# New Conjugated Carbazole Derivatives: Synthesis and Photophysical Properties Catalysed by Pd-Cu@ rGO

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## Supporting Information

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**I. Large area TEM images:**

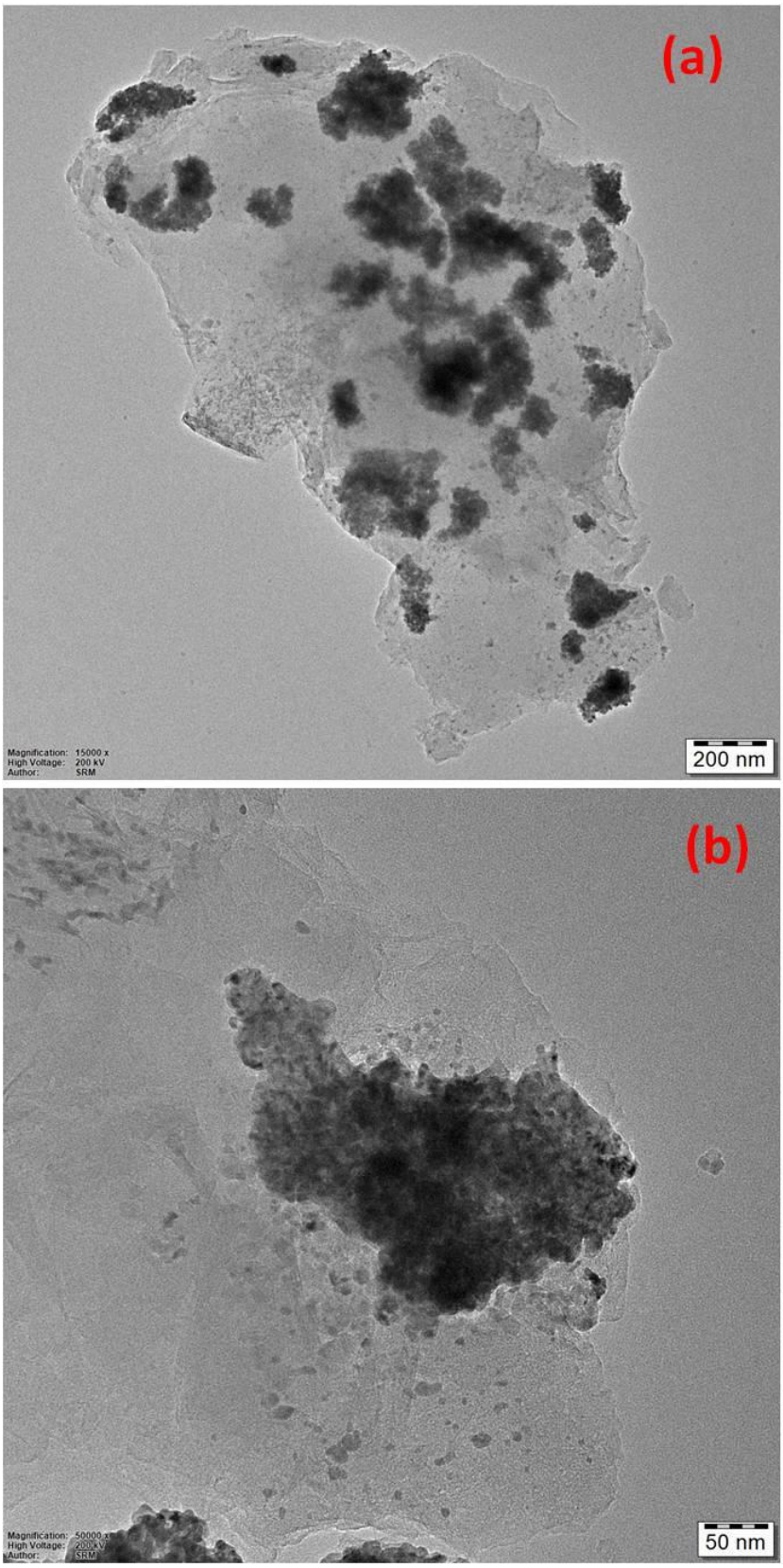



**Figure S1.** Large area TEM images (a) 200 nm scale and (b) 50 nm scale of Pd-Cu@rGO nanocomposite.

**II. SEM IMAGES (10wt%Pd &20wt%Pd):**

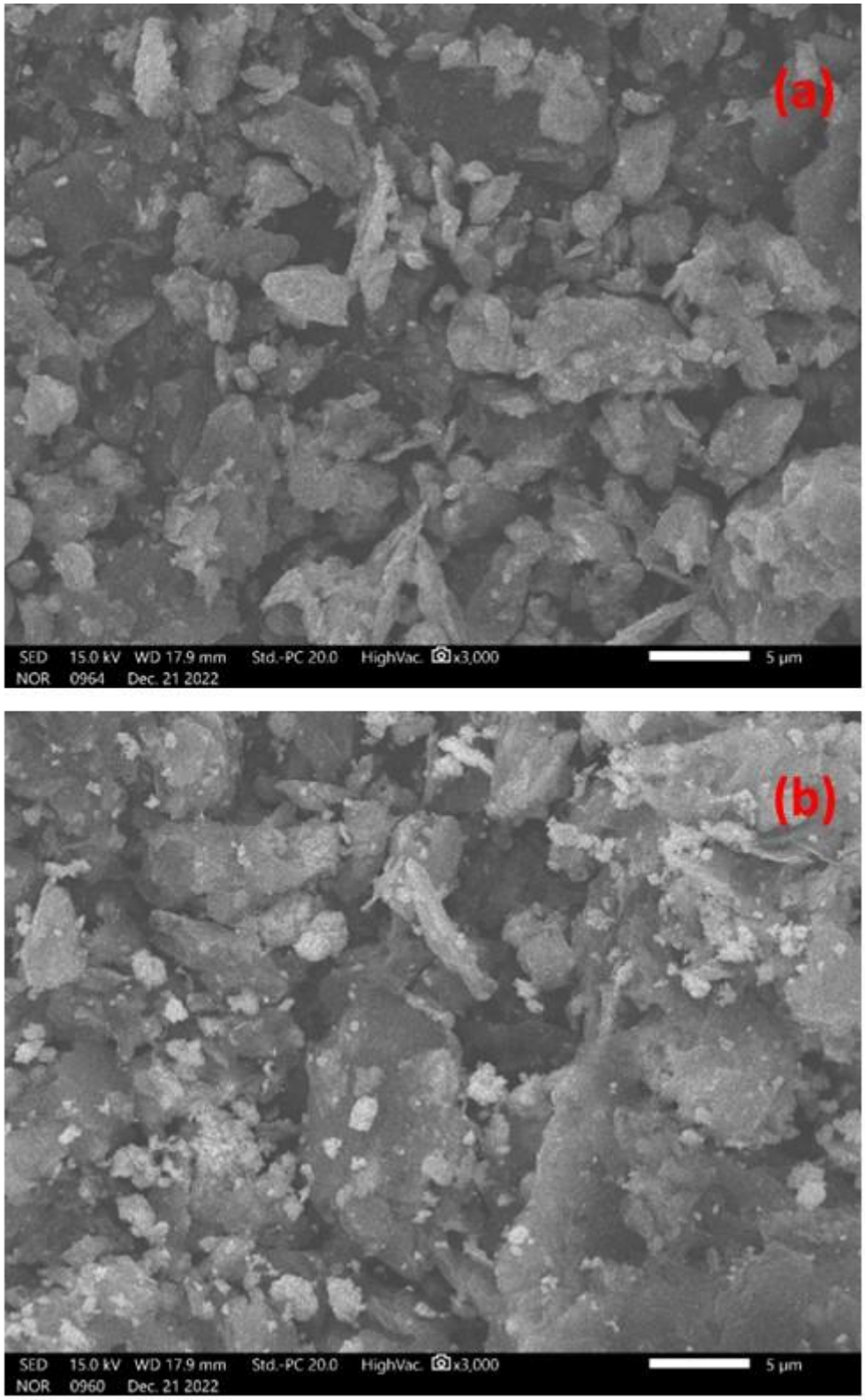



**Figure S2:** (a) SEM image of 10wt% Pd@rGO, (b) SEM image of 20wt%Pd.

**III. SEM image of Pd-Ni@rGO:**

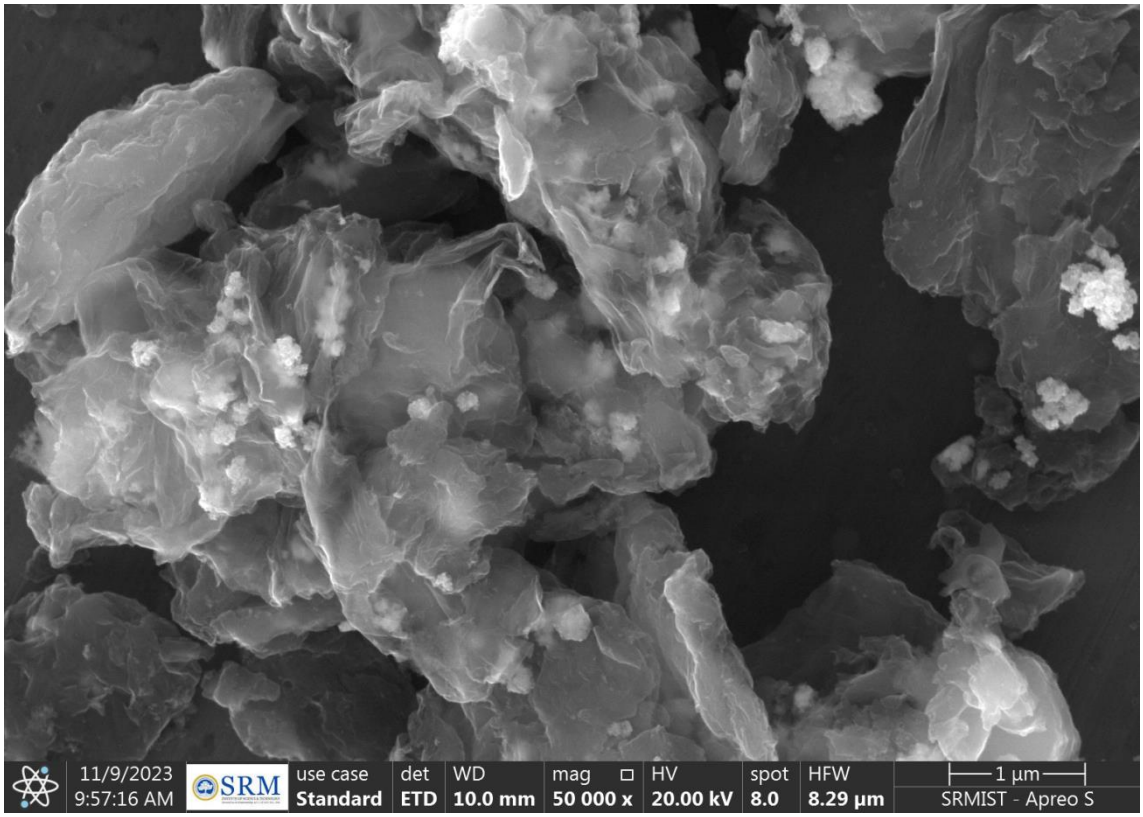



**Figure S3.** SEM image of Pd-Ni@rGO nanocomposite.

**IV. EDS Spectrum and EDS mapping of Pd-Ni@rGO:**

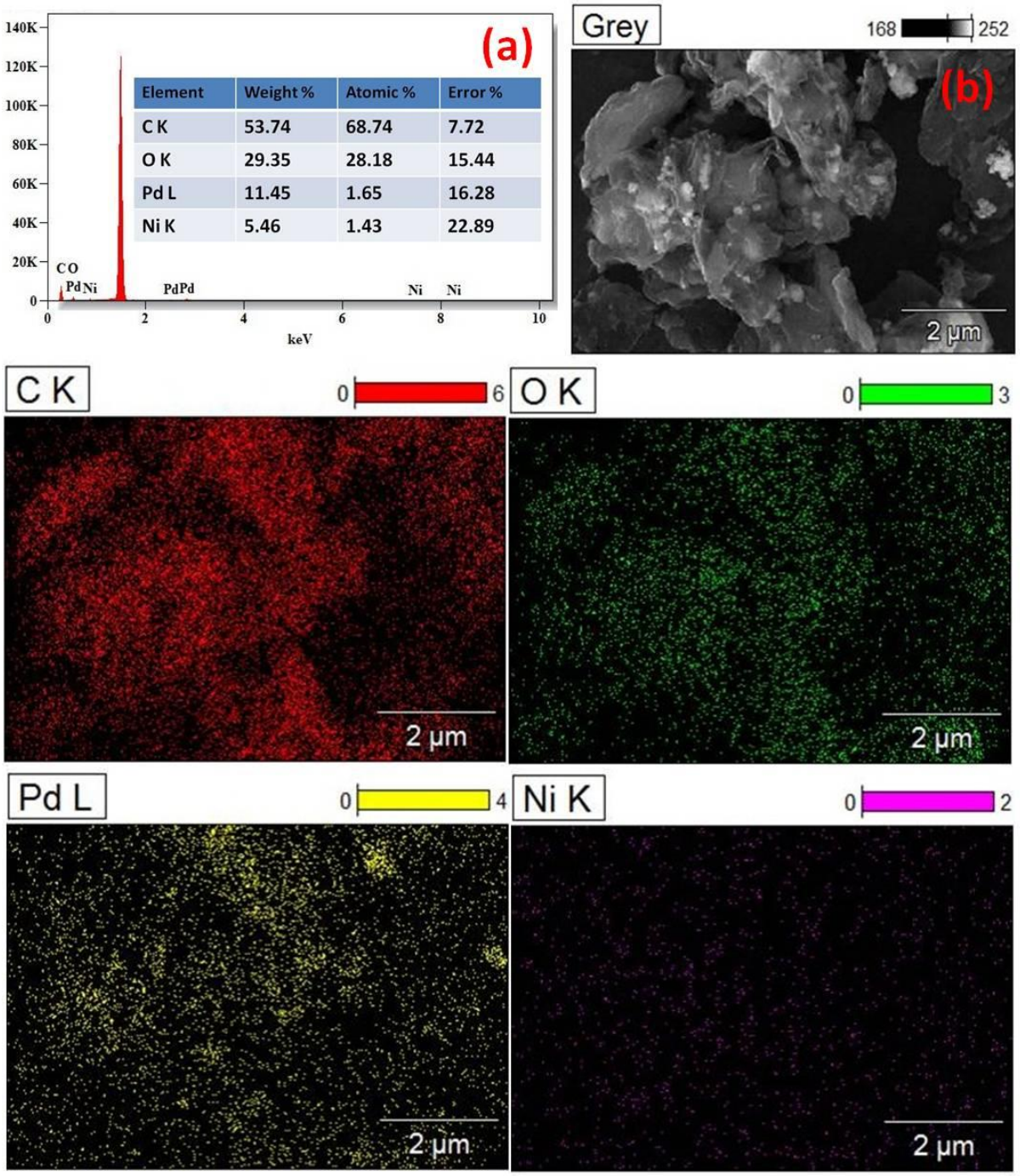


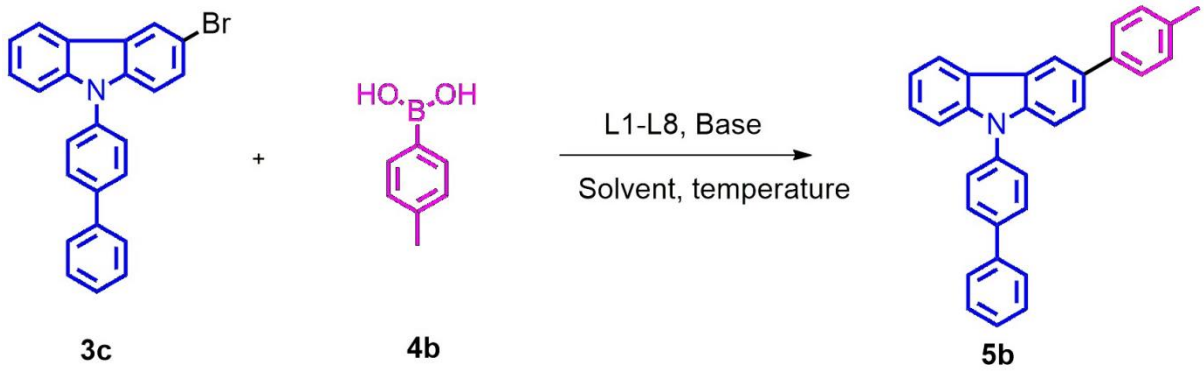

**Figure S4. (a)** EDS spectrum and (b) SEM micrograph and corresponding EDS mapping of Pd-Ni@rGO showing C (K), O (K), Pd (L) and Ni (K) images.

## V. Table S1: Comparison of results with reported literature.

| Entry | Catalyst | Metal loading | Substrate | Temperature | Time | Recyclability runs | Reference | Remarks |
|---|---|---|---|---|---|---|---|---|
| 1. | Pd-Cu@GO | Pd 29.34wt% + Cu 11.83wt% | Aryl bromides | 100 $^{O}$C | 1h | 7 | A. Gupta et al.[1] | Usage of organic solvent, high temperature, less substrate scope, high amount of catalyst. Only simple biphenyls were synthesized. |
| 2. | Pd-Cu NWs | Pd 61.80wt% + Cu 38.19wt% | Aryl bromides | 80 $^{O}$C | 2h | 5 | L. V. Jing Jing et al.[2] | High temperature, simple aryl bromides were studied. Only simple biphenyls were synthesized. |
| 3. | Pd-Co/Graphene | Pd 10wt% + Co 10wt% | Aryl iodides, bromides | 80 $^{O}$C | 2-4h | 5 | Y. S. Feng et al.[3] | High temperature, less substrate scope. Only simple biphenyls were synthesized. |
| 4. | Au/Pd NPs | Pd 16wt% + Au 7wt% | Iodo benzene | 80 $^{O}$C | 24h | 4 | M. Nasrollahzadeh et al.[4] | Requires long reaction time, high temperature and high catalytic loadings. Only simple biphenyls were synthesized. |
| 5. | Pd-Ni (20)/RGO | Ni 58.3wt% + Pd 1.9wt% | Aryl halides | 30-60 $^{O}$C | 3-24h | 5 | R. Nie et al. [5] | Long reaction time and high temperature required for bulky and electron withdrawing substrates. Only simple biphenyls were synthesized. |
| 6. | Pd-$Fe_3O_4$@C | Pd 52.5wt% | Aryl halides | RT | 2h | 10 | R. Li et al.[6] | Less substrate scope, high catalytic weight % used. Only simple biphenyls were synthesized. |
| 7. | PdAu/$Fe_3O_4$ | Pd 0.57wt%+ Au 1.42wt% | Bromo, iodo benzene | 80 $^{O}$C | 9.5h | 6 | X. Chen et al. [7] | Organic solvent was used, high temperature, long reaction time required. Only simple biphenyls were synthesized. |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8. | Pd-Cu/G | Pd 1.4 wt% + Cu 1.6 wt% | Aryl bromides | 60 $^{O}$C | 10h | 5 | X. Ma et al. [8] | High temperature, long reaction time required, less substrate scope. Only simple biphenyls were synthesized. |
| 9. | Pd/rGO | Pd 5.4wt% | Iodo benzene, bromo benzene | 80 $^{O}$C | 4h | 4 | X. Wang et al.[9] | Requires high temperature, less substrate scope. Only simple biphenyls were synthesized. |
| 10. | PdNPs@QPOSS@rGO | Pd 6.95wt% | Aryl halides | 80 $^{O}$C | 2h | 5 | S. Xia et al.[10] | Requires high temperature, less substrate scope. Only simple biphenyls were synthesized. |
| 11. | Cu/C-700/Pd | Cu 12.76wt% + Pd 0.45wt% | Aryl iodides | 120$^{0}$C | 24h | 8 | L. Sun et al. [11] | Loading of high amount of catalyst, High temperature, long reaction time. Only simple biphenyls were synthesized. |
| 12. | **Present Work** | | | | | | | |
| | Pd-Cu@rGO | Pd 10wt% + Cu 10wt% | 3-Bromo-*N*-protected carbazoles | RT | 2h | 5 | This work | 3-Bromocarbazole was used instead of simple aryl bromide, green solvents such as ionic liquids and ethanol-water (1:1) were used, photo physical properties were studied for the synthesized N-substituted carbazole derivatives. Reactions were carried out at room temperature. |

**VI. Table SII**. Optimization for SM coupling of biphenyl N-substituted 3-bromo carbazole with 4-methyl phenyl boronic acid catalyzed by rGO.




**3c** **4b** **5b**

| Entry | Catalyst | Catalyst Label | Base | Solvent | Temperature (°C) | Time (h) | Yield(%)[a] |
|---|---|---|---|---|---|---|---|
| 1. | - | | $K_2CO_3$ | EtOH+$H_2O$ | RT | 16 | NR |
| 2. | - | | $K_2CO_3$ | EtOH+$H_2O$ | 80 | 16 | NR |
| 3. | 10wt%Pd@rGO | $L_1$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 8 | 60 |
| 4. | 20wt%Pd@rGO | $L_2$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 8 | 60 |
| 5. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 98 |
| 6. | 10wt%Pd-5wt%Cu@rGO | $L_4$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 60 |
| 7. | 5wt%Pd-10wt%Cu@rGO | $L_5$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 50 |
| 8. | 10wt%Pd-10wt%Ni@rGO | $L_6$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 40 |
| 9. | 10wt%Pd-10wt%Ni@Rgo | $L_6$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 8 | 70 |
| 10. | 10wt%Pd-5wt%Ni@rGO | $L_7$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 40 |
| 11. | 5wt%Pd-10wt%Ni@rGO | $L_8$ | $K_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 30 |
| 12. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $Na_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 70 |
| 13. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $Cs_2CO_3$ | EtOH+$H_2O$ | RT | 2 | 63 |
| 14. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $NEt_3$ | EtOH+$H_2O$ | RT | 2 | 40 |
| 15. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | Toluene | RT | 2 | 40 |
| 16. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | Toluene | 80°C | 2 | 75 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 17. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | Acetonitrile | RT | 2 | 30 |
| 18. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | Acetonitrile | 80$^oC$ | 2 | 50 |
| 19. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | 1,4-dioxane | RT | 16 | 30 |
| 20. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | 1,4-dioxane | 100 | 4 | 60 |
| 21. | 10wt%Pd-10wt%Cu@rGO | $L_3$ | $K_2CO_3$ | IL[(b)] | 80 | 12 | 80 |

Reaction conditions: 9-((1,1'-Biphenyl)-4-yl)-3-bromo-9*H*-carbazole (1mmol), 4-methyl phenylboronic acid(1.1mmol), Solvent (1:1ml), catalyst (5 mg), Base (2 mmol), [a]; Isolated yield; [b] IL; 1-butyl-2-decyl-1*H*-imidazolium bromide ionic liquid) (0. 2 mmol).

