

One pot synthesis of phenanthridines using a palladium - catalyzed cyclization of aromatic ketoximes with aryl iodides via Beckmann rearrangement

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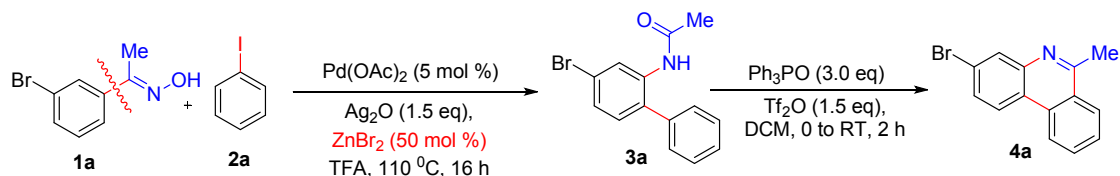
Electronic Supplementary Information (ESI)

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Experimental Section

General procedure for the synthesis of phenanthridines to aromatic ketoximes with aryl iodides catalyzed by palladium catalyst.



A 15-mL pressure tube equipped with a magnetic stirrer and septum containing $\text{Pd}(\text{OAc})_2$ (0.05 mmol, 5 mol %), Ag_2O (1.50 mmol, 1.5 equiv) and ZnBr_2 (0.5 mmol, 0.5 equiv) was evacuated and purged with nitrogen gas three times. To the tube were then added substituted oximes **1** (1.0 mmol), aryl iodides **2** (**2a-e** 3.0 mmol) and TFA solvent (2.0 mL) via syringes again the tube was evacuated and purged with nitrogen gas three times. Then, septum was taken out and covered with a screw cap immediately under nitrogen atmosphere and the reaction mixture was allowed to stir at $110\text{ }^\circ\text{C}$ for 16 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 , filtered through Celite and silica gel and the filtrate was concentrated. The crude residue was taken directly without column purification for next step.

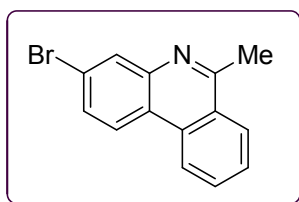
General procedure for the preparation of phenanthridines.

To a solution of Ph_3PO (3.0 equiv) in anhydrous CH_2Cl_2 (5 mL) was added Tf_2O (0.078 mL, 1.5 equiv) drop wise under nitrogen atmosphere at $0\text{ }^\circ\text{C}$. After 15 min above crude product (arylated anilide) in anhyd CH_2Cl_2 (2 mL) was added. The reaction was then warmed to r.t. and stirred until completion. The reaction was quenched by addition of sat. aq NaHCO_3 . The mixture was extracted with CH_2Cl_2 ($3 \times 10\text{ mL}$). The combined extracts were washed with brine, dried over anhyd Na_2SO_4 , and concentrated. The crude product was purified by column chromatography on silica gel using a mixture of PE and EtOAc (5:1 to 2:1, v/v) as the eluent to afford a pure product of **4a-4r**.

Spectral data and copies of ^1H and ^{13}C NMR spectra of all compounds **4a-r** and **3a-c** are listed below.

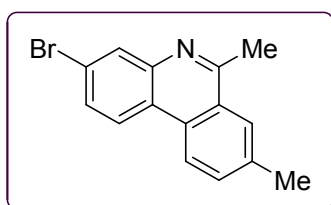
Spectral Data of Compounds 4a-r and 3a-c.

3-Bromo-6-methylphenanthridine (4a):¹ Colorless solid; eluent (10% ethyl acetate in



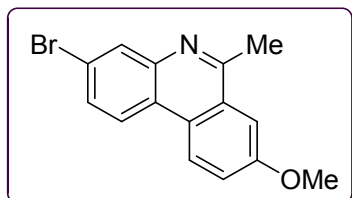
hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.54 (d, *J* = 8.0 Hz, 1 H), 8.34 (dd, *J* = 8.0, 4.0 Hz, 1 H), 8.26 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 7.83 (t, *J* = 8.0 Hz, 1 H), 7.72- 7.66 (m, 2 H), 3.02 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 160.5, 144.5, 132.4, 131.9, 131.2, 129.8, 128.0, 126.9, 126.0, 123.7, 122.8, 122.5, 122.4, 23.5. HRMS (ESI): calc. for [(C₁₄H₁₀BrN)H] (M+H) 272.0075, measured 272.0078.

3-Bromo-6,8-dimethylphenanthridine (4b): Colorless solid; eluent (10% ethyl acetate in



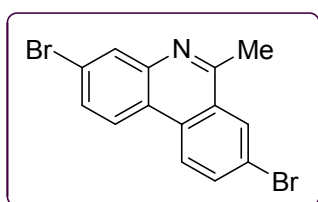
hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.44 (d, *J* = 8.0 Hz, 1 H), 8.32 (d, *J* = 8.0 Hz, 1 H), 8.26 (s, 1 H), 7.98 (s, 1 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 3.02 (s, 3 H), 2.62 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.8, 144.1, 137.7, 132.5, 131.6, 129.8, 129.2, 126.1, 125.8, 123.2, 122.6, 121.9, 121.6, 23.3, 21.8. HRMS (ESI): calc. for [(C₁₅H₁₂BrN)H] (M+H) 286.0231, measured 286.0235.

3-Bromo-8-methoxy-6-methylphenanthridine (4c): Colorless solid; eluent (15% ethyl



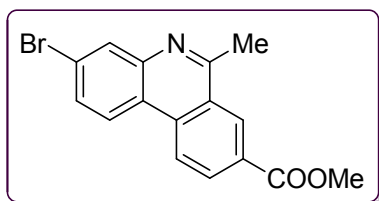
acetate in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.42 (d, *J* = 8.0 Hz, 1 H), 8.25 (d, *J* = 8.0 Hz, 1 H), 8.23 (s, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.46 (s, 1 H), 7.45 (d, *J* = 8.0 Hz, 1 H), 3.99 (s, 3 H), 2.99 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.2, 158.9, 143.4, 131.5, 129.5, 127.1, 126.4, 123.9, 122.9, 122.6, 121.2, 121.1, 106.9, 55.6, 23.4. HRMS (ESI): calc. for [(C₁₅H₁₂BrNO)H] (M+H) 302.0181, measured 302.0184.

3,8-Dibromo-6-methylphenanthridine (4d): Colorless solid; eluent (10% ethyl acetate in



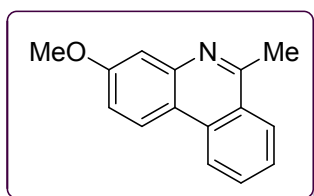
hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.42 (d, *J* = 8.0 Hz, 1 H), 8.35 (s, 1 H), 8.32 (d, *J* = 8.0 Hz, 1 H), 8.29 (s, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 3.02 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.0, 144.3, 134.1, 131.9, 130.8, 129.9, 129.3, 127.1, 124.1, 123.2, 122.8, 121.9, 121.7, 23.3. HRMS (ESI): calc. for [(C₁₄H₉Br₂N)H] (M+H) 349.9180, measured 349.9183.

Methyl 3-bromo-6-methylphenanthridine-8-carboxylate (4e): Brown solid; eluent (15% ethyl acetate in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.93



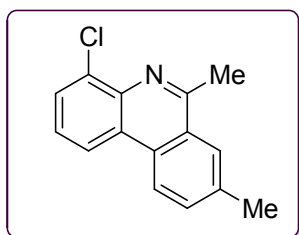
(s, 1 H), 8.62 (dd, $J = 8.0, 4.0$ Hz, 1 H), 8.46 (d, $J = 8.0, 4.0$ Hz, 1 H), 8.41 (d, $J = 8.0$ Hz, 1 H), 8.31 (s, 1 H), 7.75 (dd, $J = 8.0, 4.0$ Hz, 1 H), 4.05 (s, 3 H), 3.11 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 166.4, 160.7, 145.3, 135.2, 132.0, 130.7, 129.9, 128.99, 128.97, 125.3, 123.9, 123.7, 122.5, 121.9, 52.6, 23.4. **HRMS (ESI):** calc. for $[(\text{C}_{16}\text{H}_{12}\text{BrNO}_2)\text{H}]$ (M+H) 330.0130, measured 330.0135.

3-Methoxy-6-methylphenanthridine (4f):² Colorless solid; eluent (15% ethyl acetate in



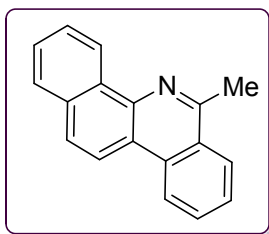
hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.47 (d, $J = 8.0$ Hz, 1 H), 8.37 (d, $J = 8.0$ Hz, 1 H), 8.15 (d, $J = 8.0$ Hz, 1 H), 7.78 (t, $J = 8.0$ Hz, 1 H), 7.59 (t, $J = 8.0$ Hz, 1 H), 7.53 (s, 1 H), 7.24 (dd, $J = 8.0, 4.0$ Hz, 1 H), 3.96 (s, 3 H), 3.02 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.1, 159.3, 144.8, 132.8, 130.7, 126.5, 126.2, 124.8, 123.1, 121.7, 117.7, 117.4, 108.9, 55.5, 23.0. **HRMS (ESI):** calc. for $[(\text{C}_{15}\text{H}_{13}\text{NO})\text{H}]$ (M+H) 224.1075, measured 224.1080.

4-Chloro-6,8-dimethylphenanthridine (4g): Colorless solid; eluent (10% ethyl acetate in



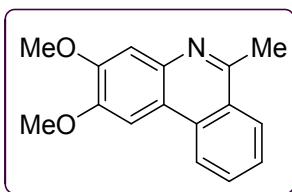
hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.48 (d, $J = 8.0$ Hz, 1 H), 8.41 (dd, $J = 8.0, 4.0$ Hz, 1 H), 8.02 (s, 1 H), 7.79 (dd, $J = 8.0, 4.0$ Hz, 1 H), 7.71 (d, $J = 8.0$ Hz, 1 H), 7.52 (t, $J = 8.0$ Hz, 1 H), 3.13 (s, 3 H), 2.63 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 160.1, 138.6, 138.3, 133.2, 132.8, 130.3, 128.8, 126.4, 126.3, 125.9, 125.6, 122.5, 120.8, 23.2, 21.8. **HRMS (ESI):** calc. for $[(\text{C}_{15}\text{H}_{12}\text{ClN})\text{H}]$ (M+H) 242.0737, measured 242.0738.

6-Methylbenzo[c]phenanthridine (4h):² Colorless solid; eluent (10% ethyl acetate in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 9.48 (d, $J = 8.0$ Hz, 1 H), 8.70 (d, $J = 8.0$ Hz, 1 H), 8.53 (d, $J = 8.0$ Hz, 1 H), 8.30 (d, $J = 8.0$ Hz, 1 H), 7.98 (d, $J = 8.0$ Hz, 2 H), 7.87 (t, $J = 8.0$ Hz, 1 H), 7.79 – 7.67 (m, 3 H), 3.20 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 157.6, 140.4, 133.2, 132.8, 131.8, 130.1, 127.5, 127.1, 126.84, 126.81, 126.7, 126.4, 126.1, 124.7, 122.6,



120.3, 119.8, 23.6. **HRMS (ESI):** calc. for [(C₁₈H₁₃N)H] (M+H) 244.1126, measured 244.1129.

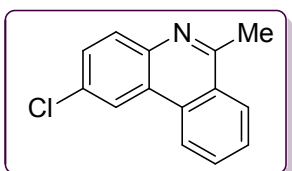
2,3-Dimethoxy-6-methylphenanthridine (4i): Colorless solid; eluent (20% ethyl acetate in



hexanes). **¹H NMR (CDCl₃, 400 MHz):** δ 8.46 (d, *J* = 8.2 Hz, 1 H), 8.19 (d, *J* = 8.2 Hz, 1 H), 7.81 (s, 1 H), 7.80 (t, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.55 (s, 1 H), 4.11 (s, 3 H), 4.05 (s, 3 H), 3.03 (s, 3 H). **¹³C NMR (CDCl₃, 100 MHz):** δ 156.7, 150.9, 148.9, 132.3,

130.3, 129.5, 126.7, 126.3, 125.0, 121.8, 117.8, 109.2, 101.7, 56.1, 22.8. **HRMS (ESI):** calc. for [(C₁₆H₁₅NO₂)H] (M+H) 254.1181, measured 254.1187.

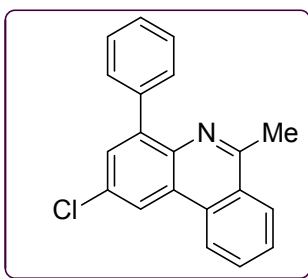
2-Chloro-6-methylphenanthridine(4ja):³ Colorless solid; eluent (10% ethyl acetate in



hexanes). **¹H NMR (CDCl₃, 400 MHz):** δ 8.53 (d, *J* = 8.0 Hz, 1 H), 8.47 (s, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 1 H), 7.87 (t, *J* = 8.0 Hz, 1 H), 7.74 (t, *J* = 8.0 Hz, 1 H), 7.64 (dd, *J* = 8.0, 4.0, Hz, 1 H), 3.04 (s, 3 H). **¹³C NMR (CDCl₃, 100 MHz):** δ 159.2, 141.8,

132.2, 131.5, 130.8, 130.6, 129.1, 128.0, 126.6, 125.9, 124.8, 122.3, 121.6, 23.23. **HRMS (ESI):** calc. for [(C₁₄H₁₀ClN)H] (M+H) 228.0580, measured 228.0584.

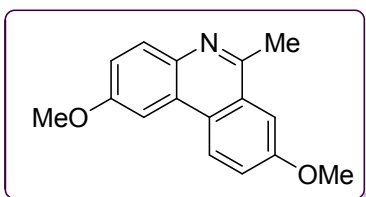
2-Chloro-6-methyl-4-phenylphenanthridine (4jb): Colorless solid; eluent (10% ethyl



acetate in hexanes). **¹H NMR (CDCl₃, 400 MHz):** δ 8.58 (d, *J* = 8.0 Hz, 1 H), 8.50 (s, 1 H), 8.21 (d, *J* = 8.0 Hz, 1 H), 7.86 (t, *J* = 8.0, Hz, 1 H), 7.78 – 7.72 (m, 4 H), 7.52 (t, *J* = 8.0, Hz, 2 H), 7.45 (t, *J* = 8.0, Hz, 1 H), 2.97 (s, 3 H). **¹³C NMR (CDCl₃, 100 MHz):** δ 158.4, 142.3, 139.4, 138.7, 131.7, 131.6, 131.0, 130.5, 130.0, 127.9, 127.8, 127.5, 126.4, 125.7, 125.4, 122.6, 120.8, 23.6. **HRMS (ESI):** calc.

for [(C₂₀H₁₄ClN)H] (M+H) 304.0893, measured 304.0895.

2,8-Dimethoxy-6-methylphenanthridine (4ka):⁴ Colorless solid; eluent (20% ethyl acetate



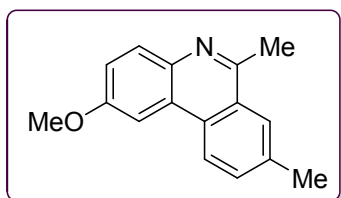
in hexanes). **¹H NMR (CDCl₃, 400 MHz):** δ 8.40 (d, *J* = 8.0, Hz, 1 H), 8.00 (dd, *J* = 8.0, 4.0 Hz, 1 H) 7.74 (s, 1 H), 7.42 (s, 1 H), 7.40 (d, *J* = 8.0, Hz, 1 H), 7.28 - 7.25 (m, 1 H), 3.98 (s, 6 H), 2.96 (s, 3 H). **¹³C NMR (CDCl₃, 100 MHz):** δ 158.6, 158.0,

155.2, 137.7, 130.3, 127.2, 126.4, 124.8, 123.9, 120.5, 117.4, 106.6, 102.4, 55.5, 55.4, 22.9.

HRMS (ESI): calc. for $[(C_{16}H_{15}NO_2)H]$ (M+H) 254.1181, measured 254.1184.

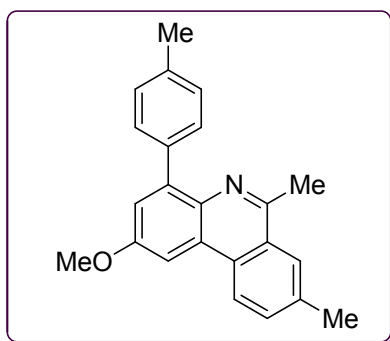
2,8-Dimethoxy-4-(4-methoxyphenyl)-6-methylphenanthridine (4kb): HRMS (ESI): calc. for $[(C_{23}H_{21}NO_3)H]$ (M+H) 360.1600, measured 360.1604.

2-Methoxy-6,8-dimethylphenanthridine (4la): Colorless solid; eluent (15% ethyl acetate in



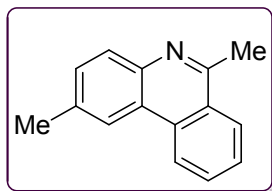
hexanes). **1H NMR (CDCl₃, 400 MHz):** δ 8.43 (d, $J = 8.0$, Hz, 1 H), 8.02 (d, $J = 8.0$, Hz, 1 H), 7.96 (s, 1 H), 7.84 (s, 1 H), 7.64 (d, $J = 8.0$, Hz, 1 H), 7.31 (dd, $J = 8.0, 4.0$, Hz, 1 H), 4.00 (s, 3 H), 3.00 (s, 3 H), 2.61 (s, 3 H). **^{13}C NMR (CDCl₃, 100 MHz):** δ 157.9, 155.9, 138.3, 137.3, 131.9, 130.4, 129.9, 126.1, 124.8, 122.2, 117.8, 102.9, 55.6, 23.0, 21.8. **HRMS (ESI):** calc. for $[(C_{16}H_{15}NO)H]$ (M+H) 238.1232, measured 238.1233.

2-Methoxy-6,8-dimethyl-4-(p-tolyl)phenanthridine (4lb): Colorless solid; eluent (15%



ethyl acetate in hexanes). **1H NMR (CDCl₃, 400 MHz):** δ 8.48 (dd, $J = 8.0, 4.0$ Hz, 1 H), 7.96 (s, 1 H), 7.88 (t, $J = 8.0$ Hz, 1 H), 7.70 (dd, $J = 8.0, 4.0$, Hz, 2 H), 7.65 (d, $J = 8.0$, Hz, 1 H), 7.37 (t, $J = 8.0$, Hz, 1 H), 7.32 (d, $J = 8.0$, Hz, 2 H), 4.04 (s, 3 H), 2.93 (s, 3 H), 2.62 (s, 3 H), 2.46 (s, 3 H). **^{13}C NMR (CDCl₃, 100 MHz):** δ 157.2, 155.1, 141.9, 137.2, 136.8, 136.1, 131.5, 130.9, 130.1, 128.4, 125.9, 125.4, 122.5, 118.6, 102.3, 55.6, 23.5, 21.8, 21.3. **HRMS (ESI):** calc. for $[(C_{23}H_{21}NO)H]$ (M+H) 328.1701, measured 32.1703.

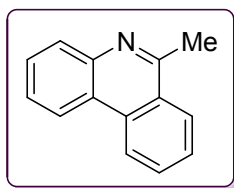
2,6-Dimethylphenanthridine (4ma):³ Colorless solid; eluent (10% ethyl acetate in hexanes).



1H NMR (CDCl₃, 400 MHz): δ 8.60 (d, $J = 8.0$ Hz, 1 H), 8.30 (s, 1 H), 8.19 (d, $J = 8.0$ Hz, 1 H), 8.00 (d, $J = 8.0$ Hz, 1 H), 7.81 (t, $J = 8.0$ Hz, 1 H), 7.67 (t, $J = 8.0$ Hz, 1 H), 7.53 (dd, $J = 8.0, 4.0$ Hz, 1 H), 3.03 (s, 3 H), 2.61 (s, 3 H). **^{13}C NMR (CDCl₃, 100 MHz):** δ 157.7, 141.8, 136.0, 132.25, 130.24, 130.2, 128.9, 127.0, 126.4, 125.7, 123.5, 122.2, 121.5, 23.2, 21.8. **HRMS (ESI):** calc. for $[(C_{15}H_{13}N)H]$ (M+H) 208.1126, measured 208.1128.

2,6-Dimethyl-4-phenylphenanthridine (4mb): HRMS (ESI): calc. for $[(C_{21}H_{17}N)H]$ (M+H) 284.1439, measured 284.1432.

6-Methylphenanthridine (4na):⁴ Colorless solid; eluent (10% ethyl acetate in hexanes). ¹H

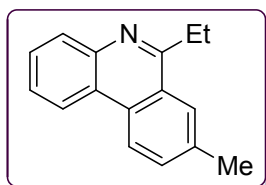


NMR (CDCl₃, 400 MHz): δ 8.62 (d, J = 8.0 Hz, 1 H), 8.54 (d, J = 8.0 Hz, 1 H), 8.22 (d, J = 8.0 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 7.85 (t, J = 8.0 Hz, 1 H), 7.74 – 7.68 (m, 2 H), 7.63 (t, J = 8.0 Hz, 1 H), 3.06 (s, 3 H). ¹³C

NMR (CDCl₃, 100 MHz): δ 158.9, 143.4, 132.5, 130.6, 129.1, 128.7, 127.3, 126.6, 126.4, 125.8, 123.7, 122.3, 121.9, 23.2. **HRMS (ESI):** calc. for [(C₁₄H₁₁N)H] (M+H) 194.0970, measured 194.0972.

