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Construction of Benzo[a]carbazole Derivatives via Diels-Alder Reaction of Arynes with Vinylindoles

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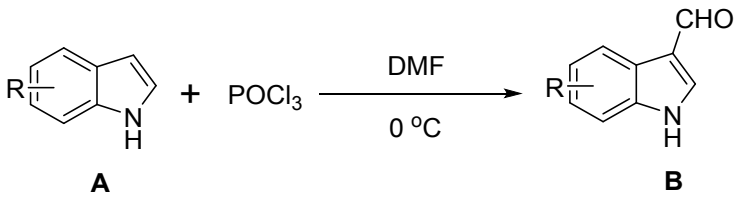
Supporting Information

1) General Information

NMR spectra of the products **3b-3d**, **3f-3o**, **3q-3t'** and **3v-3v'** were recorded using Bruker Avance-500 instruments, calibrated to TMS (^{1}H NMR spectra) and $CDCl_3$ (^{13}C NMR spectra) as the internal reference (0.00 ppm for ^{1}H NMR spectra and 77.00 ppm for ^{13}C NMR spectra). NMR spectra of the products **3a**, **3e**, **3p** and **3u** were recorded using Bruker Avance-500 instruments, calibrated to residual CD_2Cl_2 as the internal reference (5.32 ppm for ^{1}H NMR spectra and 54.00 ppm for ^{13}C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography or GC-MS analysis. Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh).

2) Synthesis of Starting Materials[1-4]

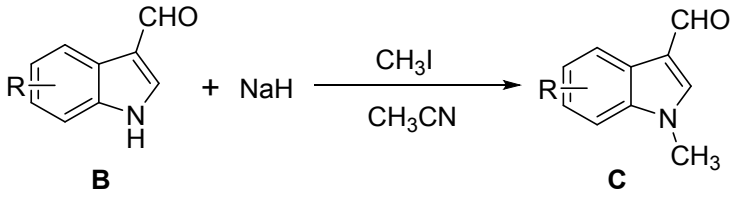
(i) General Procedure for the Synthesis of indole-3-carboxaldehyde derivatives[1]



A **B**

To a solution of phosphorus chloride oxide (7.5 mmol, 1.5 equiv) in anhydrous DMF (10.0 mL) at 0 ºC under dry nitrogen atmosphere, DMF (2.0 mL) and indole derivatives **A** (5.0 mmol, 1.0 equiv) was added to the system and the resulting mixture was stirred at room temperature. After being stirred for 1h, the reaction mixture was poured into cold saturated $NaHCO_3$ solution (aqueous) and stirred for 30 min. The reaction mixture was extracted by EtOAc for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, concentrated under reduced pressure and purified by silica gel flash column chromatography to provide desired products **B** in moderate to excellent yields.

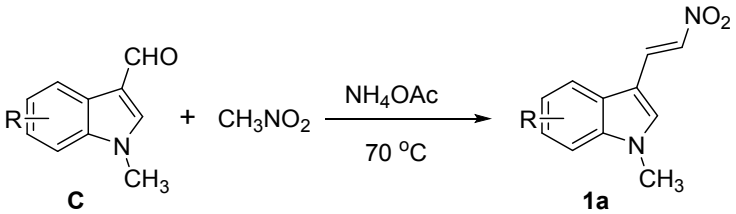
(ii) General Procedure to synthesis the N-substituted indole-3-carboxaldehyde[1]



B **C**

N-substituted indole-3-carboxaldehyde **C** was prepared by the treatment of indole-3-carboxaldehyde **B** (5.0 mmol, 1.0 equiv) with NaH (7.5 mmol, 1.5 equiv) in CH_3CN (8.0 mL) followed by the addition of CH_3I (7.5 mmol, 1.5 equiv). After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with water and extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, after removal of the solvent and the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2:1) to provide the **C** as a solid.

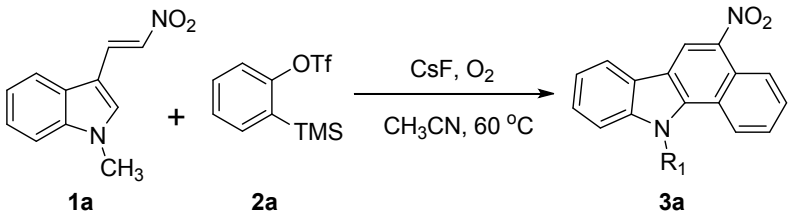
(iii) General Procedure for the Synthesis of N-substituted-3-vinylindoles (1a)[1]



C **1a**

The stirred mixture of N-substituted indole-3-carboxaldehyde **C** (1.0 mmol, 1.0 equiv) and NH_4OAc (1.5 mmol, 1.5 equiv) in CH_3NO_2 (2.0 mL) was heated at 70 ºC for 6 h. Then the reaction mixture was filtered, the solid was washed with H_2O and residue was further purified by re-crystallization from hot methanol to afford **1a** as a yellow solid.

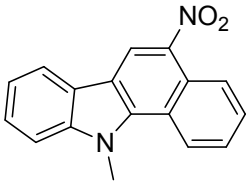
3) Typical Procedures



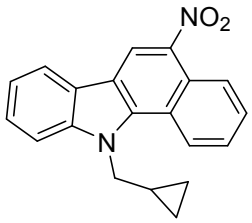
1a **2a** **3a**

The stirred mixture of N-methyl-3-vinylindoles **1a** (0.3 mmol), **2a** (0.45 mmol, 1.5 equiv) and CsF (0.9 mmol, 3.0 equiv) in CH_3CN (2.0 mL) at 60 °C for 6 h under dry O_2 atmosphere. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, organic layer was dried over Na_2SO_4. Then removal of the solvent, the crude product was purified by column chromatography (petroleum ether/ethyl acetate, 10:1) to provide the desired products **3a** as a yellow solid.

4) Characterization Data

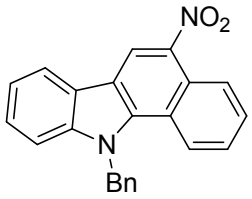


11-methyl-5-nitro-11H-benzo[a]carbazole (3a): yellow solid, isolated yield 95% (78 mg); mp: 206.9-207.7 °C; **^{1}H NMR** (CD_2Cl_2, 500 MHz) δ = 8.92 (s, 1H), 8.85 (d, *J* = 8.5 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.74-7.67 (m, 2H), 7.60-7.56 (m, 2H), 7.40-7.38 (m, 1H), 4.26 (s, 3H); **^{13}C NMR** (CD_2Cl_2, 125 MHz) δ = 142.1, 139.7, 138.9, 127.9, 126.6 (2C), 125.8, 125.0, 123.3, 123.2, 122.4, 121.6, 120.2, 120.2, 116.8, 110.2, 34.6; HRMS (ESI, m/z) calcd for $[C_{17}H_{12}N_2O_2]Na^+$: 299.0791; Found 299.0791.

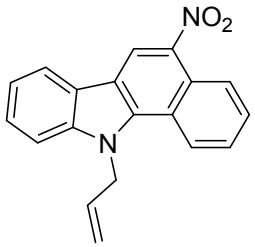


11-(cyclopropylmethyl)-5-nitro-11H-benzo[a]carbazole (3b): yellow solid, isolated yield 87% (82 mg); mp: 151.0-152.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.87 (d, *J* = 8.0 Hz, 1H), δ = 8.87 (s, 1H), 8.64 (d, *J* = 9.5 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.69-7.64 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 4.58 (d, *J* = 5.5 Hz, 2H), 1.44-1.39 (m, 1H), 0.59-0.55 (m, 2H), 0.43-0.40 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.6, 139.4, 137.8, 127.4, 126.3, 126.2, 125.4, 124.8, 123.0, 122.6, 121.6, 121.2, 119.8, 119.7, 116.8, 110.1, 48.8,

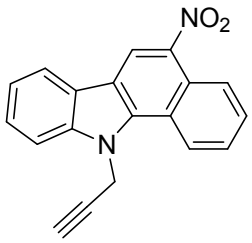
10.8, 3.6; HRMS (ESI, m/z) calcd for $[C_{20}H_{16}N_2O_2]H^+$: 317.1285; Found 317.1289.



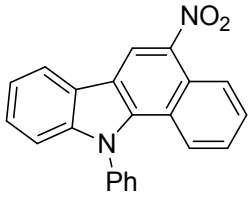
11-benzyl-5-nitro-11H-benzo[a]carbazole (3c): yellow solid, isolated yield 85% (90 mg); mp: 211.1-212.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.96 (s, 1H), 8.85 (d, *J* = 9.0 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.45-7.39 (m, 3H), 7.32-7.27 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 2H), 5.80 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.9, 139.8, 138.3, 136.0, 129.2, 127.9, 127.6, 127.5, 126.5, 125.7, 125.4, 124.7, 123.1, 122.6, 122.5, 121.8, 121.4, 119.7, 116.9, 109.9, 49.8; HRMS (ESI, m/z) calcd for $[C_{23}H_{16}N_2O_2]H^+$: 353.1285; Found 353.1290.



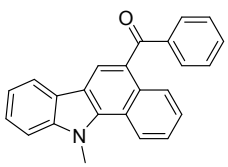
11-allyl-5-nitro-11H-benzo[a]carbazole (3d): yellow solid, isolated yield 83% (75 mg); mp: 140.0-141.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.97 (s, 1H), 8.89 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 6.31-6.24 (m, 1H), 5.32 (d, *J* = 10.5 Hz, 1H), 5.24 (t, *J* = 1.5 Hz, 2H), 5.01 (d, *J* = 17.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.6, 139.6, 138.3, 131.7, 127.6, 126.5, 126.4, 125.4, 124.8, 123.1, 122.7, 121.6, 121.4, 119.9, 119.8, 117.7, 116.8, 109.9, 48.5. HRMS (ESI, m/z) calcd for $[C_{19}H_{15}N_2O_2]H^+$: 303.1128; Found 303.1129.



5-nitro-11-(prop-2-yn-1-yl)-11H-benzo[a]carbazole (3e): yellow solid, isolated yield 75% (68 mg); mp: 229.0-209.5 °C; **^{1}H NMR** (CD_2Cl_2, 500 MHz) δ = 8.98 (s, 1H), 8.84 (t, *J* = 5.0 Hz, 1H), 8.78 (t, *J* = 5.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.79-7.75 (m, 2H), 7.67-7.60 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 5.43 (s, 2H), 2.57 (s, 1H); **^{13}C NMR** (CD_2Cl_2, 125 MHz) δ = 141.7, 140.8, 138.3, 128.3, 127.3, 127.2, 125.9, 125.2, 123.7, 123.6, 122.4, 122.2, 120.6, 120.1, 117.6, 110.2, 78.2, 74.8, 37.1; HRMS (ESI, m/z): calcd for $[C_{19}H_{12}N_2O_2]H^+$: 301.0972; Found 301.0973.

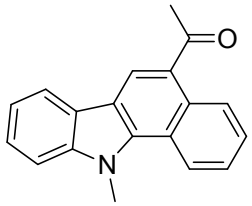


5-nitro-11-phenyl-11H-benzo[a]carbazole (3f): yellow solid, isolated yield 72% (73 mg); mp: 198.0-199.2 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.11 (s, 1H), 8.86 (d, *J* = 9.0 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 7.69-7.68 (m, 3H), 7.61 (t, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.48-7.40 (m, 4H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 143.0, 140.1, 138.8, 138.4, 130.5, 129.7, 128.7, 127.6, 126.4, 126.0, 125.4, 124.7, 123.1, 122.7, 121.9, 121.5, 120.0, 119.7, 117.1, 111.0; HRMS (ESI, m/z) calcd for $[C_{22}H_{14}N_2O_2]H^+$: 339.1128; Found 339.1132.

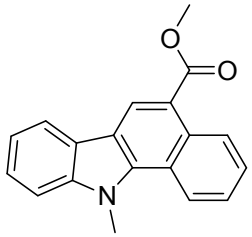


(11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3g): yellow solid, isolated yield 96% (96 mg); mp: 155.0-155.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.69 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J*

= 7.5 Hz, 1H), 8.27 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.56-7.46 (m, 5H), 7.27 (t, *J* = 8.0 Hz, 1H), 4.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.0, 141.1, 139.6, 137.3, 132.6, 131.5, 130.4, 128.3, 127.9, 127.4, 125.9, 125.6, 125.3, 123.9, 123.0, 122.7, 122.3, 120.3, 119.6, 116.9, 109.3, 34.1; HRMS (ESI, m/z) calcd for $[C_{24}H_{17}NO]H^+$: 336.1383; Found 336.1385.

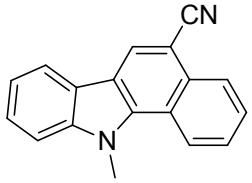


1-(11-methyl-11H-benzo[a]carbazol-5-yl)ethanone (3h): yellow solid, isolated yield 99% (81 mg); mp: 163.0-163.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.19 (d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.35 (s, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.51-7.47 (m, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 4.01 (s, 3H), 2.74 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.5, 141.0, 137.7, 130.7, 127.7, 126.6, 126.4, 125.3, 125.2, 124.3, 122.9, 122.5, 122.1, 120.3, 119.3, 116.5, 109.3, 33.8, 29.6; HRMS (ESI, m/z) calcd for $[C_{19}H_{15}NO]H^+$: 274.1226; Found 274.1226.

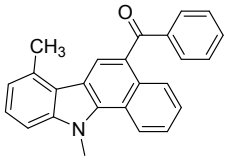


methyl 11-methyl-11H-benzo[a]carbazole-5-carboxylate (3i): yellow solid, isolated yield 94% (82 mg); mp: 168.0-168.8 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.24 (d, *J* = 8.5 Hz, 1H), 8.78 (s, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.14 (s, 3H), 4.02 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 168.3, 141.0, 138.0, 131.5, 127.2, 126.0, 125.2, 125.0, 125.0, 123.0, 122.5, 122.2, 120.3, 119.6, 118.0, 117.1, 109.2, 51.9, 34.0; HRMS (ESI, m/z) calcd

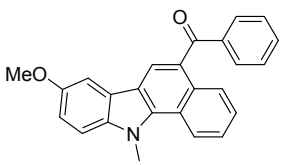
for $[C_{19}H_{15}NO_2]H^+$: 290.1176; Found 290.1179.



11-methyl-11H-benzo[a]carbazole-5-carbonitrile (3j): yellow solid, isolated yield 99% (76 mg); mp: 191.8-192.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.43 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 8.19 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.63-7.56 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 4.05 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.7, 137.3, 131.6, 126.6, 126.5, 126.4, 126.3, 125.9, 122.4, 122.0, 121.7, 120.9, 119.5, 119.3, 117.5, 109.3, 100.6, 33.7; HRMS (ESI, m/z) calcd for $[C_{18}H_{12}N_2]H^+$: 257.1073; Found 257.1071.

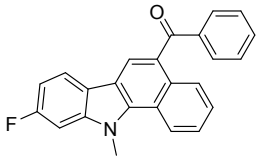


(7,11-dimethyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3k): yellow solid, isolated yield 97% (102 mg); mp: 176.0-176.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.73 (d, *J* = 8.5 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 7.93 (d, *J* = 7.0 Hz, 2H), 7.63-7.48 (m, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 8.56 (d, *J* = 4.0 Hz, 2H), 7.06 (t, *J* = 4.0 Hz, 1H), 4.34 (s, 3H), 2.72 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.1, 141.3, 139.6, 137.4, 132.6, 132.5, 130.9, 130.4, 128.2, 127.6, 127.2, 126.2, 125.8, 125.4, 125.0, 122.5, 122.4, 122.1, 121.5, 117.7, 107.1, 34.4, 20.8; HRMS (ESI, m/z) calcd for $[C_{25}H_{19}NO]H^+$: 350.1539; Found 350.1543.

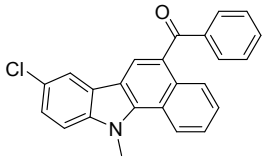


(8-methoxy-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3l): yellow solid, isolated yield 96% (105 mg); mp: 176.2-176.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.62 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 8.5 Hz, 1H), 8.20 (s, 1H), 7.92 (d, *J* = 7.0 Hz, 2H), 7.61-7.52 (m, 3H),

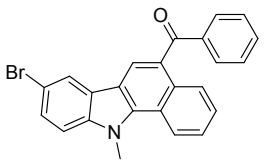
7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (s, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.09 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 4.23 (s, 3H), 3.86 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.9, 154.5, 139.8, 137.6, 136.0, 132.5, 131.4, 130.4, 128.3, 127.4, 127.3, 125.8, 125.5, 124.1, 123.2, 122.8, 122.2, 116.5, 114.9, 110.1, 101.5, 55.9, 34.1; HRMS (ESI, m/z) calcd for $[C_{25}H_{19}NO_2]H^+$: 366.1487; Found 366.1496.



