Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

One-pot access to tetrahydro benzo[*c*]carbazoles from simple ketones using O_2 as oxidant

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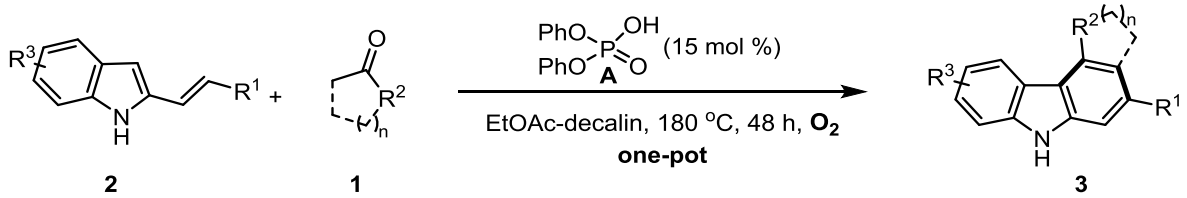
Experimental Section:

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen/argon atmosphere. Ethylacetate was obtained from SRL India. All other solvents were obtained from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized under UV light or by dipping into $KMnO_4$ or DNP solution. Silica gel (particle size 100-200 mesh) was purchased from SRL India for performing column chromatography by using mixture of hexanes and ethylacetate eluent. The ^{1}H NMR spectroscopic data were recorded with a Bruker 400 or 500 or 600 MHz instruments. ^{13}C NMR proton decoupled carbon spectra were similarly recorded at 101 or 126 or 151 MHz instruments by using a broadband decoupled mode $^{13}C\{^{1}H\}$. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16) or DMSO-d_6 (δ= 2.50, 39.52). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, dd: doublet of doublets, m: multiplet. Infrared (IR) spectra were recorded by Perkin Elmer FTIR spectrometer, and reported in terms of wave number (cm^{-1}). High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method using a time-of-flight (TOF) mass analyzer.

Synthesis of 2-Alkenyl Indoles (2): 2-Alkenyl Indoles **2** were synthesized according to known literature procedure.[1,2]

General Procedure I (GP I): One-Pot Synthesis of Carbazole



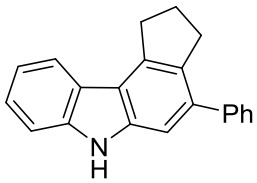
To a mixture of (*E*)-2-styryl-1*H*-indole derivative **2** (0.20 mmol, 1.0 equiv) and diphenyl phosphate (15 mol%, 7.5 mg) in a screw cap seal reaction tube, 1.3 mL of ethyl acetate and 2.7 mL of decalin were added successively. Then the electrophile **1** (0.40 mmol, 2.0 equiv) was added and air of the reaction tube was replaced by purging with pure oxygen. Next, the resulting mixture was stirred at 180 ºC for 48 hours. The progress of the reaction was monitored by TLC. On complete consumption of all the intermediates as indicated by TLC, the crude residue was diluted with ethylacetate, and transferred to a round bottom flask. After evaporating the ethylacetate under *vacuo*, the crude product was purified by silica gel column chromatography by using ethylacetate /hexane as eluent to obtain the pure desired carbazoles **3**.

5-Phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3aa):

The titled compound **3aa** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3aa** (48.3 mg, 0.16 mmol, 81%) was isolated as a pale-yellow solid after column chromatography on silica gel by using 6% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, *J* = 7.6 Hz, 1H), 7.88 (s, 1H), 7.50-7.38 (m, 7H), 7.31-7.27 (m, 1H), 7.13 (s, 1H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.08-2.02 (m, 2H), 1.87-1.81 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 143.0, 140.8, 140.0, 137.5, 132.8, 129.6, 128.1, 126.8, 126.1, 125.0, 124.0, 123.2, 120.9, 119.3, 110.5, 109.5, 29.0, 28.8, 23.6, 23.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3405, 3054, 2926, 1699, 1600, 1453, 1263, 1115, 1030, 854. **HRMS (ESI)**: calculated for $C_{22}H_{20}N$ (**[M+H]$^+$**): 298.1590; found 298.1596.

4-Phenyl-1,2,3,6-tetrahydrocyclopenta[*c*]carbazole (3ab):

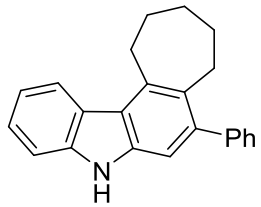
The titled compound **3ab** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and cyclopentanone (35.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ab** (26.2 mg, 0.09 mmol, 46%) was isolated as a white foamy solid after



column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26-7.23 (m, 2H), 3.49 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.29-2.25 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 142.6, 140.3, 139.4, 138.2, 136.6, 133.8, 129.0, 128.4, 126.8, 125.5, 123.6, 122.0, 119.6, 119.3, 110.5, 108.7, 32.5, 26.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3393, 2919, 1711, 1599, 1454, 1261, 1027, 863. **HRMS (ESI)**: calculated for $C_{21}H_{18}N$ (**[M+H]$^+$**): 284.1434; found 284.1439.

6-Phenyl-1,2,3,4,5,8-hexahydrocyclohepta[*c*]carbazole (3ac):

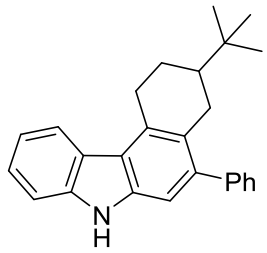
The titled compound **3ac** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-



indole (43.9 mg, 0.20 mmol, 1.0 equiv) and cycloheptanone (47.3 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ac** (28.3 mg, 0.09 mmol, 45%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.31 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.44-7.39 (m, 4H), 7.38-7.35 (m, 3H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 1H), 3.60-3.59 (m, 2H), 2.90-2.88 (m, 2H), 1.96-1.84 (m, 4H), 1.65 (t, *J* = 4.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 143.8, 140.5, 140.1, 139.5, 138.0, 133.2, 129.8, 128.0, 126.6, 125.2, 123.8, 122.7, 120.9, 119.3, 110.6, 109.3, 32.3, 31.0, 30.5, 28.6, 26.9. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3408, 2920, 1714, 1600, 1454, 1268, 853. **HRMS (ESI)**: calculated for $C_{23}H_{22}N$ (**[M+H]$^+$**): 312.1747; found 312.1749.

3-(*tert*-Butyl)-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ad):

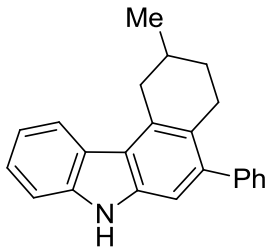
The titled compound **3ad** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-



indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 4-*tert*-butylcyclohexanone (61.7 mg, 0.40 mmol, 2.0 equiv). The carbazole **3ad** (40.5 mg, 0.11 mmol, 57%) was isolated as a white solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 7.6 Hz, 1H), 8.00 (s, 1H), 7.46-7.35 (m, 7H), 7.26-7.23 (m, 1H), 7.16 (s, 1H), 3.71-3.66 (m, 1H), 3.37-3.28 (m, 1H), 2.75-2.71 (m, 1H), 2.53-2.46 (m, 1H), 2.26-2.21 (m, 1H), 1.55-1.43 (m, 2H), 0.90 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 142.9, 141.0, 140.0, 137.4, 132.7, 129.6, 128.1, 126.8, 126.5, 125.0, 124.0, 123.1, 120.6, 119.3, 110.5, 109.7, 45.0, 32.6, 30.3, 30.1, 27.4,

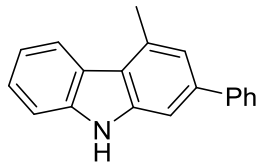
24.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3432, 2938, 2864, 1608, 1453, 1364, 1267, 860, 701. **HRMS (ESI)**: calculated for $C_{26}H_{28}N$ (**[M+H]**$^+$): 354.2216; found 354.2212.

2-Methyl-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ae):



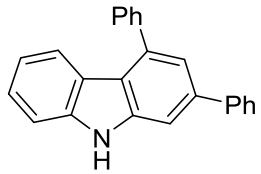
The titled compounds **3ae**+**3ae'** were synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 3-methylcyclohexanone (49.1 μL, 0.40 mmol, 2.0 equiv). The mixture of carbazoles **3ae** and its regioisomer **3ae'** (**3ae**: **3ae′** = 4.4:1, 41.9 mg, 0.13 mmol, 67%) was isolated as a white solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) δ 8.23 (d, *J* = 7.8 Hz, 1H), 8.00 (s, 1H), 7.45-7.40 (m, 7H), 7.27-7.25 (m, 1H), 7.16 (s, 1H), 3.67-3.63 (m, 1H), 2.97-2.92 (m, 1H), 2.83-2.77 (m, 1H), 2.73-2.69 (m, 1H), 2.09-2.04 (m, 1H), 1.92-1.90 (m, 1H), 1.45-1.40 (m, 1H), 1.24 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 143.1, 140.7, 140.1, 137.6, 132.9, 129.6, 128.1, 126.8, 125.8, 125.1, 124.1, 123.3, 120.8, 119.4, 110.5, 109.5, 37.5, 31.9, 29.2, 29.0, 22.6. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3388, 2920, 1714, 1600, 1440, 1265, 1103, 957, 701. **HRMS (ESI)**: calculated for $C_{23}H_{22}N$ (**[M+H]**$^+$): 312.1747; found 312.1749.

4-Methyl-2-phenyl-9*H*-carbazole (3af):



The titled compound **3af** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and acetone (29.6 μL, 0.40 mmol, 2.0 equiv). The carbazole **3af** (33.4 mg, 0.13 mmol, 65%) was isolated as a white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.19 (d, *J* = 8.0 Hz, 1H), 8.11 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.49-7.41 (m, 5H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29-7.27 (m, 2H), 2.94 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 142.1, 140.3, 140.1, 139.3, 133.7, 128.9, 127.6, 127.2, 125.4, 123.9, 122.7, 121.4, 120.9, 119.7, 110.5, 106.8, 21.0. **HRMS (ESI)**: calculated for $C_{19}H_{16}N$ (**[M+H]**$^+$): 258.1277; found 258.1275.

2,4-Diphenyl-9*H*-carbazole (3ag):

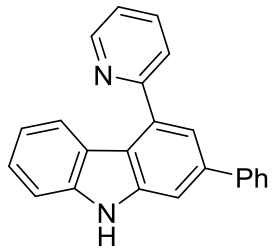


The titled compound **3ag** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and acetophenone (46.7 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ag** (26.9 mg, 0.08 mmol, 42%) was isolated as a white solid after column chromatography on silica gel

by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.23 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.64 (s, 1H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.51-7.50 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.38-7.35 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 141.8, 141.4, 140.7, 140.4, 139.2, 138.1, 129.4, 129.0, 128.6, 127.8, 127.7, 127.3, 125.9, 123.0, 122.6, 121.0, 120.3, 119.4, 110.6, 108.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3410, 3056, 2922, 1715, 1600, 1457, 1323, 1155, 997, 858. **HRMS (ESI)**: calculated for $C_{24}H_{18}N$ (**[M+H]$^+$**): 320.1434; found 320.1434.

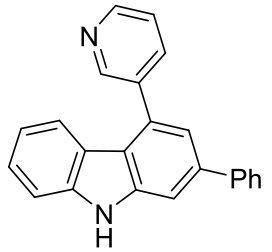
2-Phenyl-4-(pyridin-2-yl)-9*H*-carbazole (3ah):

The titled compound **3ah** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 2-acetylpyridine (44.9 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ah** (27.7 mg, 0.09 mmol, 43%) was isolated as a yellow solid after column chromatography on silica gel by using 11% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.87 (d, *J* = 4.4 Hz, 1H), 8.51 (s, 1H), 7.88 (td, *J* = 7.6, 1.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.55-7.54 (m, 2H), 7.45-7.40 (m, 3H), 7.36-7.32 (m, 3H), 7.04-7.00 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 159.7, 149.7, 141.6, 141.0, 140.6, 139.1, 136.7, 136.4, 128.9, 127.7, 127.3, 126.0, 124.5, 122.9, 122.7, 122.5, 121.0, 120.1, 119.3, 110.7, 109.3. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3399, 2922, 1737, 1591, 1457, 1323, 1146, 997, 862, 733. **HRMS (ESI)**: calculated for $C_{23}H_{17}N_2$ (**[M+H]$^+$**): 321.1386; found 321.1393.



2-phenyl-4-(pyridin-3-yl)-9*H*-carbazole (3ai):

The titled compound **3ai** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 3-acetylpyridine (44.9 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ai** (28.2 mg, 0.09 mmol, 44%) was isolated as a yellow solid after column chromatography on silica gel by using 18% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.97 (s, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.48 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.68 (s, 1H), 7.52-7.44 (m, 5H), 7.40-7.36 (m, 3H), 7.03 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 150.1, 149.0, 141.4, 140.8, 140.4, 139.4, 137.1, 136.9, 134.0, 129.0, 127.6, 127.5, 126.2, 123.5, 122.5, 122.1, 121.2, 120.3, 119.7, 110.9, 108.9. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3152, 3050, 1610, 1567, 1458, 1324, 1141, 1028, 814, 764. **HRMS (ESI)**: calculated for $C_{23}H_{17}N_2$ (**[M+H]$^+$**): 321.1386; found 321.1403.



5-Phenyl-1,2,4,7-tetrahydro-3*H*-benzo[*c*]carbazol-3-one (3aj):

The titled compound **3aj** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 1,4-cyclohexanedione (44.9 mg, 0.40 mmol, 2.0 equiv). The carbazole **3aj** (26.3 mg, 0.08 mmol, 42%) was isolated as a white solid after column chromatography on silica gel by using 7% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.24 (d, *J* = 8.4 Hz, 1H), 8.16 (s, 1H), 7.49-7.42 (m, 4H), 7.39-7.36 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.29-7.26 (m, 2H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.63 (s, 2H), 2.75 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 211.3, 141.5, 140.3, 140.1, 138.3, 131.8, 129.5, 128.5, 127.3, 125.8, 123.3, 122.7, 122.6, 120.2, 119.8, 110.9, 110.6, 43.3, 38.0, 26.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3293, 3054, 2922, 1693, 1600, 1456, 1269, 1029, 863. **HRMS (ESI)**: calculated for $C_{22}H_{17}NNaO$ (**[M+Na]$^+$**): 334.1202; found 334.1201.

5-Phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazol-1-one (3ak):

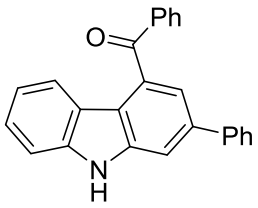
The titled compound **3ak** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 1,2-cyclohexanedione (44.9 mg, 0.40 mmol, 2.0 equiv). The carbazole **3ak** (28.7 mg, 0.09 mmol, 46%) was isolated as a yellow solid after column chromatography on silica gel by using 5% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 9.17 (d, *J* = 8.4 Hz, 1H), 8.30 (s, 1H), 7.52 (s, 1H), 7.49-7.46 (m, 3H), 7.44-7.41 (m, 2H), 7.40-7.38 (m, 2H), 7.29-7.26 (m, 1H), 2.92 (t, *J* = 6.0 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 2.09-2.05 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.5, 141.6, 141.0, 139.5, 138.8, 136.4, 129.6, 129.2, 128.4, 127.4, 127.2, 127.0, 122.7, 120.8, 119.8, 117.2, 110.3, 40.5, 29.5, 23.5. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3271, 2950, 1648, 1454, 1303, 1159, 1022, 876, 737. **HRMS (ESI)**: calculated for $C_{22}H_{18}NO$ (**[M+H]$^+$**): 312.1383; found 312.1389.

1-(2-Phenyl-9*H*-carbazol-4-yl)ethan-1-one (3al):

The titled compound **3al** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 2,3-butanedione (34.8 μL, 0.40 mmol, 2.0 equiv). The carbazole **3al** (34.9 mg, 0.12 mmol, 61%) was isolated as a yellow solid after column chromatography on silica gel by using 7% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.74 (d, *J* = 8.4 Hz, 1H), 8.36 (s, 1H), 7.89 (d, *J* = 1.2 Hz, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.53-7.49 (m, 2H), 7.48-7.45 (m, 2H), 7.42 (t, *J* = 7.5 Hz,

1H), 7.28-7.26 (m, 1H), 2.86 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 201.4, 141.2, 141.0, 140.9, 138.4, 134.4, 129.2, 127.8, 127.6, 127.2, 125.6, 122.2, 121.7, 120.1, 119.9, 113.2, 110.5, 29.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3280, 1650, 1416, 1323, 1234, 1146, 1003, 856. **HRMS (ESI)**: calculated for $C_{20}H_{16}NO$ (**[M+H]$^+$**): 286.1226; found 286.1232.

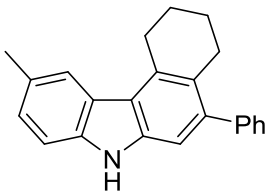
Phenyl(2-phenyl-9*H*-carbazol-4-yl)methanone (3am):



The titled compound **3am** was synthesized according to the **GP I** by using (*E*)-2-styryl-1*H*-indole (43.9 mg, 0.20 mmol, 1.0 equiv) and 1-phenyl-1,2-propanedione (59.3 mg, 0.40 mmol, 2.0 equiv). The carbazole **3am** (28.6 mg, 0.08 mmol, 41%) was isolated as a yellow sticky solid after column chromatography on silica gel by using 7% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.38 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.67-7.60 (s, 3H), 7.55 (s, 1H), 7.51-7.35 (m, 7H), 7.11 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 197.9, 141.0, 140.8, 140.6, 138.4, 137.9, 133.6, 133.4, 130.8, 129.1, 128.7, 127.64, 127.59, 126.7, 123.8, 121.8, 121.1, 120.5, 120.1, 111.7, 110.7. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3404, 3057, 2922, 1596, 1458, 1249, 1024, 869, 734. **HRMS (ESI)**: calculated for $C_{25}H_{18}NO$ (**[M+H]$^+$**): 348.1383; found 348.1376.

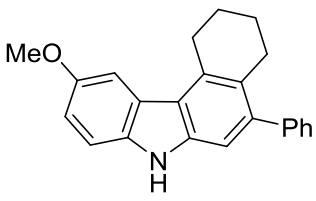
10-Methyl-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ba):

The titled compound **3ba** was synthesized according to the **GP I** by using (*E*)-5-methyl-2-styryl-1*H*-indole (46.7 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ba** (38.9 mg, 0.12 mmol, 62%) was isolated as a white solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.00 (s, 1H), 7.90 (s, 1H), 7.45-7.42 (m, 2H), 7.40-7.36 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.13 (s, 1H), 3.46 (t, *J* = 6.3 Hz, 2H), 2.71 (t, *J* = 6.3 Hz, 2H), 2.56 (s, 3H), 2.05-2.01 (m, 2H), 1.83-1.79 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 143.1, 140.6, 138.3, 137.8, 132.8, 129.7, 128.5, 128.1, 126.7, 126.3, 125.9, 124.2, 123.3, 120.8, 110.1, 109.5, 29.0, 28.9, 23.6, 23.2, 21.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3397, 2927, 1697, 1600, 1448, 1301, 1030, 700. **HRMS (ESI)**: calculated for $C_{23}H_{22}N$ (**[M+H]$^+$**): 312.1747; found 312.1751.



10-Methoxy-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ca):

The titled compound **3ca** was synthesized according to the **GP I** by using (*E*)-5-methoxy-2-styryl-1*H*-indole (49.9 mg, 0.20 mmol, 1.0 equiv) and



cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ca** (34.9 mg, 0.11 mmol, 53%) was isolated as a white sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (s, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.45-7.36 (m, 5H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.13 (s, 1H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.95 (s, 3H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.05-1.99 (m, 2H), 1.83-1.77 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 153.7, 143.0, 140.9, 138.4, 135.1, 132.8, 129.6, 128.1, 126.8, 125.8, 124.6, 121.0, 113.4, 110.8, 109.6, 107.2, 56.4, 29.0, 28.7, 23.6, 23.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3408, 2926, 1580, 1486, 1297, 1210, 1031. **HRMS (ESI)**: calculated for $C_{23}H_{22}NO$ (**[M+H]$^+$**): 328.1696; found 328.1703.

10-Chloro-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3da):

The titled compound **3da** was synthesized according to the **GP I** by using (*E*)-5-chloro-2-styryl-1*H*-indole (50.7 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3da** (45.8 mg, 0.14 mmol, 69%) was isolated as a white solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 1H), 8.00 (s, 1H), 7.44 (d, *J* = 6.8 Hz, 2H), 7.39-7.32 (m, 5H), 7.14 (s, 1H), 3.40 (t, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 5.6 Hz, 2H), 2.03-2.01 (m, 2H), 1.82-1.81 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 142.7, 141.6, 138.3, 138.1, 133.1, 129.6, 128.1, 126.9, 126.6, 125.08, 125.05, 124.7, 122.7, 120.2, 111.3, 109.6, 29.0, 28.7, 23.5, 23.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3417, 2926, 1705, 1601, 1447, 1287, 1028. **HRMS (ESI)**: calculated for $C_{22}H_{19}ClN$ (**[M+H]$^+$**): 332.1201; found 332.1196.

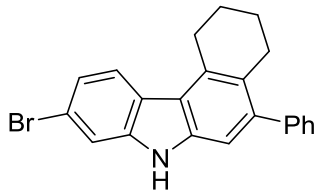
10-Bromo-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ea):

The titled compound **3ea** was synthesized according to the **GP I** by using (*E*)-5-bromo-2-styryl-1*H*-indole (59.6 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ea** (54.3 mg, 0.14 mmol, 72%) was isolated as a white solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 8.01 (s, 1H), 7.49 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.47-7.43 (m, 2H), 7.40-7.37 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 1H), 3.39 (t, *J* = 6.6 Hz, 2H), 2.70 (t, *J* = 6.2 Hz, 2H), 2.05-1.99 (m, 2H), 1.83-1.78 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 142.7, 141.6, 138.6, 137.9, 133.1, 129.6, 128.1, 127.7, 126.9, 126.7, 125.7, 125.6, 120.1, 112.1, 111.8, 109.6, 29.0, 28.7, 23.5, 23.0. **FTIR**: ν_{max}

(neat)/ cm^{-1} = 3416, 2924, 1712, 1600, 1452, 1288, 1026, 580. **HRMS (ESI)**: calculated for $C_{22}H_{19}BrN$ (**[M+H]**$^+$): 376.0695; found 376.0696.

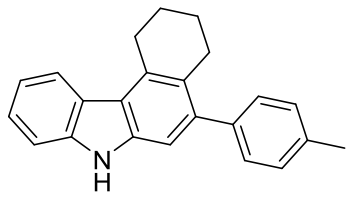
9-Bromo-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3fa):

The titled compound **3fa** was synthesized according to the **GP I** by using (*E*)-6-bromo-2-styryl-1*H*-indole (59.6 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3fa** (46.1 mg, 0.12 mmol, 61%) was isolated as a yellow solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.56-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.39-7.37 (m, 3H), 7.34 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.16-7.14 (m, 1H), 3.39 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.04-1.98 (m, 2H), 1.83-1.77 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 142.8, 141.4, 140.8, 137.6, 132.9, 129.6, 128.1, 126.9, 126.8, 124.2, 123.0, 122.6, 120.4, 118.7, 113.4, 109.6, 29.0, 28.7, 23.5, 23.1. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3410, 2923, 1712, 1600, 1438, 1623, 1026, 903. **HRMS (ESI)**: calculated for $C_{22}H_{19}BrN$ (**[M+H]**$^+$): 376.0695; found 376.0691.



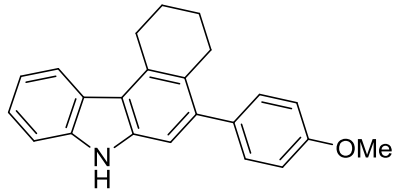
5-(*p*-Tolyl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ga):

The titled compound **3ga** was synthesized according to the **GP I** by using (*E*)-2-(4-methylstyryl)-1*H*-indole (46.7 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ga** (52.5 mg, 0.17 mmol, 84%) was isolated as a white solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.23 (d, *J* = 7.8 Hz, 1H), 8.02 (s, 1H), 7.46-7.42 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 3H), 7.18 (s, 1H), 3.49 (t, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 5.7 Hz, 2H), 2.47 (s, 3H), 2.05-2.04 (m, 2H), 1.85-1.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 140.8, 140.1, 140.0, 137.5, 136.4, 132.8, 129.5, 128.8, 126.3, 125.0, 124.1, 123.2, 120.8, 119.3, 110.4, 109.5, 29.1, 28.8, 23.6, 23.2, 21.4. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3397, 2928, 1607, 1440, 1330, 1261, 1115, 1030. **HRMS (ESI)**: calculated for $C_{23}H_{22}N$ (**[M+H]**$^+$): 312.1747; found 312.1752.



5-(4-Methoxyphenyl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ha):

The titled compound **3ha** was synthesized according to the **GP I** by using (*E*)-2-(4-methoxystyryl)-1*H*-indole (49.9 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The



carbazole **3ha** (34.3 mg, 0.10 mmol, 52%) was isolated as a white solid after column chromatography on silica gel by using 3% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.43-7.39 (m, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.26-7.23 (m, 1H), 7.14 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 3.46 (t, *J* = 6.3 Hz, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 2.04-2.00 (m, 2H), 1.84-1.80 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 158.6, 140.4, 140.0, 137.5, 135.4, 132.8, 130.7, 126.4, 125.0, 124.1, 123.2, 120.8, 119.3, 113.5, 110.4, 109.6, 55.4, 29.1, 28.8, 23.7, 23.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3350, 2925, 1713, 1607, 1512, 1240, 1032, 827, 731. **HRMS (ESI)**: calculated for $C_{23}H_{22}NO$ (**[M+H]$^+$**): 328.1696; found 328.1701.

5-(2-Fluorophenyl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ia):

The titled compound **3ia** was synthesized according to the **GP I** by using (*E*)-2-(2-fluorostyryl)-1*H*-indole (47.5 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ia** (39.8 mg, 0.13 mmol, 63%) was isolated as a white sticky solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.26 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 7.49-7.45 (m, 2H), 7.44-7.40 (m, 1H), 7.37 (td, *J* = 7.5, 1.6 Hz, 1H), 7.31-7.30 (m, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.23-7.20 (m, 2H), 3.52-3.49 (m, 2H), 2.75-2.63 (m, 2H), 2.09-2.07 (m, 2H), 1.92-1.85 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 160.0 (d, 244.6 Hz), 140.1, 137.4, 134.2, 132.9, 132.0 (d, 4.5 Hz), 130.2 (d, 16.6 Hz), 129.0 (d, 7.6 Hz), 127.0, 125.2, 124.0 (d, 3.0 Hz), 123.3, 121.6, 119.4, 115.6 (d, 22.7 Hz), 110.5, 109.8, 28.7, 27.9, 23.4, 23.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) -114.32. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3398, 2929, 1710, 1604, 1454, 1261, 1117, 1027, 929. **HRMS (ESI)**: calculated for $C_{22}H_{19}FN$ (**[M+H]$^+$**): 316.1496; found 316.1502.

5-(2-Nitrophenyl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ja):

The titled compound **3ja** was synthesized according to the **GP I** by using (*E*)-2-(2-nitrostyryl)-1*H*-indole (52.9 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ja** (35.1 mg, 0.10 mmol, 51%) was isolated as a yellow solid after column chromatography on silica gel by using 6% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.18 (d, *J* = 8.0 Hz, 1H), 8.02-7.98 (m, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.43-7.38 (m, 3H), 7.25-7.21 (m, 1H), 7.04 (s, 1H), 3.50-3.36 (m, 2H), 2.54-2.45 (m, 2H), 2.05-1.96 (m, 2H), 1.85-1.78 (m,

2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 149.5, 140.0, 137.5, 137.2, 135.7, 133.0, 132.7, 132.5, 128.2, 126.1, 125.3, 124.1, 123.9, 123.2, 121.6, 119.4, 110.5, 108.1, 28.6, 28.2, 23.2, 23.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3405, 2924, 1711, 1606, 1521, 1345, 1264, 1160, 1032, 850, 729. **HRMS (ESI)**: calculated for $C_{22}H_{19}N_2O_2$ (**[M+H]$^+$**): 343.1441; found 343.1447.