6-Methyl-4-phenylphenanthridine (4nb): **HRMS (ESI):** calc. for [(C₂₀H₁₅N)H] (M+H) 270.1283, measured 270.1286.

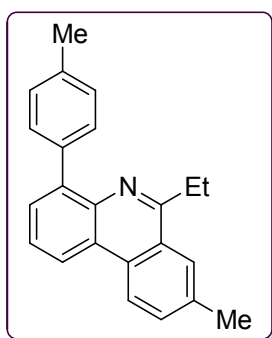
6-Ethyl-8-methylphenanthridine (4oa): Colorless solid; eluent (10% ethyl acetate in



hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.64 (d, J = 8.0 Hz, 1 H), 8.58 (d, J = 8.0 Hz, 1 H), 8.51 (d, J = 8.0 Hz, 1 H), 8.18 (s, 1 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.84 – 7.78 (m, 2 H), 3.72 (q, J = 8.0 Hz, 2 H), 2.69 (s, 3 H), 1.59 (t, J = 8.0 Hz, 3 H). ¹³C NMR (CDCl₃, 100 MHz):

δ 163.3, 137.8, 133.2, 131.2, 129.4, 128.7, 127.9, 126.9, 126.1, 124.7, 123.8, 122.5, 121.8, 28.4, 21.8, 13.9. **HRMS (ESI):** calc. for [(C₁₆H₁₅N)H] (M+H) 222.1283, measured 222.1286.

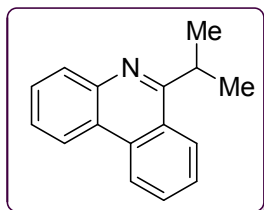
6-Ethyl-8-methyl-4-(*p*-tolyl)phenanthridine (4ob): Colorless solid; eluent (10% ethyl



acetate in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.58 (d, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 8.04 (s, 1 H), 7.77 (t, J = 8.0 Hz, 3 H), 7.65 (t, J = 8.0 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 3.37 (q, J = 8.0 Hz, 2 H), 2.63 (s, 3 H), 2.49 (s, 3 H), 1.46 (t, J = 8.0 Hz, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 161.2, 140.6, 137.2, 137.0, 136.5, 131.7, 131.2, 130.8, 129.2, 128.3, 125.8, 125.2, 125.1, 124.1, 122.6, 120.9, 28.6, 21.9, 21.3, 12.2. **HRMS (ESI):** calc. for [(C₂₃H₂₁N)H] (M+H)

312.1752, measured 312.1755.

6-Isopropylphenanthridine (4pa):³ Colorless semisolid; eluent (10% ethyl acetate in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.67 (d, *J* = 8.0 Hz, 1 H),

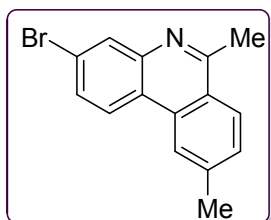


8.55 (d, *J* = 8.0 Hz, 1 H), 8.34 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 7.84 (t, *J* = 8.0 Hz, 1 H), 7.74 – 7.69 (m, 2 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 4.03 (sept, *J* = 4.0 Hz, 1 H), 1.56 (d, *J* = 4.0 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz): δ 165.9, 143.5, 133.1, 130.1, 129.7, 128.5, 127.1,

126.2, 125.7, 124.6, 123.4, 122.6, 121.8, 31.5, 21.9. HRMS (ESI): calc. for [(C₁₆H₁₅N)H] (M+H) 222.1283, measured 222.1285.

6-Isopropyl-4-phenylphenanthridine (4pb): HRMS (ESI): calc. for [(C₂₂H₁₉N)H] (M+H) 298.1596, measured 298.1591.

3-Bromo-6,9-dimethylphenanthridine (4qa): Colorless solid; eluent (10% ethyl acetate in

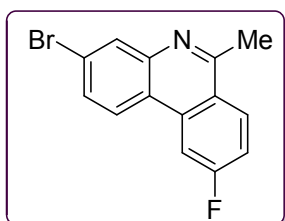


hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.37 (d, *J* = 8.0 Hz, 1 H), 8.35 (s, 1 H), 8.29 (s, 1 H), 8.12 (d, *J* = 8.0 Hz, 1 H), 7.69 (dd, *J* = 8.0, 4.0, Hz, 1 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 3.03 (s, 3 H), 2.66 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 160.1, 144.1, 141.7, 132.3, 131.3, 129.5, 129.4, 126.7, 123.8, 123.4, 122.5, 122.3, 121.9, 22.9, 22.2. HRMS

(ESI): calc. for [(C₁₅H₁₂BrN)H] (M+H) 286.0231, measured 286.0235.

3-Bromo-6,7-dimethylphenanthridine (4qb): (ESI): calc. for [(C₁₅H₁₂BrN)H] (M+H) 286.0231, measured 286.0235.

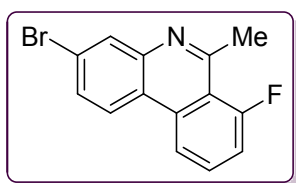
3-Bromo-9-fluoro-6-methylphenanthridine (4ra): Colorless solid; eluent (10% ethyl



acetate in hexanes). ¹H NMR (CDCl₃, 400 MHz): δ 8.26 (s, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 8.12 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 8.0 Hz, 1 H), 3.02 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz): δ 165.1, 162.6, 159.5, 144.8, 134.5, 134.4(F-coupling), 131.9, 129.6, 129.5(F-coupling), 123.5, 123.0, 122.7, 122.1,

122.1(F-coupling), 116.7, 116.5(F-coupling), 107.4, 107.2(F-coupling), 23.4. HRMS (ESI): calc. for [(C₁₄H₉BrFN)H] (M+H) 289.9981, measured 289.9983.

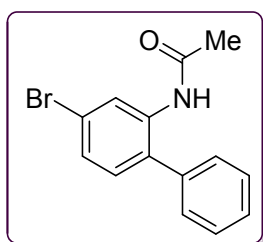
3-Bromo-7-fluoro-6-methylphenanthridine (4rb): Colorless solid; eluent (10% ethyl



acetate in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.36 (d, $J = 8.0$ Hz, 1 H), 8.33 (d, $J = 8.0$ Hz, 1 H), 8.29 (s, 1 H), 7.70 (td, $J = 8.0, 4.0$ Hz, 1 H), 7.72 (d, $J = 8.0$ Hz, 1 H), 7.38 (dd, $J = 12.0, 8.0$ Hz, 1 H due to F-coupling), 3.15 (d, $J = 8.0$ Hz, 3 H due to F-coupling).

HRMS (ESI): calc. for $[(\text{C}_{14}\text{H}_9\text{BrFN})\text{H}]$ (M+H) 289.9981, measured 289.9983.

N-(4-Bromo-[1,1'-biphenyl]-2-yl)acetamide (3a): Colorless solid; eluent (25% ethyl acetate

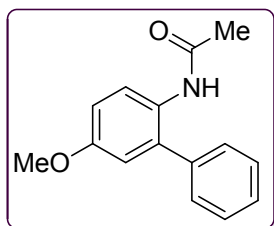


in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.53 (s, 1 H), 7.50 (t, $J = 8.0$ Hz, 2 H), 7.44 (t, $J = 8.0$ Hz, 1 H), 7.34 (d, $J = 8.0$ Hz, 2 H), 7.30 (d, $J = 8.0$ Hz, 1 H), 7.17 (s, 1 H), 7.10 (d, $J = 8.0$ Hz, 1 H), 2.02 (s, 3 H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 168.2, 137.0, 135.8, 131.1, 130.6, 129.2, 129.0, 128.3, 127.2, 124.0, 122.0, 24.6. **HRMS (ESI):** calc. for

$[(\text{C}_{14}\text{H}_{12}\text{BrNO})\text{H}]$ (M+H) 290.0181, measured 290.0182.

N-(5-Methoxy-[1,1'-biphenyl]-2-yl)acetamide (3b): Colorless solid; eluent (35% ethyl

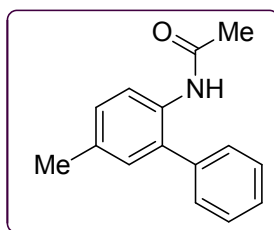


acetate in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.00 (d, $J = 8.0$ Hz, 1 H), 7.48 (t, $J = 8.0$ Hz, 2 H), 7.42 (d, $J = 8.0$ Hz, 1 H), 7.37 (d, $J = 8.0$ Hz, 2 H), 6.98 (bs, 1 H), 6.91 (dd, $J = 8.0, 4.0$ Hz, 1 H), 6.81 (s, 1 H), 3.81 (s, 3 H), 2.00 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ

168.4, 156.4, 138.2, 134.7, 129.0, 128.9, 127.9, 127.6, 124.3, 115.4,

113.4, 55.5, 24.2. **HRMS (ESI):** calc. for $[(\text{C}_{15}\text{H}_{15}\text{NO}_2)\text{H}]$ (M+H) 242.1181, measured 242.1184.

N-(5-Methyl-[1,1'-biphenyl]-2-yl)acetamide (3c): Colorless solid; eluent (25% ethyl acetate



in hexanes). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.09 (d, $J = 8.0$ Hz, 1 H), 7.48 (t, $J = 8.0$ Hz, 2 H), 7.42 (d, $J = 8.0$ Hz, 1 H), 7.37 (d, $J = 8.0$ Hz, 2 H), 7.18 (d, $J = 8.0$ Hz, 1 H), 7.07 (s, 2 H), 2.36 (s, 3 H), 2.02 (s, 3 H).

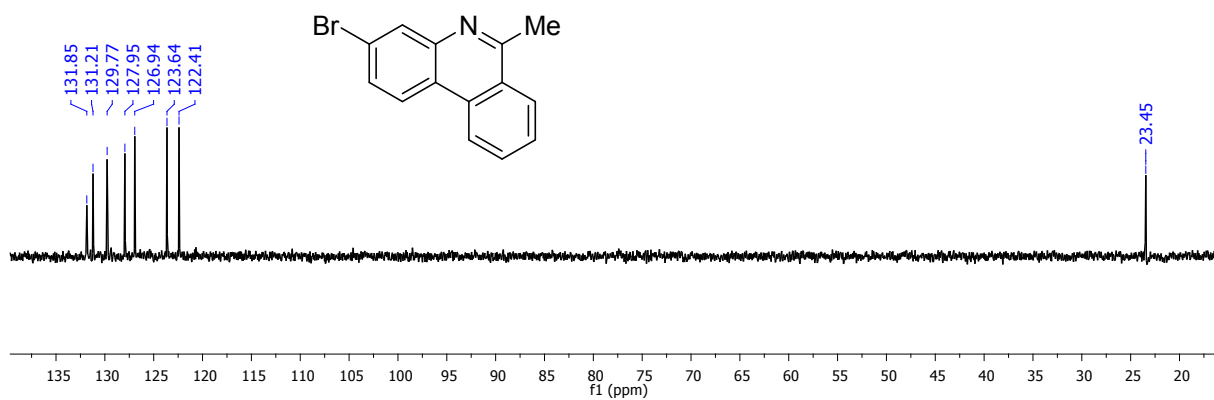
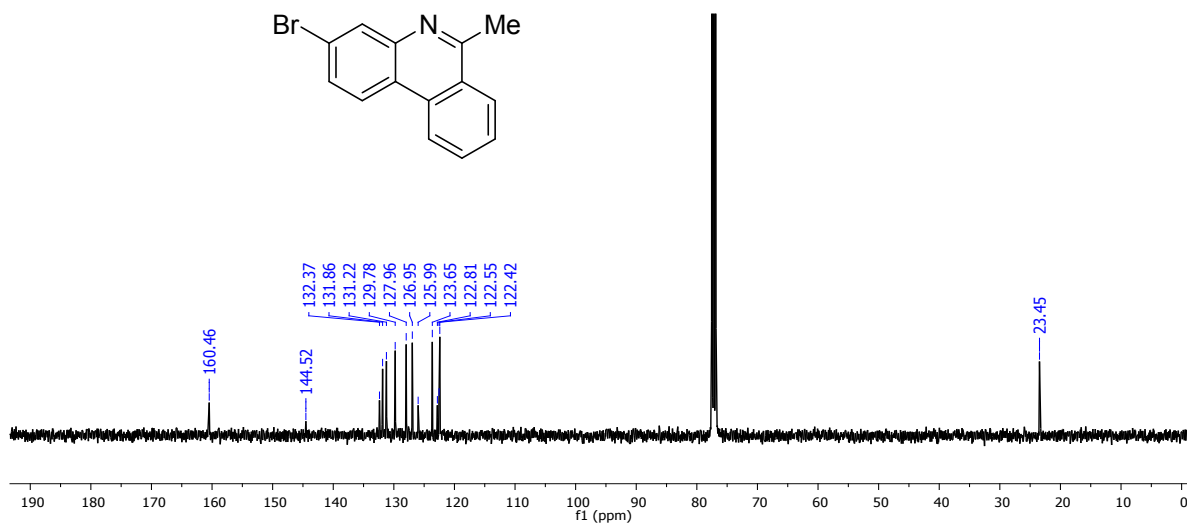
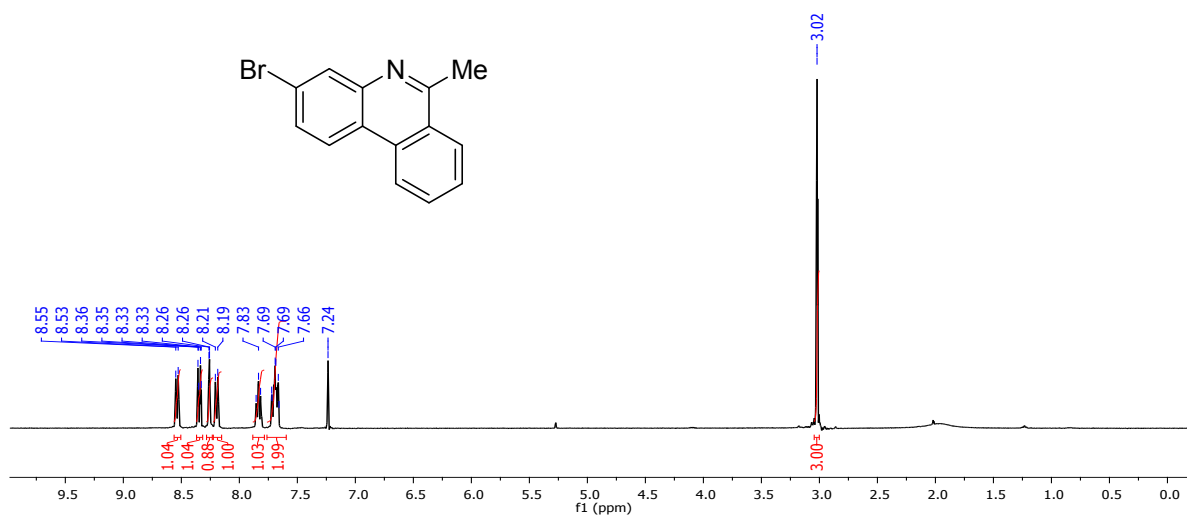
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 168.3, 138.3, 134.1, 132.5, 132.0, 130.6, 129.1, 128.9, 128.9, 127.8, 122.0, 24.4, 20.8. **HRMS (ESI):**

calc. for $[(\text{C}_{15}\text{H}_{15}\text{NO})\text{H}]$ (M+H) 226.1232, measured 226.1235.

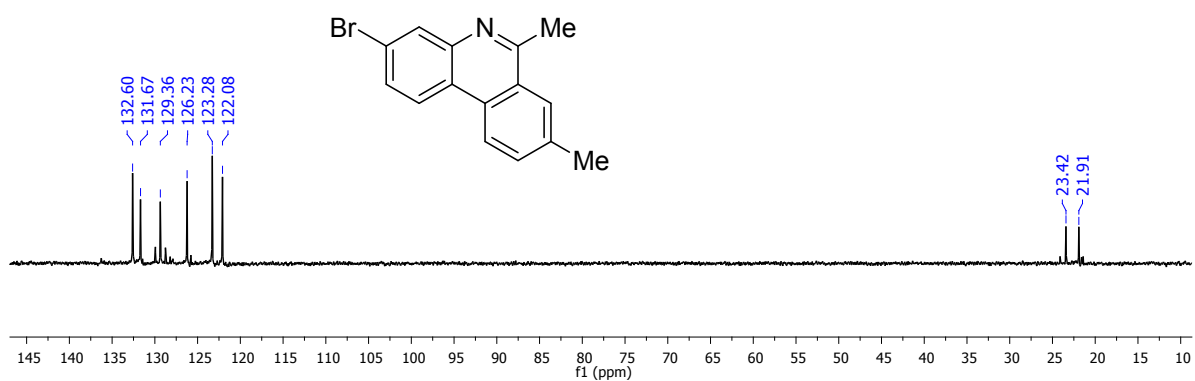
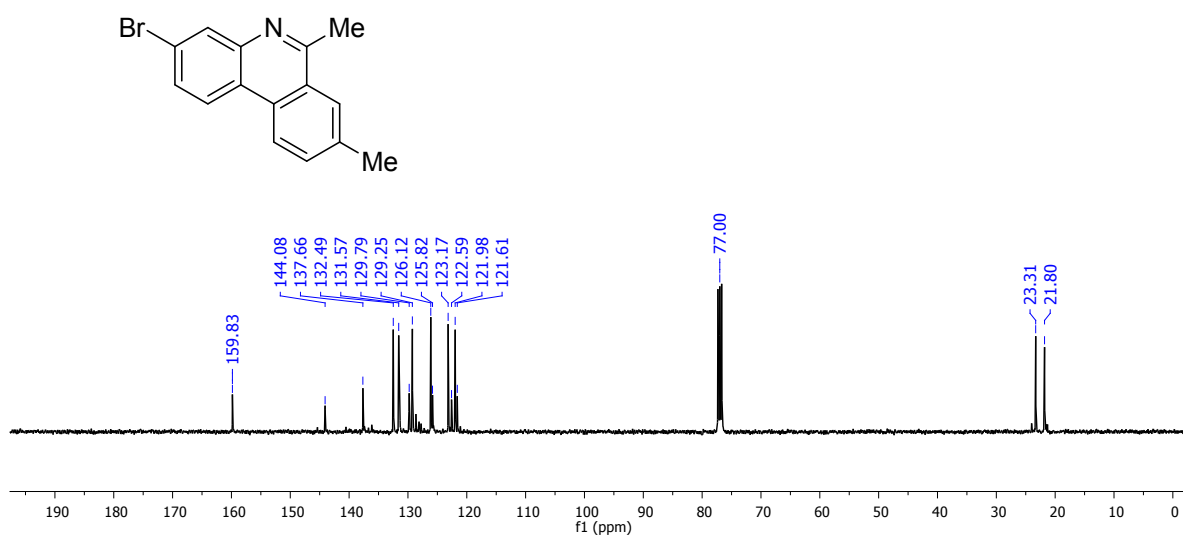
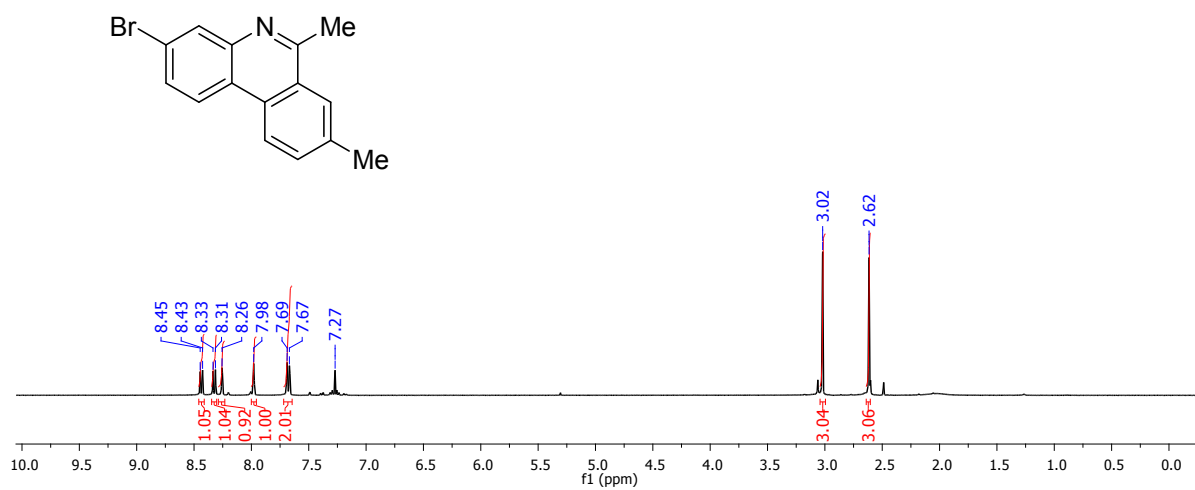
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1. R. K. Chinnagolla and J. Masilamani, *Chem. Commun.*, 2014, **50**, 2442-2444.
2. J. Heng, A. Xiaode, T. Kun, Z. Tianyi, Z. Yan and Y. Shouyun, *Angew. Chem. Int. Ed.*, 2015, **54**, 4055-4059.
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4. X. Jie, D. Qing-Li, L. Guan-Sai, W. Shaozhong, C. Lin and Y. Zhu-Jun, *SYNLETT* 2010, **11**, 1674-1678.