**VII. SEM image of Pd-Cu@rGO:**

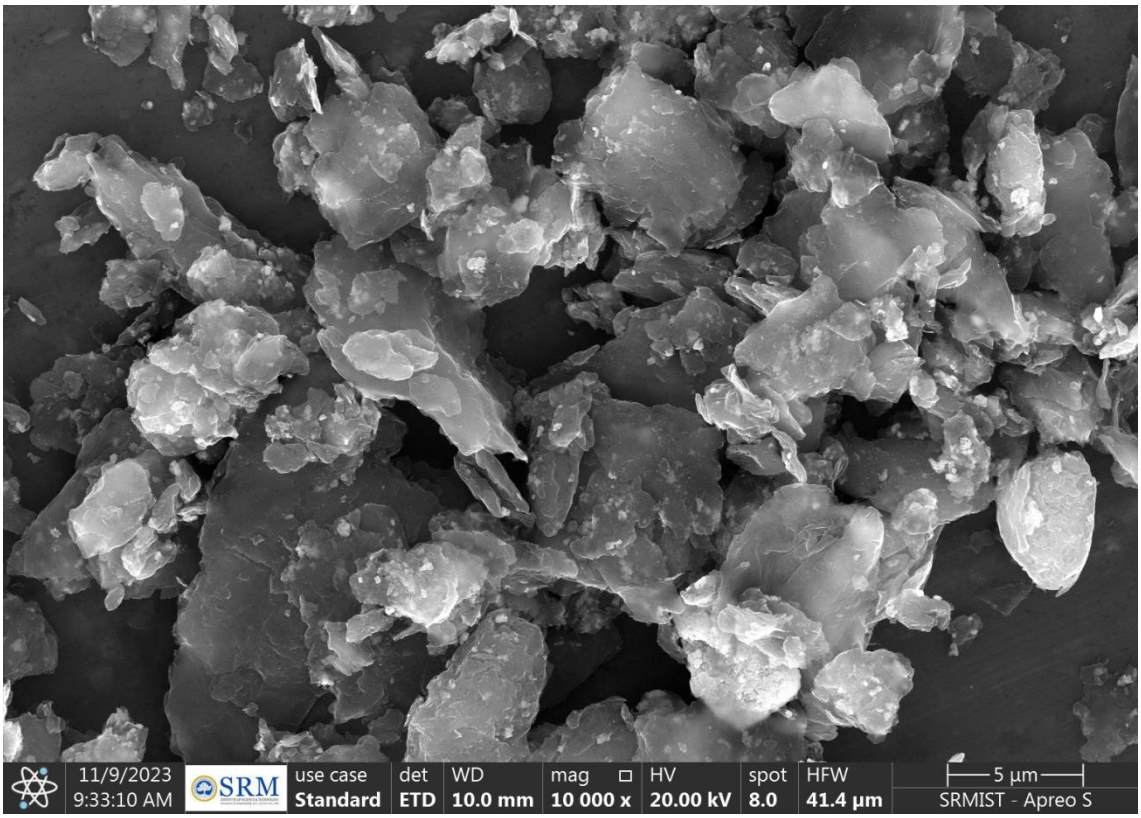



**Figure S5.** SEM image of Pd-Cu@rGO nanocomposite.

**VIII. SEM image of recoverd Pd-Cu@rGO:**

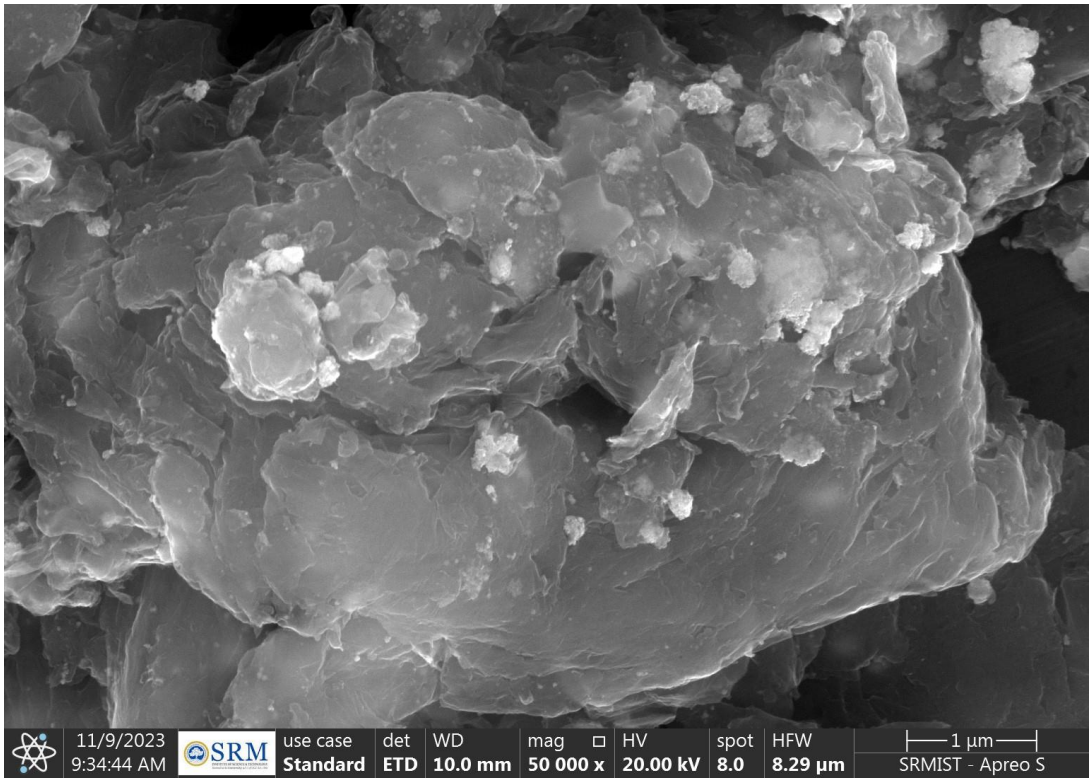



**Figure S6(a).** SEM image of recovered Pd-Cu@rGO nanocomposite (after 5 cycles).

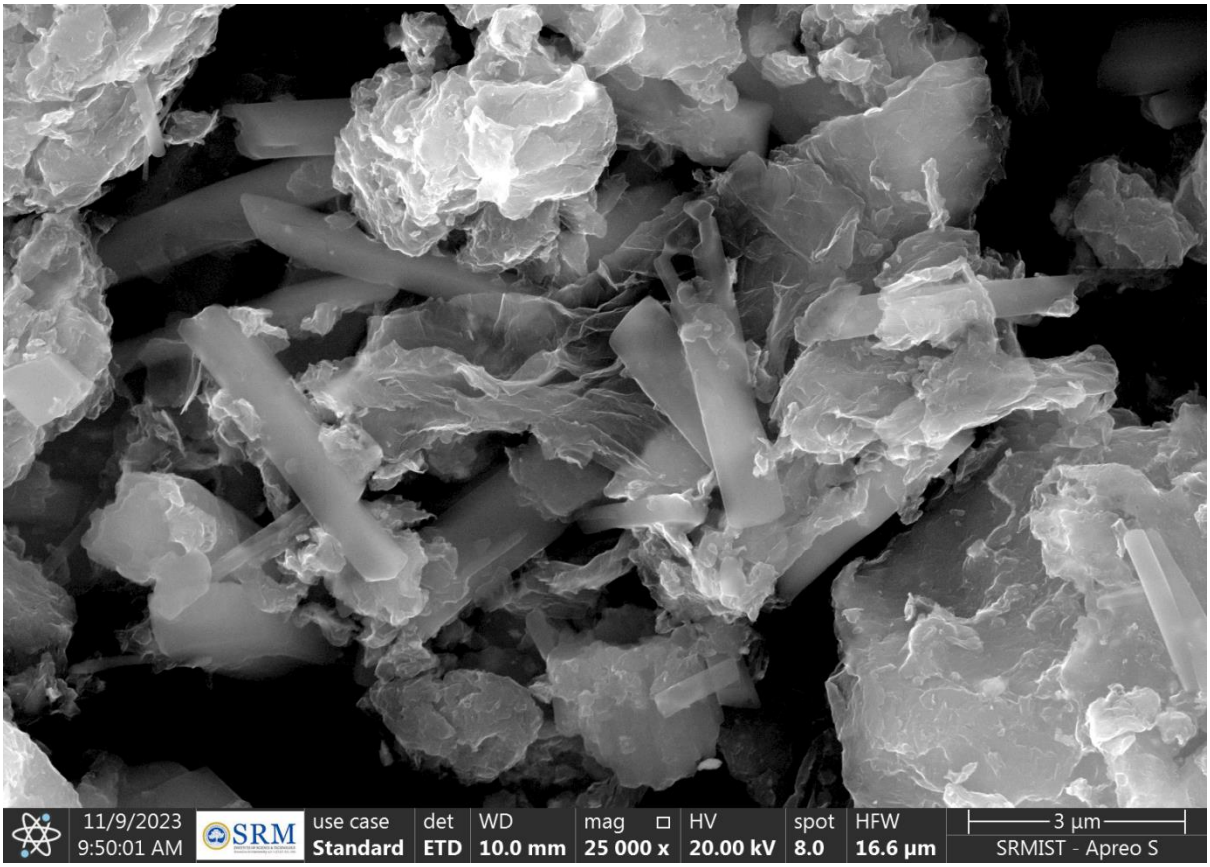



**Figure S6(b).** SEM image of recovered Pd-Cu@rGO nanocomposite (after 7 cycles).

**IX. EDS Spectrum and EDS mapping of recovered Pd-Cu@rGO:**

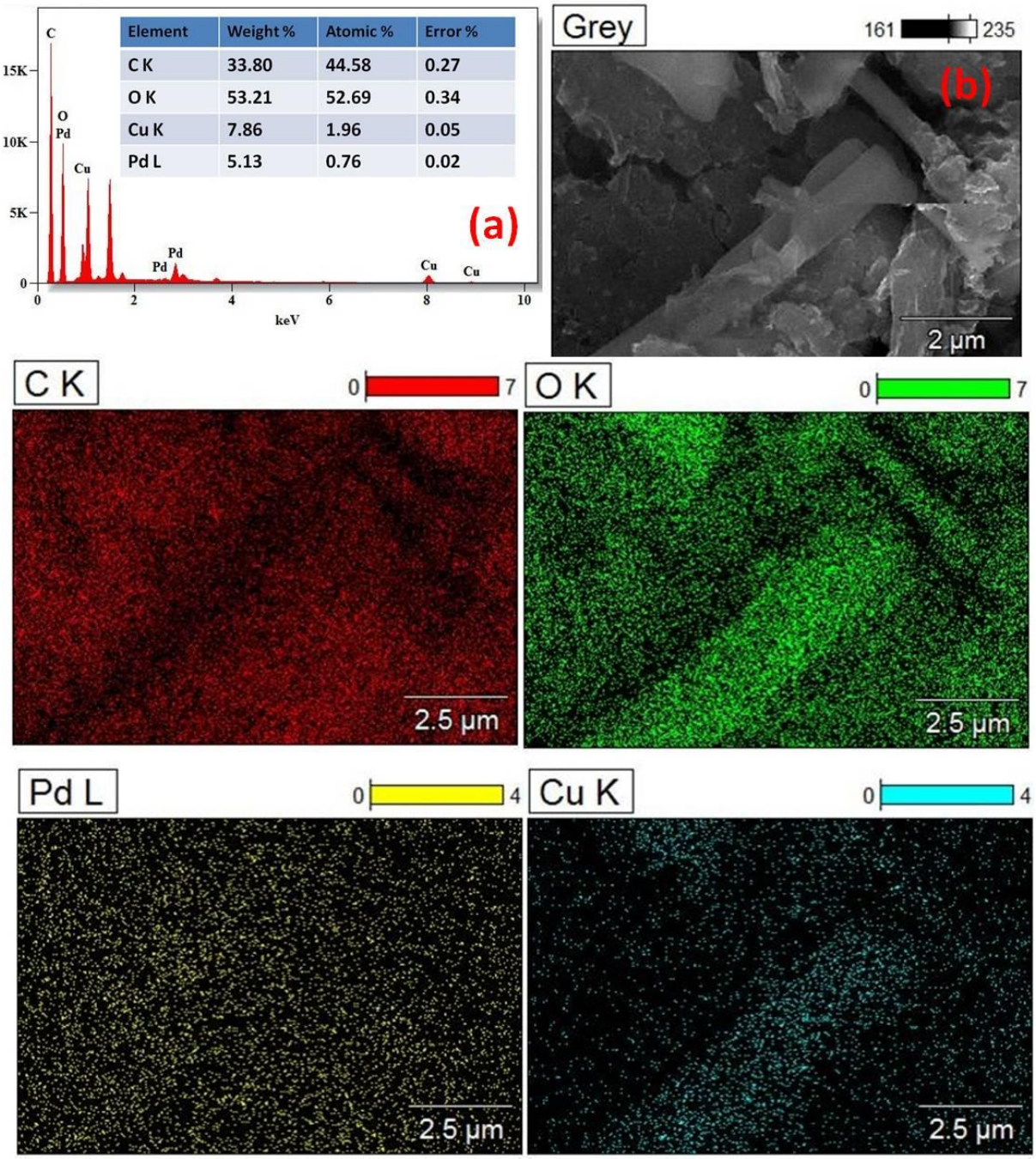



**Figure S7.** (a) EDS spectrum and (b) SEM micrograph and corresponding EDS mapping of recovered Pd-Cu@rGO(after 7 cycles) showing C (K), O (K), Pd (L) and Cu (K) images.

**X. CV:**

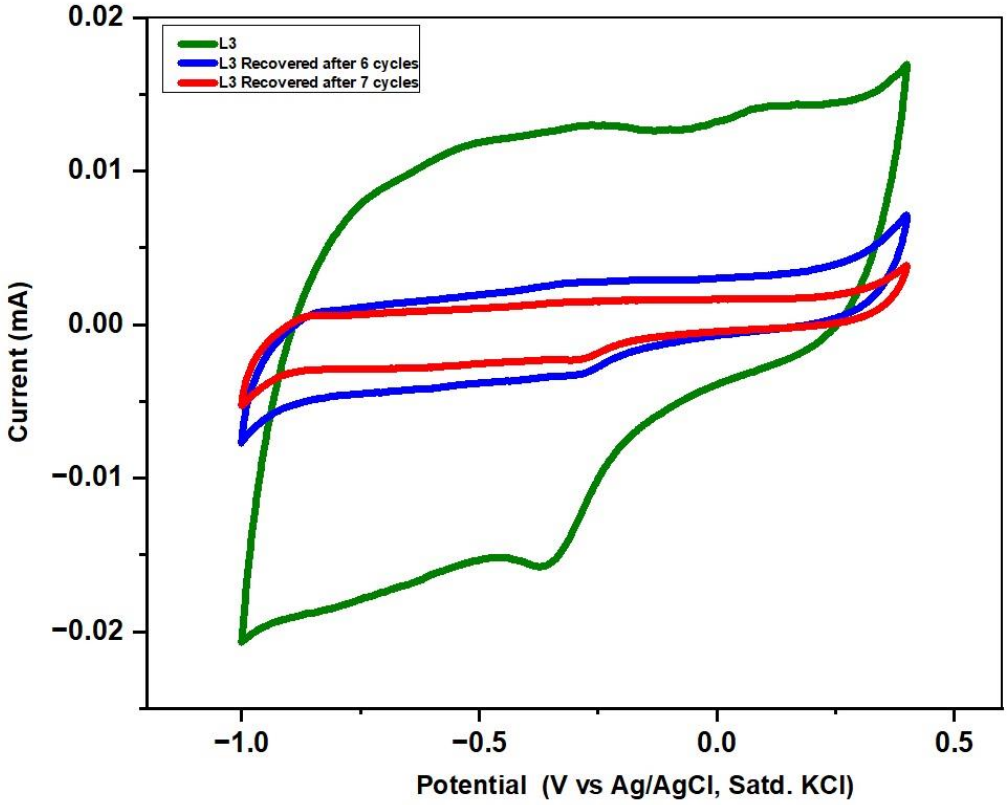
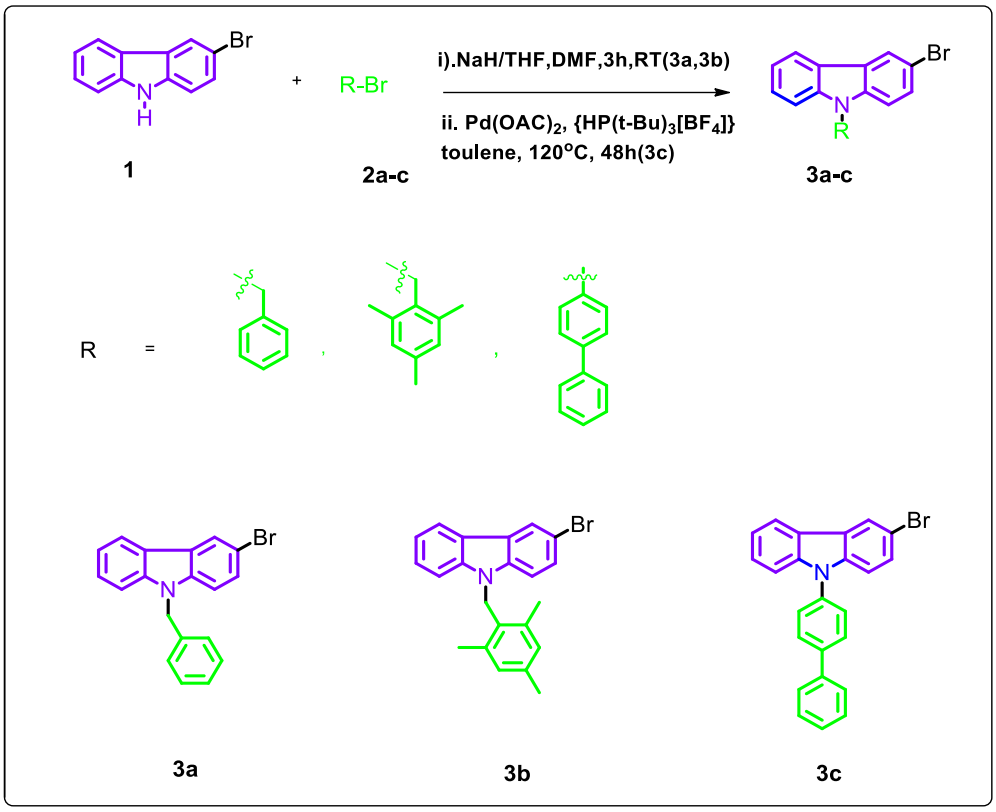



**Figure S8.** Cyclic voltammograms of (a) fresh 10wt% Pd- 10 wt% Cu@rGO **(L3)** and (b) recovered 10wt% Pd- 10 wt% Cu@rGO after 6 consecutive cycles of SM reaction samples **(L3 recovered after 6cycles)** (c) recovered 10wt% Pd- 10 wt% Cu@rGO after 7 consecutive cycles of SM reaction samples **(L3 recovered after 7cycles)** recorded in Nitrogen-saturated 1 M KOH electrolyte with a scan rate of 50 mV/s in a potential range of -1.0 to 0.4 V vs Ag/AgCl (satd. KCl).

## XI. Preparation of *N*-protected Carbazoles (3a-c)




### a) Preparation of *N*-benzyl/2',4',6'-trimethyl benzyl-carbazoles (3a& 3b)[12,13a-c]

In a dried 25 mL round-bottomed flask, DMF (5 mL) and NaH (2.5 eq) were taken and the resulting solution was added to the solution of 3-bromocarbazole (1 eq) in THF (10mL) at 0 °C. After stirring for 30 minutes at room temperature, benzyl bromide(1eq) was added to the solution and the reaction was continued overnight at room temperature, the solution was quenched with ice-water (20 mL), extracted with EtOAc (30 mL X 3). After washing the combined organic layers with water (2 mL X 5) and brine, the organic phase was dried with anhydrous $Na_2SO_4$. After that, the organic phase is concentrated, and the solvent is evaporated under rotovapor to get the pure compound **3a**. A similar procedure was adopted to compound **3b**.

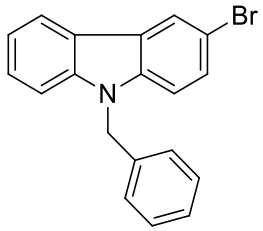
### b) Preparation of *N*-biphenyl-3-bromo-carbazoles (3c)[12]

A mixture of $NaO^tBu$ (2.8 g, 29.1 mmol), $Pd(OAc)_2$ (0.2 mmol), and $[HPt\text{-}Bu)_3\{BF_4\}]$ (0.2 mmol) was dissolved in toluene (10 mL) in a 25 mL oven-dried flask. 3-bromocarbazole (1 mmol) and biphenyl bromide (1 mmol) were added. The reaction was heated at reflux temperature for

48 h. Then, the reaction mixture was cooled to room temperature, the mixture was quenched by addition of 2 M HCl (aq) (25 mL). The mixture was extracted with dichloromethane (25 mL X 3), dried over anhydrous $Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. Finally, the product was isolated by column chromatography using 20: 80 ethyl acetate: hexane as eluents to produce product **3c.**

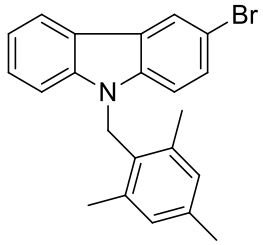
## XII. Characterization Data

### 3a. 9-Benzyl-3-bromo-9*H*-carbazole[14]




Colourless solid; M.P. 196-198$^{O}$C. Yield: 98%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.23 (d, *J* = 1.6 Hz, 1H, Ar-H), 8.08 (d, *J* = 7.6Hz, 1H, Ar-H), 7.50-7.43 (m, 2H, Ar-H), 7.37 (d, *J* = 8.4Hz, 1H, Ar-H), 7.26-7.21 (m, 5H, Ar-H), 7.11-7.09 (m, 2H, Ar-H), 5.49 (s, 2H, Ar-C$\underline{H}_2$). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 140.99 (Ar-C), 139.29 (Ar-C), 136.72 (Ar-C), 128.89 (Ar-C), 128.53 (Ar-C), 127.66 (Ar-C), 126.65 (Ar-C), 126.35 (Ar-C), 124.81 (Ar-C), 123.18 (Ar-C), 122.03 (Ar-C), 120.64 (Ar-C), 119.70 (Ar-C), 112.10 (Ar-C), 110.45 (Ar-C), 109.18 (Ar-C), 46.68 (Ar-$\underline{C}H_2$). Anal. calcd. for $C_{19}H_{14}N^+$ $[M]^+$: C, 67.87; H, 4.20; N, 4.17%; Found: C, 67.84; H, 4.22; N, 4.20 %.

