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Supporting Information

Synthesis of Dibenzo[*a*,*c*]carbazoles from 2-(2-Halophenyl)-indoles and Iodobenzenes via Palladium-Catalyzed Dual C–H Functionalization

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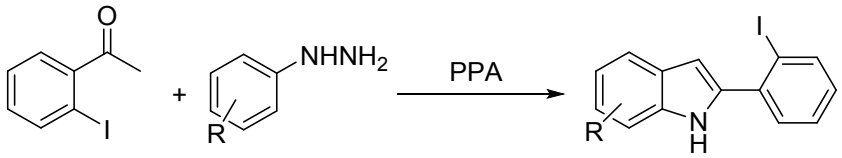
Contents

1) General Information

NMR spectra of the products **3aa-3ea**, **3ia**, **3la-3oa, 3ab** and **3ad-3ap** 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 product **3ja-3ka** and **3ac** were recorded using Bruker Avance-500 instruments, calibrated to residual DMSO-*d6* as the internal reference (2.50 ppm for ^{1}H NMR spectra and 40.00 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).

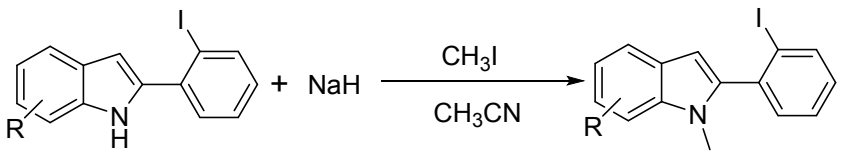
2) Synthesis of Starting Materials

Preparation of 2-(2-iodophenyl)-1*H*-indoles



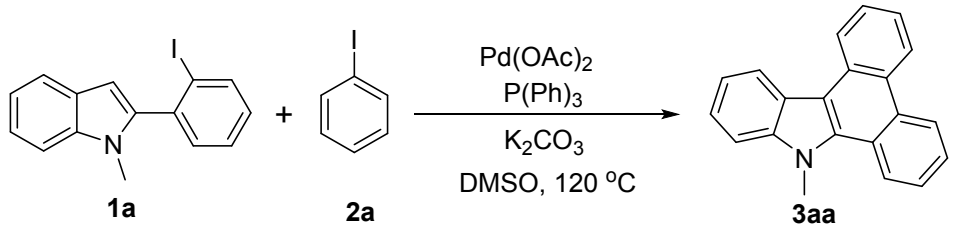
The stirred mixture of 1-(2-iodophenyl)ethanone (5.0 mmol, 1.0 equiv), phenylhydrazine (6.0 mmol, 1.2 equiv) and PPA (15.0 g) were heated at 110 ºC for 6 h. Then, the reaction mixture was poured into cold water and stirred for 5 min. Next, the mixture was extracted by EtOAc for several times. The combined 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 2-(2-iodophenyl)-1*H*-indoles in moderate to excellent yields.

Preparation of *N*-substituted-2-(2-iodophenyl)-indoles



N-substituted-2-(2-iodophenyl)-indoles was prepared by the treatment of **2-(2-**iodophenyl)-1*H*-indoles (2.0 mmol, 1.0 equiv) with NaH (3.0 mmol, 1.5 equiv) in CH_3CN (8 mL) followed by the addition of CH_3I (3.0 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, 100:1) to provide the *N*-substituted-2-(2-iodophenyl)-indoles as a solid.

3) Typical Procedures



The sealed Schlenk tube was charged with 2-(2-iodophenyl)-indoles **1** (0.3 mmol), iodobenzenes **2** (0.6 mmol), $Pd(OAc)_2$ (3.4 mg, 5 mol%, 0.015 mmol), PhP_3 (7.9 mg, 10 mol%, 0.03 mmol), K_2CO_3 (124.3 mg, 3.0 equivalent, 0.9 mmol) and DMSO (2 mL). Then the mixture was stirred at 120 °C (oil bath temperature). After the reaction was finished, the reaction mixture was cooled to room temperature, quenched by water and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over Na_2SO_4, and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford benzo[*a*,*c*]carbazoles **3**.

