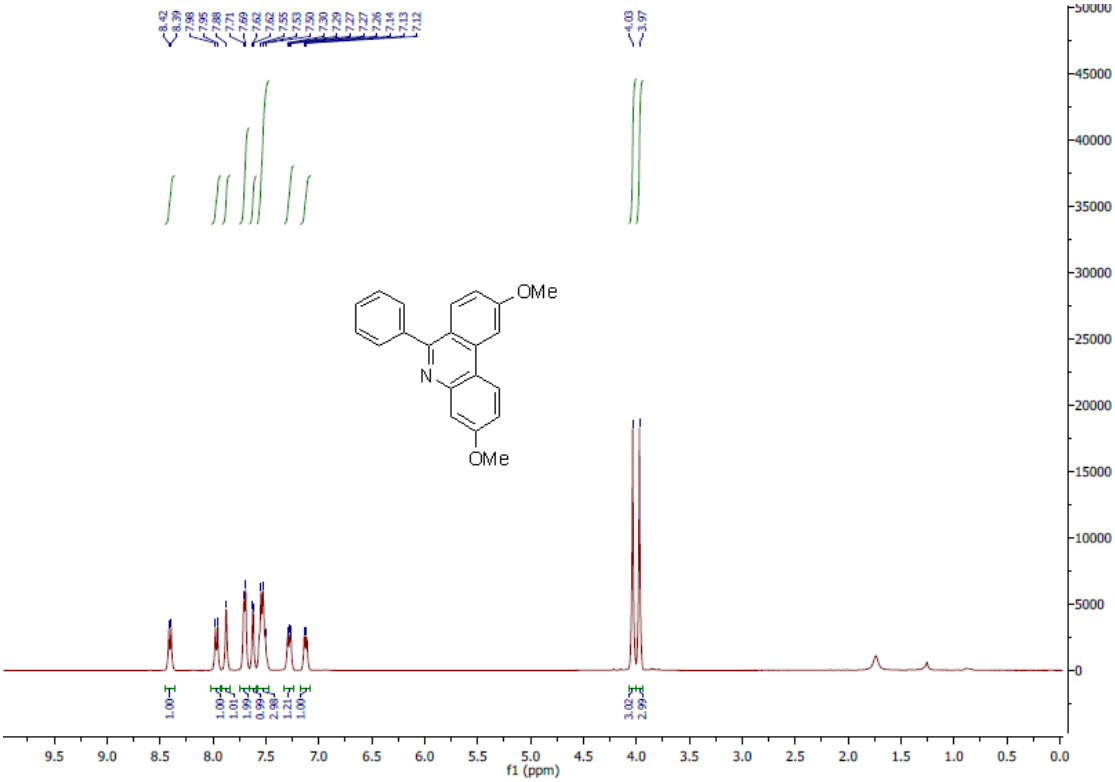


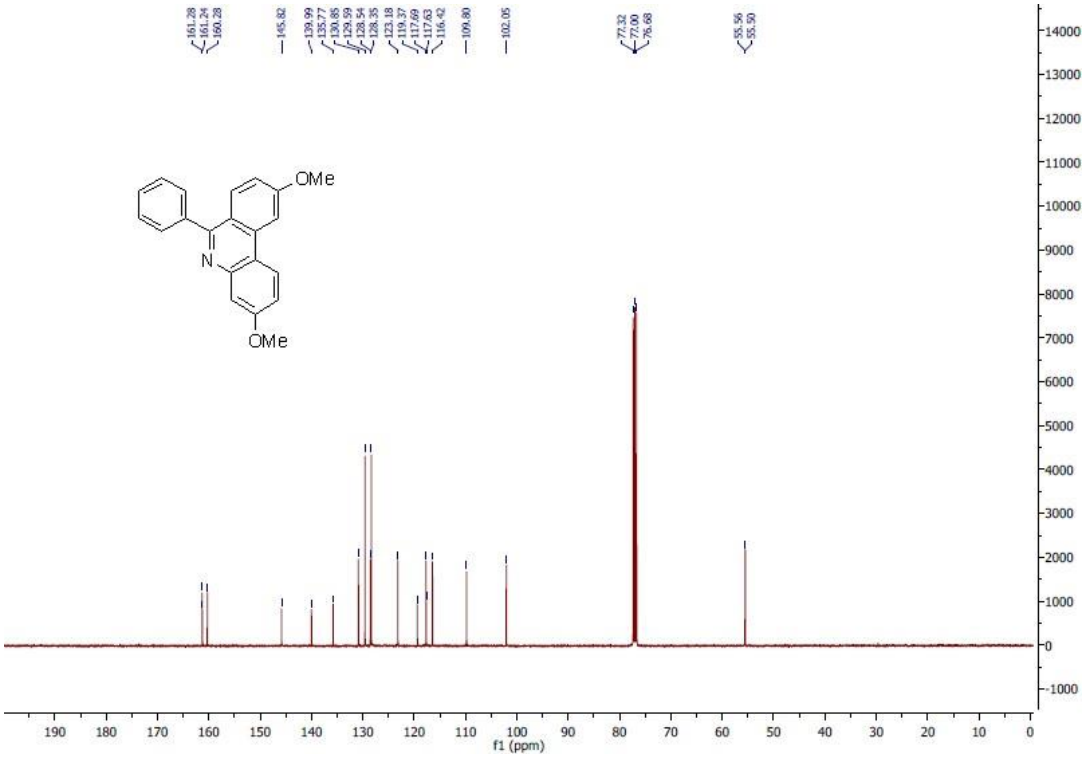
^{1}H and ^{13}{C} spectra of **5n**



