**Supporting Information**

# Catalyst- and solvent-free, pot, atom and step economic synthesis of tetrahydroquinazolines by an aza-Diels–Alder reaction strategy

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Electronic Supplementary Material (ESI) for Green Chemistry


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## General Information

All the commercially available reagents were used as received. Melting points were measured with a Buchi M-560 melting point apparatus and are uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400 instrument. $^{1}H$ nuclear magnetic resonance (NMR) spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Hertz (Hz). $^{13}C$ NMR spectra were recorded on an Advance DPX 75 MHz FT-NMR spectrometer and Chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm). Mass spectra were recorded on ESQUIRE 3000 Mass spectrometer. All experiments were monitored by thin layer chromatography (TLC). TLC was performed on a pre-coated silica gel plates (Merck). After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by stating $KMnO_4$ and warming in a hot air oven. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate-hexane as eluent.

## Microwave Instrumentation

All microwave reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. The multitude microwave has a twin magnetron (2.45 GHz) with maximum output power of 1400 W. The output power can be controlled in unpulsed control mode over whole power which is adjustable in 1 W increment. A Motorola 68xxx series microprocessor system control is used to measure power, pressure, time and temperature during the reaction. The temperature and pressure were monitored throughout the reaction by an infrared detector. The temperature can be measured from 0 to 280 $^{o}C$ with uncertainty ±1%. The temperature during the MW reaction was monitored by an externally calibrated IR sensor. The pressure can be measured from 0 to 86 bar with uncertainty ±0.2 bar. The MW power is initially set at 700 W and the reaction is run. However, during the course of the reaction, once the set temperature and pressure limit is reached, the reactor automatically adjusts the power by lowering it.

**Table S1** Optimization studies for the preparation of tetrahydroquinolines

| Entry | Solvent | Time (min) | Microwave power (W) | Yield(%)[a] |
|---|---|---|---|---|
| 1 | Ethanol | 5 | 500 | 10 |
| 2 | Ethanol | 5 | 700 | 25 |
| 3 | Ethanol | 5 | 800 | 19 |
| 4 | Ethanol | 6 | 700 | 30 |
| 5 | Ethanol | 7 | 700 | 30 |
| 6 | Methanol | 7 | 700 | 20 |
| 7 | DCM | 7 | 700 | NR |
| 8 | Chloroform | 7 | 700 | Trace |
| 9 | Acetonitrile | 7 | 700 | Trace |
| 10 | DMSO | 7 | 700 | NR |
| 11 | Water | 7 | 700 | NR |
| 12 | DMF | 7 | 700 | NR |
| 13 | Toluene | 7 | 700 | NR |
| 14 | Hexane | 7 | 700 | NR |
| 15 | Neat | 7 | 700 | 82 |
| 16 | Neat | 8 | 700 | 81 |
| 17 | Neat | 7 | 600 | 75 |
| 18 | Neat | 7 | 800 | 76 |

**Table S2** Synthesis of tetrahydroquinolines employing urea as source of ammonia

| Entry | Solvent | Time (min) | Microwave power (W) | Yield(%)[a] |
|---|---|---|---|---|
| 1 | Neat | 7 | 700 | 30 |
| 2 | Neat | 10 | 700 | 28 |
| 3 | Neat | 7 | 800 | 20 |
| 4 | Ethanol | 7 | 700 | NR |
| 5 | Methanol | 7 | 700 | NR |
| 6 | DCM | 7 | 700 | NR |
| 7 | Chloroform | 7 | 700 | NR |
| 8 | Toluene | 7 | 700 | NR |
| 9 | Hexane | 7 | 700 | NR |
| 10 | Water | 7 | 700 | NR |

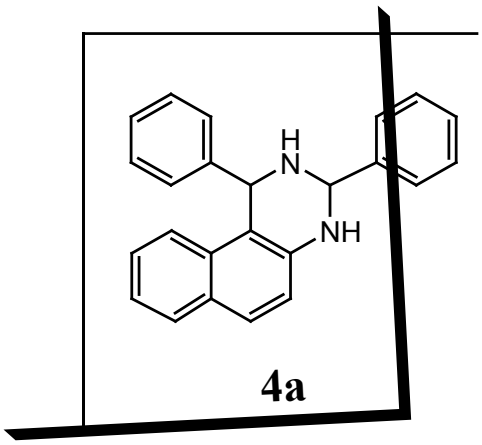
**General procedure for the preparation of tetrahydroquinazolines 4a-m under microwave irradiation:**

2-naphthylamine (1mmol), aldehyde (2.2 mmol), ammonium acetate (1.2 mmol) were mixed and irradiated in a closed vessel in absence of any solvent in a Synthos 3000 microwave reactor at 700 watt,10 bar and 90 $^{0}$C for 6 min. The final product is purified by column chromatography by using 1.5:8.5 ethyl acetate:hexane as eluent.

**General procedure for the preparation of tetrahydroquinazolines 4a-m under thermal condition:**

A mixture of 2-naphthylamine (1mmol), aldehyde (2.2mmol), ammonium acetate (1.2mmol) were heated in an open round bottomed flask on a preheated oil bath at 150 $^{0}$C for 8 h. The progress of the reaction was monitored by TLC. The final product is purified by column chromatography by using 1.5:8.5 ethyl acetate:hexane as eluent.

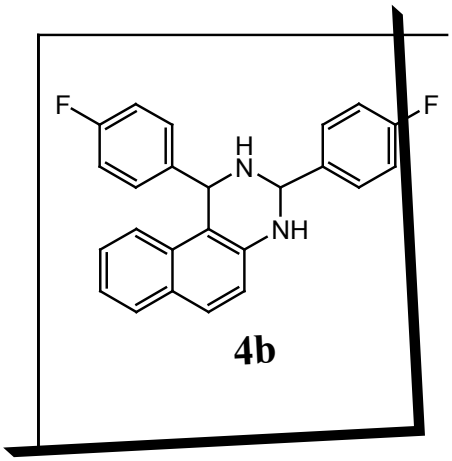
**Characterization data for tetrahydroquinazolines 4a-m**




**4a**

**2,4-Diphenyl-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4a)**

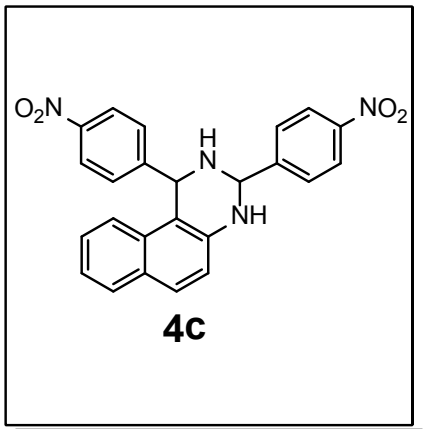
Off white solid, solid m.p. 170-172$^0$C, $^1$H NMR (300MHz, $CDCl_3$) δ 7.69-6.89 (m, Ar, 16H), 5.71 (s, 1H), 5.07 (s, 1H), 4.43 (s, br,1H), 2.01(s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 144.4, 141.3. 141.2, 132.1, 129.3, 128.9, 128.8, 128.7, 128.6, 128.3, 128.0, 127.1, 126.9, 126.7, 122.3, 122.0, 118.4, 112.0, 63.9, 56.1. MS (GCMS, m/z) 336.1 $[M]^+$. ; Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.66; H, 5.94; N, 8.40.




**4b**

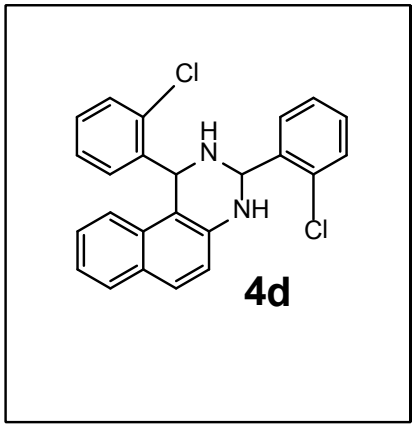
**2,4-Di(4-fluorophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4b)**

Off white solid, solid m.p. 168-170$^0$C, $^1$H NMR (300MHz, $CDCl_3$) δ 7.70-6.90 (m, Ar, 14H), 5.67 (s, 1H), 5.01 (s, 1H), 4.42 (s, br,1H), 2.02(s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 161.2, 160.4, 140.9, 131.7, 130.9, 130.8, 129.1, 128.6, 128.5, 128.1, 126.8, 124.6, 124.2, 122.3, 122.1, 118.3, 115.8, 115.3, 115.0, 111.4, 63.2, 55.4. MS (GCMS, m/z) 372.1 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2F_2$: C, 77.40; H, 4.87; N, 7.52. Found: C, 77.44; H, 4.91; N, 7.50.



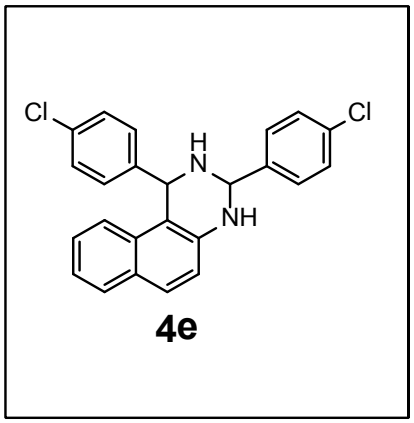

**2,4-Di(4-nitrophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4c)**

Yellow solid, m.p. 178-180$^0$C $^1$H NMR (300MHz, $CDCl_3$) δ 8.34-6.93 (m, Ar, 14H), 5.75 (s, 1H), 5.04 (s, 1H), 4.52 (s, br, 1H), 3.82 (s, br,1H), MS (GCMS, m/z) 364.2 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_4O_4$: C, 67.60; H, 4.25; N, 13.14. Found: C, 67.66; H, 4.28; N, 13.18




**2,4-Di(2-chlorophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4d)**

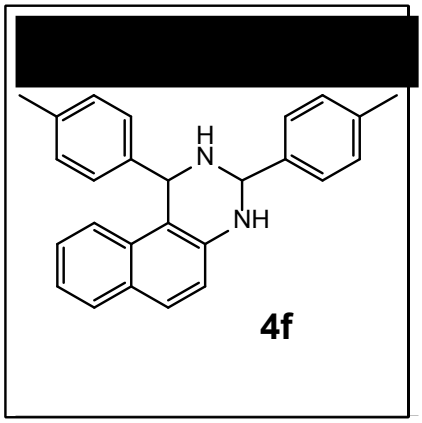
White solid, m.p. 157-159$^0$C $^1$H NMR (300MHz, $CDCl_3$) δ 7.90-6.96 (m, Ar, 14H), 6.13 (s, 1H), 5.54 (s, 1H), 4.30 (s, br,1H), 2.65 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 141.9, 140.8, 137.9, 133.5, 133.4, 131.6, 131.4, 129.9, 129.8, 129.7, 128.9, 128.6, 128.5, 128.3, 127.9, 127.4, 126.8, 126.1, 122.3, 122.1, 118.4, 111.3, 60.6, 53.7. MS (GCMS, m/z) 404 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2Cl_2$: C, 71.12; H, 4.48; N, 6.91. Found: C, 71.16; H, 4.50; N, 6.98