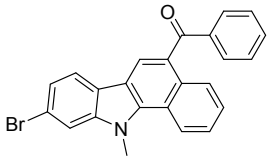
(9-fluoro-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3m): yellow solid, isolated yield 98% (104 mg); mp: 185.0-185.9 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.56 (d, *J* = 8.5 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.82-7.79 (m, 1H), 7.60-7.45 (m, 5H), 7.11 (d, *J* = 9.5 Hz, 1H), 6.96 (t, *J* = 8.5 Hz, 1H), 4.15 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.9, 161.7 (d, *J* = 240.4 Hz), 141.6 (d, *J* = 12.1 Hz), 139.5 (2C), 137.5, 132.7, 131.0, 130.4, 128.4, 128.3, 127.3, 125.8 (d, *J* = 6.2 Hz), 123.1, 122.5, 122.0, 120.5 (d, *J* = 10.4 Hz), 119.2, 116.6, 108.5 (d, *J* = 24.3 Hz), 96.2 (d, *J* = 26.9 Hz), 34.2; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}FNO]H^+$: 354.1289; Found 354.1293.



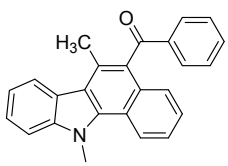
(8-chloro-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3n): yellow solid, isolated yield 98% (108 mg); mp: 211.9-212.5 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.68 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.18 (s, 1H), 7.93 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 1.0 Hz, 2H), 4.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.8, 139.4, 139.3, 137.7, 132.7, 131.7, 130.4, 128.4, 128.3, 127.5, 126.2, 125.8 (2C), 125.3, 123.9, 123.5, 122.6, 122.2, 119.1, 115.9, 110.4, 34.2; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}ClNO]H^+$: 370.0993; Found 370.0998.



(8-bromo-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3o): yellow solid, isolated yield 99% (123 mg); mp: 222.6-223.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.60 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.12 (s, 1H), 8.03 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.63-7.55 (m, 3H), 7.51-7.47 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 4.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.8, 139.6, 139.4, 137.5, 132.7, 131.7, 130.4, 128.4 (2C), 127.9, 127.4, 126.2, 125.9, 124.5, 123.4, 122.6, 122.2, 122.2, 115.8, 113.2, 110.8, 34.2; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}BrNO]H^+$: 414.0488; Found 414.0488.

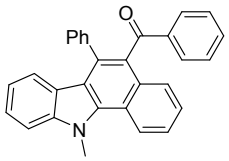


(9-bromo-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3p): yellow solid, isolated yield 97% (120 mg); mp: 226.1-227.2 °C; **^{1}H NMR** (CD_2Cl_2, 500 MHz) δ = 8.73 (d, *J* = 8.5 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.21 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.67-7.62 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 4.32 (s, 3H); **^{13}C NMR** (CD_2Cl_2, 125 MHz) δ = 197.9, 142.3, 139.9, 137.9, 133.1, 131.9, 130.7, 129.1, 128.8, 127.8, 126.4, 126.3, 123.7, 123.5, 123.1, 122.8, 122.3, 121.2, 119.1, 116.9, 113.0, 34.7; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}BrNO]H^+$: 414.0488; Found 414.0488.

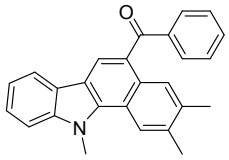


(6,11-dimethyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3q): yellow solid, isolated yield 85% (89 mg); mp: 138.5-139.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.74 (d, *J* = 8.5 Hz, 1H),

7.94 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.56-7.48 (m, 7H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.36 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 208.1, 141.2, 138.5, 135.8, 132.3, 132.1, 130.7, 128.9, 128.7, 128.3, 126.0, 125.8, 125.3, 124.8, 122.8, 122.5, 121.8, 119.6, 116.7, 115.3, 109.0, 34.3, 33.5; HRMS (ESI, m/z) calcd for $[C_{25}H_{19}NO]H^+$: 350.1539; Found 350.1542.

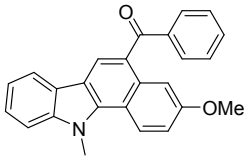


(11-methyl-6-phenyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3r): yellow solid, isolated yield 88% (108 mg); mp: 201.0-202.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.80 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29-7.22 (m, 7H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.43 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 200.2, 141.2, 139.1, 138.0, 136.0, 133.8, 132.9, 130.5, 130.1, 129.5, 129.5, 128.1, 127.7, 126.9, 125.7, 125.3, 124.8, 122.8, 122.4, 121.9, 121.6, 119.6, 117.1, 115.3, 108.9, 34.3; HRMS (ESI, m/z) calcd for $[C_{30}H_{21}NO]H^+$: 412.1696; Found 412.1698.

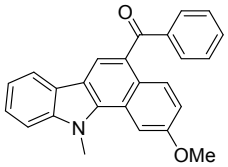


phenyl(2,3,11-trimethyl-11H-benzo[a]carbazol-5-yl)methanone (3s): yellow solid, isolated yield 95% (103 mg); mp: 237.0-238.0 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.36 (s, 2H), 8.20 (s, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50-7.46 (m, 2H), 7.26 (t, *J* = 7.0 Hz, 1H), 4.29 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.2, 141.0, 139.8, 137.1, 135.6, 135.1, 132.5, 130.5, 130.4, 128.3, 127.1, 127.1, 124.9, 123.3, 123.1, 122.1, 121.5, 120.1, 119.4, 116.3, 109.2, 34.0, 20.7, 20.3; HRMS (ESI,

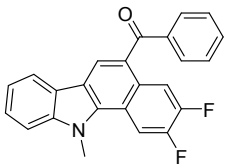
m/z) calcd for $[C_{26}H_{21}NO]H^+$: 364.1696; Found 364.1698.



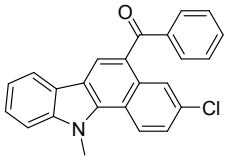
(3-methoxy-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3t): yellow solid, isolated yield 49% (54 mg), (3r : 3r' = 1.1 : 1, in total : 94%); mp: 226.0-227.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.65 (d, *J* = 9.5 Hz, 1H), 8.33 (s, 1H), 8.20 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54-7.47 (m, 4H), 7.30-7.28 (m, 2H), 4.36 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.3, 157.8, 141.1, 140.2, 138.3, 133.6, 132.4, 130.4, 128.3, 126.2, 125.8, 125.0, 123.8, 123.2, 120.3, 119.4, 117.6, 117.5, 115.6, 109.2, 106.7, 55.2, 34.1; HRMS (ESI, m/z) calcd for $[C_{25}H_{19}NO_2]H^+$: 366.1489; Found 366.1493.



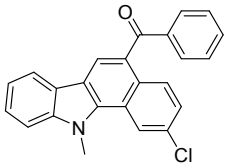
(2-methoxy-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3t'): yellow solid, isolated yield 45% (48 mg), (3r : 3r' = 1.1 : 1, in total : 94%); mp: 165.0-166.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.52 (d, *J* = 9.5 Hz, 1H), 8.15 (s, 1H), 8.07 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53-7.47 (m, 4H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 9.5 Hz, 2.0 Hz, 1H), 4.37 (s, 3H), 4.00 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 198.0, 157.2, 141.2, 139.7, 136.8, 132.5, 130.5, 129.0, 128.3, 128.0, 126.5, 125.3, 124.0, 123.1, 122.1, 120.2, 119.7, 117.4, 116.0, 109.3, 103.6, 55.4, 33.9; HRMS (ESI, m/z) calcd for $[C_{25}H_{19}NO_2]H^+$: 366.1489; Found 366.1495.



(2,3-difluoro-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3u): yellow solid, isolated yield 94% (105 mg); mp: 224.0-224.6 °C; **^{1}H NMR** (CD_2Cl_2, 500 MHz) δ = 8.60-8.55 (m, 1H), 8.51-8.47 (m, 1H), 8.33 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.56-7.51 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.33 (s, 3H); **^{13}C NMR** (CD_2Cl_2, 125 MHz) δ = 197.4, 149.8 (dd, *J* = 241.6 Hz, 9.6 Hz), 149.3 (dd, *J* = 250.6 Hz, 18.9 Hz), 141.6, 140.0, 137.2, 133.0, 130.7, 129.3 (d, *J* = 6.6 Hz), 128.8, 126.8, 126.2, 125.7, 123.1, 121.0, 120.0, 120.0 (d, *J* = 7.1 Hz), 117.5, 114.8 (d, *J* = 18.9 Hz), 110.0, 109.8 (d, *J* = 19.0 Hz), 34.2; HRMS (ESI, m/z) calcd for $[C_{24}H_{15}F_2NO]H^+$: 372.1195; Found 372.1200.



(3-chloro-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3v): yellow solid, isolated yield 47% (52 mg), (3t : 3t' = 1 : 1, in total : 93%); mp: 194.0-195.1 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.63 (s, 1H), 8.52 (d, *J* = 9.0 Hz, 1H), 8.28 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.56-7.47 (m, 5H), 7.30 (t, *J* = 7.0 Hz, 1H), 4.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.6, 141.2, 139.4, 136.2, 132.7, 131.5, 130.5, 129.7, 129.0, 128.4, 127.6, 126.4, 125.8, 124.2, 123.4, 122.7, 121.4, 120.6, 119.8, 117.8, 109.5, 34.0; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}ClNO]H^+$: 370.0993; Found 370.0998.



(2-chloro-11-methyl-11H-benzo[a]carbazol-5-yl)(phenyl)methanone (3v'): yellow solid, isolated yield 46% (51 mg), (3t : 3t' = 1 : 1, in total : 93%); mp: 156.8-157.6 °C; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.67 (s, 1H), 8.63 (d, *J* = 9.0 Hz, 1H), 8.30 (s, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.57-7.49 (m, 5H), 7.30 (t, *J* = 8.0 Hz, 1H), 4.35 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 197.4, 141.2, 139.4, 137.2, 132.7, 132.4, 132.3, 130.5, 128.4,

126.7, 126.6, 126.3, 125.6, 125.2, 123.7, 122.9, 121.0, 120.6, 119.7, 117.1, 109.4, 34.2; HRMS (ESI, m/z) calcd for $[C_{24}H_{16}ClNO]H^+$: 370.0993; Found 370.0997.

5) X-ray crystallographic studies for 3c.

The single crystals of **3c** suitable for X-ray analysis were grown in solution of hexane, diethyl ether and ethyl acetate as co-solvent. Data collections for **3c** were performed at 25 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Cu Kα radiation (λ = 1.54184 Å). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package for **3c**. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) for **3c** to yield the reflection data file. The structures of **3c** were solved by use of SHELXTL program. Refinement was performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **3c** are summarized in **Table S1**. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1059087 (**3c**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/deposit.

Table S1. Crystal data and structure refinement for 3c.

Identification code	3c
Empirical formula	$C_{23}H_{16}N_2O_2$
Formula weight	352.38
Temperature/K	180.01(10)
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 5.7929(3) Å α = 90°

	b = 14.5941(5) Å β = 105.323(5)°
	c = 10.6740(5) Å γ = 90°
Volume	870.32(7) $Å^3$
Z	2
Density (calculated)	1.345 mg/mm^3
Absorption coefficient	0.697 m/mm^{-1}
F(000)	368.0
Crystal size/mm^3	0.1 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184 Å)
Theta range for data collection	8.59 to 133.116°
Index ranges	$-6 \leq h \leq 4$, $-17 \leq k \leq 17$, $-12 \leq l \leq 12$
Reflections collected	4998
Independent reflections	2662 [R_{int} = 0.0304, R_{sigma} = 0.0273]
Data/restraints/parameters	2662/1/244
Goodness-of-fit on F^2	1.133
Final R indexes [I>=2σ (I)]	R_1 = 0.0846, wR_2 = 0.2608
Final R indexes [all data]	R_1 = 0.0859, wR_2 = 0.2617
Largest diff. peak/hole	0.41/-0.43 e $Å^{-3}$

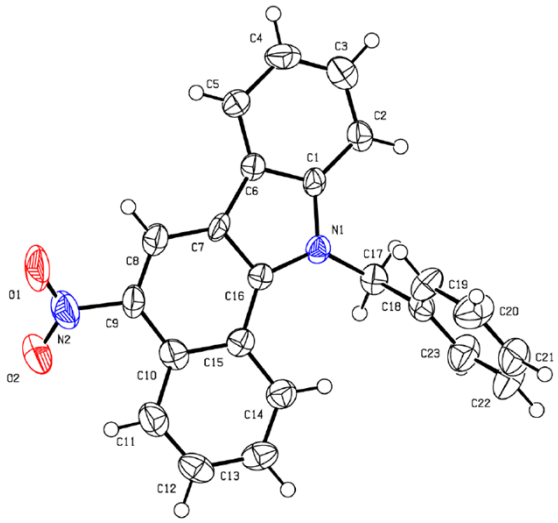


Figure S1. **OPTEP structure of 3c**

6) References

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2 L. Shi, D. Zhang, R. Lin, C. Zhang, X. Li and N, Jiao, *Tetrahedron. Lett*., 2014, **55**, 2243.