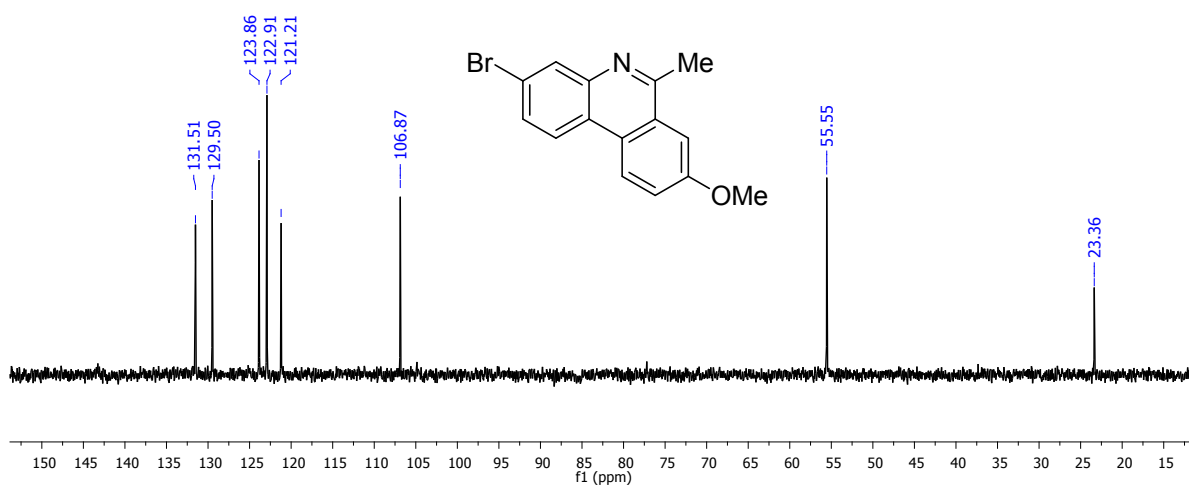
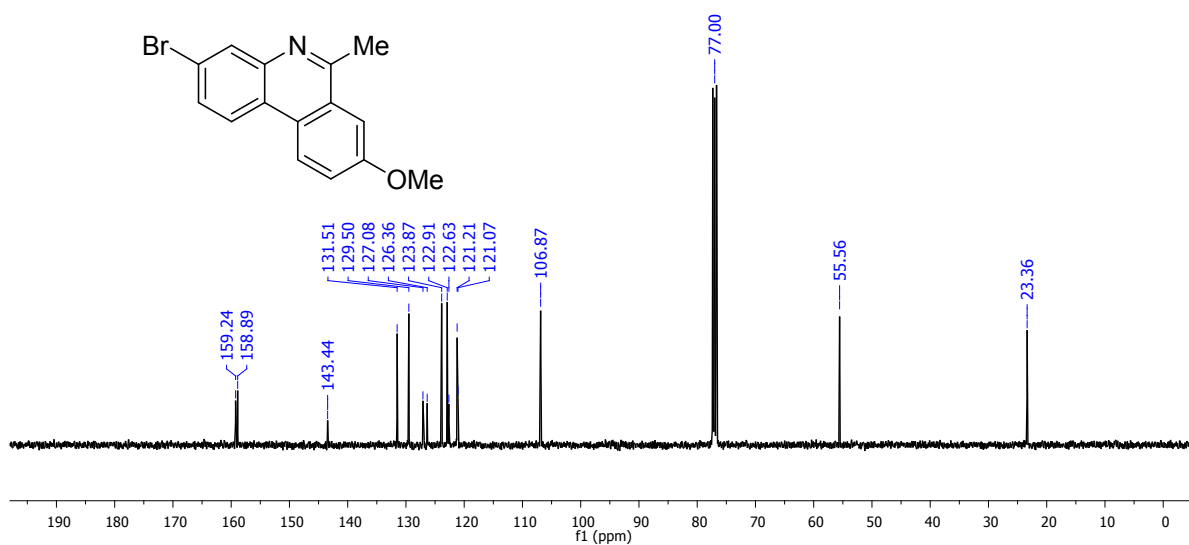
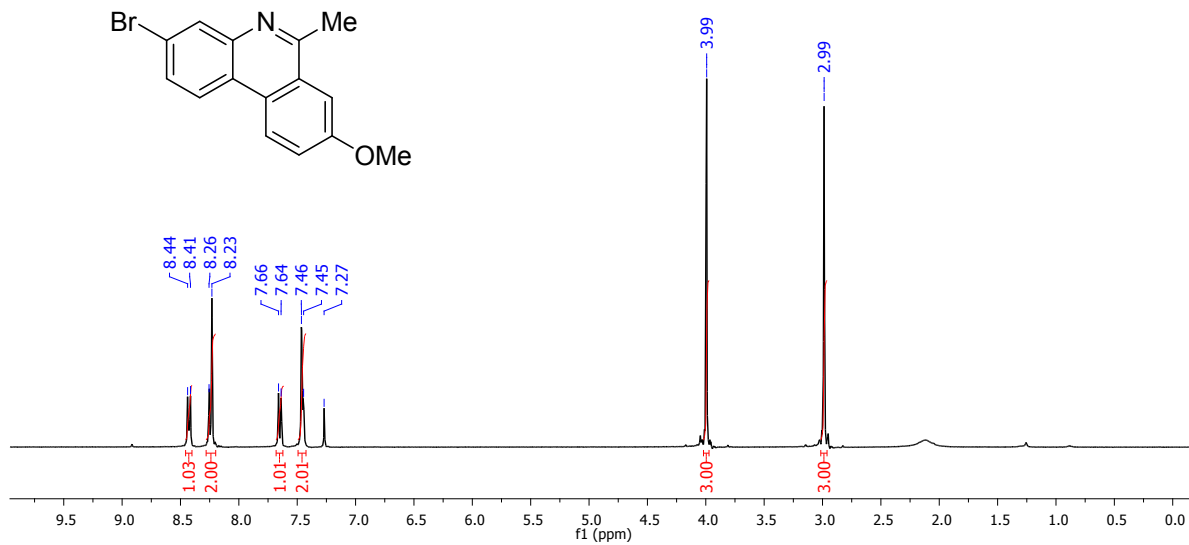
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4a.



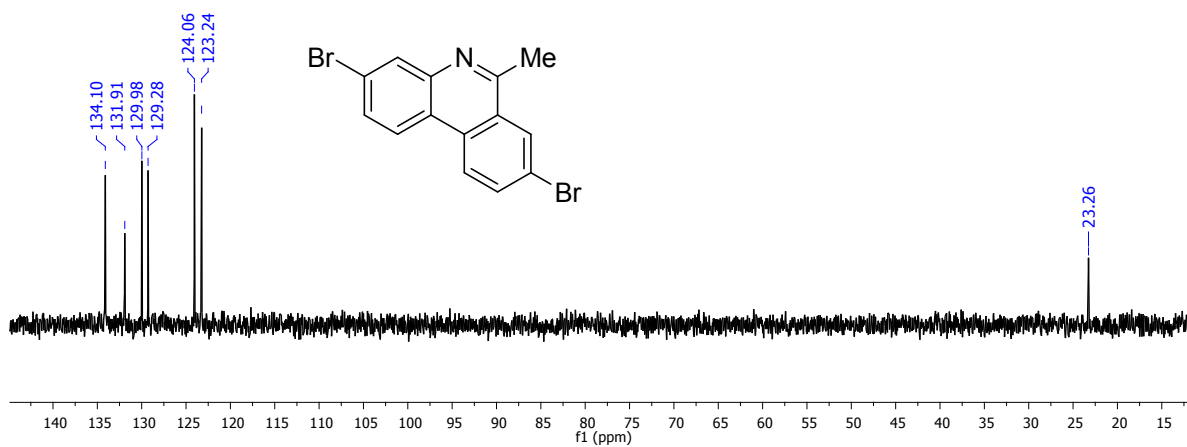
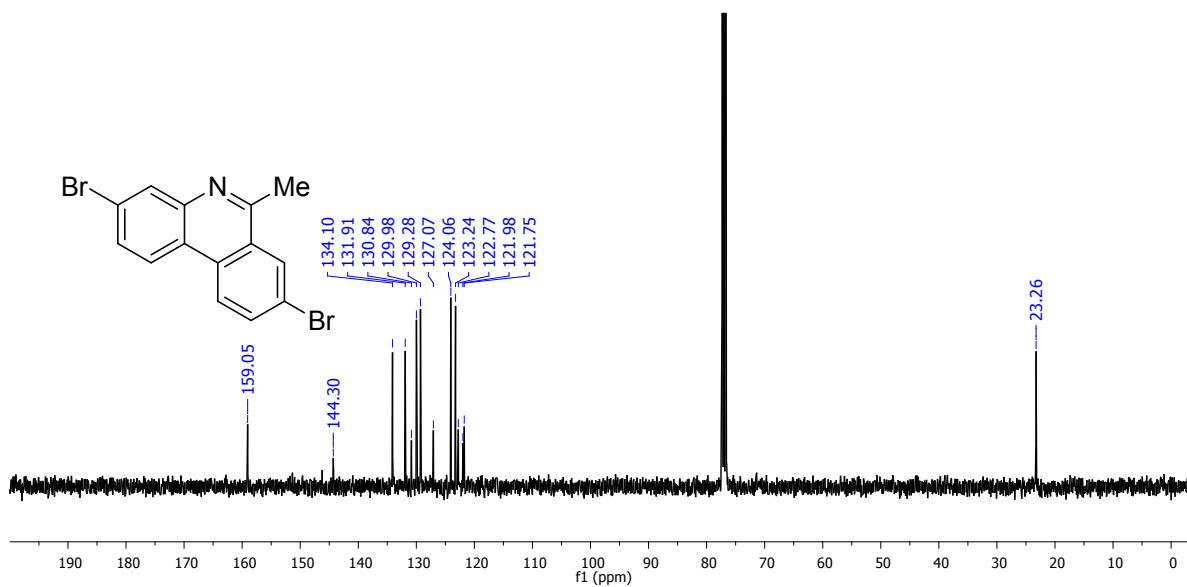
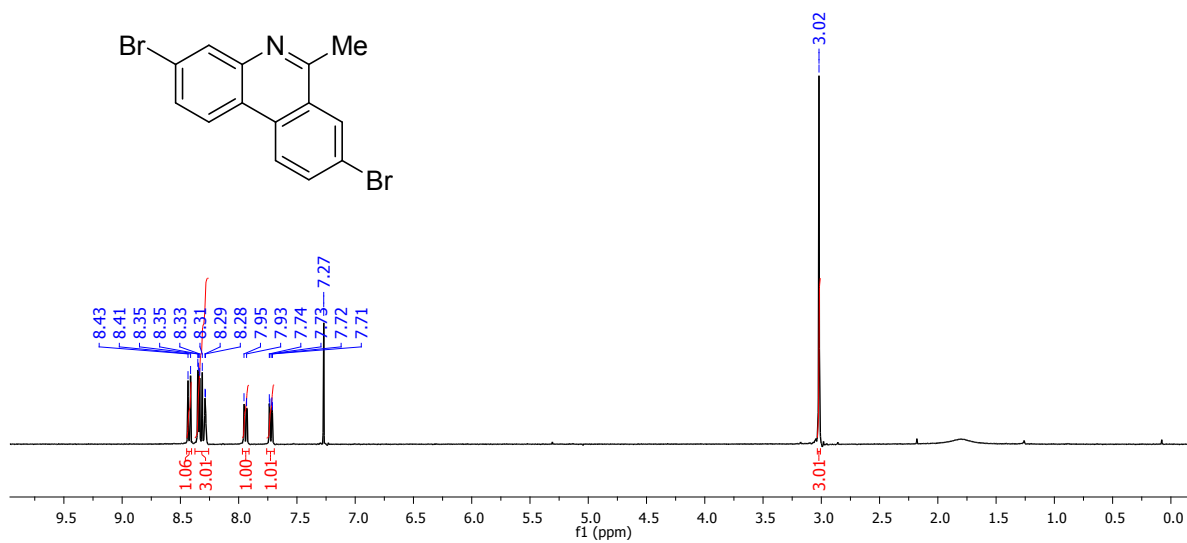
H^1, C^{13} and DEPT NMR Spectra's of compound of 4b.



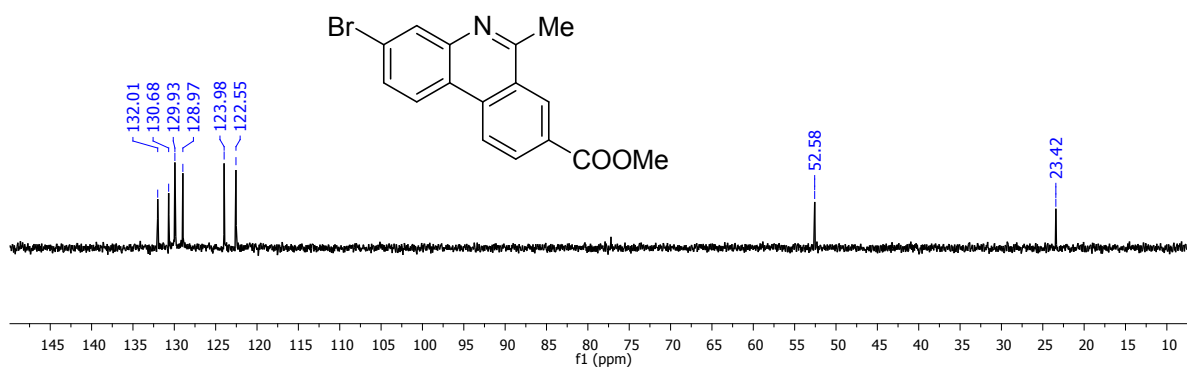
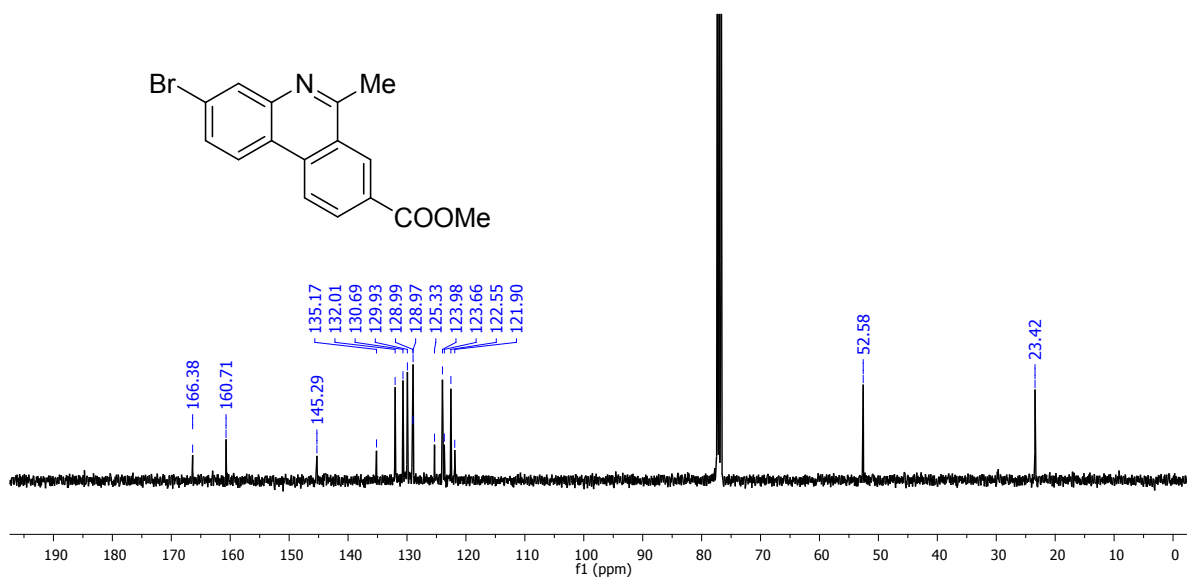
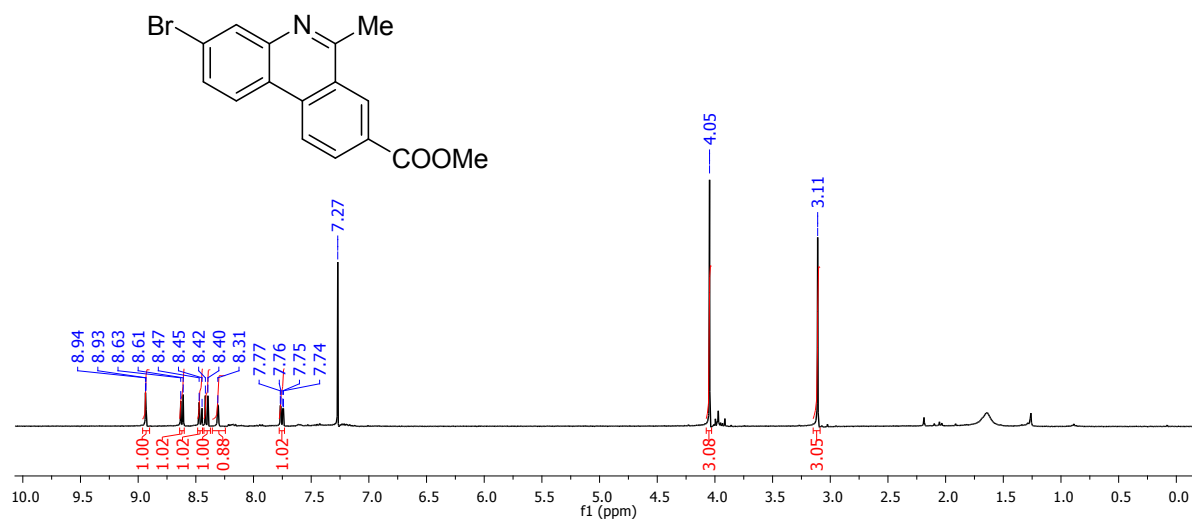
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4c.



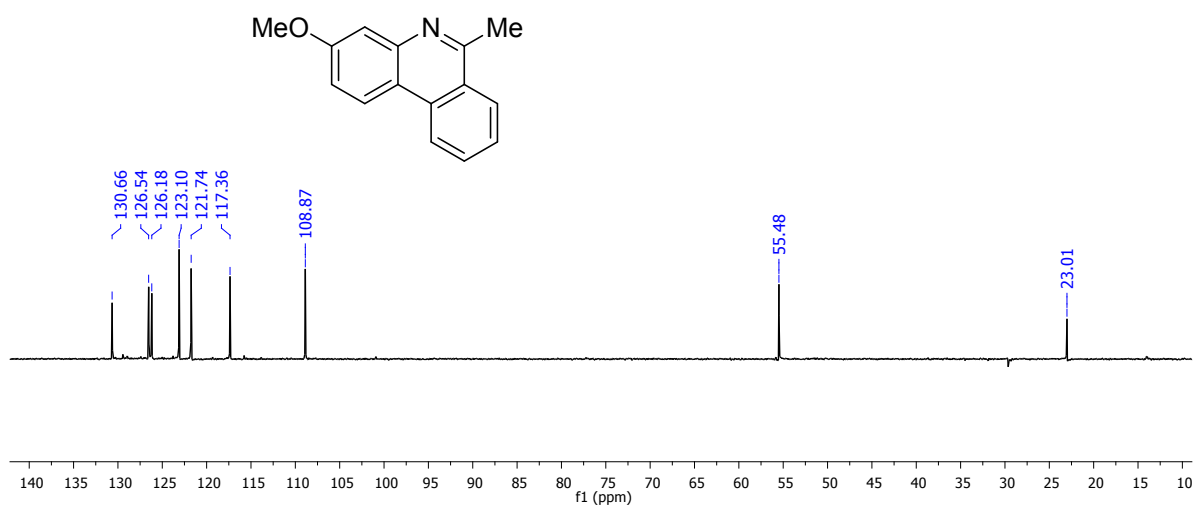
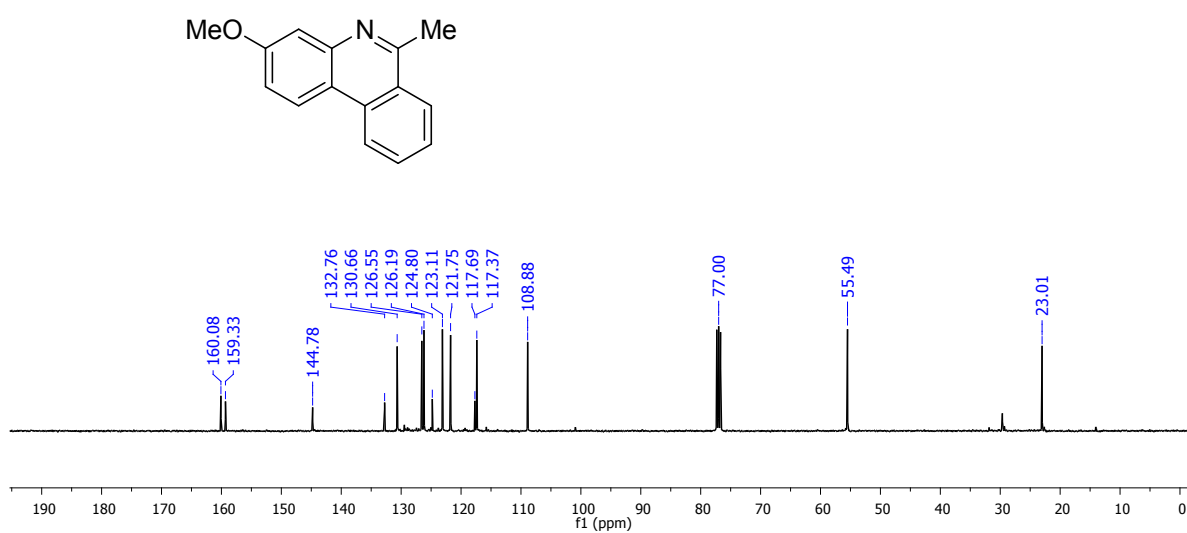
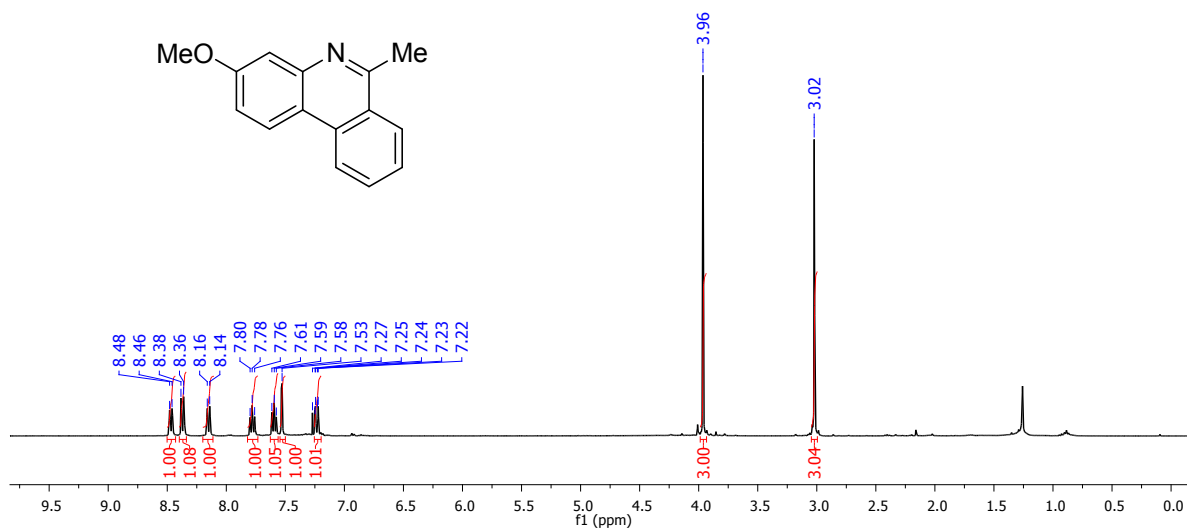
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4d.