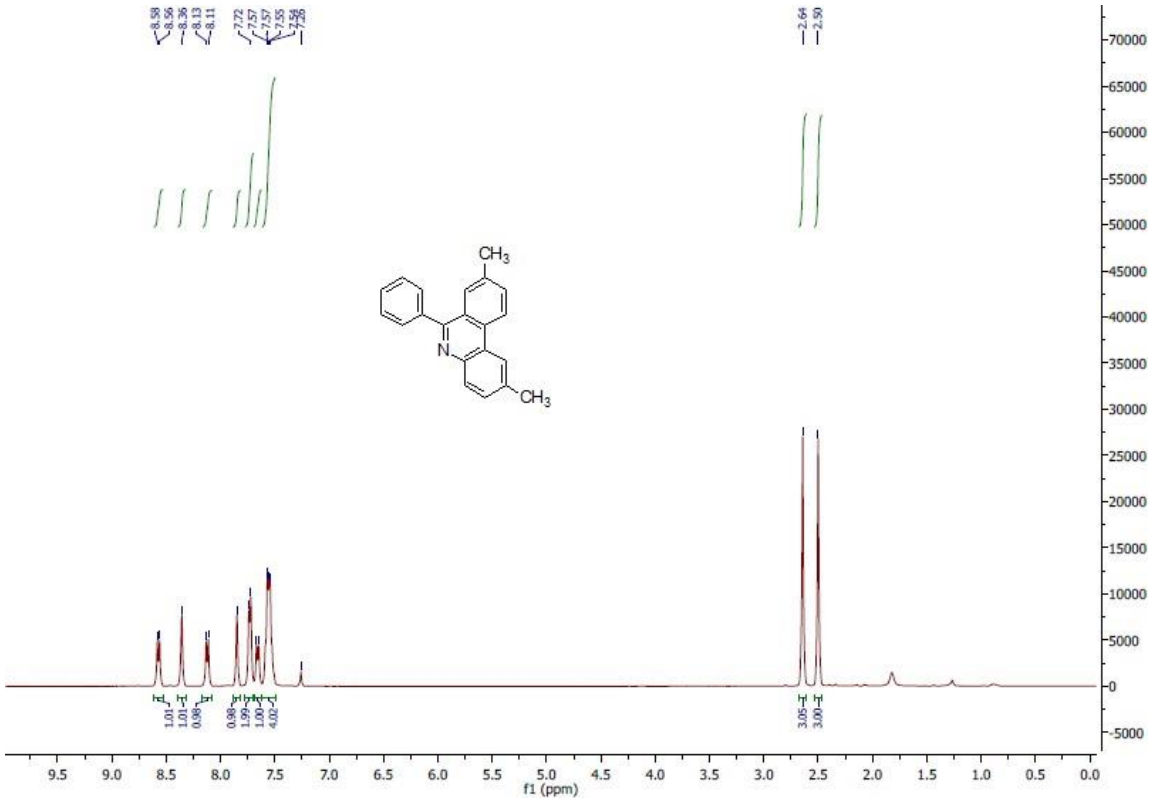


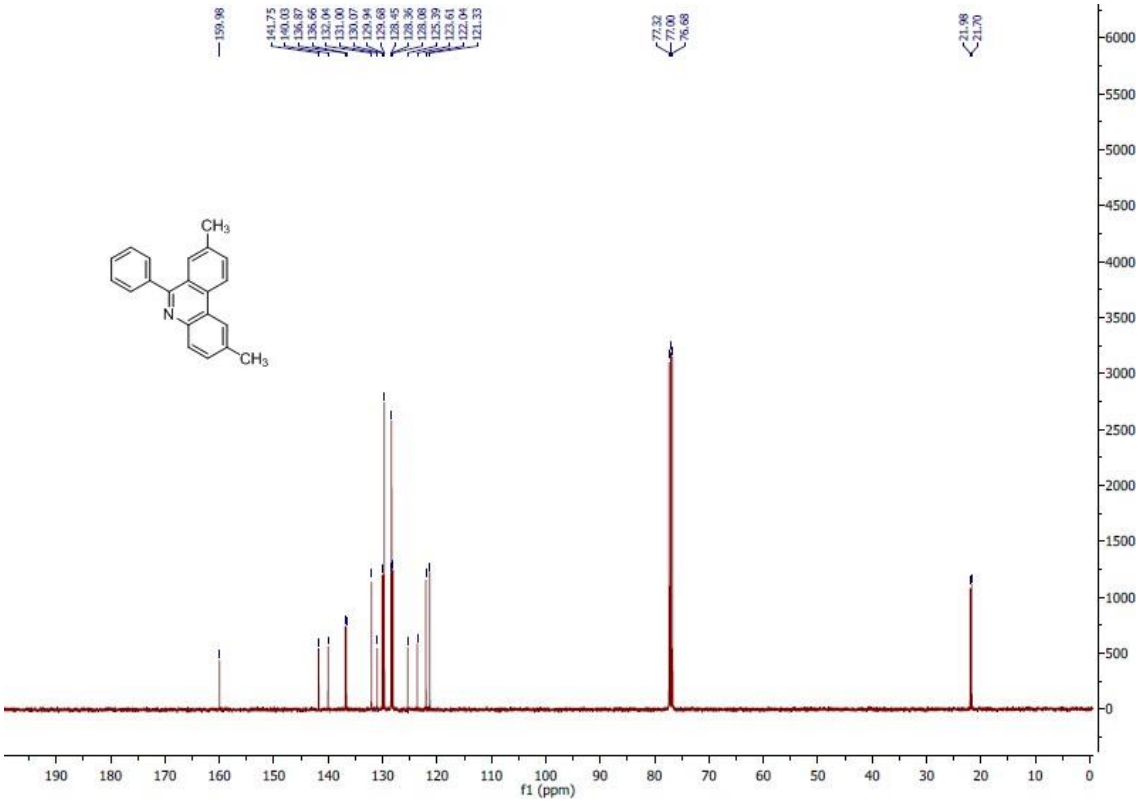
^{1}H and ^{13}{C} spectra of **5o**