3 D. S. Giorgio, I. Irene and S. Aldo, *Synlett*., 2006, **9**, 1319.

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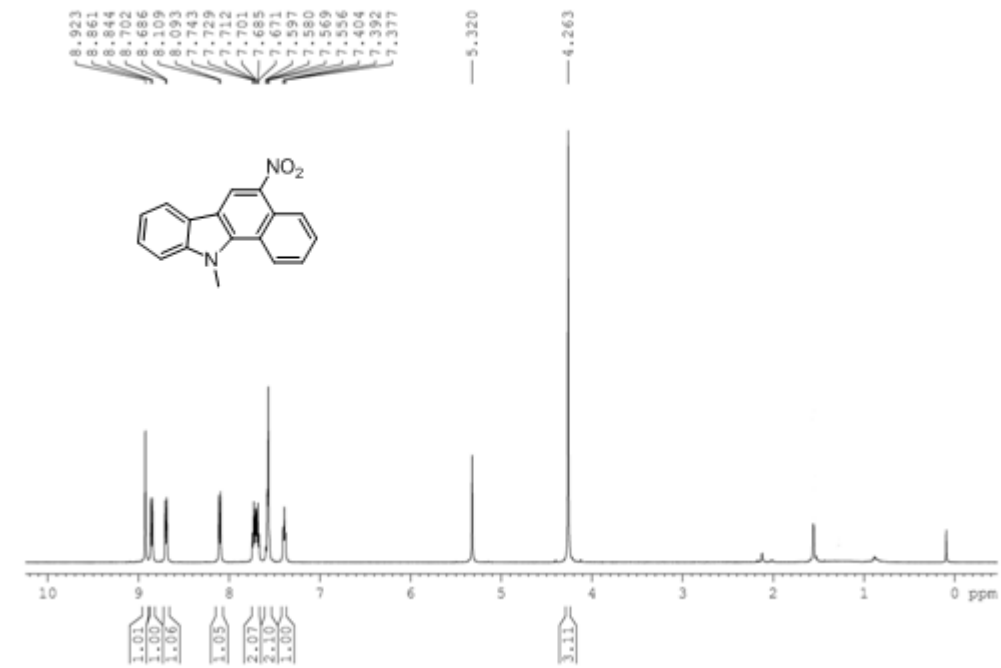
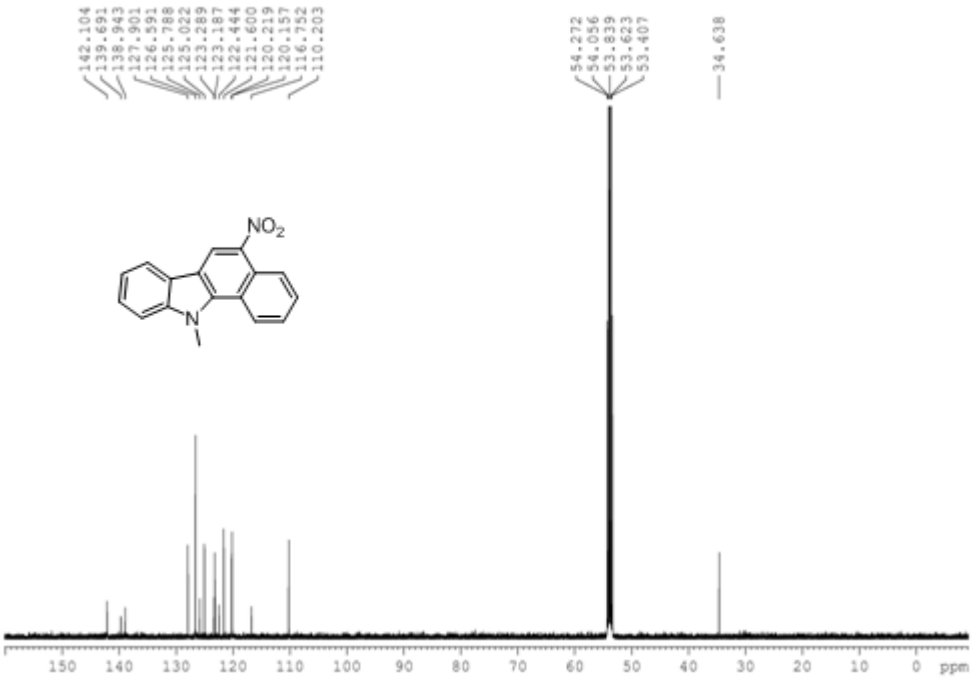
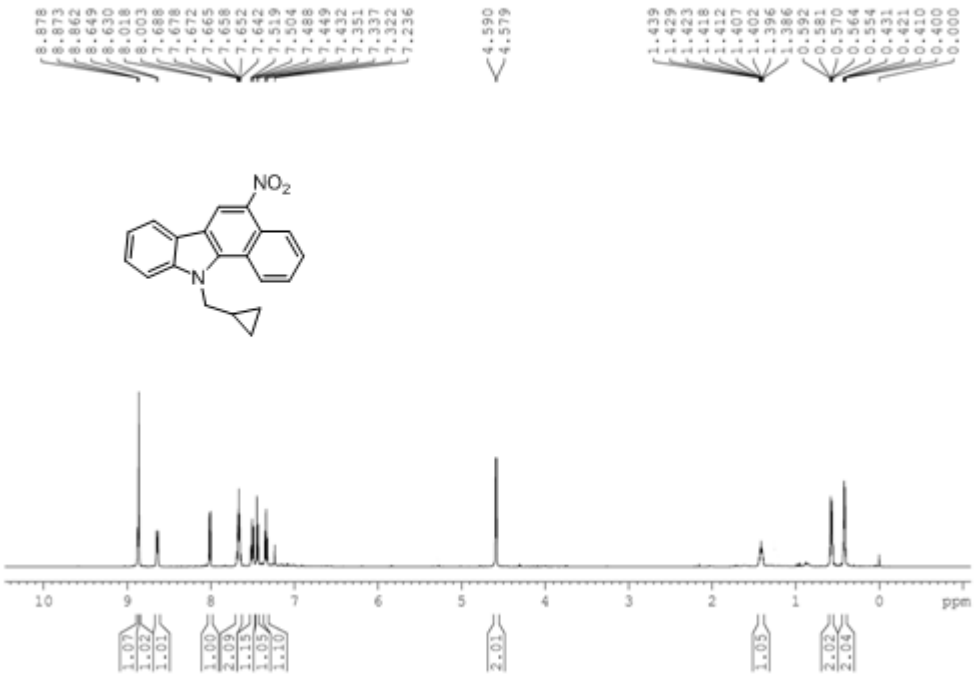
7) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

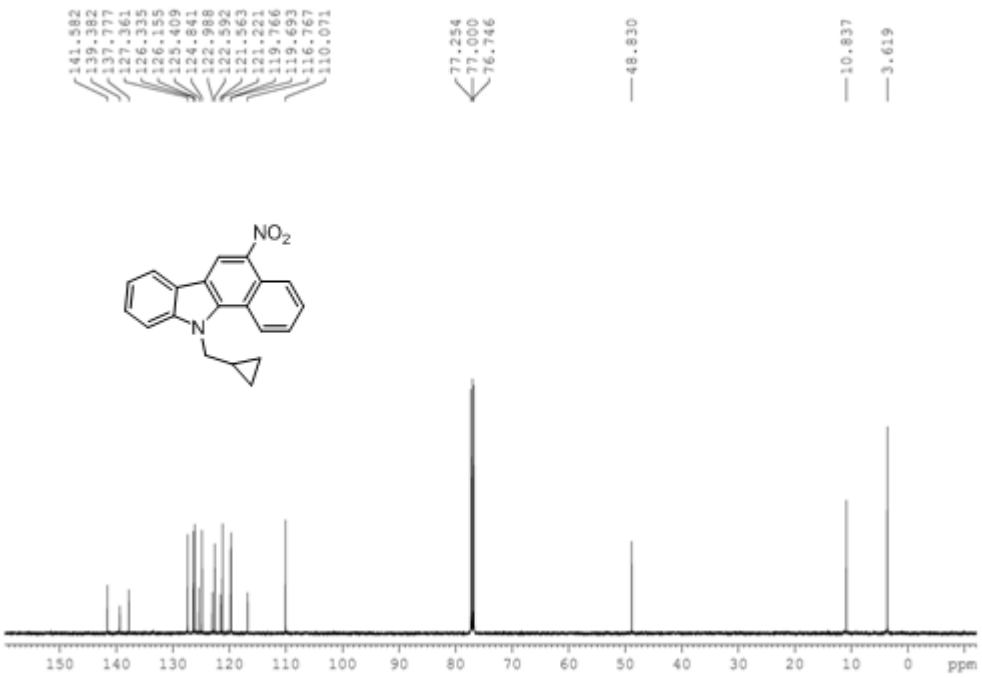
^{1}H and ^{13}C Spectrum of Compound **3a**



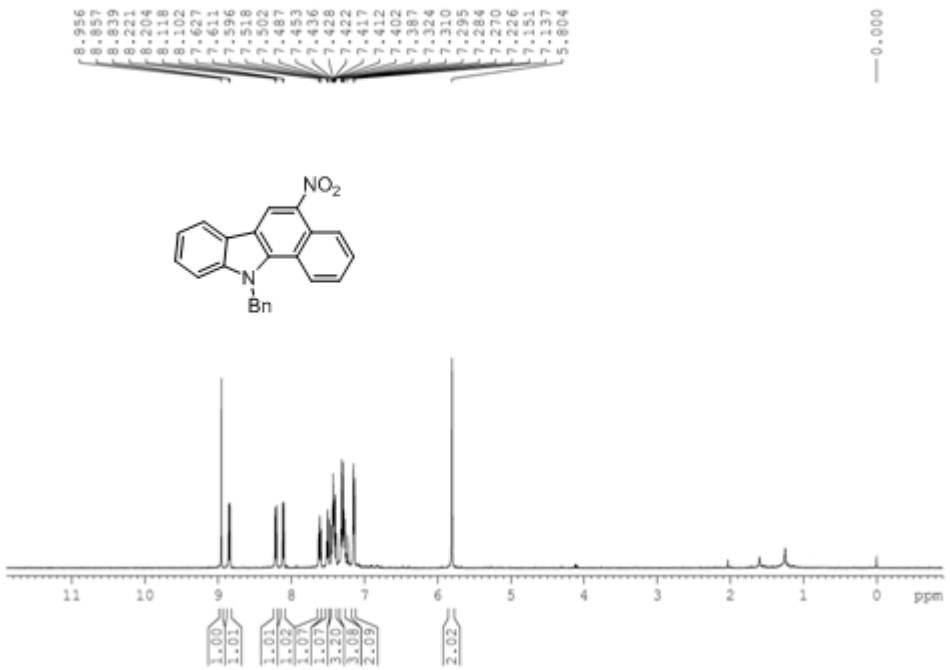


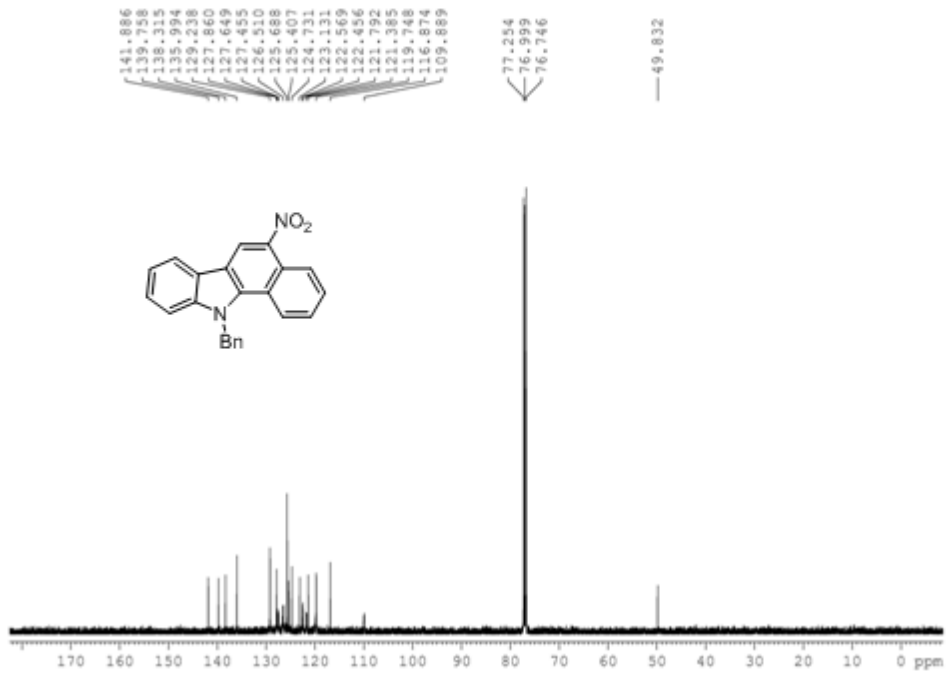
^{1}H and ^{13}C Spectrum of Compound **3b**



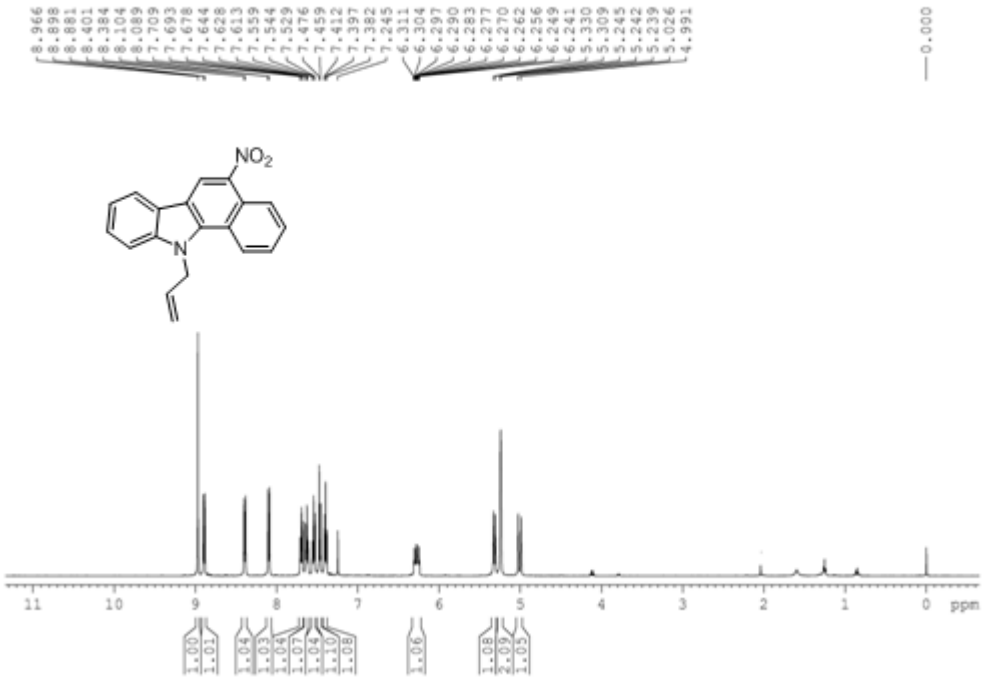


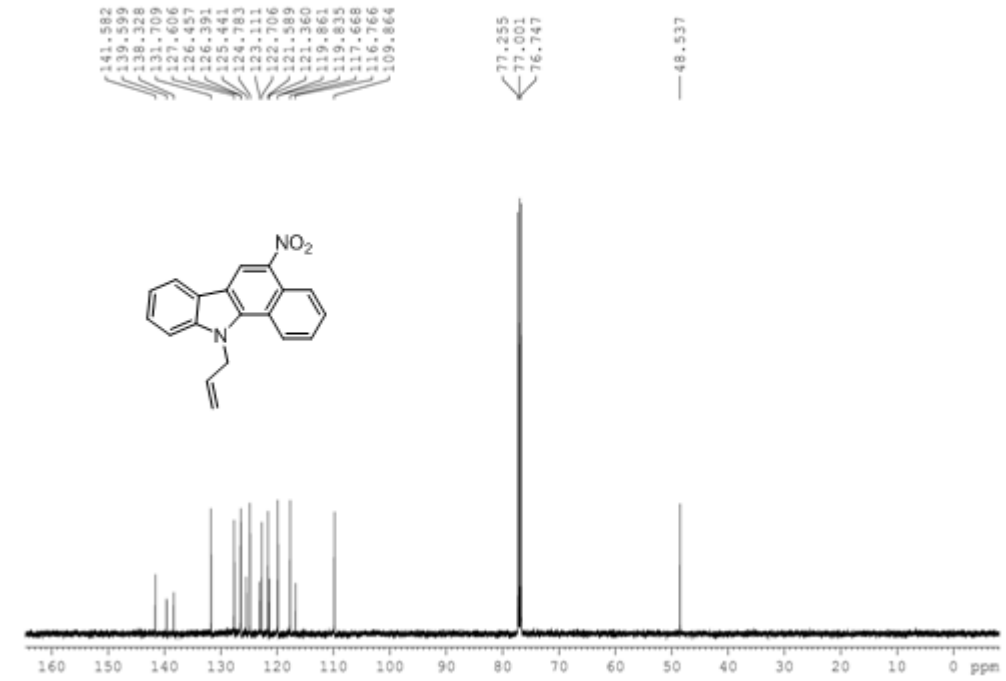
^{1}H and ^{13}C Spectrum of Compound **3c**