5-(Naphthalen-1-yl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ka):

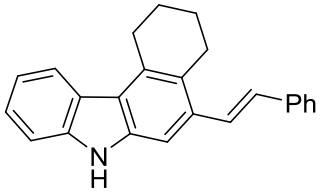
The titled compound **3ka** was synthesized according to the **GP I** by using (*E*)-2-(2-(naphthalen-1-yl)vinyl)-1*H*-indole (53.9 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ka** (52.3 mg, 0.15 mmol, 75%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 2% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.26 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 7.95-7.89 (m, 2H), 7.58-7.47 (m, 3H), 7.44-7.35 (m, 4H), 7.30-7.26 (m, 1H), 7.17 (s, 1H), 3.53-3.46 (m, 2H), 2.54-2.47 (m, 1H), 2.40-2.33 (m, 1H), 2.03-1.97 (m, 2H), 1.77-1.71 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 140.9, 140.0, 138.8, 137.5, 133.7, 132.7, 132.6, 128.3, 127.4, 126.9, 126.6, 126.1, 125.8, 125.5, 125.1, 124.1, 123.2, 121.2, 119.4, 110.5, 110.1, 28.8, 28.0, 23.4, 23.2. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3411, 2926, 1703, 1607, 1452, 1263, 1126, 956, 730. **HRMS (ESI)**: calculated for $C_{26}H_{22}N$ (**[M+H]$^+$**): 348.1747; found 348.1751.

5-(Thiophen-2-yl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3la):

The titled compound **3la** was synthesized according to the **GP I** by using (*E*)-2-(2-(thiophen-2-yl)vinyl)-1*H*-indole (45.1 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3la** (49.2 mg, 0.16 mmol, 81%) was isolated as a pale-yellow sticky solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.20 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.37 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.33 (s, 1H), 7.27-7.23 (m, 1H), 7.14-7.12 (m, 1H), 7.10 (dd, *J* = 3.2, 1.2 Hz, 1H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.92 (t, *J* = 6.2 Hz, 2H), 2.08-2.00 (m, 2H), 1.89-1.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 144.0, 140.2, 137.3, 133.2, 132.5, 127.1, 127.0, 126.9, 125.3, 125.1, 123.9, 123.3, 121.6, 119.5, 110.6, 110.5, 29.1, 28.9, 23.6, 23.0. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3407, 2923, 1712, 1607, 1447, 1264, 825. **HRMS (ESI)**: calculated for $C_{22}H_{18}NS$ (**[M+H]$^+$**): 304.1154; found 304.1156.

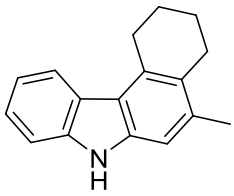
(*E*)-5-Styryl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3ma):

The titled compound **3ma** was synthesized according to the **GP I** by using 2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)-1*H*-indole (49.1 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3ma** (27.3 mg, 0.08 mmol, 42%) was isolated as a white solid after column chromatography on silica gel by using 1.5% ethylacetate in hexane as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 8.16 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.57-7.51 (m, 4H), 7.44-7.37 (m, 4H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 16.0 Hz, 1H), 3.40 (t, *J* = 6.0 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 2.03-1.95 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 140.3, 138.1, 138.0, 135.3, 132.9, 130.1, 128.9, 128.0, 127.6, 126.7, 126.6, 125.2, 124.2, 123.1, 121.6, 119.4, 110.4, 105.3, 28.8, 27.5, 23.4, 22.9. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3379, 3026, 2928, 1597, 1448, 1330, 1263, 1135, 959, 840. **HRMS (ESI)**: calculated for $C_{24}H_{22}N$ (**[M+H]$^+$**): 324.1747; found 324.1740.



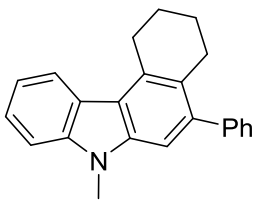
5-Methyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3na):

The titled compound **3na** was synthesized according to the **GP I** by using (*E*)-2-(prop-1-en-1-yl)-1*H*-indole (31.4 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3na** (17.1 mg, 0.07 mmol, 36%) was isolated as a yellowish sticky solid after column chromatography on silica gel by using 1% ethylacetate in hexane as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.14 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H), 7.42-7.34 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.12 (s, 1H), 3.38 (t, *J* = 5.8 Hz, 2H), 2.76 (t, *J* = 5.6 Hz, 2H), 2.39 (s, 3H), 2.04-1.92 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 139.6, 137.8, 135.2, 132.6, 127.1, 124.5, 124.3, 122.8, 119.8, 119.1, 110.3, 109.1, 28.7, 27.2, 23.5, 23.0, 20.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3403, 3054, 2922, 1715, 1606, 1454, 1263, 1081, 966, 850. **HRMS (ESI)**: calculated for $C_{17}H_{18}N$ (**[M+H]$^+$**): 236.1434; found 236.1439.



7-Methyl-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (3oa):[3]

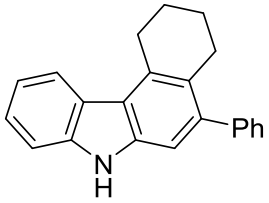
The titled compound **3oa** was synthesized according to the **GP I** by using (*E*)-1-methyl-2-styryl-1*H*-indole (46.7 mg, 0.20 mmol, 1.0 equiv) and cyclohexanone (41.4 μL, 0.40 mmol, 2.0 equiv). The carbazole **3oa** (49.4 mg, 0.16 mmol, 79%) was isolated as a white solid after column chromatography on silica gel by using 0.5% ethylacetate in hexane as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.22 (d, *J* = 7.8 Hz, 1H), 7.49-7.41 (m, 6H), 7.39-7.36 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 3.83 (s, 3H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.05-2.01 (m, 2H), 1.84-1.80 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$):



δ (ppm) 143.4, 141.5, 140.6, 139.1, 132.9, 129.7, 128.1, 126.8, 125.6, 124.9, 123.5, 123.2, 120.3, 118.8, 108.2, 107.6, 29.1, 29.0, 28.8, 23.7, 23.3.

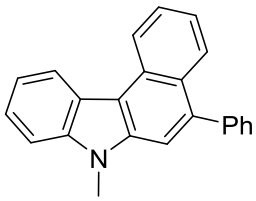
Gram-scale synthesis of 3aa:

To a mixture of (*E*)-2-styryl-1*H*-indole derivative **2** (3.0 mmol, 1.0 equiv) and diphenyl phosphate (15 mol %, 112.6 mg) in a screw cap 30 mL seal reaction tube, 3.0 mL of ethyl acetate and 6.0 mL of decalin were added. After addition of electrophile **1** (6.0 mmol, 2.0 equiv), air of the reaction tube was replaced by purging with pure oxygen. Next, the resulting mixture was stirred at 180 ºC for 48 hours. The progress of the reaction was monitored by TLC. On complete consumption of all the intermediates as indicated by TLC, the crude residue was diluted with ethylacetate, and transferred to a round bottom flask. After evaporating the ethylacetate in *vacuo*, the crude product was purified by silica gel column chromatography by using 6% ethylacetate in hexane as eluent to obtain the pure desired tetrahydro benzo[*c*]carbazole **3aa** (0.70 g, 2.34 mmol, 78%) as a pale-yellow solid.



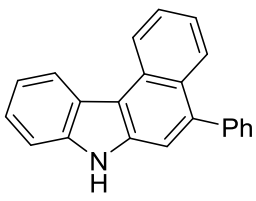
Synthesis of compound 4:[3]

The compound 7-methyl-5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole **3oa** (77.9 mg, 0.25 mmol, 1.0 equiv) and iodine (12.7mg, 0.05 mmol, 20 mol %) were taken in a screw cap seal reaction tube. The reaction tube was purged with oxygen gas and then 0.5 mL of toluene was added. The resulting mixture was stirred at 160 ºC for 24 hours. The progress of the reaction was monitored by TLC. On complete consumption, the crude residue was diluted with ethylacetate, and carefully transferred to a round bottom flask. After evaporating the ethylacetate in *vacuo*, the crude product was purified by silica gel column chromatography by using 1% ethylacetate in hexane as eluent to obtain the pure desired benzo[*c*]carbazole **4** (68.5 mg, 0.22 mmol, 89%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.88 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.62-7.59 (m, 3H), 7.56-7.46 (m, 5H), 7.43-7.39 (m, 2H), 4.00 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 141.8, 140.3, 139.7, 138.1, 130.51, 130.46, 128.4, 127.7, 127.6, 127.5, 126.9, 124.3, 123.6, 123.5, 122.9, 122.2, 120.0, 114.6, 111.9, 109.2, 29.4.



Synthesis of compound 5:

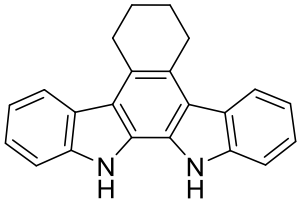
The titled compound **5** was synthesized using 5-phenyl-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole **3aa** (74.4 mg, 0.25 mmol, 1.0 equiv) and iodine



(12.7mg, 0.05 mmol, 20 mol %) by following the procedure as described above for the synthesis of benzocarbazole **4**. The silica gel column chromatography was performed by using 2% ethylacetate in hexane as eluent to obtain the pure desired benzo[*c*]carbazole **5** (63.9 mg, 0.22 mmol, 87%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.87 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.35 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.57-7.40 (m, 10H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 141.5, 139.9, 138.8, 136.7, 130.5, 128.4, 128.0, 127.7, 127.4, 126.9, 124.5, 124.1, 123.7, 123.2, 122.2, 120.5, 115.2, 113.7, 111.3. **FTIR**: ν_{max} (neat)/ cm^{-1} = 3415, 3051, 2924, 1594, 1495, 1352, 1279, 1146, 1021, 865. **HRMS (ESI)**: calculated for $C_{22}H_{16}N$ (**[M+H]**$^{+}$): 294.1277; found 294.1282.

Synthesis of compound 6:

To a mixture of 5-(2-nitrophenyl)-2,3,4,7-tetrahydro-1*H*-benzo[*c*]carbazole (85.6 mg, 0.25 mmol, 1.0 equiv) and $P(OEt)_3$ (0.5 mL) in a screw cap seal reaction tube, decalin (1.5 mL) was added and the resulting mixture was stirred at 180 ºC for 12 hours. The progress of the reaction was monitored by TLC. On complete consumption, the crude residue was diluted with ethylacetate, and transferred to a round bottom flask. After evaporating the ethylacetate in *vacuo*, the crude product was purified by silica gel column chromatography by using 10% ethylacetate in hexane as eluent to obtain the pure desired indolo[2,3-*a*]carbazole **6** (66.2 mg, 0.21 mmol, 85%) as a white solid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ (ppm) 11.00 (s, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 3.38 (s, 4H), 2.03 (s, 4H). **^{13}C NMR** (126 MHz, DMSO-d_6): δ (ppm) 139.2, 124.1, 123.9, 123.7, 122.4, 122.0, 118.7, 118.5, 111.3, 27.9, 22.8. **FTIR**: ν_{max} (neat)/ cm^{-1} = 2924, 1567, 1457, 1326, 1225, 1033, 742. **HRMS (ESI)**: calculated for $C_{22}H_{19}N_2$ (**[M+H]**$^{+}$): 311.1543; found 311.1540.



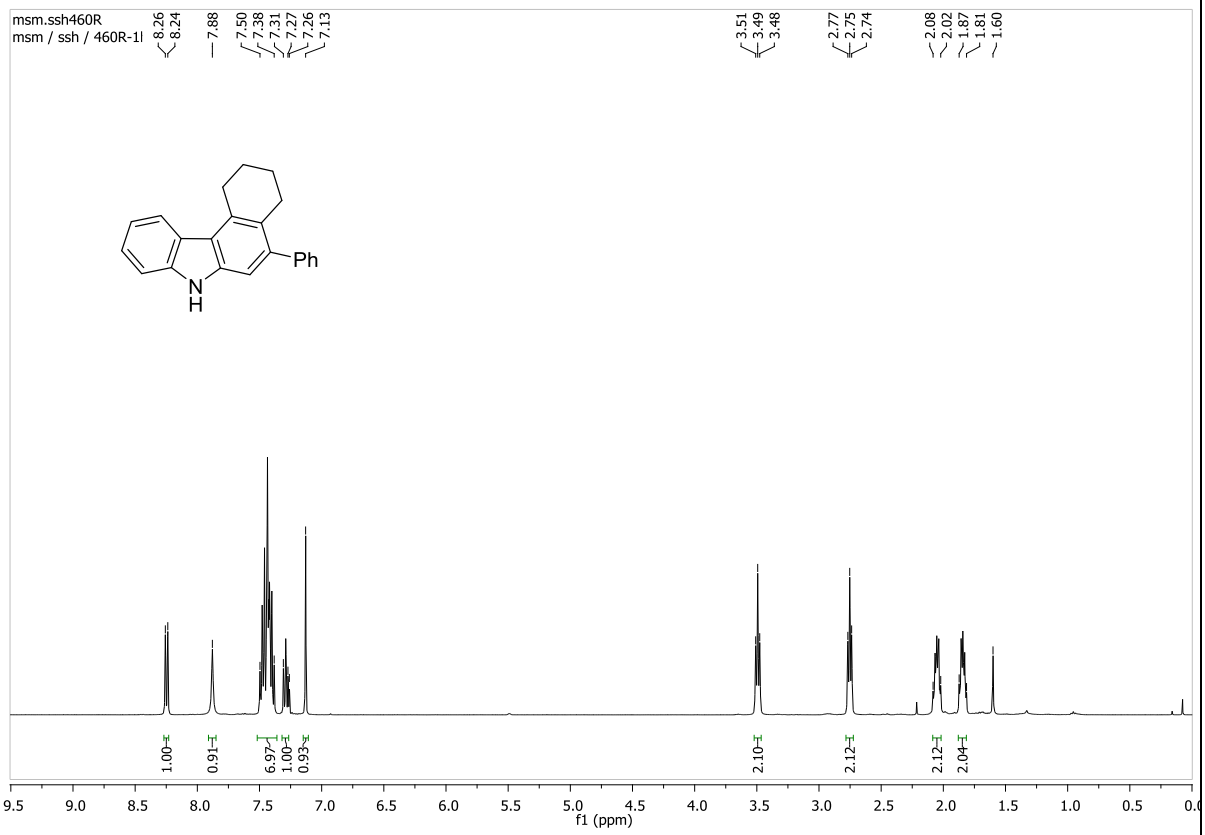
References:

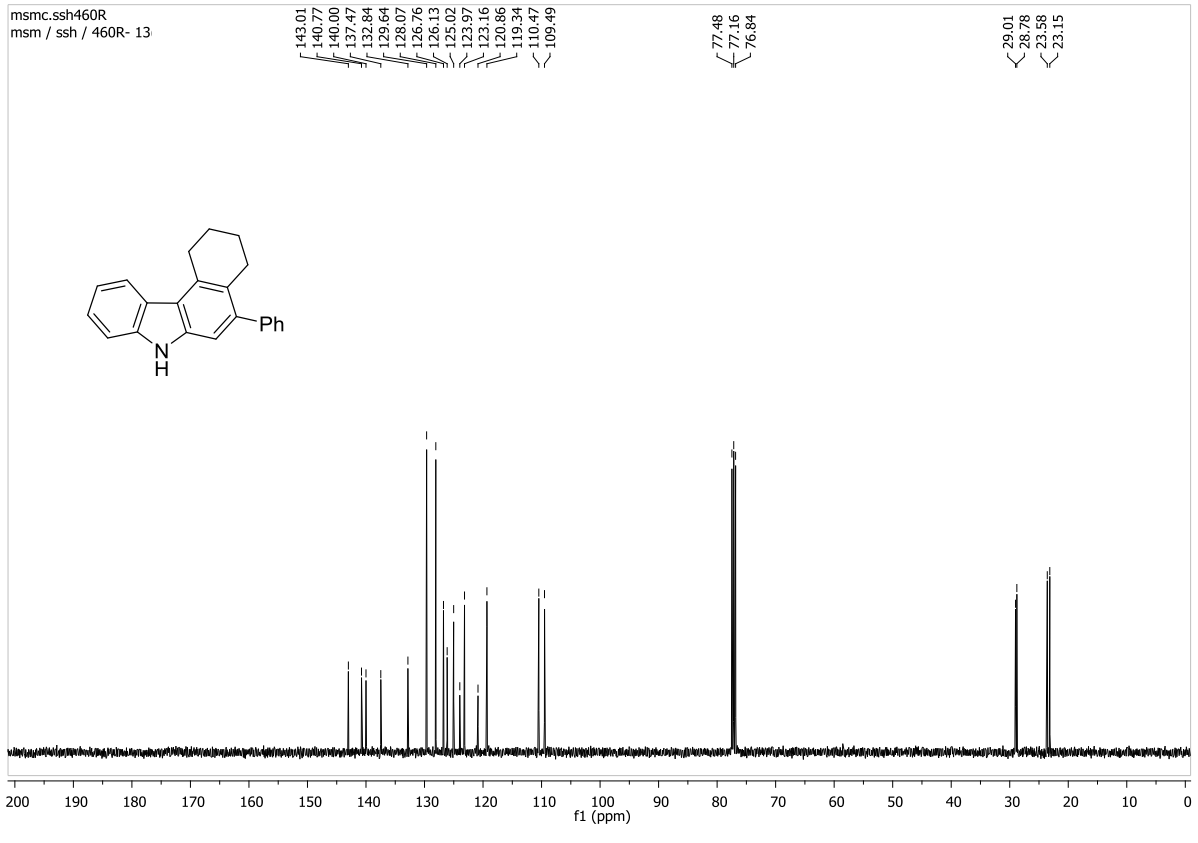
(1) Banerjee, A.; Sahu, S.; Maji, M. S. *Adv. Synth. Catal.* **2017**, *359*, 1860.

(2) Rojas-Martín, J.; Veguillas, M.; Ribagorda, M.; Carreño, M. C. *Org. Lett.* **2013**, *15*, 5686.

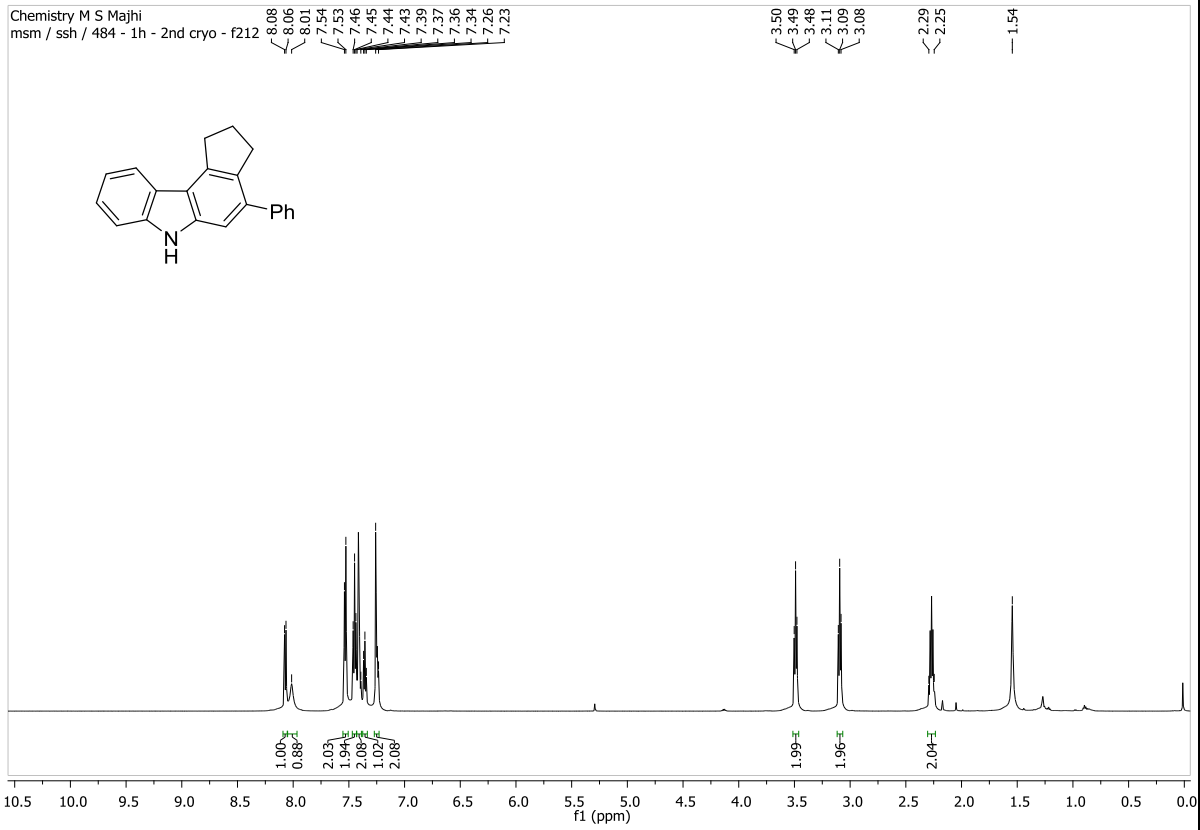
(3) Chen, S.; Li, Y.; Ni, P.; Huang, H.; Deng, G-J. *Org. Lett.* **2016**, *18*, 5384.

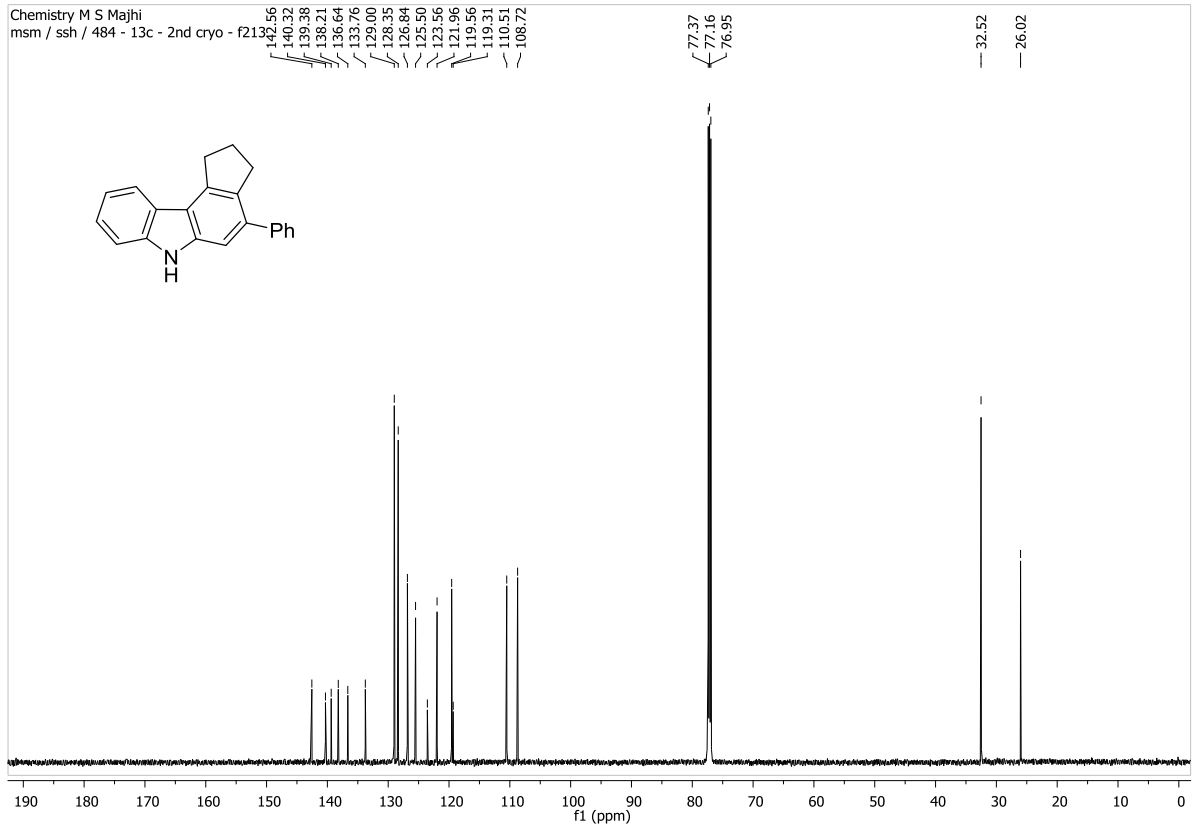
^{1}H NMR and ^{13}C NMR Spectra of Compound **3aa**



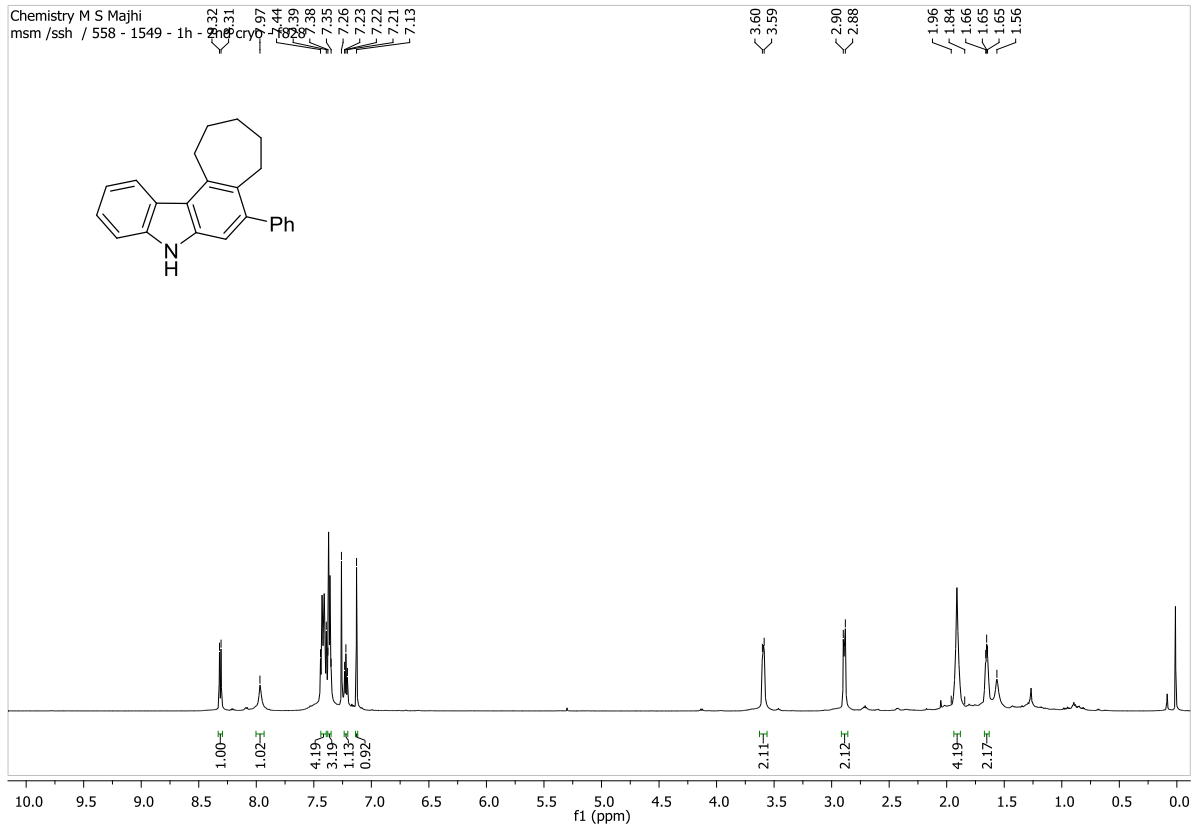


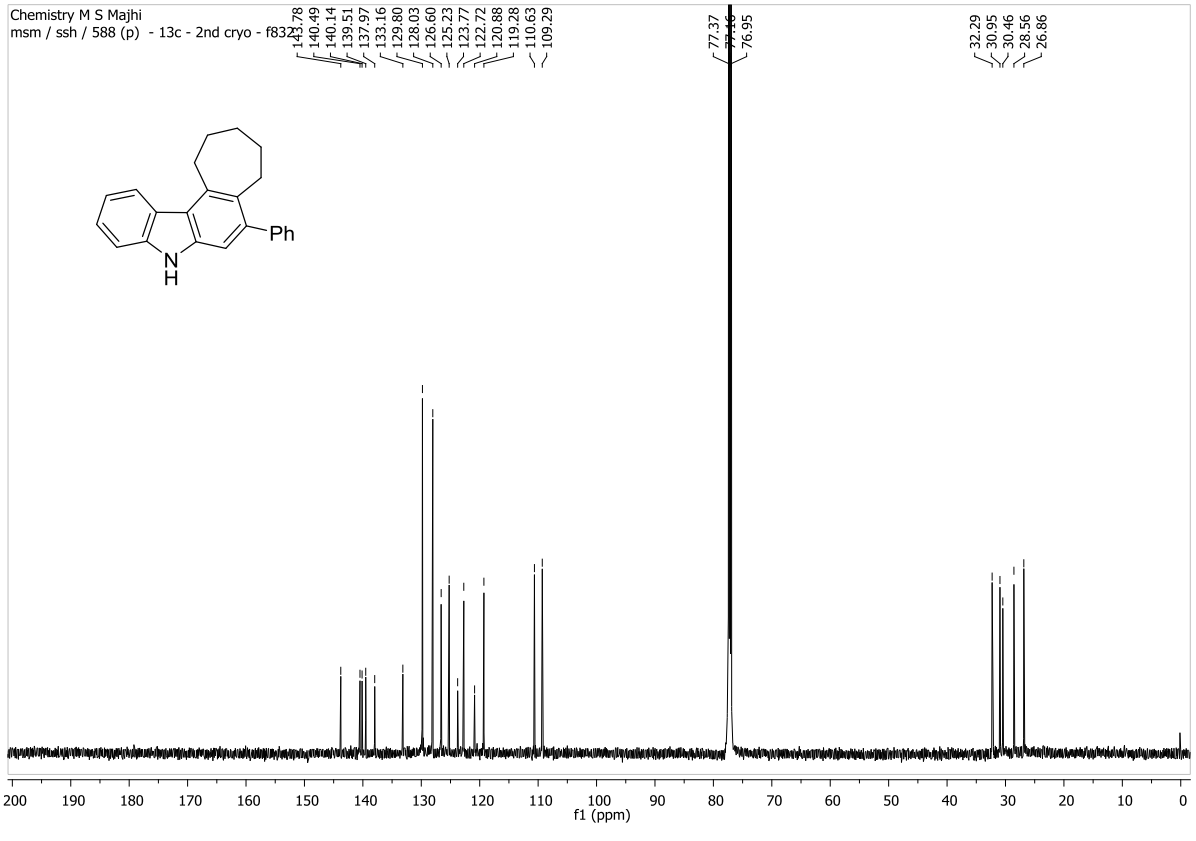
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ab**