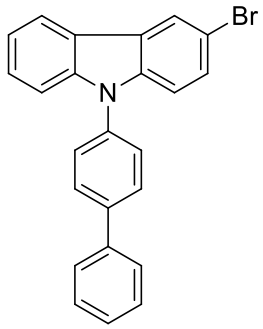
### 3b. 3-Bromo-9-(2,4,6-trimethylbenzyl)-9*H*-carbazole




Colourless solid; M.P. 144-146$^{O}$C. Yield: 98%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.16 (d, *J* = 2Hz, 1H, Ar-H), 8.02 (d, *J* = 7.6Hz, 1H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.23-7.15 (m, 3H, Ar-H), 6.93-6.87 (m, 2H, Ar-H), 5.38 (s, 2H, Ar-C$\underline{H}_2$-), 2.28 (s, 3H, Ar-C$\underline{H}_3$), 2.12 (s, 6H, Ar-$[CH_3]_2$). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.08 (Ar-C), 139.32 (Ar-C), 137.76 (Ar-C), 137.54 (Ar-C),

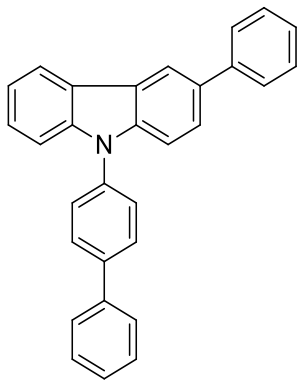
129.82 (Ar-C), 129.07 (Ar-C), 128.30 (Ar-C), 126.42 (Ar-C), 124.86 (Ar-C), 122.91 (Ar-C), 122.00 (Ar-C), 120.41 (Ar-C), 119.36 (Ar-C), 117.78 (Ar-C), 110.95 (Ar-C), 109.61 (Ar-C), 43.26 (Ar-$\underline{C}H_2$), 21.01 (Ar-$CH_3$), 20.42 (Ar-$\underline{C}H_3$). Anal. calcd. for $C_{22}H_{20}N^+$ $[M]^+$: C, 69.85; H, 5.33; N, 3.70%; Found: C, 69.82; H,5.36; N, 3.67%.

**3c. 9-([1,1'-Biphenyl]-4-yl)-3-bromo-9*H*-carbazole**




Colourless solid; M.P. 154-156$^O$C. Yield: 97%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.26 (d, *J* = 1.6Hz, 1H, Ar-H), 8.10-8.08 (m, 1H, Ar-H), 7.82-7.80 (m, 2H, Ar-H), 7.69-7.67 (m, 2H, Ar-H), 7.60-7.58 (m, 2H, Ar-H), 7.52-7.48 (m, 3H, Ar-H), 7.45-7.41 (m, 3H, Ar-H), 7.34-7.28 (m, 2H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.22 (Ar-C), 140.70 (Ar-C), 140.16 (Ar-C), 139.56 (Ar-C), 129.03 (Ar-C), 128.66 (Ar-C), 127.79 (Ar-C), 127.29 (Ar-C), 127.18 (Ar-C), 126.75 (Ar-C), 125.20 (Ar-C), 123.10 (Ar-C), 122.37 (Ar-C), 120.55 (Ar-C), 120.42 (Ar-C), 112.77 (Ar-C), 111.38 (Ar-C), 110.12 (Ar-C). Anal. calcd. for $C_{24}H_{16}N^+$ $[M]^+$: C, 72.37; H, 4.05; N, 3.52%; Found: C, 72.35; H, 4.03; N, 3.54 %.

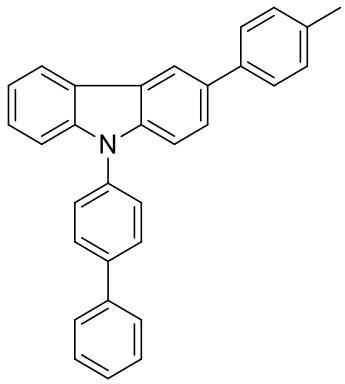
**5a. 9-([1,1'-Biphenyl]-4yl)-3-phenyl-9*H*-carbazole**




Colourless solid; M.P. 120-122$^O$C. Yield: 90%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.35 (s, 1H, Ar-H), 8.19 (d, *J* = 6Hz, 1H, Ar-H), 7.79 (d, *J* = 6.8Hz, 2H, Ar-H), 7.71 (d, *J* = 6.4Hz, 2H, Ar-H),

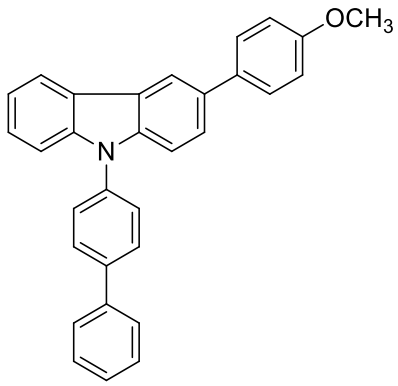
7.67-7.60 (m, 5H, Ar-H), 7.50-7.28 (m, 10H, Ar-H). $^{13}$C NMR ( 100MHz, $CDCl_3$): δ (ppm): 142.06 ( Ar-C), 141.38 (Ar-C), 140.41 (Ar-C), 140.31 (Ar-C), 136.88 (Ar-C), 133.65 (Ar-C), 129.06 (Ar-C), 128.88 (Ar-C), 128.61 (Ar-C), 127.75 (Ar-C), 127.43 (Ar-C), 127.31 (Ar-C), 127.22 (Ar-C), 126.67 (Ar-C), 126.27 (Ar-C), 125.62 (Ar-C), 124.06 (Ar-C), 123.66 (Ar-C), 120.49 (Ar-C), 120.25 (Ar-C), 118.93 (Ar-C), 110.18 (Ar-C), 110.09 (Ar-C). Anal. calcd. for $C_{30}H_{21}N^+$ $[M]^+$: C, 91.11; H, 5.35; N, 3.54%; Found: C,91.13; H, 5.33; N, 3.51 %.

**5b. 9-([1,1'-Biphenyl]-4-yl)-3-(p-tolyl)-9*H*-Carbazole.**



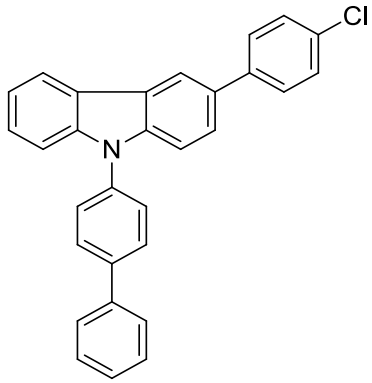
Colourless solid; M.P.150-151$^O$C. Yield: 98%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.34 (d, *J* = 1.2Hz, 1H, Ar-H), 8.20 (d, *J*= 7.6Hz, 1H, Ar-H), 7.83 -7.81 (m, 2H, Ar-H), 7.70-7.61 (m, 7H, Ar-H), 7.52-7.39 (m, 6H, Ar-H), 7.33-7.28 (m, 3H, Ar-H), 2.42 (s, 3H, Ar-C$\underline{H}_3$). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 145.01 (Ar-C), 140.35 (Ar-C), 140.30 (Ar-C), 140.21 (Ar-C), 136.88 (Ar-C), 136.31 (Ar-C), 135.56 (Ar-C), 129.56 (Ar-C), 129.01 (Ar-C), 128.58 (Ar-C), 127.70 (Ar-C), 127.28 (Ar-C),127.21 (Ar-C), 127.20 (Ar-C), 126.16 (Ar-C), 125.45 (Ar-C), 123.97 (Ar-C), 123.61 (Ar-C), 120.52 (Ar-C), 120.43 (Ar-C), 120.13 (Ar-C), 118.64 (Ar-C), 110.08 (Ar-C), 110.01 (Ar-C), 21.16 (Ar-$\underline{C}H_3$). HRMS(EI+): Cacld for $C_{31}H_{23}N^+(M)^+$: 410.52, Found: 410.1903

**5c. 9-([1,1'-Biphenyl]-4-yl)-3-(4-methoxyphenyl)-9*H*-Carbazole.**



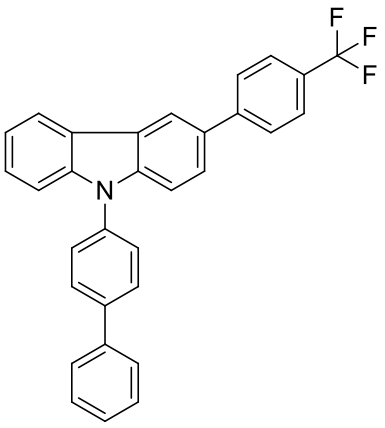
Colourless solid; M.P. 136-138$^{O}$C. Yield: 97%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.22 (d, *J* = 1.2Hz, 1H, Ar-H), 8.11 (d, *J* = 7.6Hz, 1H, Ar-H), 7.73 (d, *J* = 8.4Hz, 2H, Ar-H), 7.61-7.51 (m, 8H, Ar-H), 7.43-7.32 (m, 6H, Ar-H), 7.24 (t, *J* = 7.6 & 7.2 Hz, 1H, Ar-H), 6.92 (d, *J* = 8.8Hz, 1H, Ar-H), 3.78 (s, 3H, Ar-OC$\underline{H}_3$). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 158.73 (Ar-C), 141.32 (Ar-C), 140.33 (Ar-C), 140.30 (Ar-C), 140.04 (Ar-C), 136.91 (Ar-C), 134.67 (Ar-C), 133.32 (Ar-C), 129.01 (Ar-C), 128.57 (Ar-C), 128.35 (Ar-C), 127.70 (Ar-C), 127.27 (Ar-C), 127.18 (Ar-C), 126.15 (Ar-C), 125.31 (Ar-C), 123.99 (Ar-C), 123.61 (Ar-C), 120.42 (Ar-C), 120.11 (Ar-C), 118.40 (Ar-C), 114.30 (Ar-C), 110.09 (Ar-C), 110.01 (Ar-C), 55.44 (Ar-O$\underline{C}H_3$). Anal. calcd. for $C_{31}H_{23}N^{+}$ $[M]^{+}$: C, 87.50; H, 5.45; N, 3.29%; Found: C,87.52; H, 5.43; N, 3.31 %.

**5d. 9-([1,1'-Biphenyl]-4-yl)-3-(4-chlorophenyl)-9*H*-Carbazole.**



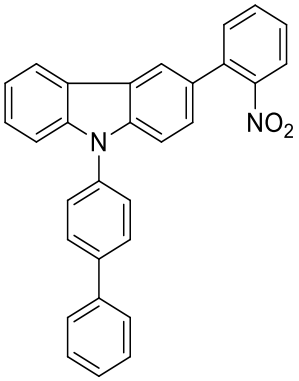

Colourless solid; M.P. 144-146$^{O}$C. Yield: 85%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.31 (s, 1H, Ar-H), 8.19 (d, *J* = 6.8Hz, 1H, Ar-H), 7.82 (d, *J* = 7.6Hz, 2H, Ar-H), 7.69-7.62 (m, 6H, Ar-H), 7.50-7.42 (m, 8H, Ar-H), 7.33-7.23 (m, 2H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.39 (Ar-C), 140.49 (Ar-C), 140.24 (Ar-C), 136.72 (Ar-C), 132.65 (Ar-C), 132.28 (Ar-C), 129.02 (Ar-C), 128.93 (Ar-C), 128.61 (Ar-C), 128.55 (Ar-C), 127.75 (Ar-C), 127.28 (Ar-C), 127.18 (Ar-C), 126.36 (Ar-C), 125.30 (Ar-C), 124.05 (Ar-C), 123.46 (Ar-C), 120.44 (Ar-C), 120.29 (Ar-C), 118.74 (Ar-C), 110.25 (Ar-C), 110.10 (Ar-C). Anal. calcd. for $C_{30}H_{20}N^{+}$ $[M]^{+}$: C, 83.81; H, 4.69; N, 3.26%; Found: C, 83.79; H, 4.71; N, 3.24 %.

**5e. 9-[(1,1'-Biphenyl]-4-yl)-3-(4-[trifloromethyl]-phenyl-9*H*-Carbazole**




Colourless solid; M.P. 165-167$^0$C. Yield: 91%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.36 (d, *J* = 1.2 Hz, 1H, Ar-H), 8.21 (d, *J* = 7.6Hz, 1H, Ar-H), 7.83-7.80 (m, 4H, Ar-H), 7.72-7.62 (m, 7H, Ar-H), 7.54-7.39 (m, 6H, Ar-H), 7.35-7.31 (m, 1H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 145.00 (Ar-C), 141.46 (Ar-C), 140.82 (Ar-C), 140.61 (Ar-C), 140.21 (Ar-C), 136.62 (Ar-C), 131.94 (Ar-C), 129.04 (Ar-C), 128.64 (Ar-C), 127.78 (Ar-C), 127.48 (Ar-C), 127.30 (Ar-C), 127.19 (Ar-C), 126.49 (Ar-C), 125.77 (Ar-C), 125.74 (Ar-C), 125.46 (Ar-C), 124.12 (Ar-C), 123.41 (Ar-C), 123.17 (Ar-C), 120.47 (Ar-C), 120.41 (Ar-C), 119.12 (Ar-C), 110.37 (Ar-C), 110.17 (Ar-C). Anal. calcd. for $C_{31}H_{20}N^+$ $[M]^+$: C, 80.33; H, 4.35; N, 3.02%; Found: C, 80.35; H, 4.37; N, 3.04 %.

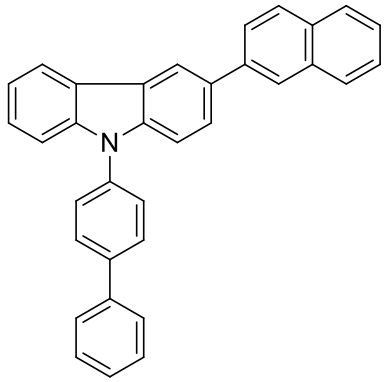
**5f. 9-([1,1'-Biphenyl]-4-yl)-3-(2-nitrophenyl)-9*H*-Carbazole**




Yellow Colour solid; M.P. 152-153$^0$C. Yield: 81%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.58 (t, *J* = 2, & 2Hz, 1H, Ar-H), 8.39 (d, *J* = 1.6Hz, 1H, Ar-H), 8.23-8.16 (m, 2H, Ar-H), 8.04 (d, *J* = 8Hz, 1H, Ar-H), 7.85 (d, *J* = 8.4Hz, 2H, Ar-H), 7.71-7.60 (m, 6H, Ar-H), 7.56-7.40 (m, 6H, Ar-H). 7.36-7.33 (m, 1H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 148.85 (Ar-C), 143.67 (Ar-C), 141.50 (Ar-C), 140.94 (Ar-C), 140.68 (Ar-C), 140.18 (Ar-C), 136.52 (Ar-C), 133.15 (Ar-C), 130.79 (Ar-C), 129.69 (Ar-C), 129.04 (Ar-C), 128.67 (Ar-C), 127.80 (Ar-C), 127.30 (Ar-C), 127.19 (Ar-C), 126.62 (Ar-C), 125.24 (Ar-C), 124.23 (Ar-C), 123.30 (Ar-C), 121.95 (Ar-C), 121.29 (Ar-C), 120.52 (Ar-C),

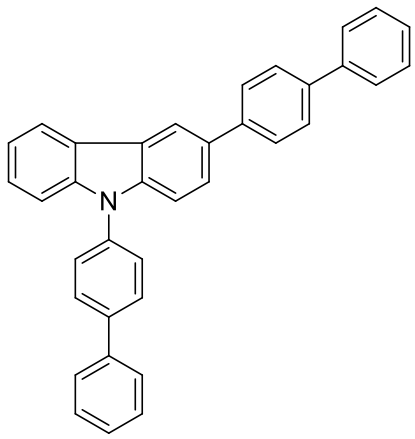
119.07 (Ar-C), 110.53(Ar-C), 110.21 (Ar-C). Anal. calcd. for $C_{30}H_{20}N_2^+$ $[M]^+$: C, 81.80; H, 4.58; N, 7.26%; Found: C, 81.78; H, 4.60; N, 7.24 %.

**5g. 9-([1,1'-Biphenyl]-4-yl)-3-(napthalen-2-yl)-9*H*-Carbazole**



Colourless solid; M.P. 146-148$^0$C. Yield: 90%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.19 (s, 1H, Ar-H), 8.08 (d, *J* = 7.6Hz, 1H, Ar-H), 7.96 (d, *J* = 8.4Hz, 1H, Ar-H), 7.87-7.76 (m, 4H, Ar-H), 7.64 (d, *J* = 8Hz, 3H, Ar-H), 7.50-7.33 (m, 12H, Ar-H), 7.25 (t, *J* = 7.2, &7.2 Hz, 1H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.33 (Ar-C), 140.93 (Ar-C), 140.44 (Ar-C), 140.30 (Ar-C), 140.22 (Ar-C), 136.90 (Ar-C), 133.93 (Ar-C), 132.72 (Ar-C), 132.23 (Ar-C), 129.01 (Ar-C), 128.62 (Ar-C), 128.29 (Ar-C), 127.71 (Ar-C), 127.39 (Ar-C), 127.35 (Ar-C), 127.20 (Ar-C), 126.40 (Ar-C), 126.21 (Ar-C), 125.98 (Ar-C), 125.73 (Ar-C), 125.47 (Ar-C), 123.52 (Ar-C), 123.48 (Ar-C), 121.77 (Ar-C), 120.46 (Ar-C), 120.19 (Ar-C), 110.03 (Ar-C), 109.58 (Ar-C). Anal. calcd. for $C_{34}H_{23}N^+$ $[M]^+$: C, 91.65; H, 5.20; N, 3.14%; Found: C, 91.67; H, 5.22; N,3.13 %.

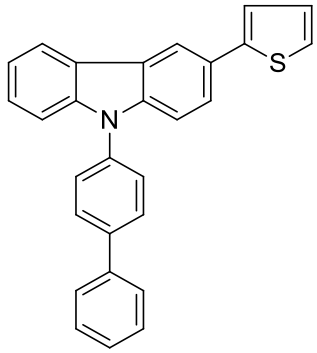
**5h. 3,9-Di([1,1'-biphenyl]-4-yl)-9*H*-Carbazole.**



Colourless solid; M.P 150-152$^0$C. Yield: 86%; $^1$HNMR (400MHz, $CDCl_3$: δ (ppm): 8.41 (d, *J* = 1.6Hz, 1H, Ar-H), 8.22 (d, *J* = 8Hz, 1H, Ar-H), 7.84- 7.79 (m, 4H, Ar-H), 7.72- 7.64 (m, 9H, Ar-H),

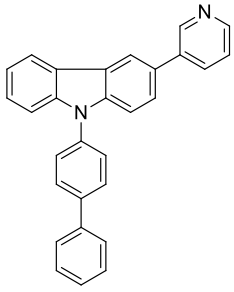
7.55-7.30 (m, 10H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.37 (Ar-C), 140.94 (Ar-C), 140.90 (Ar-C), 140.44 (Ar-C), 140.28 (Ar-C), 139.45 (Ar-C), 136.82 (Ar-C), 133.02 (Ar-C), 129.01 (Ar-C), 128.85 (Ar-C), 128.60 (Ar-C), 127.71 (Ar-C), 127.66 (Ar-C), 127.57 (Ar-C), 127.30 (Ar-C), 127.19 (Ar-C), 127.07 (Ar-C), 126.25 (Ar-C), 125.44 (Ar-C), 124.06 (Ar-C), 123.59 (Ar-C), 120.45 (Ar-C), 120.22 (Ar-C), 118.76 (Ar-C), 110.20 (Ar-C), 110.06 (Ar-C). Anal. calcd. for $C_{36}H_{25}N^+$ $[M]^+$: C, 91.69; H, 5.34; N, 2.97%; Found: C, 91.67; H, 5.36; N, 2.99 %.

**5i. 9-([1,1'-Biphenyl]-4-yl)-3-(thiophen-2-yl)-9*H*-Carbazole**



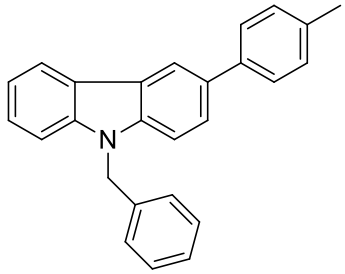

Yellow colour solid; M.P. 104-105$^O$C. Yield: 91%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.48 (d, *J* = 1.2Hz, 1H, Ar-H), 8.27 (d, *J* = 7.6Hz, 1H, Ar-H), 7.87-7.80 (m, 4H, Ar-H), 7.73-7.69 (m, 4H, Ar-H), 7.60-7.42 (m, 8H, Ar-H), 7.36 -7.32(t, *J* = 7.6, & 6.8 Hz, 1H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 143.16 (Ar-C), 141.34 (Ar-C), 140.39 (Ar-C), 140.28 (Ar-C),140.19 (Ar-C), 136.82 (Ar-C),129.03 (Ar-C), 128.58 (Ar-C), 128.44 (Ar-C), 127.73 (Ar-C),127.27 (Ar-C), 127.20 (Ar-C), 126.79 (Ar-C), 126.26 (Ar-C), 126.15 (Ar-C), 125.03 (Ar-C), 123.92 (Ar-C), 123.55 (Ar-C), 120.45 (Ar-C), 120.20 (Ar-C), 119.18 (Ar-C), 118.18 (Ar-C), 110.15 (Ar-C), 110.07 (Ar-C). Anal. calcd. for $C_{28}H_{19}N^+$ $[M]^+$: C, 83.76; H, 4.77; N, 3.49%; Found: C,83.74; H, 4.79; N, 3.47 %.