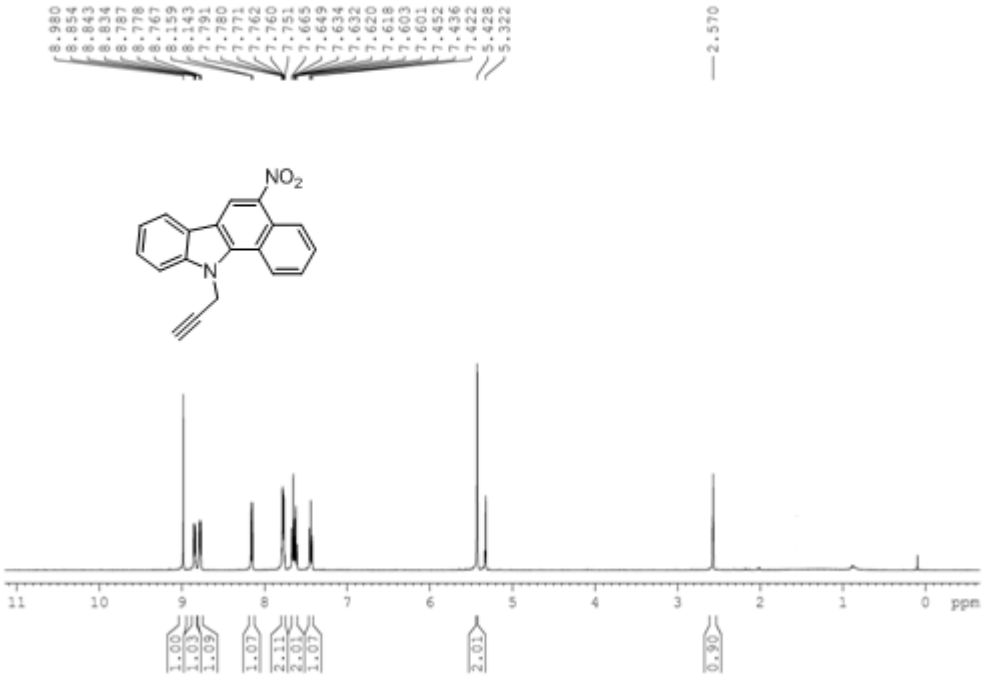


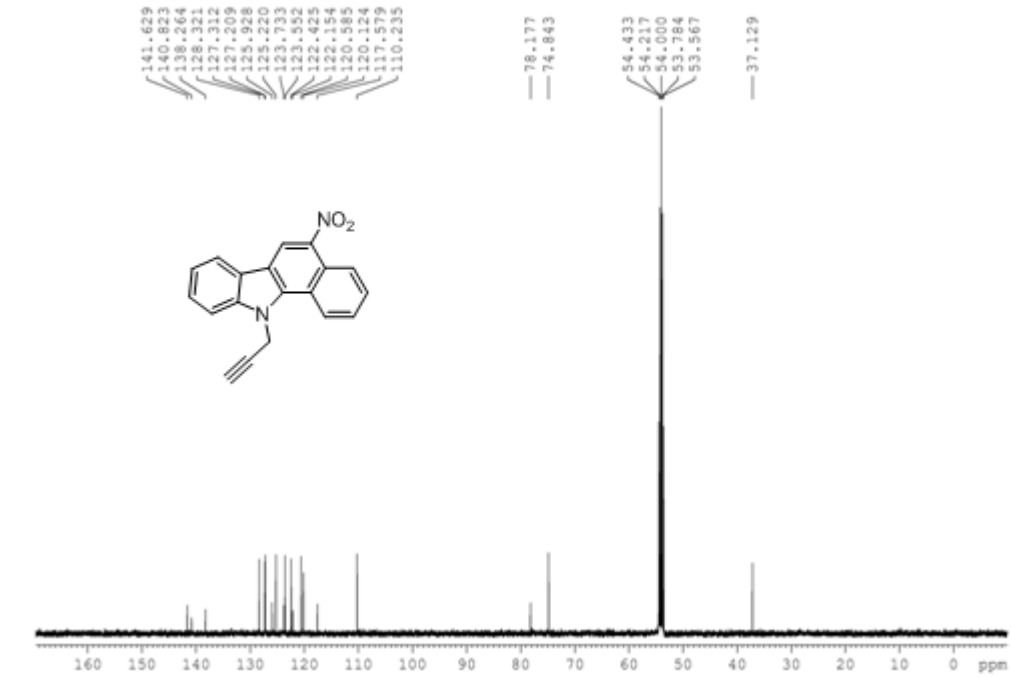
^{1}H and ^{13}C Spectrum of Compound **3d**



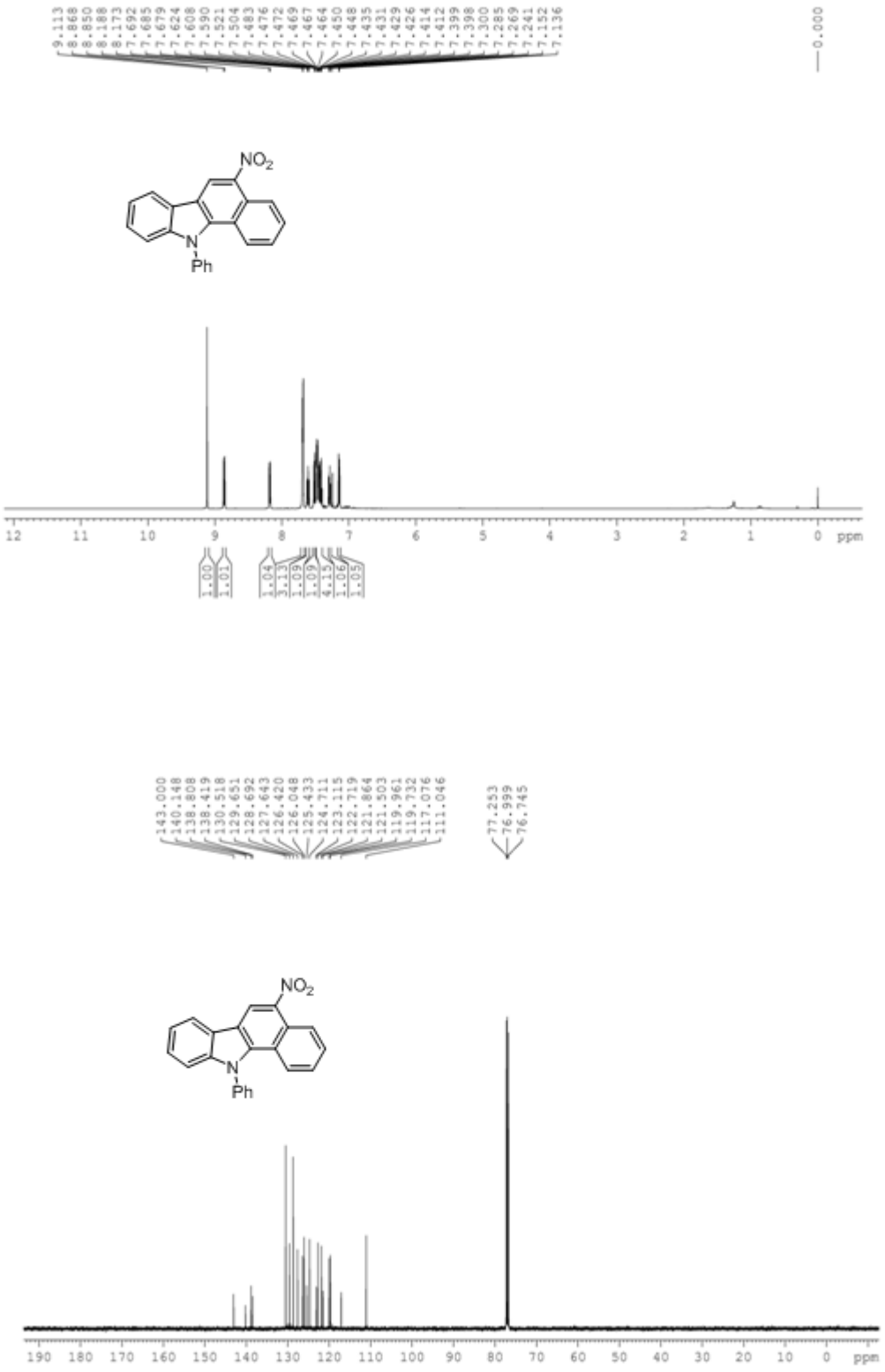


^{1}H and ^{13}C Spectrum of Compound **3e**

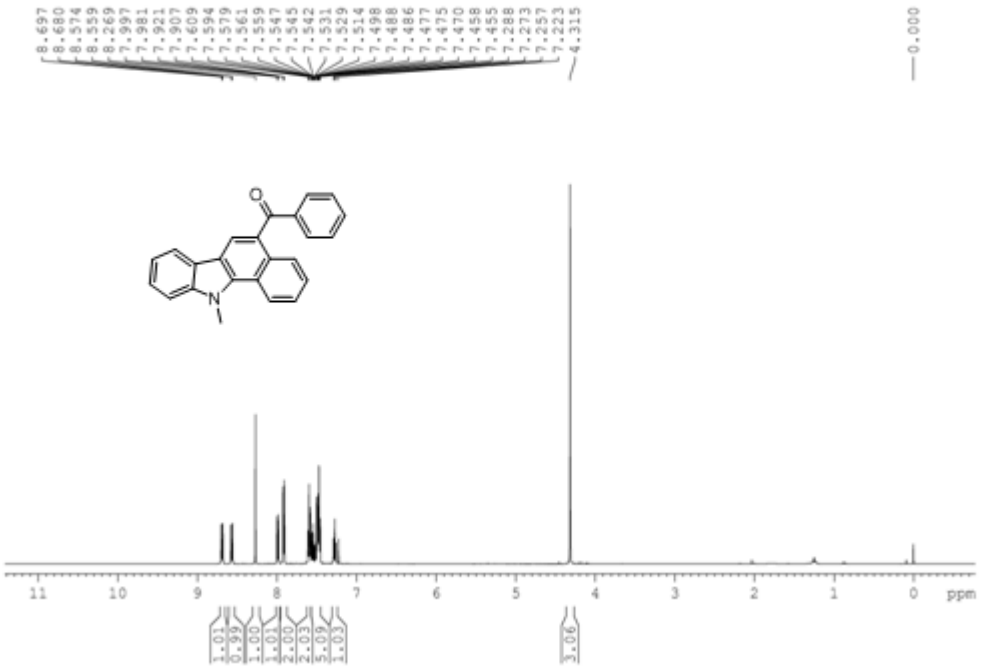


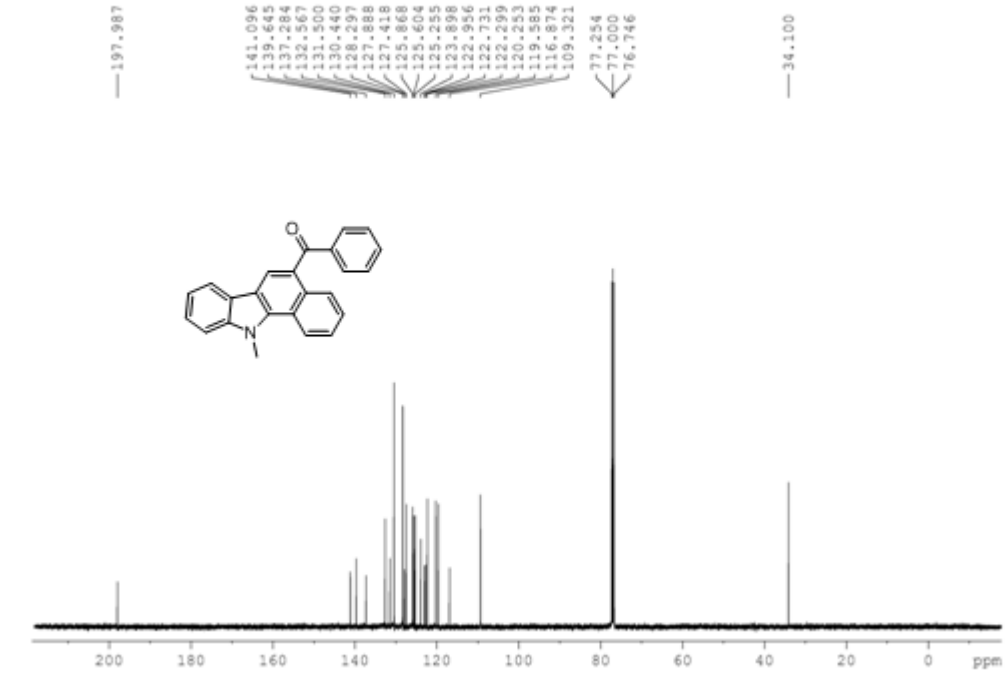


^{1}H and ^{13}C Spectrum of Compound **3f**

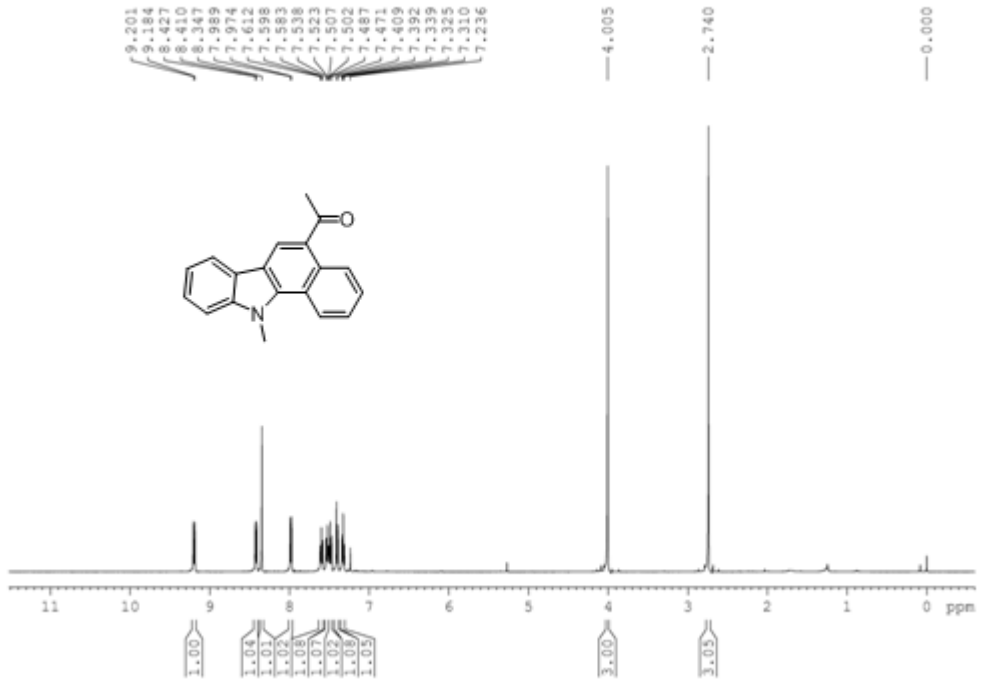


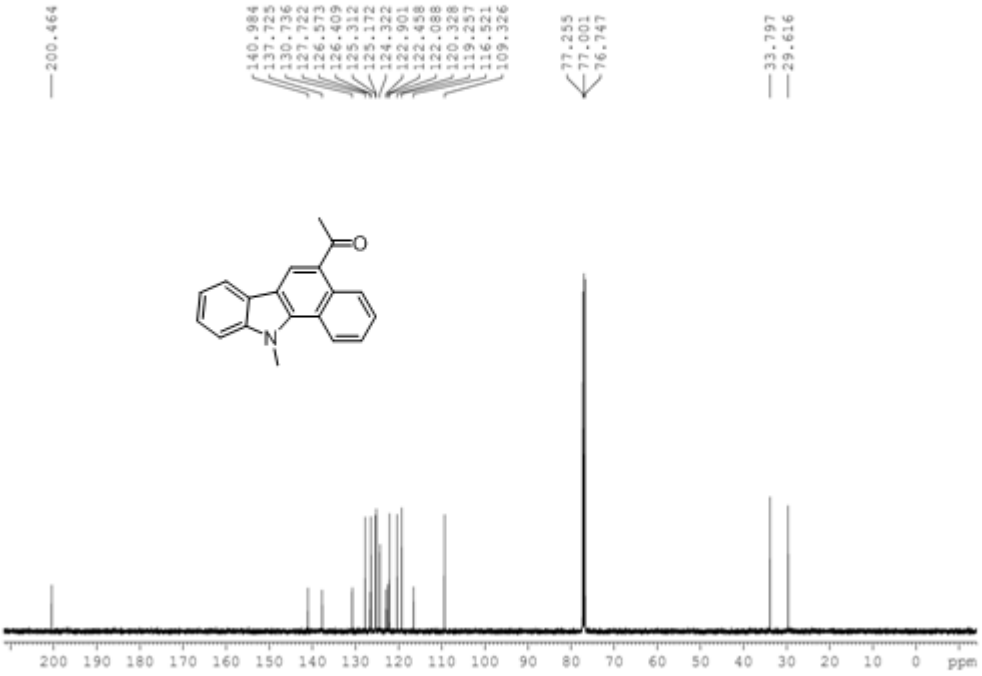
^{1}H and ^{13}C Spectrum of Compound **3g**