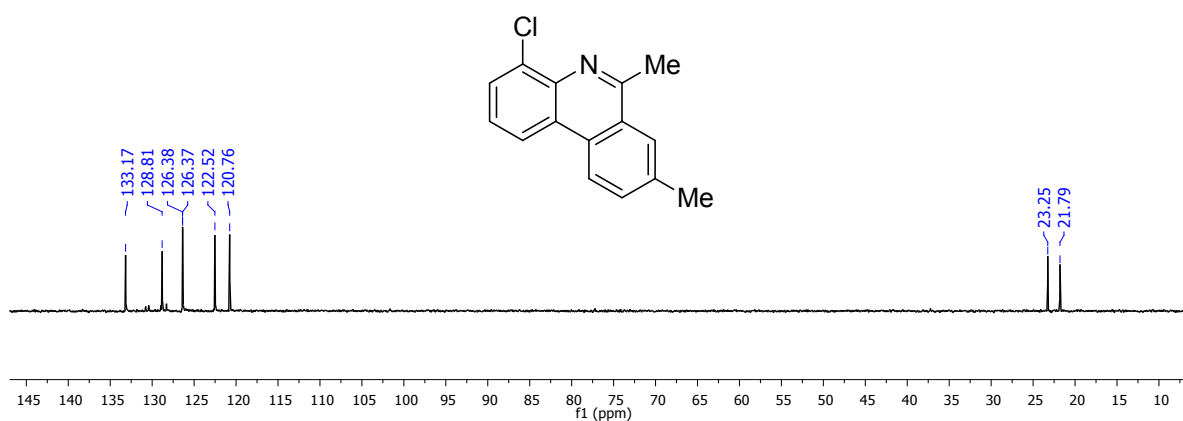
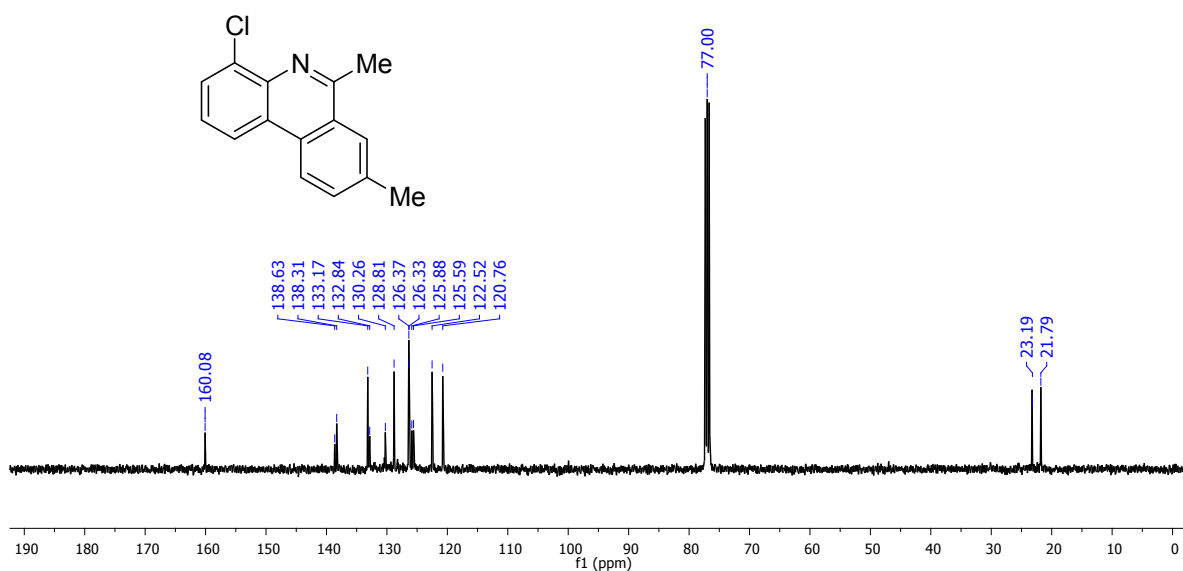
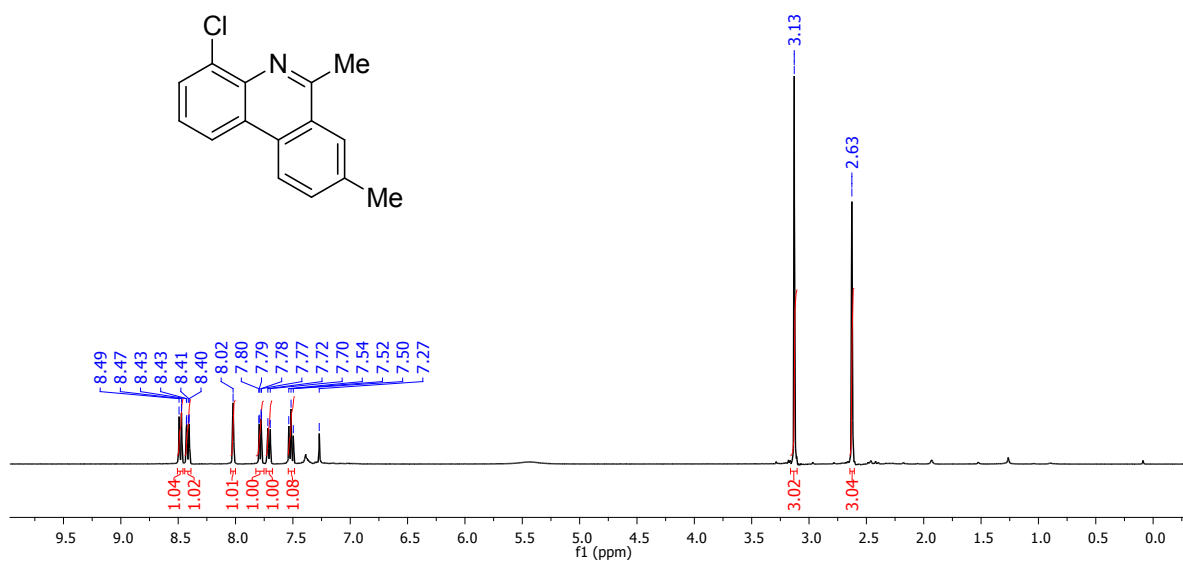
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4e.



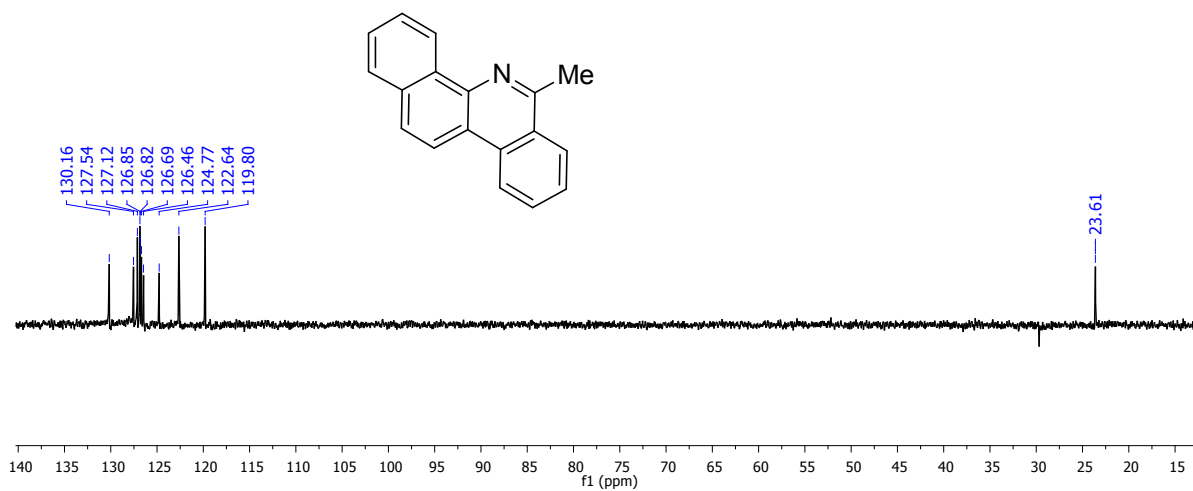
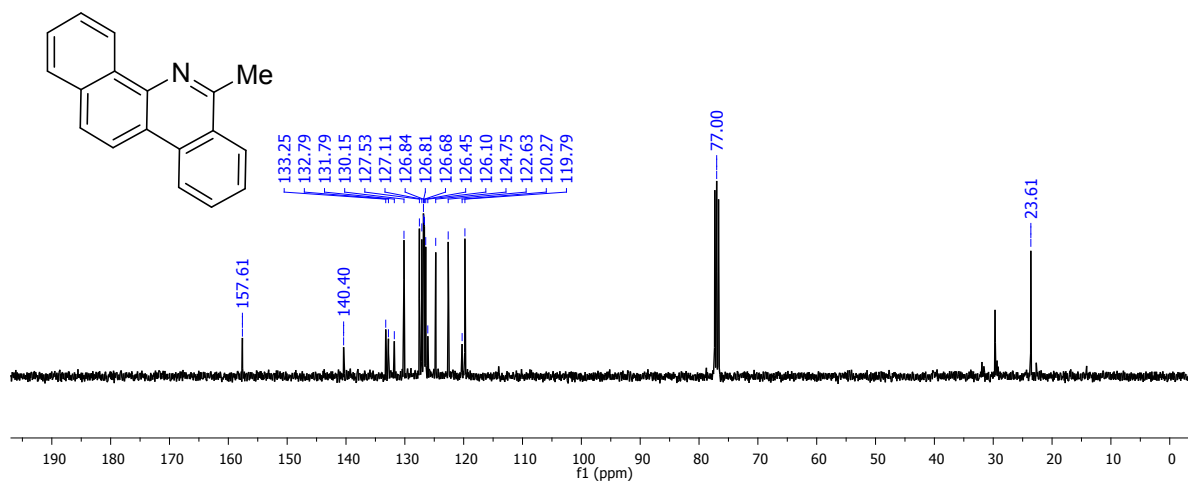
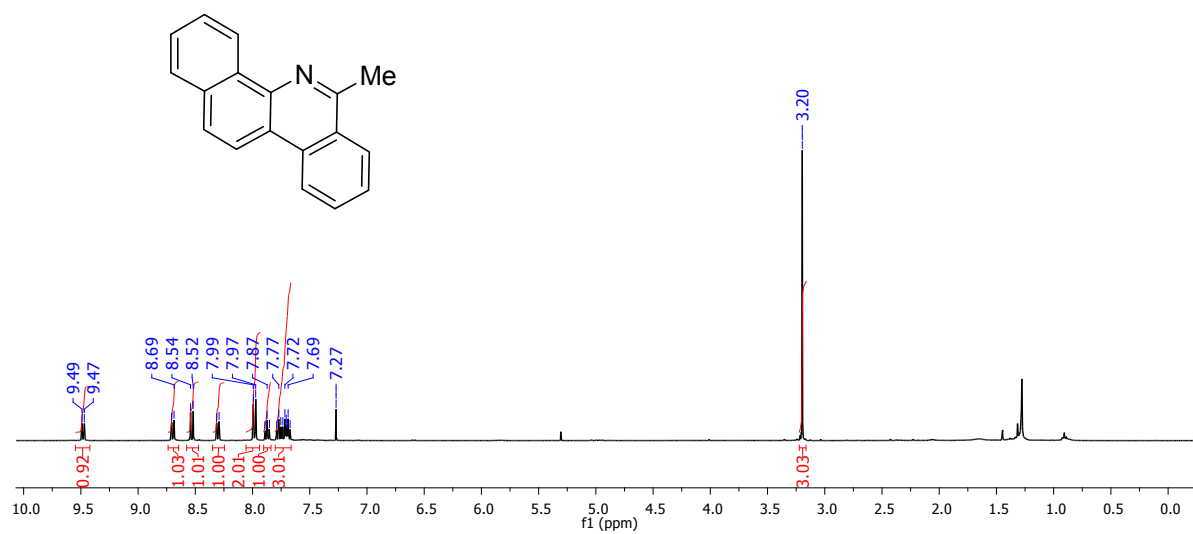
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4f.



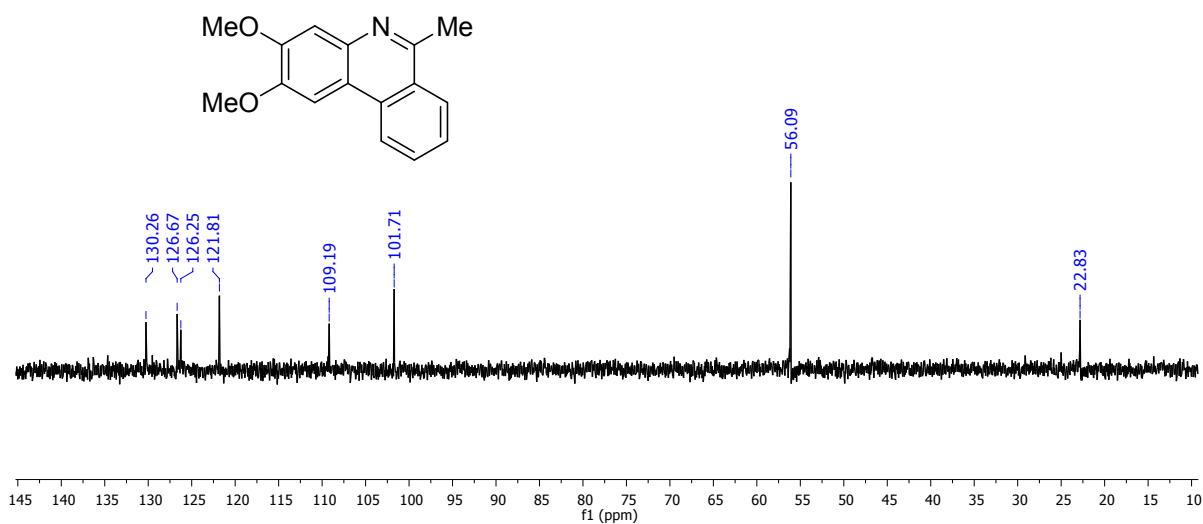
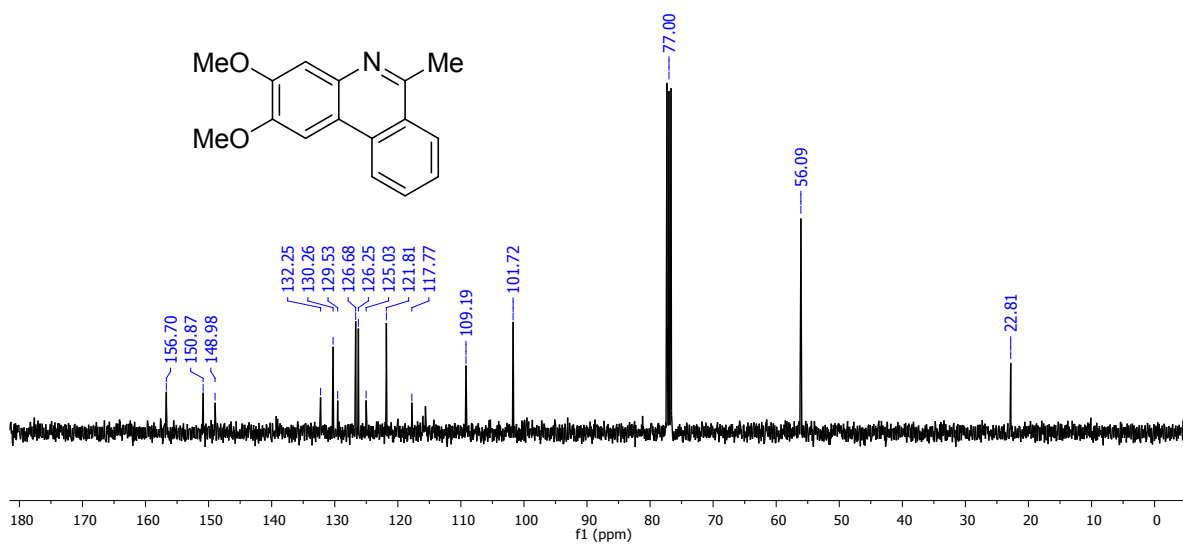
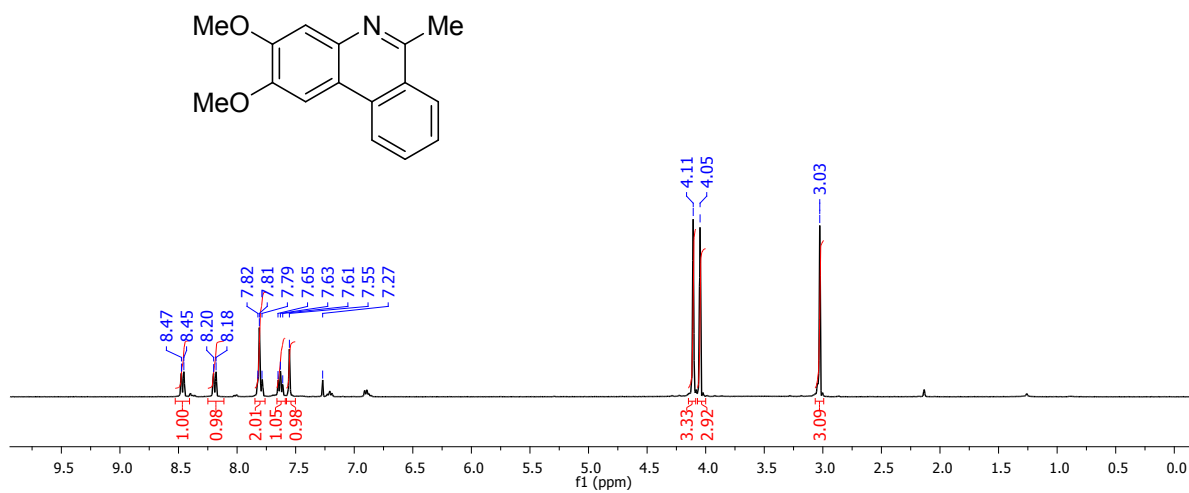
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4g.