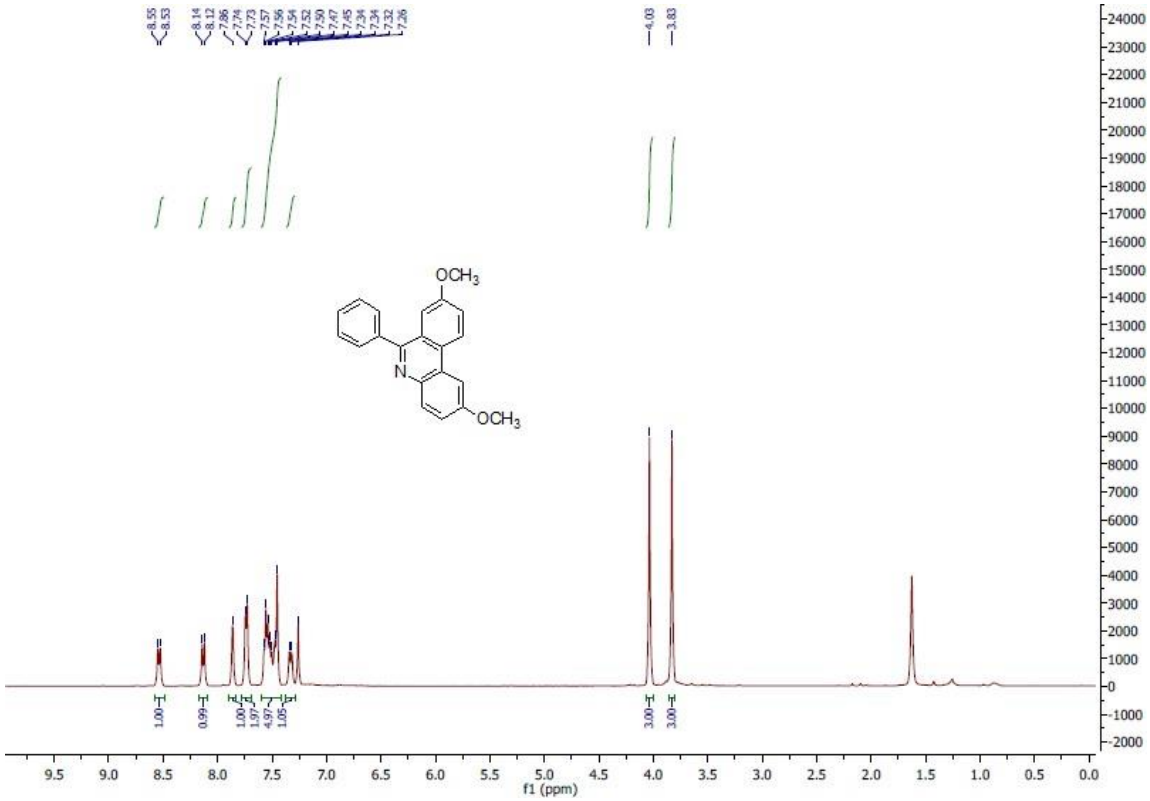


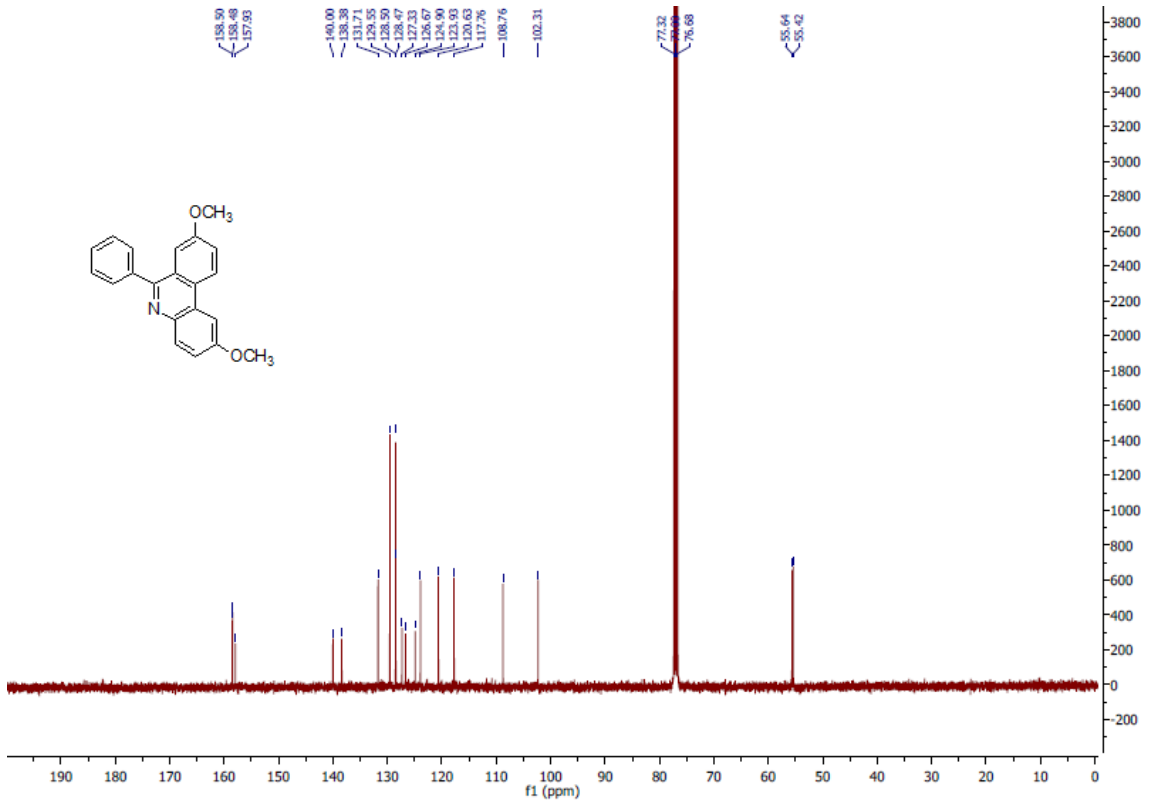
^{1}H and ^{13}{C} spectra of **5p**