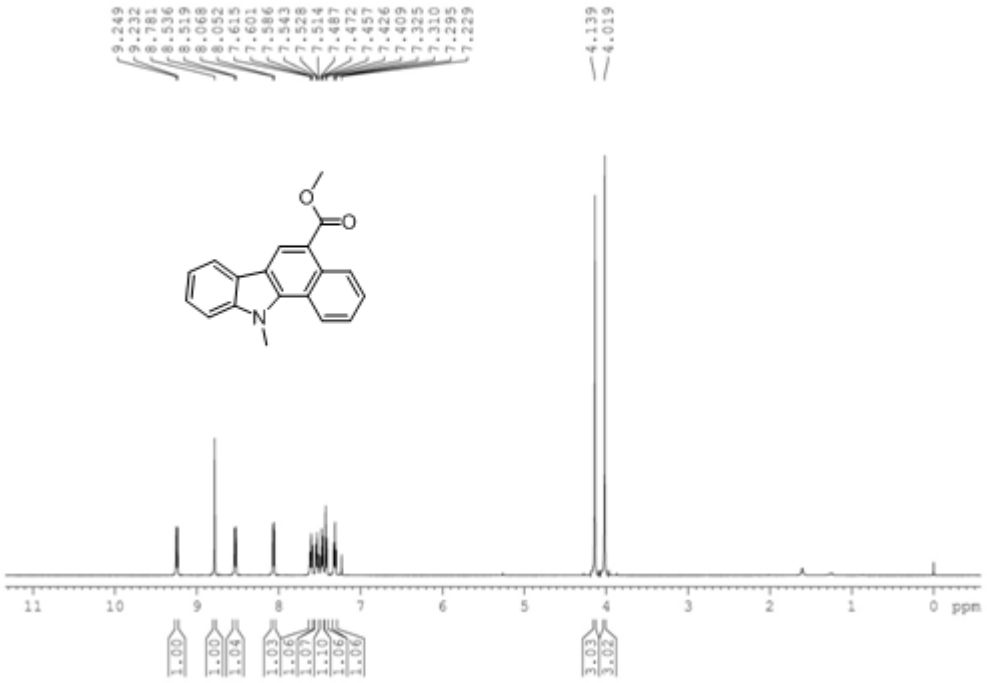


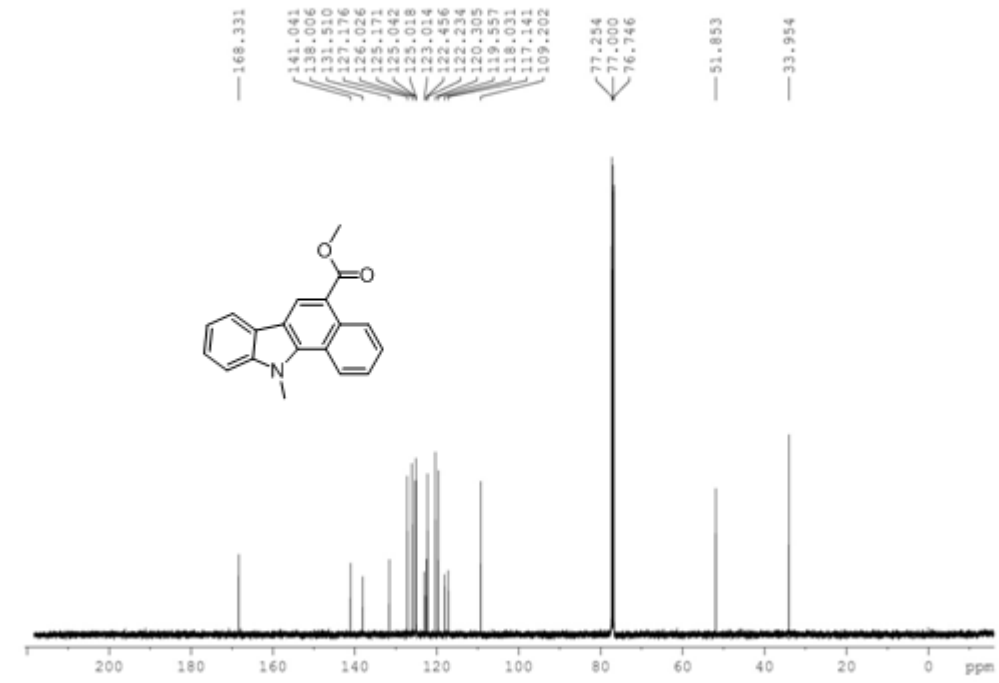
^{1}H and ^{13}C Spectrum of Compound **3h**



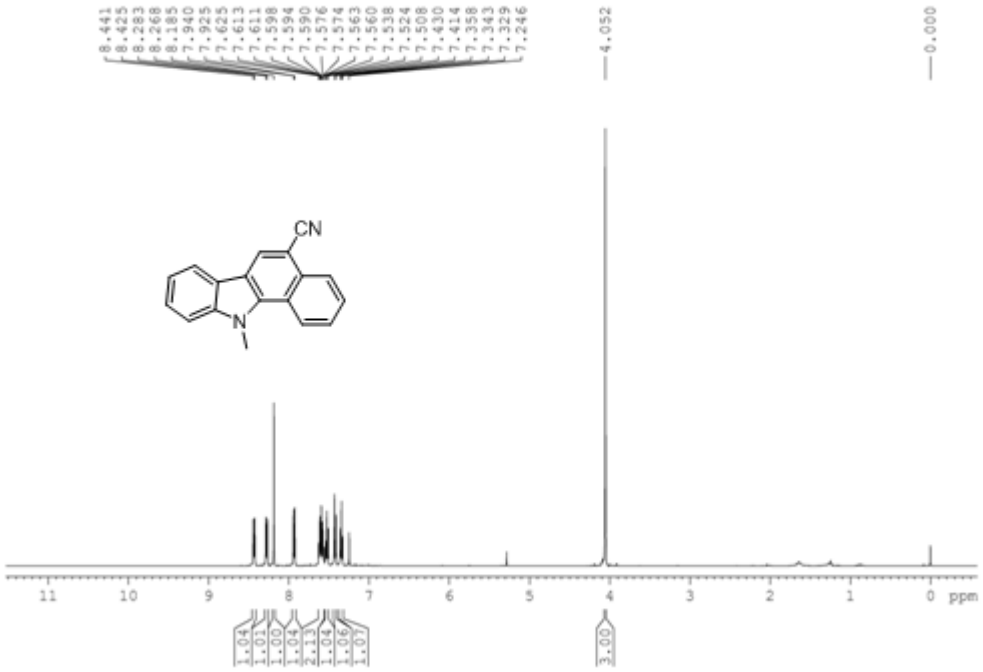


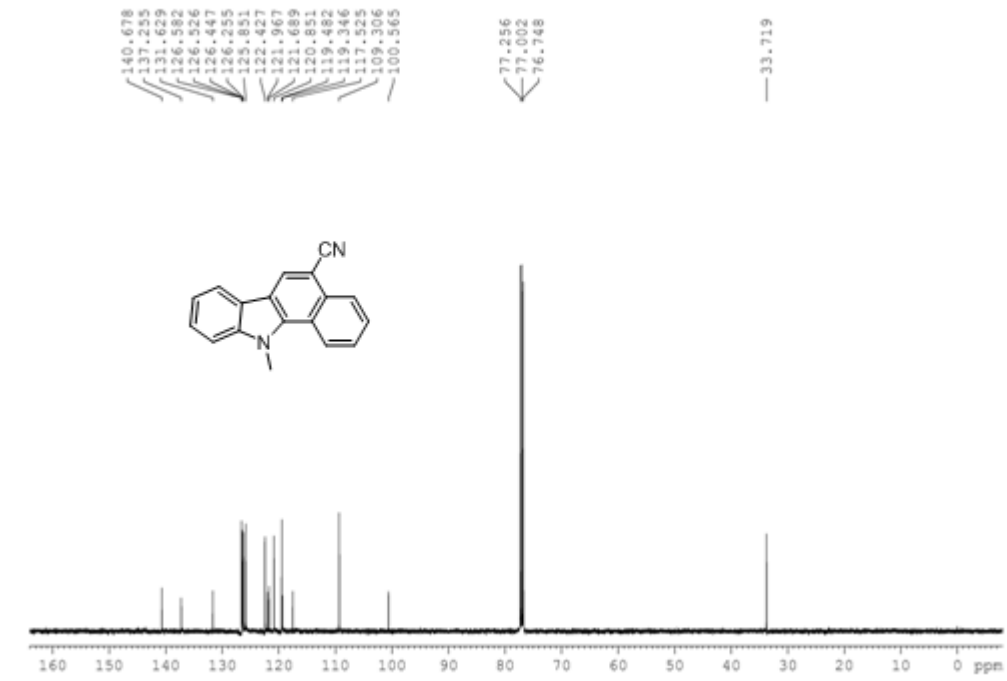
^{1}H and ^{13}C Spectrum of Compound **3i**



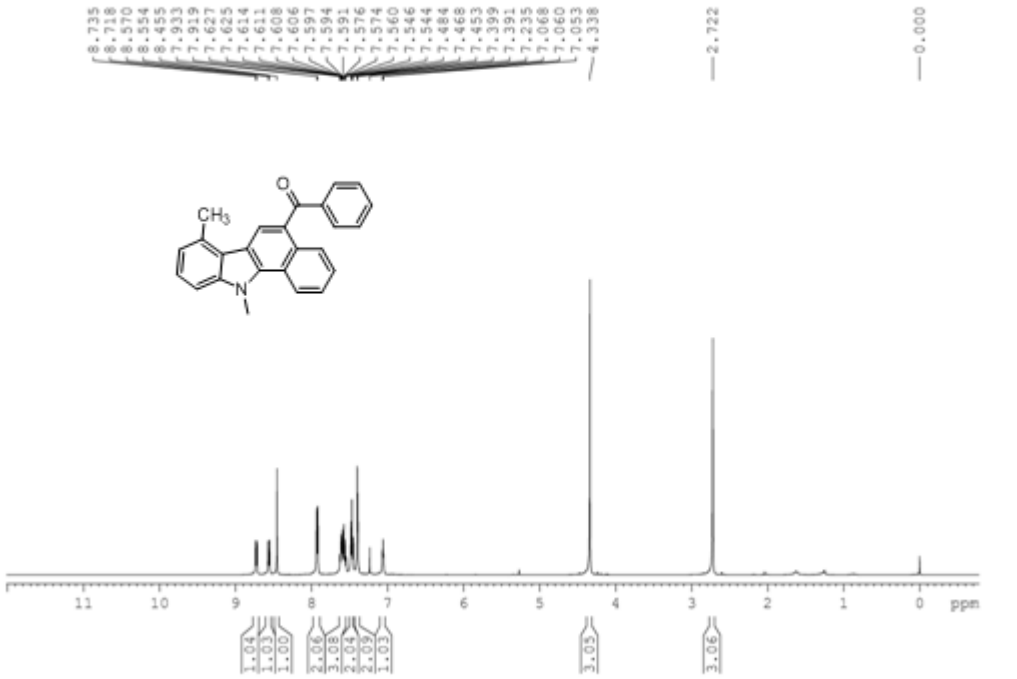


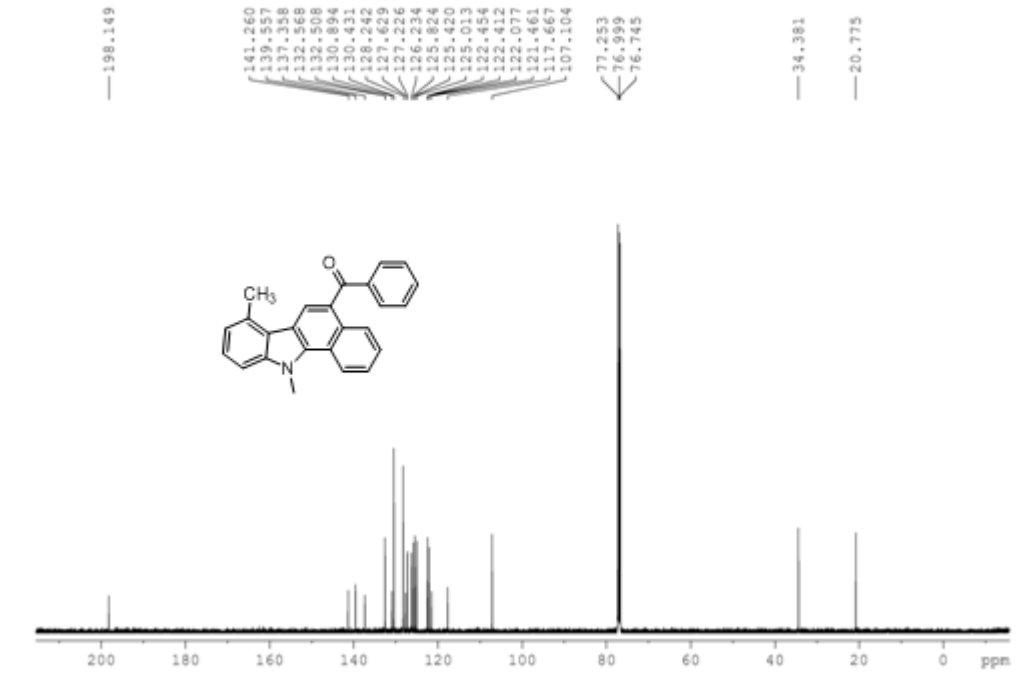
^{1}H and ^{13}C Spectrum of Compound **3j**



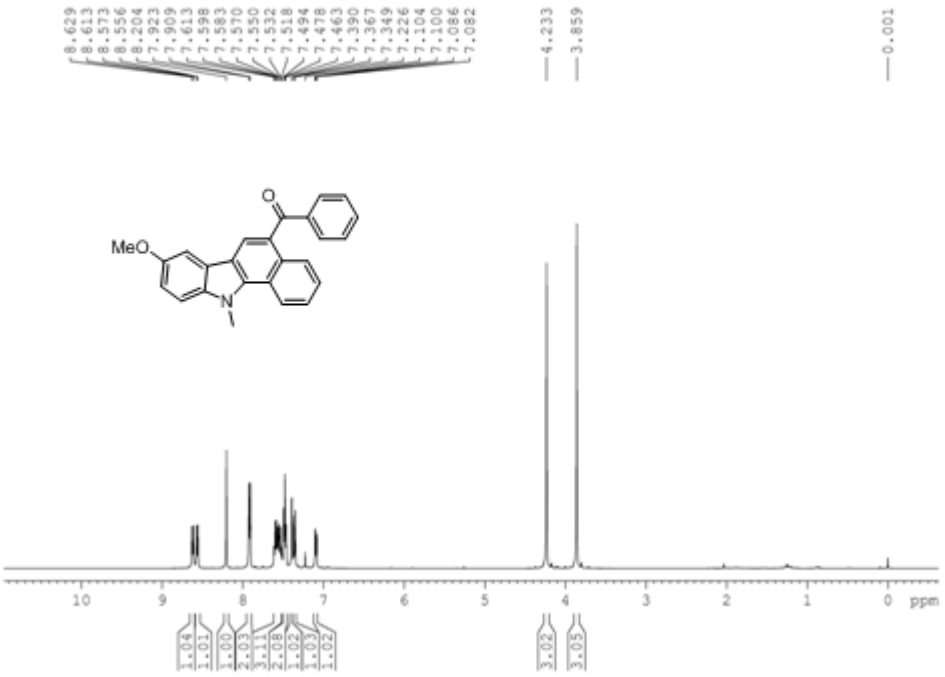


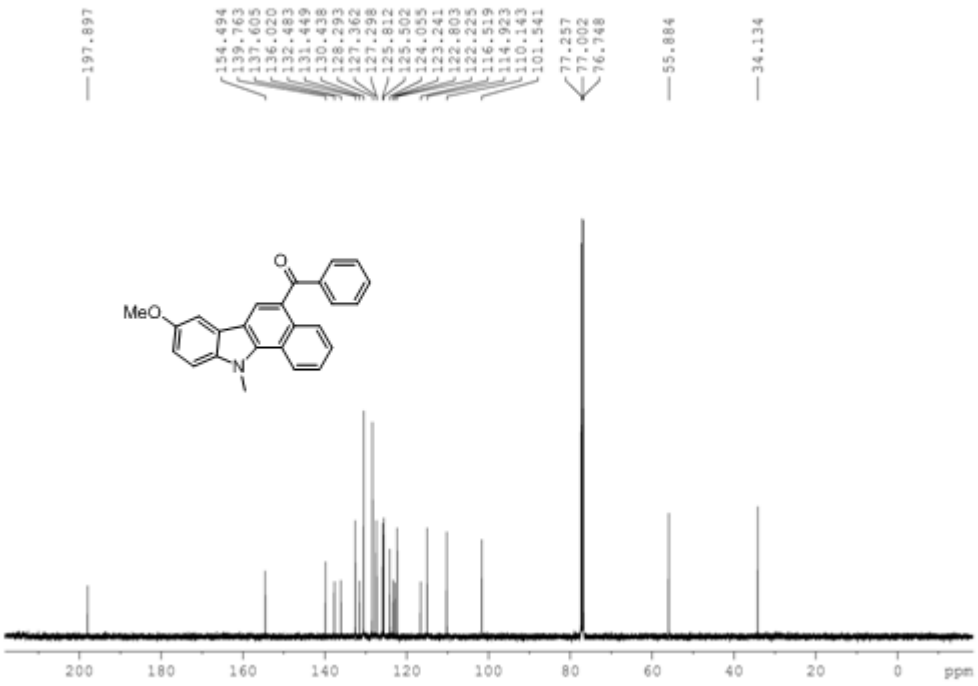
^{1}H and ^{13}C Spectrum of Compound **3k**