**4e**

**2,4-Di(4-chlorophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4e)**

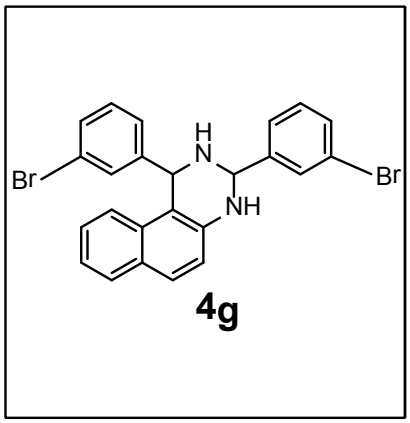
White solid, m.p. 192-194$^0$C $^1$H NMR (300MHz, DMSO-d6) δ 7.69-7.04 (m, Ar, 14H), 6.71 (s, 1H), 5.54 (s, 1H), 4.80 (s, br,1H), 3.45 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.4, 141.1, 137.5, 134.4, 132.9, 131.8, 130.6, 129.0, 128.9, 128.6, 128.4, 128.0, 126.9, 122.3, 122.1, 118.4, 63.3, 55.3. MS (GCMS, m/z) 404 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2Cl_2$: C, 71.12; H, 4.48; N, 6.91. Found: C, 71.14; H, 4.52; N, 6.96




**4f**

. **2,4-Di(4-methylphenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4f)**

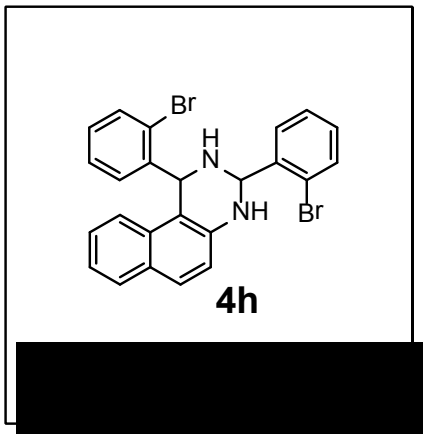
Yield: 85%. white solid, solid m.p 184-186$^0$C., $^1$H NMR (300MHz, DMSO-$d_6$) δ 7.67-7.58 (m, Ar, 2H), 7.42-7.01 (m, Ar, 12H), 6.56 (s, 1H), 5.50 (s, 1H), 4.82 (s, br,1H), 3.19 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 141.2, 138.4, 138.4, 136.6, 132.1, 129.4, 129.3, 129.1, 129.0, 128.6, 128.5, 127.9, 126.6, 126.6, 122.3, 121.9, 118.4, 112.1, 63.7, 55.8, 21.2, 21.1. MS (GCMS, m/z) 464.4 $[M]^+$. ; Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.71; H, 6.68; N, 7.61




**4g**

**2,4-Di(3-bromophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4g)**

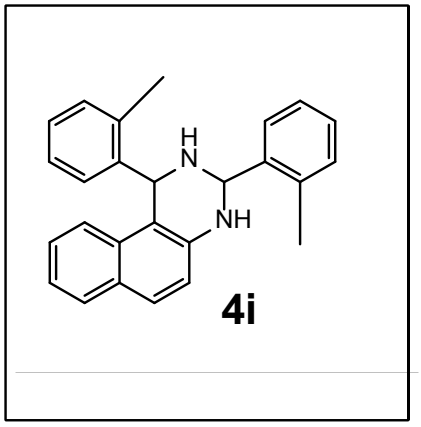
White solid, 148-150$^0$C $^1$H NMR (300MHz, $CDCl_3$) δ 7.77-6.91 (m, Ar, 14H), 5.64 (s, 1H), 5.00 (s, 1H), 4.12 (s, br, 1H), 2.15 (s, br,1H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ 146.3, 143.1, 141.0, 132.2, 132.1, 131.8, 130.4, 130.3, 129.9, 129.7, 129.1, 128.6, 128.1, 128.0, 126.9, 125.5, 122.8, 122.6, 122.3, 122.0, 118.4, 111.2, 63.3, 55.6. MS (GCMS, m/z) 494.2 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2Br_2$: C, 58.33; H, 3.67; N, 5.67. Found: C, 58.36; H, 3.70; N, 5.64




**4h**

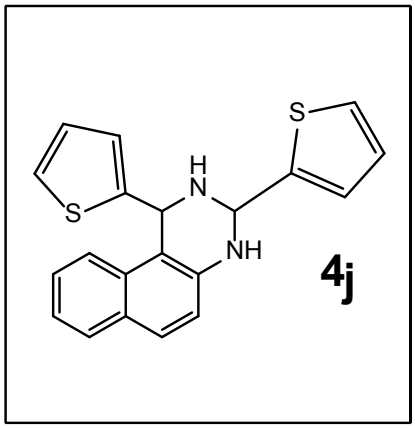
**2,4-Di(2-bromophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4h)**

White solid, m.p. 172-174$^0$C $^1$H NMR (300MHz, $CDCl_3$) δ 7.78-6.96 (m, Ar, 14H), 6.10 (s, 1H), 5.48 (s, 1H), 4.41 (s, br,1H), 2.58 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.2, 141.9, 139.3, 133.2, 133.1, 131.7, 131.5, 130.1, 129.0, 128.9, 128.5, 128.4, 128.3, 128.0, 126.8, 126.8, 124.3, 123.5, 122.3, 122.2, 118.4, 111.5, 63.1, 56.2. MS (GCMS, m/z) 494. $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2Br_2$: C, 58.33; H, 3.67; N, 5.67. Found: C, 58.36; H, 3.63; N, 5.62



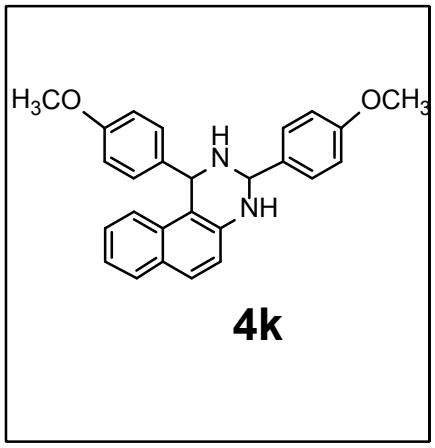

**2,4-Di(2-methylphenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4i)**

White solid, m.p. 160-163$^0$C $^1$H NMR (300MHz, $CDCl_3$) δ 7.71-6.88 (m, Ar, 14H), 5.81 (s, 1H), 5.29 (s, 1H), 4.41 (s, br, 1H), 2.05 (s, br,1H), 2.69 (s, 3H), 1.85 (s, 1H), . $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.3, 141.5, 139.2, 137.0, 136.9, 131.8, 130.7, 130.6, 130.1, 128.5, 128.5, 128.2, 128.1, 127.0, 126.6, 126.1, 125.0, 124.7, 122.3, 122.0, 118.5, 112.7, 60.3, 53.6, 19.0, 17.8 . MS (GCMS, m/z) 364.2 $[M]^+$. ; Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.66; H, 6.68; N, 7.66




**2,4-Di(thiophen-2-yl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4j)**

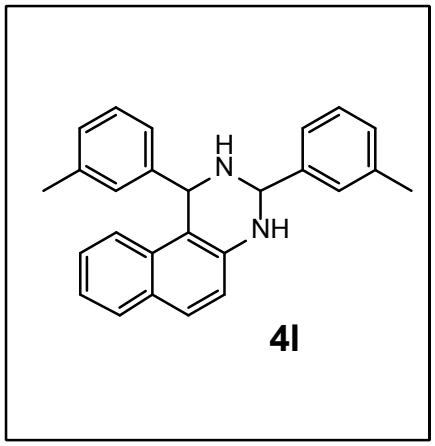
Yield: 85%. Brown gum, $^1$H NMR (300MHz, $CDCl_3$) δ 7.85-6.65 (m, Ar, 12H), 5.90 (s, 1H), 5.57 (s, 1H), 4.59 (s, br,1H), 2.40 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 148.6, 144.8, 140.2, 131.9, 129.0, 128.5, 128.2, 127.5, 126.9, 126.8, 126.6, 125.4, 125.2, 124.9, 122.3, 122.2, 118.5, 112.8, 60.5, 52.1. MS (GCMS, m/z) 348.0 $[M]^+$. ; Anal. Calcd for $C_{20}H_{19}N_2S_2$: C, 68.93; H, 4.63; N, 8.04. Found: C, 68.91; H, 4.60; N, 8.08




**4k**

**2,4-Di(2-methoxyphenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4k)**

Brown gum, $^{1}$H NMR (300MHz, $CDCl_3$) δ 7.70-6.80 (m, Ar, 14H), 5.65 (s, 1H), 5.02 (s, 1H), 4.30 (s, br, 1H), 3.78 (s, 3H), 3.77(s, 3H), 2.85 (s, br,1H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ 159.7, 158.5, 141.3, 136.5, 133.5, 132.0, 130.2, 128.6, 128.4, 128.1, 128.0, 127.9, 126.5, 122.3, 121.8, 118.4, 114.0, 112.1, 63.3, 55.5, 55.3, 55.1. MS (GCMS, m/z) 494.2 $[M]^{+}$. ; Anal. Calcd for $C_{24}H_{18}N_2Br_2$: C, 58.33; H, 3.67; N, 5.67. Found: C, 58.36; H, 3.70; N, 5.64

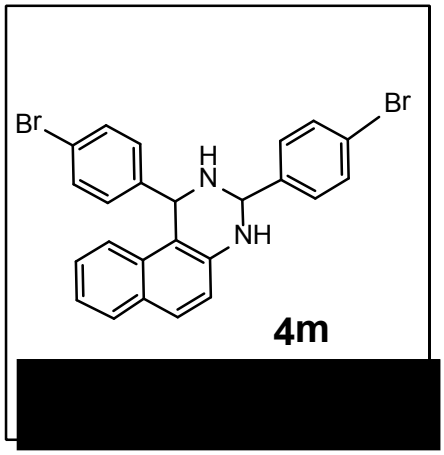



**4l**

**2,4-Di(3-methylphenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4l)**

Yield: 85%. pinkish white solid, solid m.p. 159-161$^{0}$C, $^{1}$H NMR (300MHz, $CDCl_3$) δ 7.71-6.89 (m, Ar, 14H), 5.68 (s, 1H), 5.05 (s, 1H), 4.42 (s, br,1H), 2.33 (s, 3H), 2.31(s, 3H), 2.09(s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 144.1, 141.2. 138.5, 137.9, 132.1, 129.7, 129.4, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.4, 126.6, 126.4, 123.7, 122.3, 121.9, 118.3, 112.0, 63.9,

56.3, 21.5, 21,4. MS (GCMS, m/z) 364.1 $[M]^+$. ; Anal. Calcd for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69. Found: C, 85.62; H, 6.68; N, 7.70.

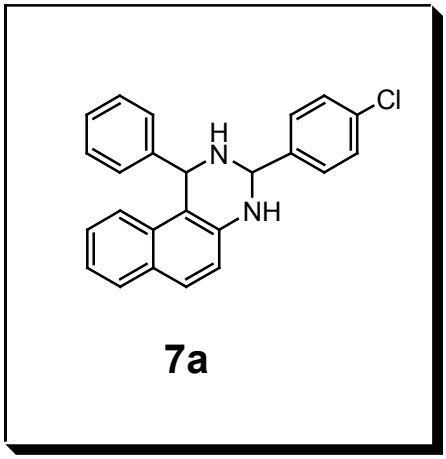



**2,4-Di(4-bromophenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (4m)**

Yield: 85%. white solid, solid m.p. 178-180$^0$C, $^1$H NMR (300MHz, DMSO-$d_6$) δ 7.69-7.04 (m, Ar, 14H), 6.71 (s, 1H), 5.52 (s, 1H), 4.79 (s, br,1H), 3.48 (s, br,1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.9, 141.1, 140.0, 132.4, 131.9, 131.4, 131.0, 129.9, 128.6, 128.3, 128.1, 126.9, 122.5, 122.3, 122.0, 121.2, 118.4, 111.5, 63.3, 55.4. MS (GCMS, m/z) 494.1 $[M]^+$. ; Anal. Calcd for $C_{26}H_{22}N_2Br_2$: C, 58.33; H, 3.67; N, 5.67. Found: C, 58.30; H, 3.70; N, 5.71

**General procedure for the preparation of tetrahydroquinazolines 7a-b under microwave irradiation:**

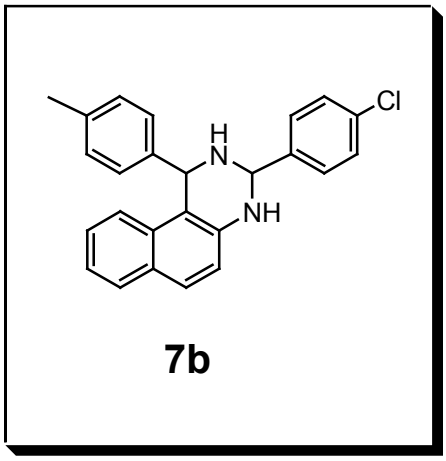
Schiff base of 2-naphthyl amine with 4-Cl benzaldehyde (1 mmol), aldehyde (1.2 mmol) and ammonium acetate(1.2mmol)were mixed and irradiated in a closed vessel in absence of any solvent in a Synthos 3000 microwave reactor at 700watt,14 bar and 70.C for 6mins. The final product is purified by column chromatography by using 1.5:8.5 ethyl acetate:hexane as eluent.