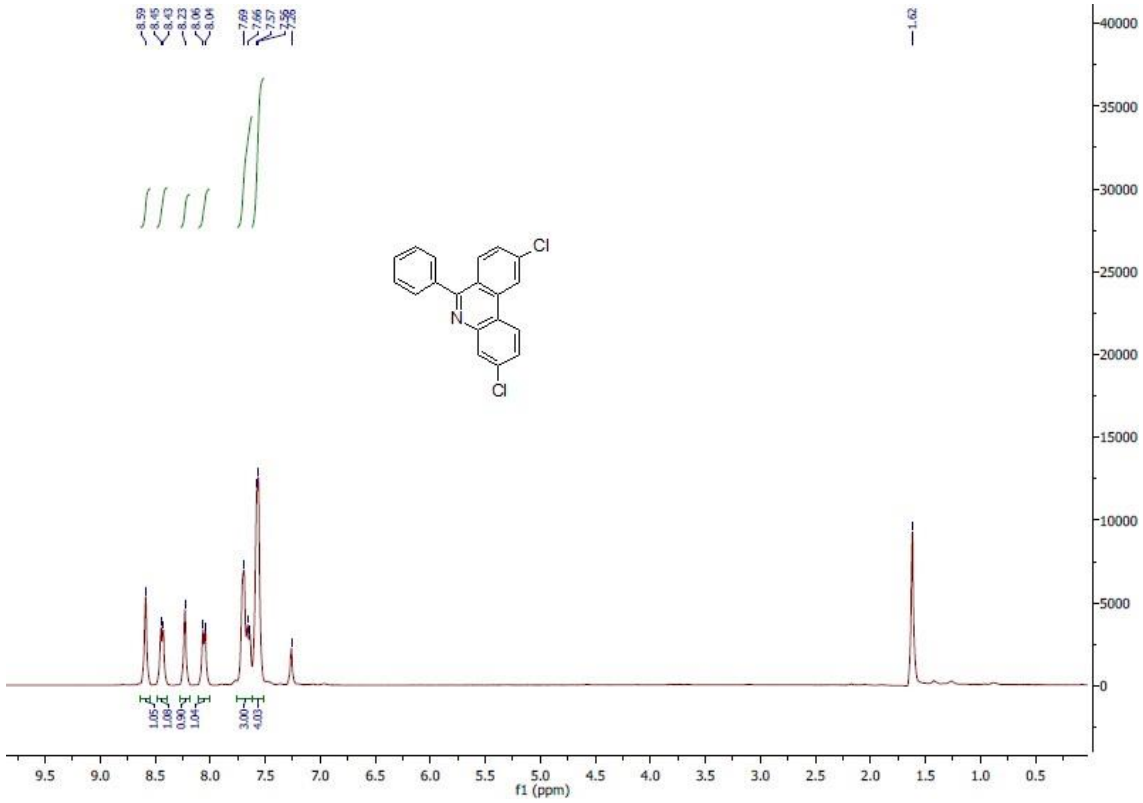


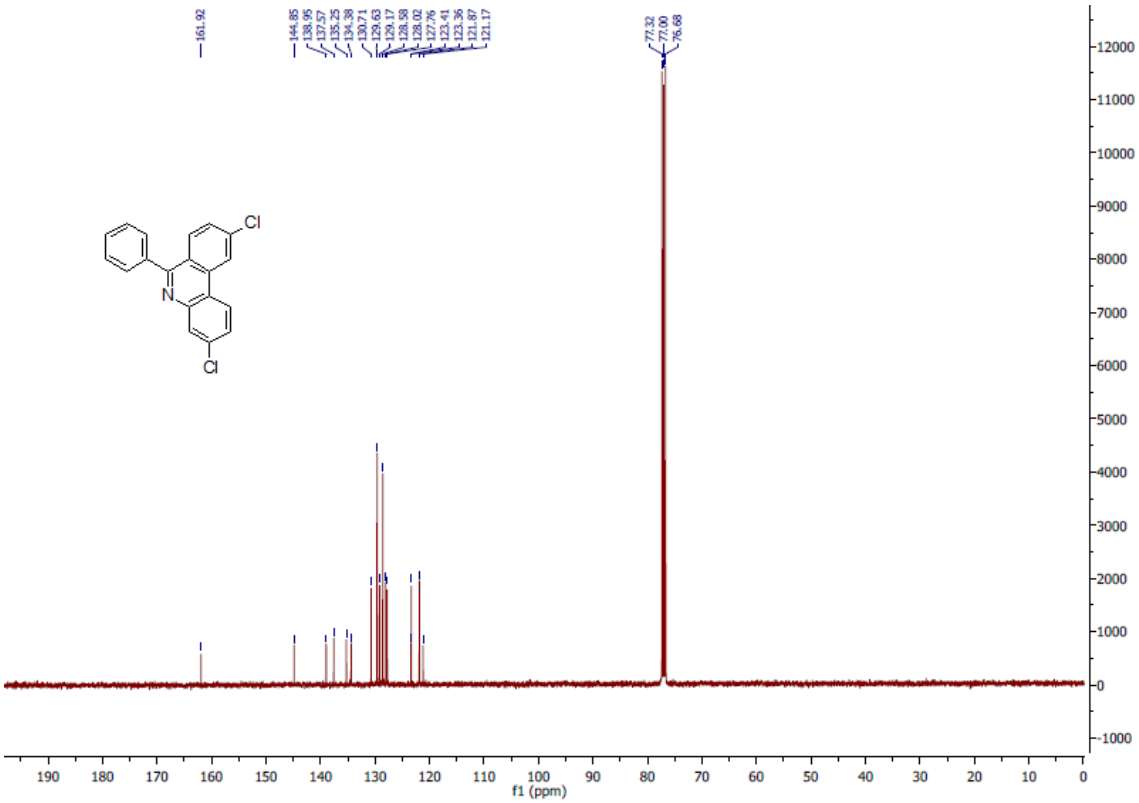
^{1}H and ^{13}{C} spectra of **5q**