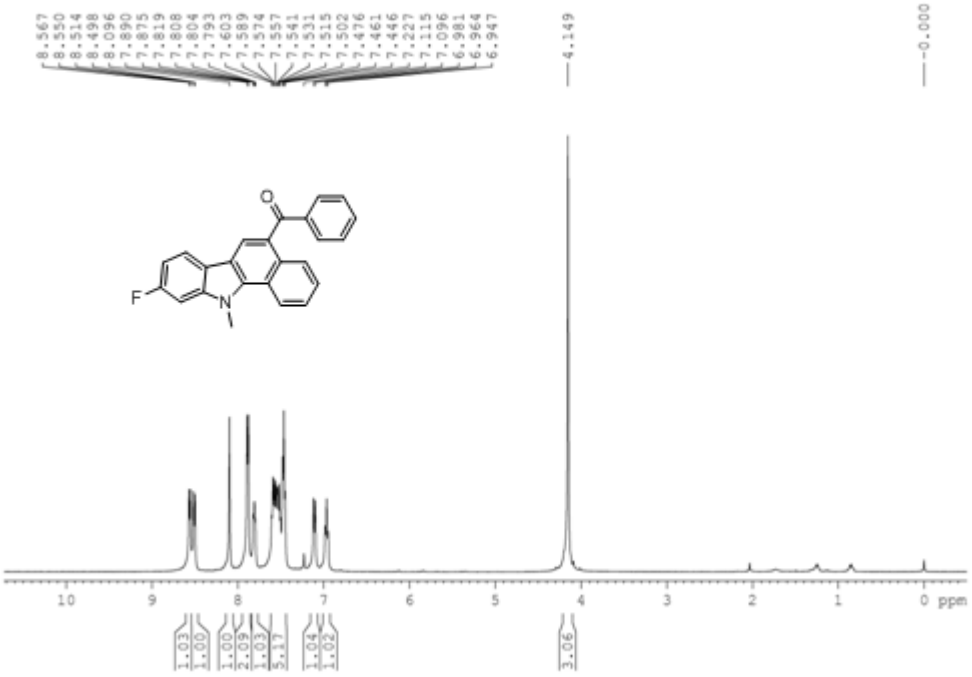


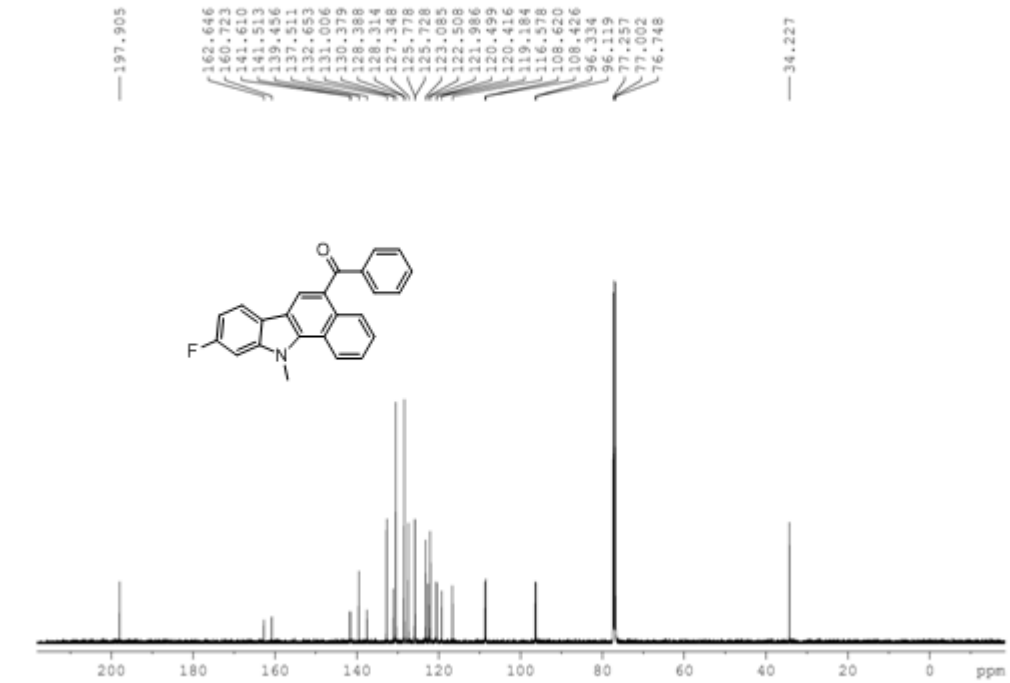
^{1}H and ^{13}C Spectrum of Compound **3l**



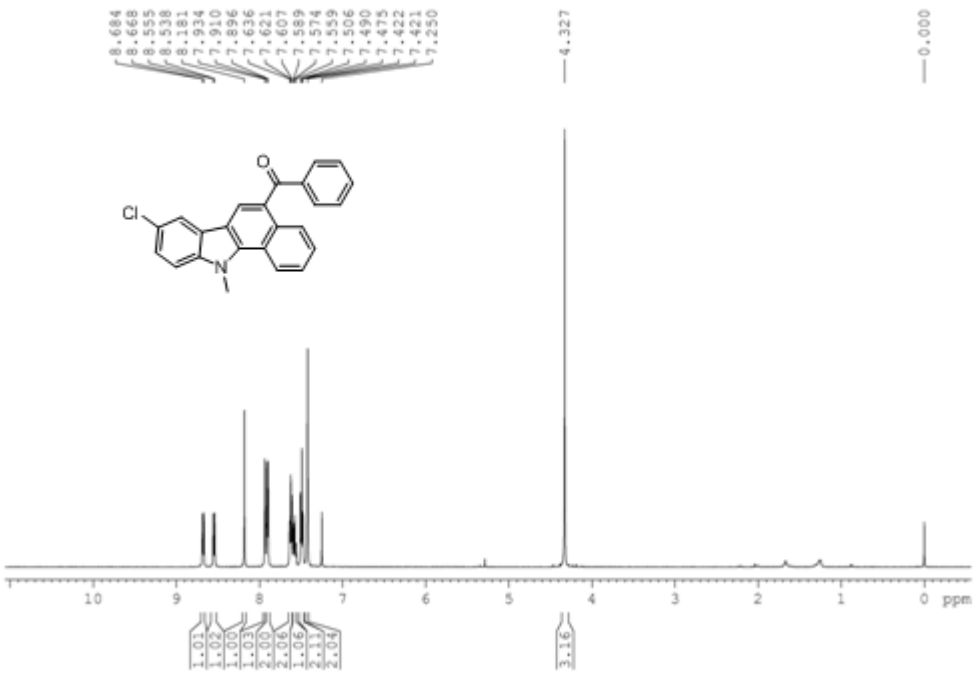


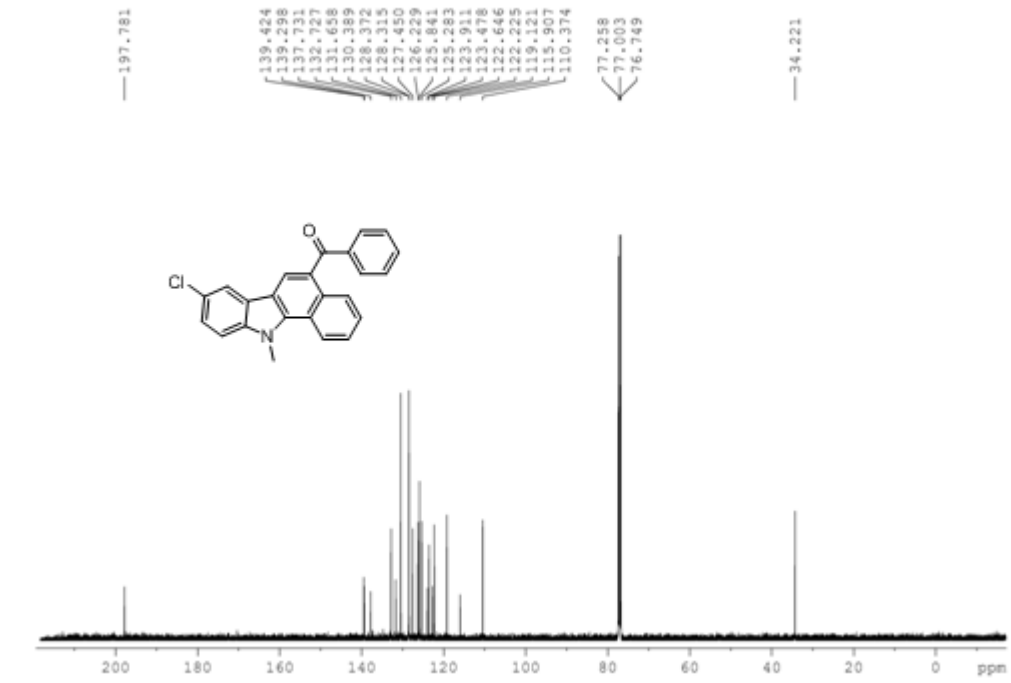
^{1}H and ^{13}C Spectrum of Compound **3m**



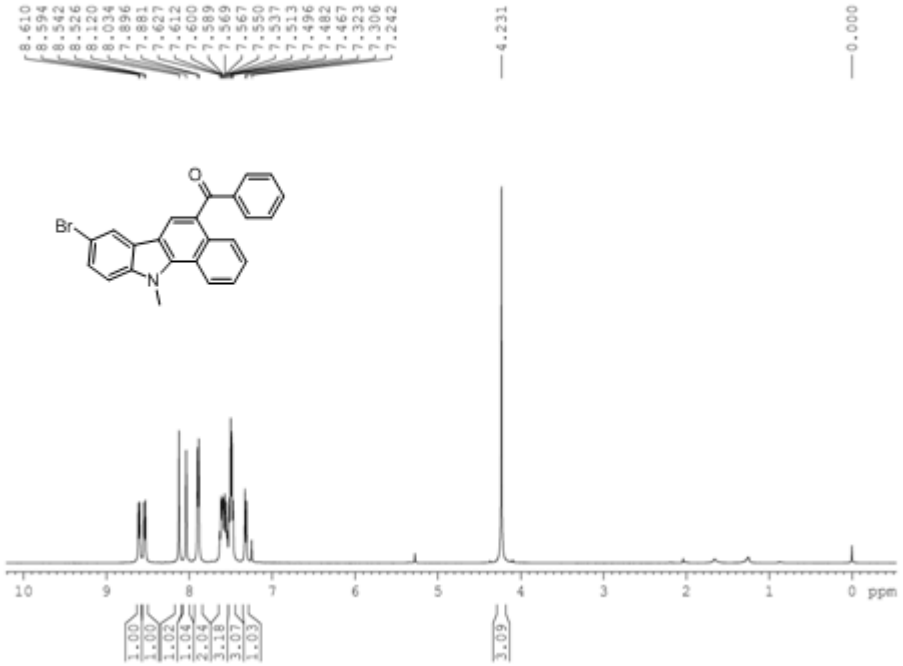


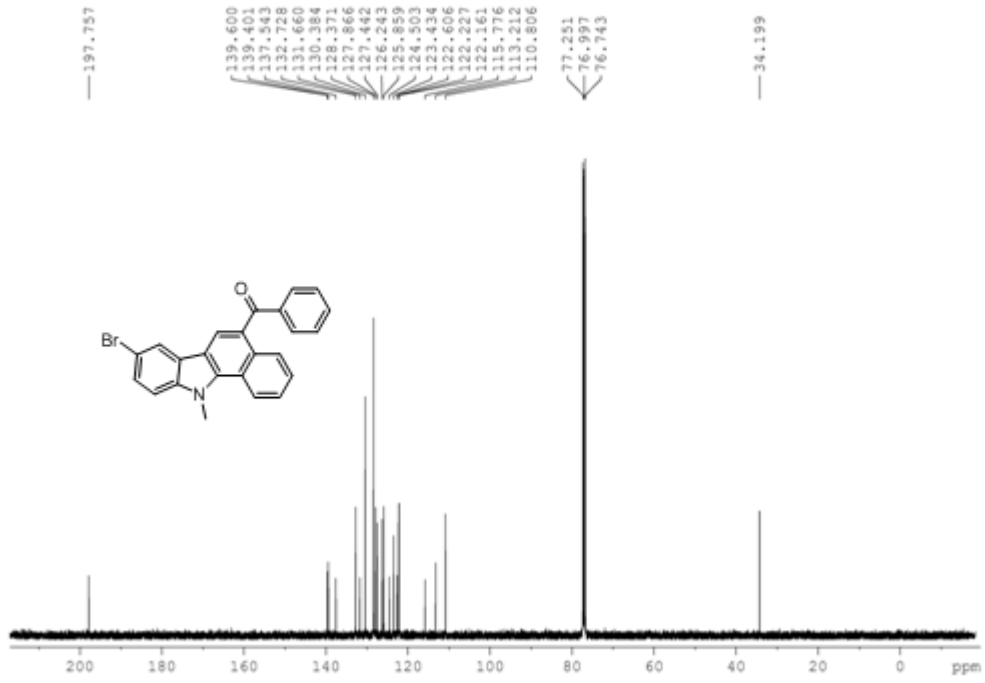
^{1}H and ^{13}C Spectrum of Compound **3n**



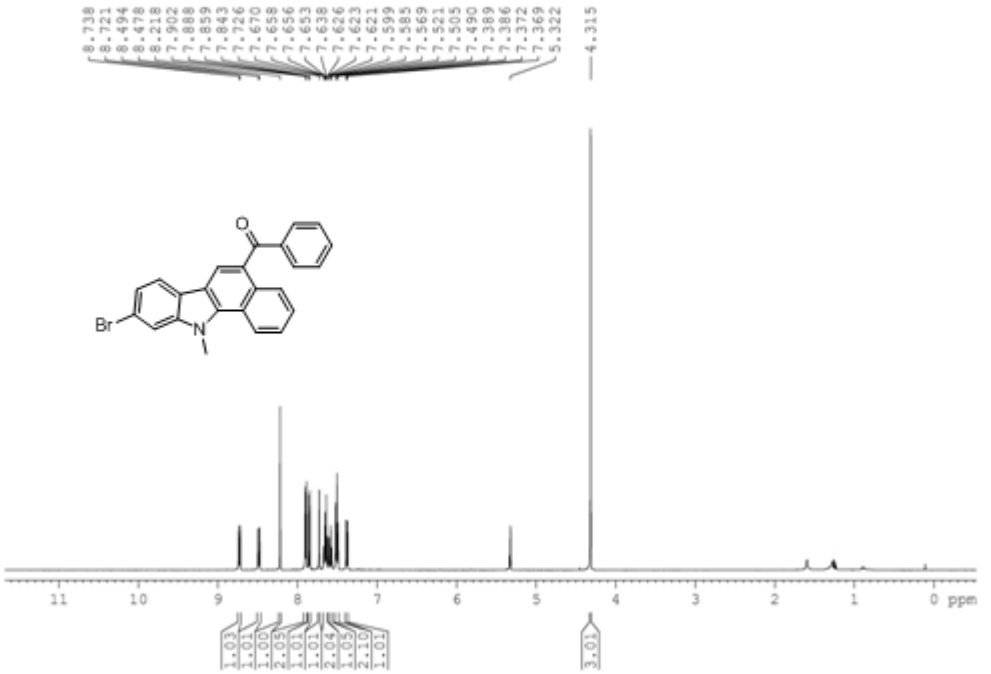


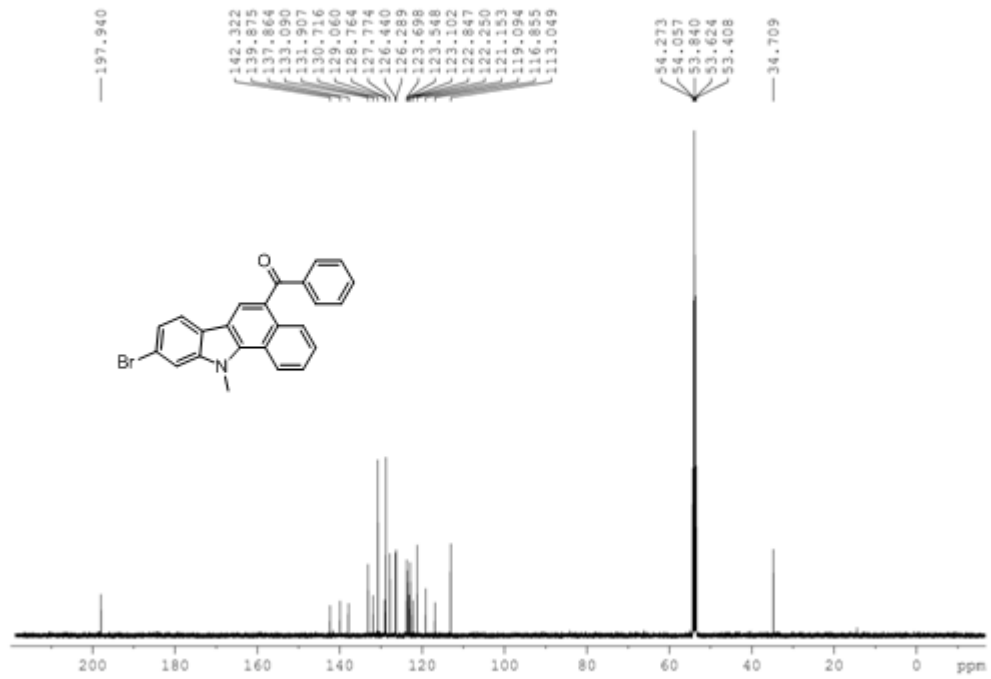
^{1}H and ^{13}C Spectrum of Compound **3o**