4) Characterization Data

9-Methyl-9*H*-dibenzo[*a*,*c*]carbazole (3aa): white solid, isolated yield 93% (78.4 mg); mp 163.5-165.2 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.75 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 7.5 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 3H), 7.41-7.40 (m, 2H), 7.34-7.30 (m, 1H), 4.10 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.5, 134.3, 130.6, 129.8, 127.1, 126.7, 125.8, 125.3, 123.8, 123.6, 123.4, 123.4, 123.4, 123.3, 123.2, 122.6, 121.6, 120.1, 113.1, 109.3, 34.1.

9-(Cyclopropylmethyl)-9*H*-dibenzo[*a*,*c*]carbazole (3ba): white solid, isolated yield 91% (87.6 mg); mp 163.2-165.0 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.83 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.69-8.65 (m, 2H), 8.57 (d, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.63-7.56 (m, 2H), 7.52-7.47 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 4.66 (d, *J* = 5.0 Hz, 2H), 1.43-1.38 (m, 1H), 0.53-0.49 (m, 2H), 0.41-0.38 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.9, 134.1, 130.9, 129.9, 127.2, 126.9, 126.3, 125.5, 124.1, 123.6, 123.6, 123.5, 123.4, 122.9, 121.8, 120.3, 113.8, 110.2, 48.6, 11.3, 3.6.

9-Benzyl-9*H*-dibenzo[*a*,*c*]carbazole (3ca): white solid, isolated yield 95% (101.7 mg); mp 193.7-195.0 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.91 (d, *J* = 8.0 Hz, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.76 (d, *J* = 8.0 Hz, 1H), 8.66-8.65 (m, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.76 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 4H), 7.36-7.28 (m, 5H), 5.93 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.2, 137.4, 134.6, 130.8, 129.9, 129.1, 127.5, 127.3, 127.0, 126.3, 125.9, 125.6, 124.0, 124.0, 123.8, 123.6, 123.4, 123.1, 122.8, 121.9, 120.8, 113.8, 109.9, 50.1; HRMS (ESI, m/z) calcd for $[C_{27}H_{19}N]H^+$: 358.1590; Found 358.1596.

9-(4-Methylbenzyl)-9*H*-dibenzo[*a*,*c*]carbazole (3da): white solid, isolated yield 93% (103.5 mg); mp 172.3-173.7 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.90 (d, *J* = 8.0 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.64 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.46-7.40 (m, 4H), 7.17-7.12 (m, 4H), 5.88 (s, 2H), 2.31 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.3, 137.1, 134.7, 134.4, 130.9, 129.9, 129.8, 127.4, 127.1, 126.4, 125.9, 125.7, 124.1, 124.0, 123.8, 123.6, 123.5, 123.2, 122.9, 121.9, 120.8, 113.8, 110.0, 50.0, 21.1; HRMS (ESI, m/z) calcd for $[C_{28}H_{21}N]H^+$: 372.1747; Found 372.1756.

4-((9*H*-dibenzo[*a*,*c*]carbazol-9-yl)methyl)benzonitrile (3ea): white solid, isolated yield 75% (86.0 mg); mp 183.7-185.6 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.85 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.60 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.58-7.52 (m, 4H), 7.42-7.36 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 3H), 5.75 (s, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 142.9, 140.9, 134.1, 132.9, 130.8, 129.6, 127.5, 127.1, 126.7, 126.4, 125.8,

124.3, 124.2, 124.1, 123.9, 123.6, 123.5, 122.8, 122.0, 121.2, 118.5, 114.2, 111.5, 109.4, 49.8; HRMS (ESI, m/z) calcd for $[C_{28}H_{18}N_2]H^+$: 383.1543; Found 383.1552.