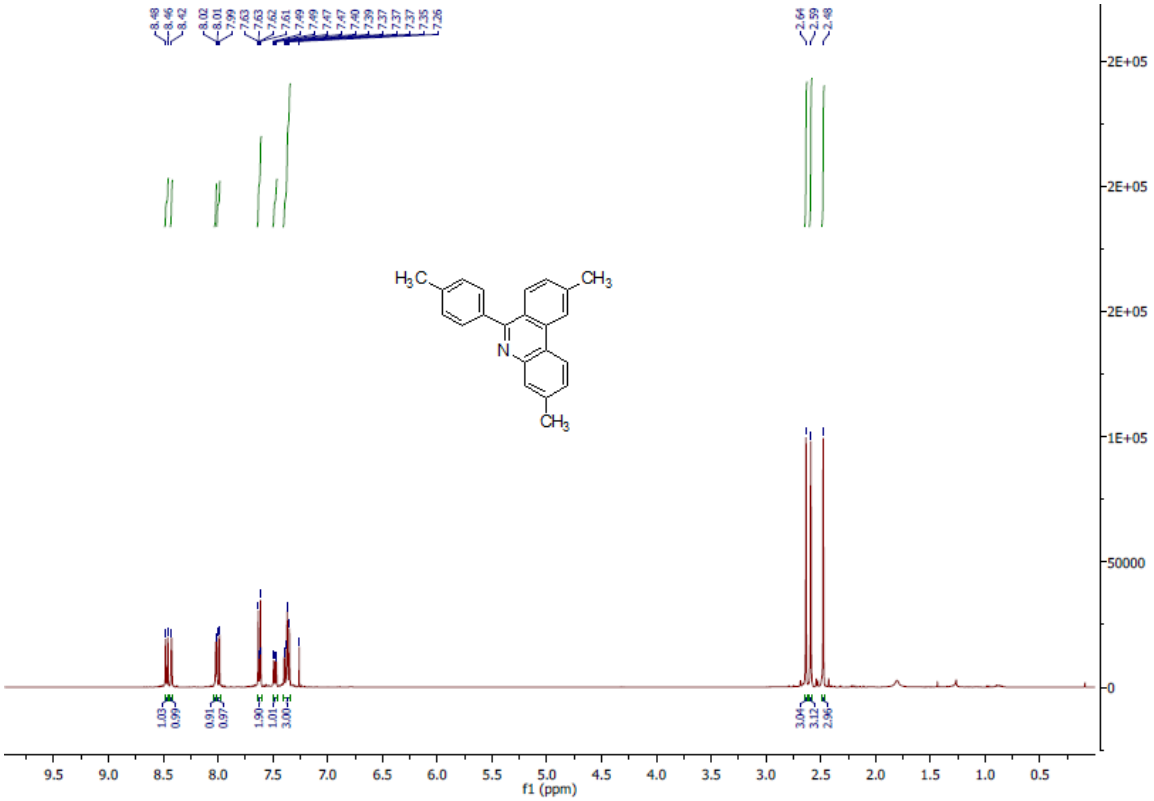


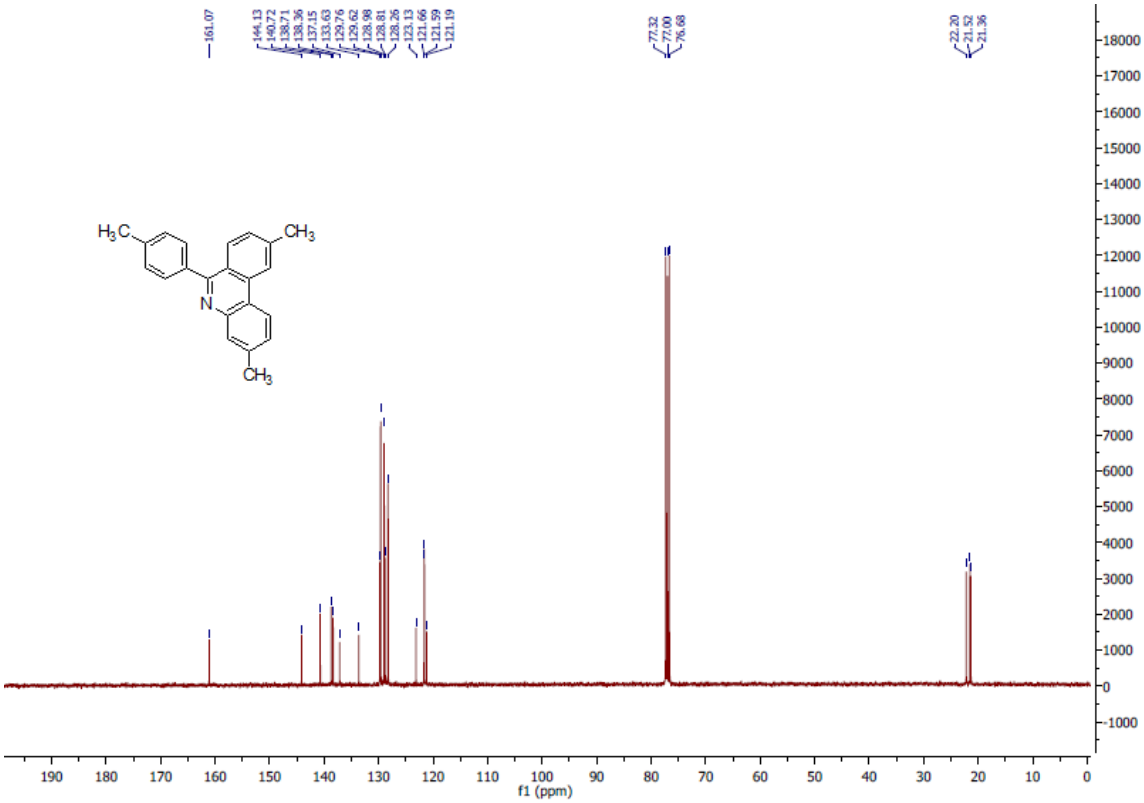
^{1}H and ^{13}{C} spectra of **5r**



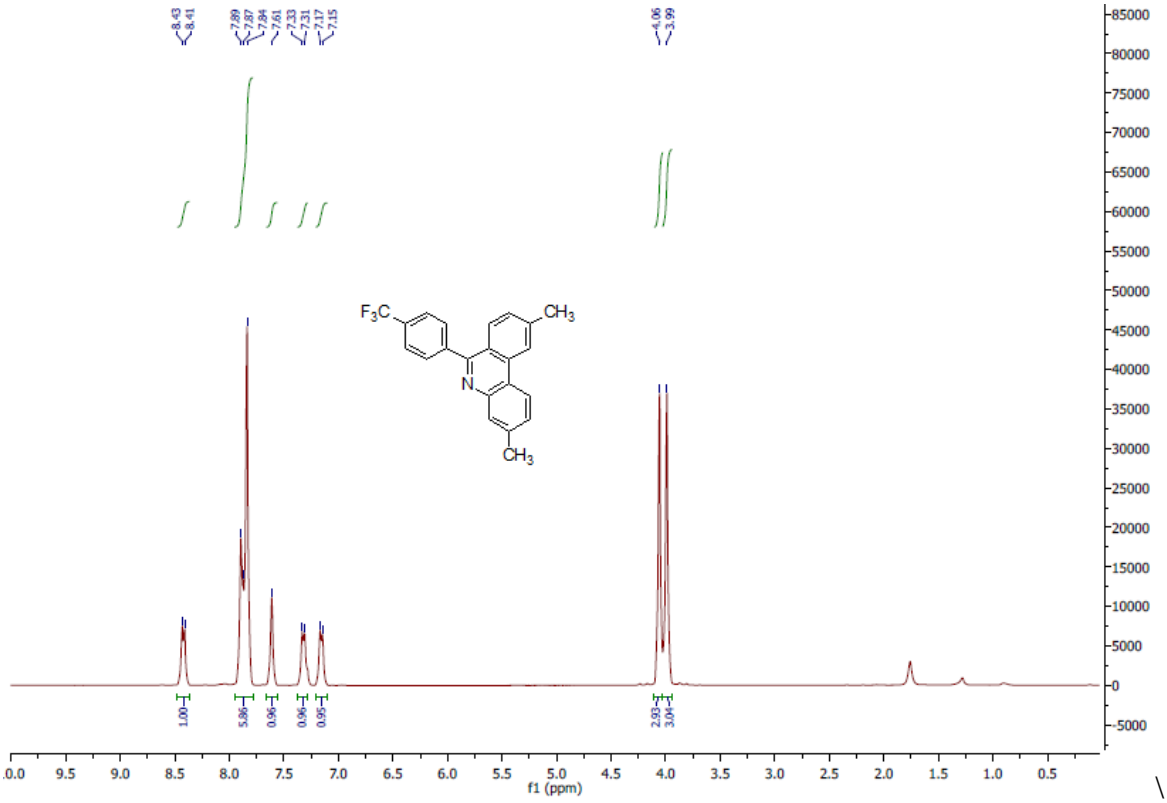