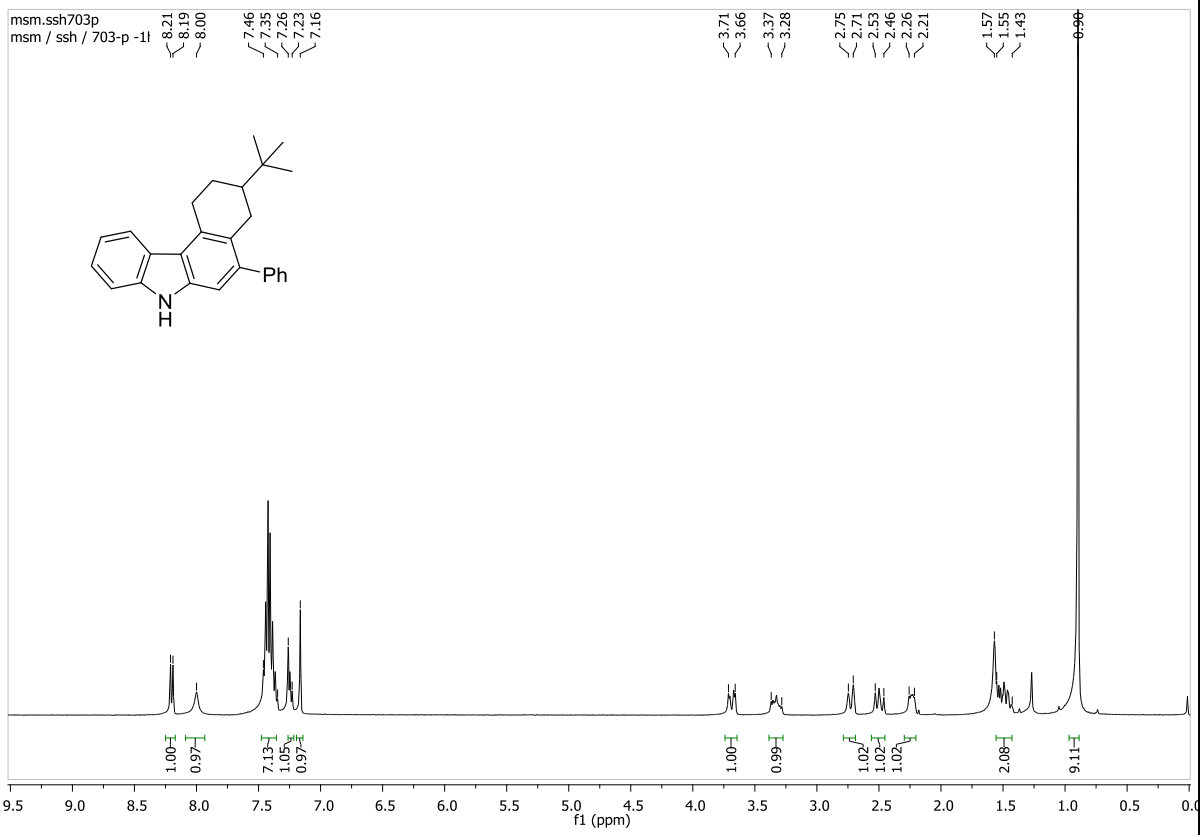


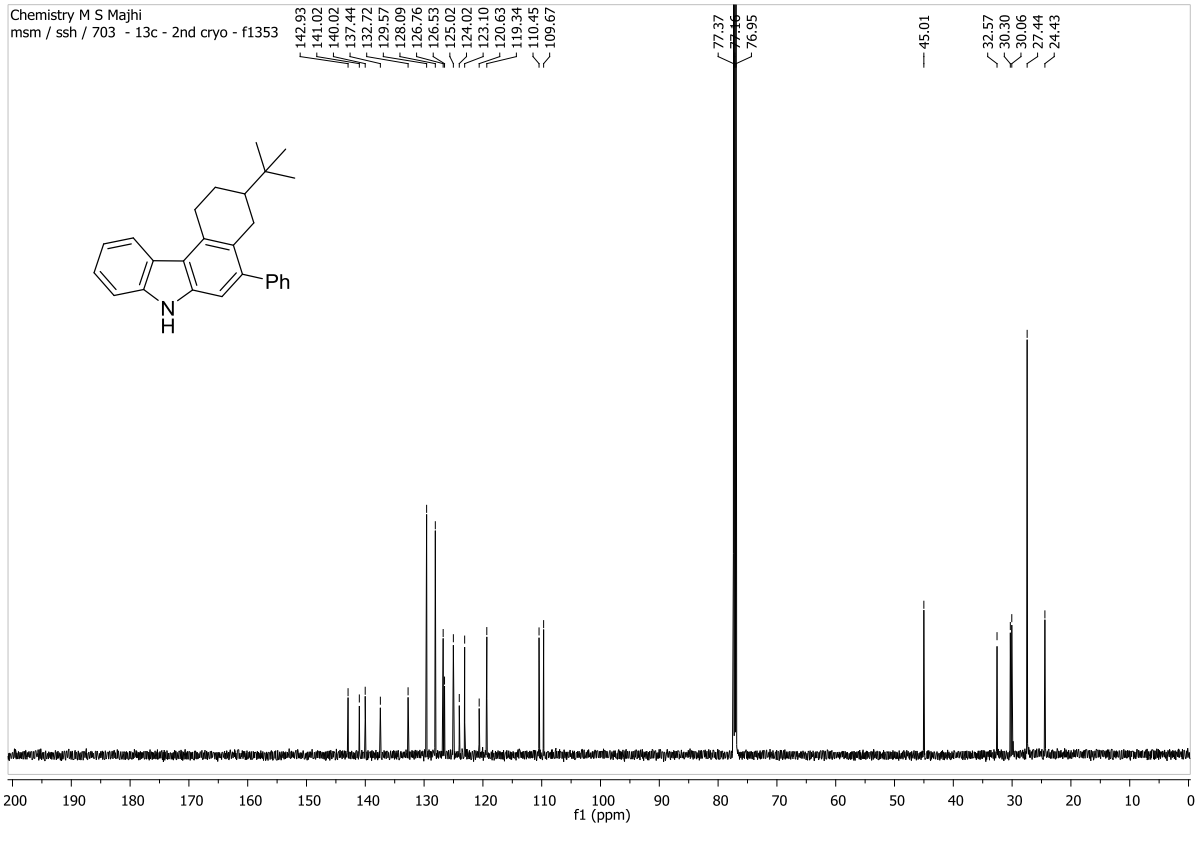
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ac**



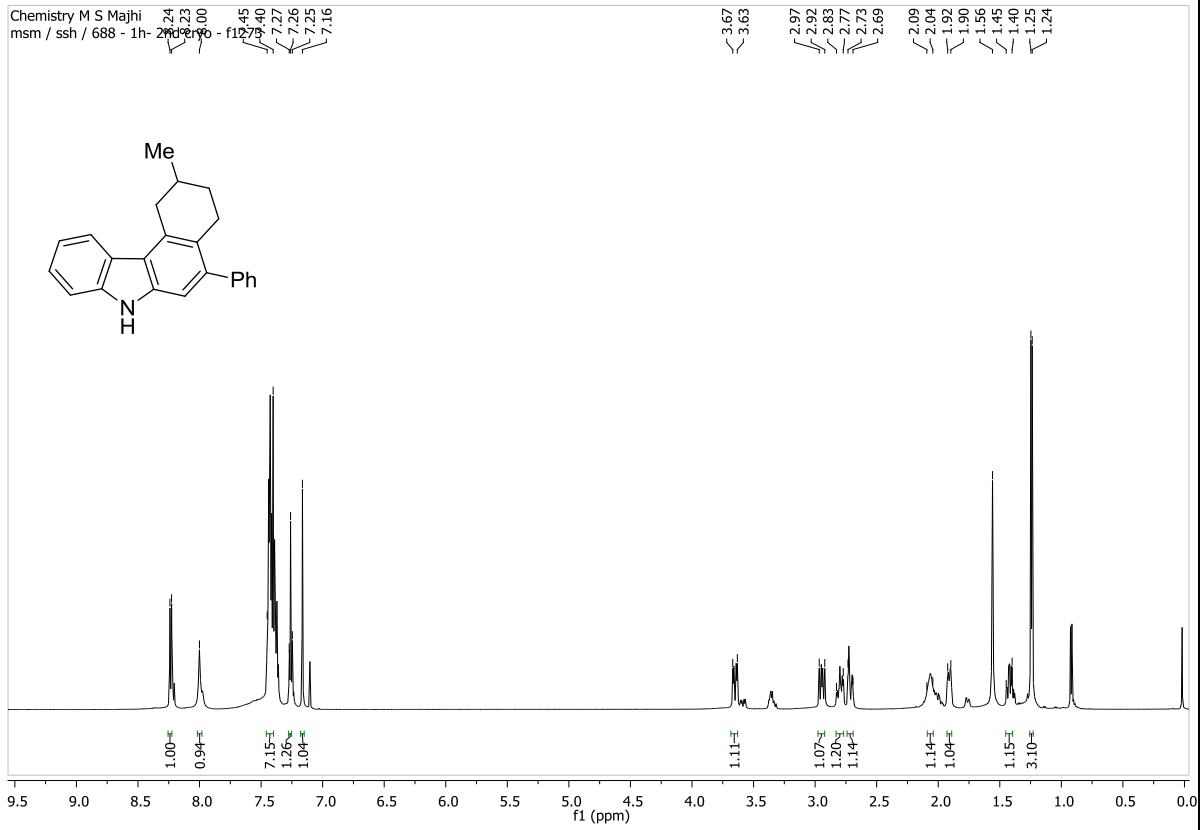


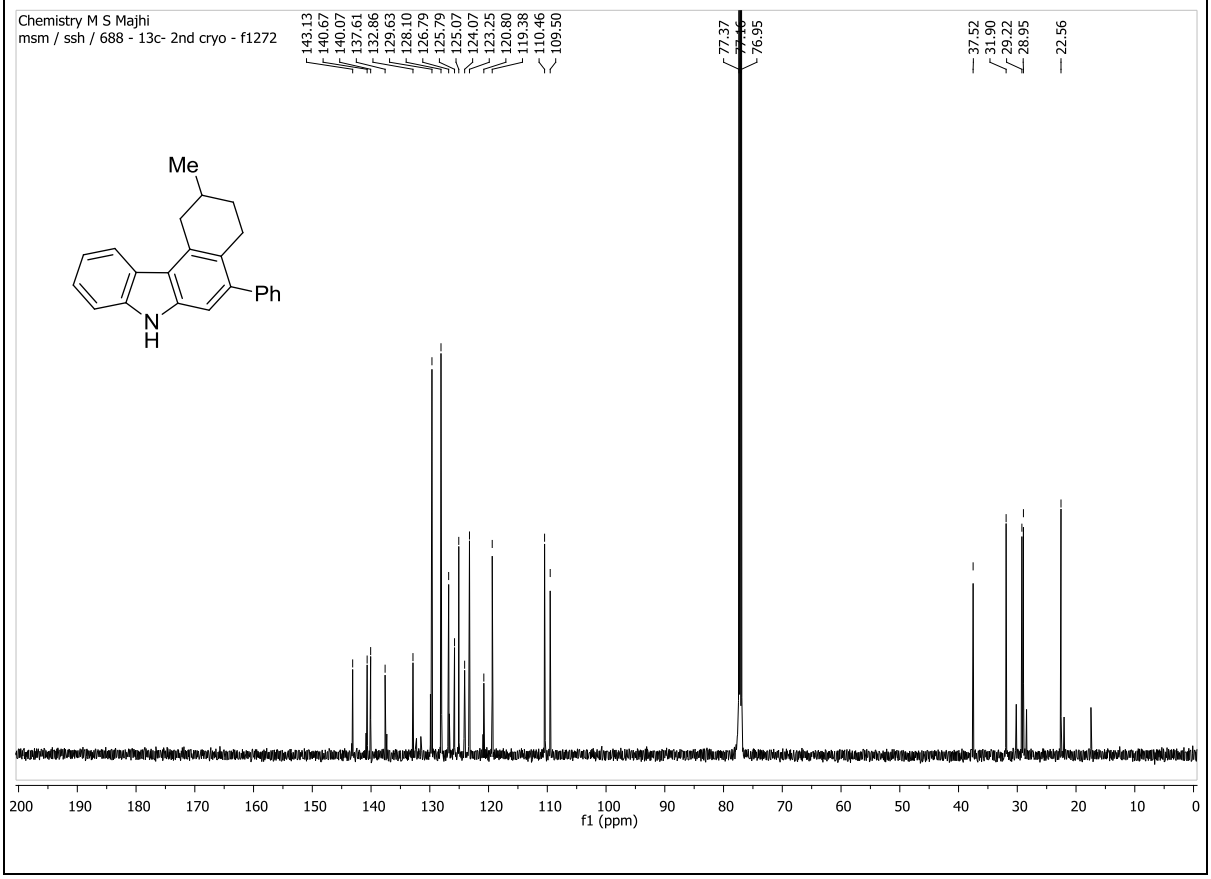
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ad**



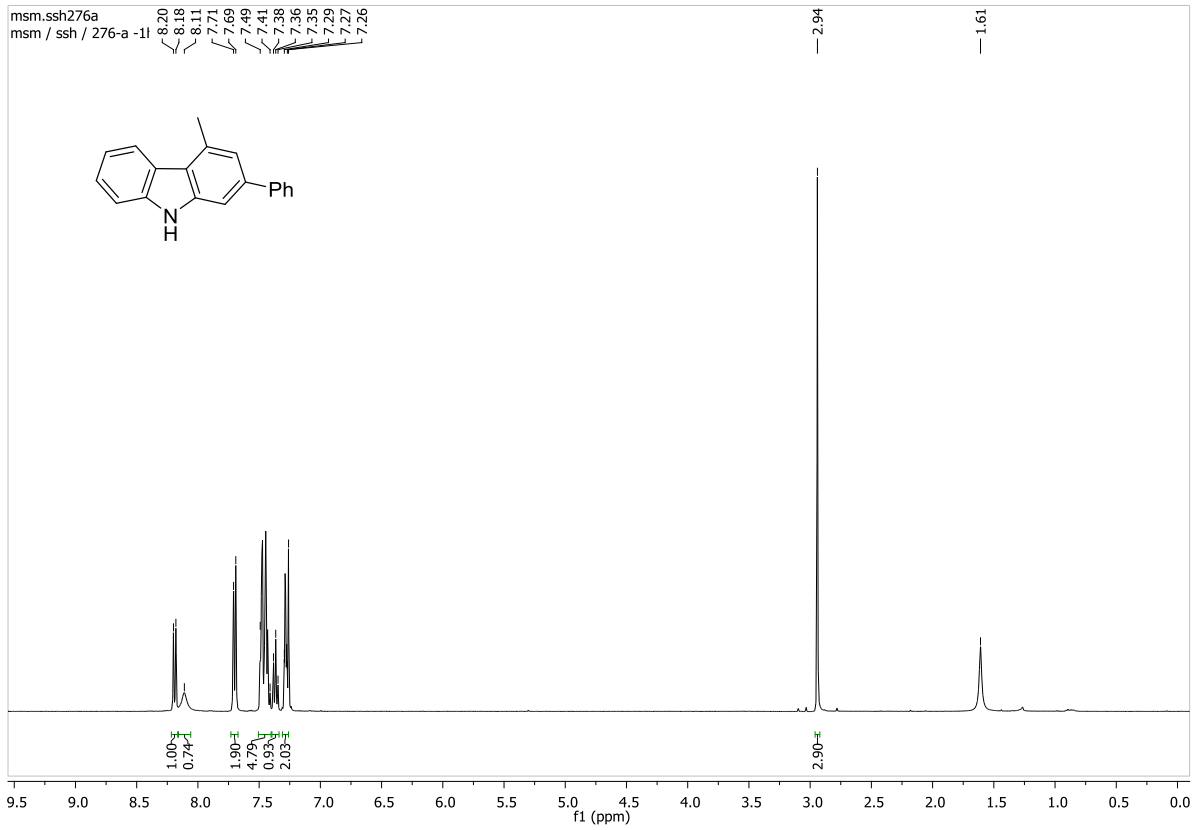


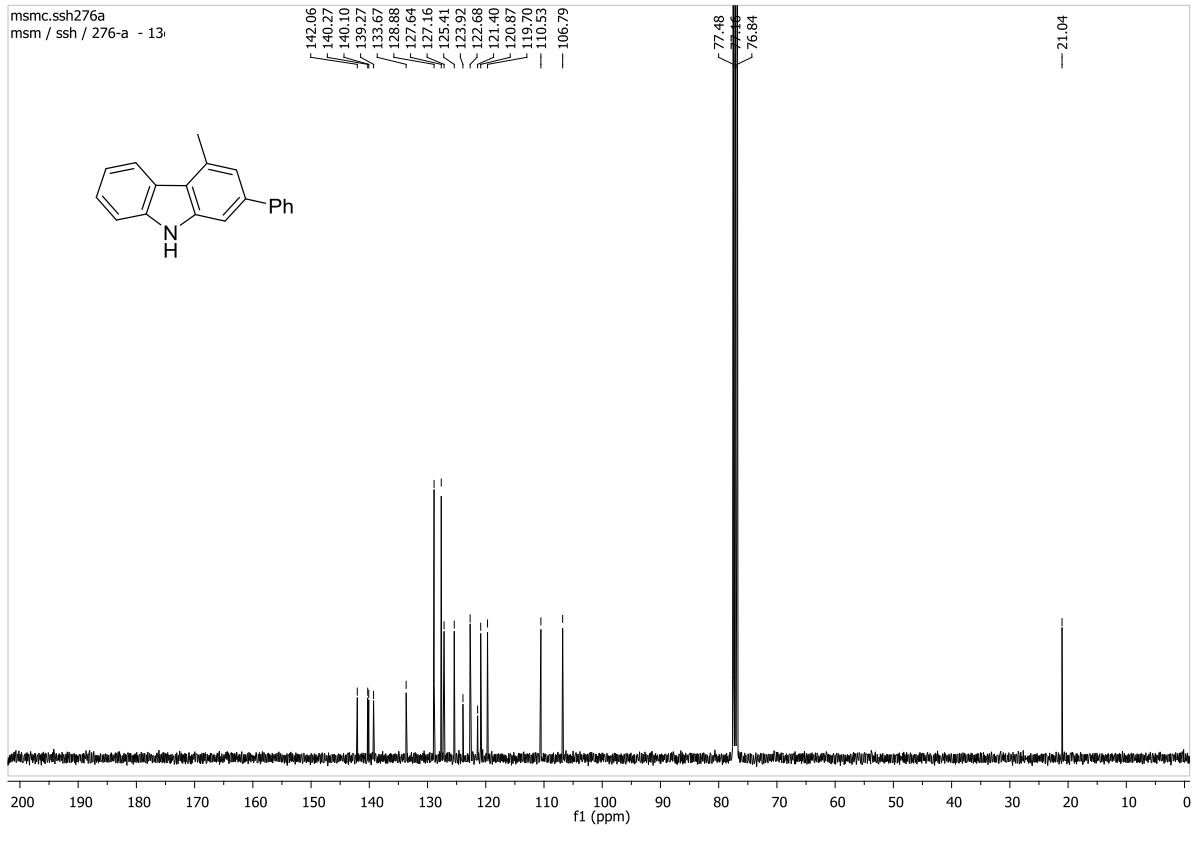
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ae**



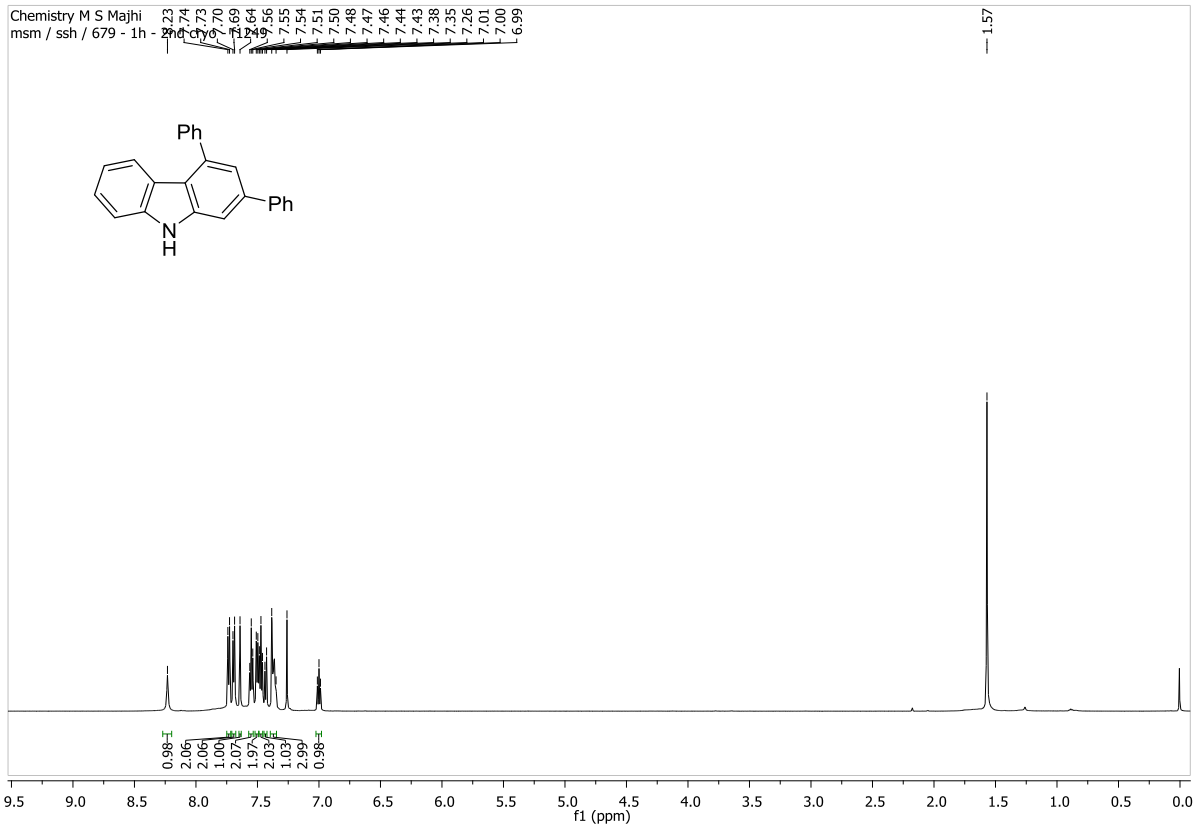


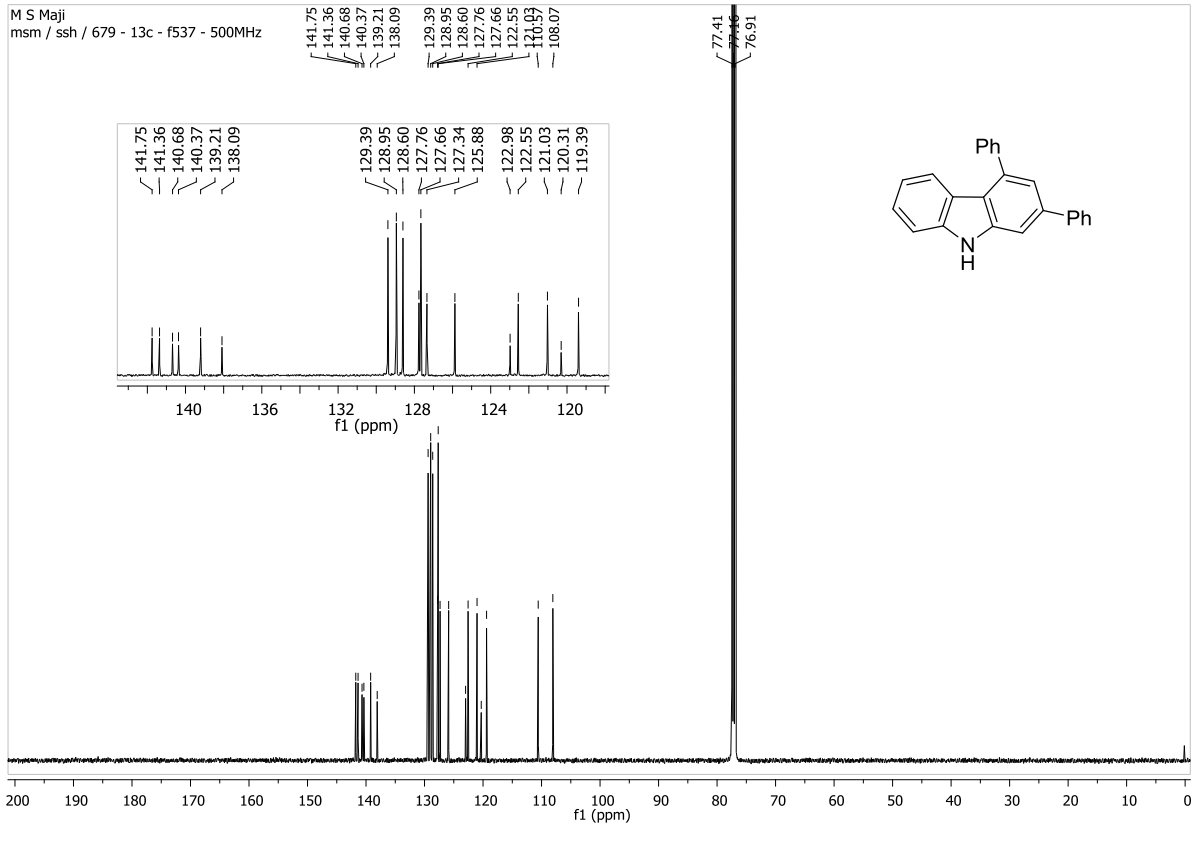
^{1}H NMR and ^{13}C NMR Spectra of Compound **3af**