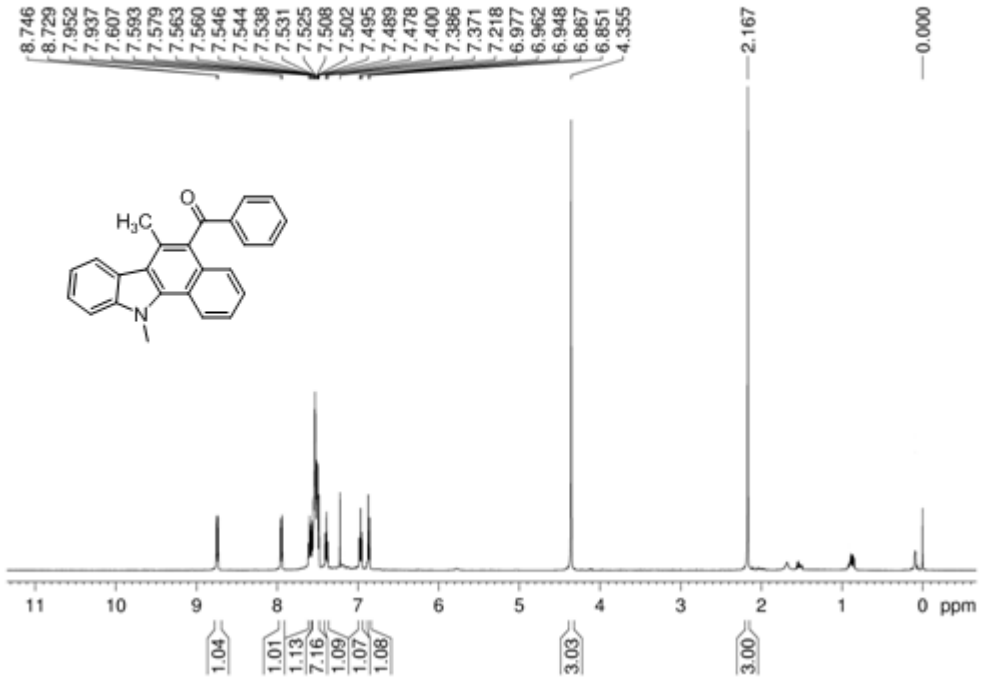


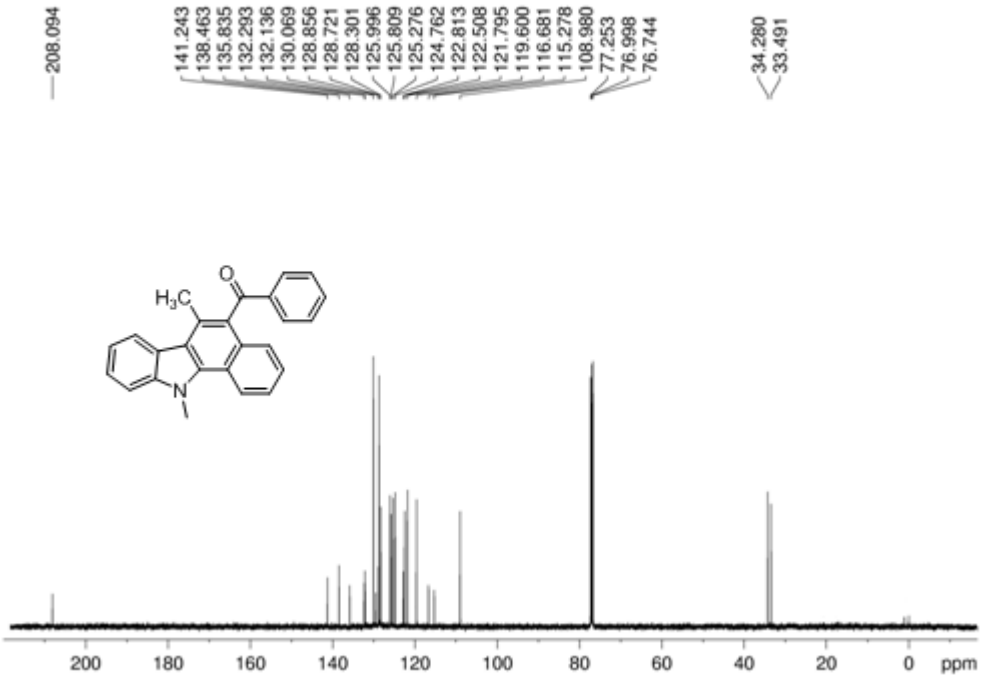
^{1}H and ^{13}C Spectrum of Compound **3p**



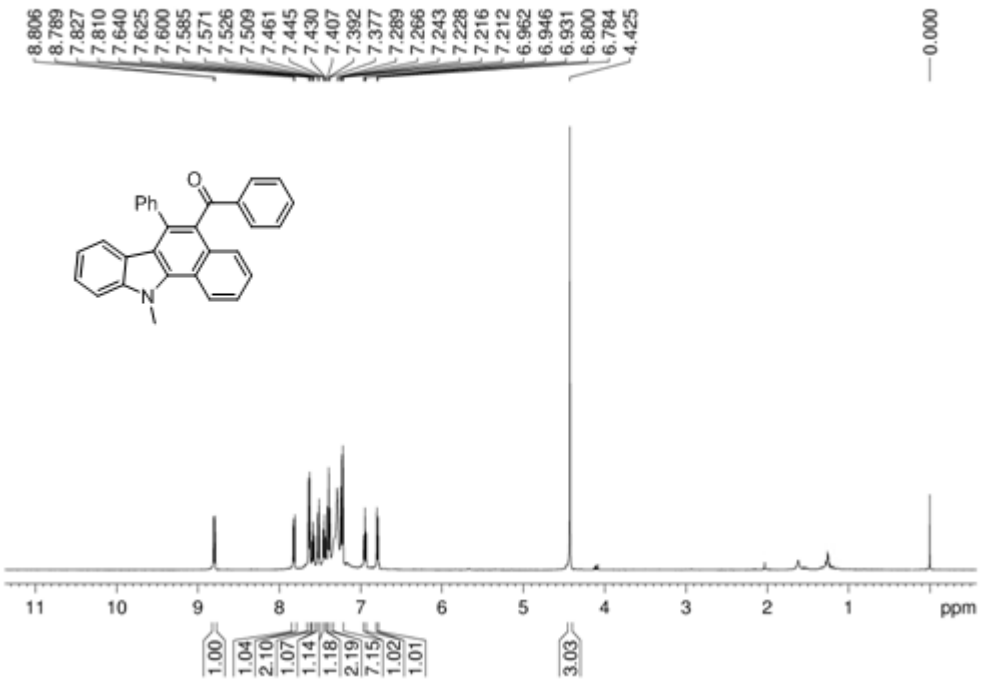


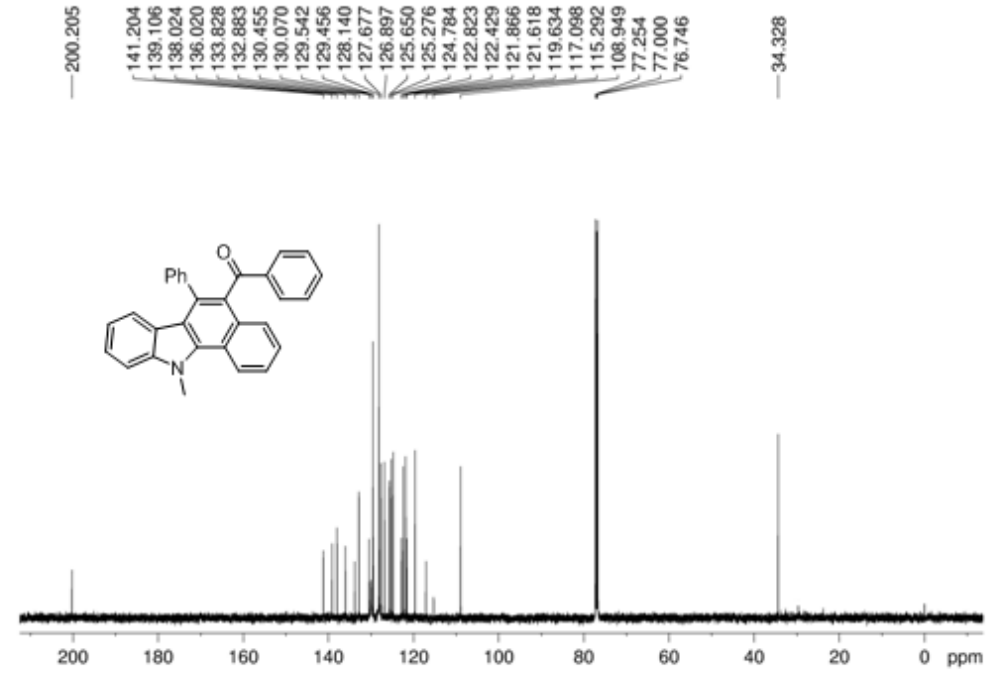
^{1}H and ^{13}C Spectrum of Compound **3q**



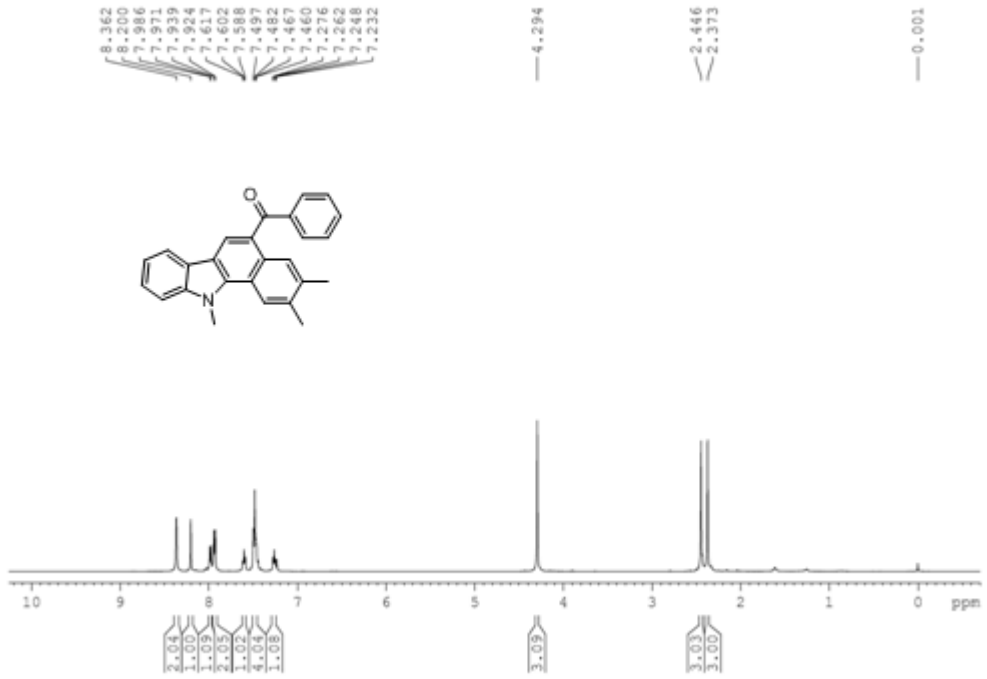


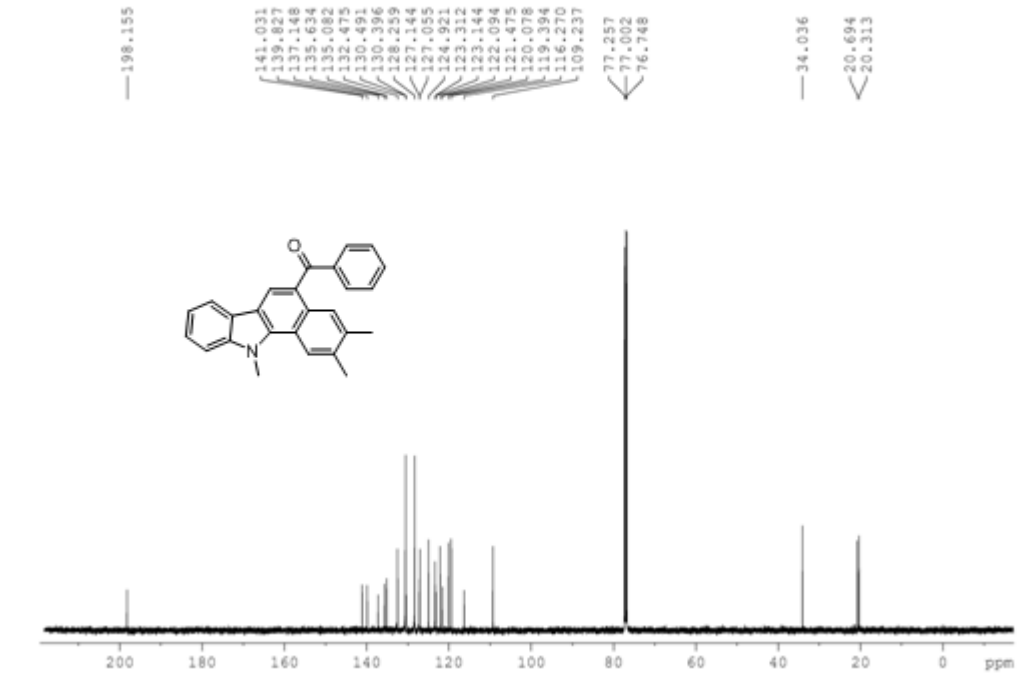
^{1}H and ^{13}C Spectrum of Compound **3r**