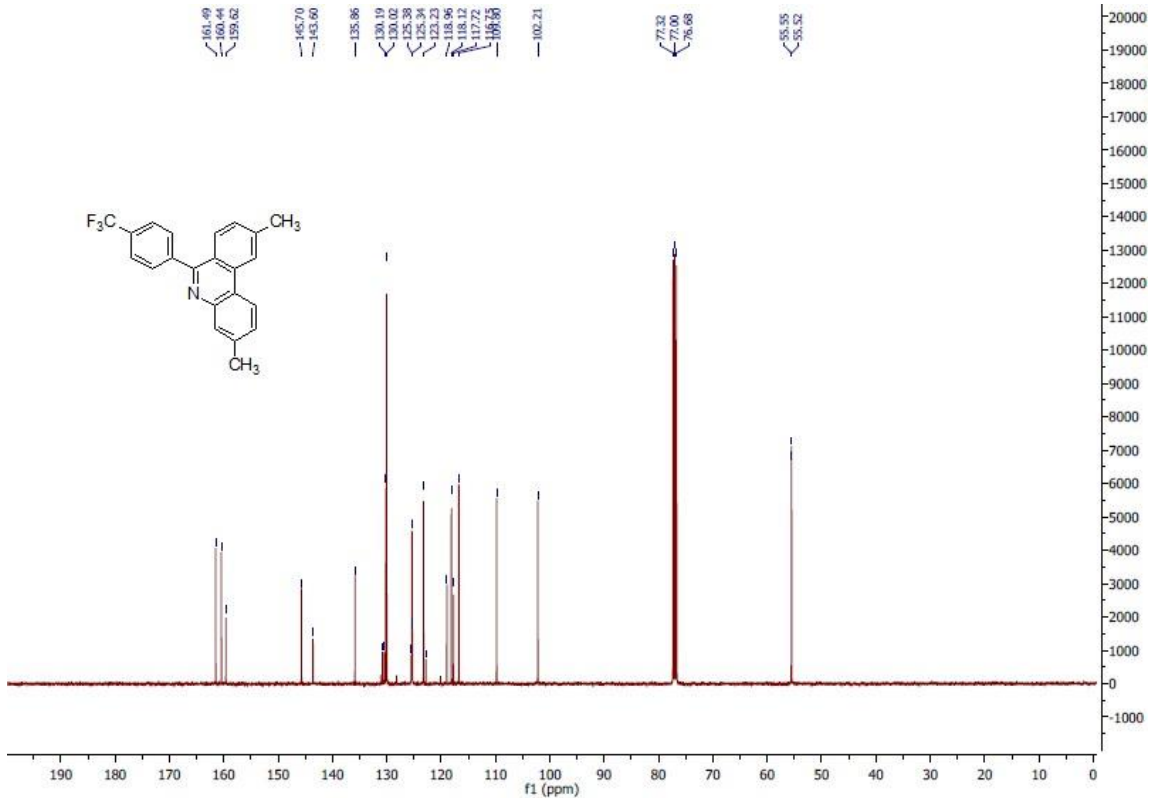
^{1}H and ^{13}{C} spectra of **5s**



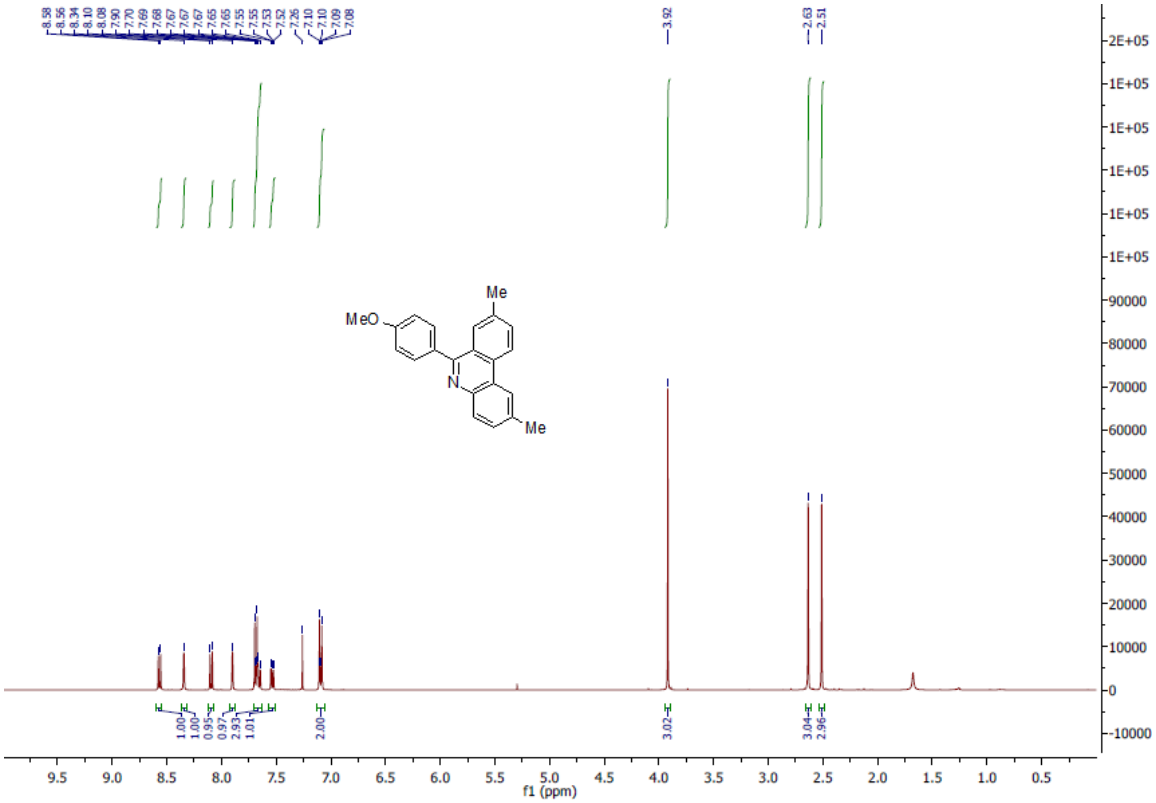