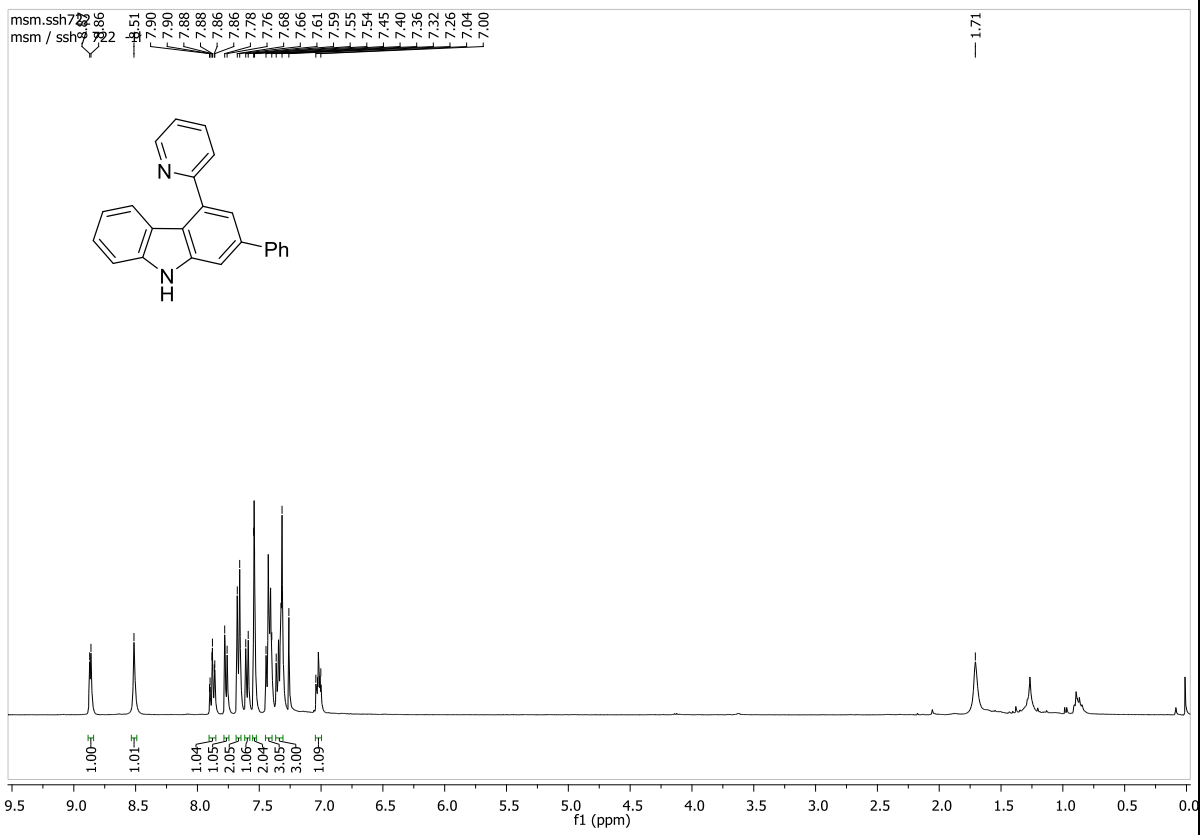


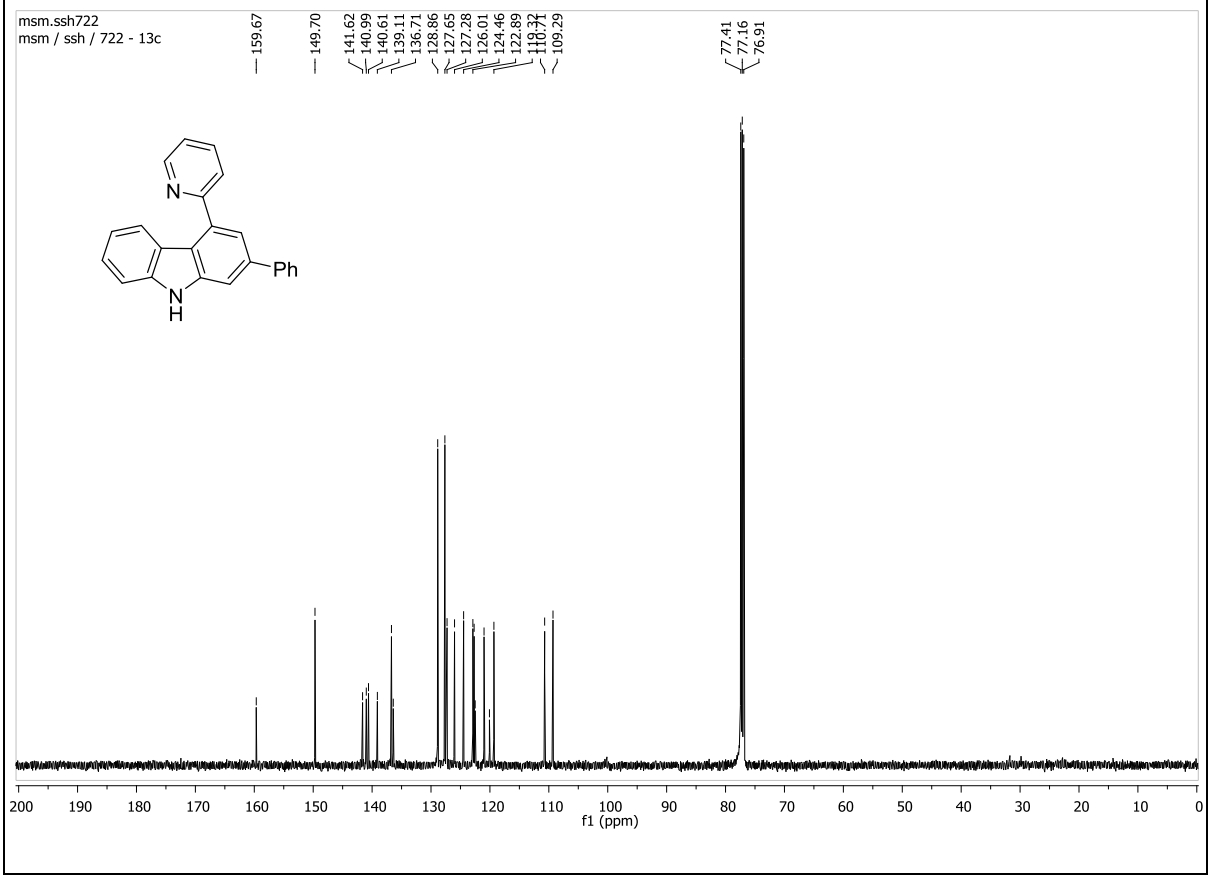
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ag**



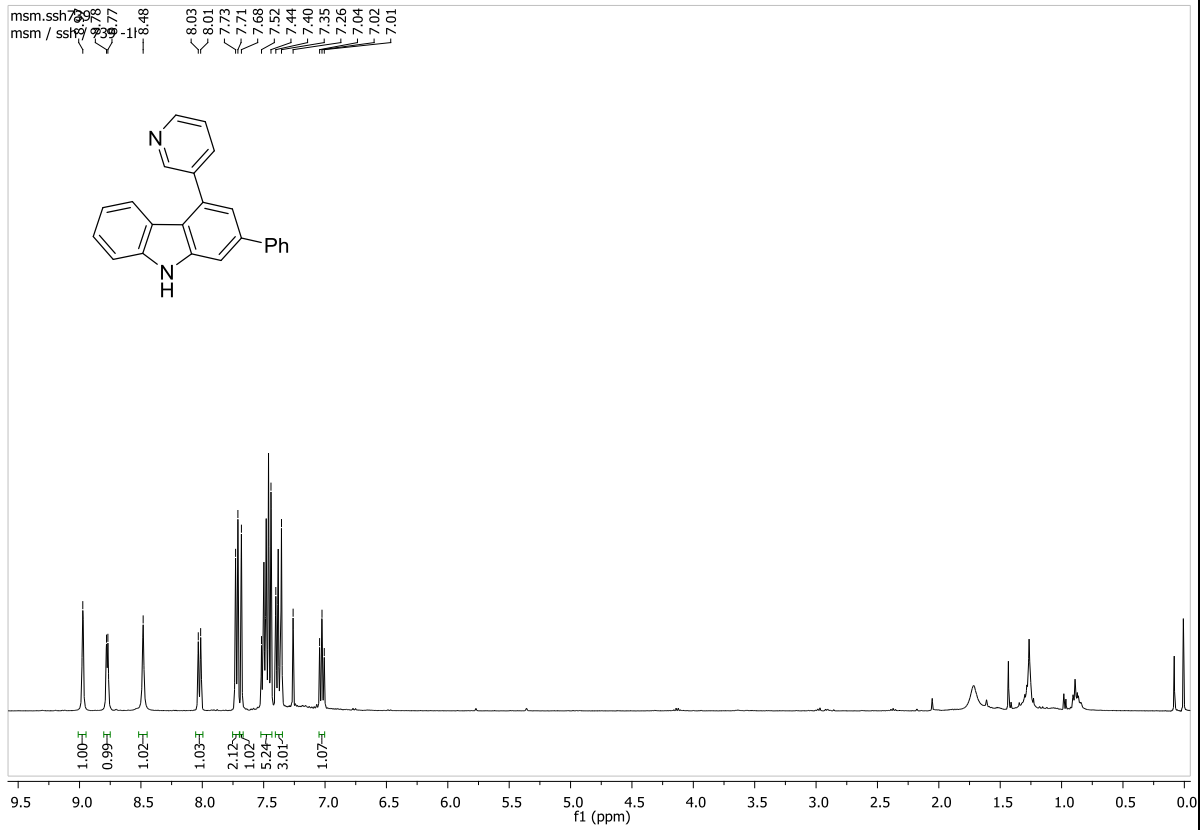


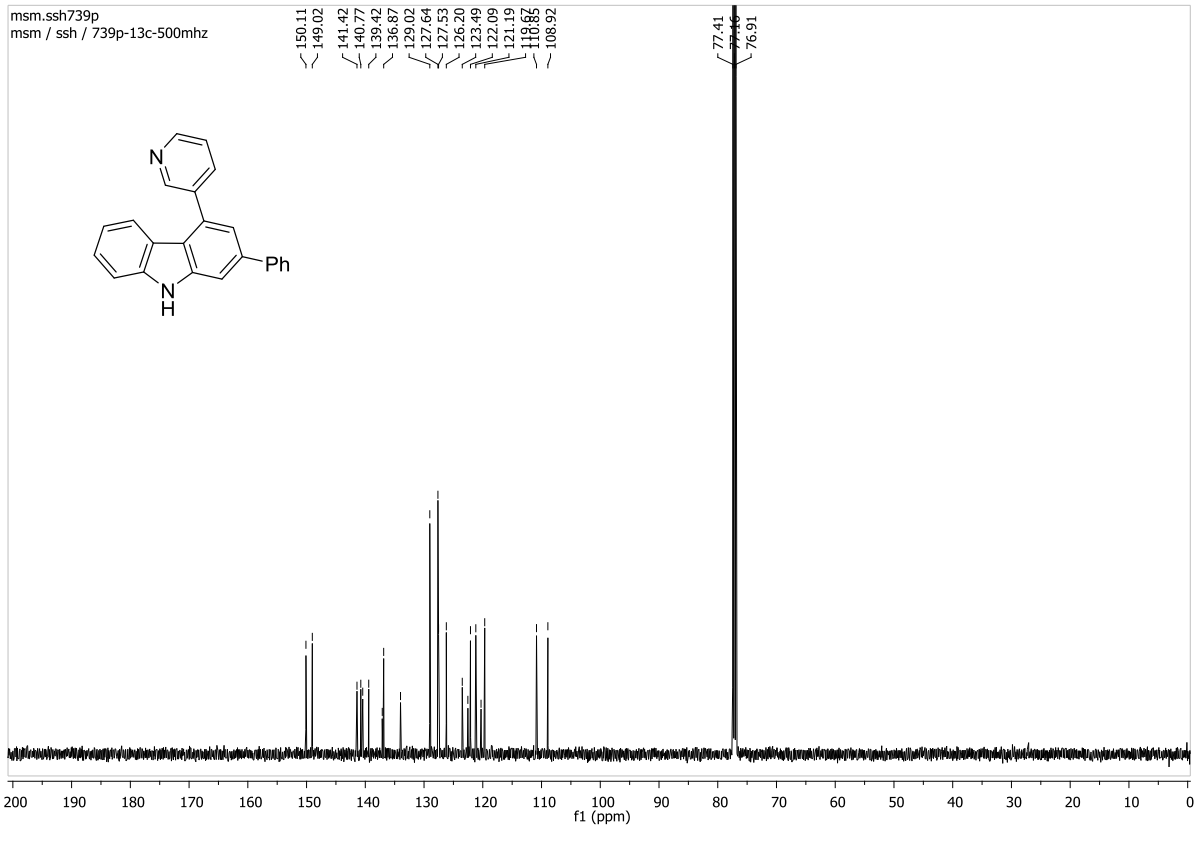
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ah**





^{1}H NMR and ^{13}C NMR Spectra of Compound **3ai**





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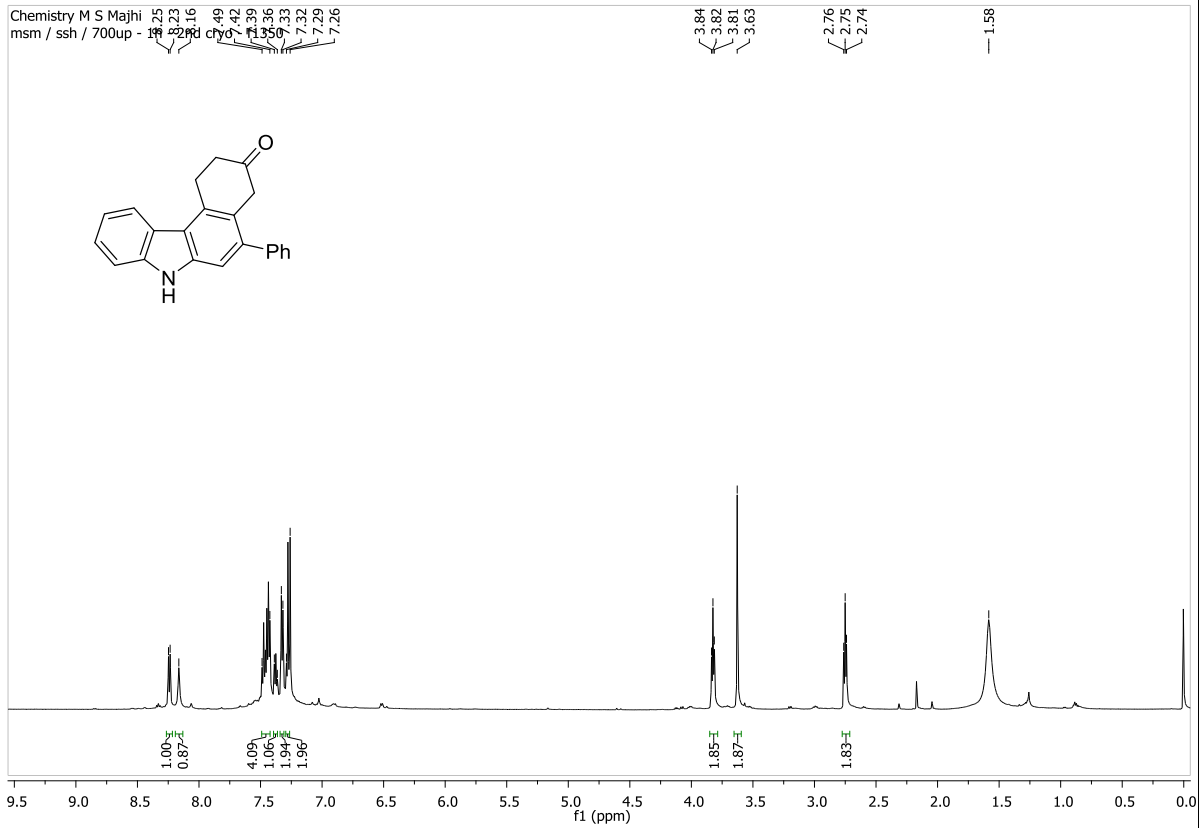

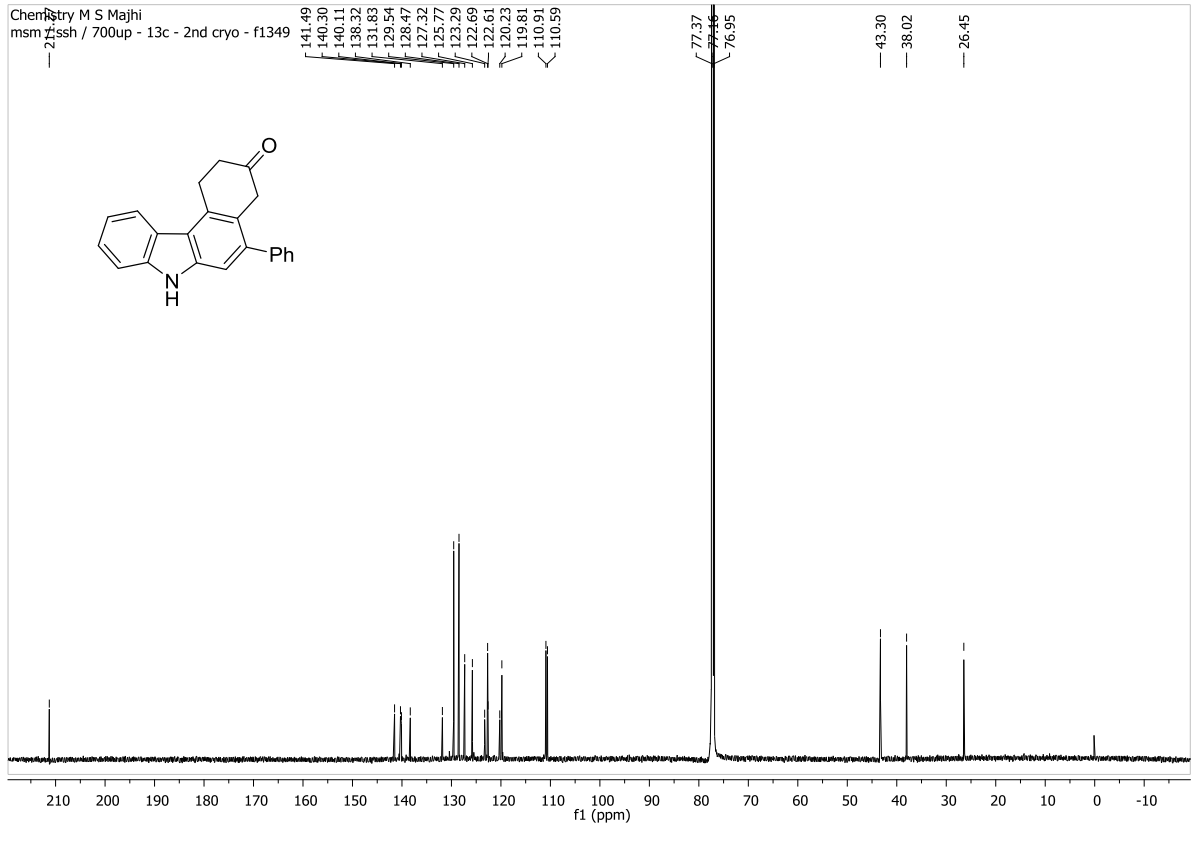

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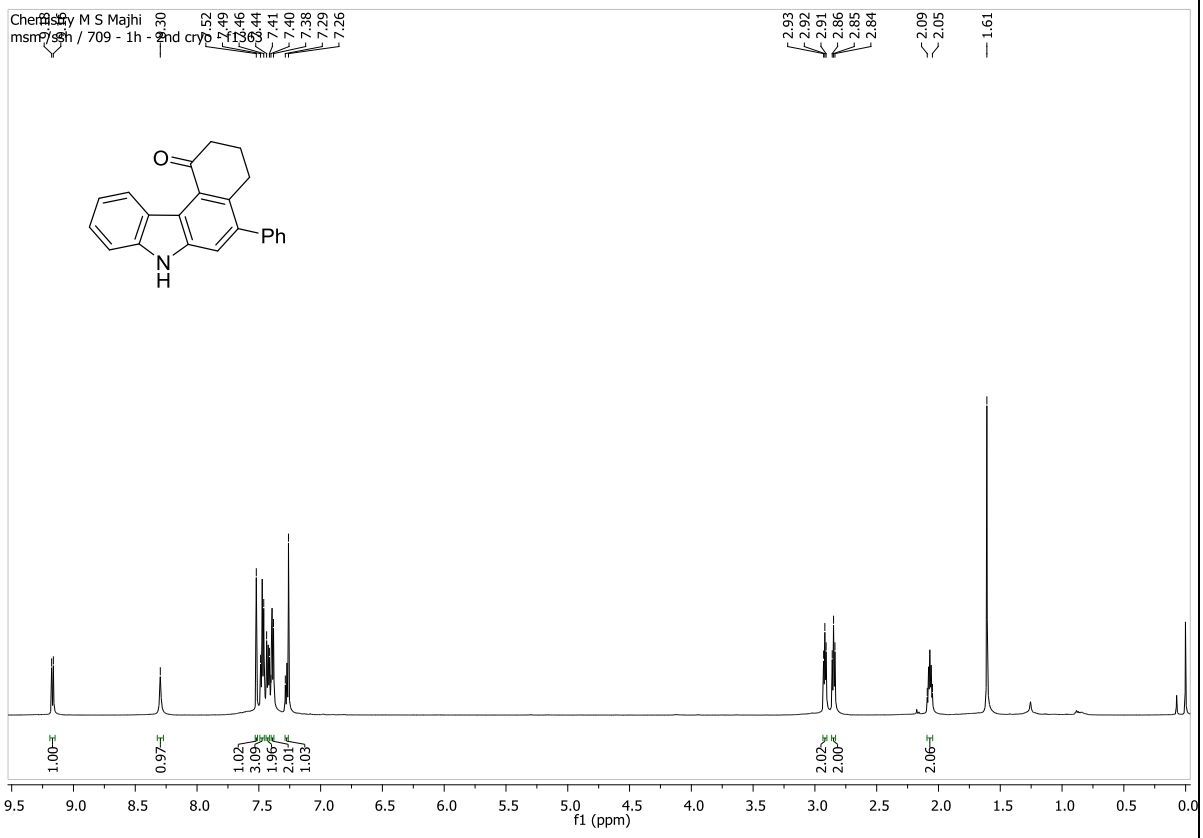
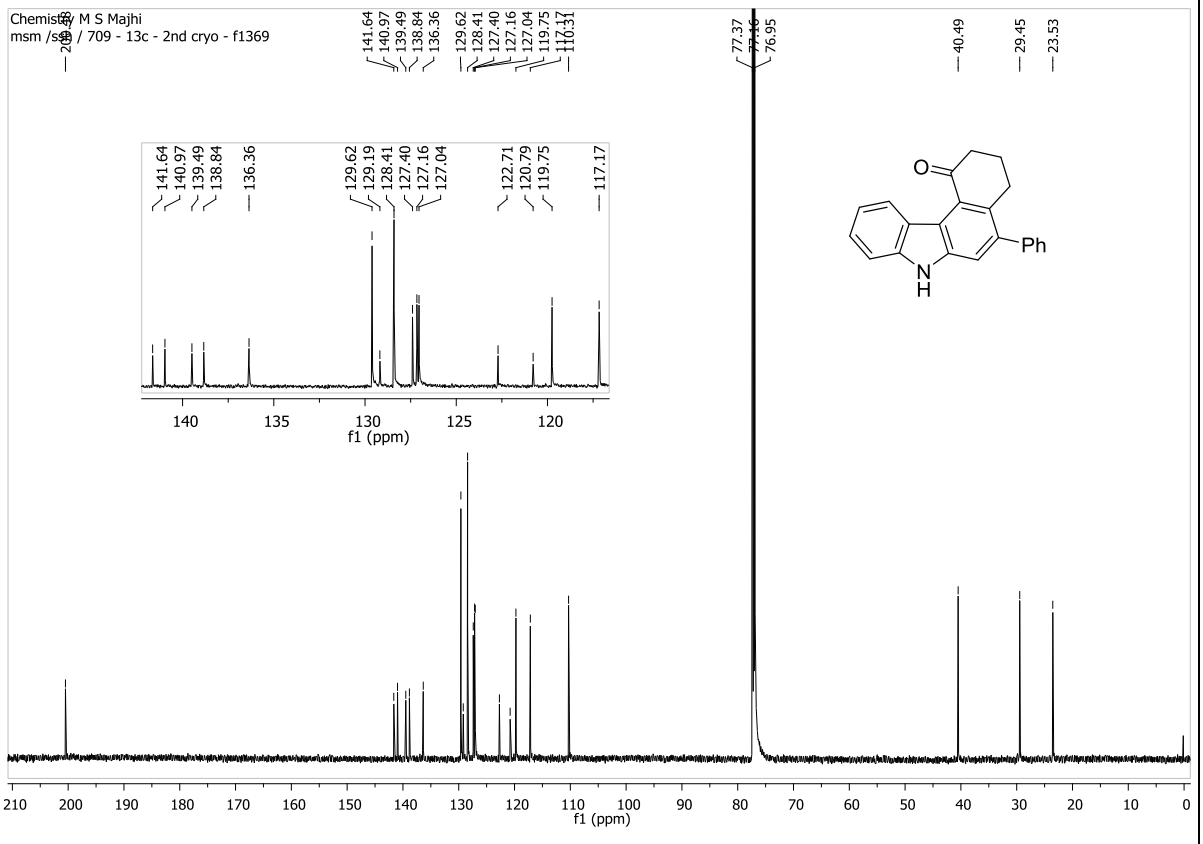
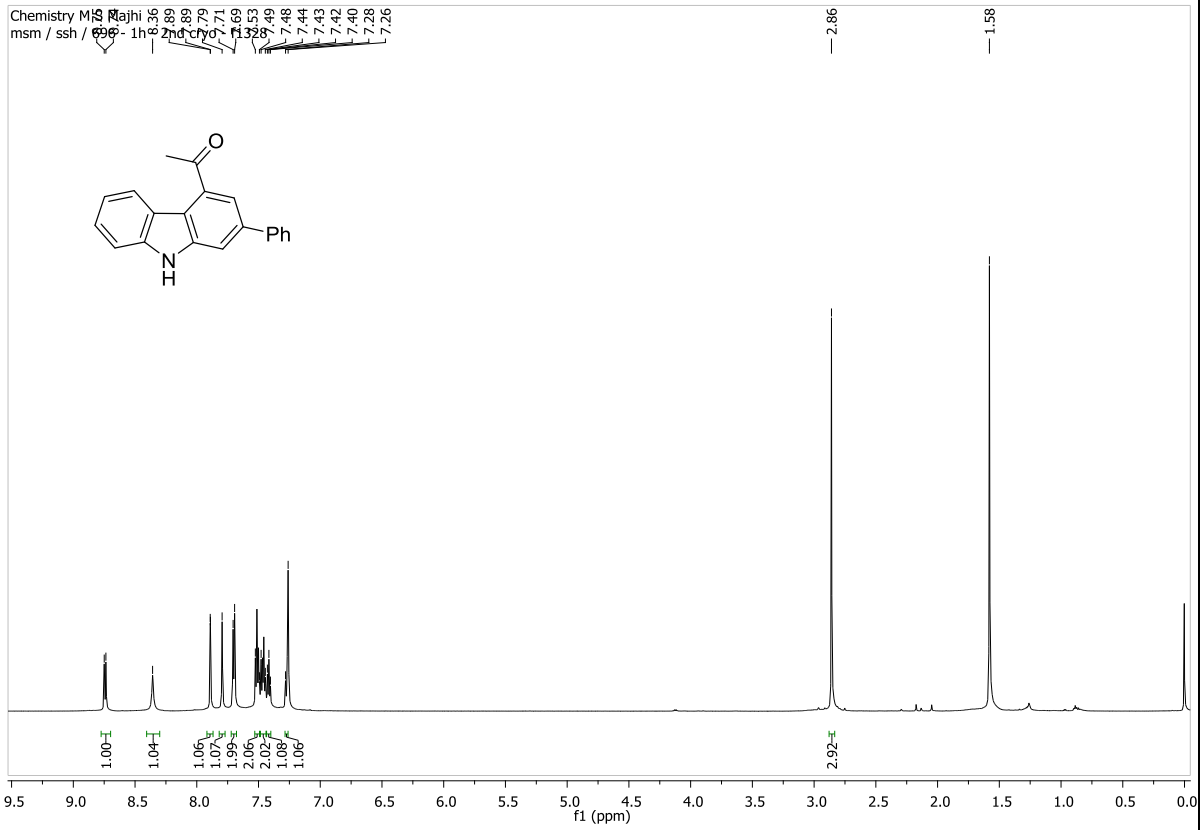
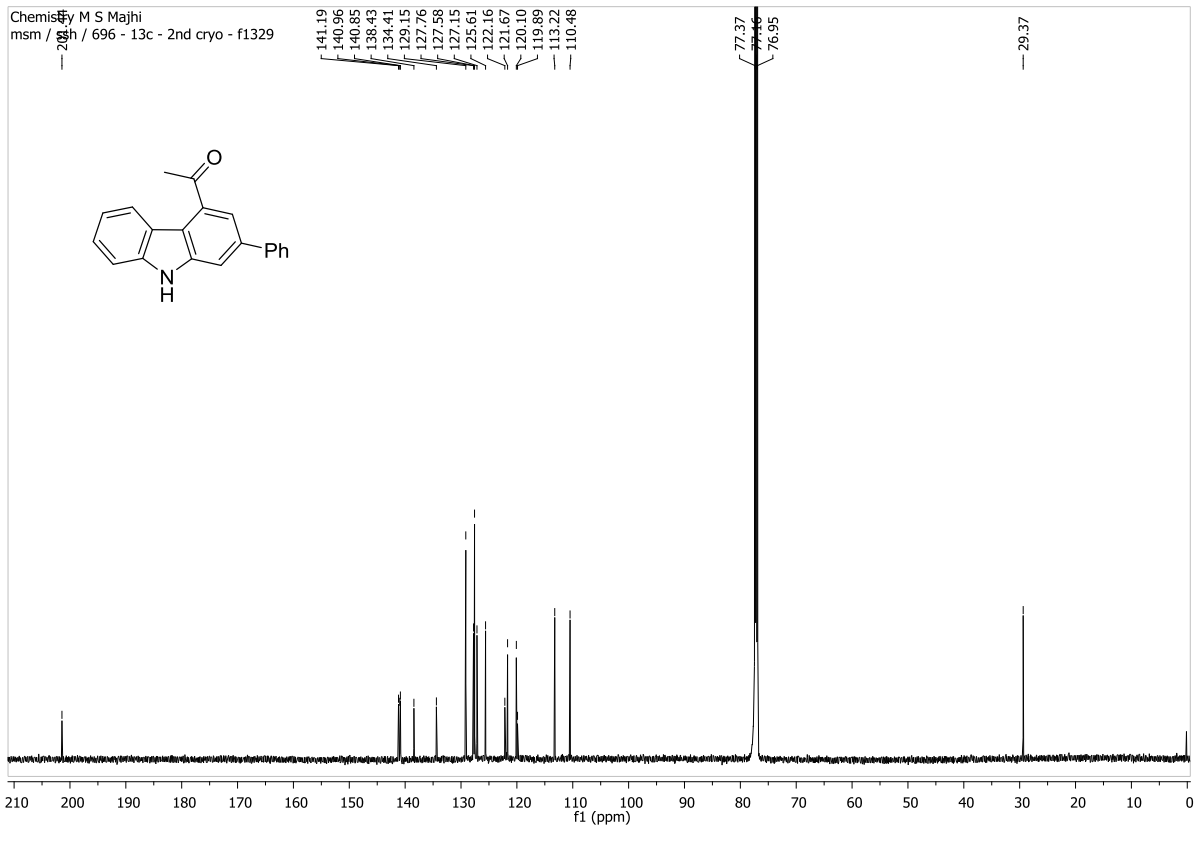