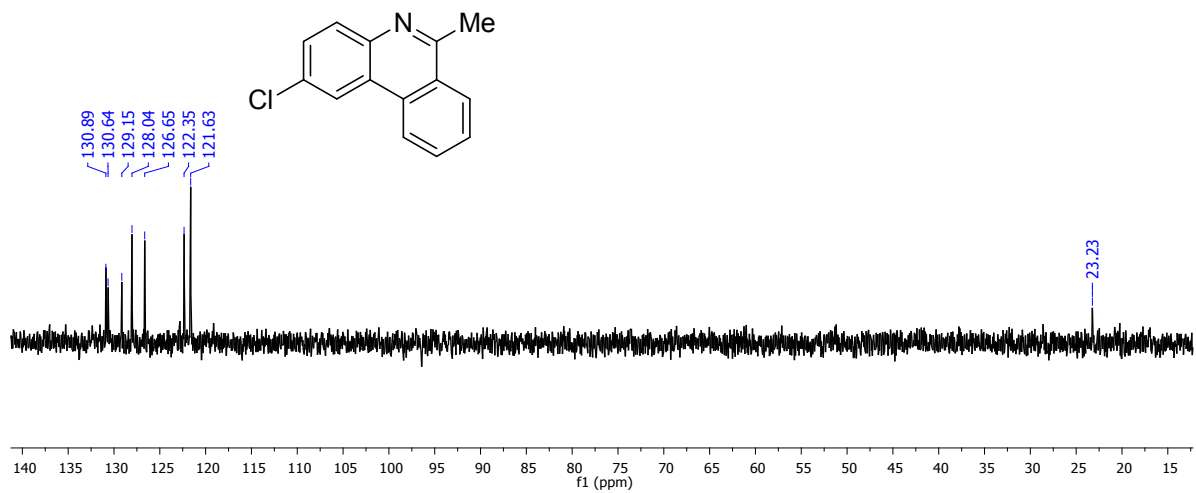
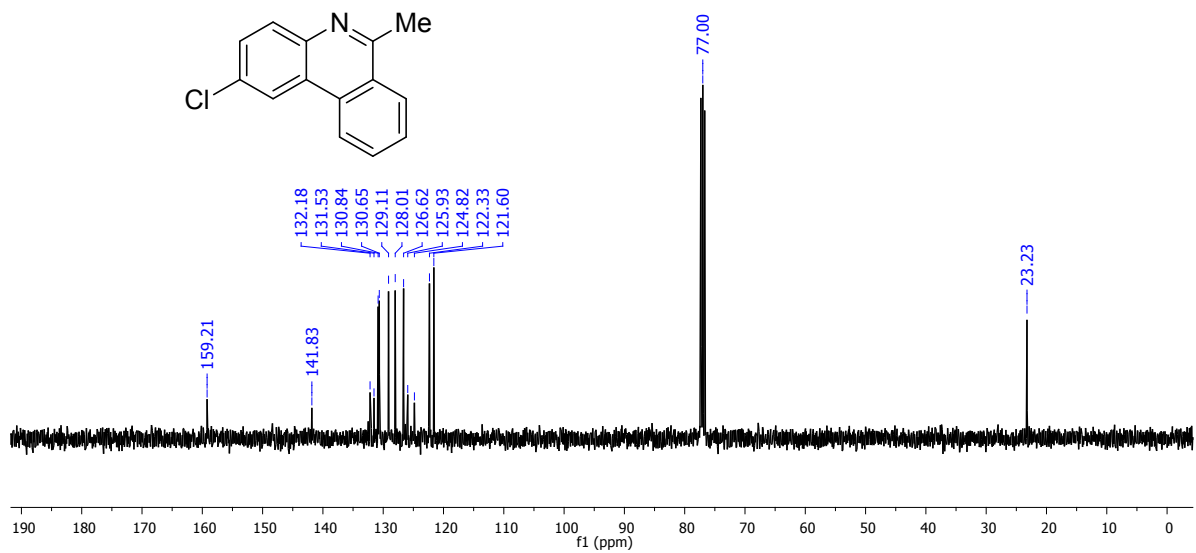
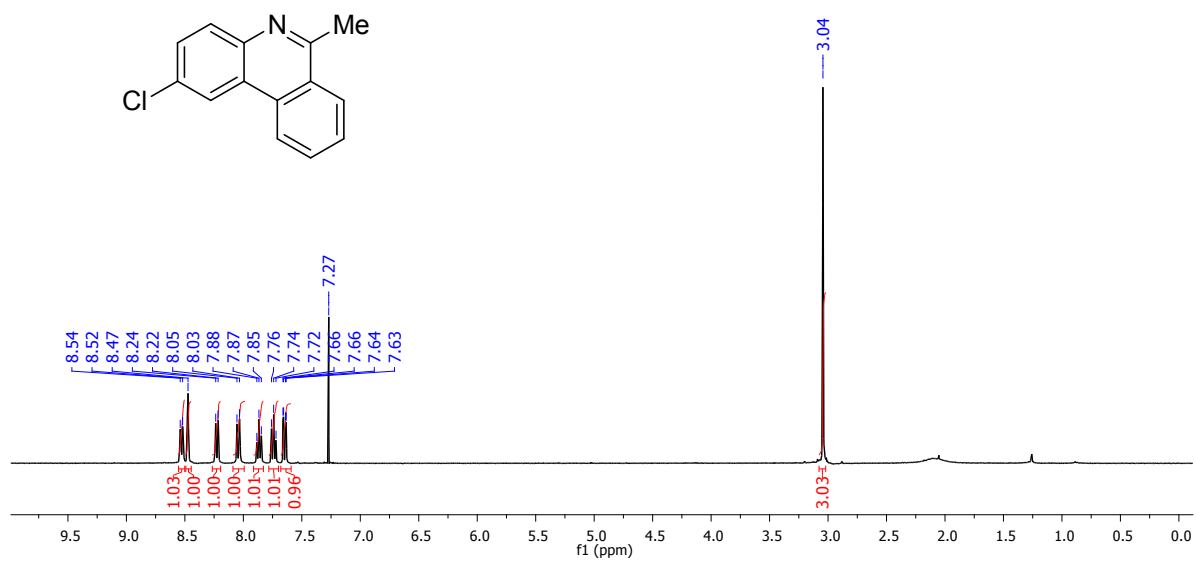
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4h.



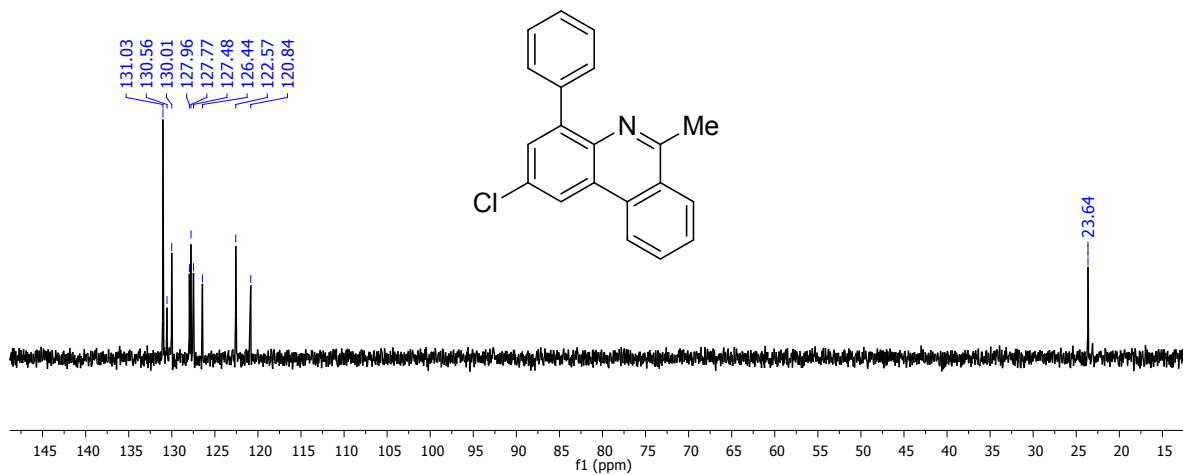
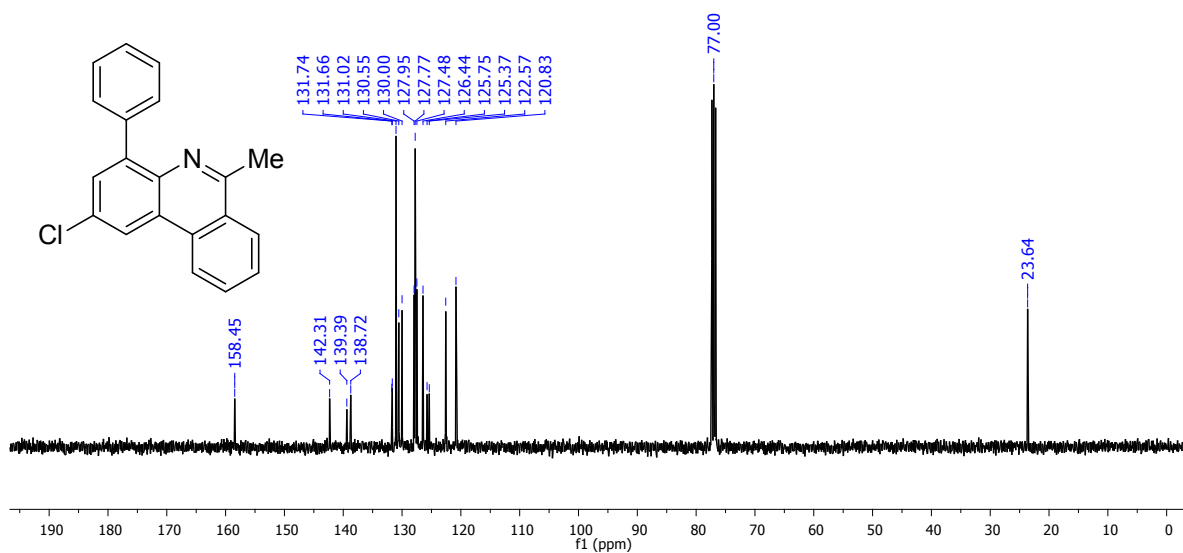
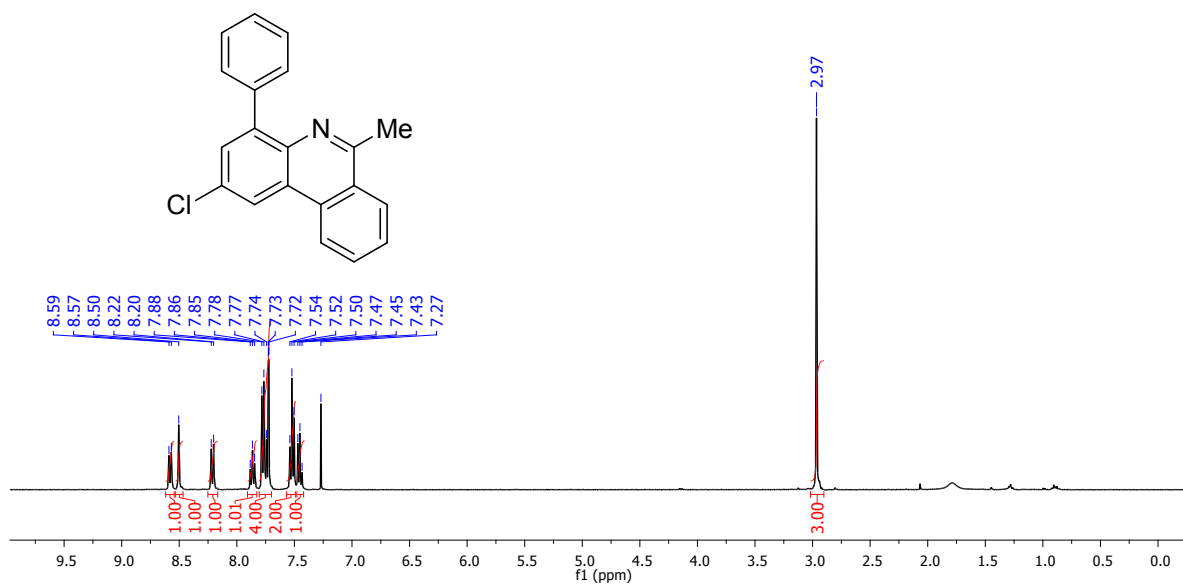
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4i.



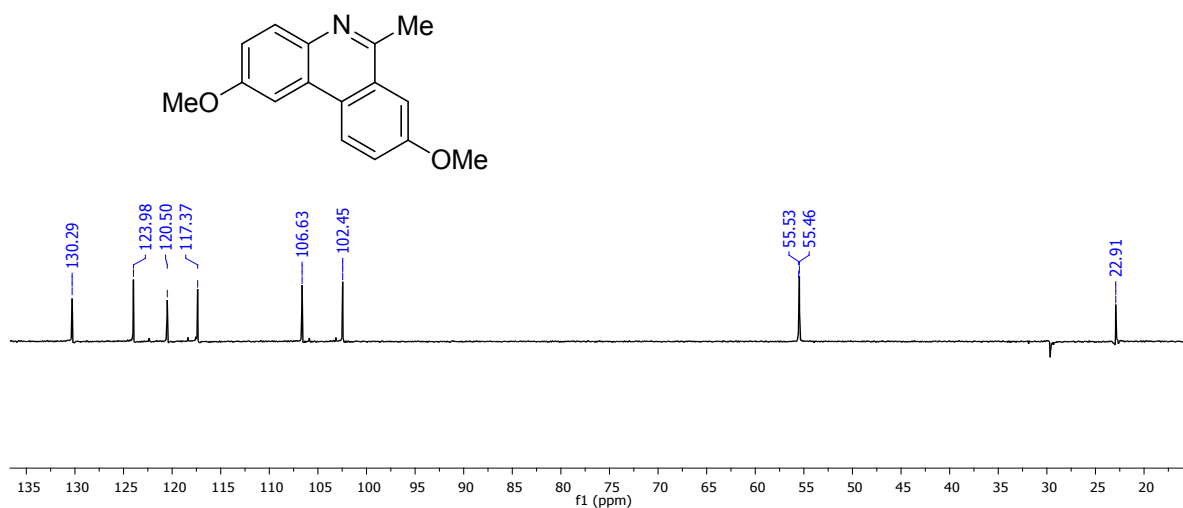
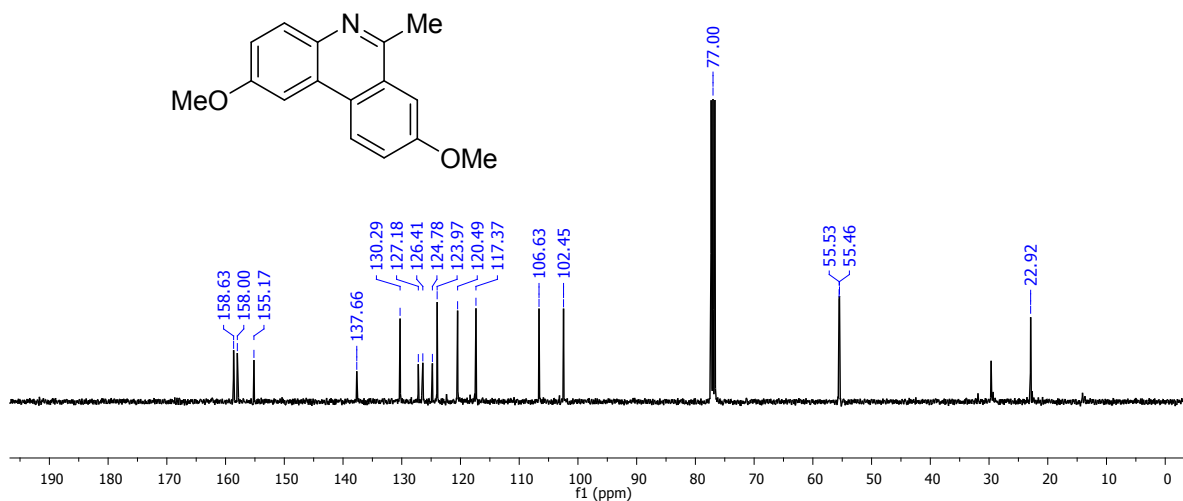
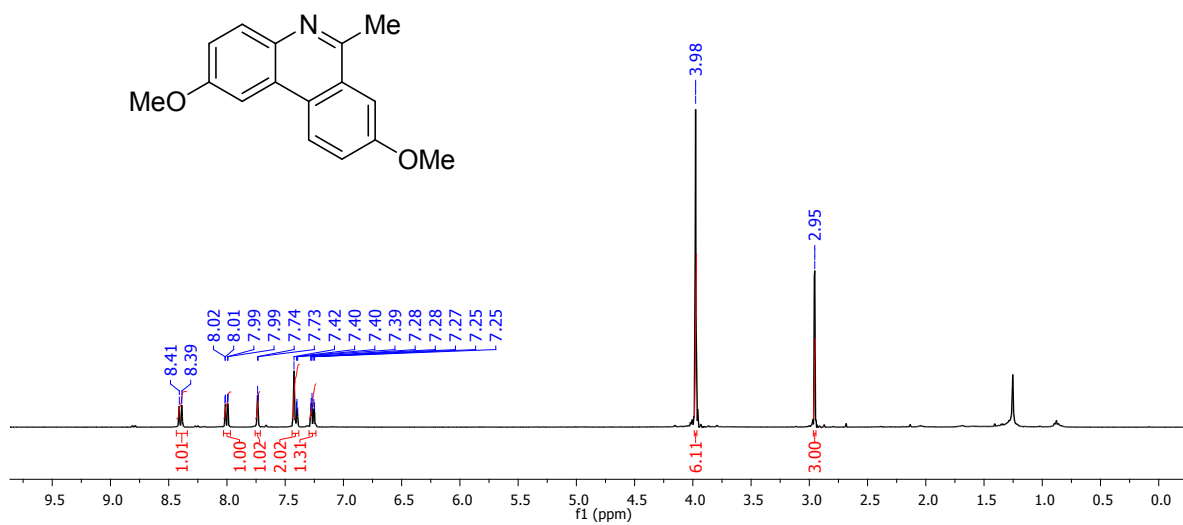
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4ja.



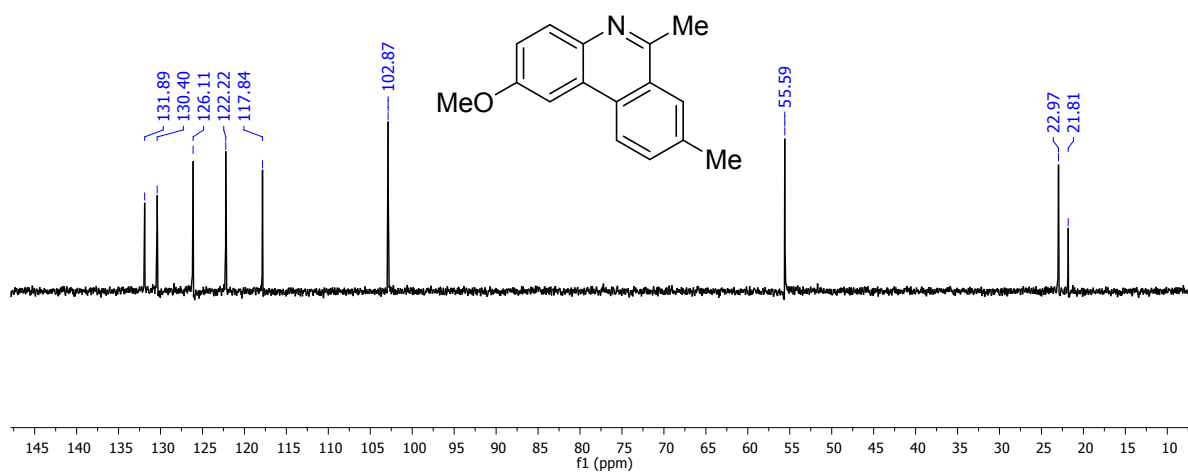
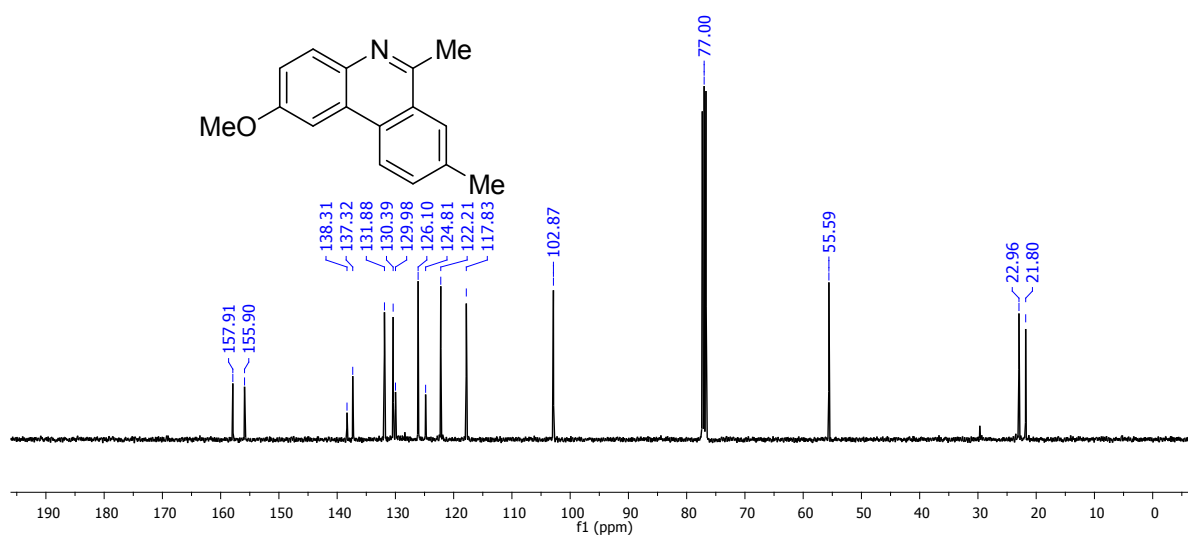
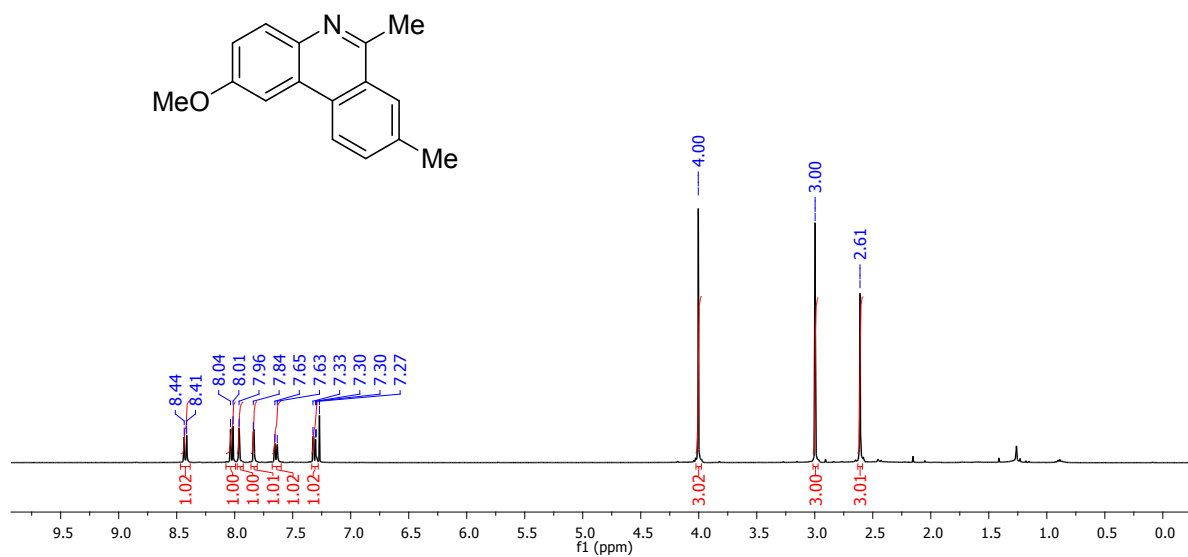
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4jb.