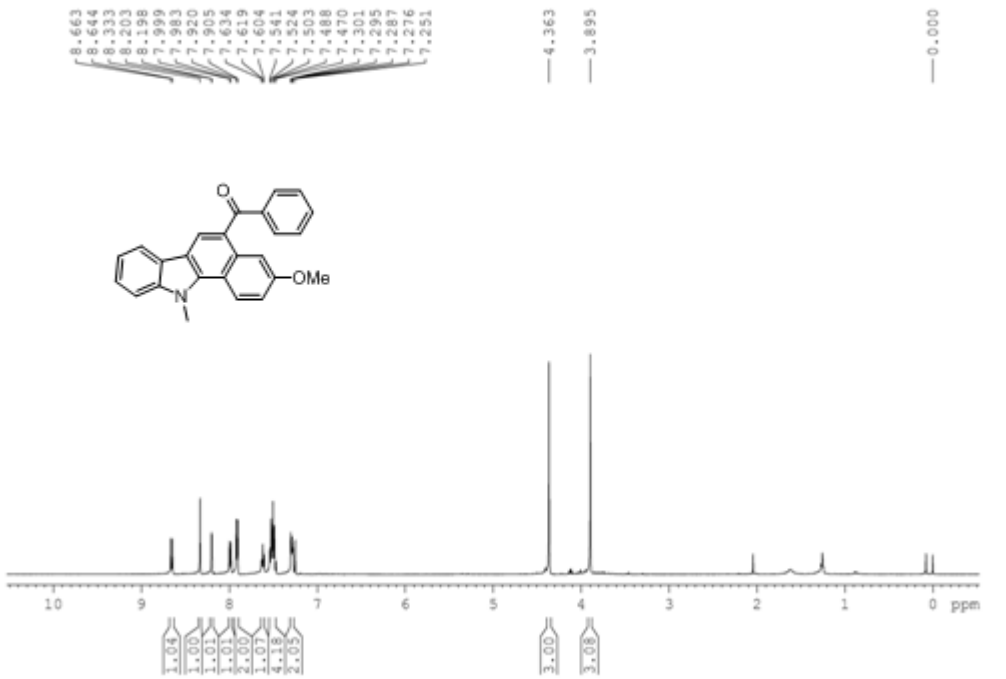


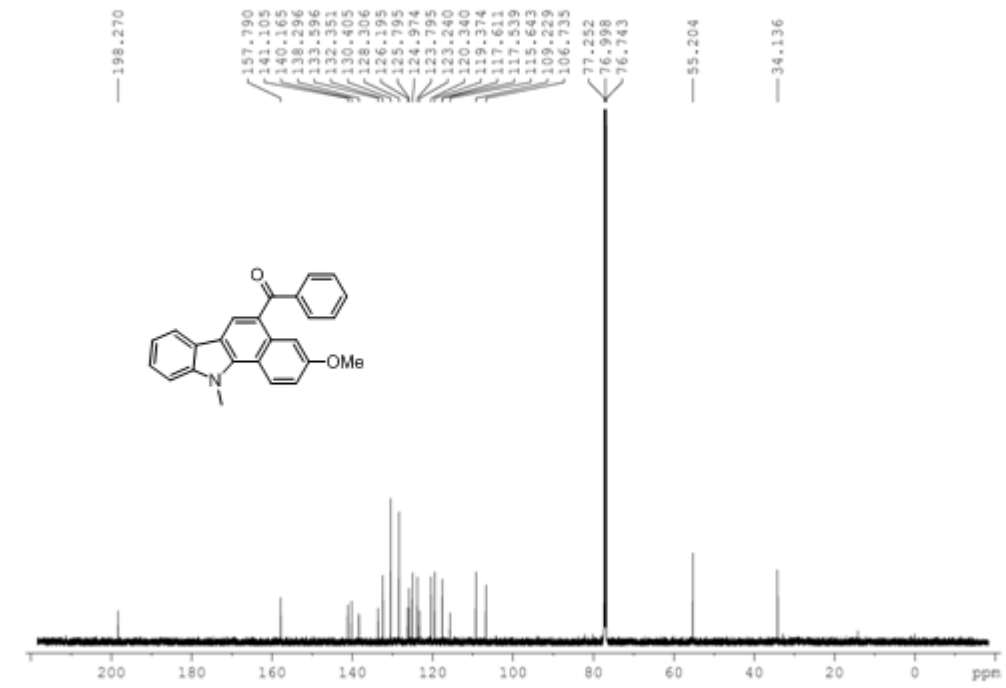
^{1}H and ^{13}C Spectrum of Compound **3s**



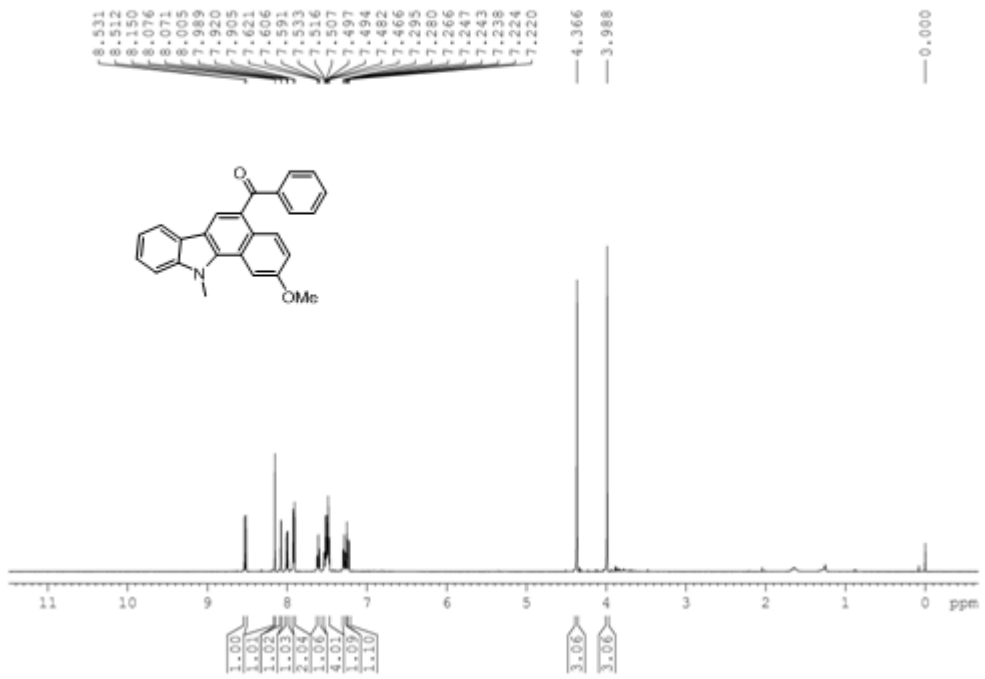


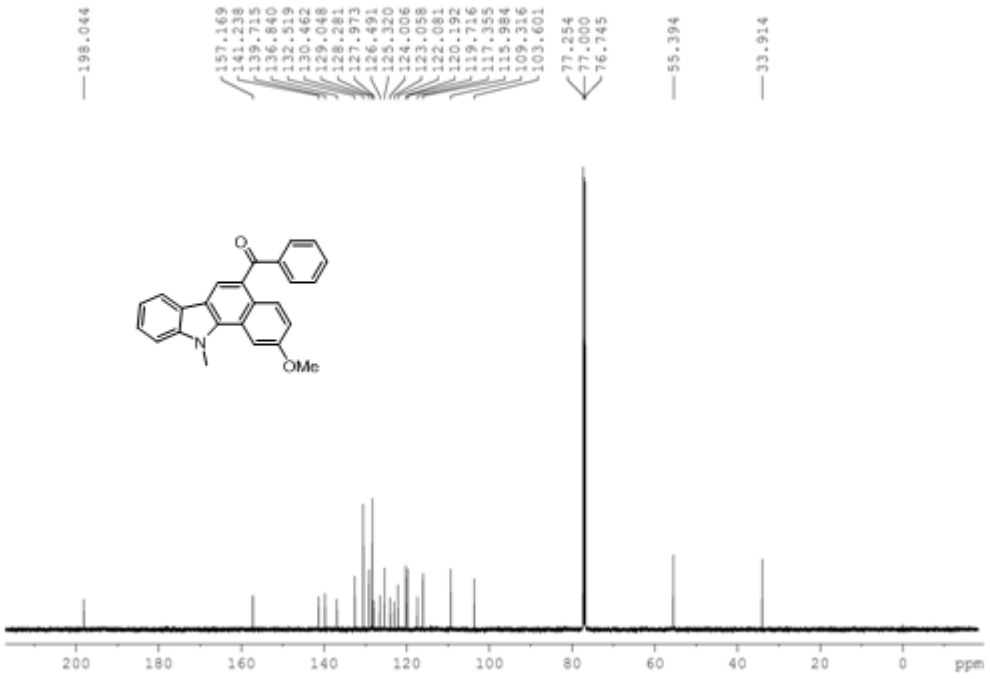
^{1}H and ^{13}C Spectrum of Compound **3t**



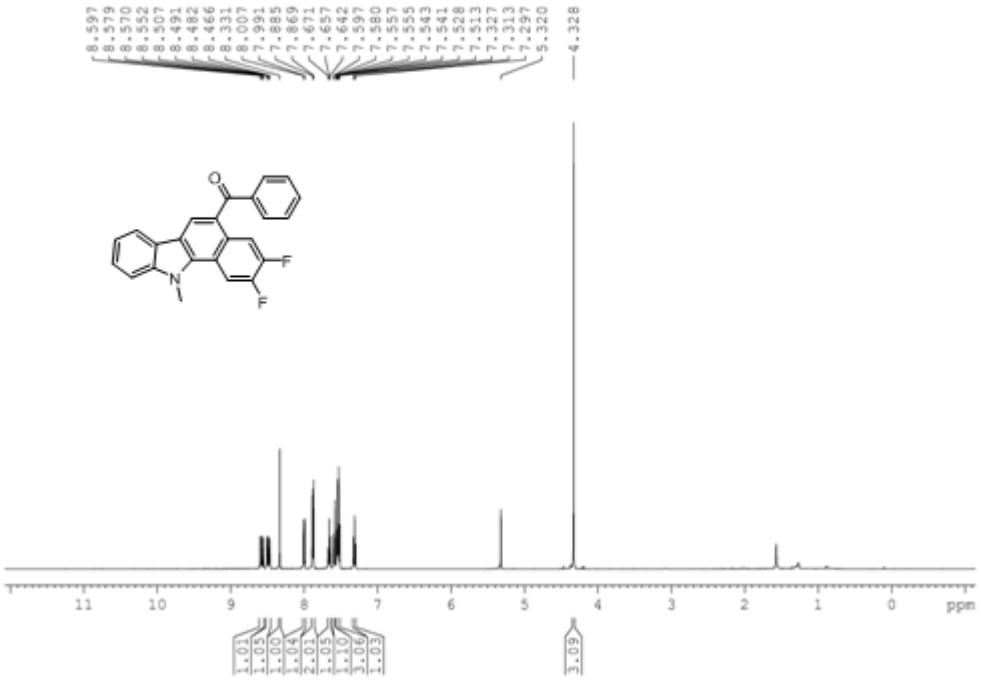


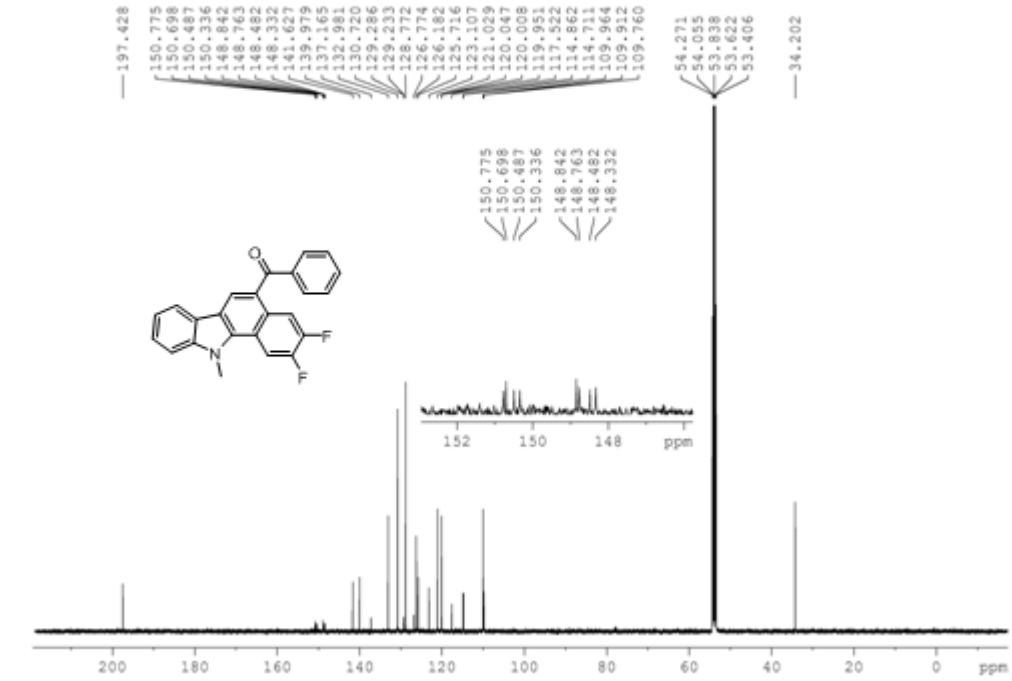
^{1}H and ^{13}C Spectrum of Compound **3t'**



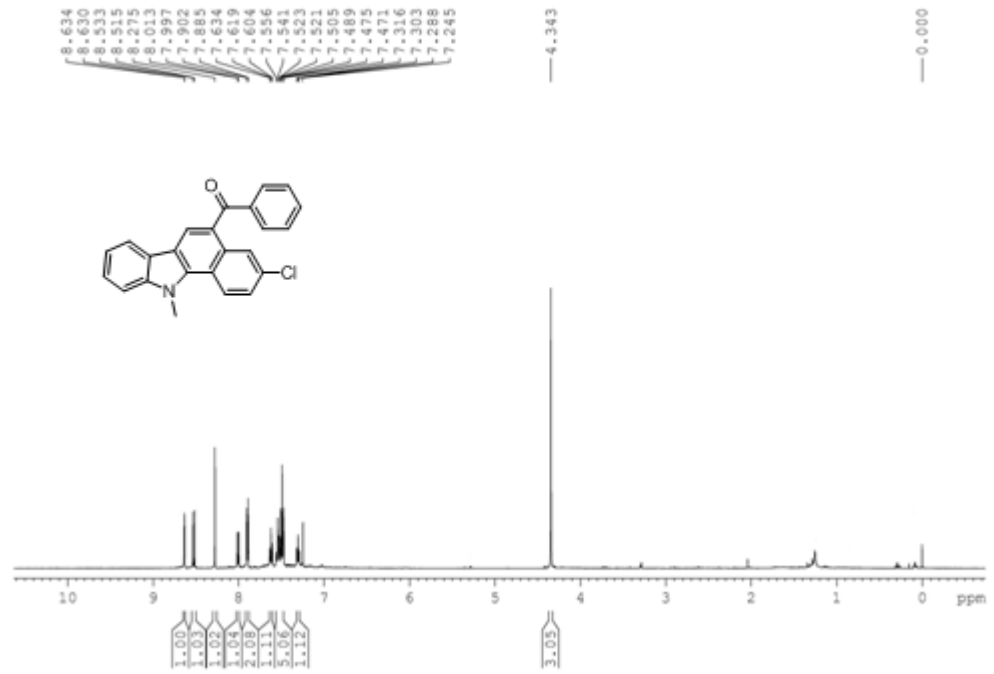


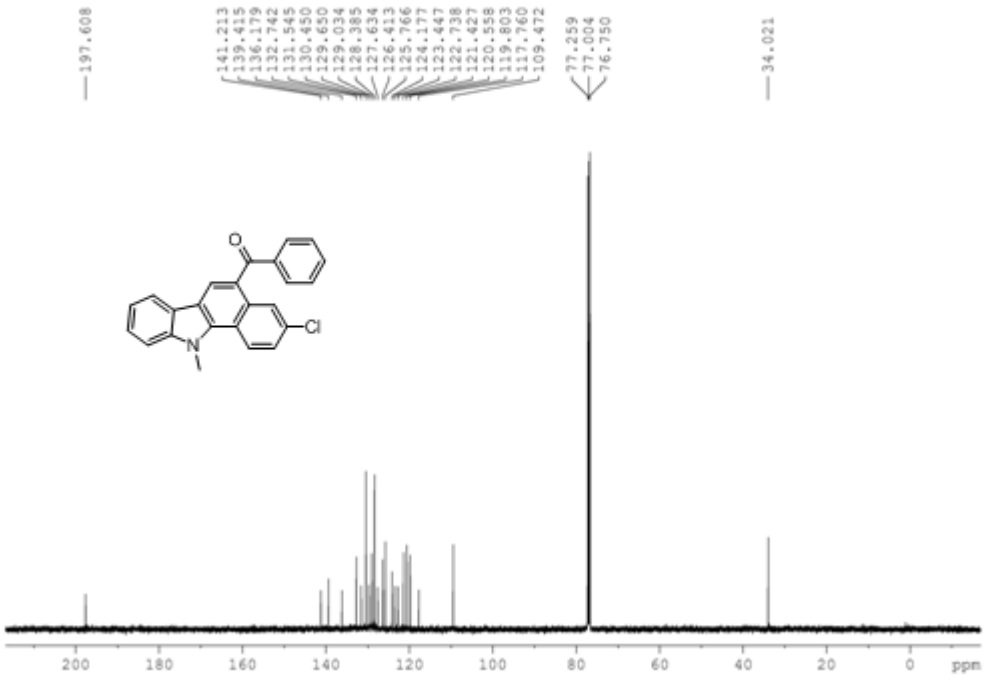
^{1}H and ^{13}C Spectrum of Compound **3u**





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





^{1}H and ^{13}C Spectrum of Compound **3v'**