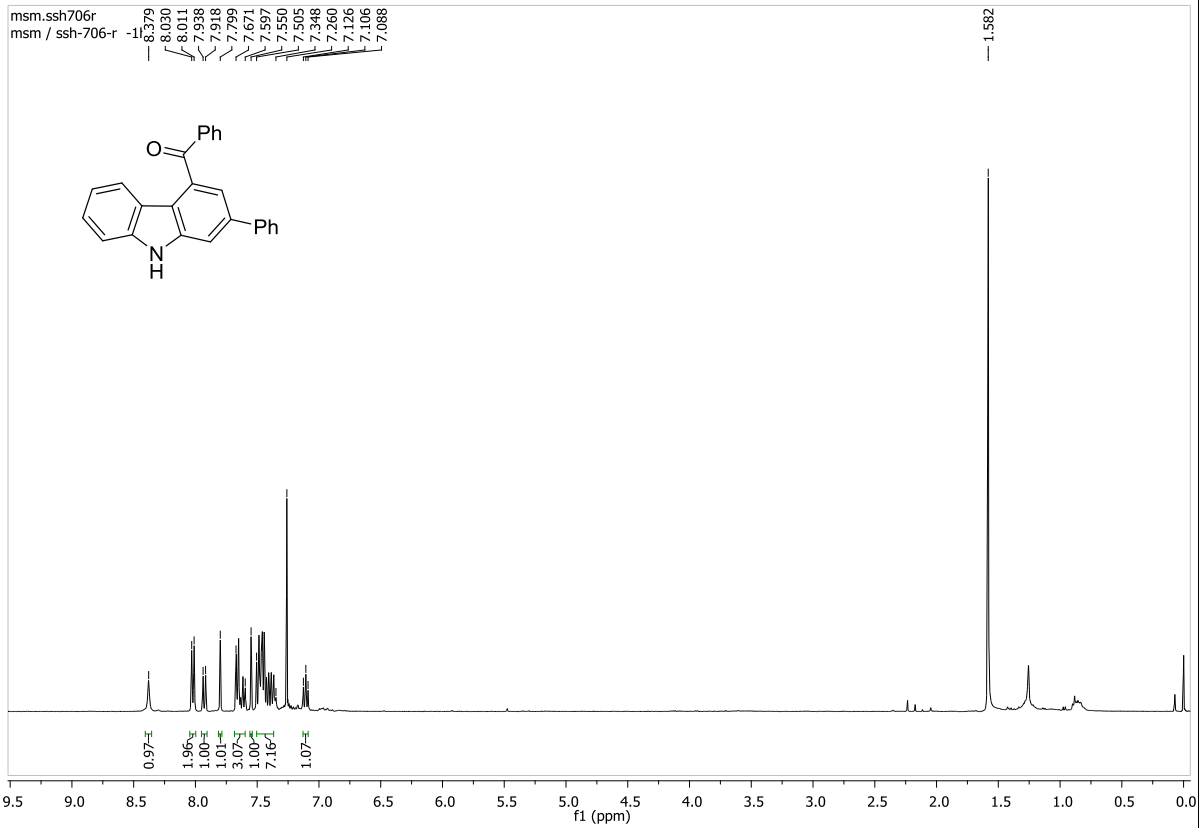


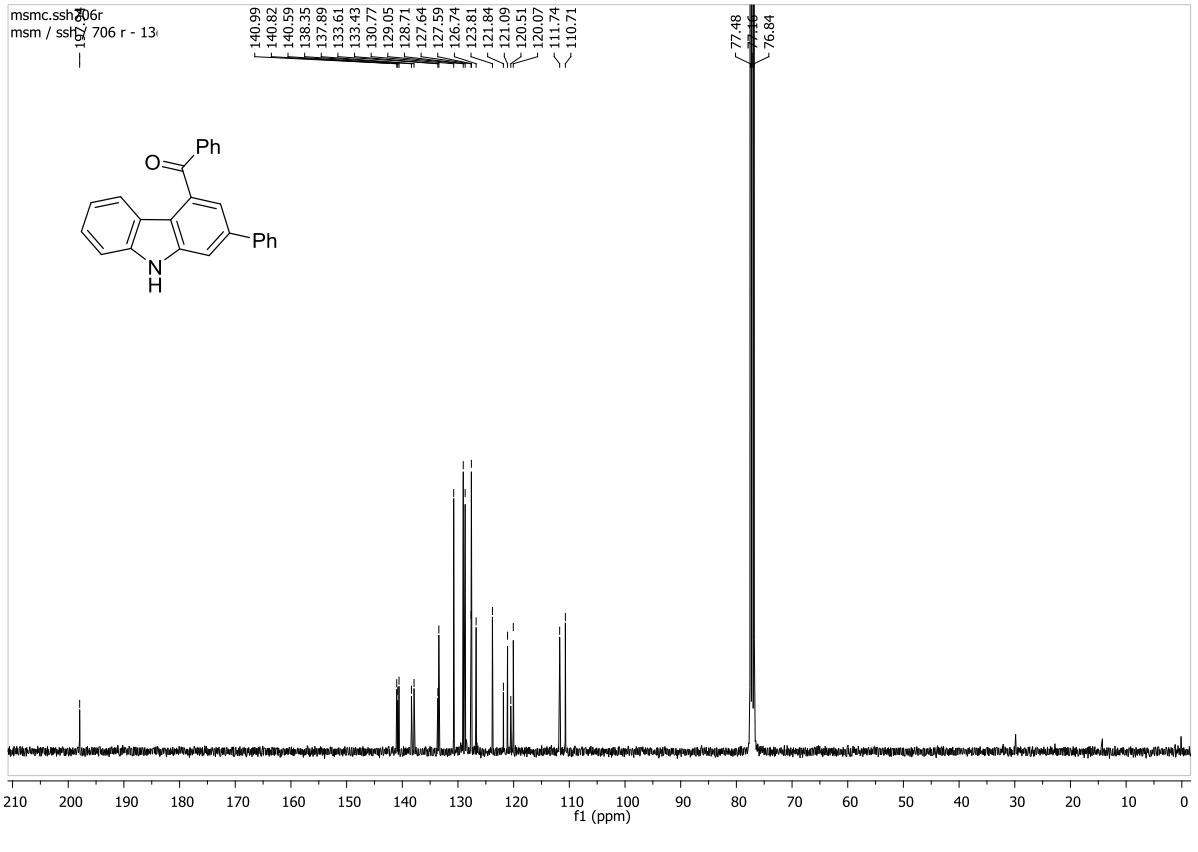
^{1}H NMR and ^{13}C NMR Spectra of Compound **3al**



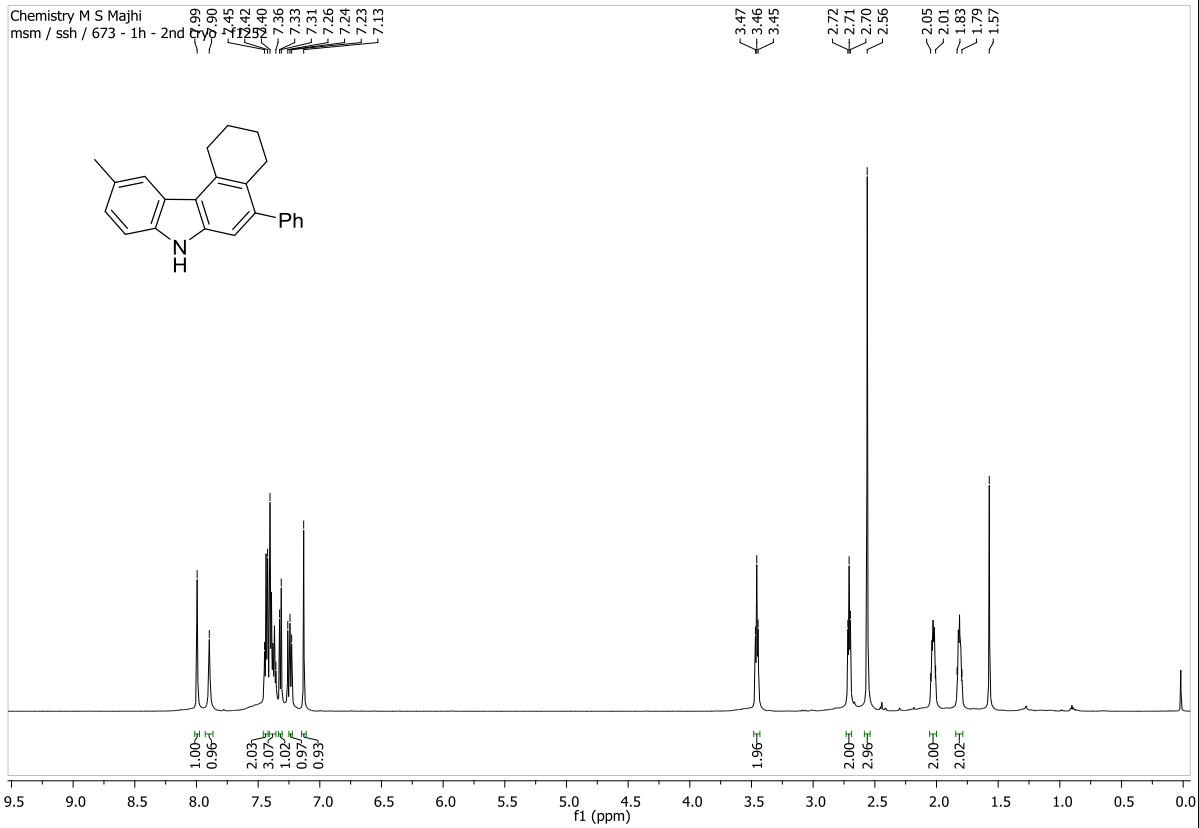


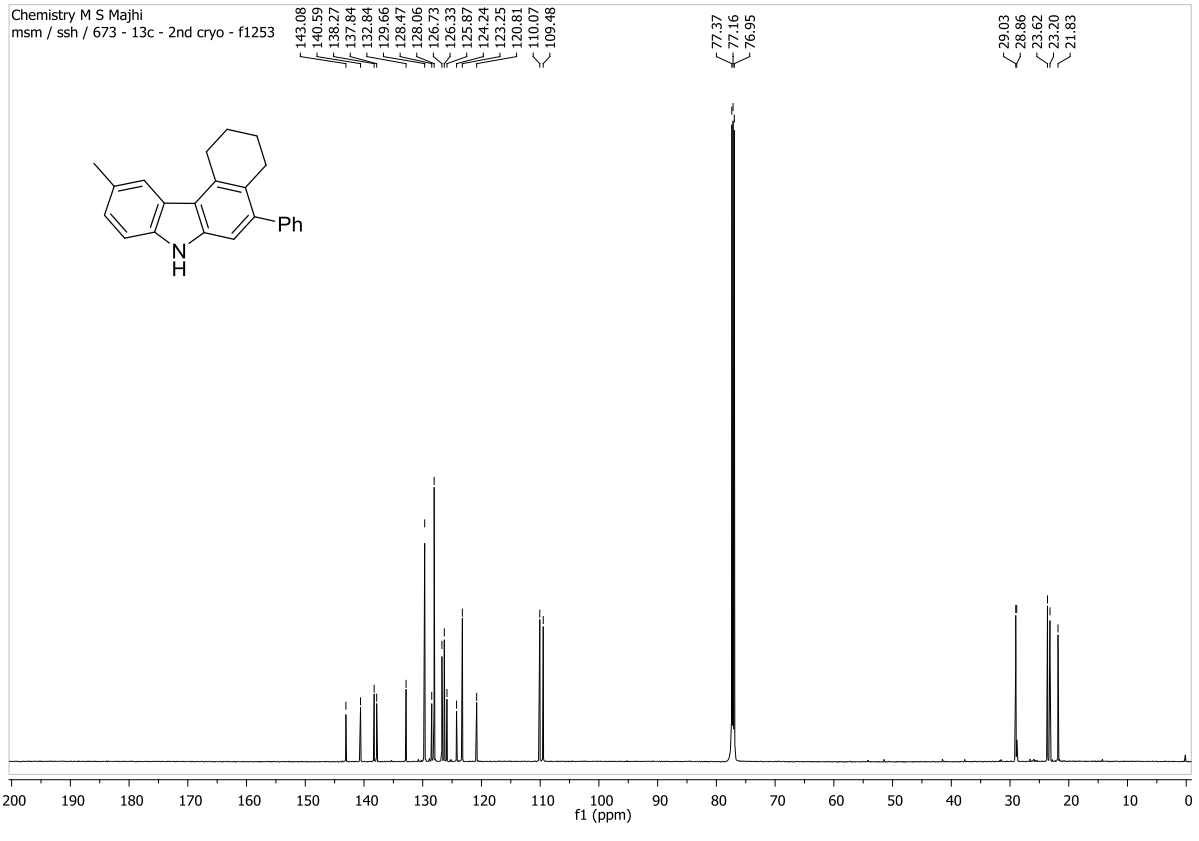
^{1}H NMR and ^{13}C NMR Spectra of Compound **3am**



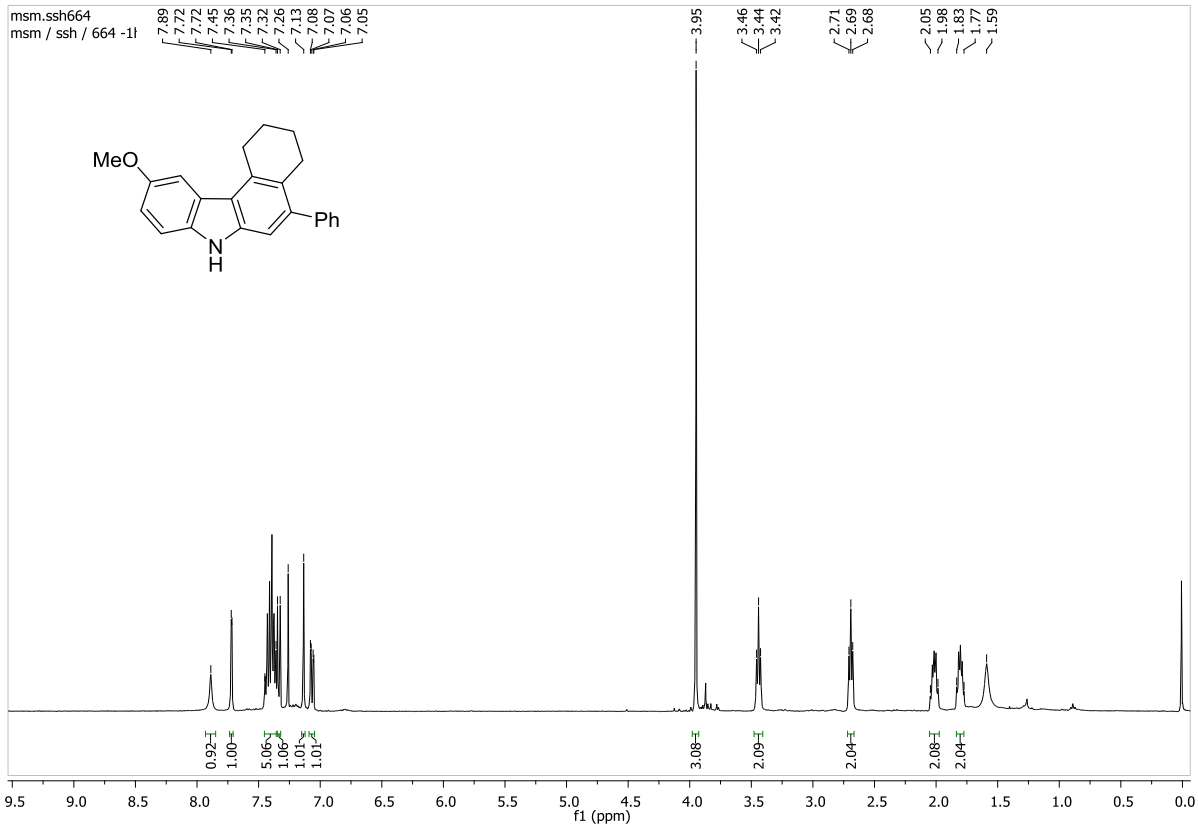


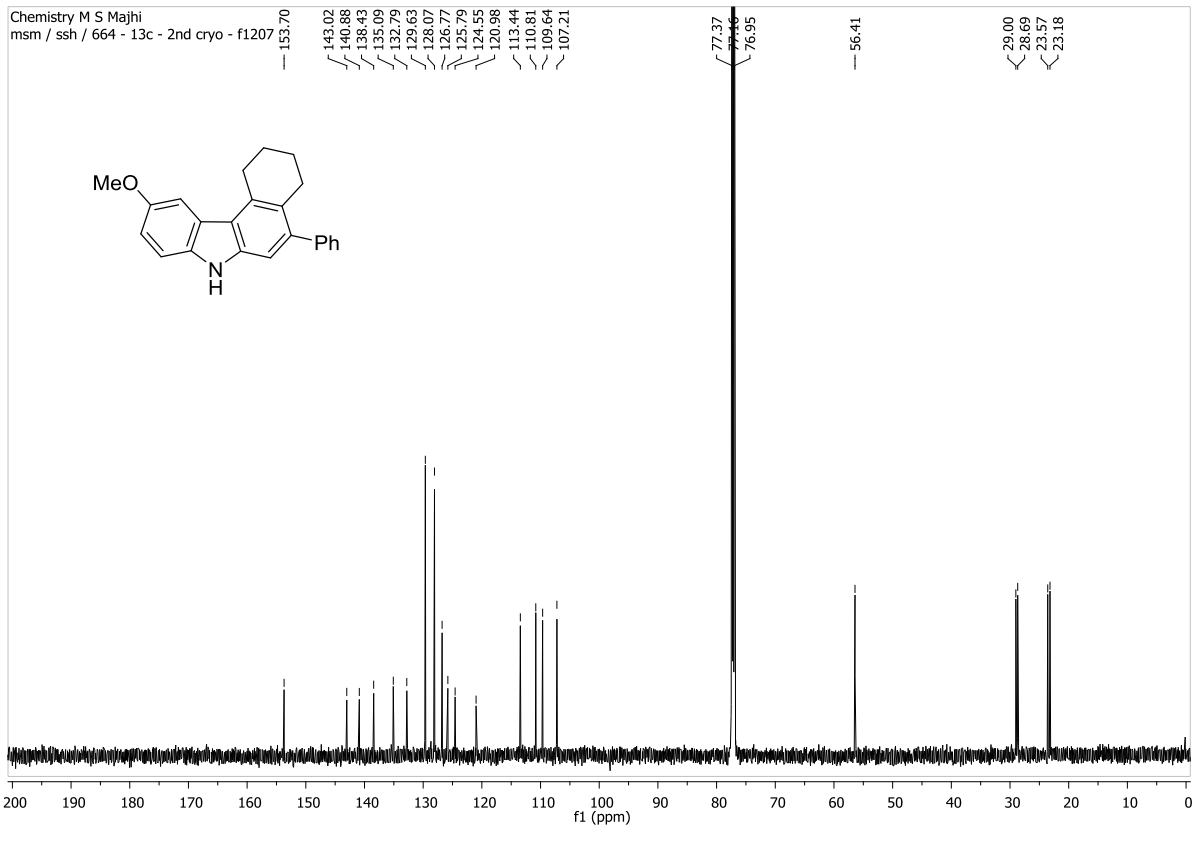
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ba**



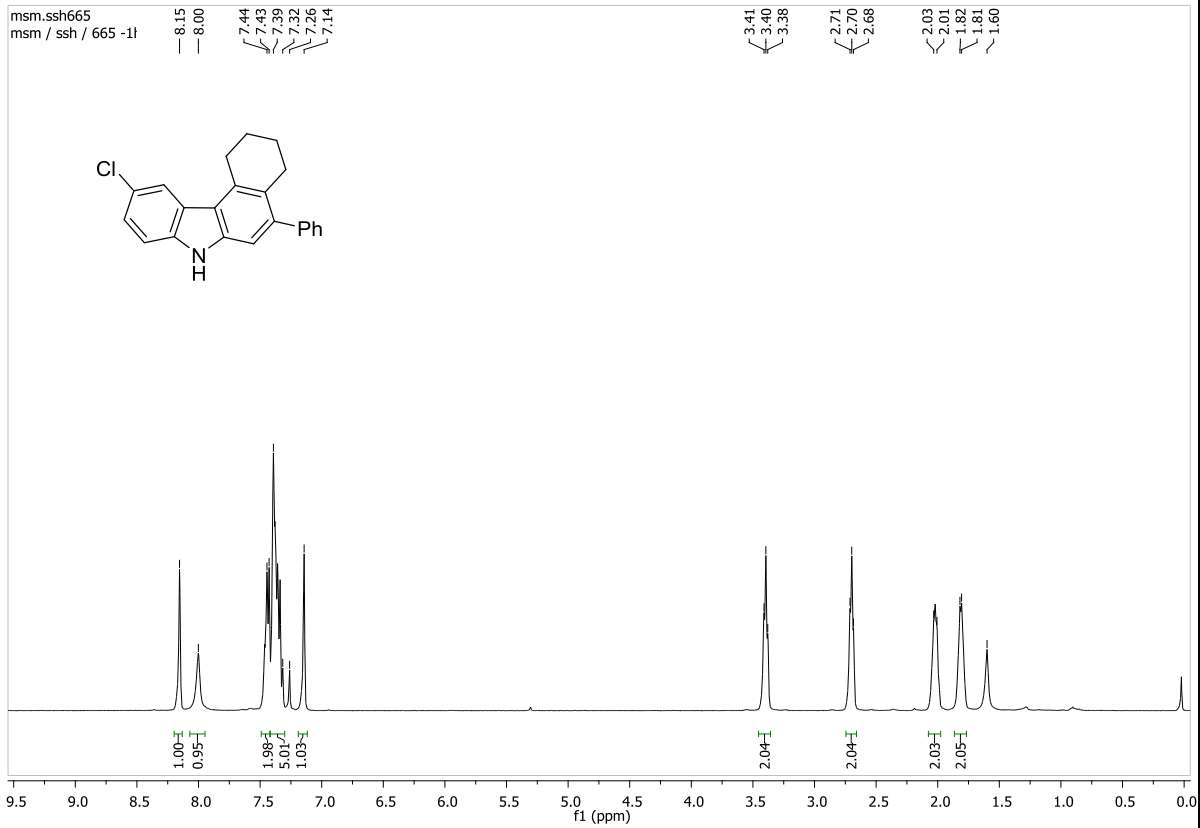


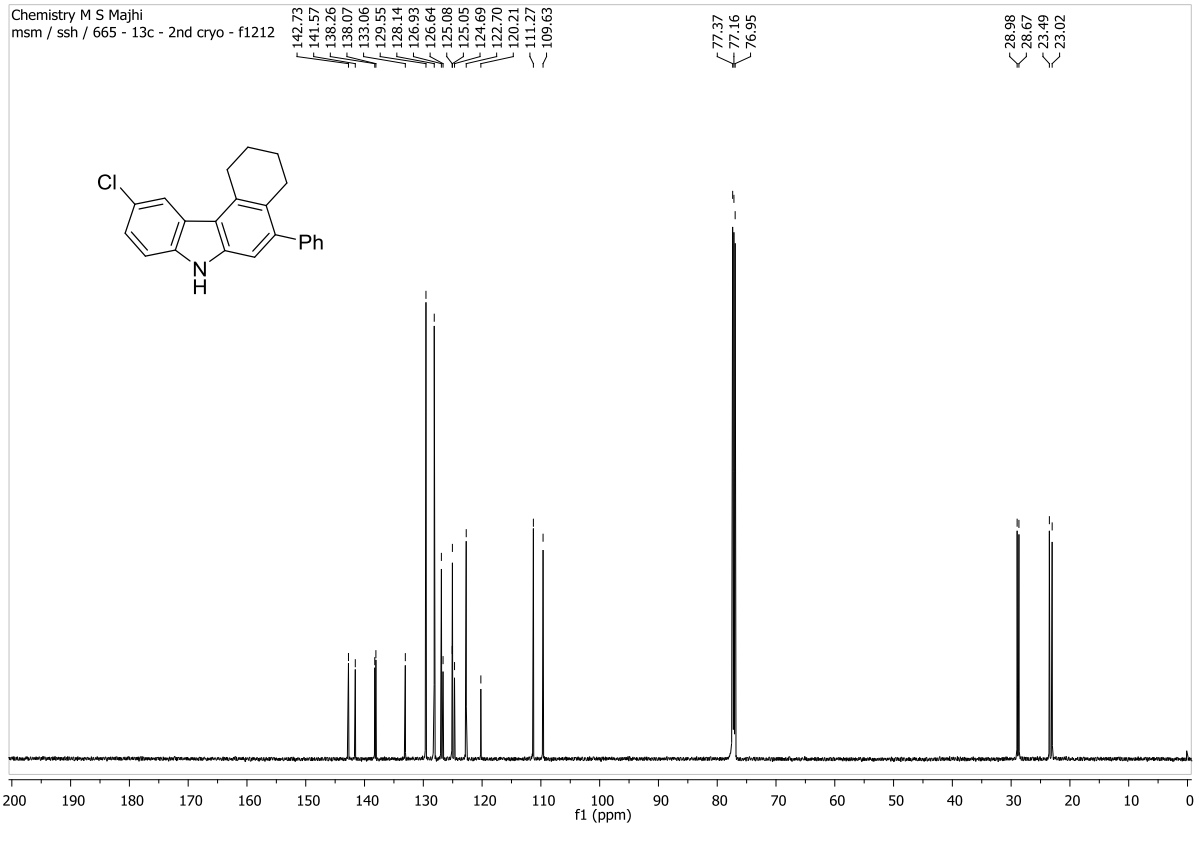
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ca**