**7a**

**2-(4-chlorophenyl) 4-phenyl-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (7a)**

White solid, m.p. 153-154$^0$C $^1$H NMR (300MHz,$CDCl_3$) δ 7.72-6.93 (m, Ar, 15H), 5.64 (s, 1H), 4.98 (s, 1H), 4.42 (s, br,1H), 2.25 (s, br,1H). MS (GCMS, m/z) 370.1 $[M]^+$. ; Anal. Calcd for $C_{24}H_{19}N_2Cl$: C, 77.72; H, 5.16; N, 7.55. Found: C, 77.76; H, 5.19; N, 7.58



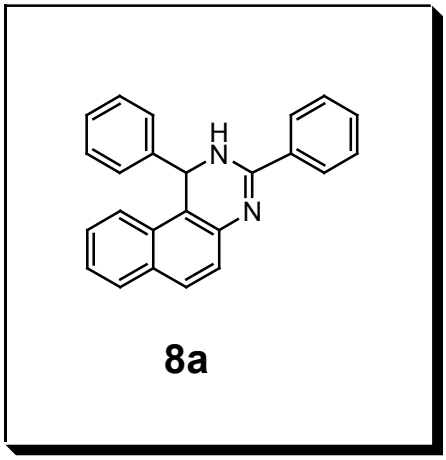

**7b**

**2-(4-chlorophenyl) 4-(4-methylphenyl)-1,2,3,4-tetrahydro-benzo[*f*]quinazoline (7b)**

White solid, m.p. 166-168$^0$C $^1$H NMR (300MHz,$CDCl_3$) δ 7.72-6.93 (m, Ar, 15H), 5.65 (s, 1H), 5.13 (s, 1H), 4.41 (s, br,1H), 2.32 (s, 3H). MS (GCMS, m/z) 370.1 $[M]^+$. ; Anal. Calcd for $C_{25}H_{21}N_2Cl$: C, 78.01; H, 5.50; N, 7.28. Found: C, 78.06; H, 5.54; N, 7.24

**General procedure for the preparation of dihydroquinazolines under thermal condition 8a-b:**

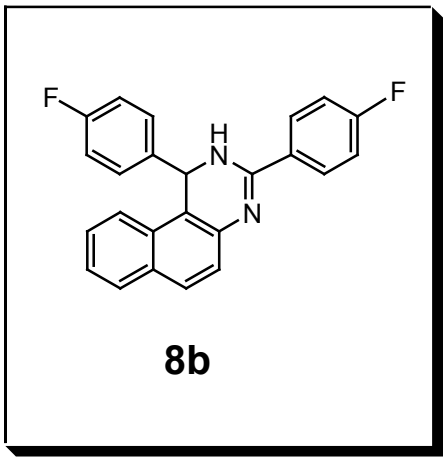
A mixture of 2-naphthylamine (1mmol), aldehyde (2.2mmol), ammonium acetate (1.2mmol) were heated on a preheated oil bath at 150 $^0$C for 15 h. The progress of the reaction is monitored by TLC. The final product is purified by column chromatography by using 1.5:8.5 ethyl acetate:hexane as eluent.




**8a**

**2,4-Diphenyl-,3,4-dihydro-benzo[*f*]quinazoline (8a)**

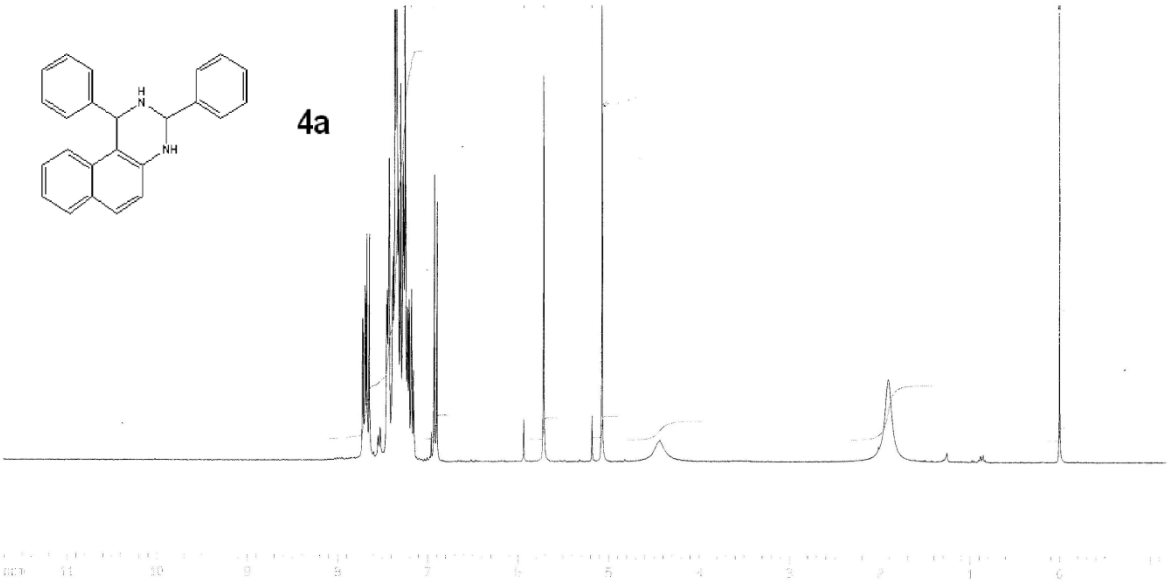
Brown gum, $^1$H NMR (300MHz, $CDCl_3$) δ 8.07-6.78 (m, Ar, 16H), 4.36 (s, 1H), 4.14 (s, br, 1H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ 154.4, 145.6, 141.9, 139.1, 135.7, 135.2, 129.6, 129.2, 129.1, 129.0, 128.8, 128.7, 128.7, 128.6, 127.4, 126.5, 126.4, 126.0, 122.1, 117.9, 104.8, 48.3. MS (GCMS, m/z) 404 $[M]^+$. ; Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.26; H, 5.40; N, 8.34