12-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ia): white solid, isolated yield 92% (82.5 mg); mp 169.3-170.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.77 (d, *J* = 7.5 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 9.5 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.63-7.60 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.40-7.37 (m, 1H), 7.18 (t, *J* = 8.5 Hz, 1H), 4.21(s, 3H); **^{13}C NMR** (DMSO-*d6*, 125 MHz) δ = 150.8 (d, *J* = 231.6 Hz), 137.4, 135.6, 130.9, 129.3, 128.3, 127.2, 126.8, 126.7, 124.6, 124.4, 124.2, 123.8, 123.6, 127 (d, *J* = 10.0 Hz), 112.5 (d, *J* = 4.1 Hz), 112.1, 111.9 (d, *J* = 4.4 Hz), 111.8, 107.0 (d, *J* = 24.6 Hz), 35.0. HRMS (ESI, m/z) calcd for $[C_{21}H_{14}FN]H^+$: 300.1183; Found 300.1189.

12-Chloro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ja): white solid, isolated yield 90% (85.1 mg); mp 191.1-192.6 °C (uncorrected); **^{1}H NMR** (DMSO-*d6*, 500 MHz) δ = 8.94-8.81 (m, 3H), 8.75 (d, *J* = 7.5 Hz, 1H), 8.59 (s, 1H), 7.85-7.59 (m, 5H), 7.48 (d, *J* = 8.0 Hz, 1H), 4.37 (s, 3H); **^{13}C NMR** (DMSO-*d6*, 125 MHz) δ = 139.2, 135.4, 131.0, 129.1, 128.4, 127.3, 127.0, 126.8, 125.4, 124.7, 124.6, 124.2, 124.0, 123.9, 123.8, 123.5, 120.9, 112.4, 112.0, 35.1; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}ClN]H^+$: 316.0886; Found 316.0894.

12-Bromo-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ka): white solid, isolated yield 83% (89.4 mg); mp 192.0-193.4 °C (uncorrected); **^{1}H NMR** (DMSO-*d6*, 500 MHz) δ = 8.96-8.94 (m, 1H), 8.85 (d, *J* = 8.5 Hz, 1H), 8.82-8.80 (m, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.70 (s, 1H), 7.81-7.73 (m, 4H), 7.59 (t, *J* = 7.5 Hz, 2H), 4.37 (s, 3H); **^{13}C NMR** (DMSO-*d6*, 125 MHz) δ = 139.5, 135.3, 131.0, 129.1, 128.4, 127.3, 127.0, 126.9, 126.7, 124.7, 124.7, 124.4, 124.3, 124.0, 123.8, 123.8, 123.5, 113.3, 112.9, 111.9, 35.1; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}BrN]H^+$: 360.0382; Found 360.0390.

9,12-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3la): white solid, isolated yield 78% (69.0 mg); mp 199.7-201.4 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.76 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 7.5Hz, 1H), 8.28 (s, 1H), 7.68(t, *J* = 7.5 Hz, 1H), 7.57-7.48(m, 3H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 4.11(s, 3H), 2.60(s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 139.1, 134.7, 130.7, 130.0, 129.4, 127.1, 126.7, 126.0, 125.3, 125.1, 124.0,

123.9, 123.5, 123.3, 122.8, 121.6, 112.9, 109.1, 34.4, 21.8; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}N]H^+$: 296.1434; Found 296.1439.

9,11,13-Trimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3ma): yellow solid, isolated yield 75% (69.5 mg); mp 205.2-206.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.80-8.77 (m, 1H), 8.70 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 8.5 Hz, 1H), 8.56-8.54 (m, 1H), 7.63-7.60 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.19 (s, 1H), 7.00 (s, 1H), 4.28 (s, 3H), 3.01 (s, 3H), 2.56 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 142.3, 135.0, 134.0, 131.1, 130.8, 129.0, 127.0, 126.1, 125.8, 125.3, 125.3, 123.9, 123.7, 123.4, 123.1, 122.8, 120.9, 115.0, 107.2, 34.8, 25.2, 21.8; HRMS (ESI, m/z) calcd for $[C_{23}H_{19}N]H^+$: 310.1590; Found 310.1595.