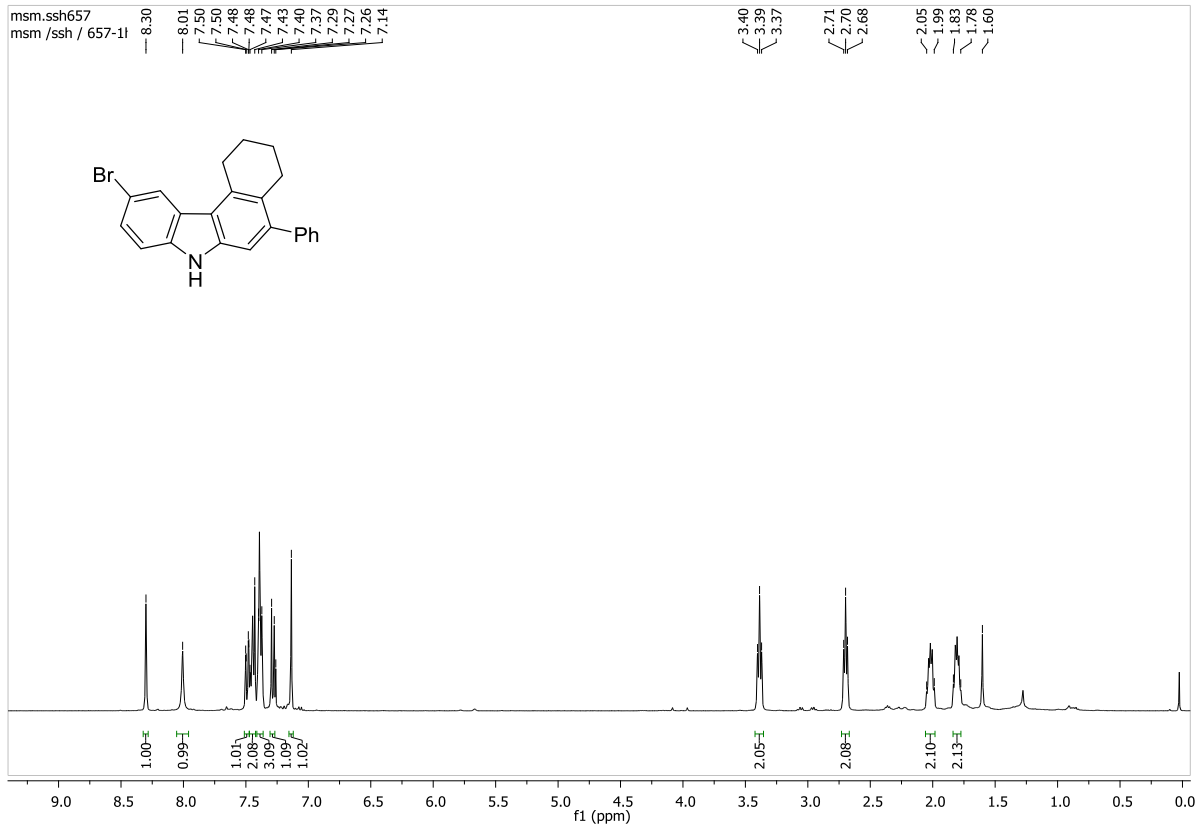


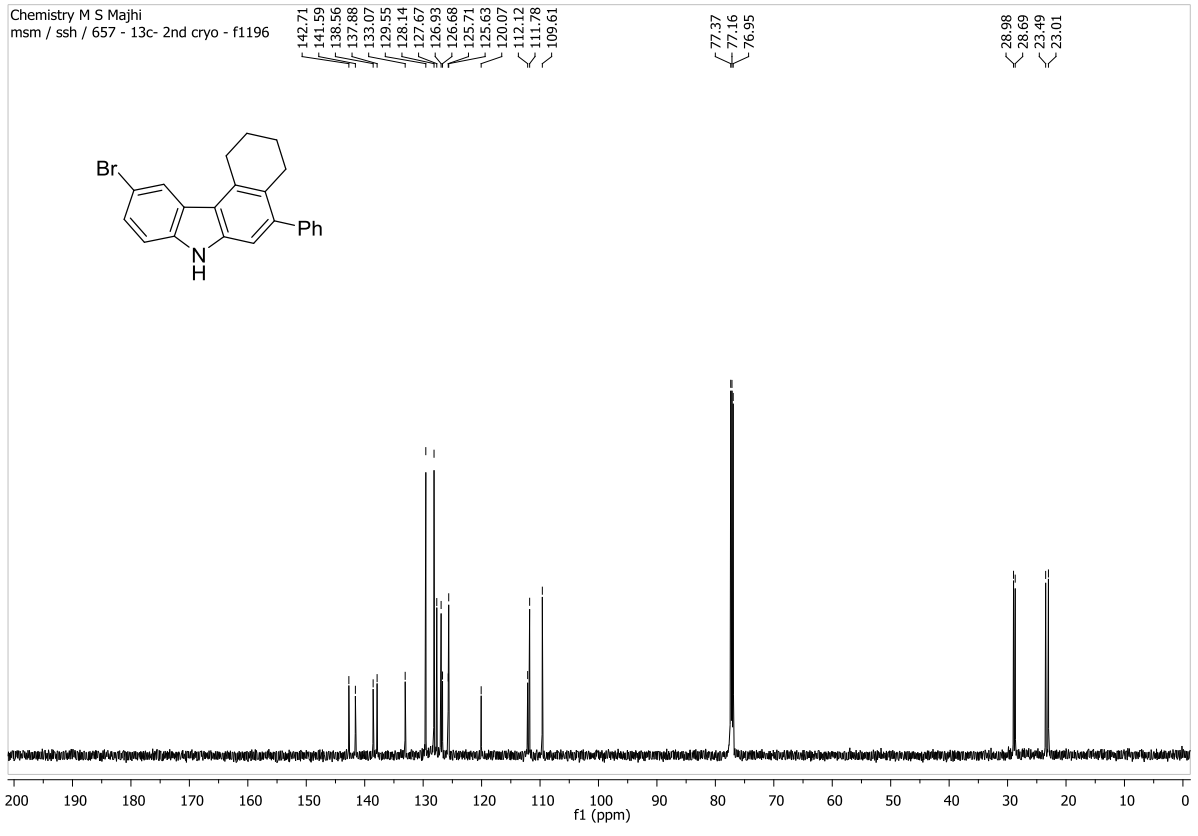
^{1}H NMR and ^{13}C NMR Spectra of Compound **3da**



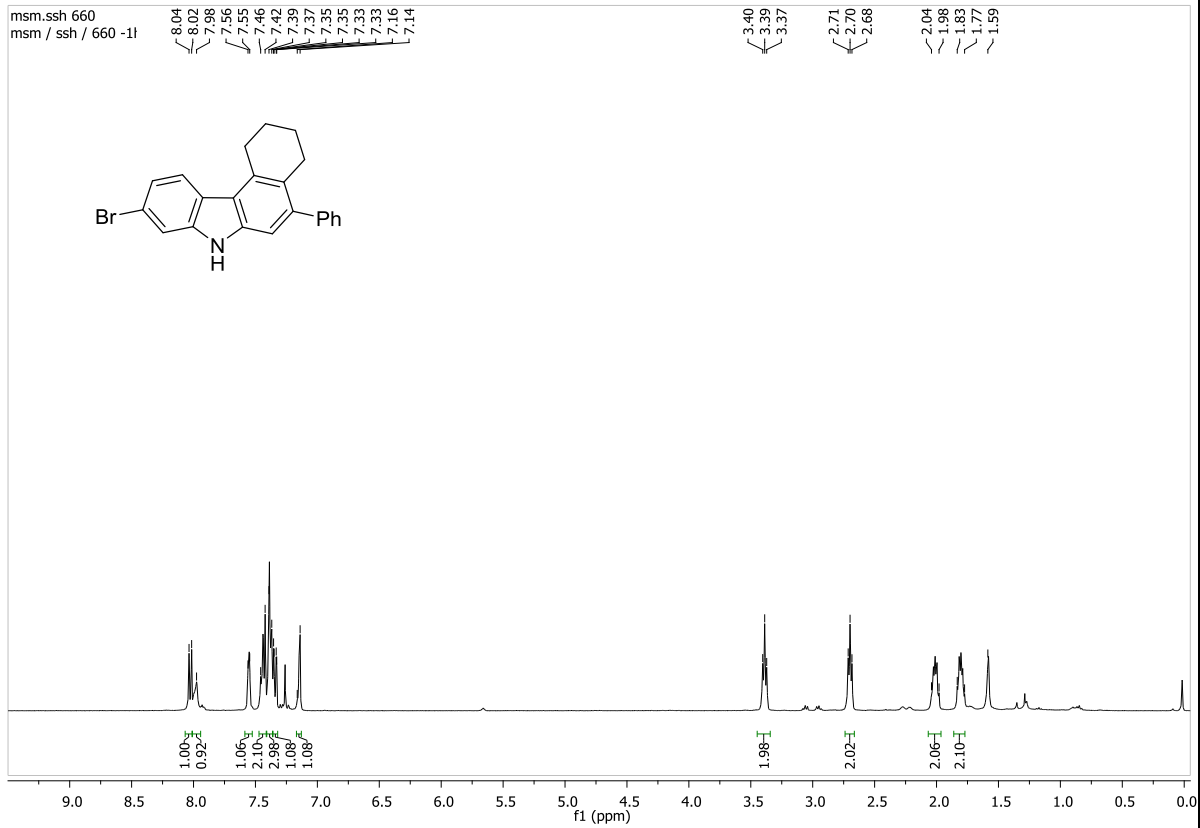


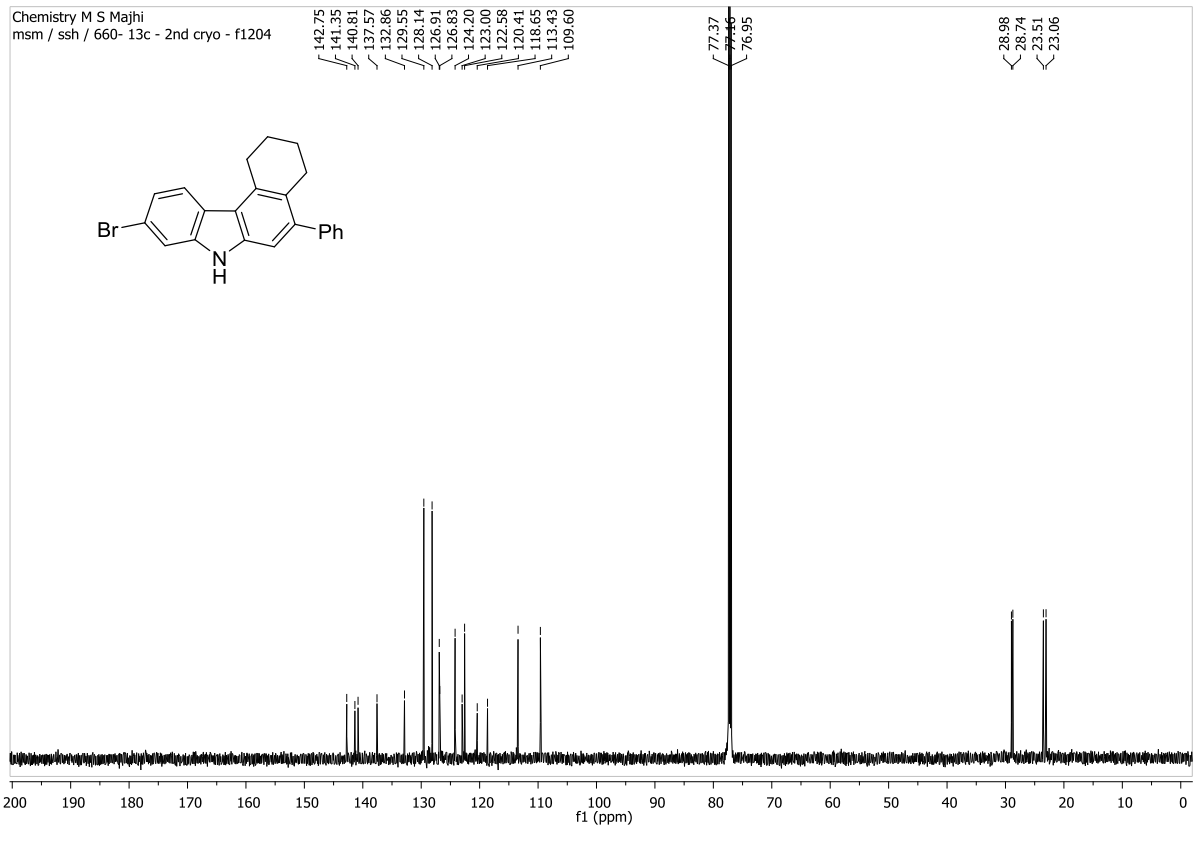
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ea**



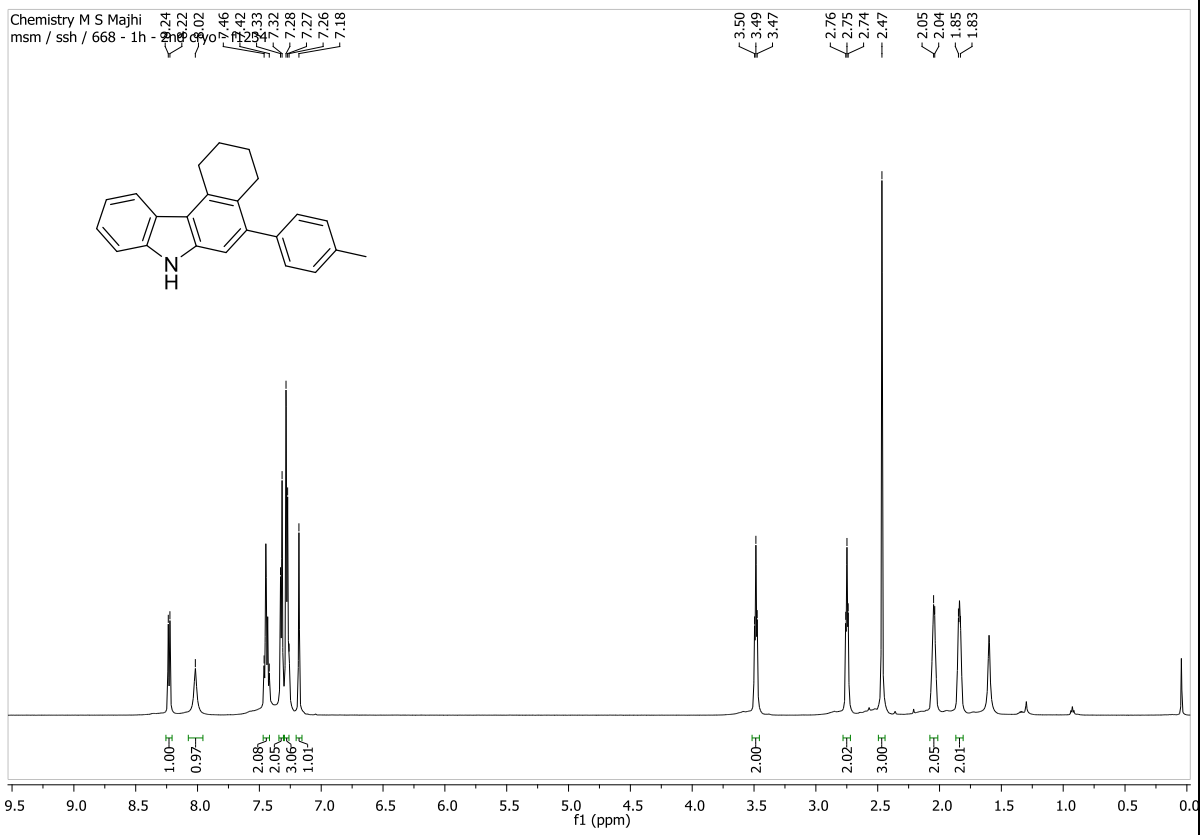


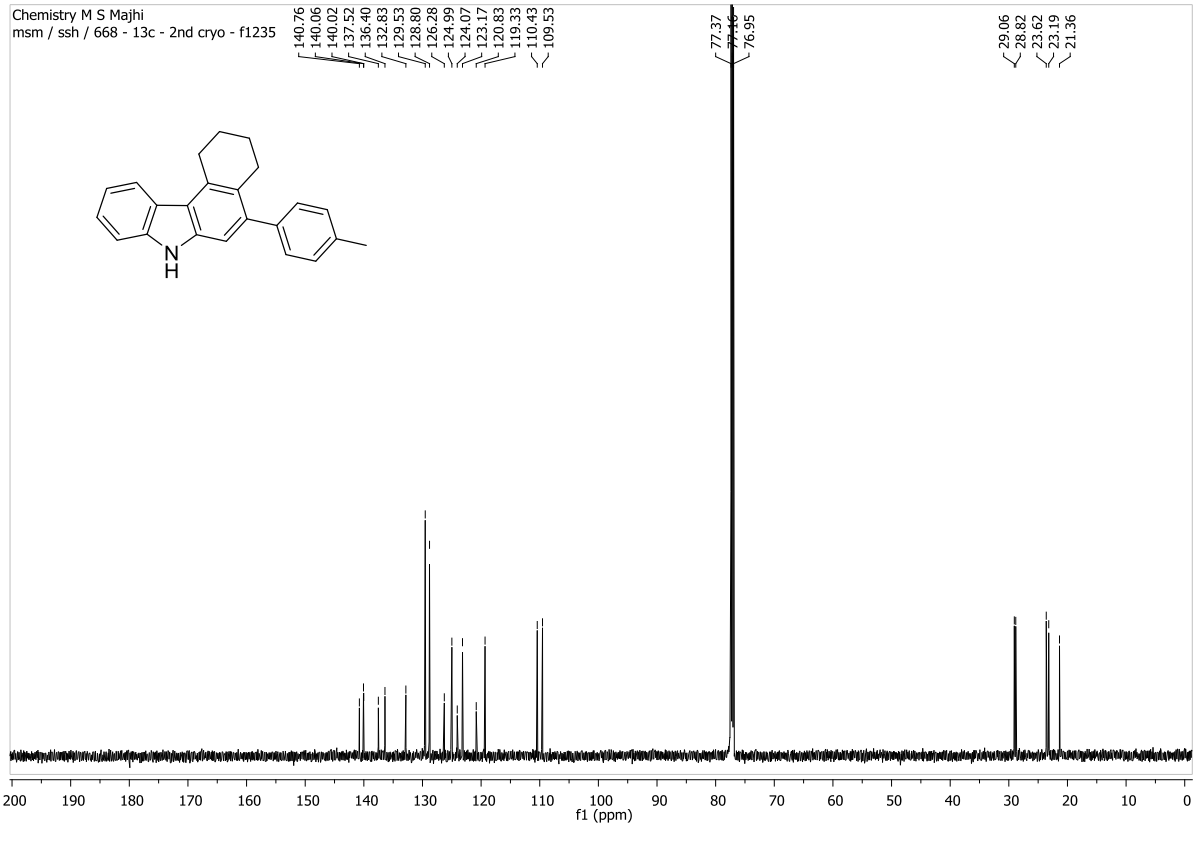
^{1}H NMR and ^{13}C NMR Spectra of Compound **3fa**



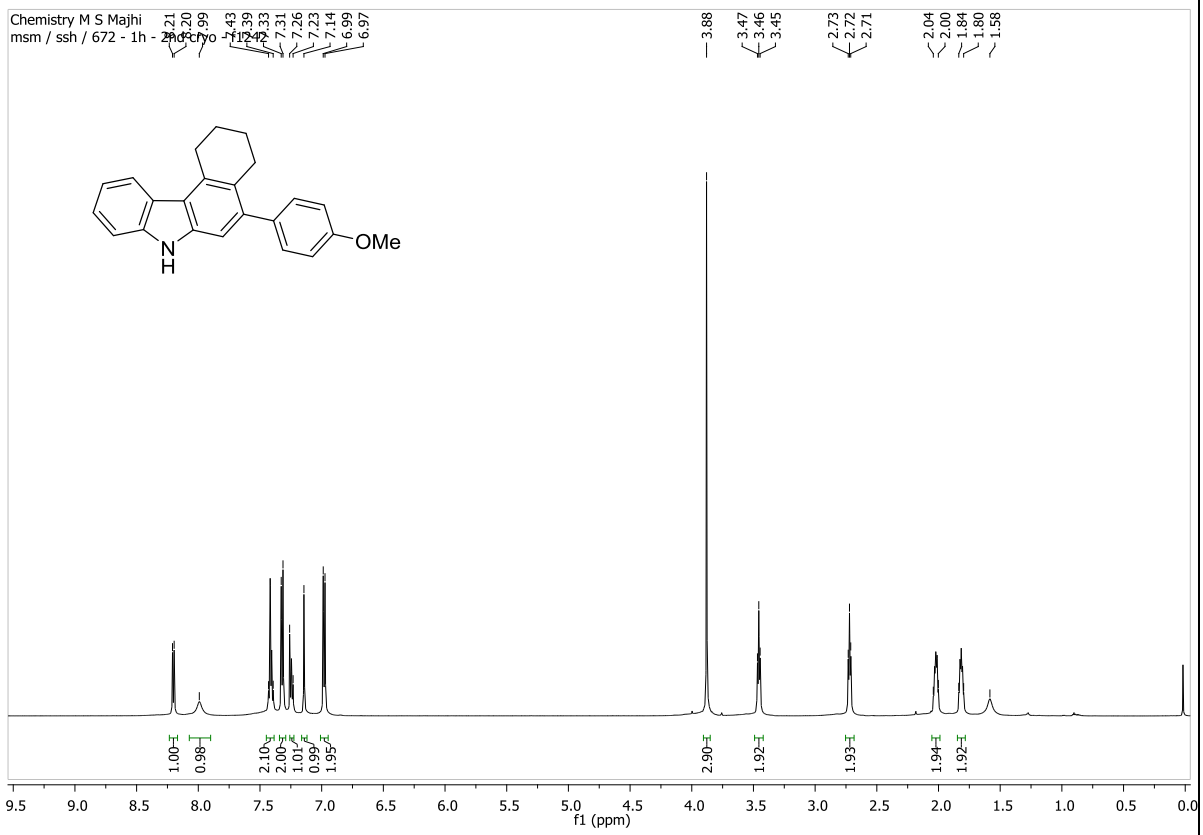


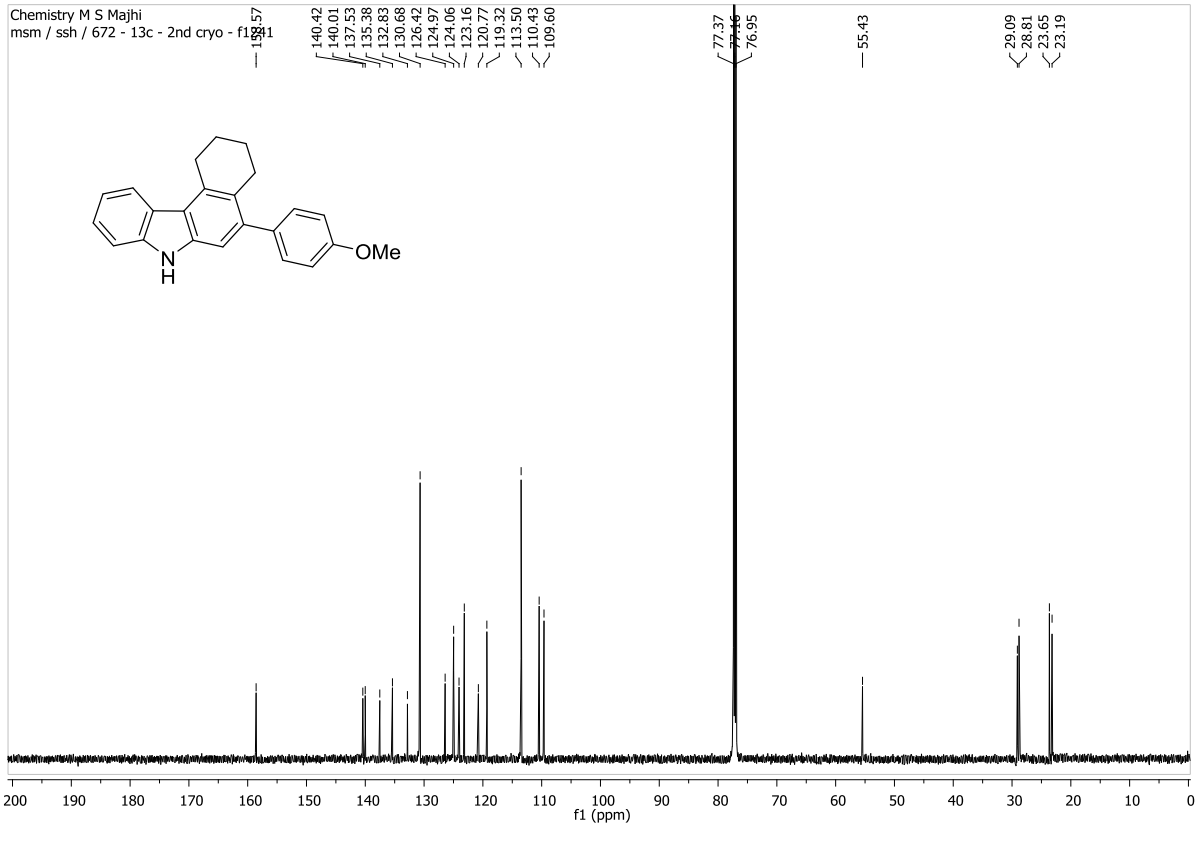
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ga**



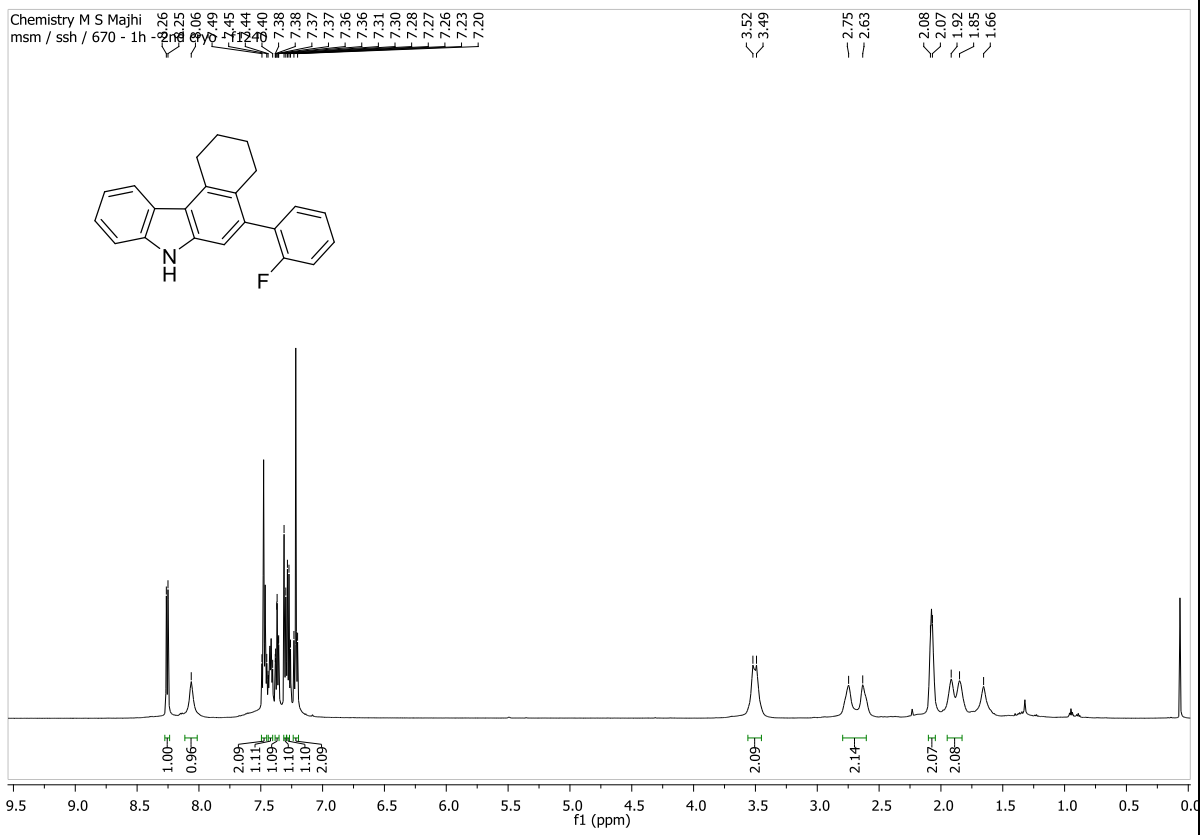


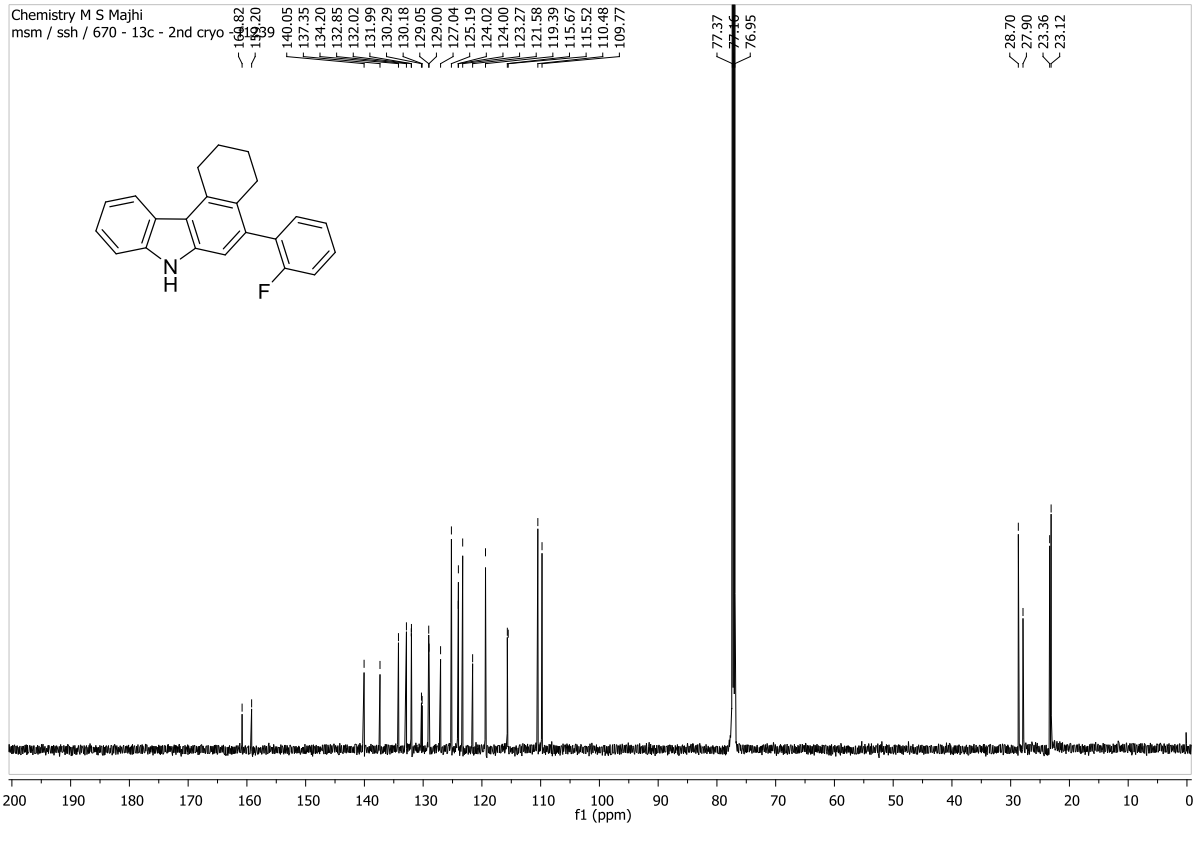
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ha**