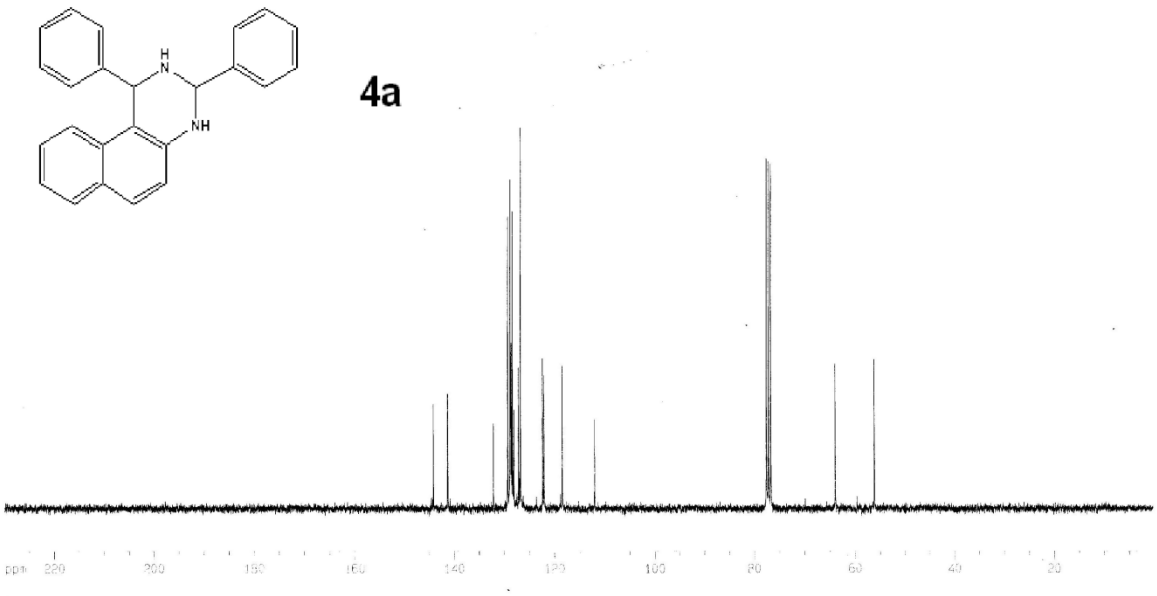


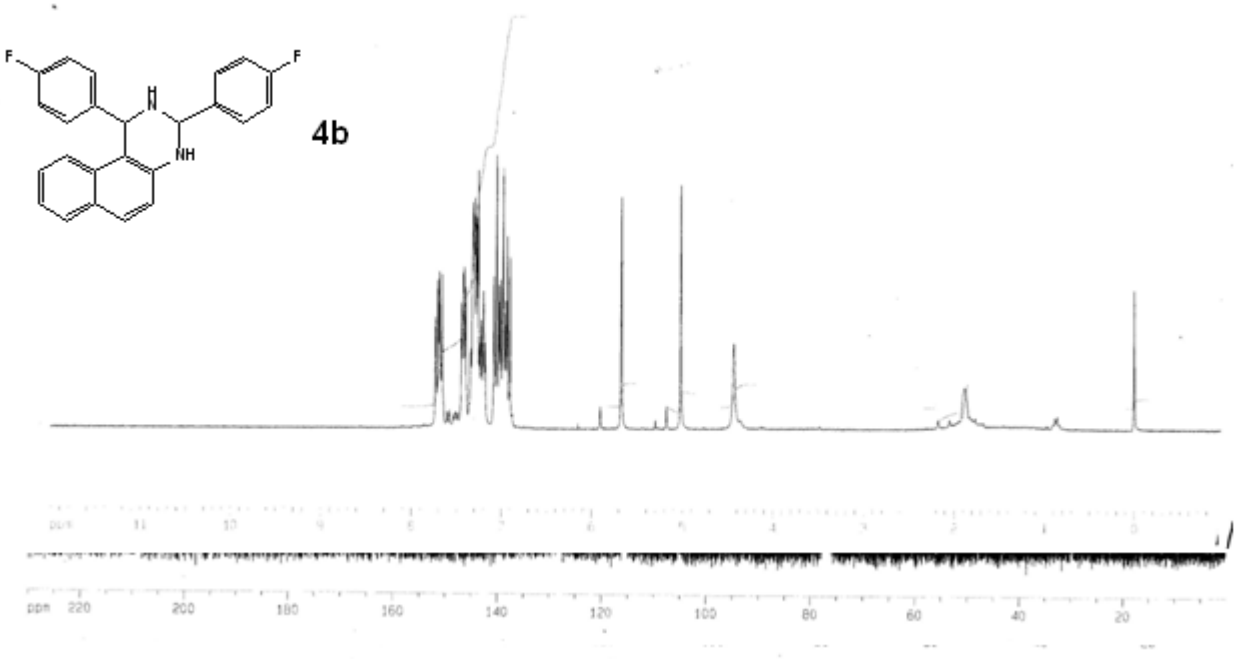

**8b**

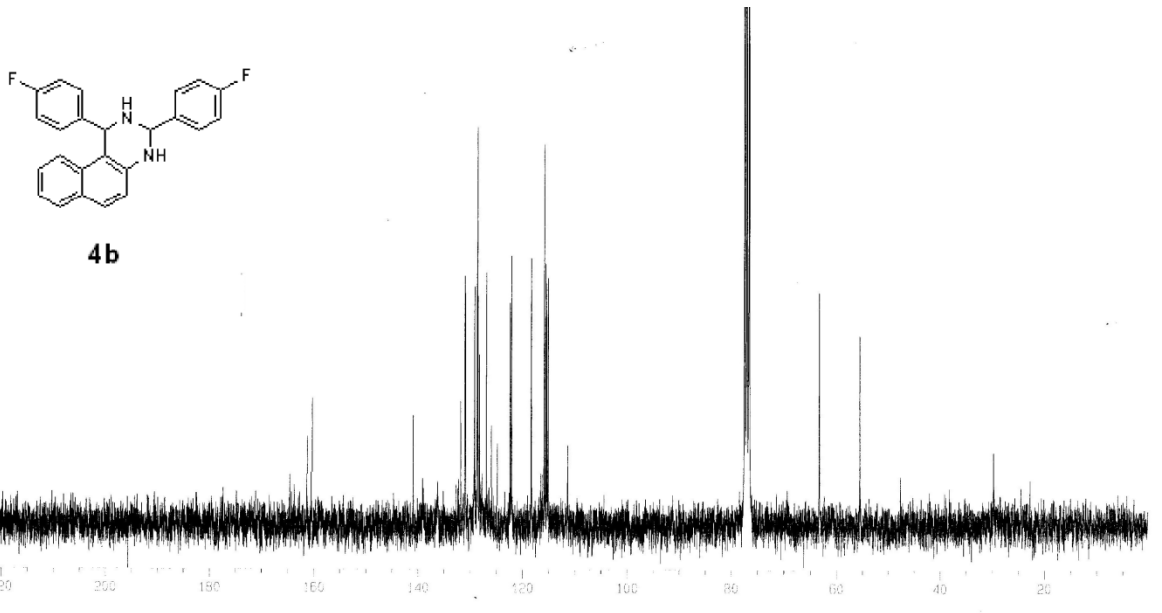
**2,4-Di(4-fluorophenyl)-,3,4-dihydro-benzo[*f*]quinazoline (8b)**

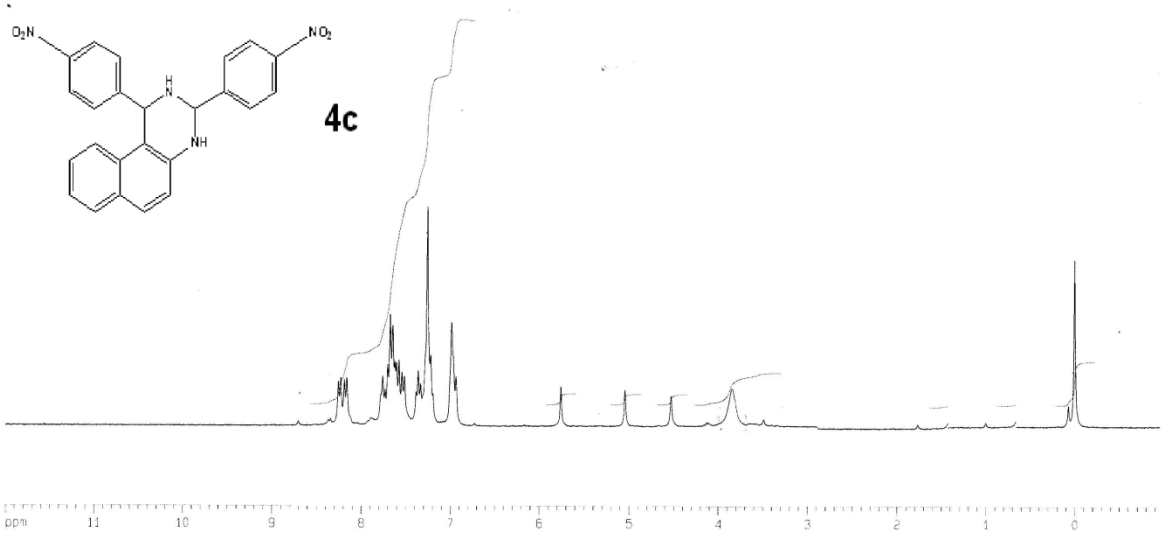
Brown gum, $^{1}$H NMR (300MHz, $CDCl_3$) δ 7.99-6.81 (m, Ar, 16H), 4.40 (s, 1H), 4.29 (s, br, 1H), $^{13}$C NMR (75 MHz, $CDCl_3$) δ 163.7, 160.5, 145.2, 135.0, 134.6, 129.3, 129.2, 129.1, 129.0,, 127.8, 127.7, 127.6, 126.4, 126.0, 122.3, 117.9, 115.6, 115.3, 105.3 47.8.. MS (GCMS, m/z) 404 $[M]^{+}$. ; Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.26; H, 5.40; N, 8.34