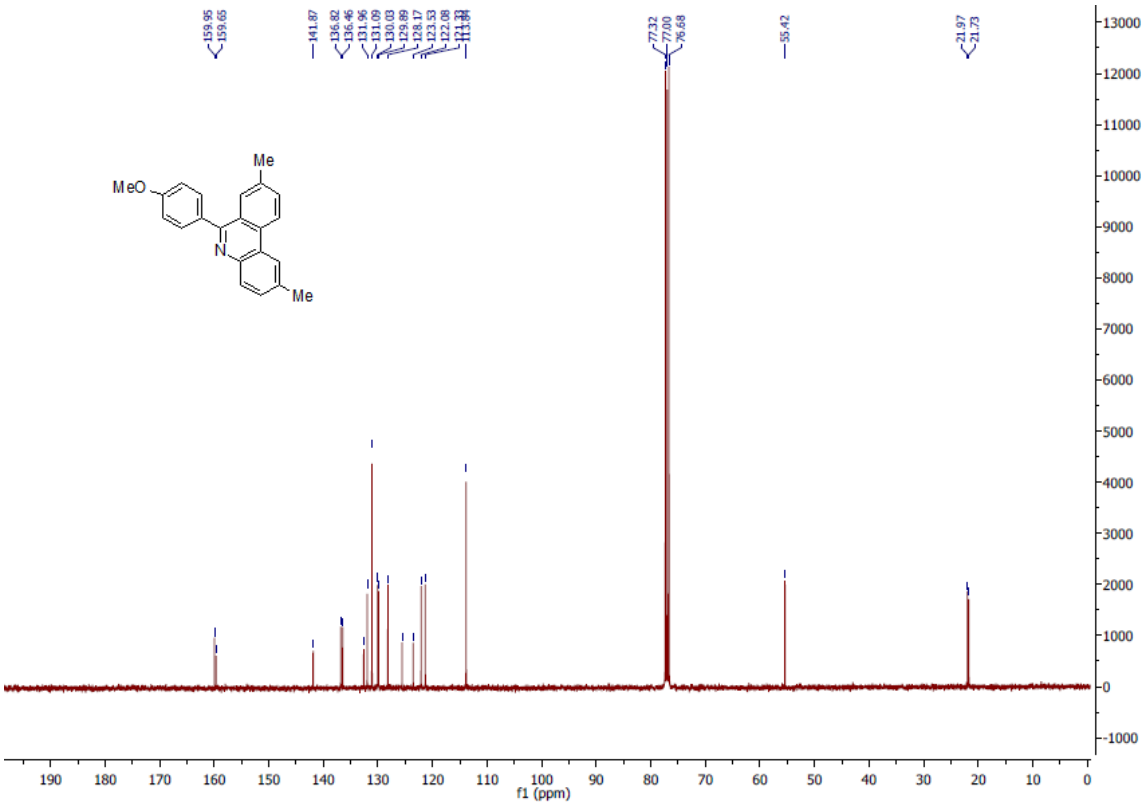
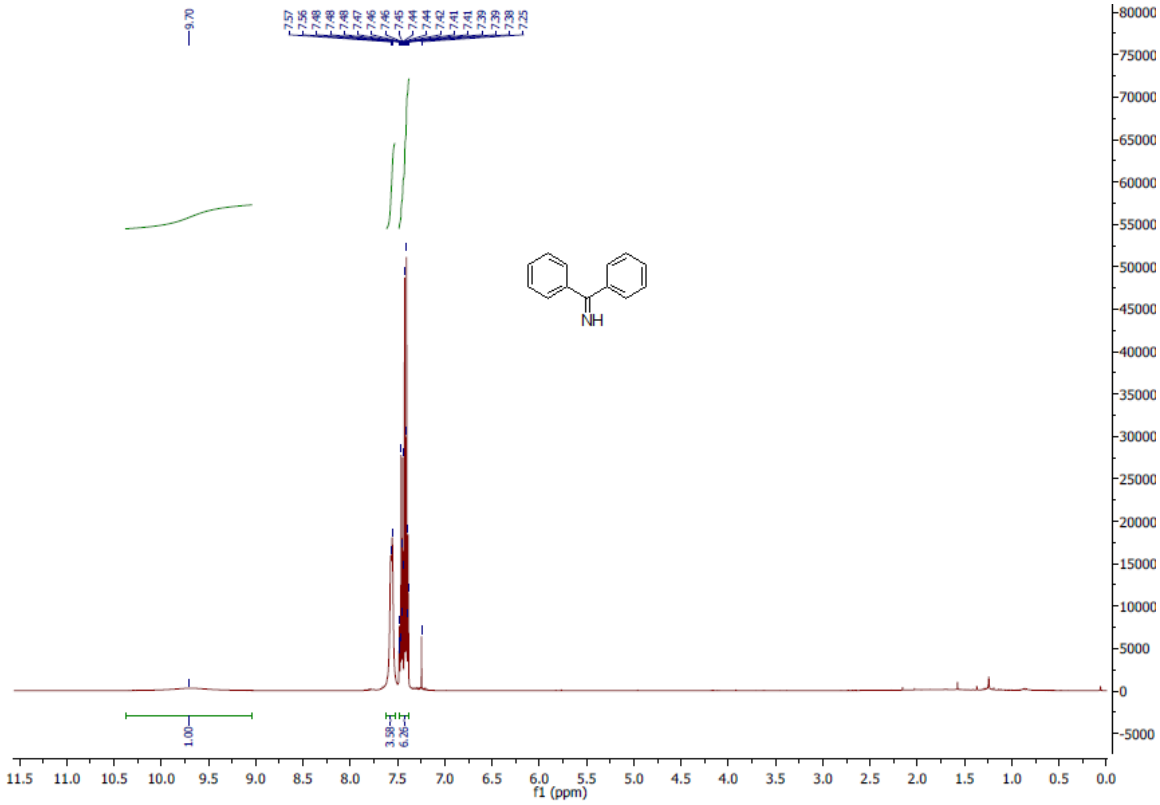
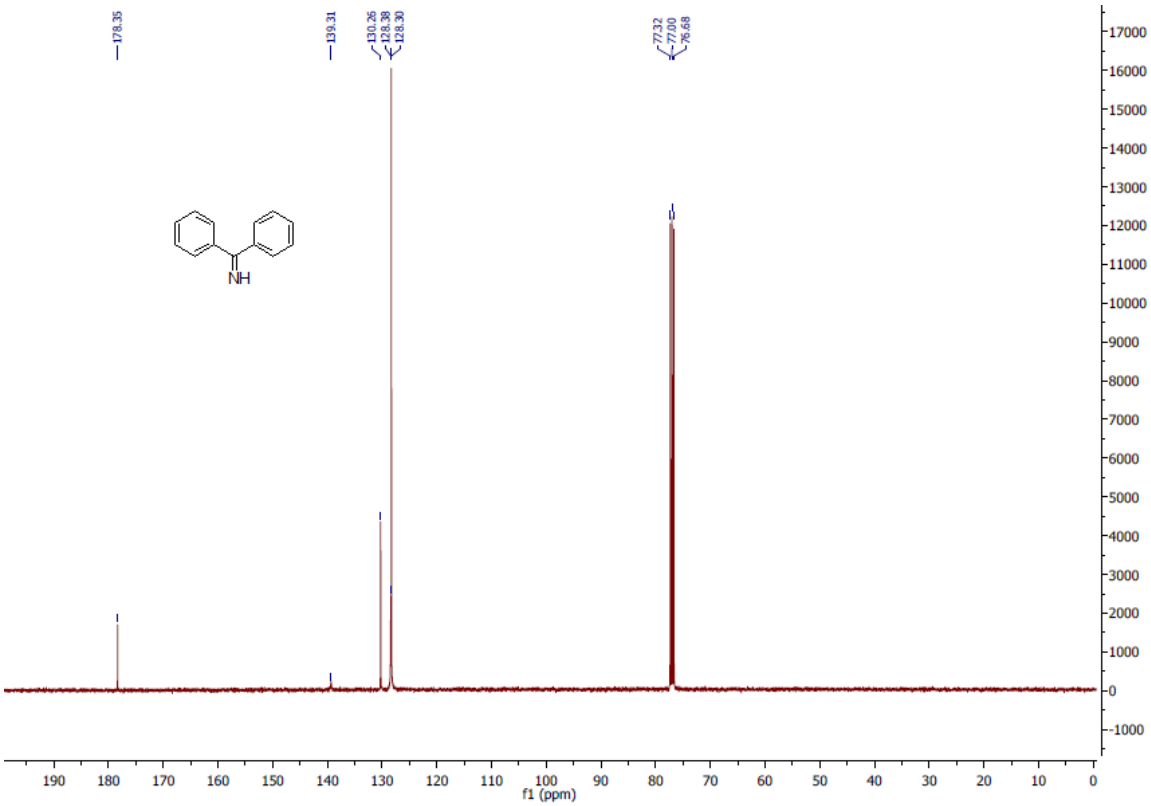
^{1}H and ^{13}{C} spectra of **5t**





^{1}H and ^{13}{C} spectra of **5u**





^{1}H and ^{13}{C} spectra of **6**