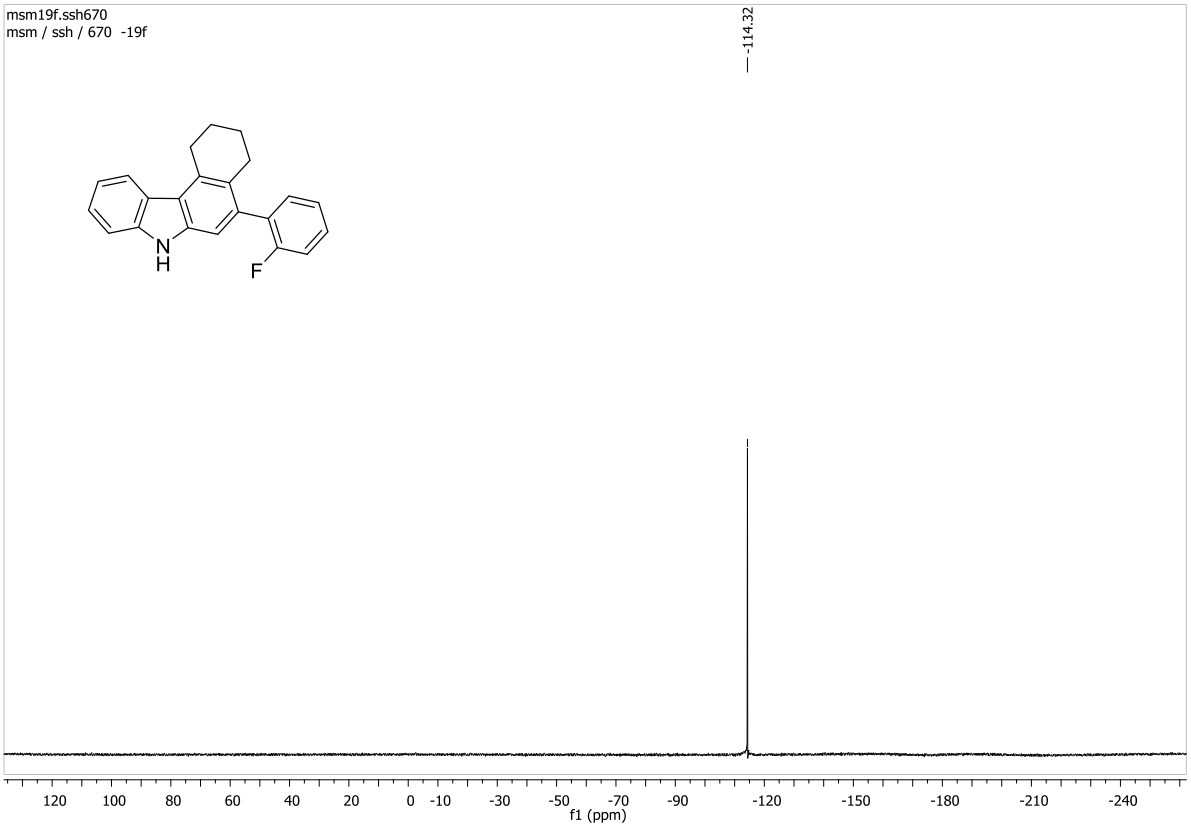


^{1}H NMR and ^{13}C NMR Spectra of Compound **3ia**

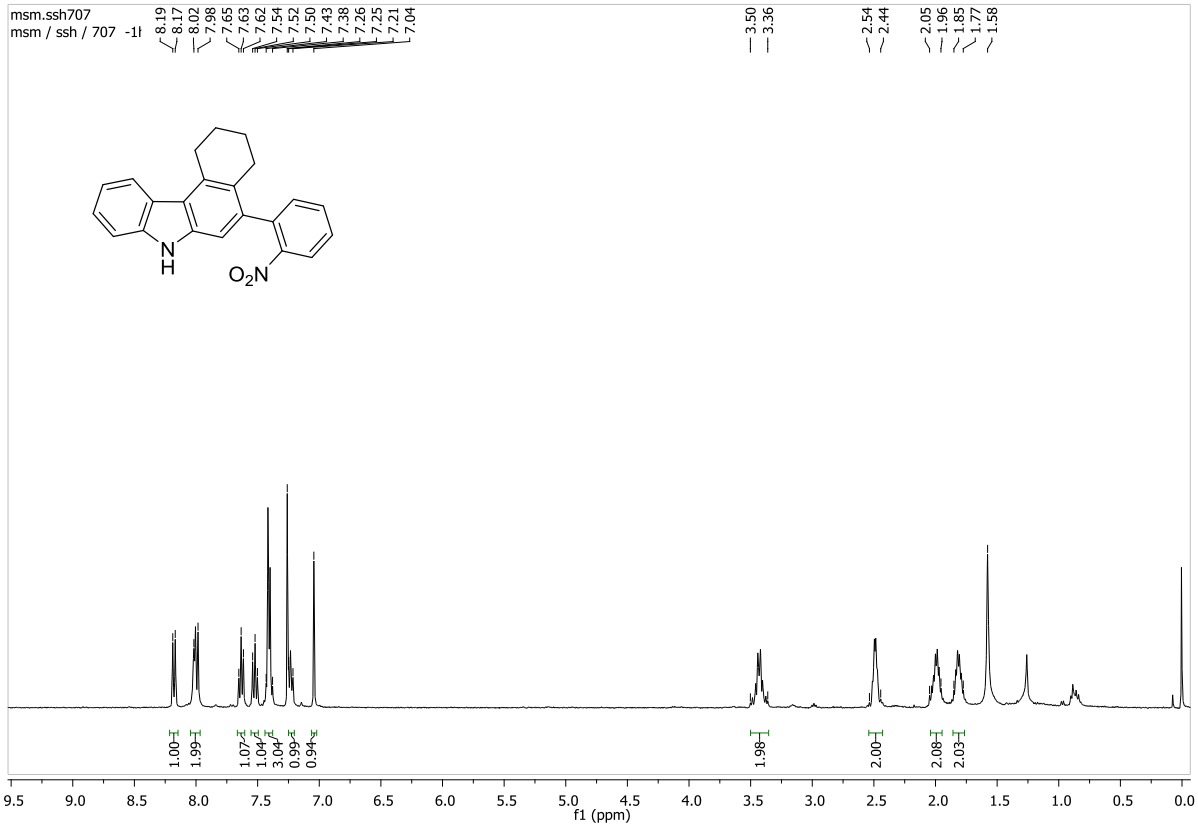


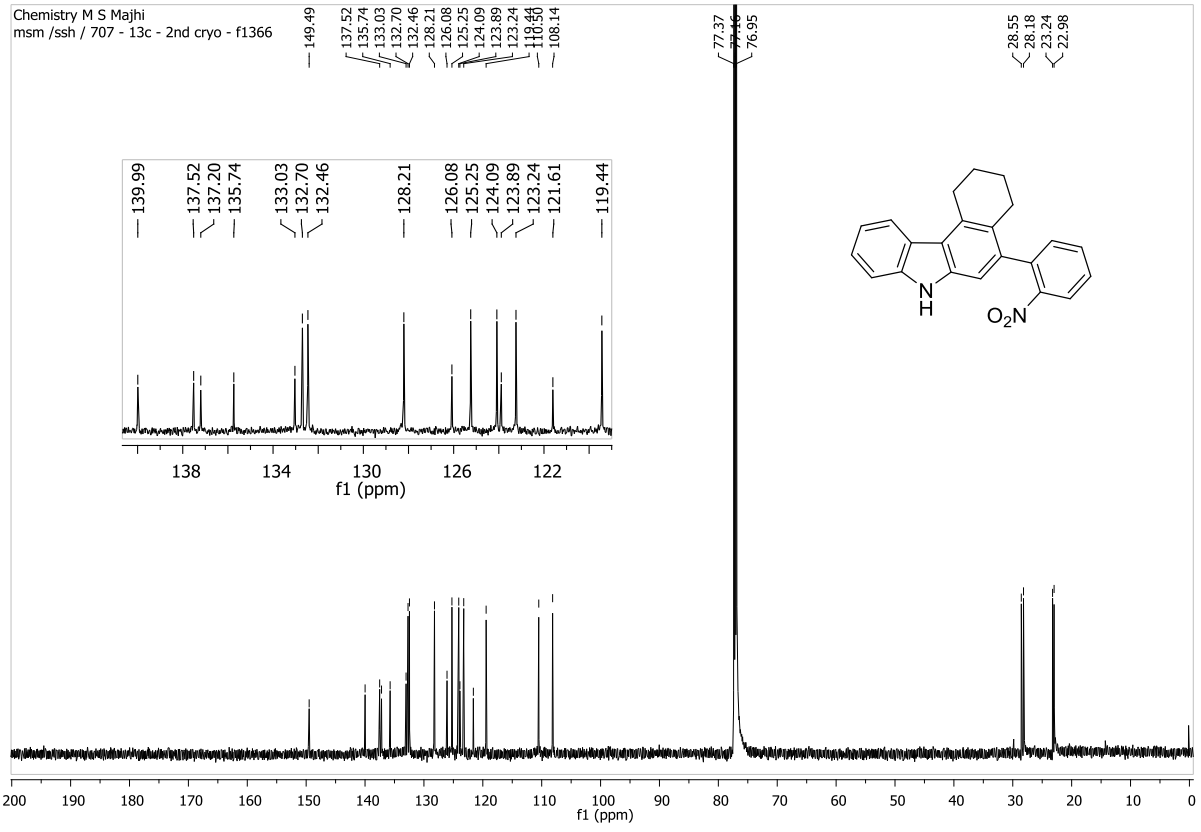


^{19}F NMR Spectra of Compound **3ia**

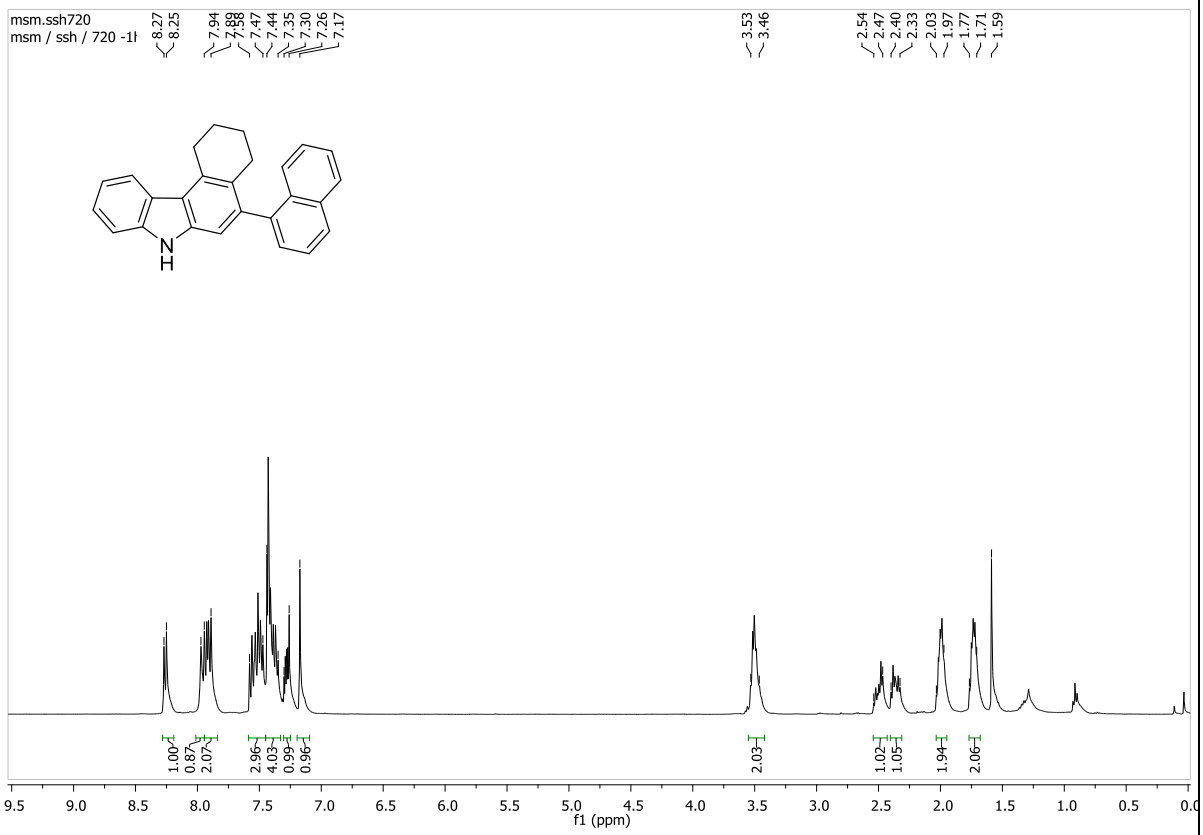


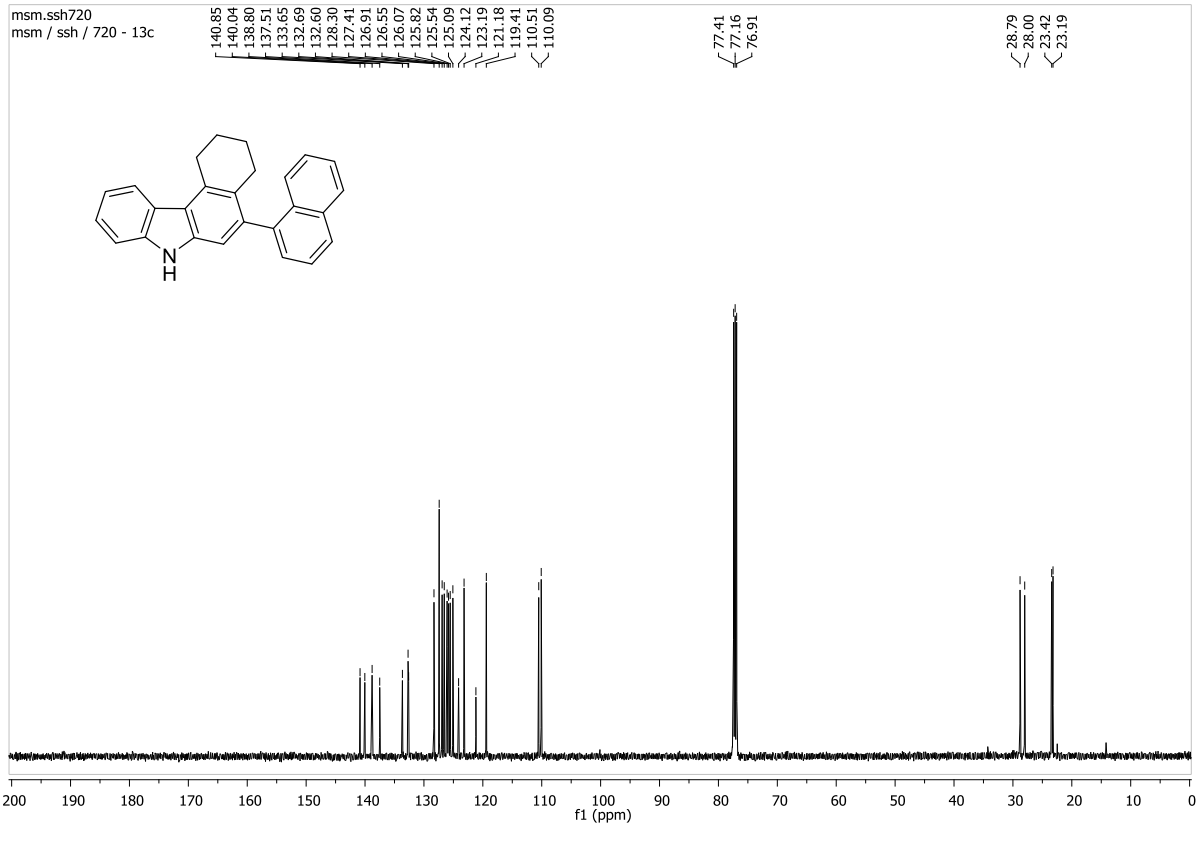
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ja**



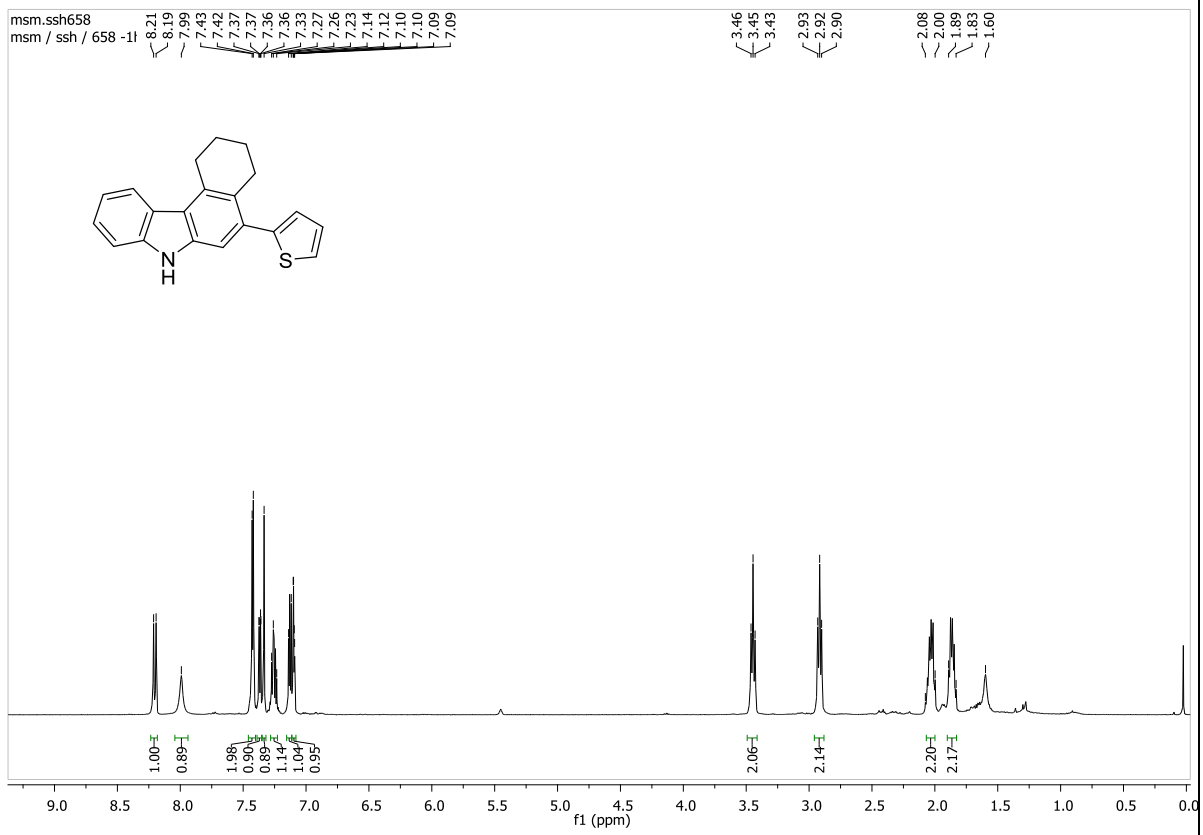


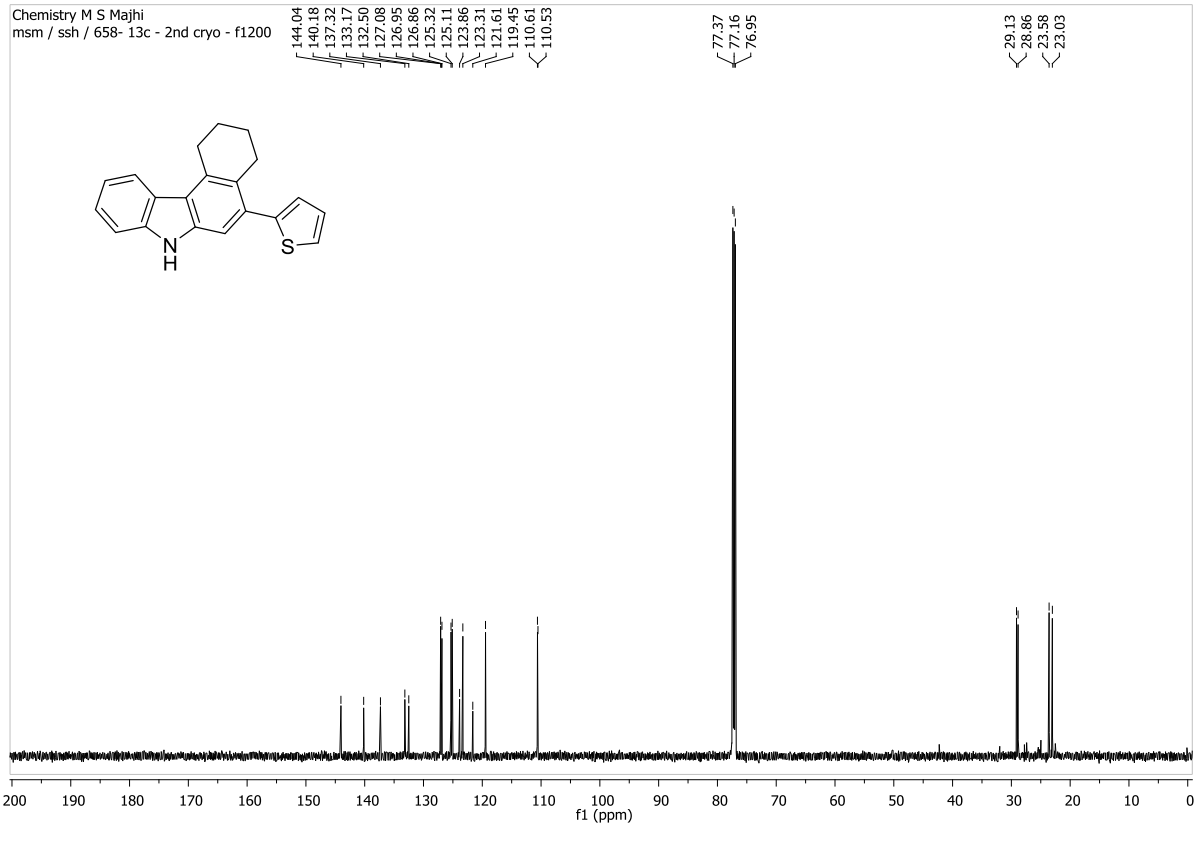
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ka**



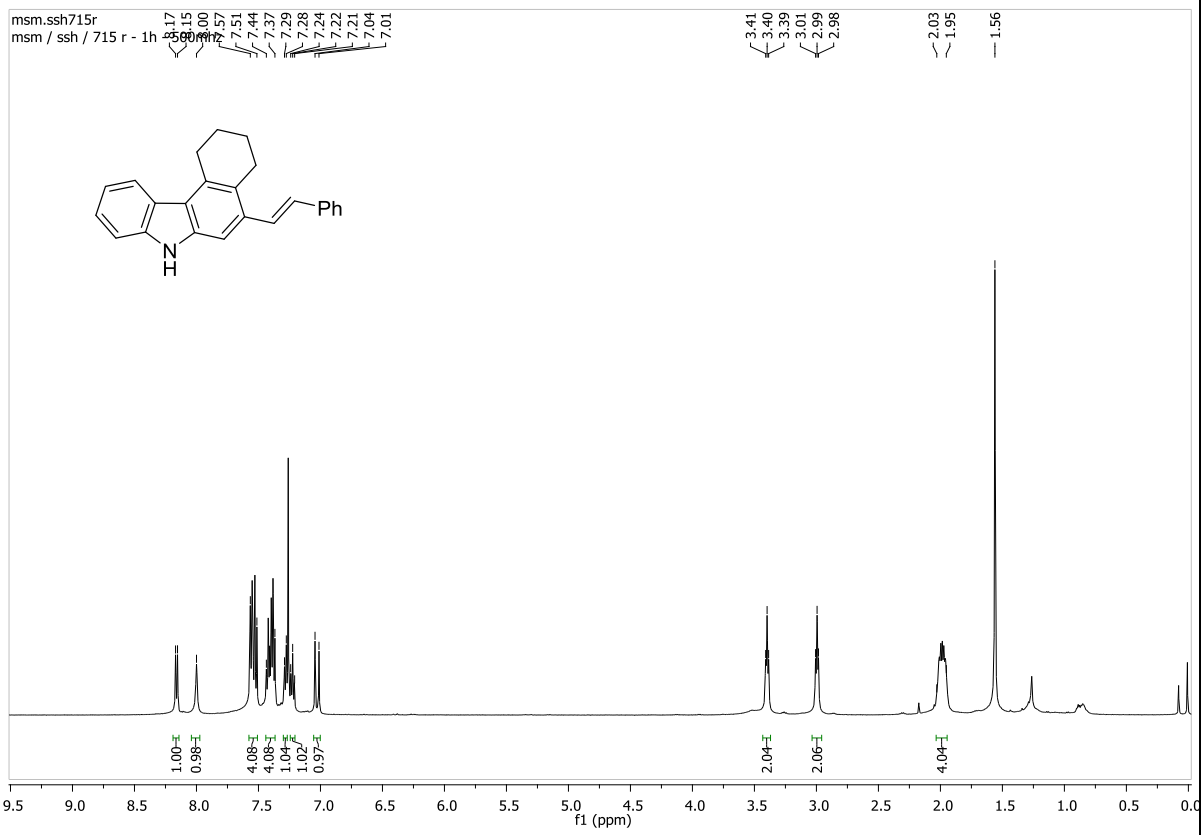


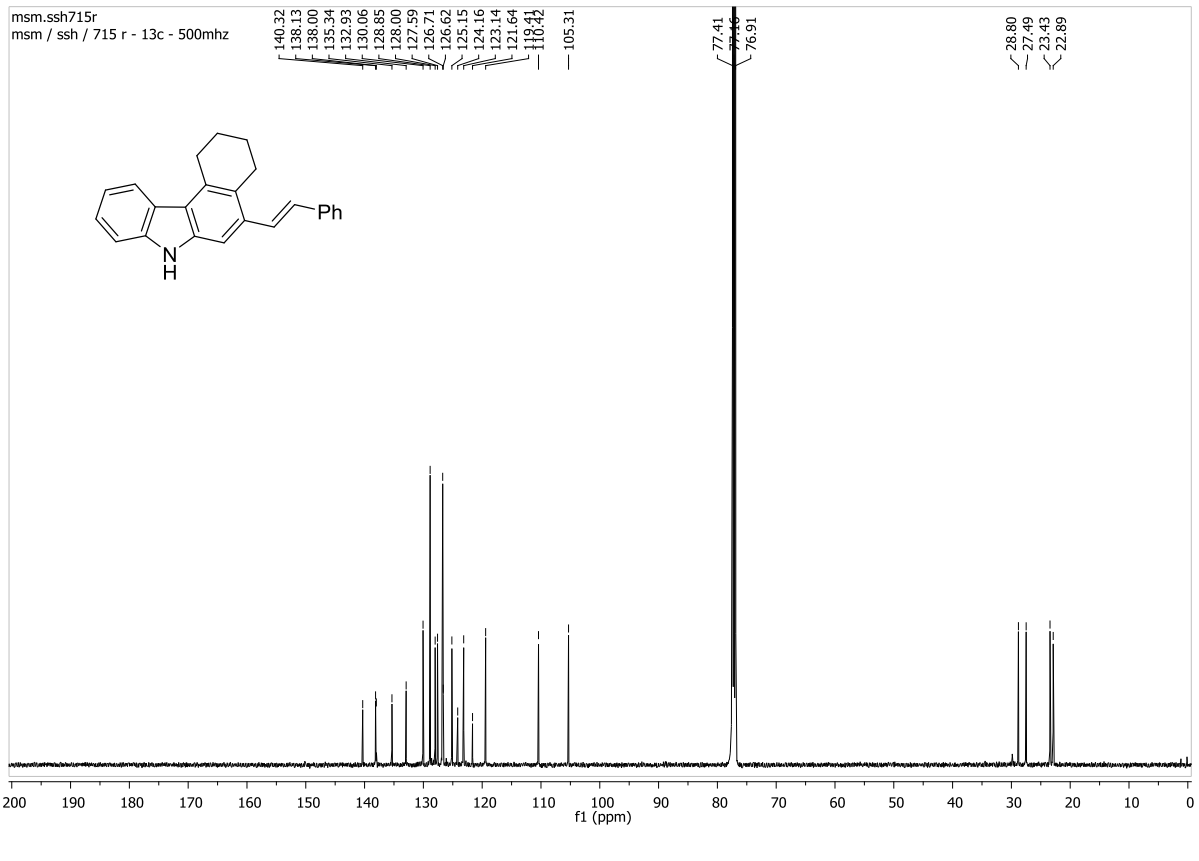
^{1}H NMR and ^{13}C NMR Spectra of Compound **3la**