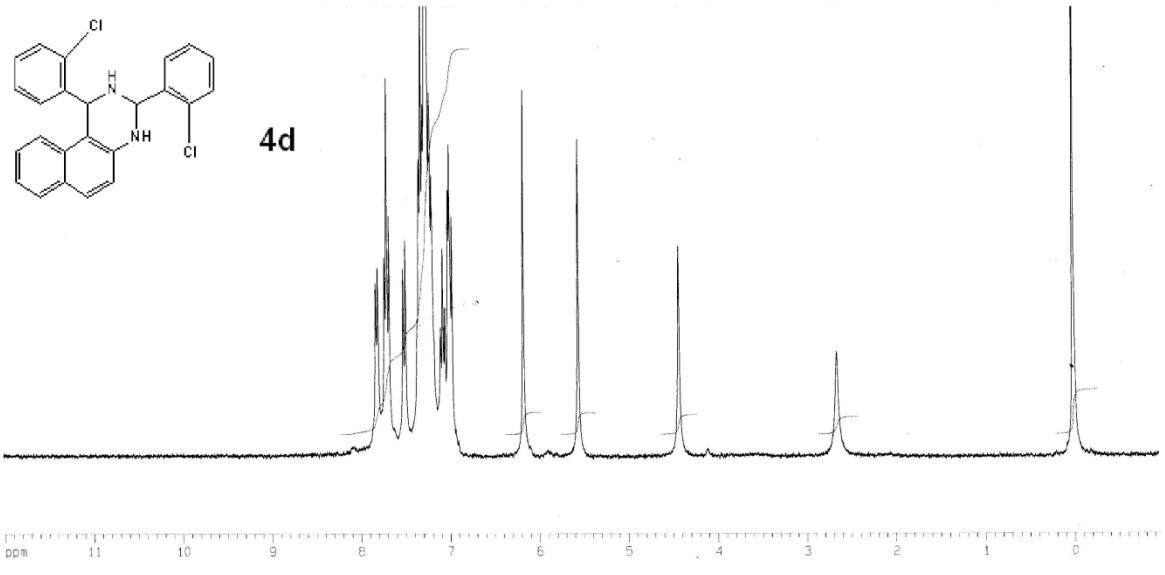


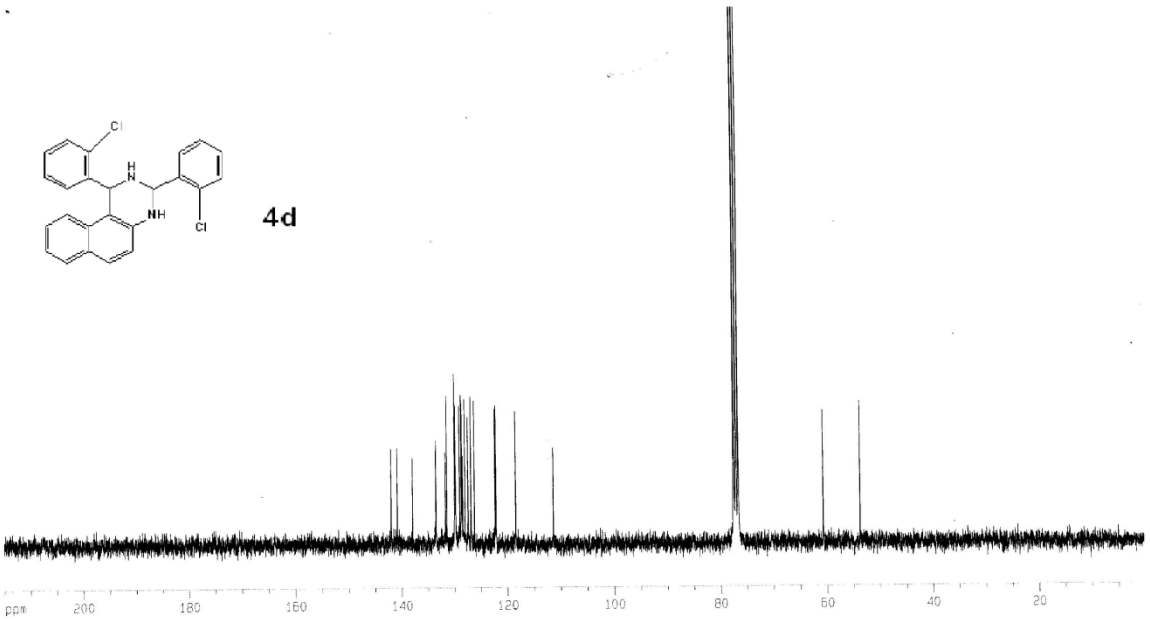



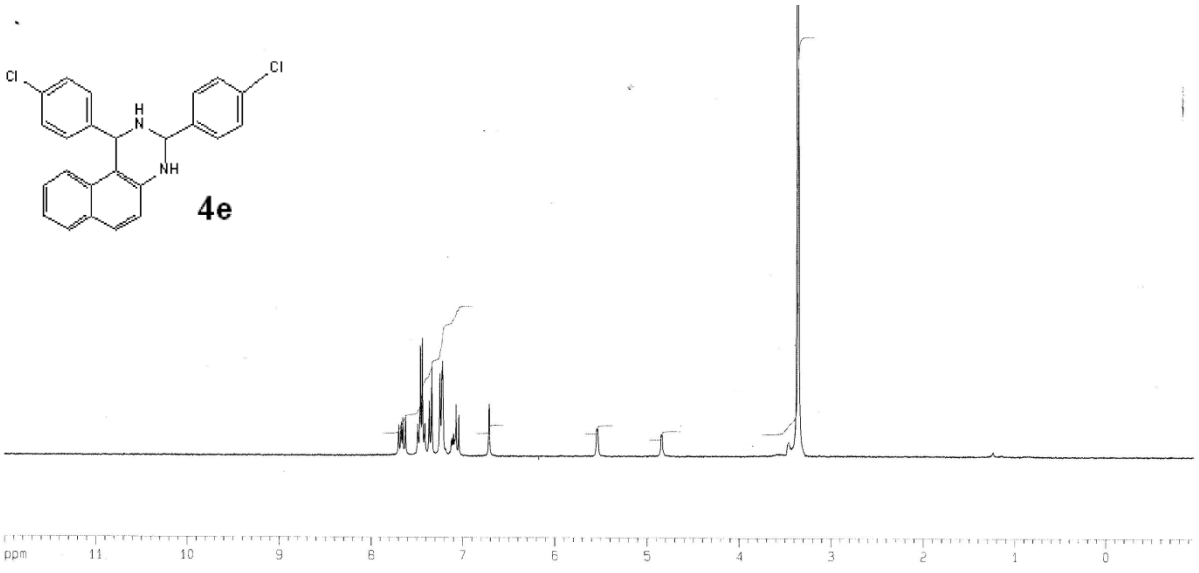


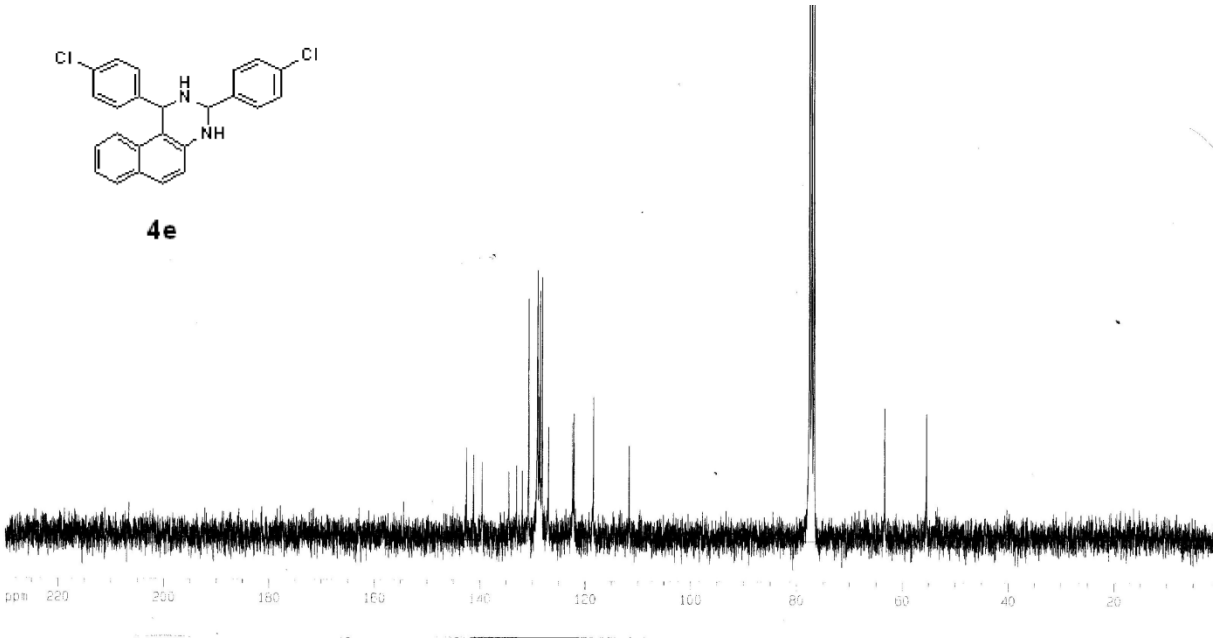




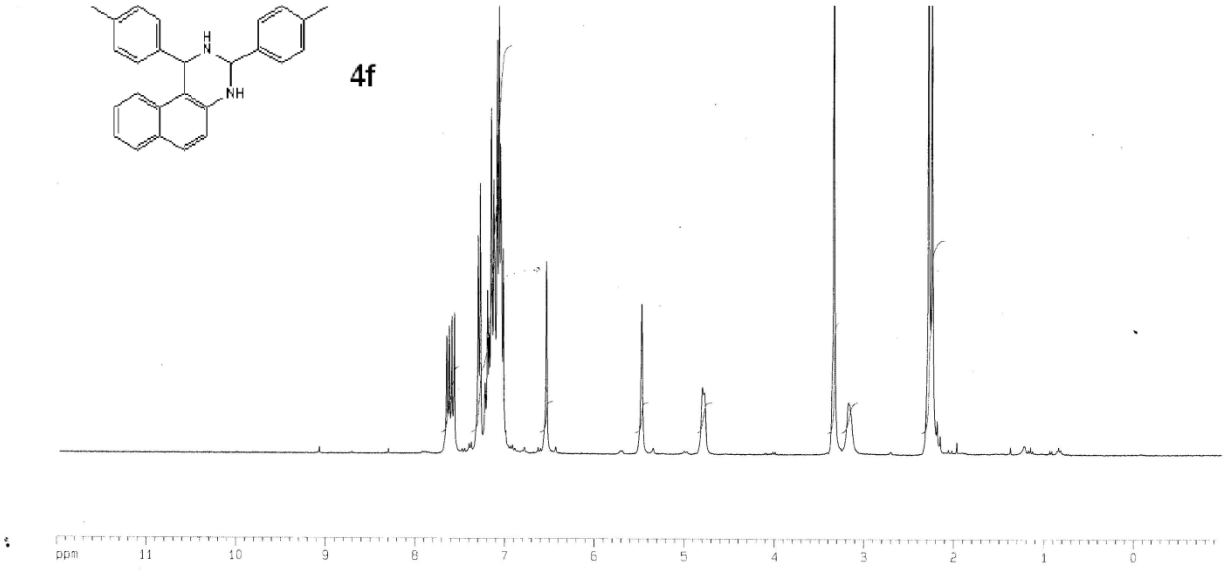
**4e**



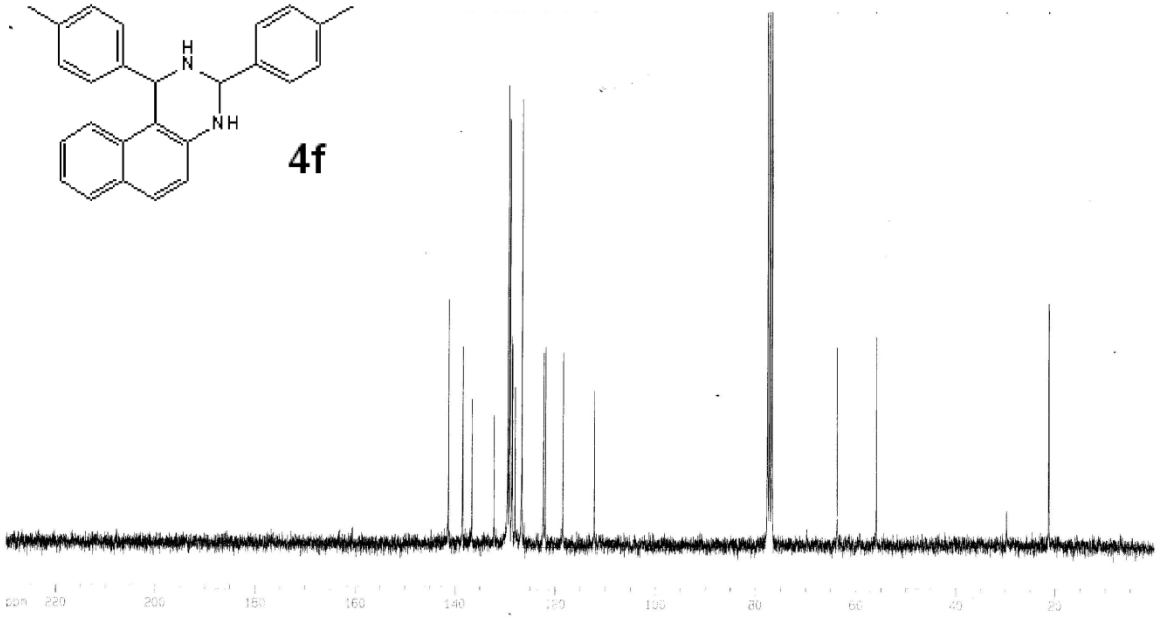