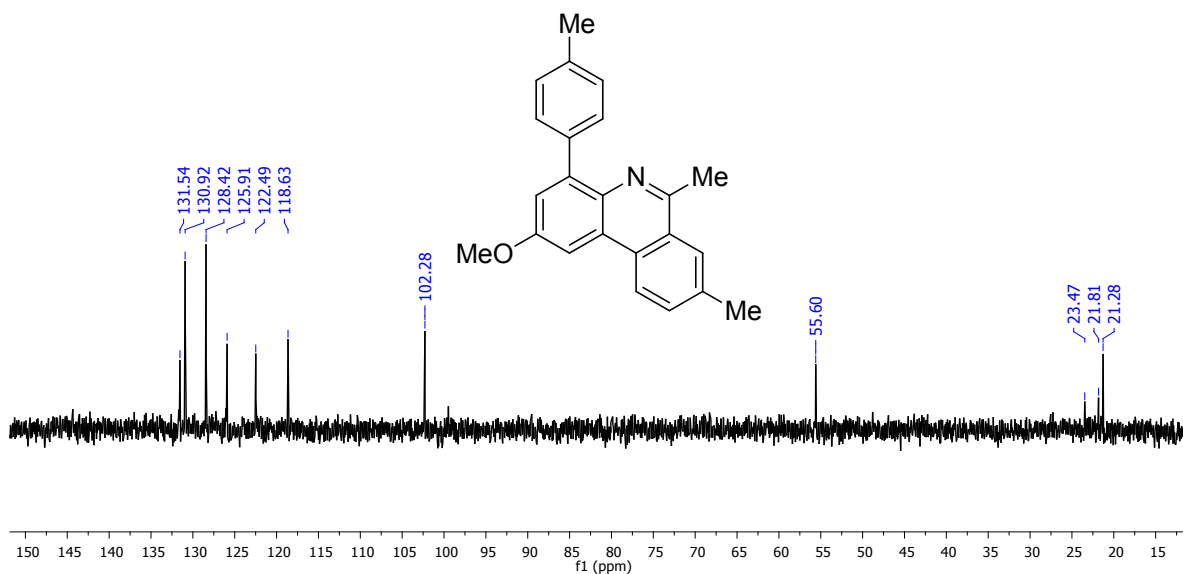
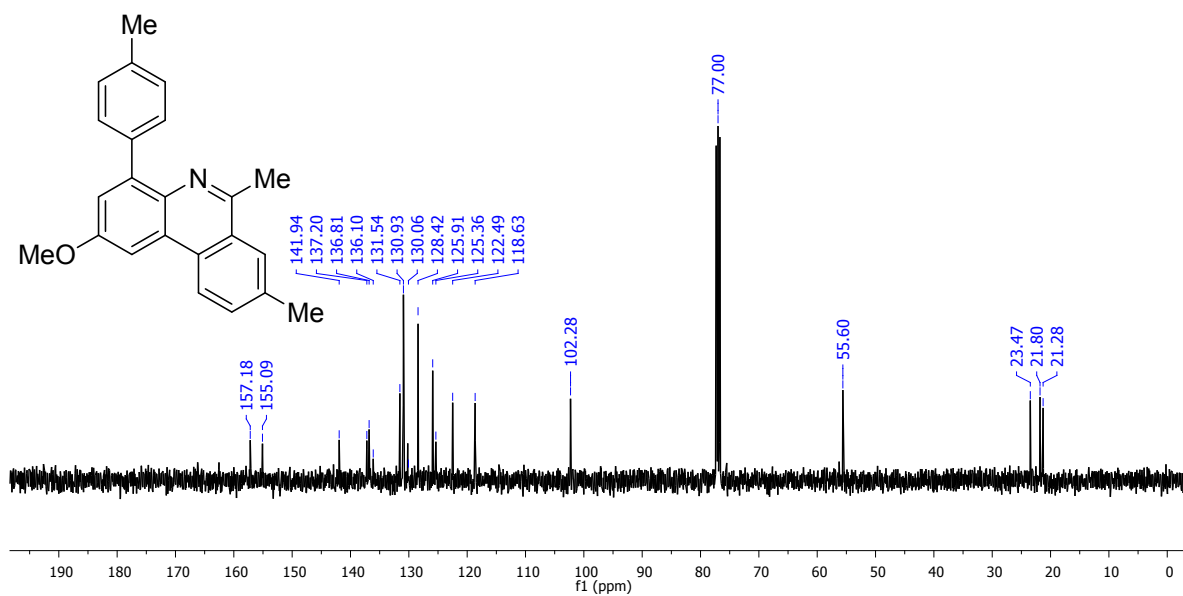
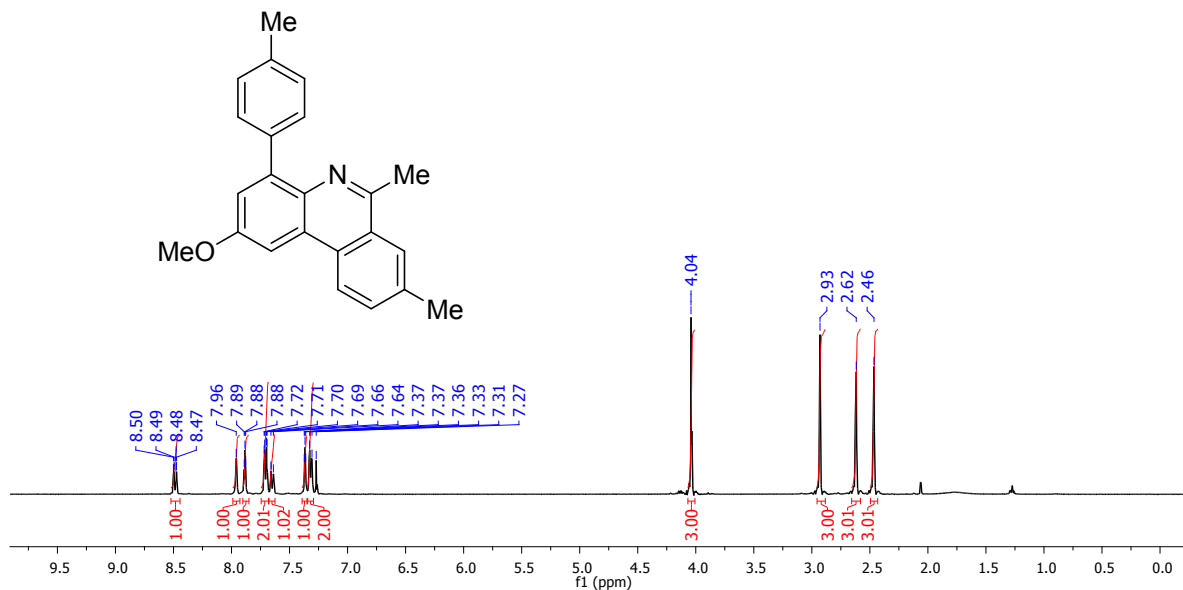
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4ka.



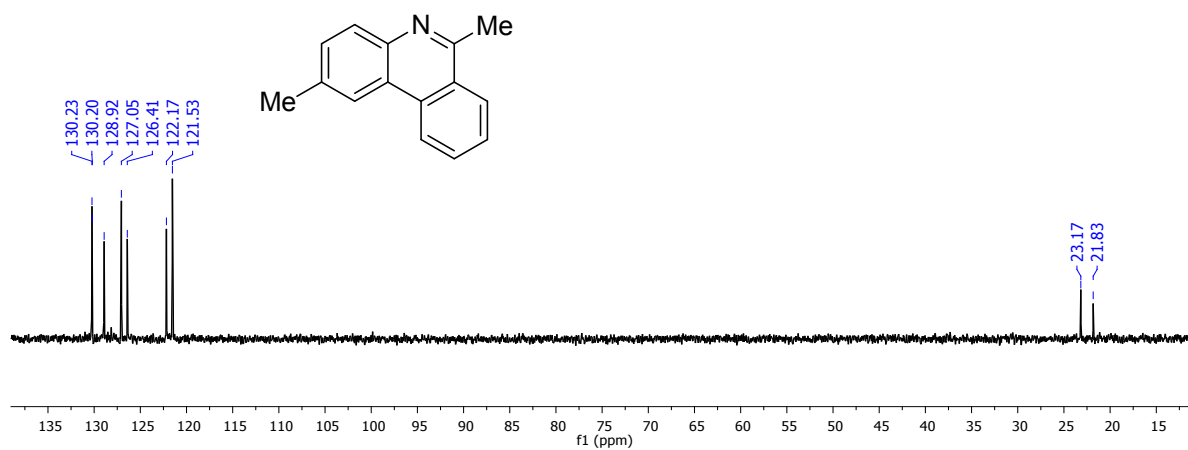
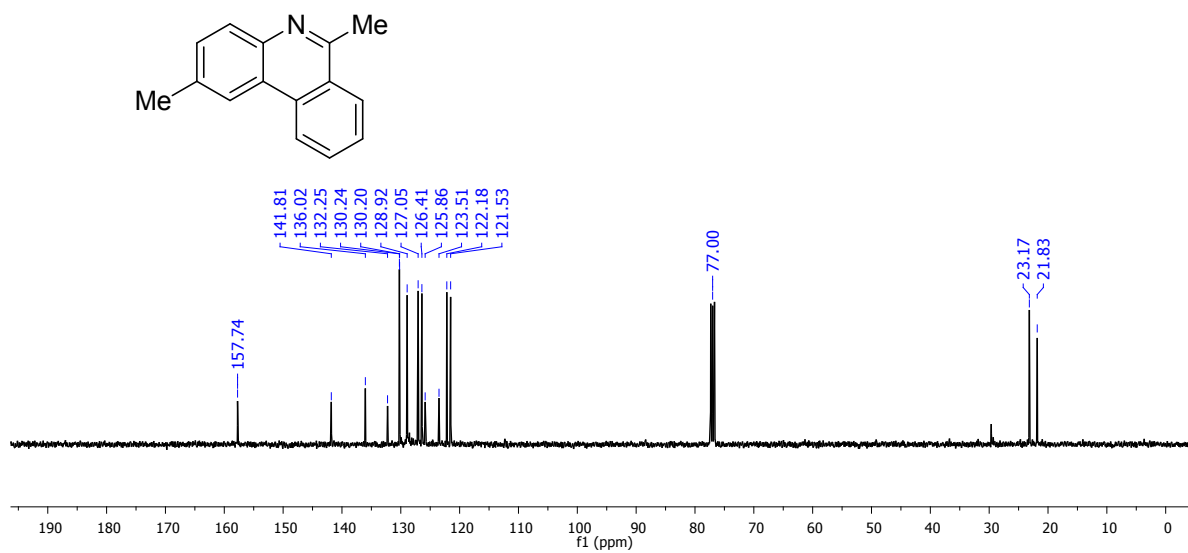
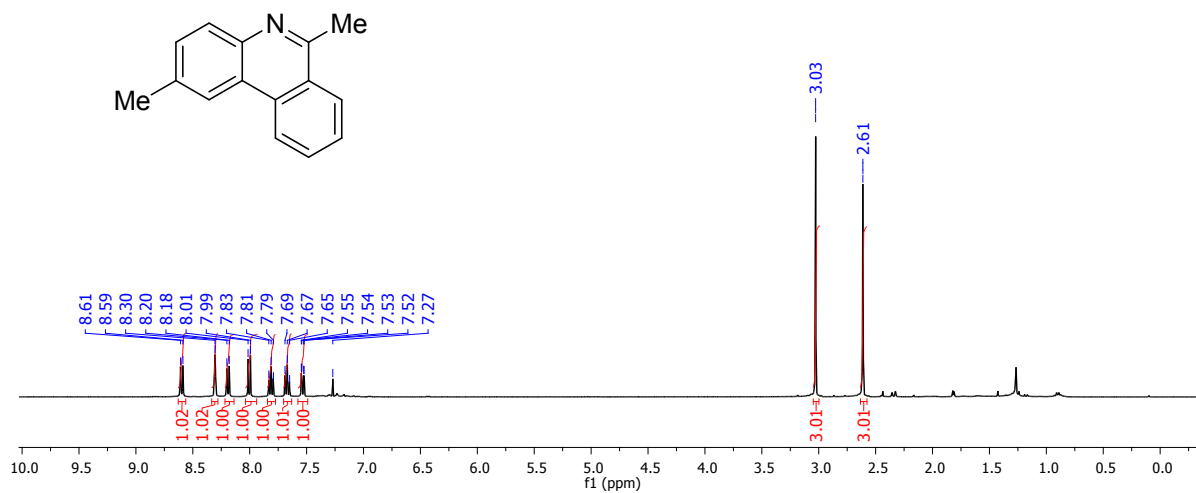
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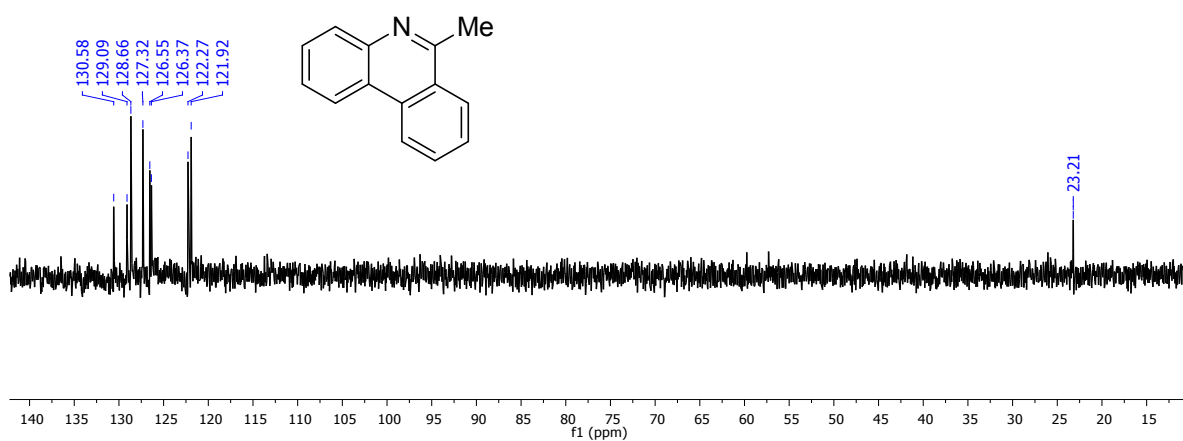
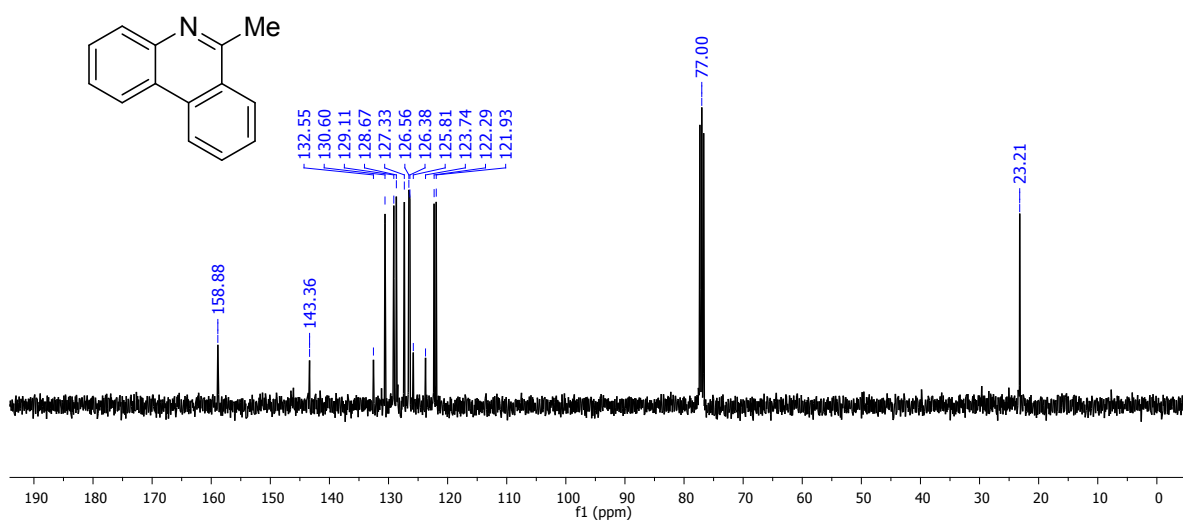
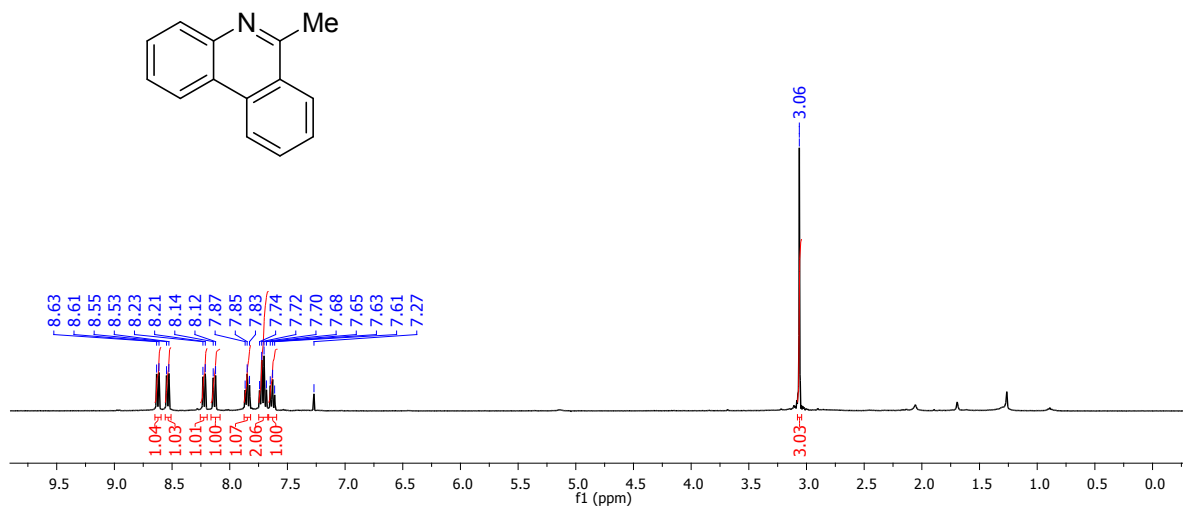
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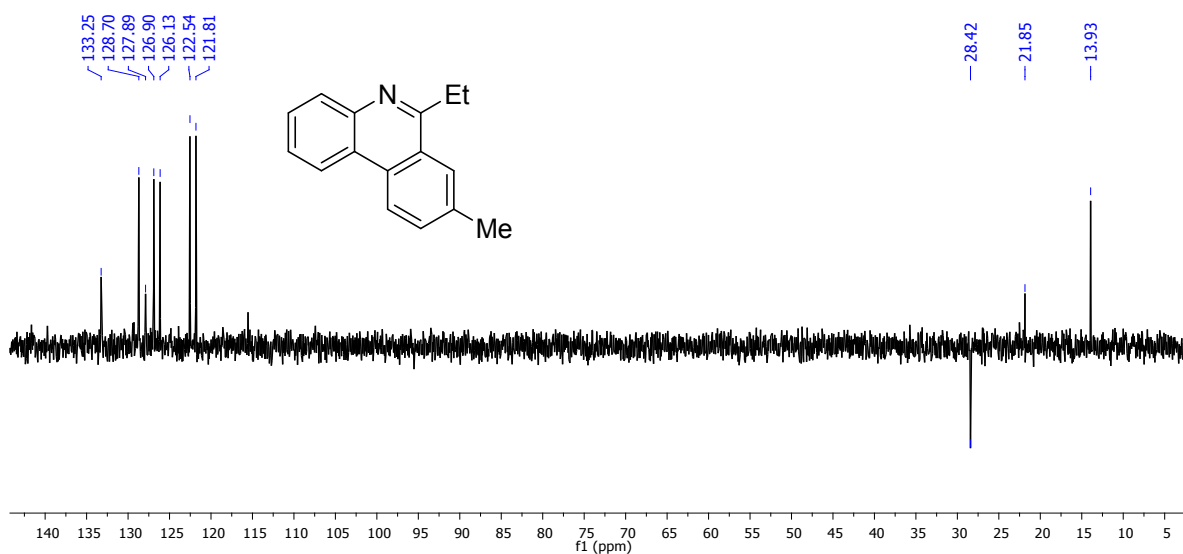
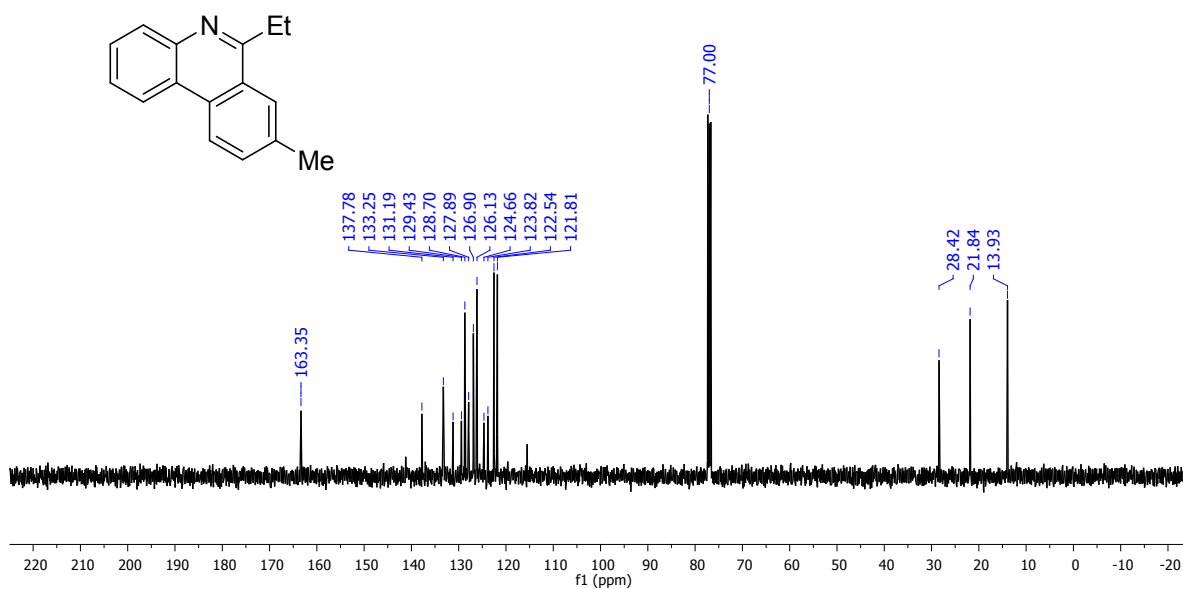
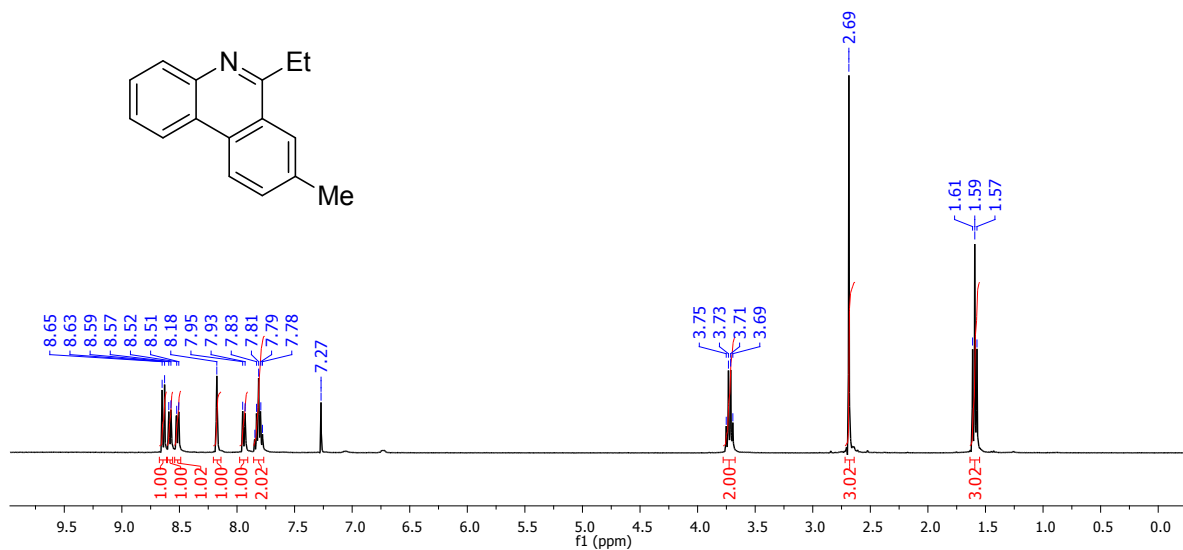
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4ma.