**5j. 9-([1,1'-Biphenyl]-4-yl)-3-(pyridin-3-yl)-9*H*-Carbazole**



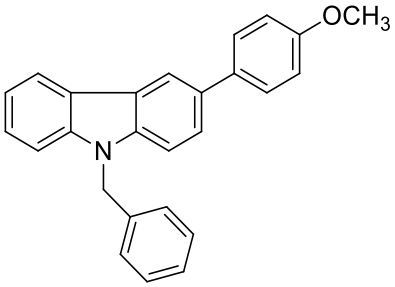
Yellow colour solid; M.P. 132-134$^{O}$C. Yield: 70%; $^{1}$H NMR (400MHz, $CDCl_3$): δ(ppm): 8.48 (d, *J* = 1.2Hz, 1H, Ar-H), 8.27 (d, *J* = 7.6Hz, 1H, Ar-H), 7.87-7.80 (m, 4H, Ar-H), 7.73-7.69 (m, 5H, Ar-H), 7.60-7.42 (m, 8H, Ar-H), 7.36 (t, *J* = 7.6, & 6.8 Hz, 1H, Ar-H). Anal. calcd. for $C_{29}H_{20}N_2^+$ $[M]^+$ : C, 87.85; H, 5.08; N, 7.07%; Found: C, 87.87; H, 5.06 ; N,7.04 %

**5k. 9-Benzyl-3-(p-tolyl)-9H-Carbazole**




Colourless solid; M.P. 105-107$^{O}$C. Yield: 97%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.31 (d, *J* = 1.6Hz, 1H, Ar-H), 8.17 (d, *J* = 8Hz, 1H, Ar-H), 7.66 (d(d), *J* = 2, & 2Hz, 1H, Ar-H), 7.60 (d, *J* = 8Hz, 2H, Ar-H), 7.45-7.35 (m, 3H, Ar-H), 7.28-7.24 (m, 6H, Ar-H), 7.17-7.15 (m, 2H, Ar-H), 5.52 (s, 2H, Ar-C$\underline{H}_2$-) 2.41 (s, 3H, Ar-C$\underline{H}_3$). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.15 (Ar-C), 140.07 (Ar-C), 139.24 (Ar-C), 137.18 (Ar-C), 136.16 (Ar-C), 132.80 (Ar-C), 129.54 (Ar-C), 128.85 (Ar-C), 127.54 (Ar-C), 127.19 (Ar-C), 126.47 (Ar-C), 126.04 (Ar-C), 125.36 (Ar-C), 123.57 (Ar-C), 123.24 (Ar-C), 120.50 (Ar-C), 119.36 (Ar-C), 118.74 (Ar-C), 109.12 (Ar-C), 109.08 (Ar-C), 46.72 (Ar-$\underline{C}H_2$-), 21.14 (Ar-$\underline{C}H_3$). HRMS(EI+): Cacld for $C_{26}H_{21}N$ $[M]^+$: 348.45, Found: 348.1726

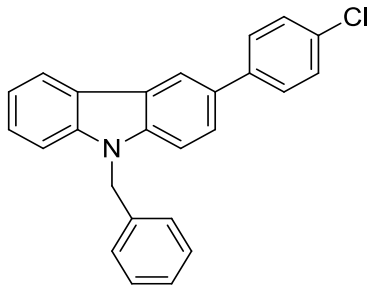
**5l. 9-Benzyl-3-(4-methoxyphenyl)-9*H*-Carbazole.**




Colourless solid; M.P. 127-129$^{O}$C. Yield: 96%; $^{1}$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.28 (d, *J* = 1.2Hz, 1H, Ar-H), 8.17 (d, *J* = 6.4Hz, 1H, Ar-H), 7.63-7.60 (m, 3H, Ar-H), 7.44-7.35 (m, 4H, Ar-H), 7.27-7.22 (m, 4H, Ar-H), 7.16 (d, *J* = 5.6Hz, 1H, Ar-H), 7.01 (d, *J* = 7.2Hz, 2H, Ar-H), 5.51(s, 2H,Ar-C$\underline{H}_2$-), 3.86 (s, 3H, Ar-OC$\underline{H}_3$). $^{13}$C NMR(100MHz, $CDCl_3$): δ (ppm): 158.64 (Ar-C), 141.14 (Ar-C), 139.88 (Ar-C), 137.18 (Ar-C), 134.77 (Ar-C), 132.53 (Ar-C), 128.84 (Ar-C), 128.31 (Ar-C), 127.52 (Ar-C), 126.46 (Ar-C), 126.03 (Ar-C),125.21 (Ar-C), 123.57 (Ar-C),123.20 (Ar-C), 120.48

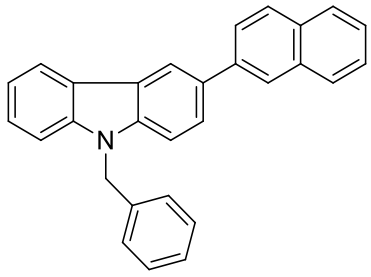
(Ar-C), 119.32 (Ar-C), 118.50 (Ar-C), 114.27 (Ar-C), 109.12 (Ar-C), 109.07 (Ar-C), 55.42 (Ar-$\underline{C}H_2$-), 46.70 (Ar-O$\underline{C}H_3$). Anal. calcd. for $C_{26}H_{21}N^+$ $[M]^+$: C, 85.92; H, 5.82; N, 3.85%; Found: C, 85.94; H, 5.84; N, 3.87 %

**5m. 9-([1,1'-Biphenyl]-4-yl)-3-(4-chlorophenyl)-9*H*-Carbazole.**




Colourless solid; M.P. 144-146$^O$C. Yield: 91%; $^1$H NMR (400MHz, $CDCl_3$): δ (ppm): 8.31 (s, 1H, Ar-H), 8.20 (d, *J* = 6.8Hz, 1H, Ar-H), 7.83 (d, *J* = 7.6Hz, 2H, Ar-H), 7.70-7.60 (m, 6H, Ar-H), 7.50-7.43 (m, 8H, Ar-H), 7.34 (d, *J* = 6.8Hz, 3H, Ar-H). $^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm): 141.39 (Ar-C), 140.49 (Ar-C), 140.24 (Ar-C), 136.73 (Ar-C), 132.65 (Ar-C), 132.28 (Ar-C), 129.03 (Ar-C), 128.94 (Ar-C), 128.62 (Ar-C), 128.56 (Ar-C), 127.75 (Ar-C), 127.29 (Ar-C), 127.19 (Ar-C), 126.37 (Ar-C), 125.30 (Ar-C), 124.06 (Ar-C), 123.47 (Ar-C), 120.45 (Ar-C), 120.29 (Ar-C), 118.75 (Ar-C), 110.25 (Ar-C), 110.11 (Ar-C). Anal. calcd. for $C_{25}H_{18}N^+$ $[M]^+$: C, 81.62; H, 4.93; N, 3.81%; Found: C, 81.64; H, 4.91; N, 3.83 %.

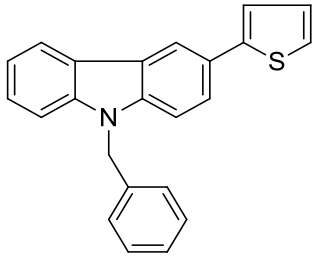
**5n. 9-Benzyl-3-(napthalen-2-yl)-9*H*-Carbazole.**




Colourless solid; M.P. 125-127$^0$C. Yield: 97%; $^1$HNMR (400MHz, $CDCl_3$): δ (ppm), 8.46 (d, *J* = 1.2Hz, 1H, Ar-H), 8.20 (m, *J* = 6Hz, 1H, Ar-H), 8.125-8.123 (m, 1H, Ar-H), 7.93-7.85 (m, 4H, Ar-H), 7.79 (d(d), *J* = 1.6 & 1.6Hz, 1H, Ar-H), 7.51-7.42 (m, 4H, Ar-H), 7.38 (d, *J* = 6.8Hz, 1H, Ar-H), 7.29-7.22 (m, 4H, Ar-H), 7.16-7.15 (m, 2H, Ar-H), 5.52 (s, 2H, Ar-C$\underline{H}_2$).$^{13}$C NMR (100MHz, $CDCl_3$): δ (ppm), 141.20 (Ar-C), 140.28 (Ar-C), 139.46 (Ar-C), 137.12 (Ar-C), 133.94 (Ar-C),

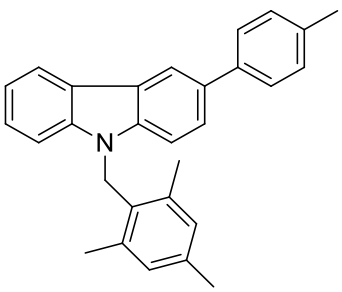
132.65 (Ar-C), 132.31 (Ar-C), 128.87 (Ar-C), 128.40 (Ar-C), 128.13 (Ar-C), 127.71 (Ar-C), 127.58 (Ar-C),126.48 (Ar-C), 126.26 (Ar-C), 126.15 (Ar-C), 125.72 (Ar-C), 125.60 (Ar-C),125.56 (Ar-C), 123.71 (Ar-C), 123.24 (Ar-C), 120.57 (Ar-C), 119.48 (Ar-C), 119.26 (Ar-C), 109.30 (Ar-C), 109.15 (Ar-C), 46.74 (Ar-$\underline{C}H_2$). Anal. calcd. for $C_{29}H_{21}N^+$ $[M]^+$: C, 90.83; H, 5.52; N, 3.65%; Found: C, 90.81; H, 5.54; N, 3.67%.

**5o. 9-Benzyl-3(thiophen-2-yl)-9*H*-Carbazole.**




Yellow colour solid; M.P. 101-103$^O$C. Yield: 90%; $^1$H NMR (400MHz, $CDCl_3$): $\delta$ (ppm), 8.33 (s, 1H, Ar-H), 8.16 (d, *J* = 6.4Hz, 1H, Ar-H), 7.68 (d(d), *J* = 1.6 ,& 1.6Hz, 1H, Ar-H), 7.50-7.49 (m, 1H, Ar-H), 7.468-7.460 (m, 1H, Ar-H), 7.44-7.40 (m, 2H, Ar-H), 7.38-7.36 ( m, 2H, Ar-H), 7.28-7.26 (m, 3H, Ar-H), 7.24-7.23 (m, 1H, Ar-H), 7.16-7.14 (m, 2H, Ar-$\underline{H}$ ), 5.53 (s, 2H, Ar-C$\underline{H}_2$). $^{13}$C NMR (100MHz, $CDCl_3$): $\delta$ (ppm): 143.24 (Ar-C), 141.13 (Ar-C), 140.02 (Ar-C), 137.08 (Ar-C), 128.83 (Ar-C), 127.69 (Ar-C), 127.53 (Ar-C), 126.75 (Ar-C), 126.43 (Ar-C) 126.10 (Ar-C), 126.04 (Ar-C), 124.91 (Ar-C), 123.46 (Ar-C), 123.12 (Ar-C), 120.48 (Ar-C), 119.39 (Ar-C), 118.96 (Ar-C), 118.27 (Ar-C), 109.15 (Ar-C), 109.09 (Ar-C), 46.86 (Ar-$\underline{C}H_2$). Anal. calcd. for $C_{23}H_{17}N^+$ $[M]^+$: C, 81.38; H, 5.05; N, 4.13%; Found: C, 81.36; H, 5.03; N, 4.15 %.

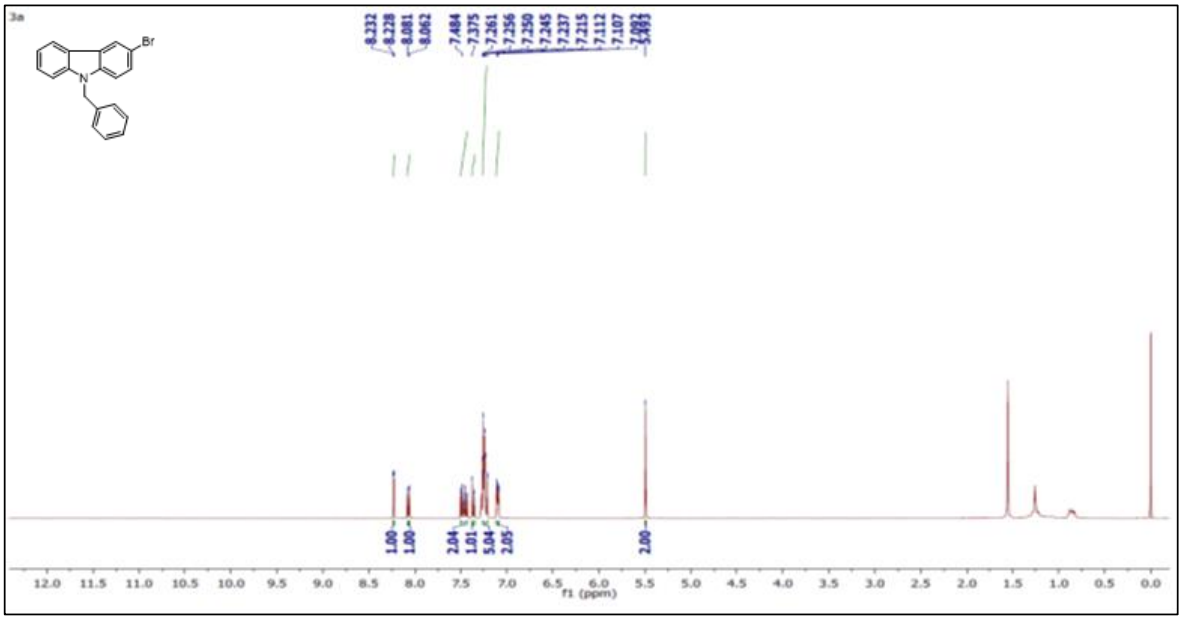
**5p. 3-(p-tolyl)-9-(2,4,6-trimethylbenzyl)-9*H*-Carbazole.**

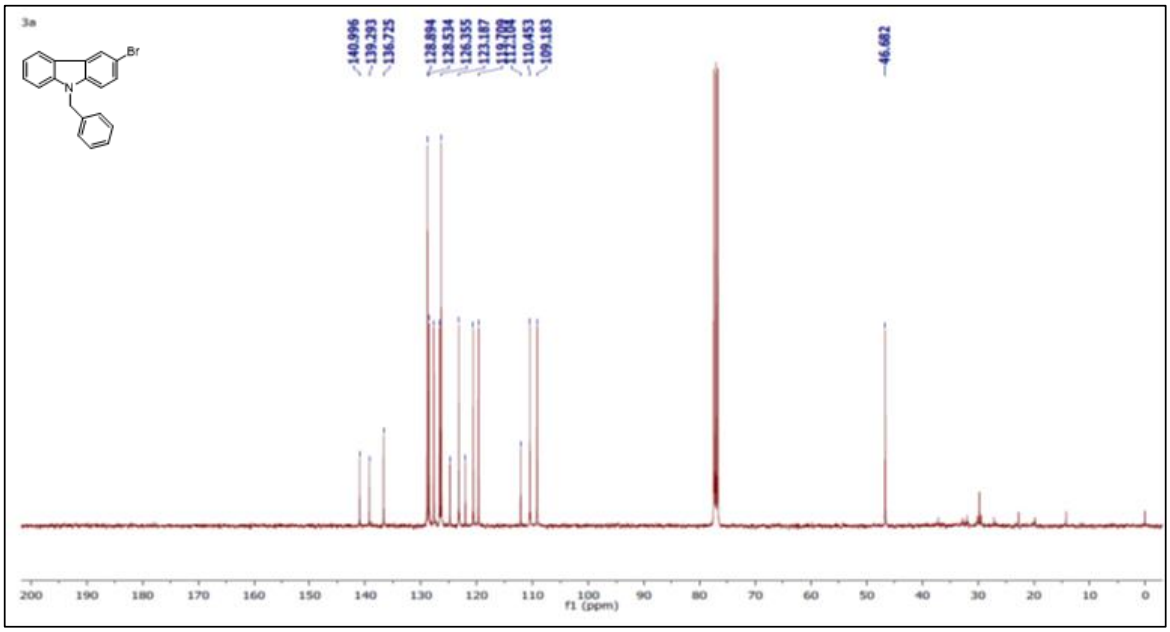



Colourless solid; M.P. 153-155$^O$C. Yield: 95%; $^1$H NMR (400MHz, $CDCl_3$): $\delta$ (ppm): 8.26 (d, *J*= 1.2Hz, 1H, Ar-H), 8.12 (d, *J* = 6.4Hz, 1H, Ar-H), 7.58-7.54 (m, 3H, Ar-H), 7.36-7.32 (m, 1H, Ar-

H), 7.26-7.12 (m, 5H, Ar-H), 6.89 (s, 2H, Ar-H), 5.43 (s, 2H,Ar-C$\underline{H}_2$-), 2.39 (s, 3H, Ar-C$\underline{H}_3$-), 2.29 (s, 3H, Ar-C$\underline{H}_3$), 2.18 (s, 6H, Ar-(C$\underline{H}_3$)$_2$). $^{13}$C NMR (100MHz,$CDCl_3$): δ (ppm): 141.26 (Ar-C), 140.14 (Ar-C), 139.20 (Ar-C), 137.64 (Ar-C), 137.59 (Ar-C), 136.05 (Ar-C), 132.29 (Ar-C), 129.78 (Ar-C), 129.49 (Ar-C), 127.08 (Ar-C), 125.81 (Ar-C), 125.10 (Ar-C), 123.60 (Ar-C), 123.24 (Ar-C),120.26 (Ar-C), 119.01 (Ar-C), 118.42 (Ar-C), 109.65 (Ar-C), 109.53 (Ar-C), 43.28 (Ar-$\underline{C}H_2$-), 21.12 (Ar-$\underline{C}H_3$), 21.02 (Ar-$\underline{C}H_3$), 20.50 (Ar-$\underline{C}H_3$). Anal. calcd. for $C_{29}H_{27}N^+$ [M]$^+$: C, 89.42; H, 6.99; N, 3.60%; Found: C, 89.44; H, 6.97; N, 3.62 %.

**XIII. Copies of ($^1$H&$^{13}$C) NMR and HRMS Spectra**

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Br
N
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139.293
136.725
128.894
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126.355
123.187
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109.183
46.682
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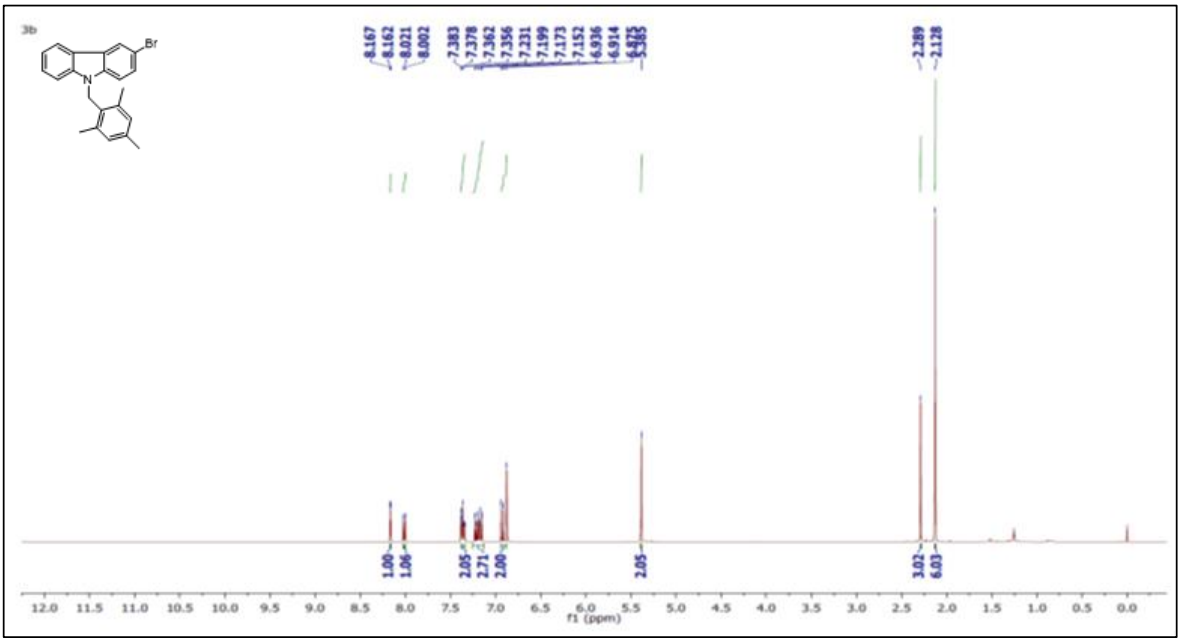
f1 (ppm)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Br
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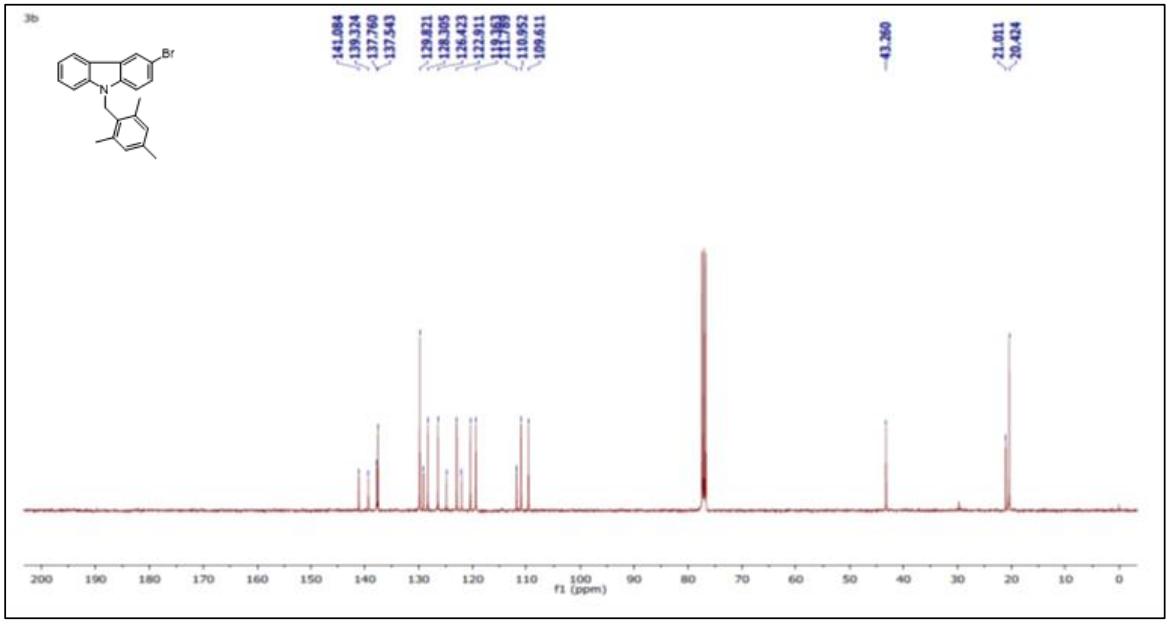
8.021
8.002
7.383
7.378
7.362
7.356
7.231
7.199
7.173
7.152
6.936
6.914
5.385
2.289
2.128
1.00
1.06
2.05
2.71
2.00
2.05
3.02
6.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Br
N
141.084
139.324
137.760
137.543
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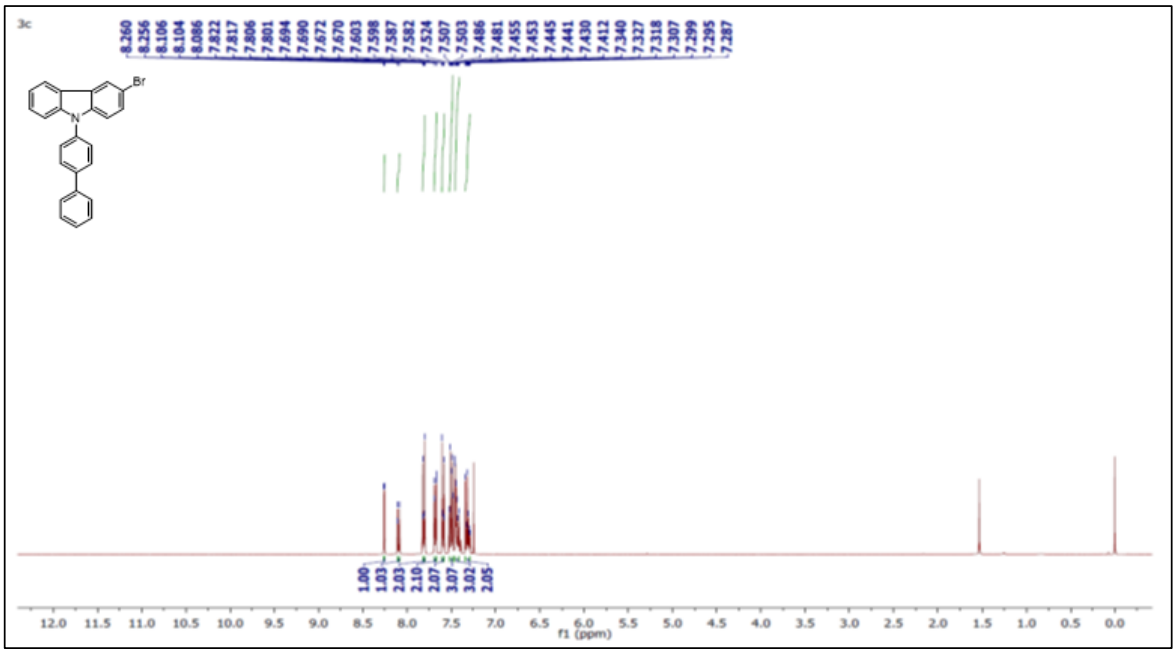
128.305
126.423
122.911
110.952
109.611
43.360
21.011
20.424
f1 (ppm)