**4f**

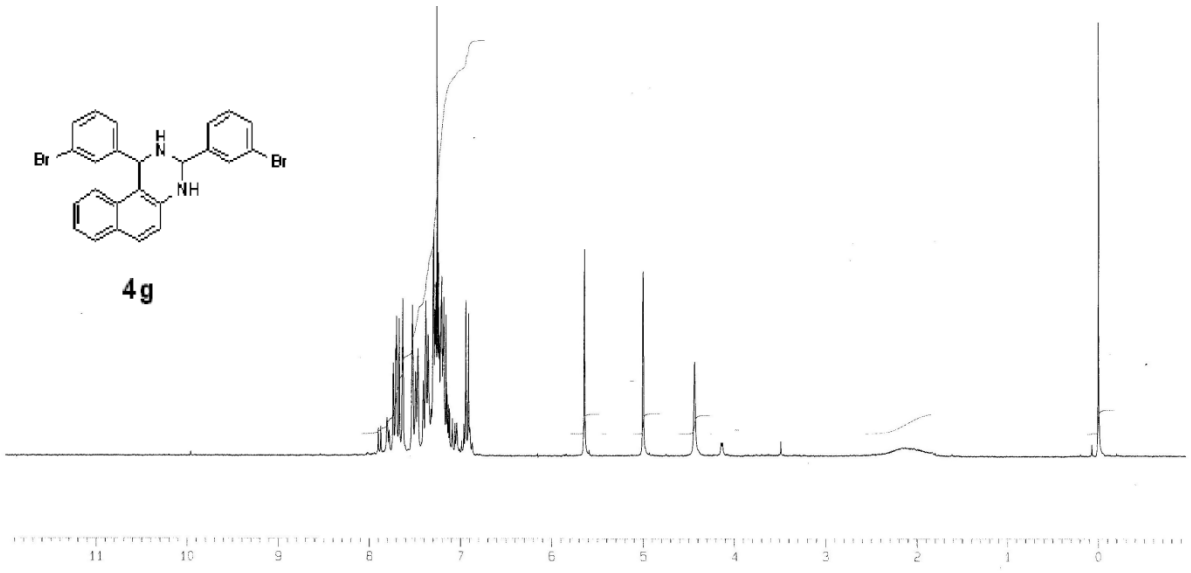


**4f**






**4g**



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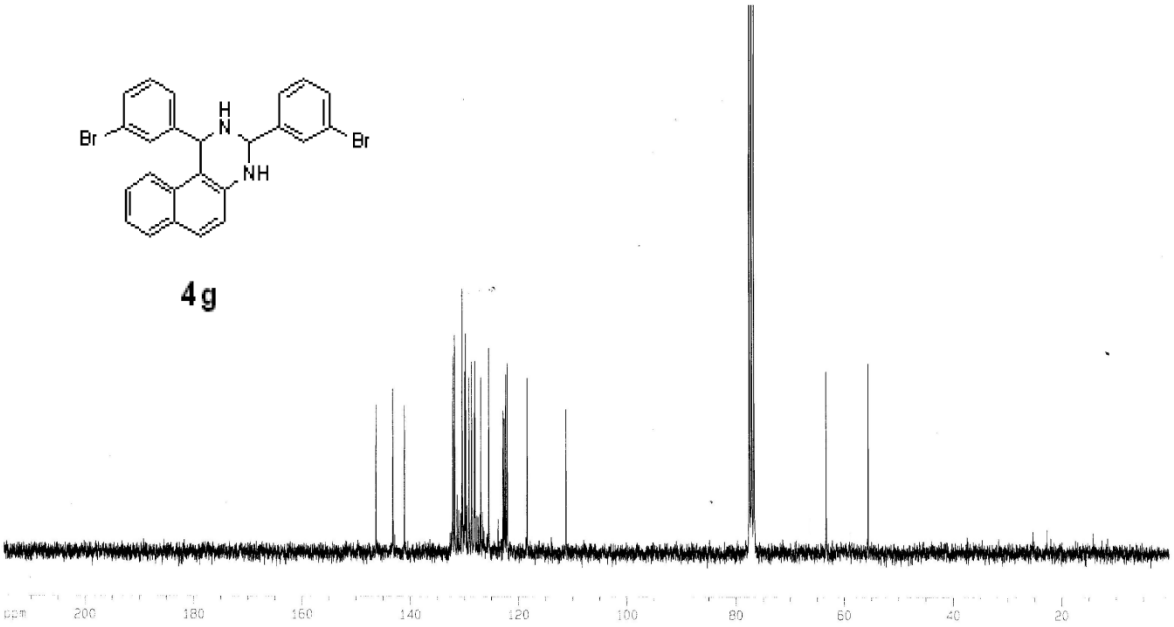
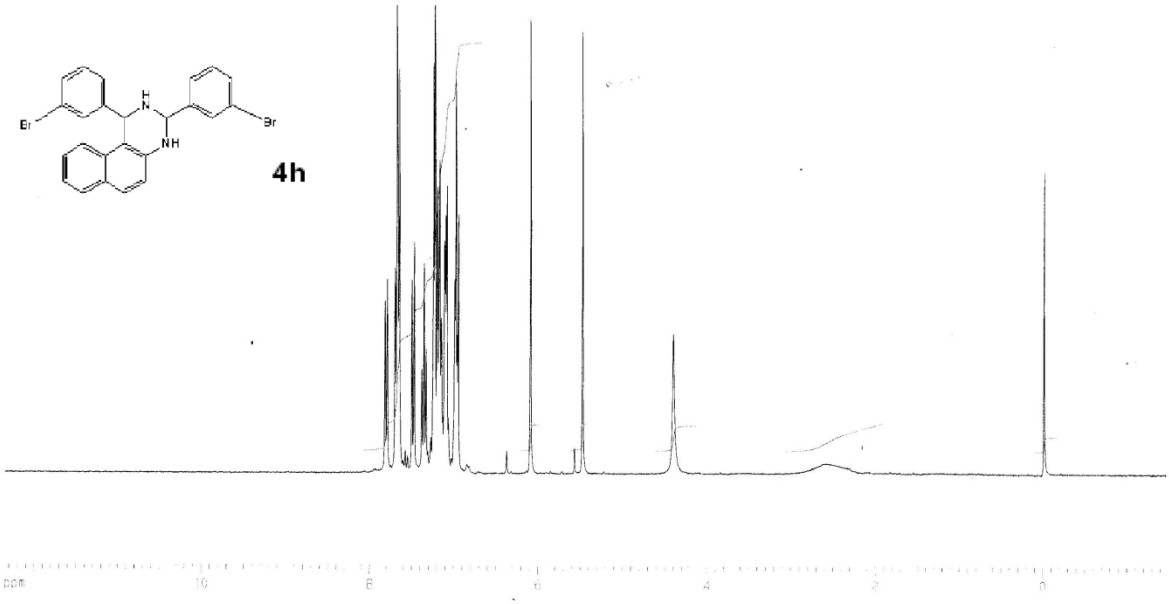
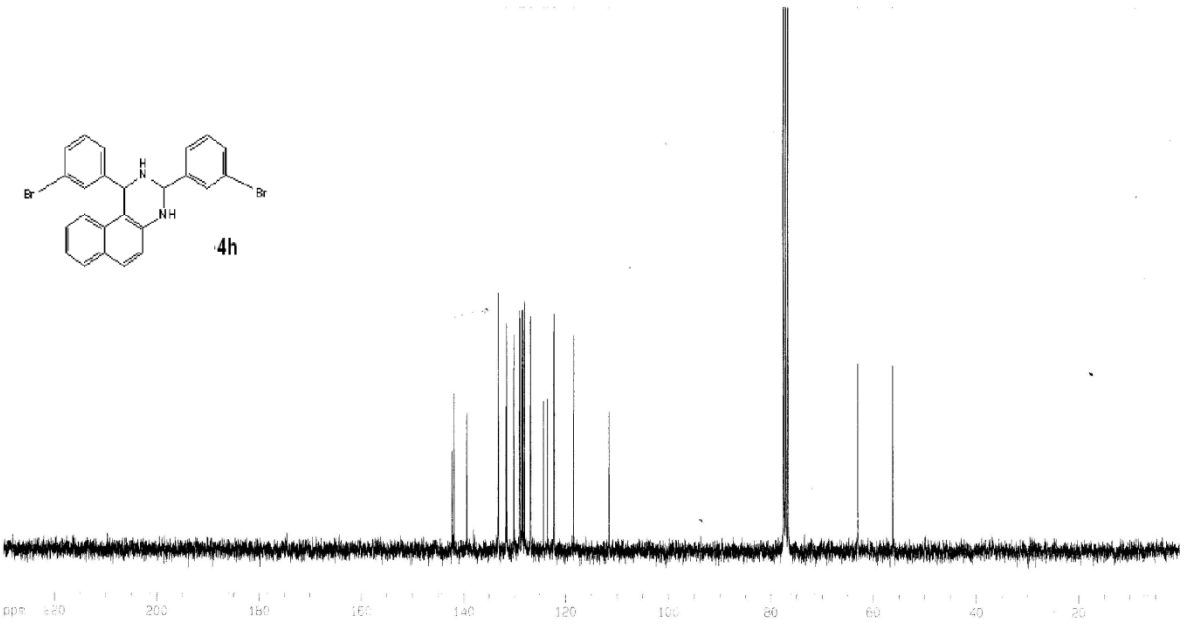