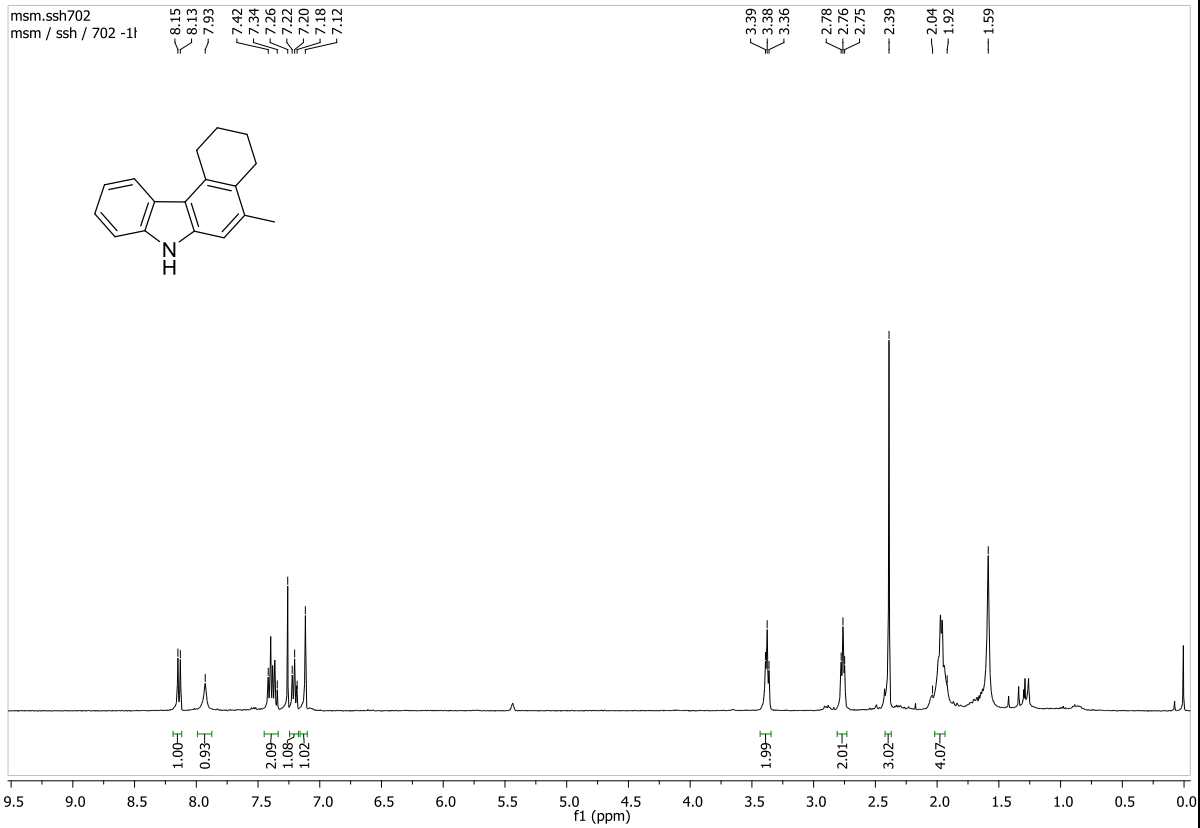


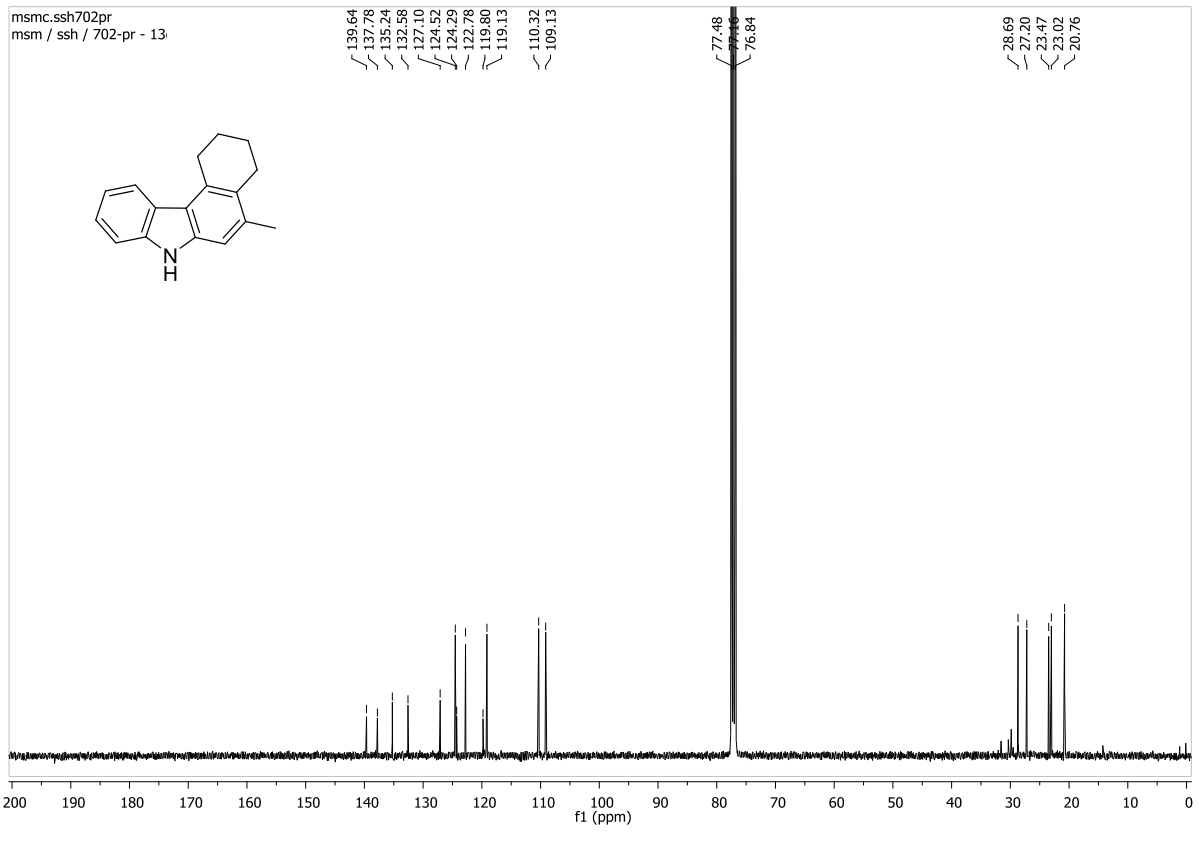
^{1}H NMR and ^{13}C NMR Spectra of Compound **3ma**



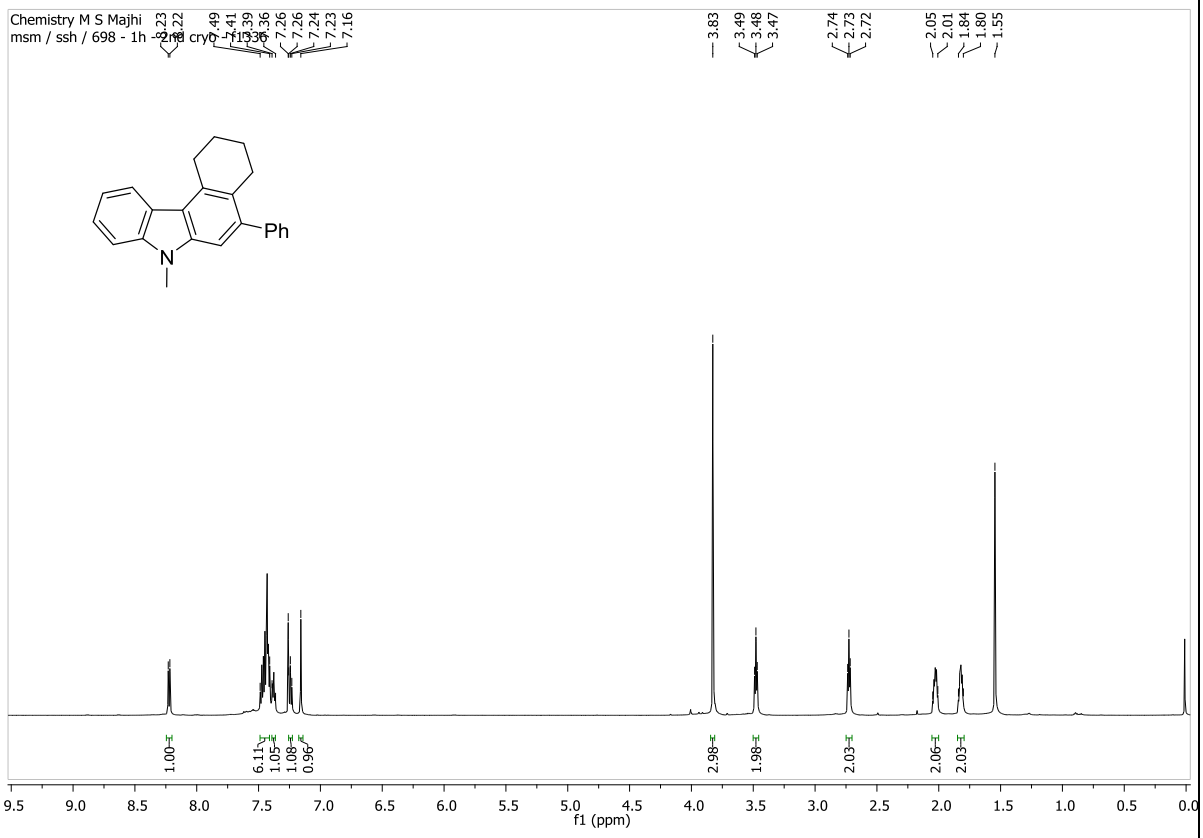


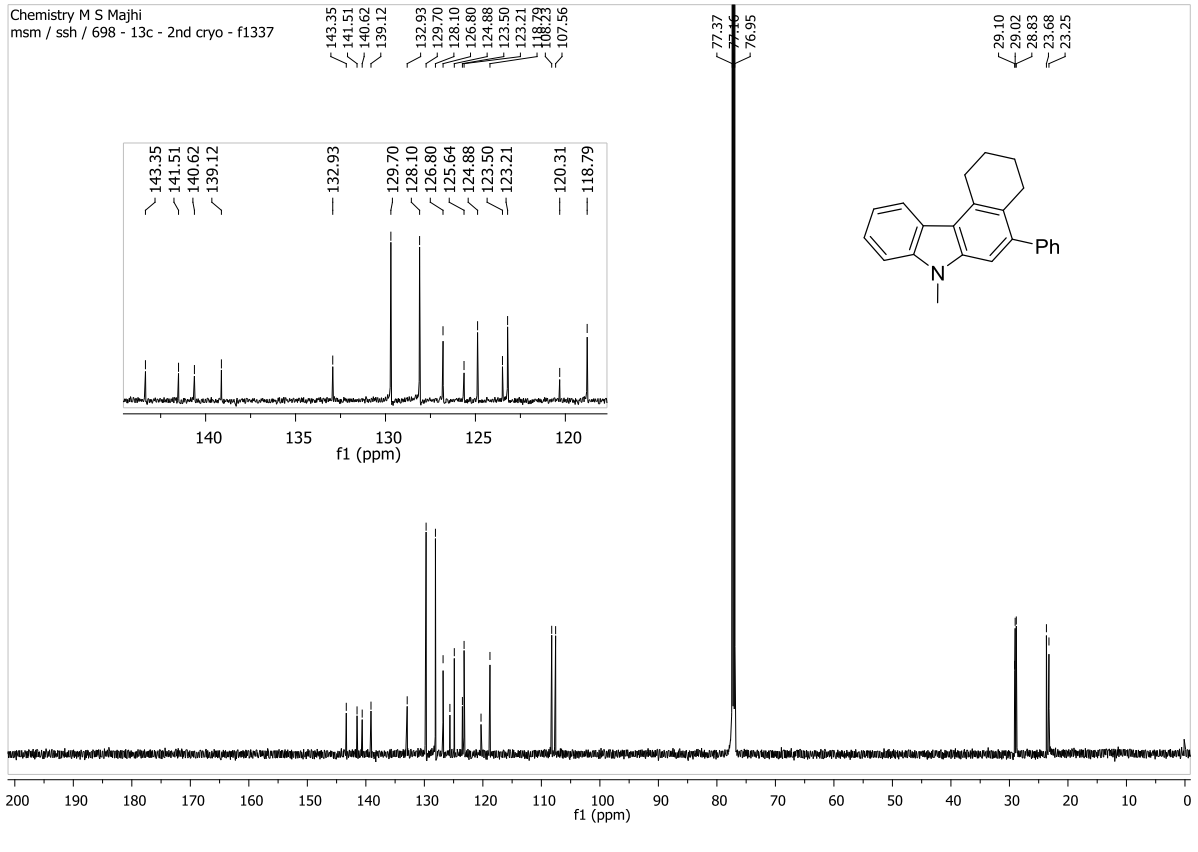
^{1}H NMR and ^{13}C NMR Spectra of Compound **3na**



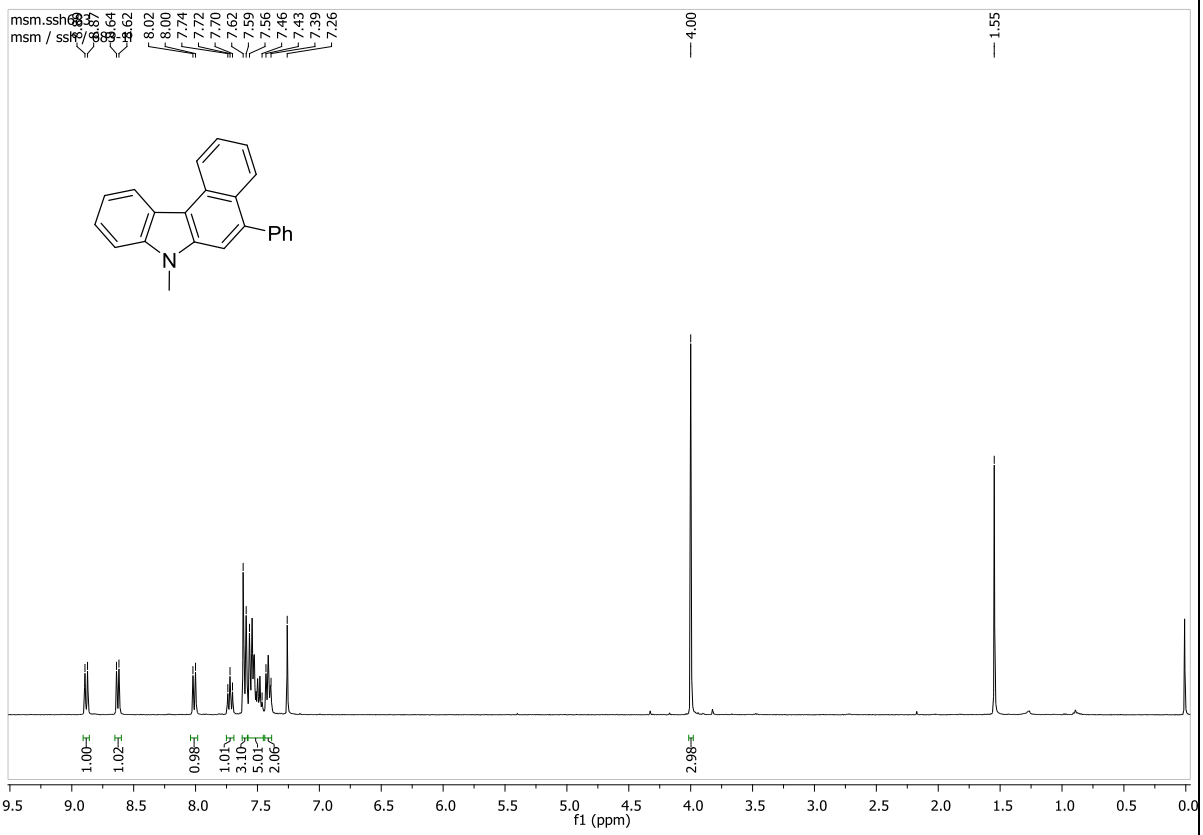


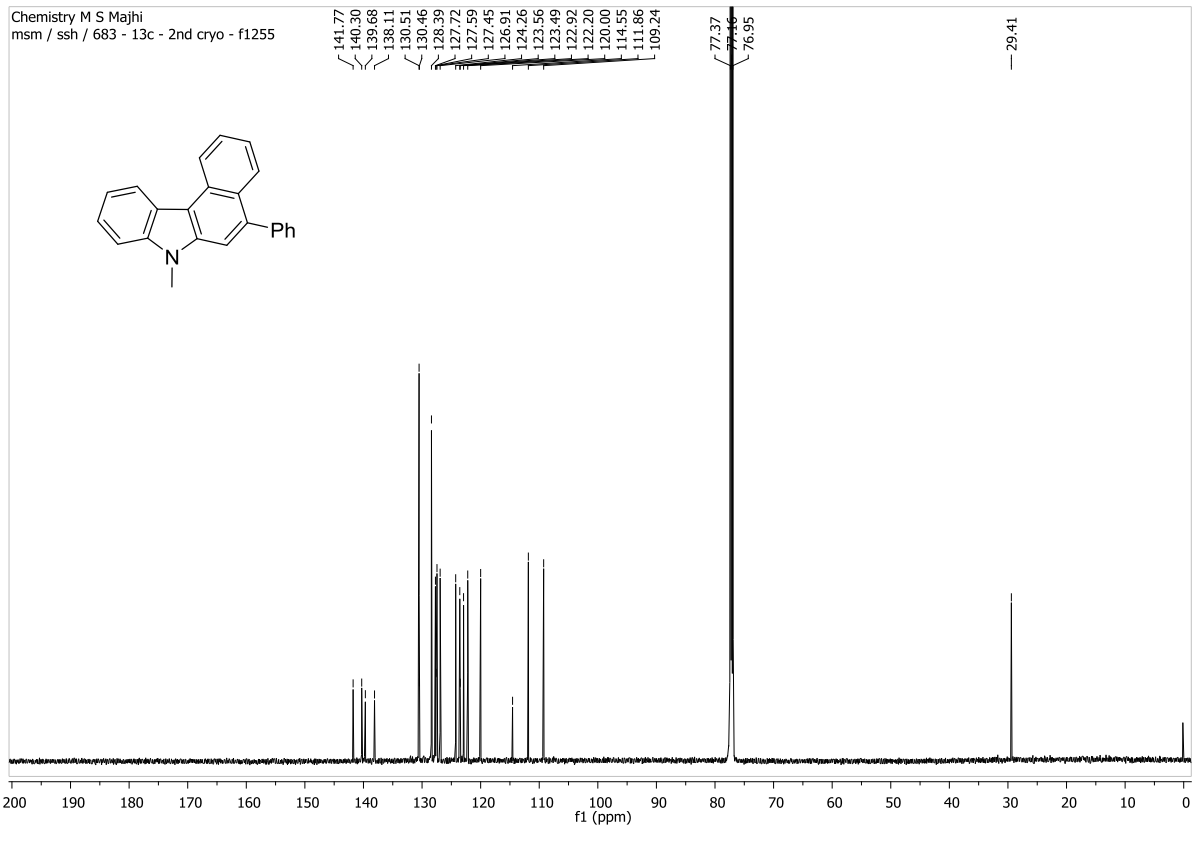
^{1}H NMR and ^{13}C NMR Spectra of Compound **3oa**



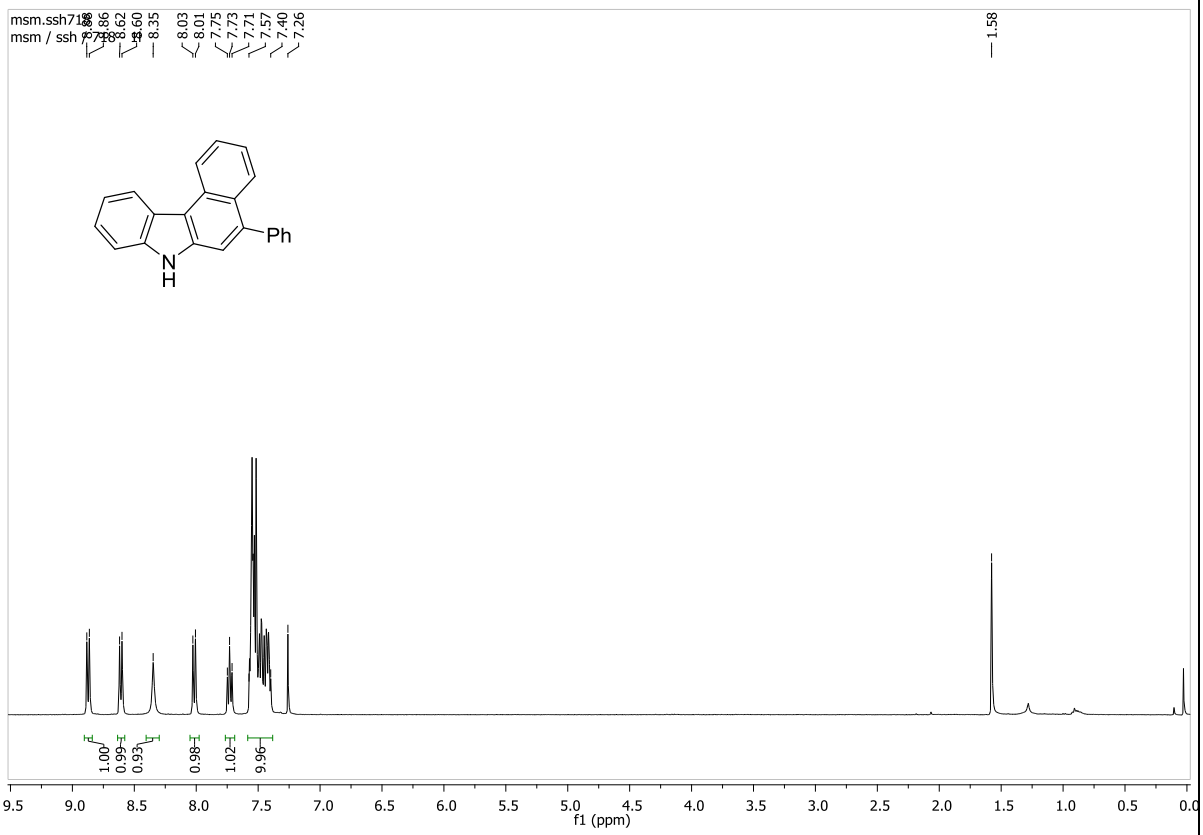


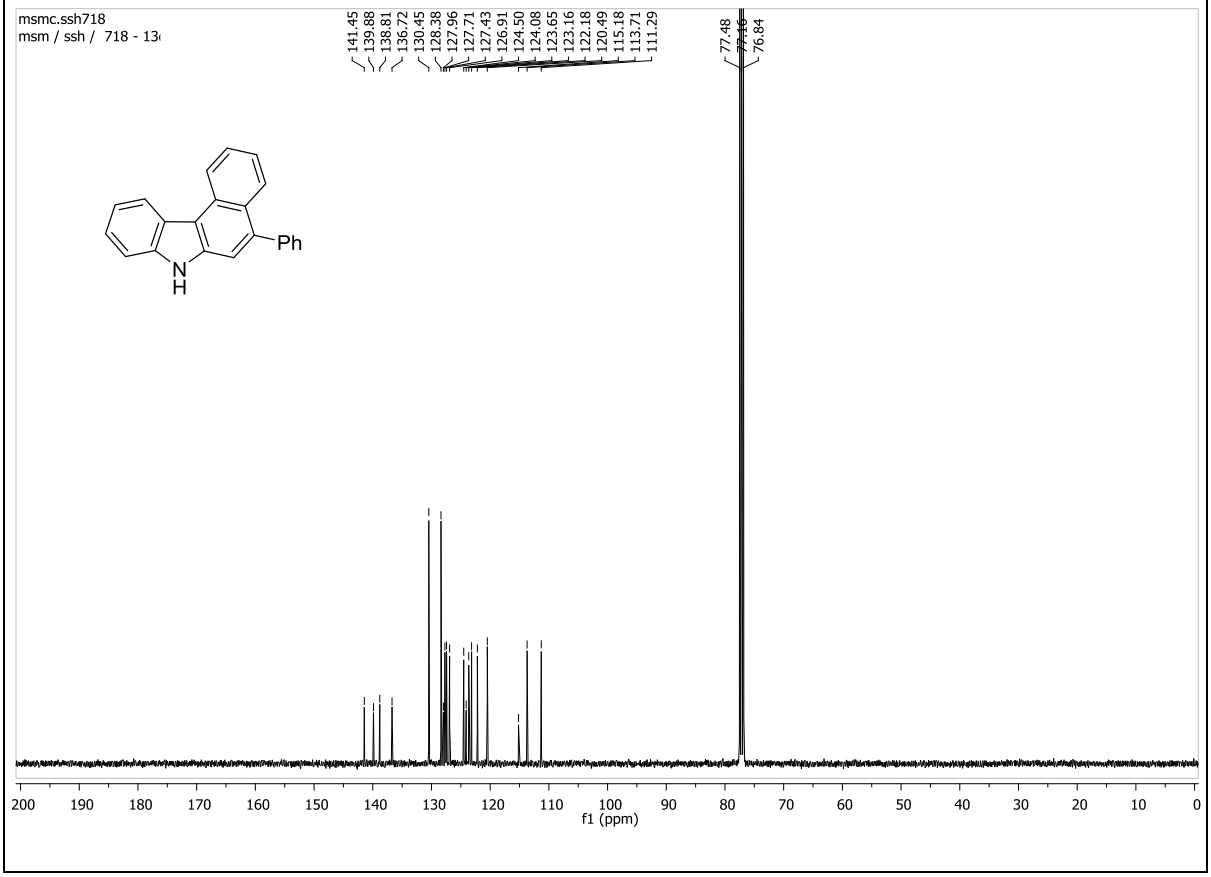
^{1}H NMR and ^{13}C NMR Spectra of Compound **4**





^{1}H NMR and ^{13}C NMR Spectra of Compound **5**





^{1}H NMR and ^{13}C NMR Spectra of Compound **6**