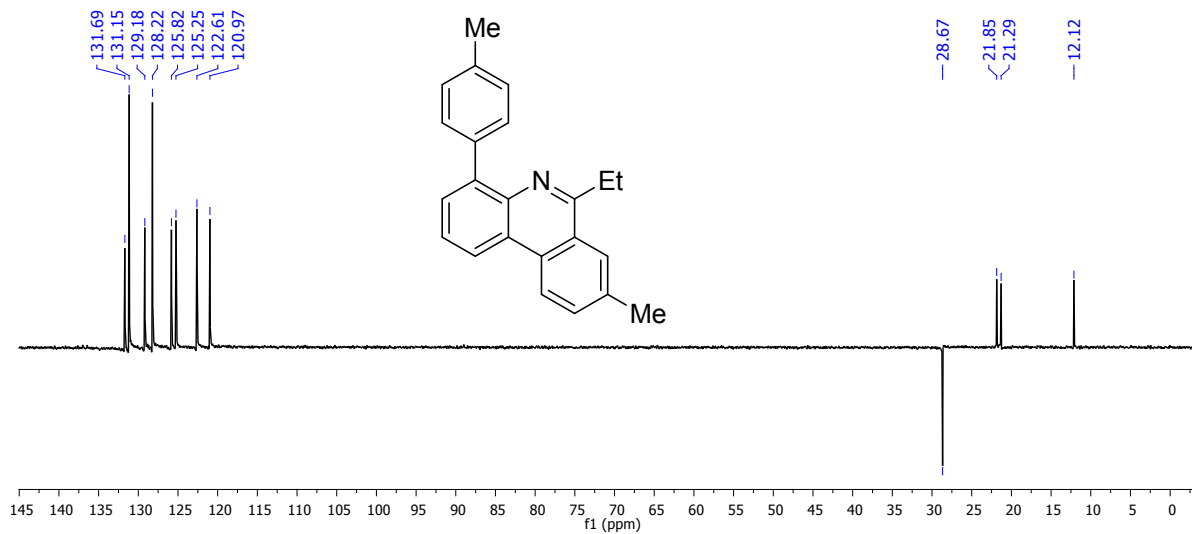
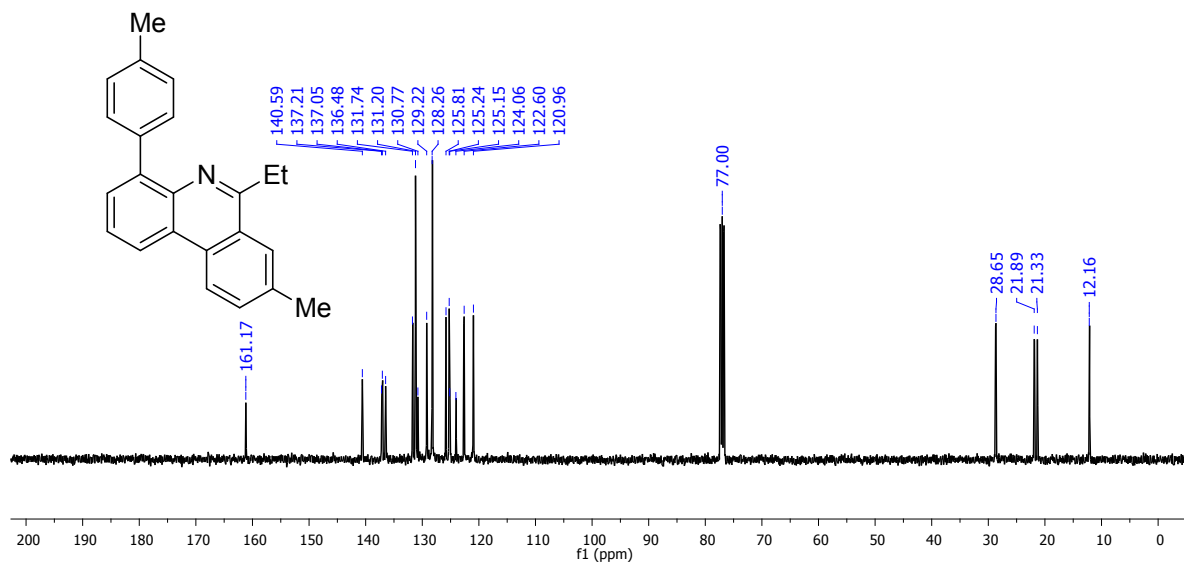
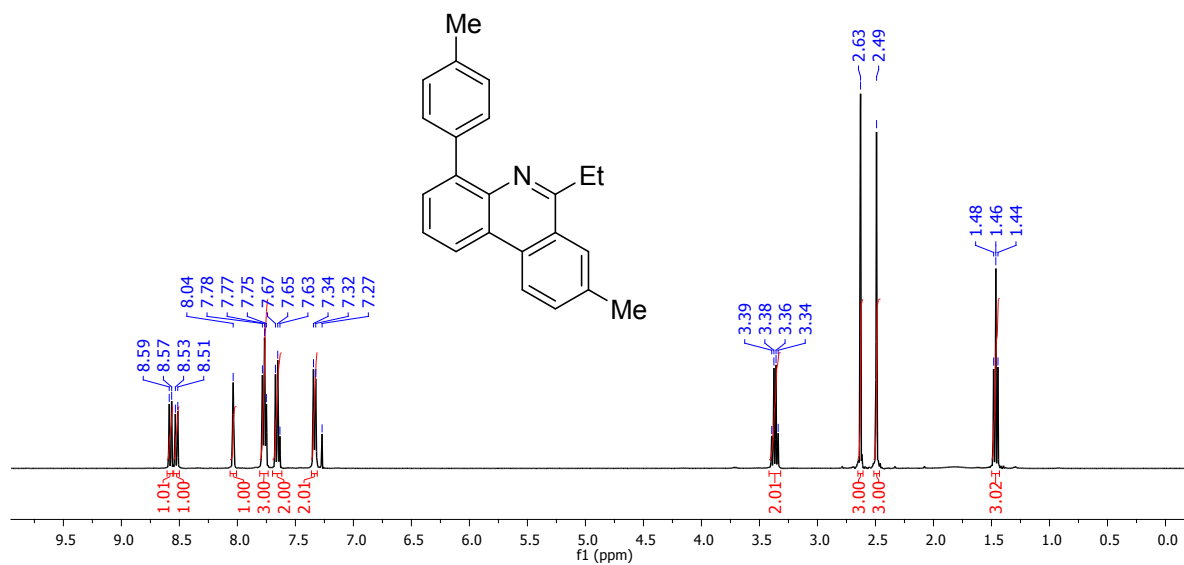
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4na.



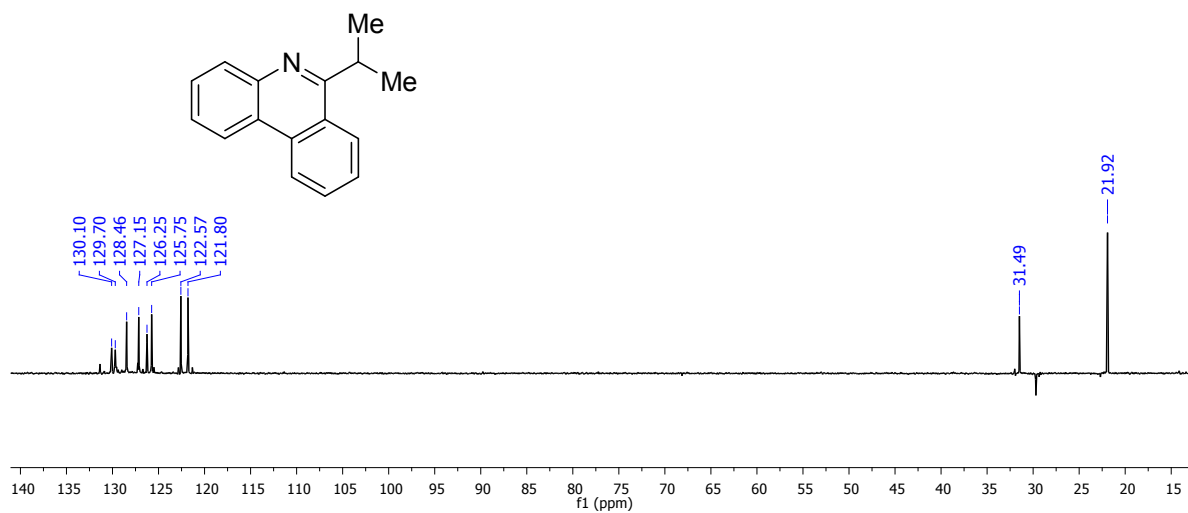
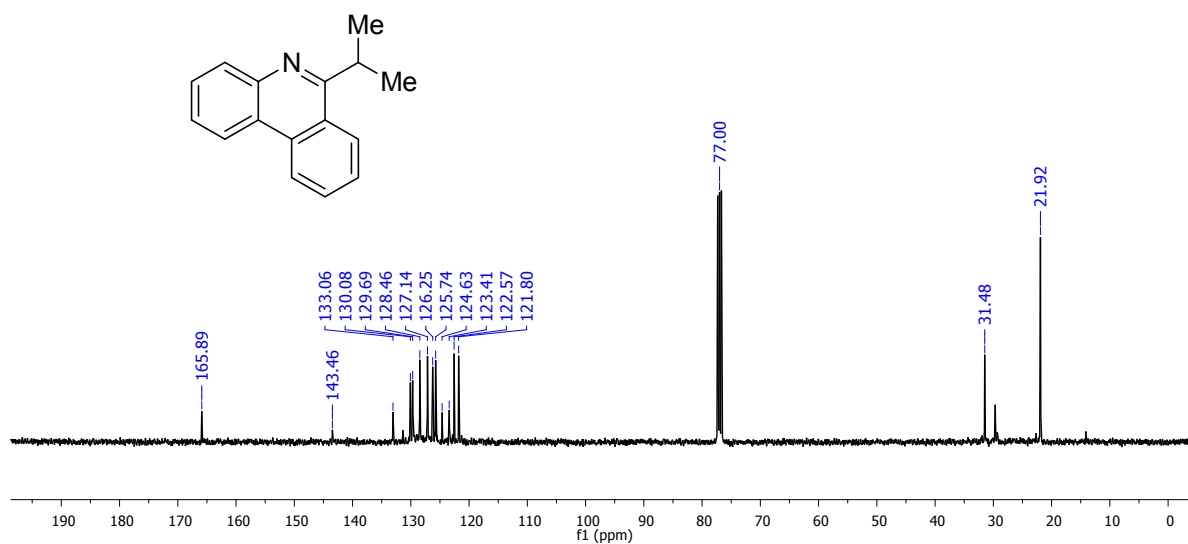
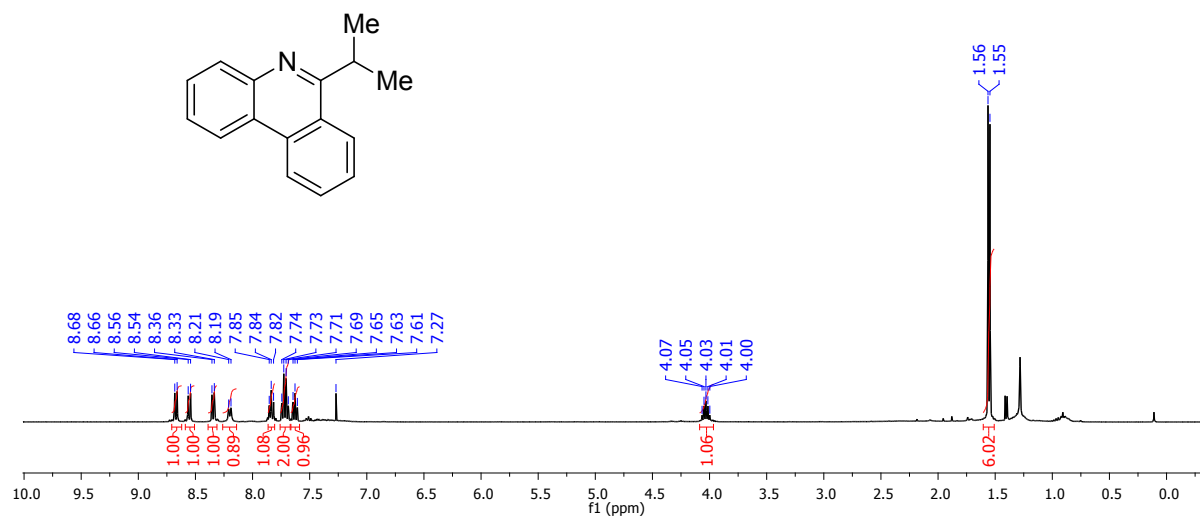
^1H , ^{13}C and DEPT NMR Spectra's of compound of 40a.



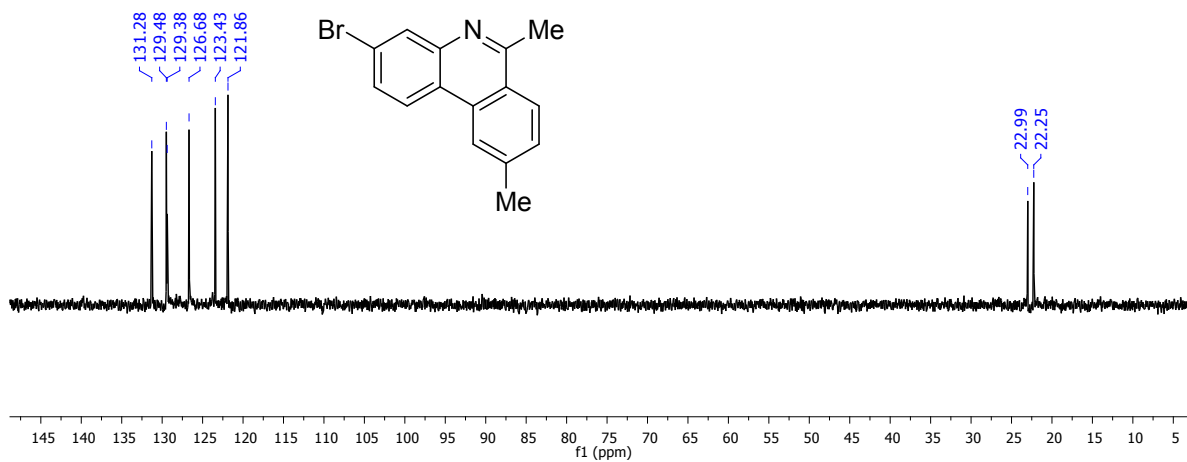
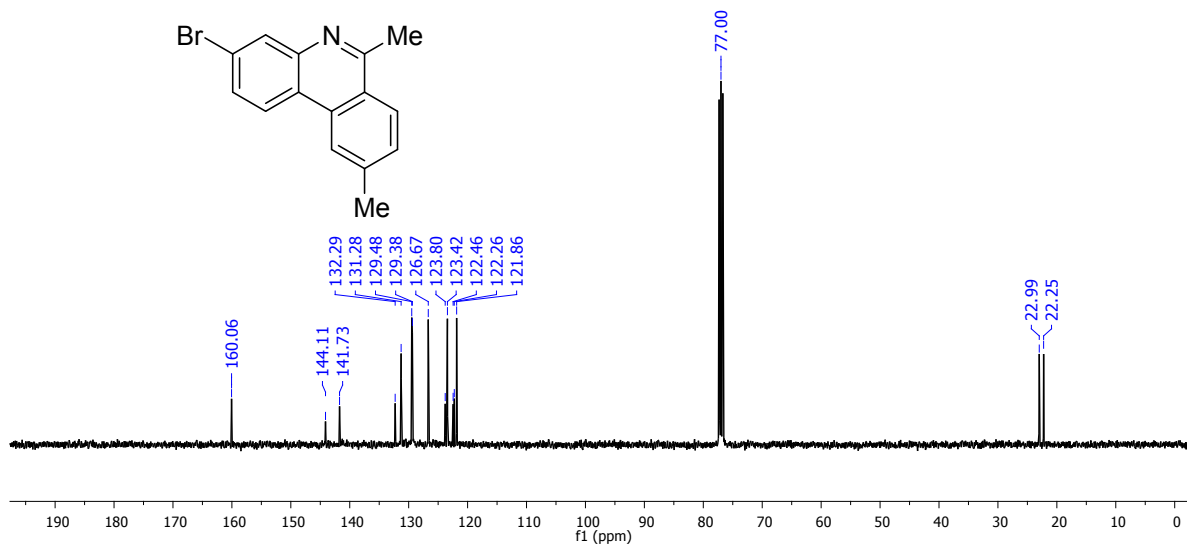
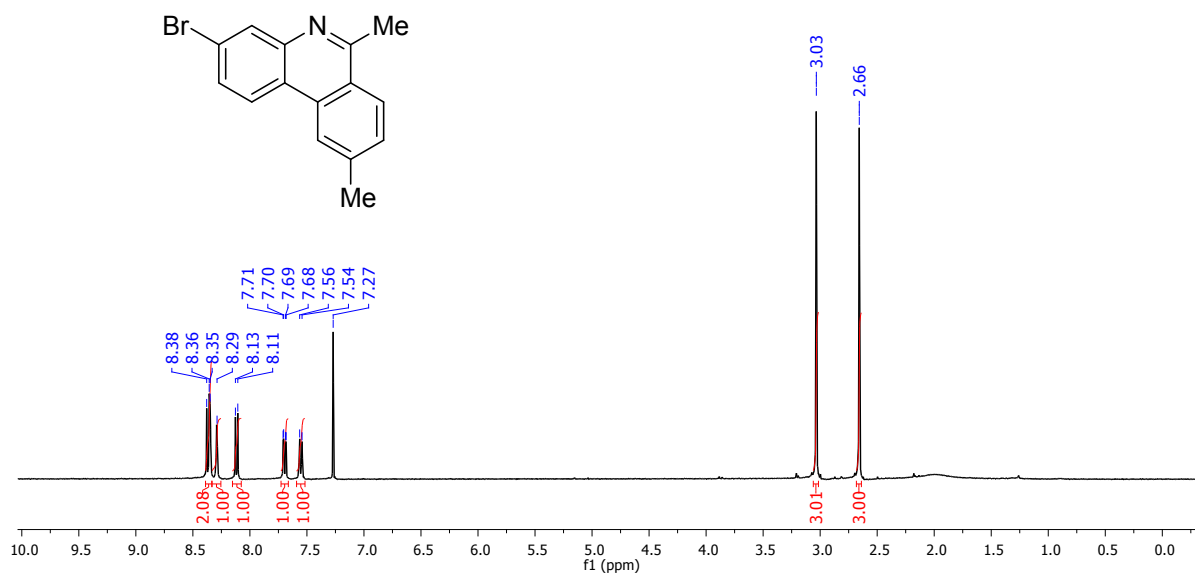
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4ob.