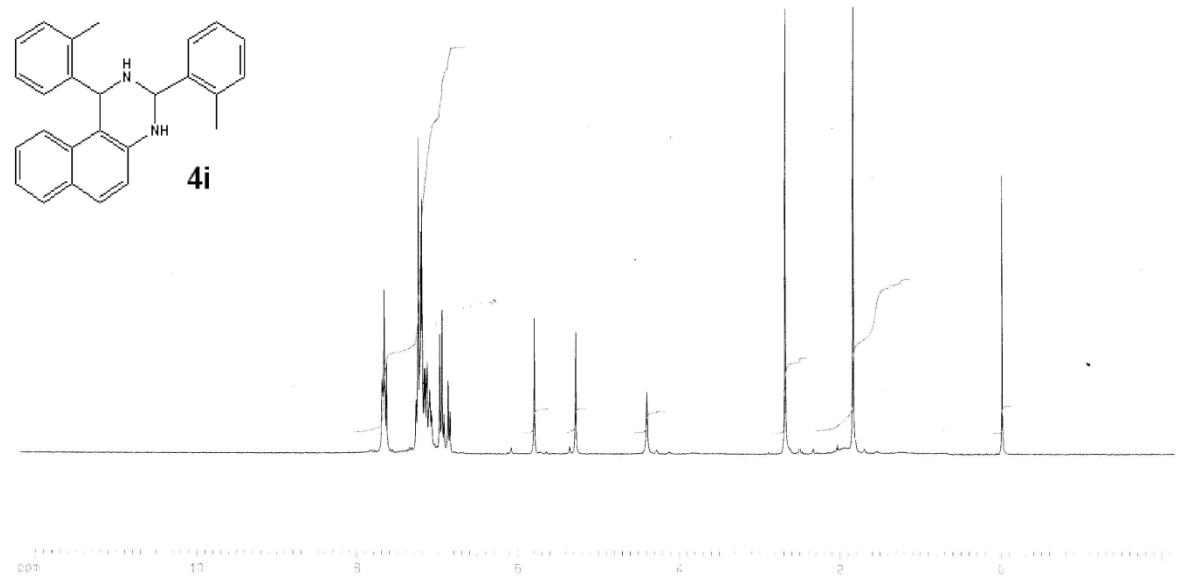


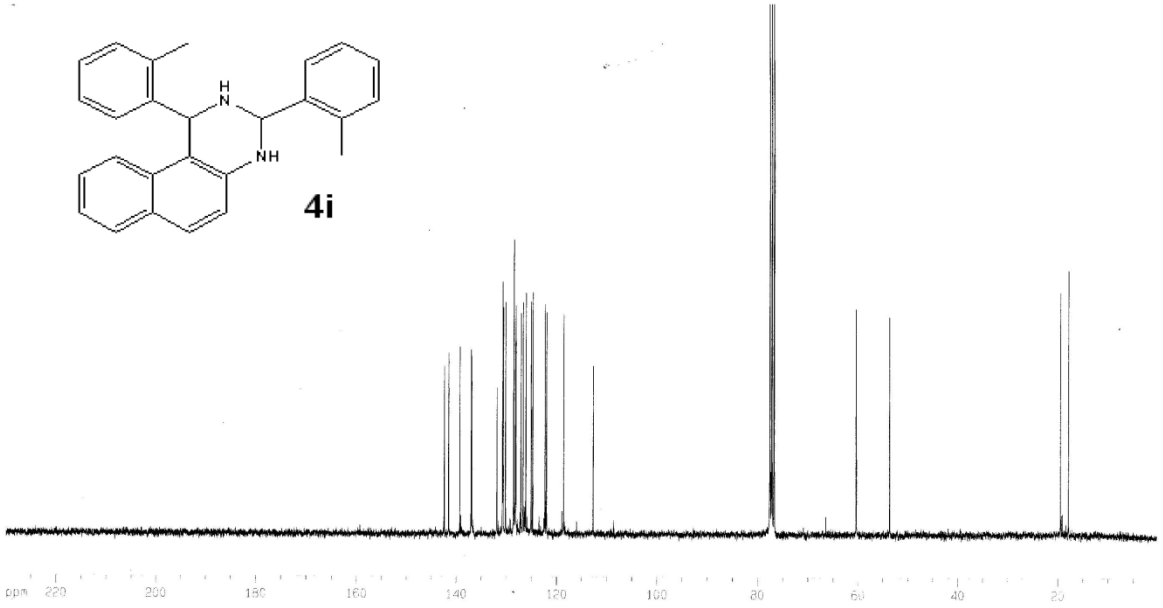


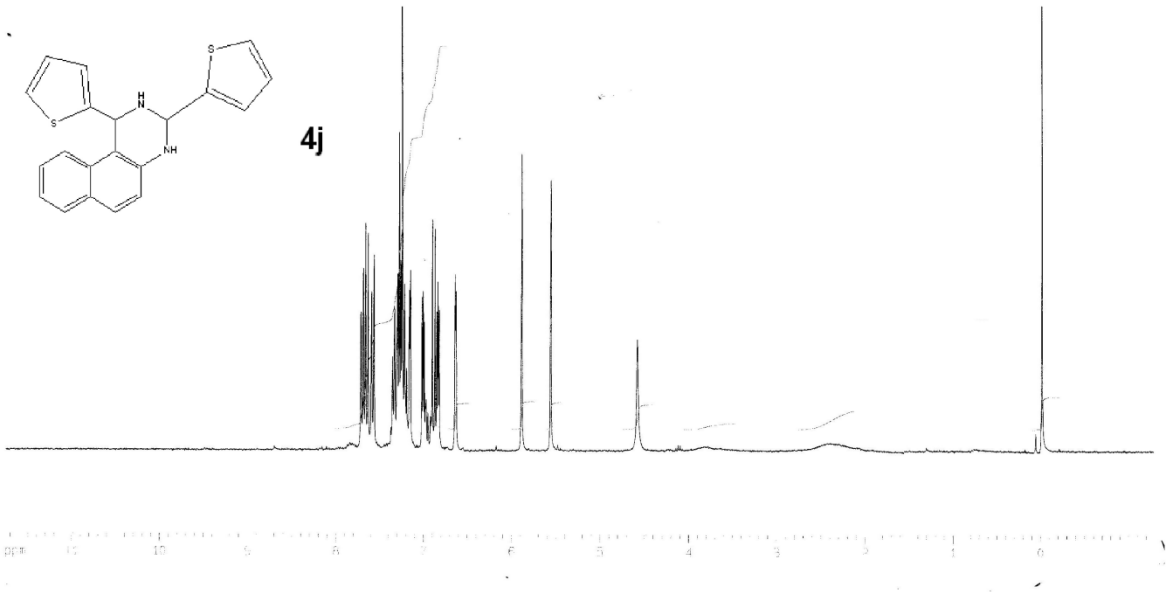
**4h**

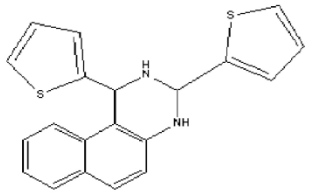




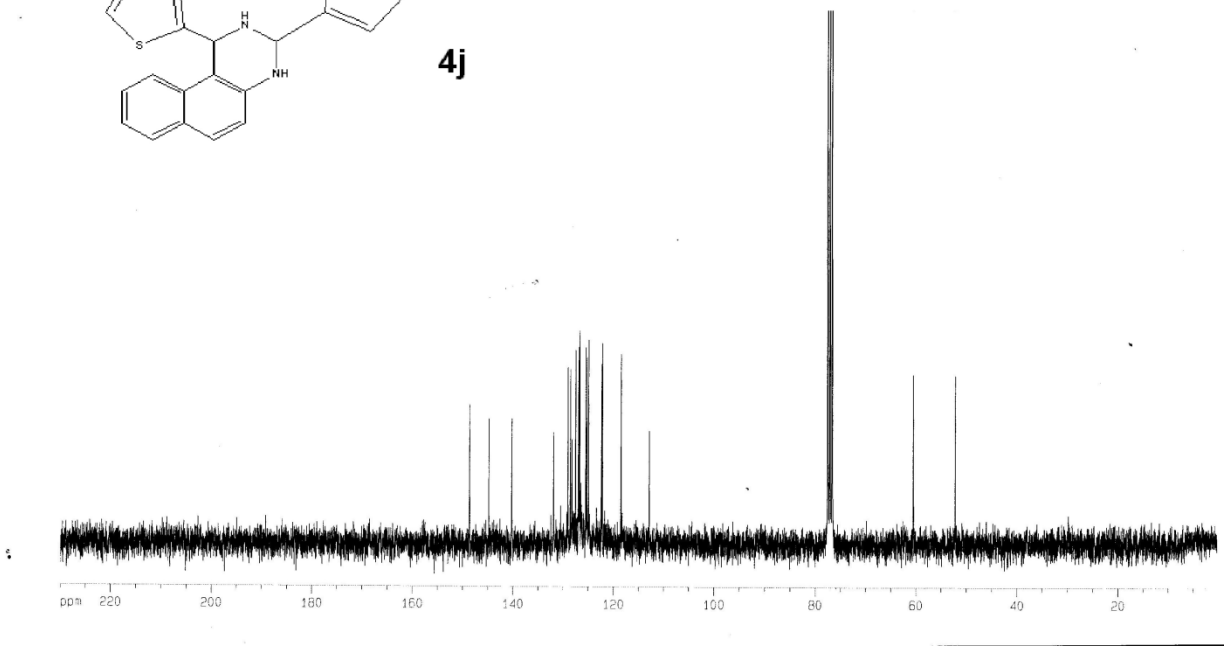







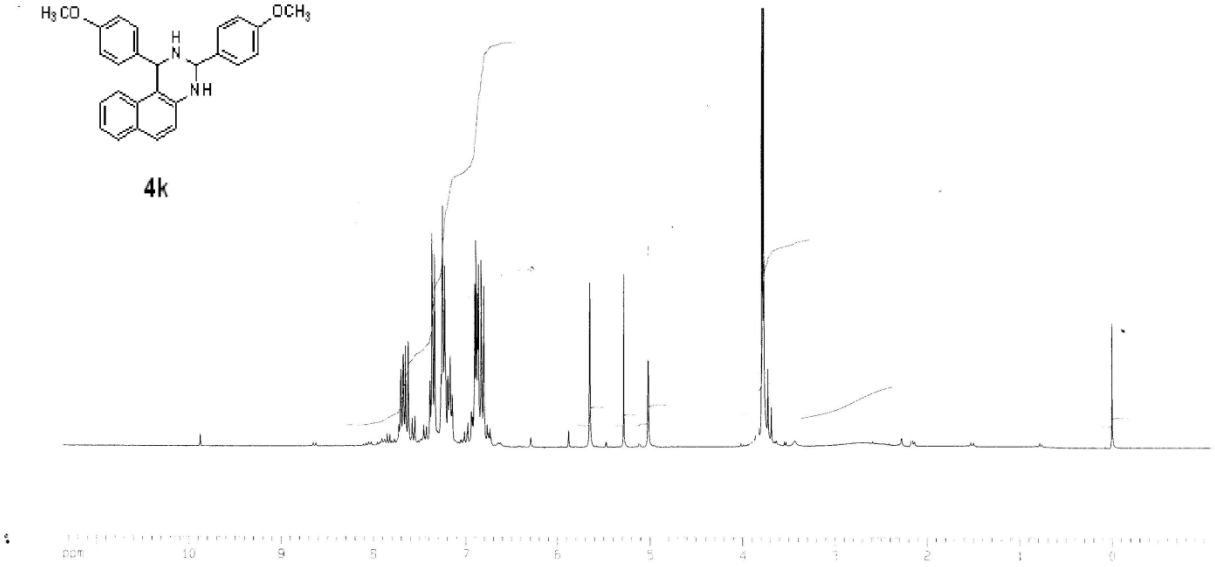

**4j**







**4k**



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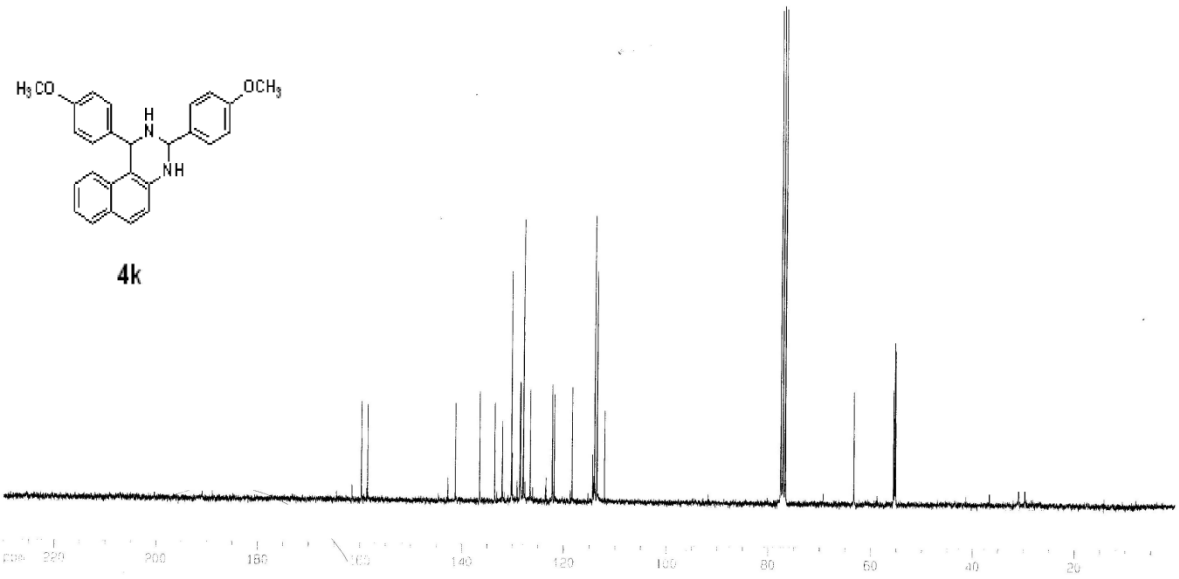




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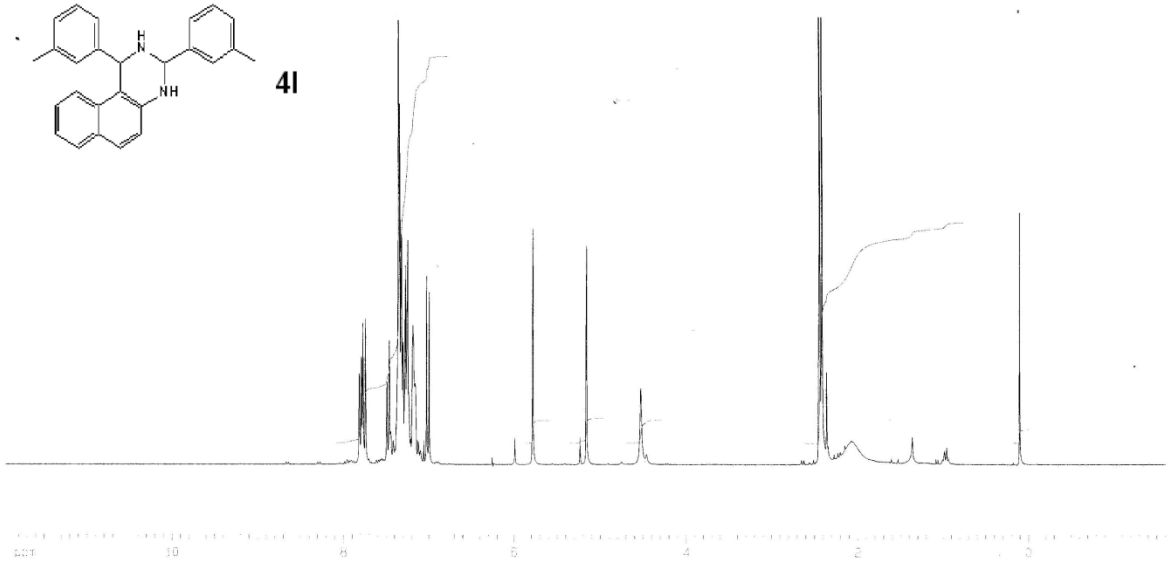