3c
Br
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8.356
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8.104
8.086
7.822
7.817
7.806
7.801
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7.690
7.672
7.670
7.603
7.598
7.587
7.582
7.524
7.507
7.503
7.486
7.481
7.455
7.453
7.445
7.441
7.430
7.412
7.340
7.327
7.318
7.307
7.299
7.295
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1.03
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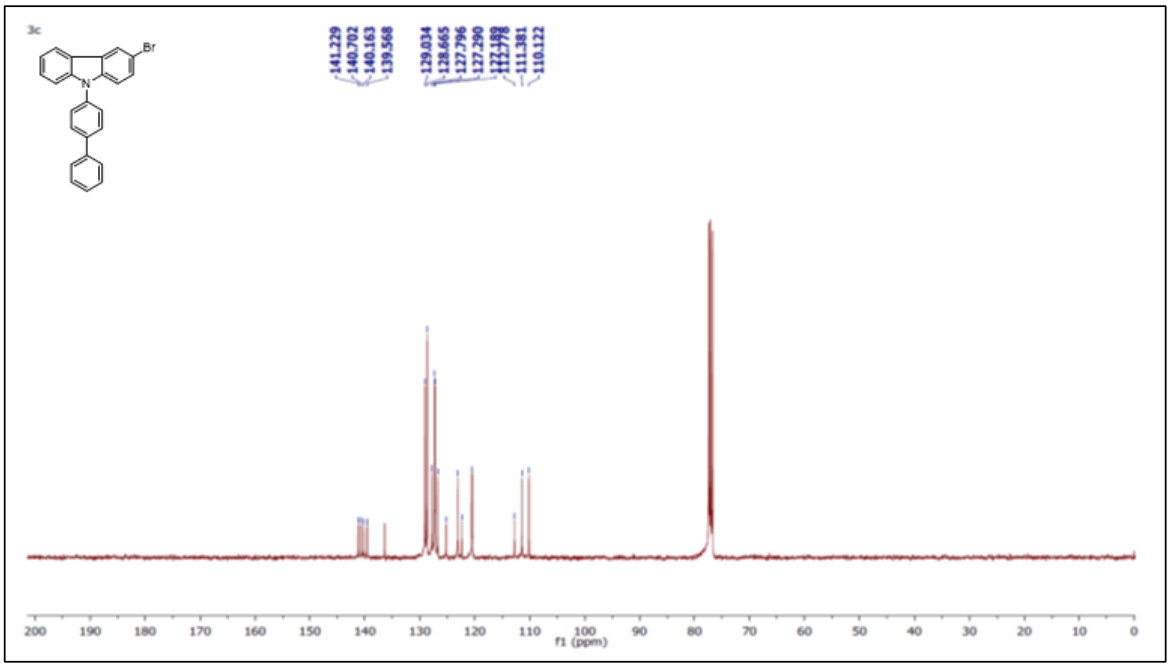
2.07
3.07
3.02
2.05
f1 (ppm)


3c
Br
N
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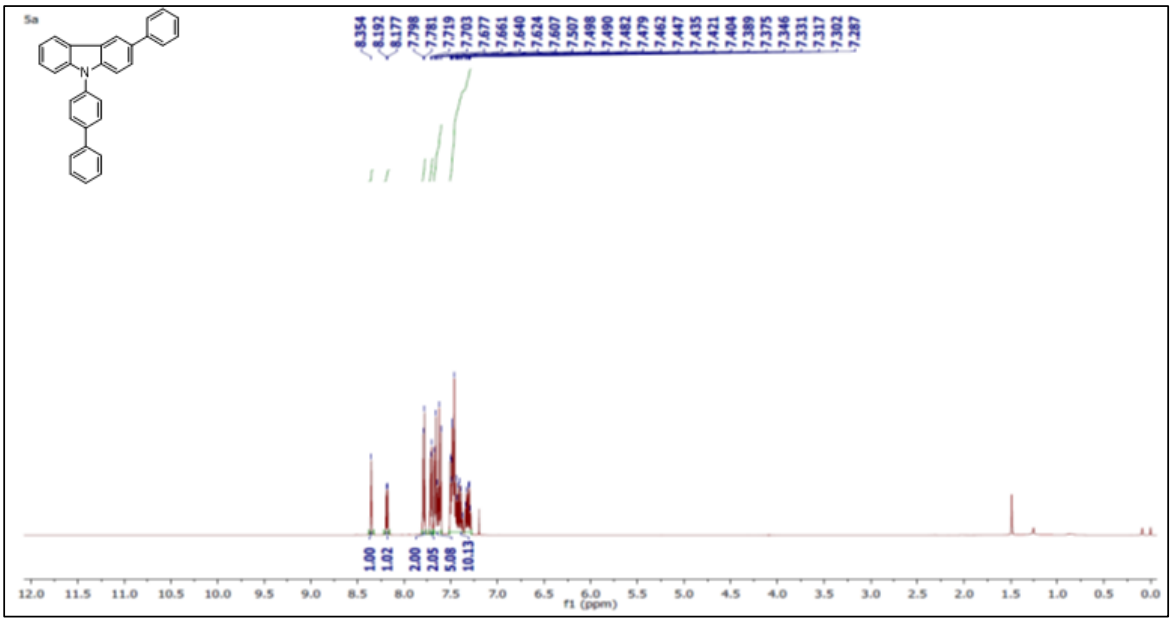
140.163
139.568
129.034
128.665
127.796
127.290
111.381
110.122
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5a
N
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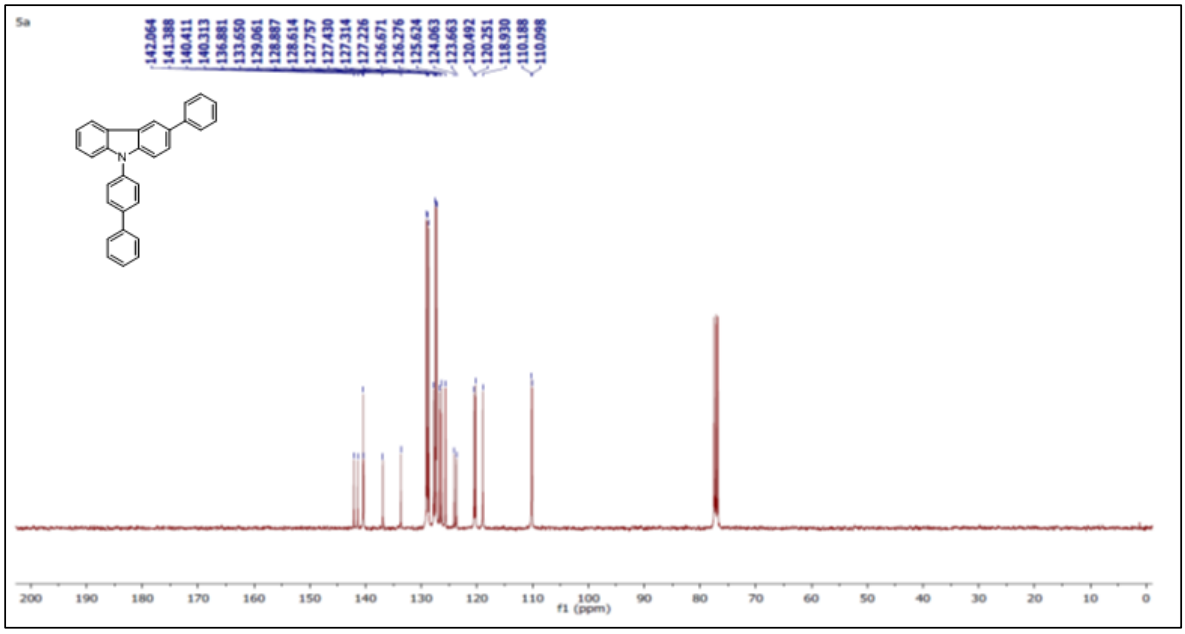
8.177
7.798
7.781
7.719
7.703
7.677
7.661
7.640
7.624
7.607
7.507
7.498
7.490
7.482
7.479
7.462
7.447
7.435
7.421
7.404
7.389
7.375
7.346
7.331
7.317
7.302
7.287
1.00
1.02
2.00
2.05
5.08
10.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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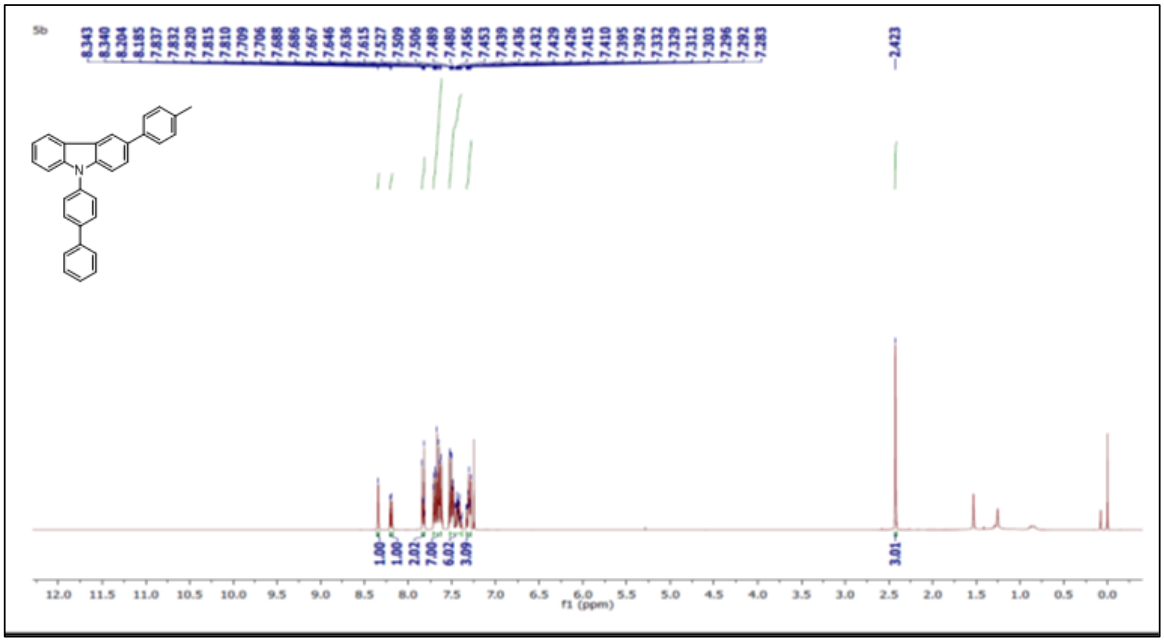
142.064
141.388
140.411
140.313
136.881
133.650
129.061
128.887
128.614
127.757
127.430
127.314
127.226
126.671
126.276
125.624
124.063
123.663
120.492
120.251
118.930
110.188
110.098
f1 (ppm)


5b
8.343
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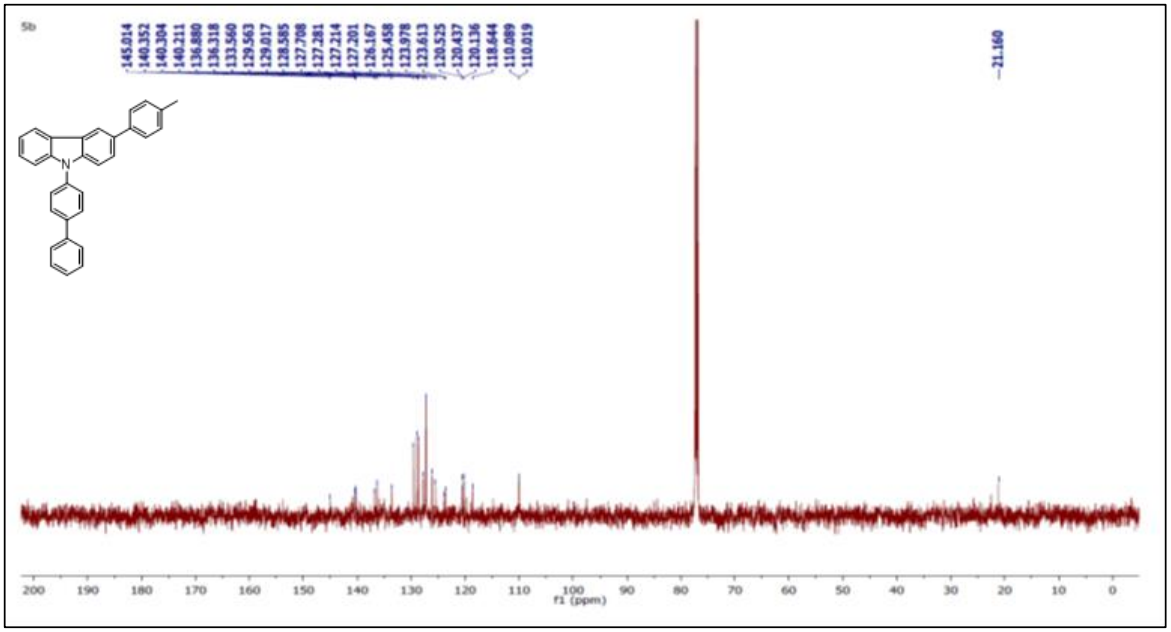
8.204
8.185
7.837
7.832
7.820
7.815
7.810
7.709
7.706
7.688
7.686
7.667
7.646
7.636
7.615
7.527
7.509
7.506
7.489
7.480
7.456
7.453
7.439
7.436
7.432
7.429
7.426
7.415
7.410
7.395
7.392
7.332
7.329
7.312
7.303
7.296
7.292
7.283
2.423
1.00
1.00
2.02
7.00
6.02
3.09
3.01
f1 (ppm)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145.014
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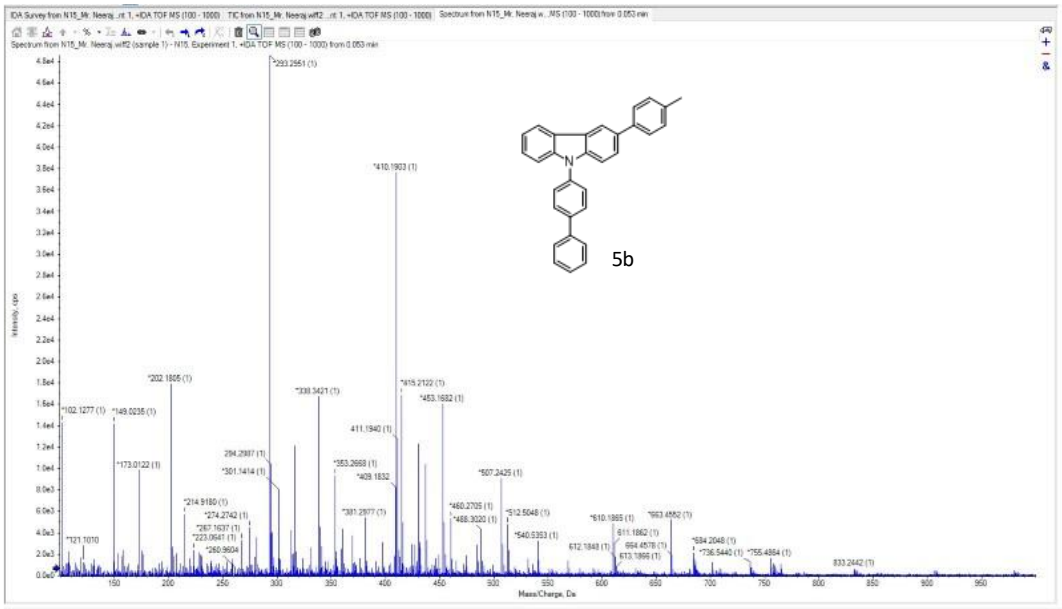
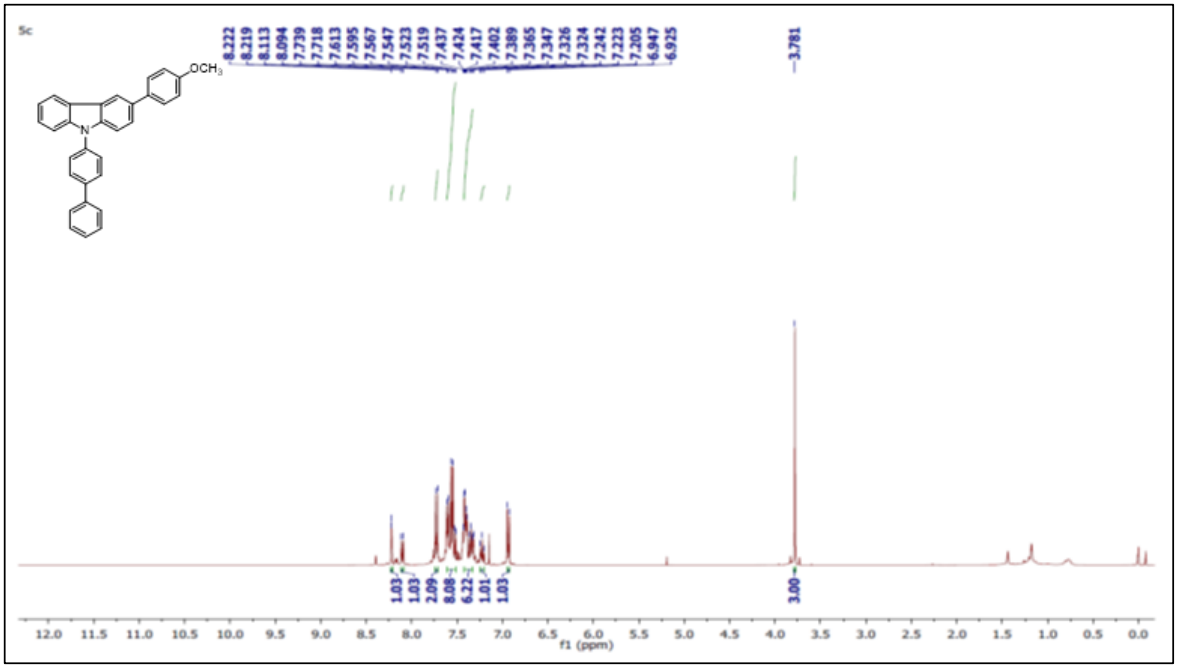
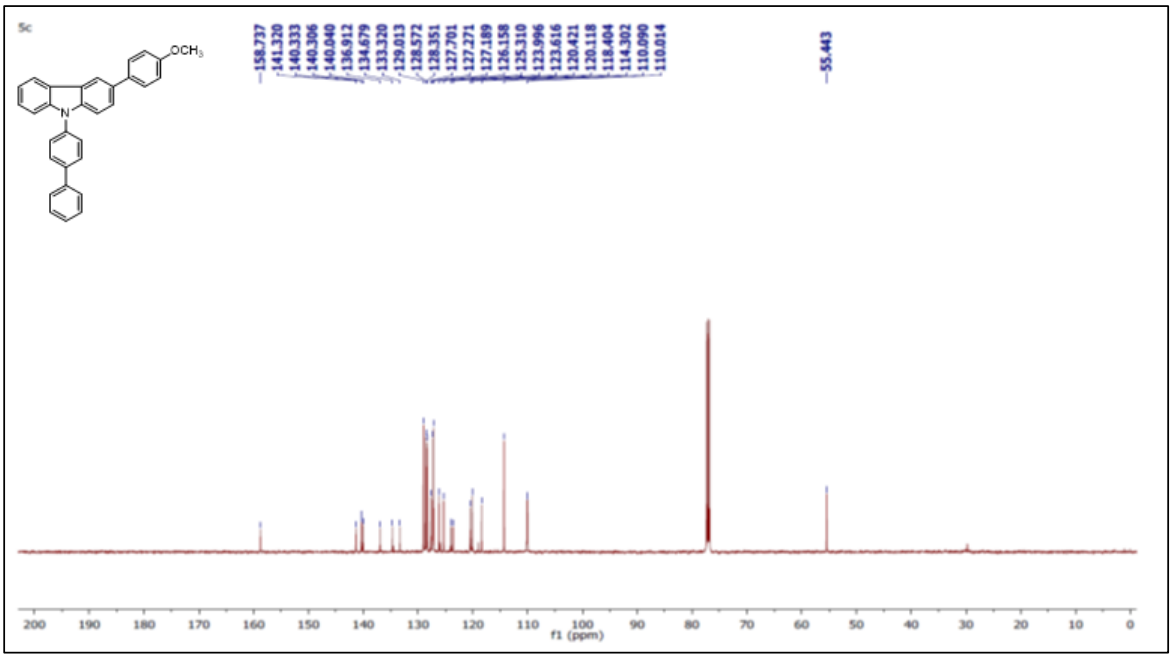
140.304
140.211
136.880
136.318
133.560
129.563
129.017
128.585
127.708
127.281
127.214
127.201
126.167
125.458
123.978
123.613
120.525
120.437
120.136
118.644
110.089
110.019
21.160
f1 (ppm)