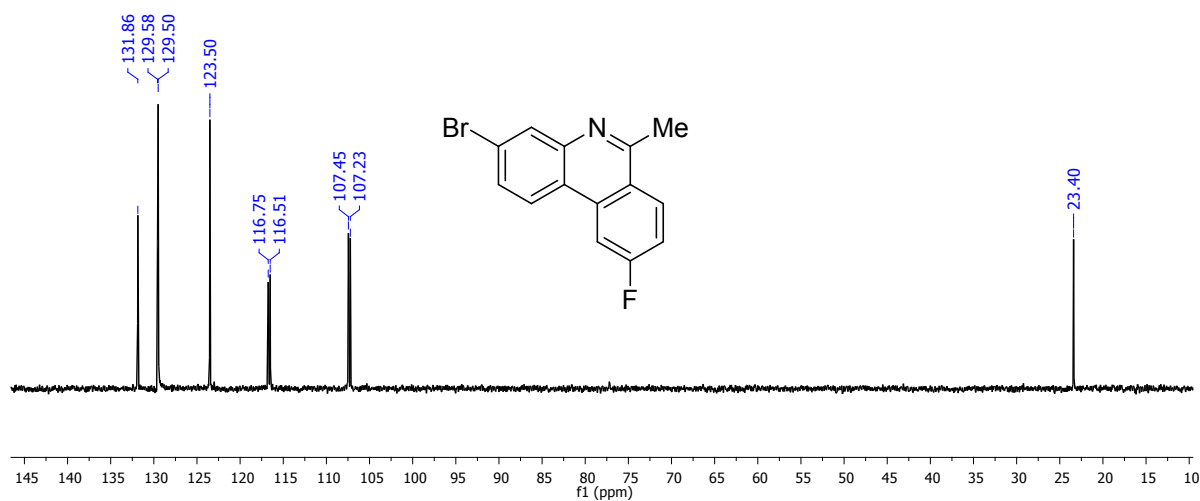
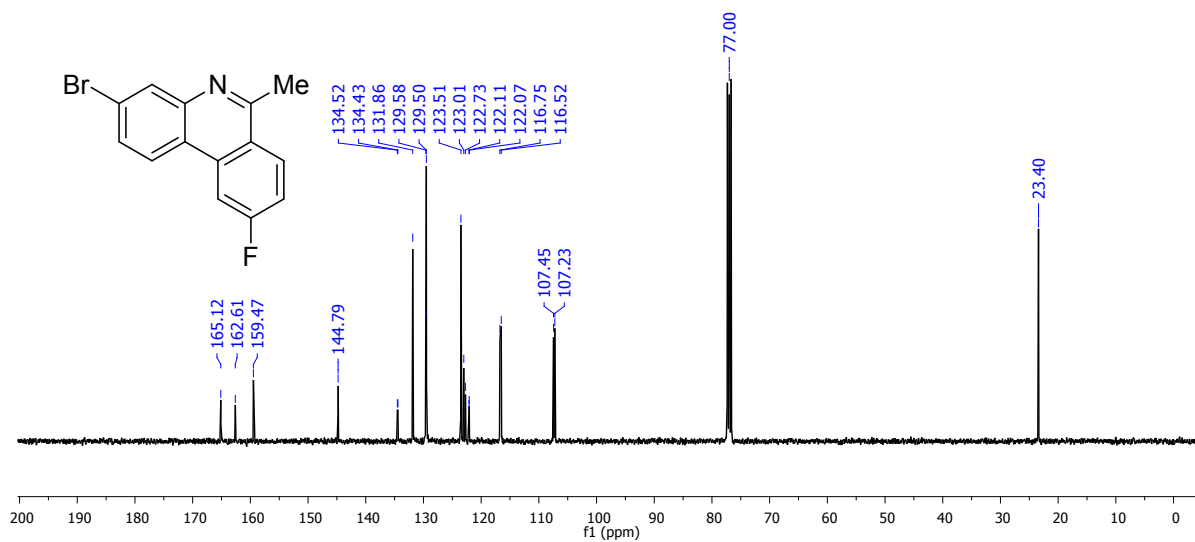
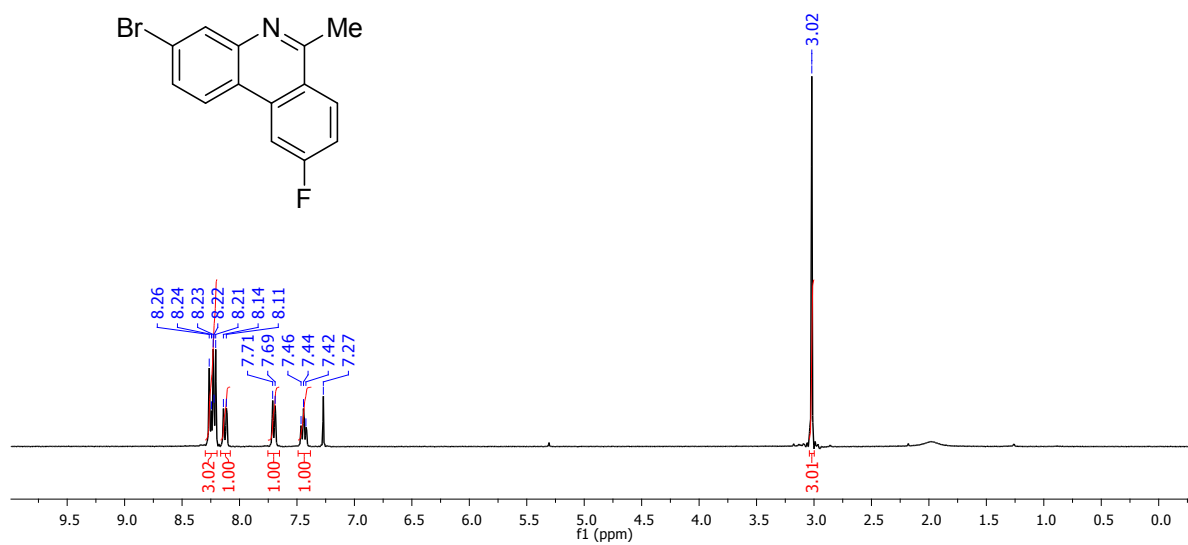
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4pa.



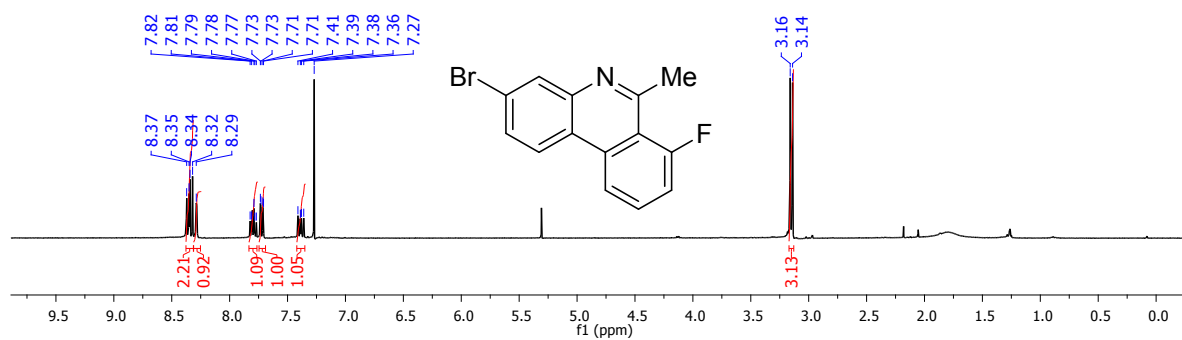
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4qa.



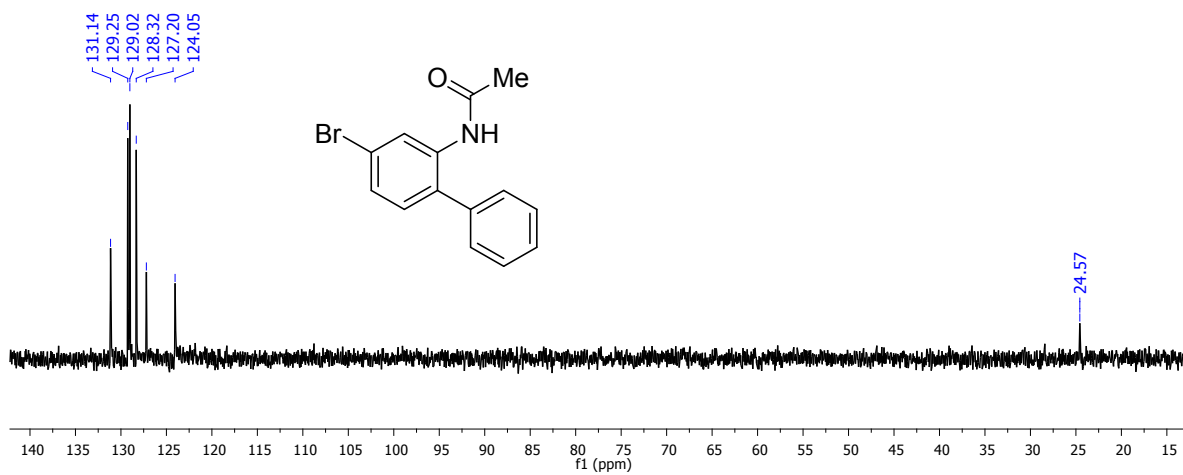
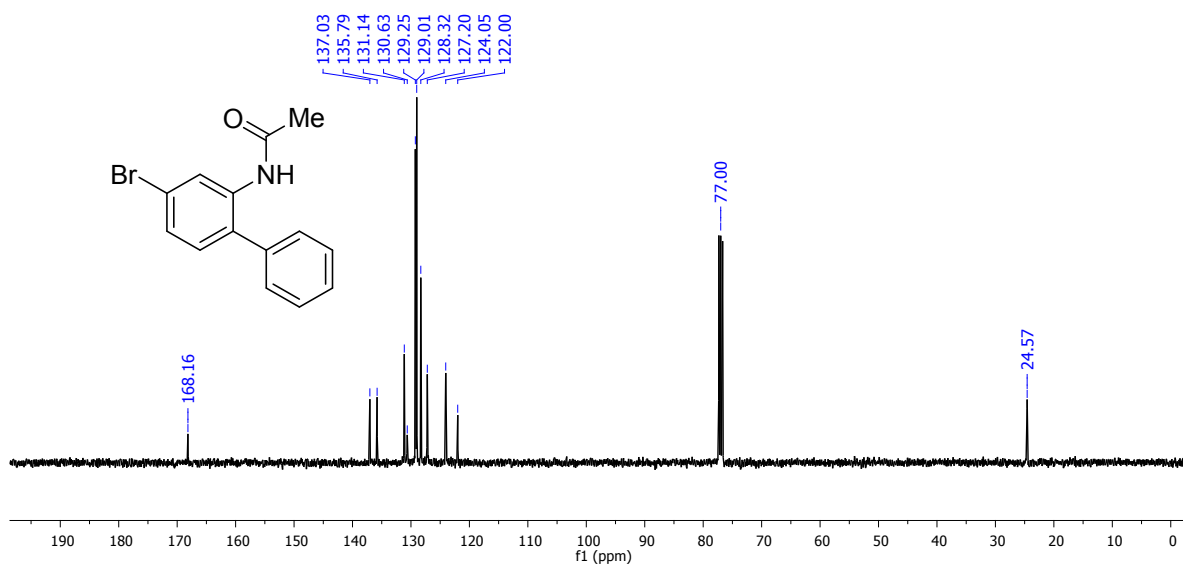
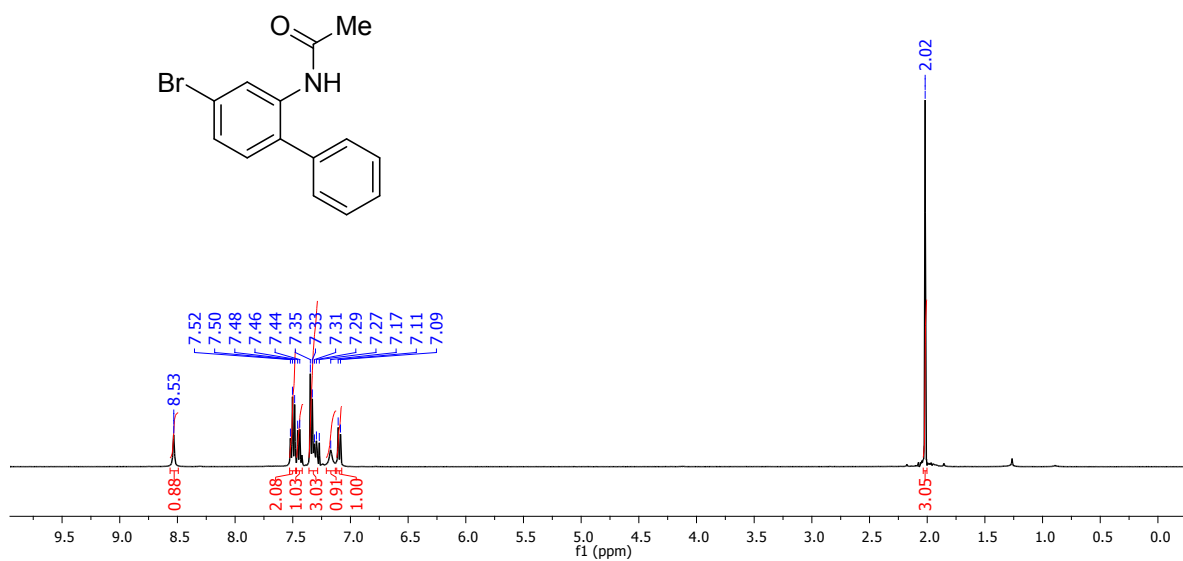
^1H , ^{13}C and DEPT NMR Spectra's of compound of 4ra.



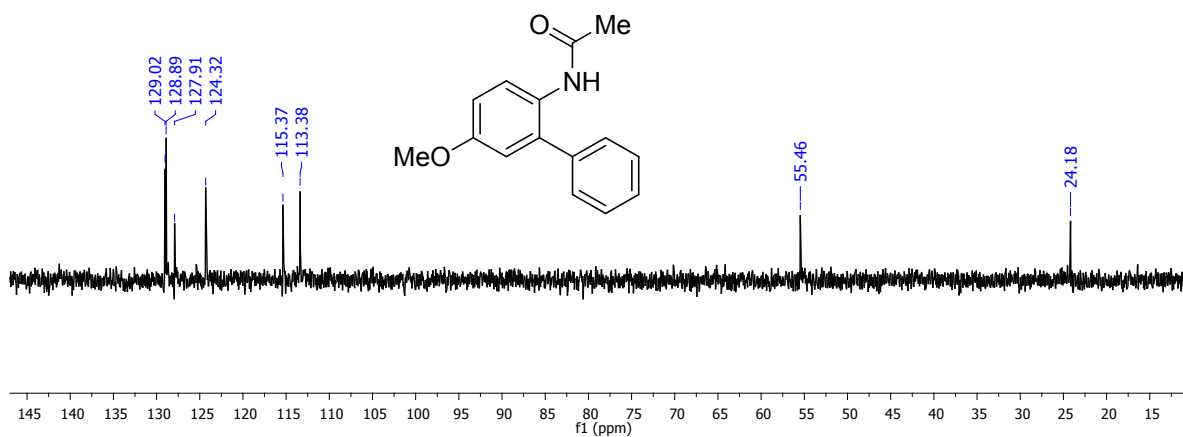
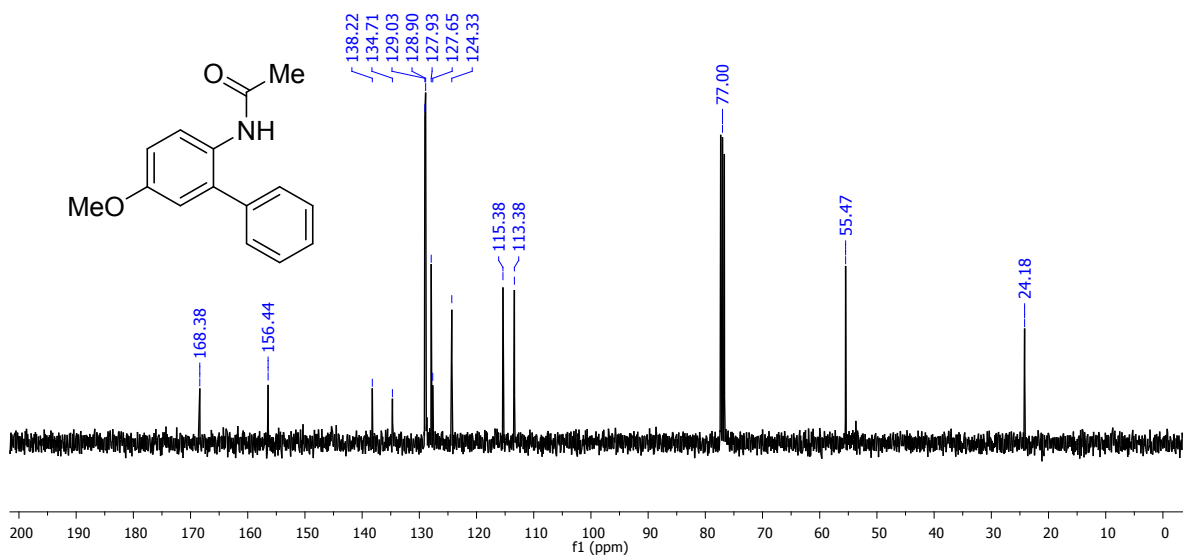
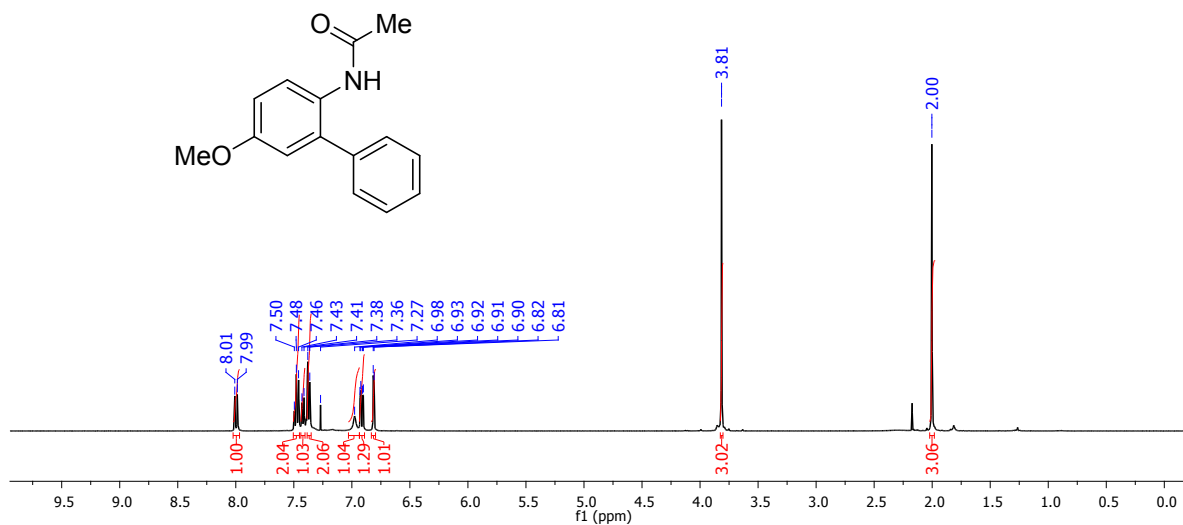
H^1 NMR Spectra's of compound of 4rb.



^1H , ^{13}C and DEPT NMR Spectra's of compound of 3a.



^1H , ^{13}C and DEPT NMR Spectra's of compound of 3b.



^1H , ^{13}C and DEPT NMR Spectra's of compound of 3c.