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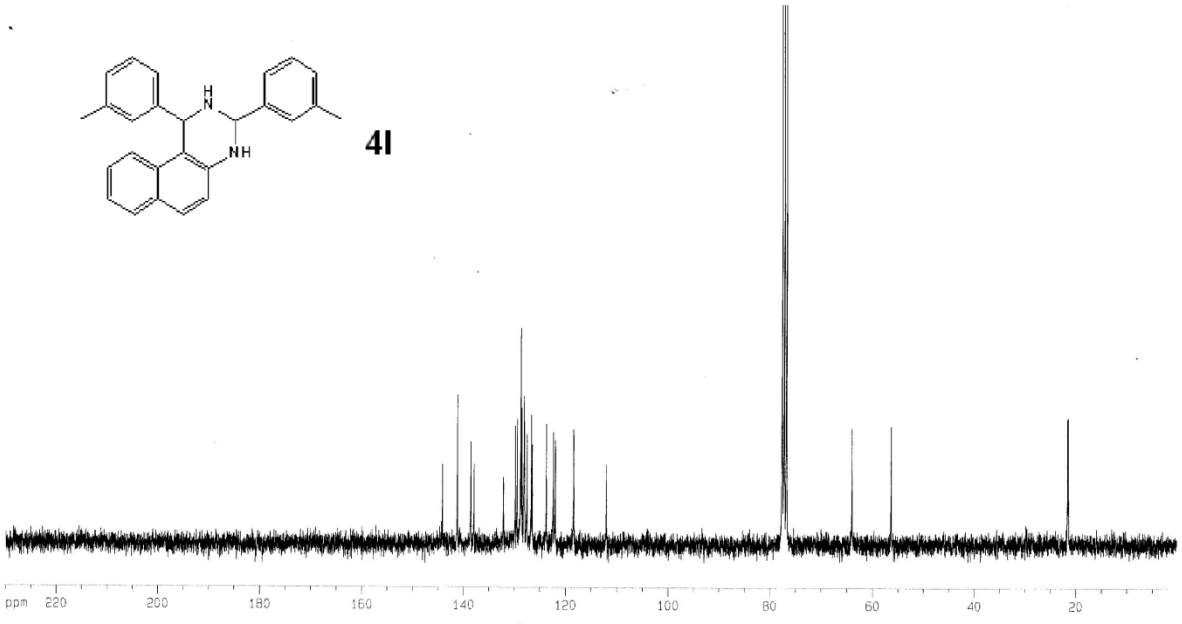
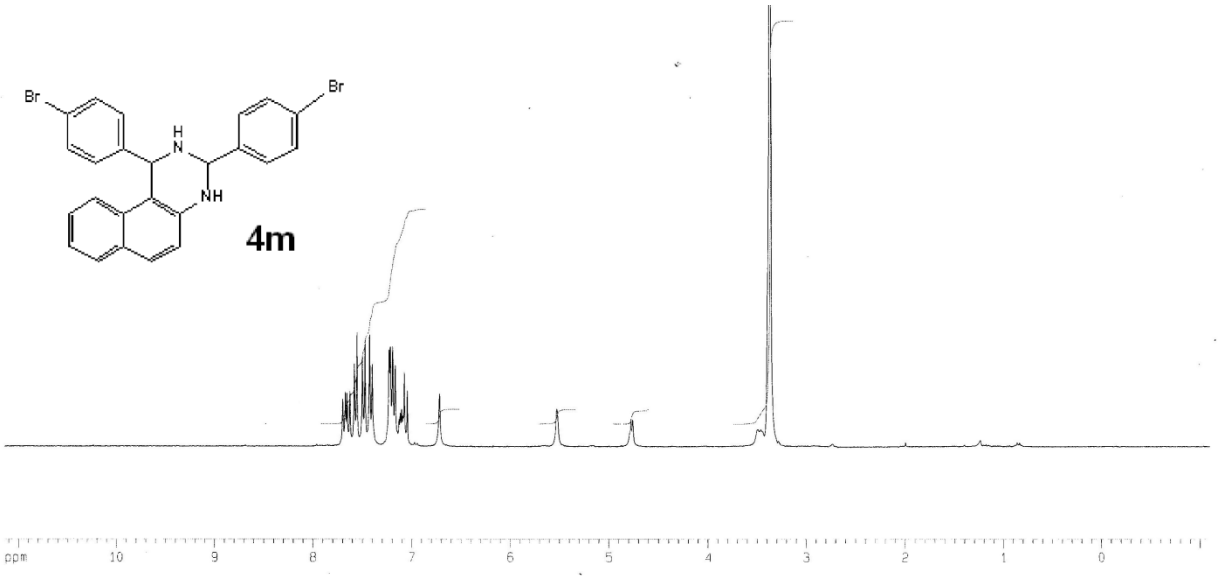
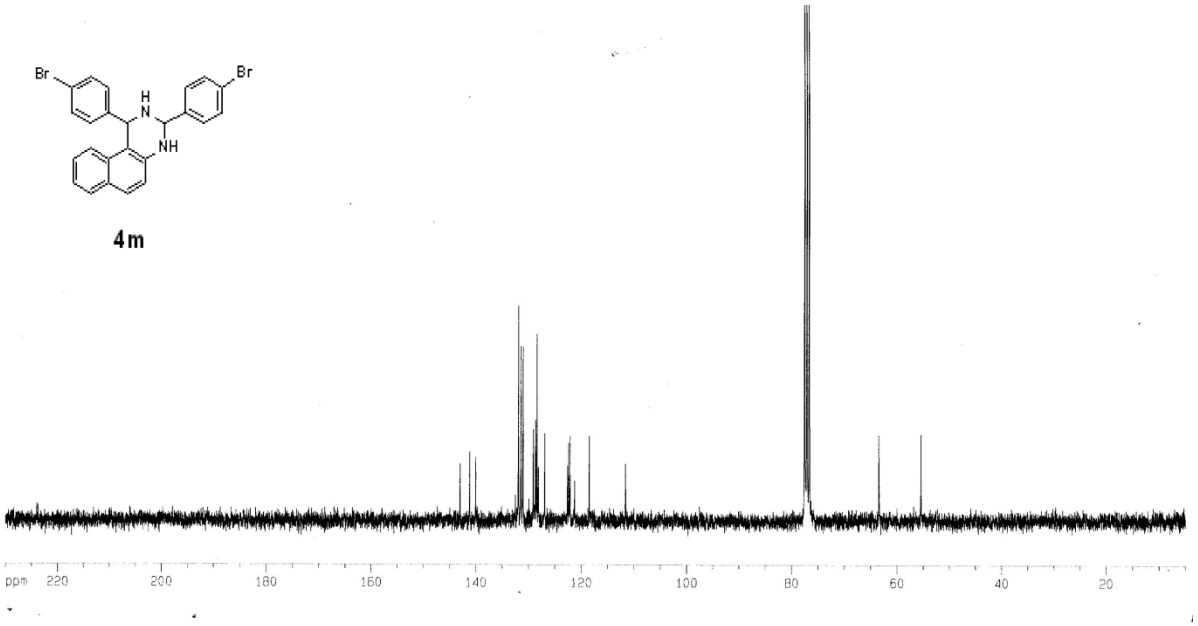




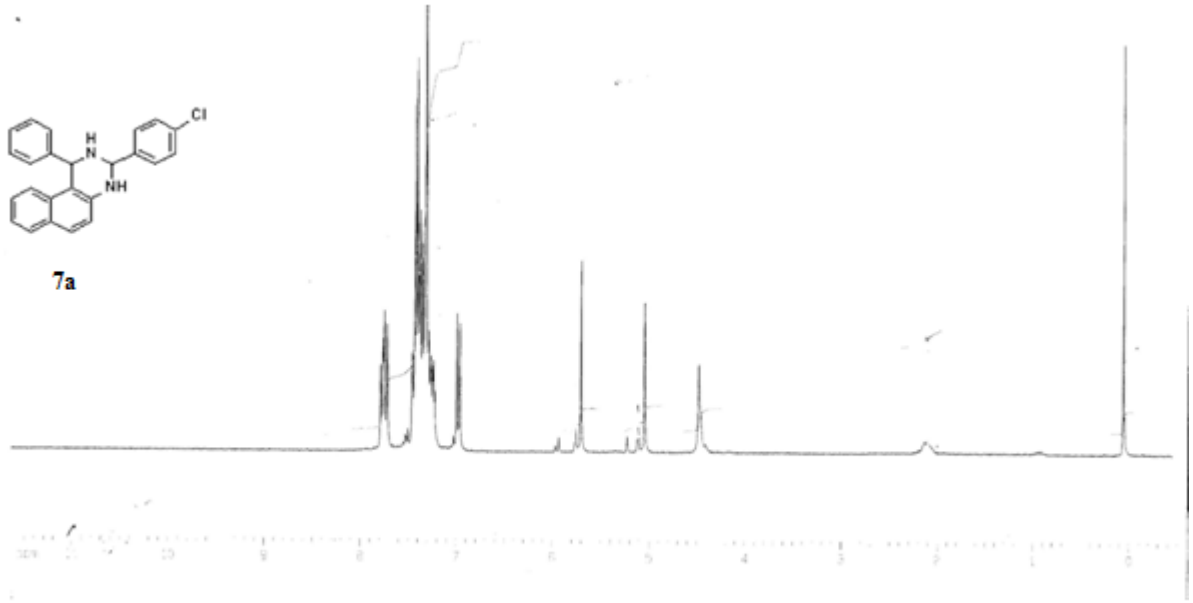


**4m**

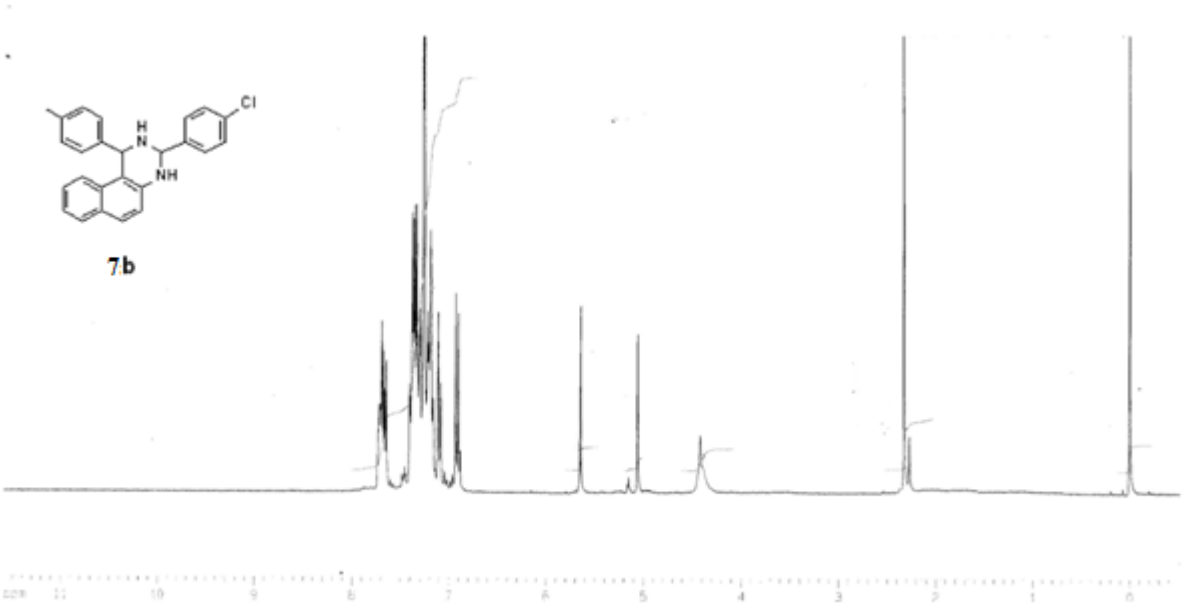




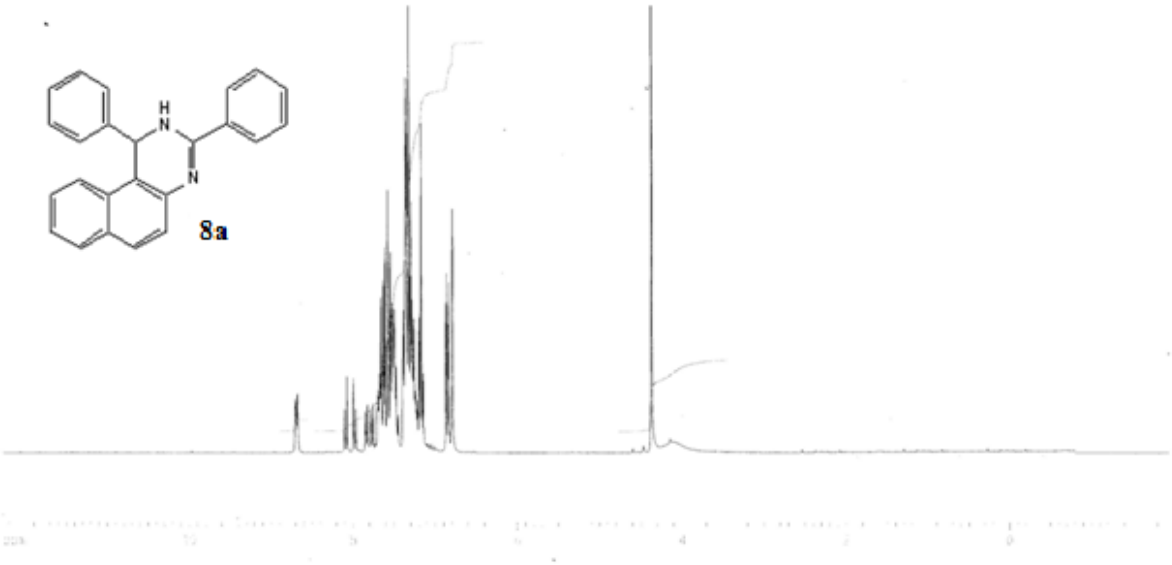

**4m**




**7a**




7b




8a