5b
Mass/Charge, Da


5c
OCH3
8.222
8.219
8.113
8.094
7.739
7.718
7.613
7.595
7.567
7.547
7.523
7.519
7.437
7.424
7.417
7.402
7.389
7.365
7.347
7.326
7.324
7.242
7.223
7.205
6.947
6.925
3.781
1.03
1.03
2.09
8.08
6.22
1.01
1.03
3.00
f1 (ppm)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140.333
140.306
140.040
136.912
134.679
133.320
129.013
128.572
128.351
127.701
127.271
127.189
126.158
125.310
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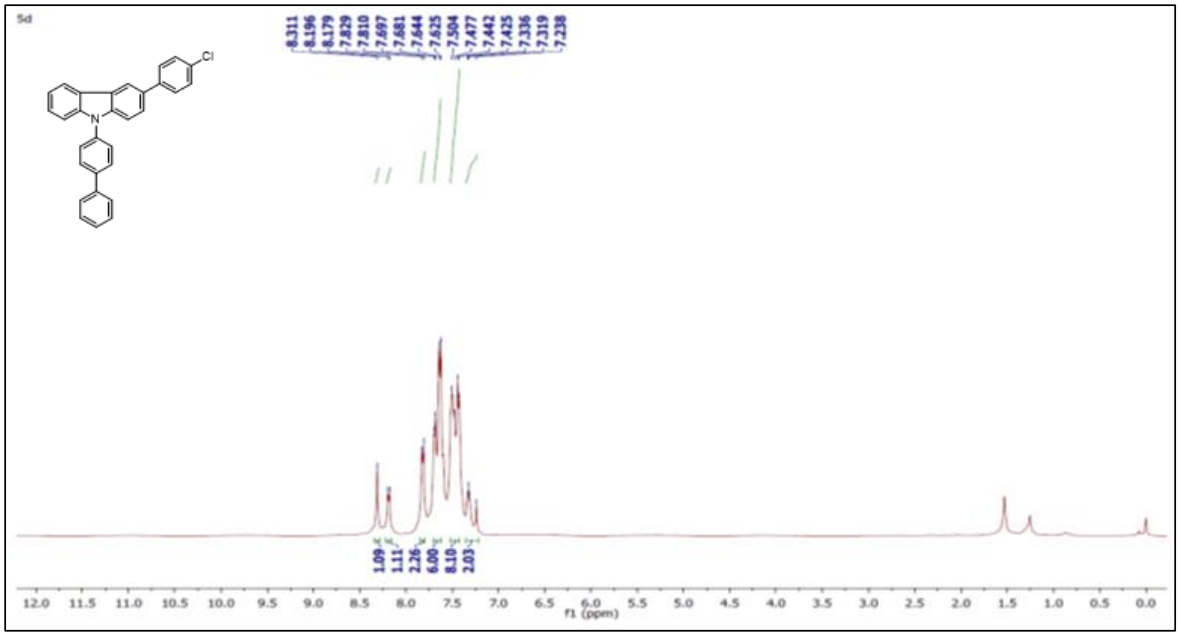
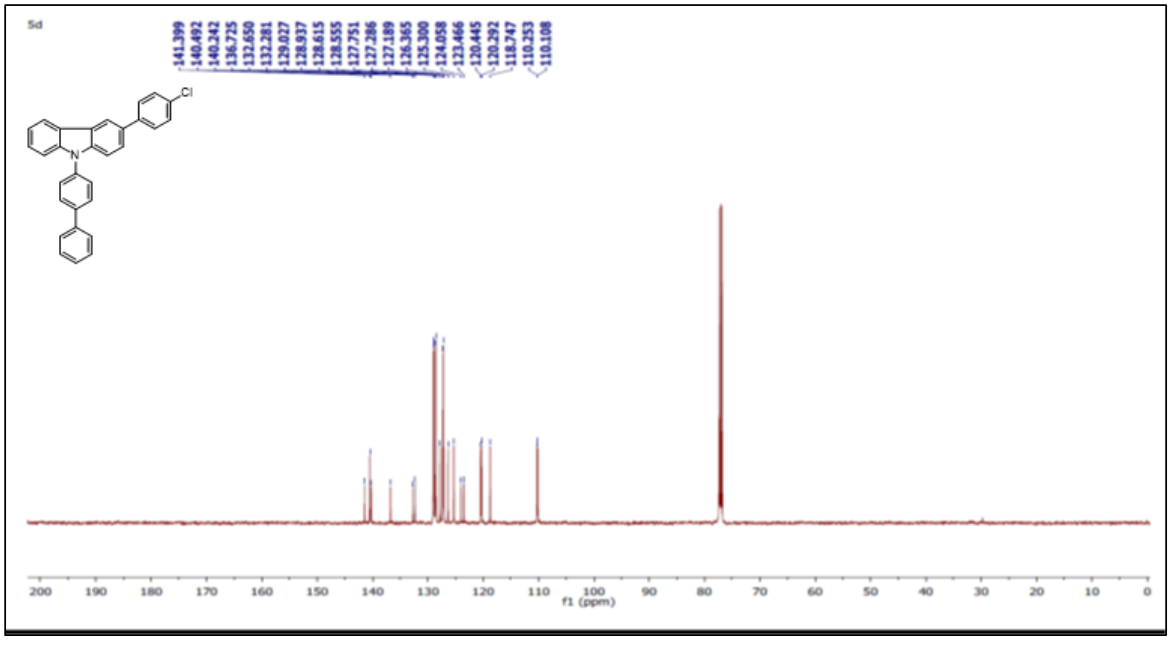
123.616
120.421
120.118
118.404
114.302
110.090
110.014
55.443
f1 (ppm)


5d
8.311
8.196
8.179
7.829
7.810
7.697
7.681
7.644
7.625
7.504
7.477
7.442
7.425
7.336
7.319
7.238
1.09
1.11
2.26
6.00
8.10
2.03
f1 (ppm)


5d
141.399
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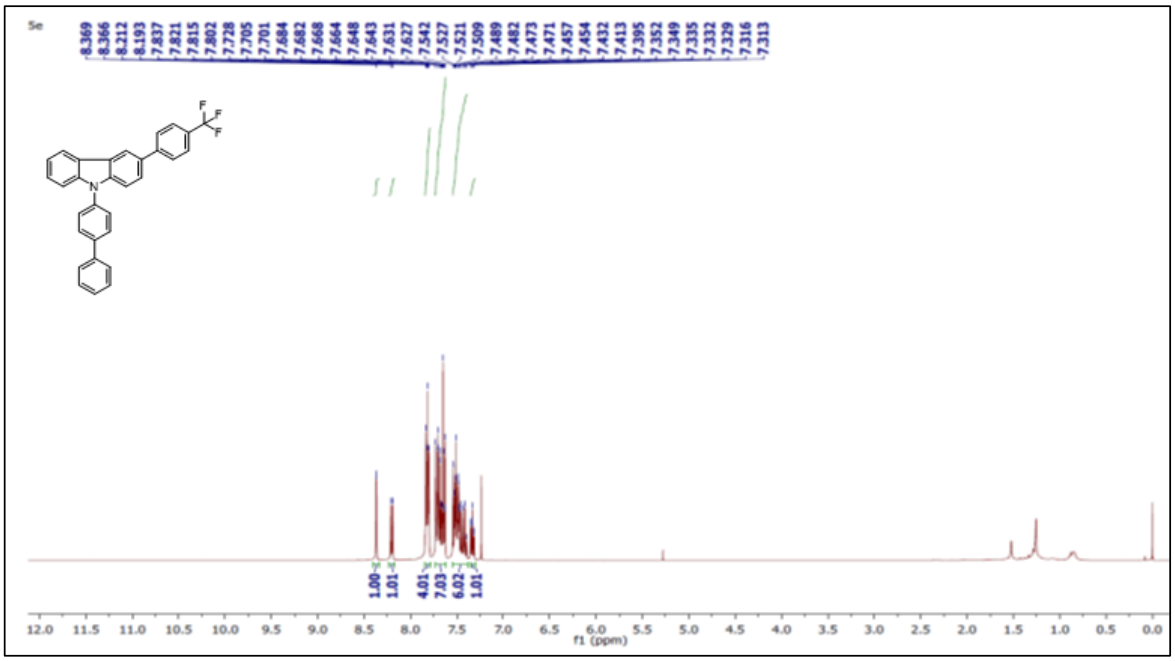
132.281
129.027
128.937
128.615
128.555
127.751
127.286
127.189
126.365
125.300
124.058
123.466
120.445
120.292
118.747
110.253
110.108
f1 (ppm)


5e
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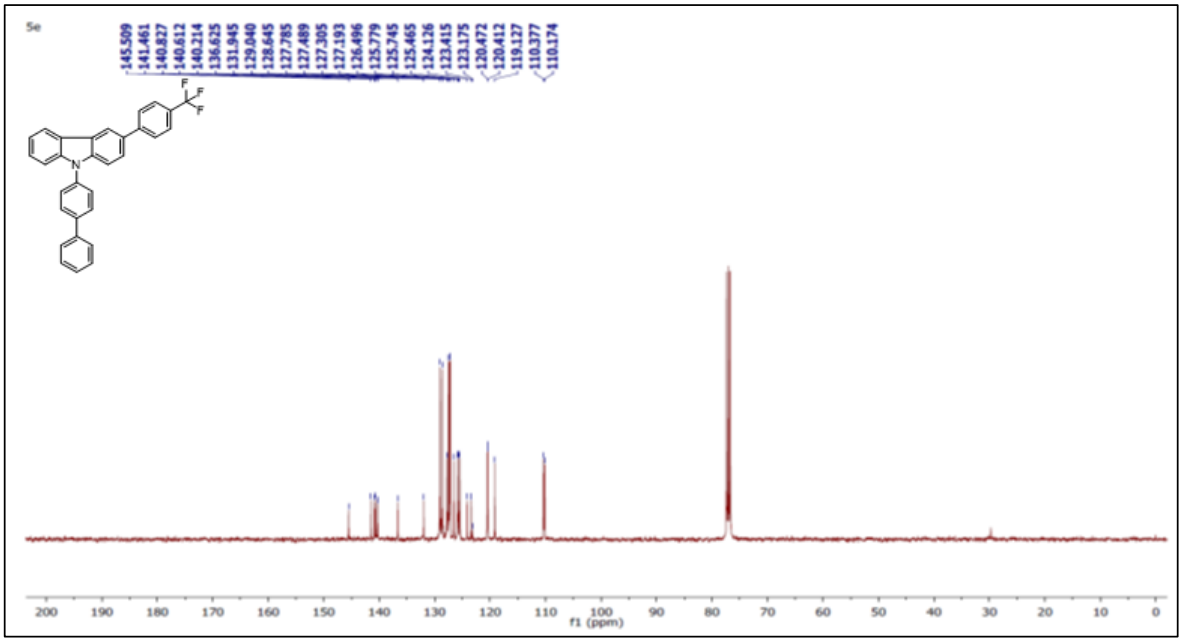
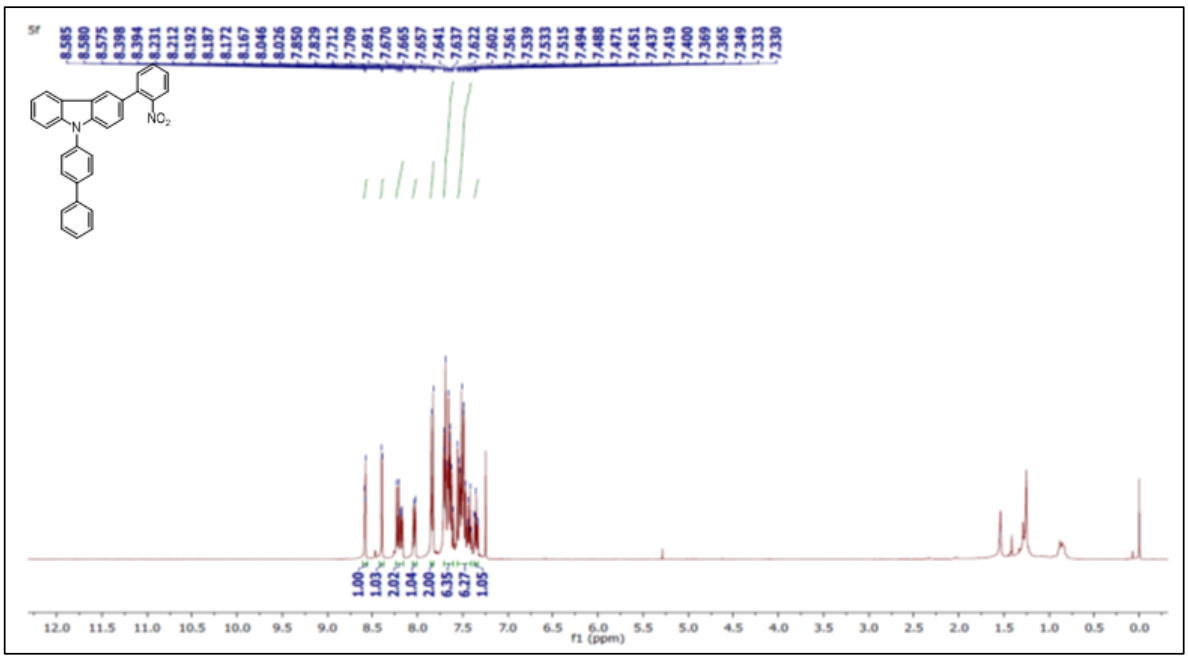
8.366
8.212
8.193
7.837
7.821
7.815
7.802
7.728
7.705
7.701
7.684
7.682
7.668
7.664
7.648
7.643
7.631
7.627
7.542
7.527
7.521
7.509
7.489
7.482
7.473
7.471
7.457
7.454
7.432
7.413
7.395
7.352
7.349
7.335
7.332
7.329
7.316
7.313
F
F
F
N
1.00
1.01
4.01
7.03
6.02
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


5e
145.509
141.461
140.827
140.612
140.214
136.625
131.945
129.040
128.645
127.785
127.489
127.305
127.193
126.496
125.779
125.745
125.465
124.126
123.415
123.175
120.472
120.412
119.127
110.377
110.174
F
F
F
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.580
8.575
8.398
8.394
8.231
8.212
8.192
8.187
8.172
8.167
8.046
8.026
7.850
7.829
7.712
7.709
7.691
7.670
7.665
7.657
7.641
7.637
7.622
7.602
7.561
7.539
7.533
7.515
7.494
7.488
7.471
7.451
7.437
7.419
7.400
7.369
7.365
7.349
7.333
7.330
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2.02
1.04
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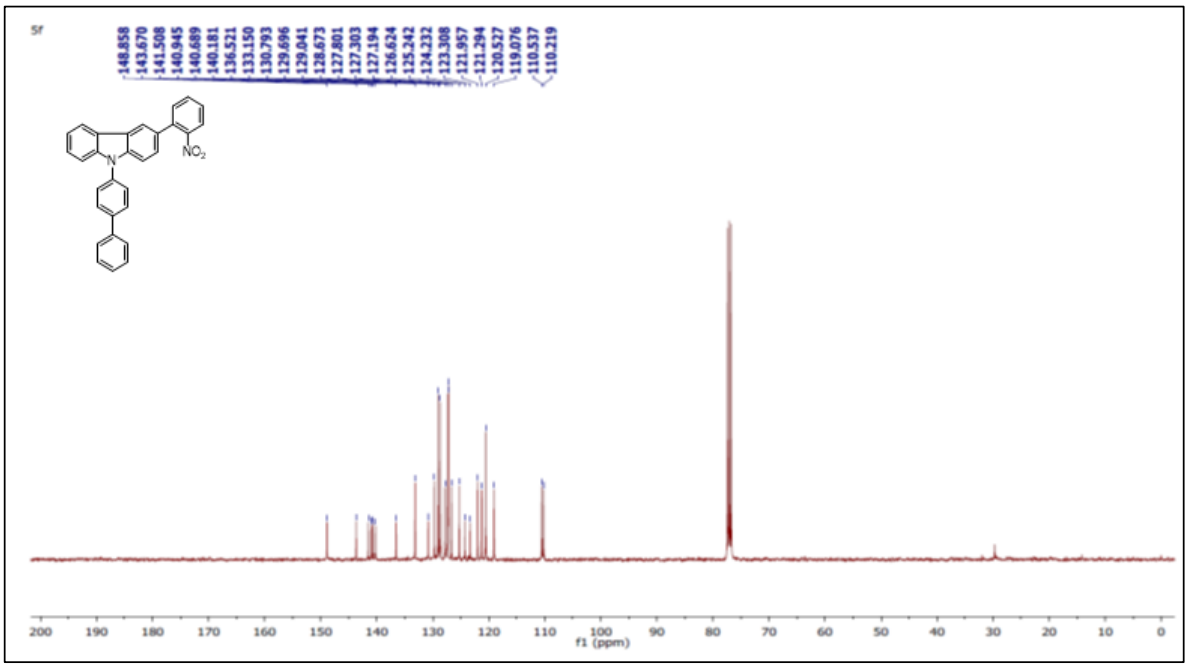
6.35
6.27
1.05
f1 (ppm)


5f
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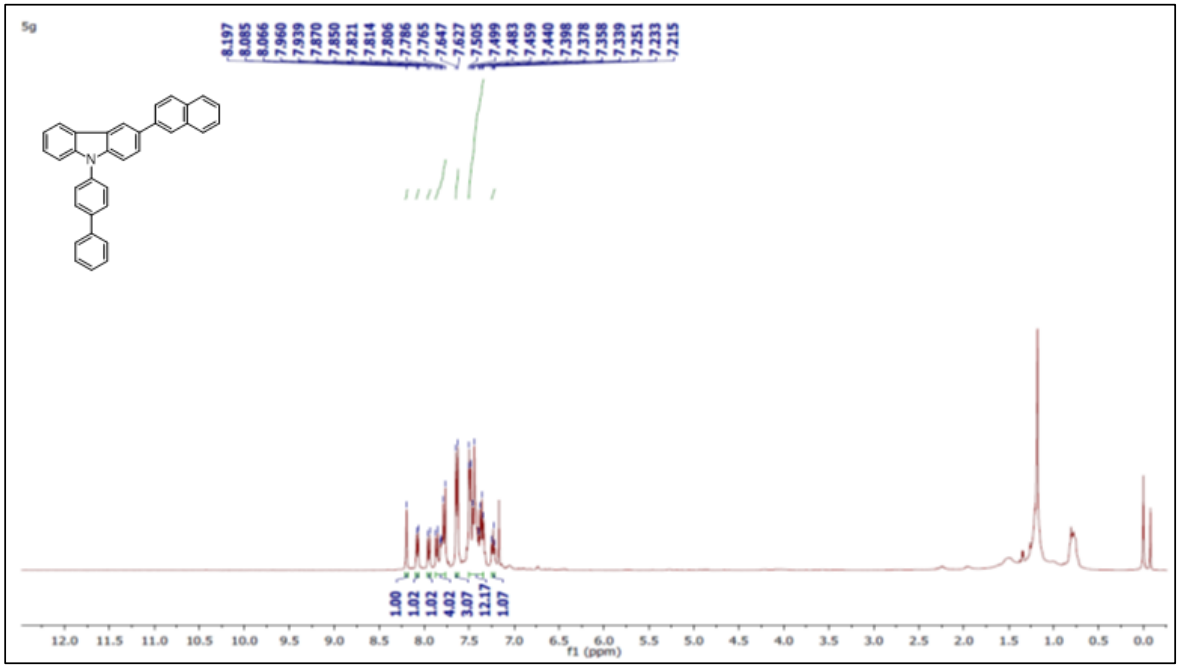
141.508
140.945
140.689
140.181
136.521
133.150
130.793
129.696
129.041
128.673
127.801
127.303
127.194
126.624
125.242
124.232
123.308
121.957
121.294
120.527
119.076
110.537
110.219
NO2
f1 (ppm)


5g
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8.085
8.066
7.960
7.939
7.870
7.850
7.821
7.814
7.806
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7.765
7.647
7.627
7.505
7.499
7.483
7.459
7.440
7.398
7.378
7.358
7.339
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1.00
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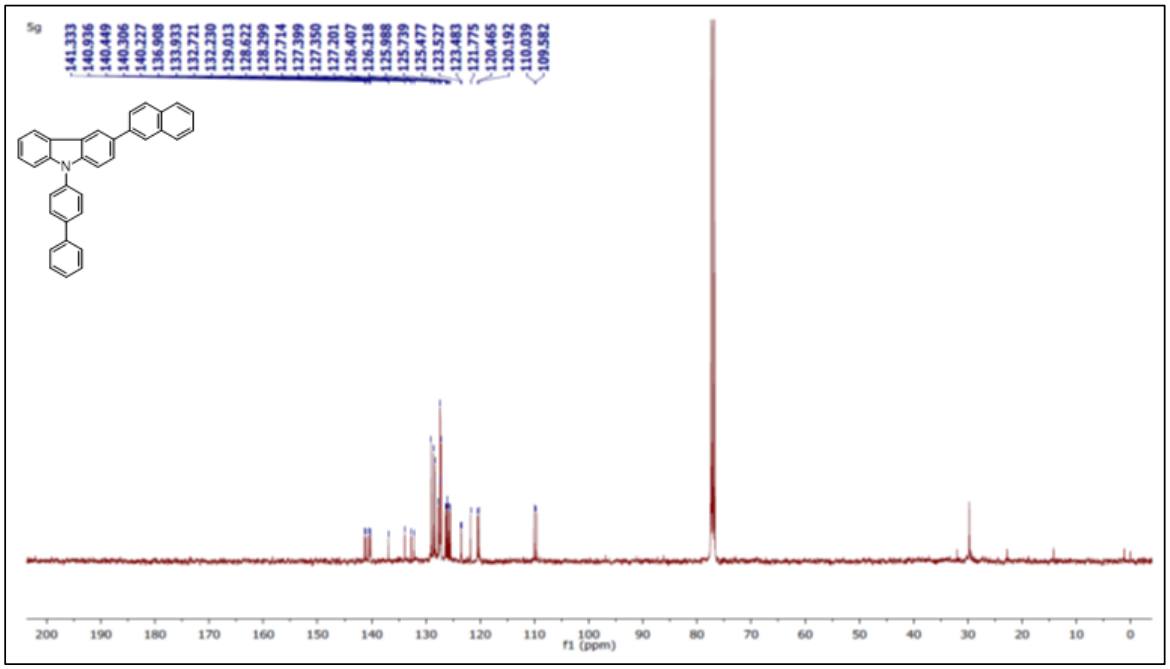
1.02
1.02
4.02
3.07
12.17
1.07
f1 (ppm)


5g
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140.227
136.908
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132.230
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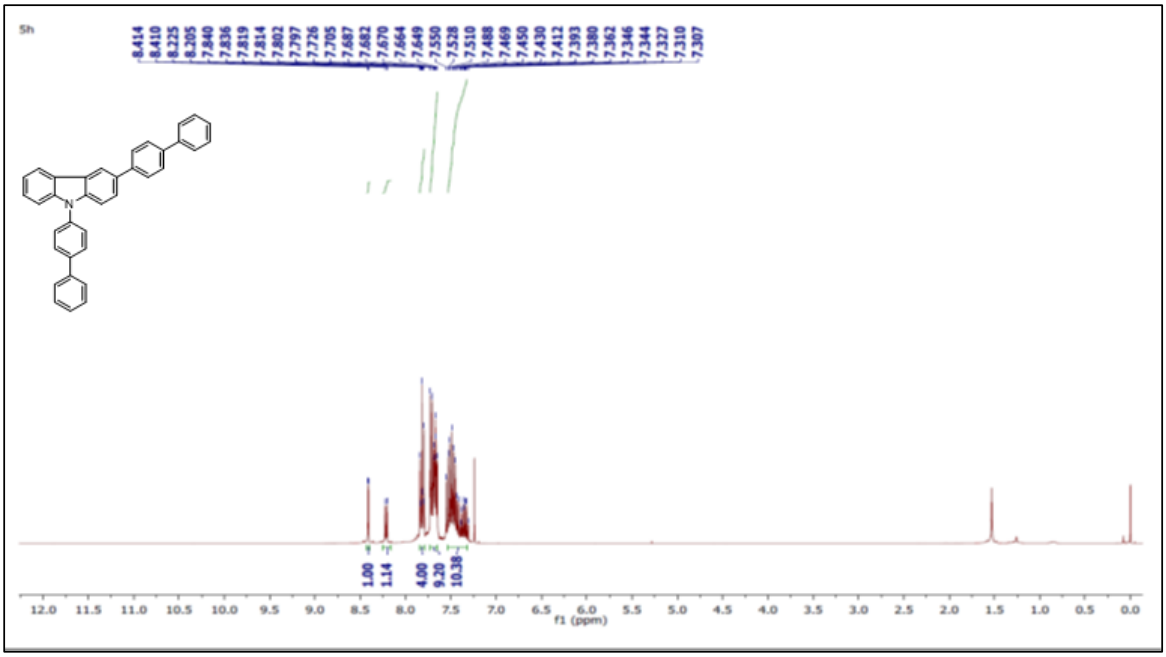
128.622
128.299
127.714
127.399
127.350
127.201
126.407
126.218
125.988
125.739
125.477
123.527
123.483
121.775
120.465
120.192
110.039
109.582
f1 (ppm)


5h
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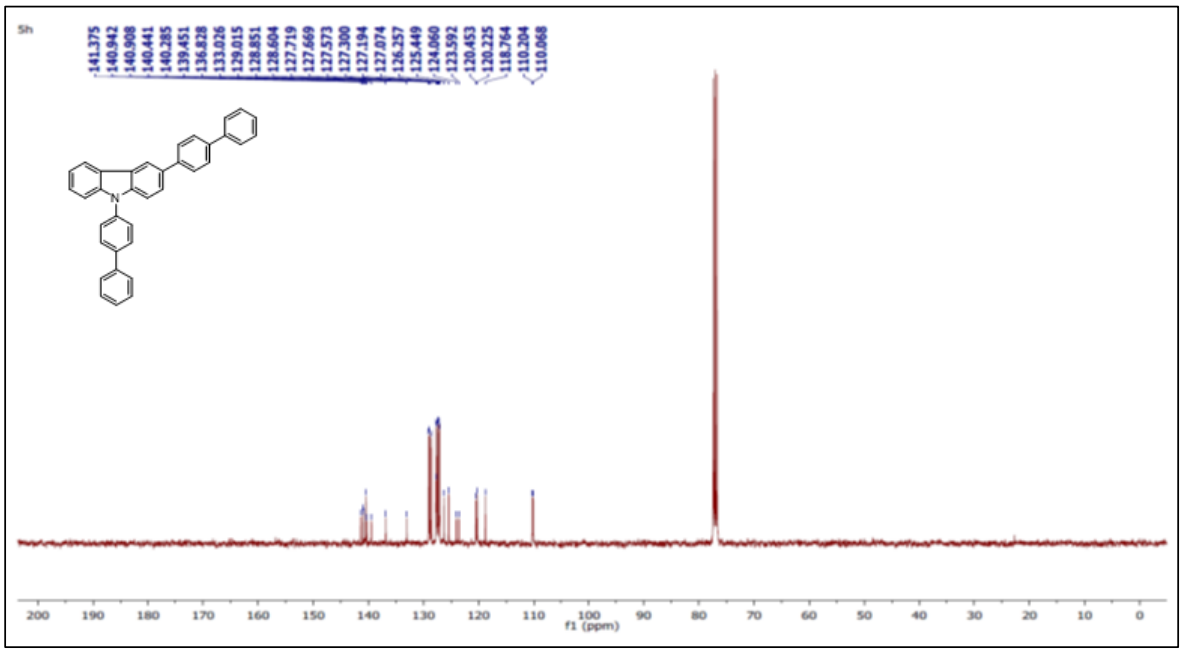
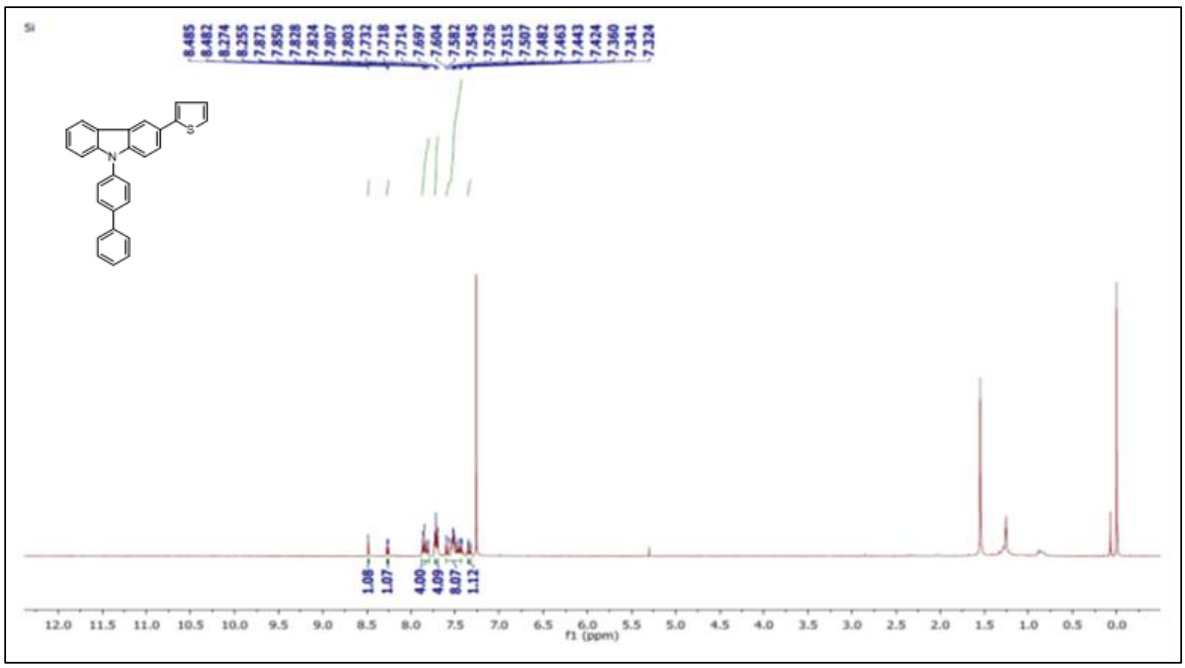
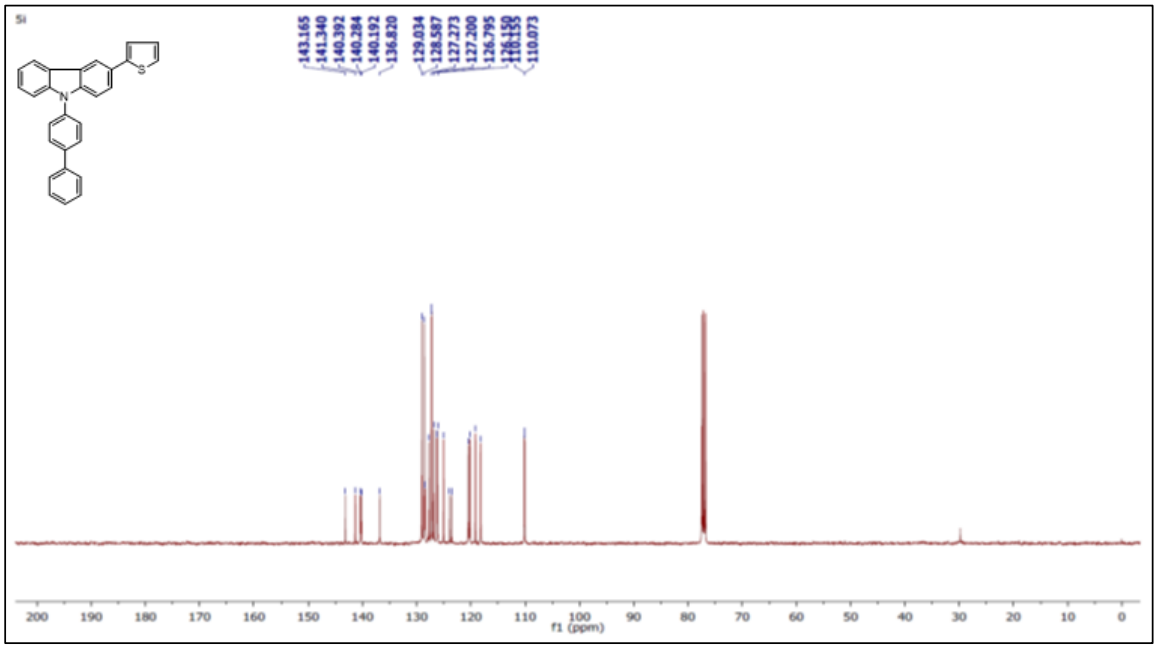
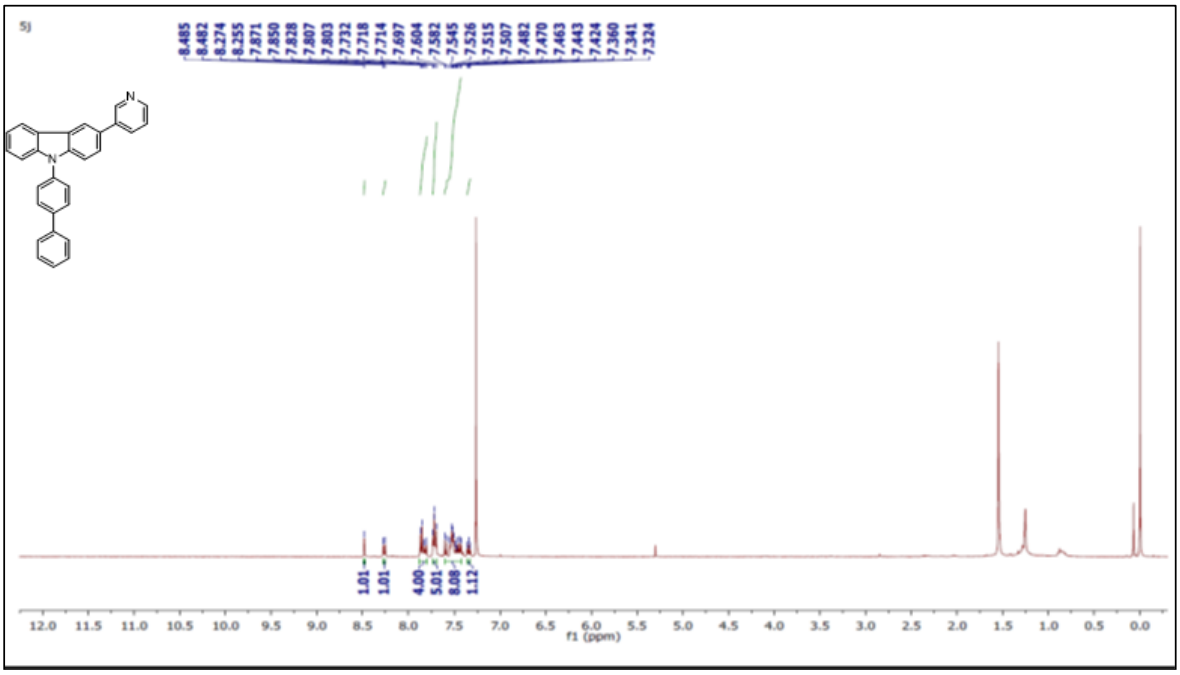
8.410
8.225
8.305
7.840
7.836
7.819
7.814
7.802
7.797
7.726
7.705
7.687
7.682
7.670
7.664
7.649
7.550
7.528
7.510
7.488
7.469
7.450
7.430
7.412
7.393
7.380
7.362
7.346
7.344
7.327
7.310
7.307
1.00
1.14
4.00
9.20
10.38
f1 (ppm)


5h
141.375
140.942
140.908
140.441
140.265
139.451
136.828
133.026
129.015
128.851
128.604
127.719
127.669
127.573
127.300
127.194
127.074
126.257
125.449
124.060
123.592
120.453
120.225
118.764
110.204
110.068
f1 (ppm)


Si
8.485
8.482
8.274
8.255
7.871
7.850
7.828
7.824
7.807
7.803
7.732
7.718
7.714
7.697
7.604
7.582
7.545
7.526
7.515
7.507
7.482
7.463
7.443
7.424
7.360
7.341
7.324
1.08
1.07
4.00
4.09
8.07
1.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Si
143.165
141.340
140.392
140.284
140.192
136.820
129.034
128.587
127.273
127.200
126.795
110.073
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


5j
8.485
8.482
8.274
8.255
7.871
7.850
7.828
7.807
7.803
7.732
7.718
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7.697
7.604
7.582
7.545
7.526
7.515
7.507
7.482
7.470
7.463
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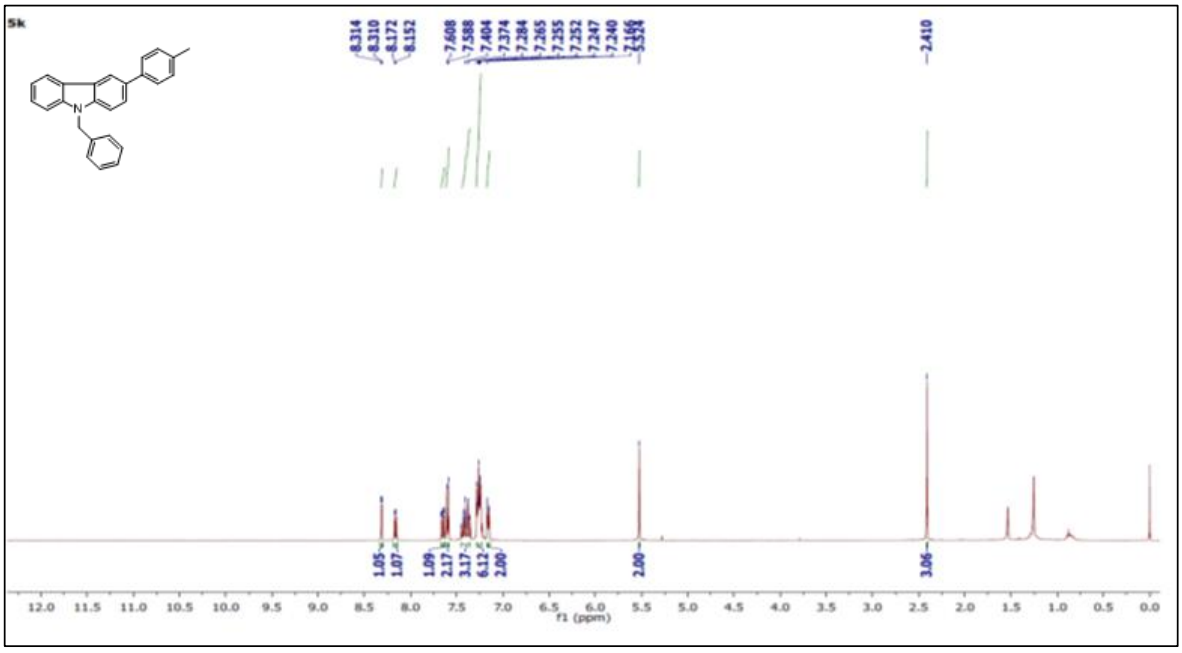
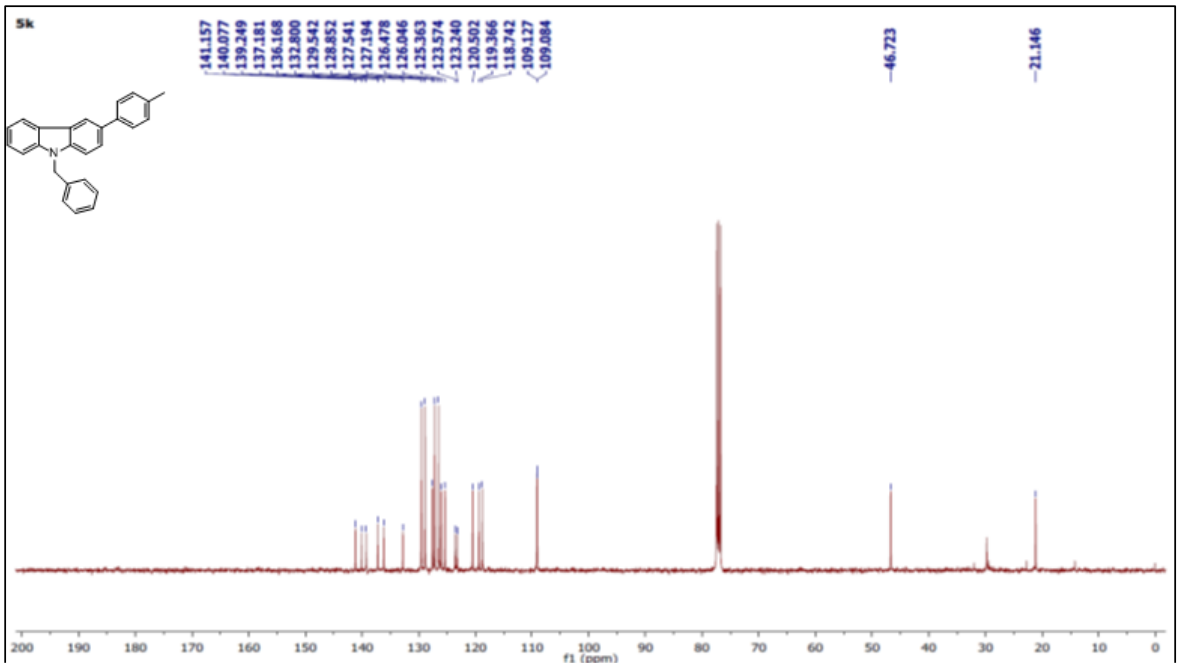
7.360
7.341
7.324
1.01
1.01
4.00
5.01
8.08
1.12
f1 (ppm)


5k
8.314
8.310
8.172
8.152
7.608
7.588
7.404
7.374
7.284
7.265
7.255
7.252
7.247
7.240
2.410
1.05
1.07
1.09
2.17
3.17
6.12
2.00
2.00
3.06
f1 (ppm)


5k
141.157
140.077
139.249
137.181
136.168
132.800
129.542
128.852
127.541
127.194
126.478
126.046
125.363
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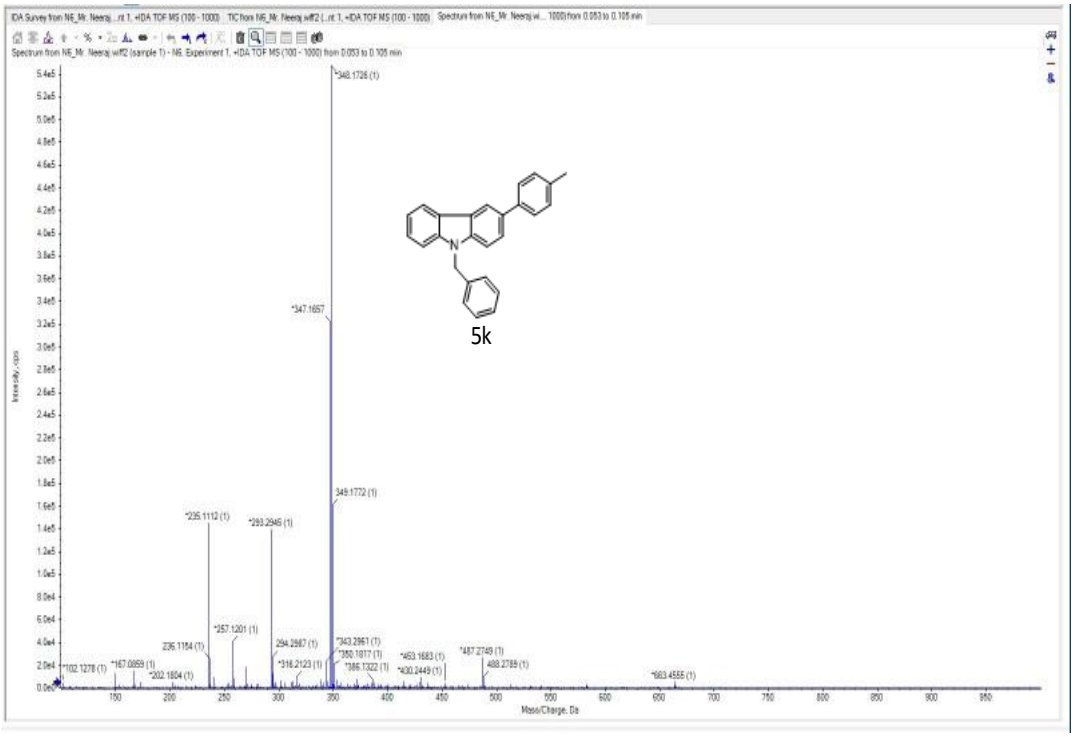
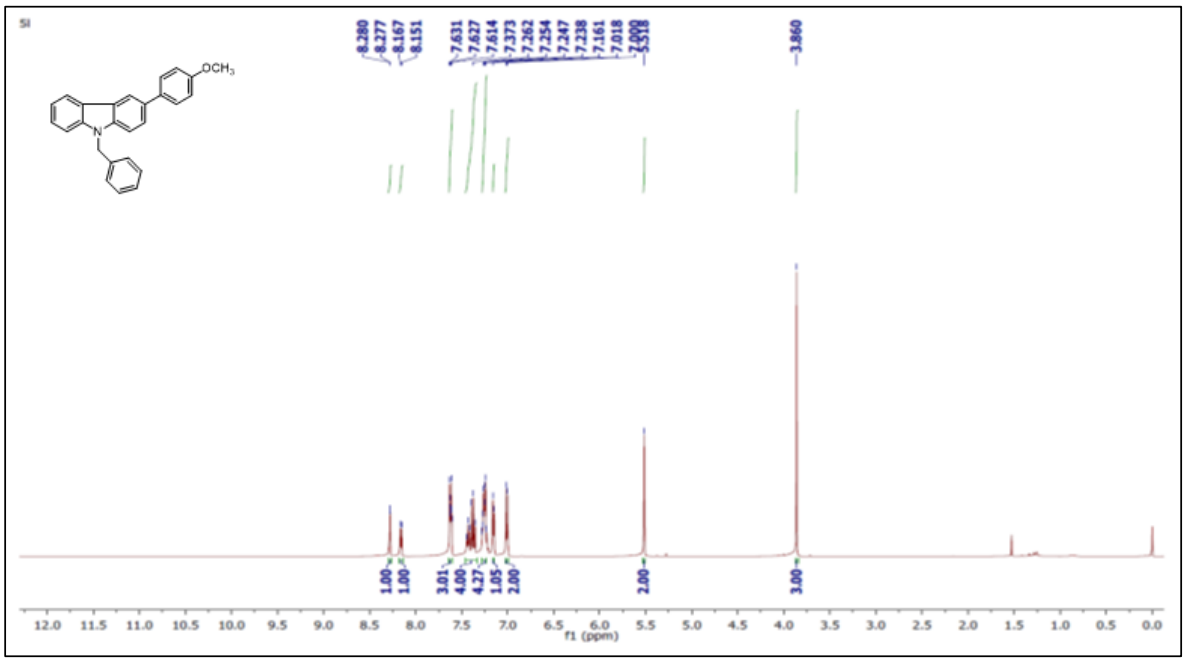
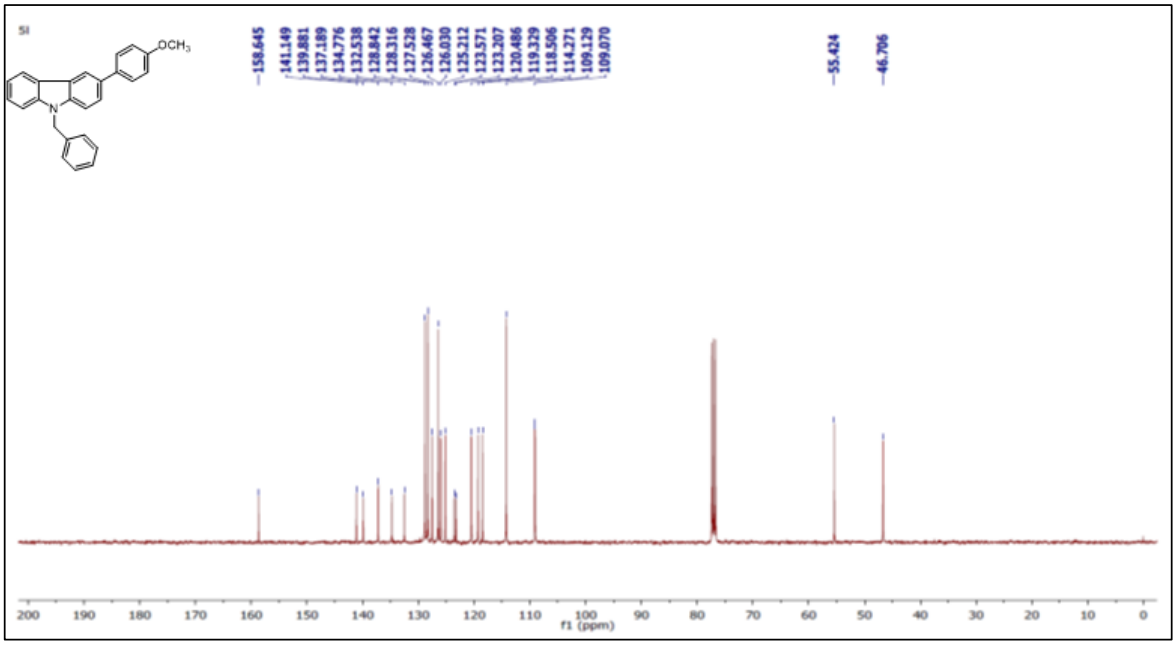
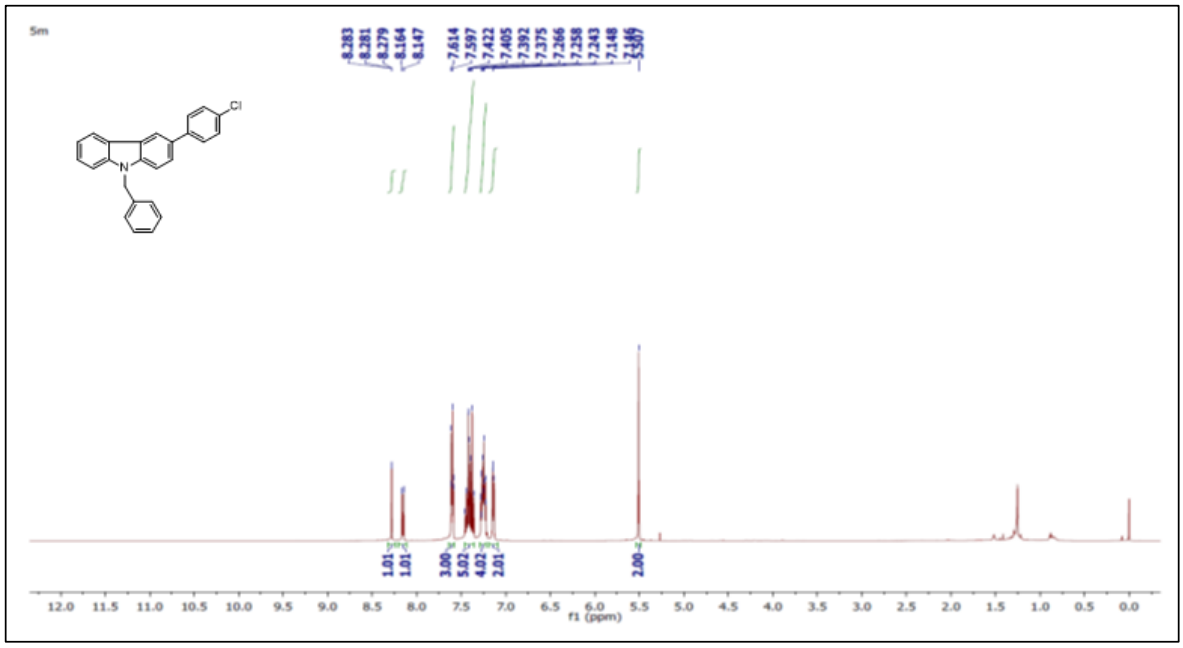
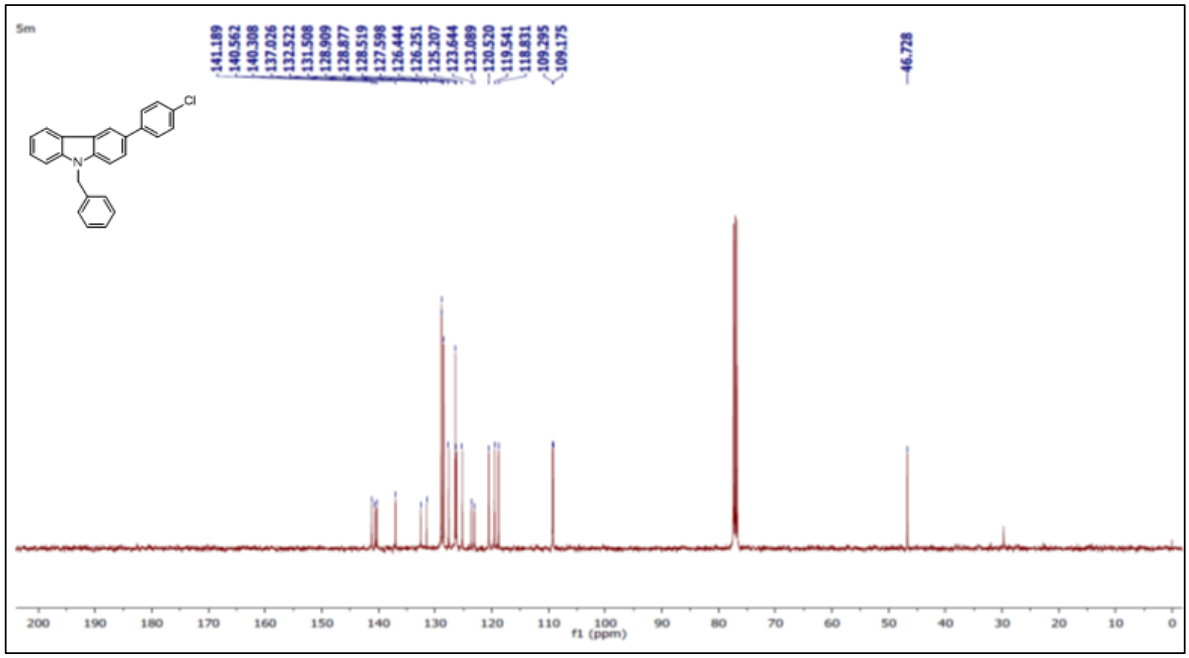
123.240
120.502
119.366
118.742
109.127
109.084
46.723
21.146
f1 (ppm)

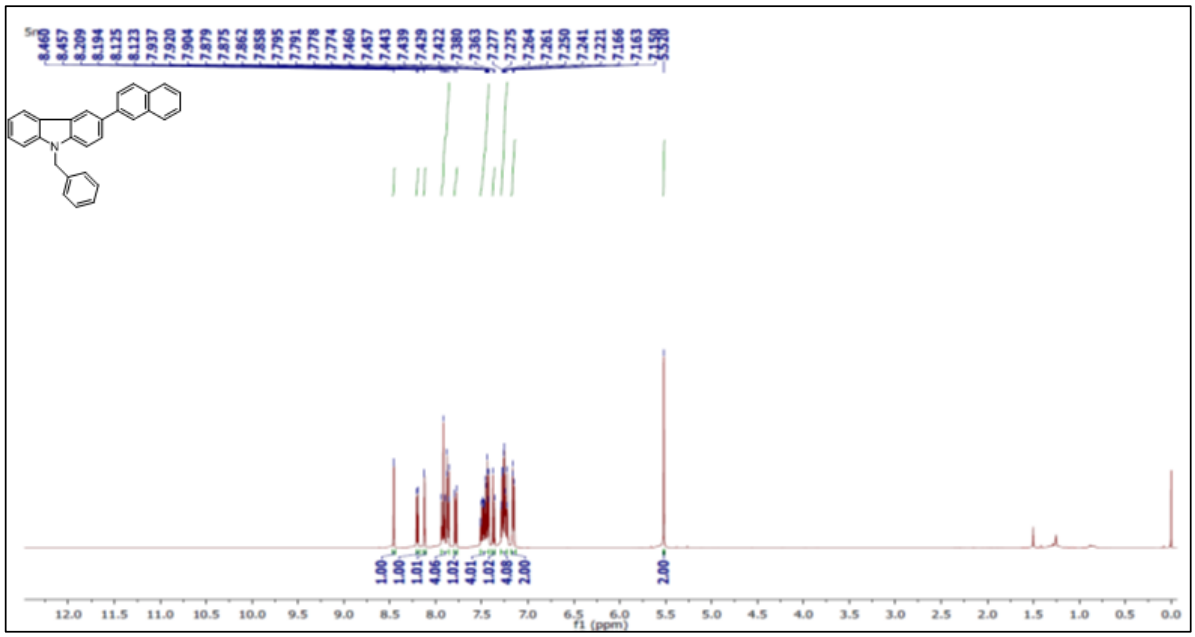

5k
Mass/Charge, Da

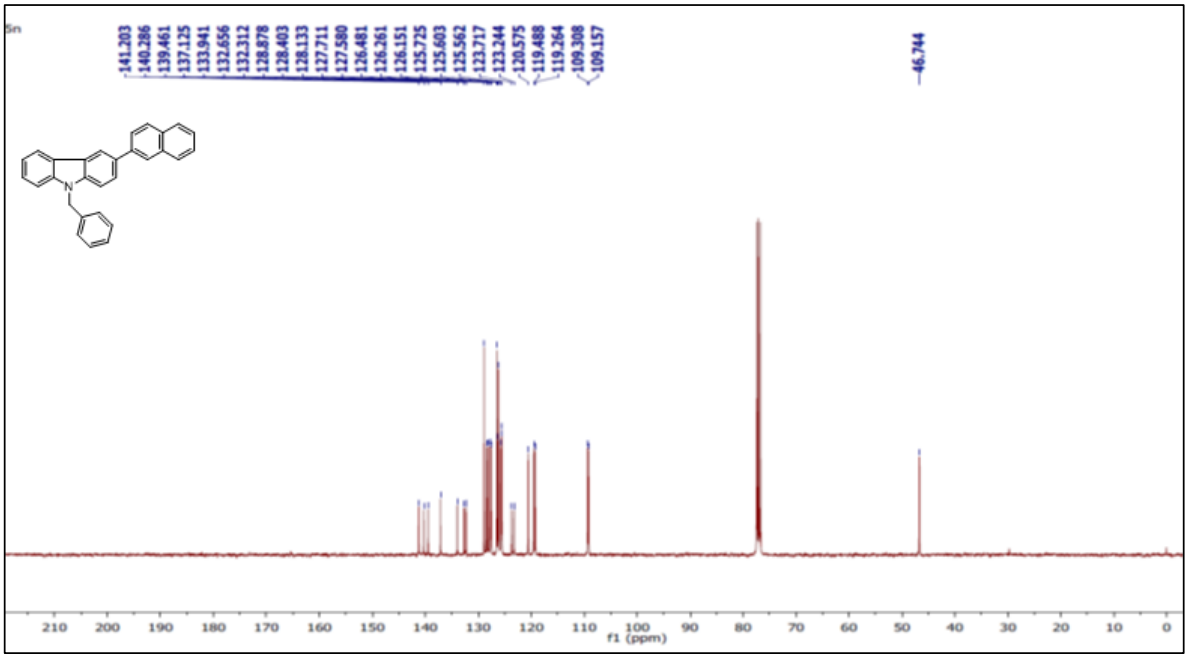

SI
OCH3
8.280
8.277
8.167
8.151
7.631
7.627
7.614
7.373
7.262
7.254
7.247
7.238
7.161
7.018
7.000
5.518
3.860
1.00
1.00
3.01
4.05
4.27
1.05
2.00
2.00
3.00
f1 (ppm)

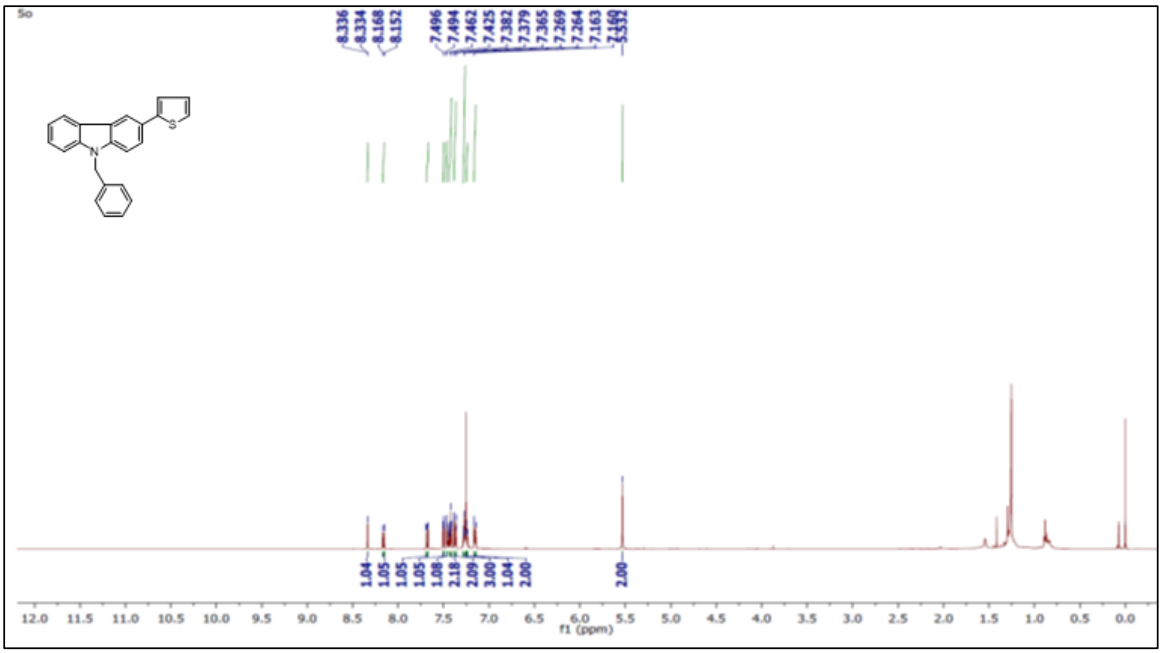

SI
OCH3
158.645
141.149
139.881
137.189
134.776
132.538
128.842
128.316
127.528
126.467
126.030
125.212
123.571
123.207
120.486
119.329
118.506
114.271
109.129
109.070
55.424
46.706
f1 (ppm)

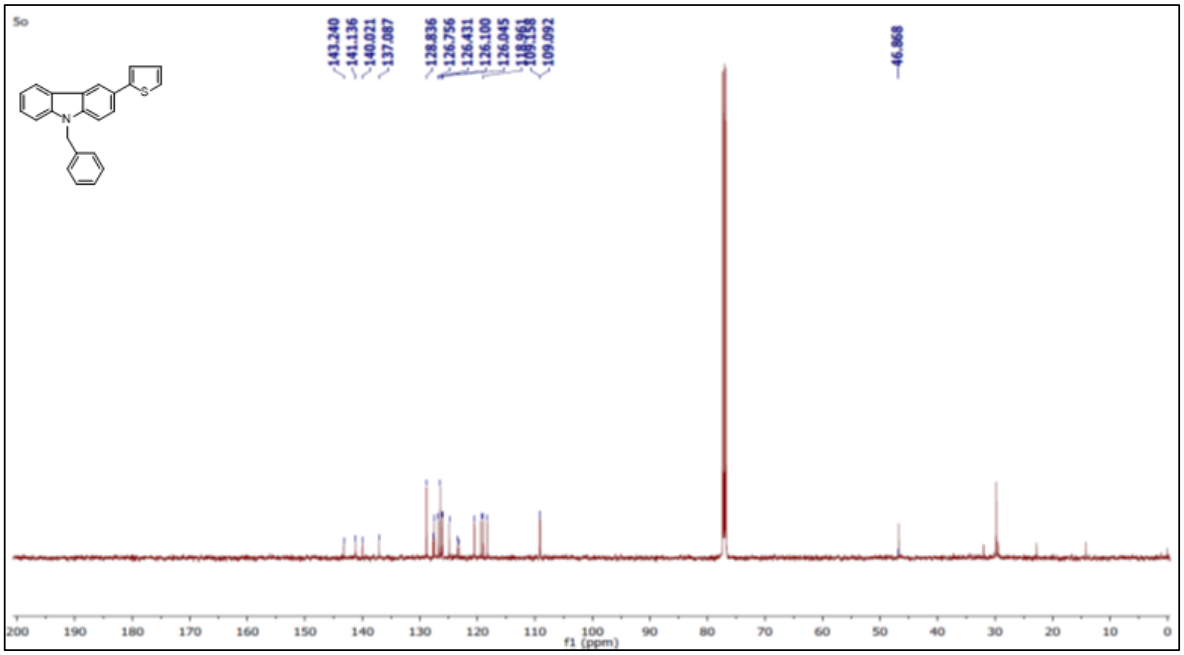

5m
8.383
8.381
8.379
8.164
8.147
7.614
7.597
7.422
7.405
7.392
7.375
7.366
7.358
7.243
7.148
5.507
Cl
N
1.01
1.01
3.00
5.02
4.02
2.01
2.00
f1 (ppm)

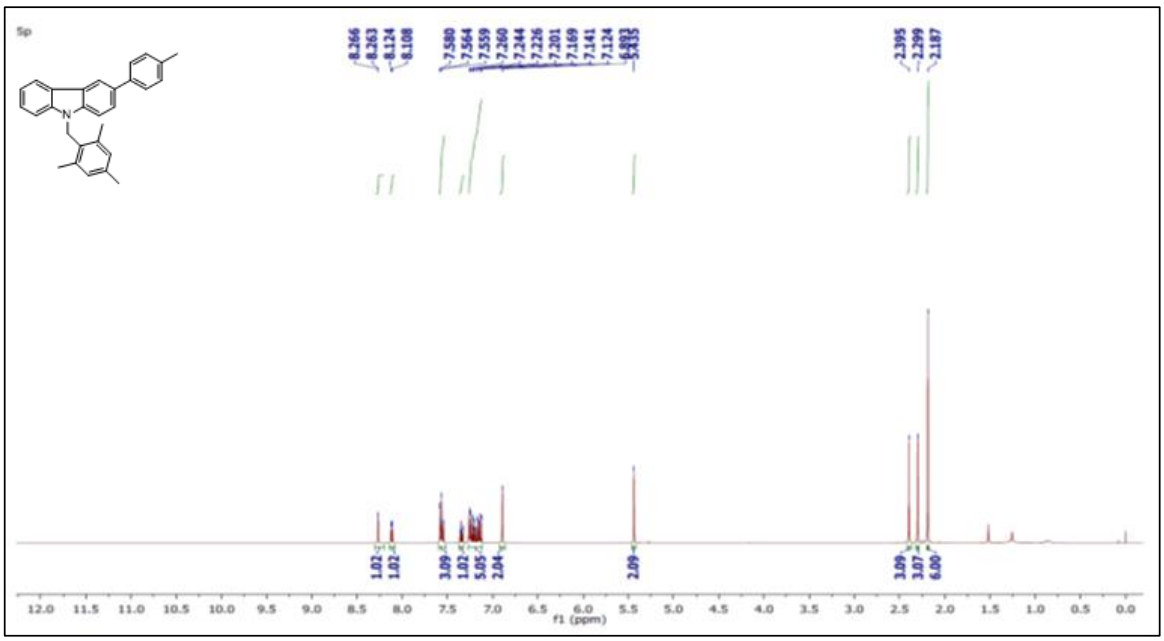

5m
141.189
140.562
140.308
137.026
132.522
131.508
128.909
128.877
128.519
127.598
126.444
126.251
125.207
123.644
123.089
120.520
119.541
118.831
109.295
109.175
46.728
Cl
N
f1 (ppm)

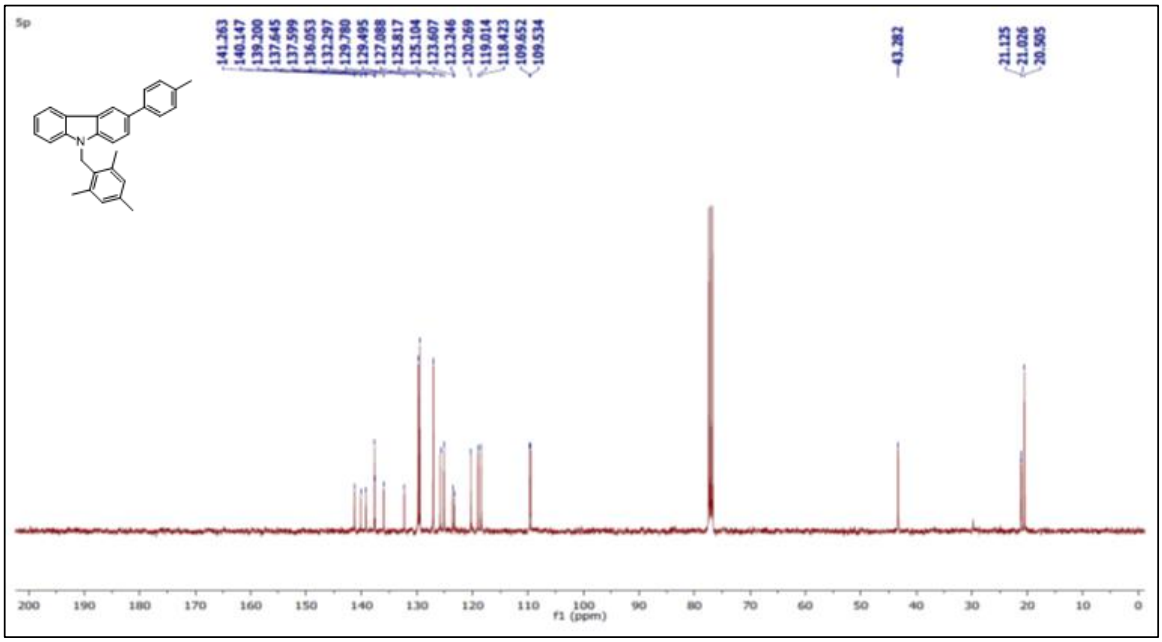

8.460
8.457
8.209
8.194
8.125
8.123
7.937
7.920
7.904
7.879
7.875
7.862
7.858
7.795
7.791
7.778
7.774
7.460
7.457
7.443
7.439
7.429
7.422
7.380
7.363
7.277
7.275
7.264
7.261
7.250
7.241
7.221
7.166
7.163
5.520
1.00
1.00
1.01
4.06
1.02
4.01
1.02
4.08
2.00
2.00
f1 (ppm)


141.203
140.286
139.461
137.125
133.941
132.656
132.312
128.878
128.403
128.133
127.711
127.580
126.481
126.261
126.151
125.725
125.603
125.562
123.717
123.244
120.575
119.488
119.264
109.308
109.157
46.744
f1 (ppm)


So
8.336
8.334
8.168
8.152
7.496
7.494
7.462
7.425
7.382
7.379
7.365
7.269
7.264
7.163
7.160
5.552
1.04
1.05
1.05
1.05
1.08
2.18
2.09
3.00
1.04
2.00
2.00
f1 (ppm)


So
143.240
141.136
140.021
137.087
128.836
126.756
126.431
126.100
126.045
109.092
46.868
f1 (ppm)


5p
8.366
8.363
8.124
8.108
7.580
7.564
7.559
7.360
7.344
7.226
7.201
7.169
7.141
7.124
2.395
2.399
2.187
1.02
1.02
3.09
1.02
5.05
2.04
2.09
3.09
3.07
6.00
f1 (ppm)


5p
141.263
140.147
139.200
137.645
137.599
136.653
132.297
129.780
129.495
127.088
125.617
125.104
123.607
123.246
120.269
119.014
118.423
109.652
109.534
43.282
21.125
21.026
20.505
f1 (ppm)

## XIV. References: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