3,9-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3ab): white solid, isolated yield 98% (86.7 mg); mp 217.1-218.6 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.84-8.83 (m, 1H), 8.74 (d, *J* = 7.5 Hz, 1H), 8.67-8.66 (m, 1H), 8.57 (d, *J* = 7.5 Hz, 1H), 8.54 (s, 1H), 7.64-7.56 (m, 4H), 7.49-7.47 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 4.36 (s, 3H), 2.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ =140.8, 134.3, 133.0, 130.9, 128.9, 127.7, 127.0, 126.0, 125.4, 124.1, 124.0, 123.6, 123.5, 123.3, 122.9, 121.8, 120.1, 109.5, 34.6, 21.9; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}N]H^+$: 296.1434; Found 296.1440.

3-Methoxy-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ac): white solid, isolated yield 82% (76.5 mg); mp 283.8-284.8 °C (uncorrected); **^{1}H NMR** (DMSO-*d6*, 500 MHz) δ = 8.96-8.57 (m, 4H), 8.29 (s, 1H), 7.79-7.73 (m, 3H), 7.47-7.34 (s, 3H), 4.38 (s, 3H), 4.01 (s, 3H); **^{13}C NMR** (DMSO-*d6*, 125 MHz) δ = 156.6, 140.9, 133.3, 130.2, 128.3, 127.3, 126.2, 125.2, 125.1, 124.3, 124.1, 124.0, 123.7, 122.7, 121.8, 120.6, 117.6, 113.0, 110.8, 106.4, 55.9, 34.9; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}NO]H^+$: 312.1383; Found 312.1390.

3-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ad): white solid, isolated yield 92% (82.5 mg); mp 187.5-189.2 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.50-8.47 (m, 1H), 8.40-8.38 (m, 1H), 8.33-8.31 (m, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 11.5 Hz, 1H), 7.45-7.43 (m, 2H), 7.34-7.33 (m, 2H), 7.29-7.22 (m, 2H), 4.00 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 159.5 (d, *J* = 240.1 Hz), 140.4, 133.7, 129.8 (d, *J* = 3.8 Hz), 128.2 (d, *J* = 7.5 Hz), 126.5, 126.2, 125.4, 125.0 (d, *J* = 8.1 Hz), 124.0, 124.0, 122.8, 122.7, 121.4, 120.1, 115.5 (d, *J* = 23.0 Hz), 112.8, 109.4, 108.5

(d, J = 8.1 Hz), 34.2; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}FN]H^+$: 300.1183; Found 300.1187.

3-Chloro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ae): white solid, isolated yield 89% (84.1 mg); mp 192.5-193.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.49-8.45 (m, 3H), 8.42-8.40 (m, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.52-7.48 (m, 3H), 7.43-7.37 (m, 2H), 7.27 (t, J = 7.0 Hz, 1H), 4.11 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.6, 134.4, 129.6, 129.1, 128.0, 127.9, 127.3, 126.6, 125.6, 124.7, 124.0, 123.9, 123.8, 122.9, 122.8, 121.5, 120.3, 112.7, 109.5, 34.3; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}ClN]H^+$: 316.0888; Found 316.0893.

9-Methyl-3-(trifluoromethyl)-9*H*-dibenzo[*a*,*c*]carbazole (3af): white solid, isolated yield 75% (78.5 mg); mp 211.3-213.1 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.77 (s, 1H), 8.61-8.59 (m, 2H), 8.40 (d, J = 7.0 Hz, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.61-7.55 (m, 2H), 7.48-7.44 (m, 2H), 7.35 (t, J = 7.5 Hz, 1H), 4.07 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.4, 135.2, 131.6, 130.1, 128.7 (d, J = 39.9 Hz), 126.6, 125.9, 125.8, 124.7 (q, J = 32.0 Hz), 123.9, 123.9, 123.8, 123.7, 122.9, 122.8, 121.5, 120.6, 120.6, 120.5, 112.4, 109.6, 34.2; HRMS (ESI, m/z) calcd for $[C_{22}H_{14}F_3N]H^+$: 350.1151; Found 350.1157.

1,9-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3ag): white solid, isolated yield 74% (65.5 mg); mp 164.6-165.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.68 (d, J = 7.5 Hz, 1H), 8.49 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 1H), 7.57-7.50 (m, 3H), 7.48-7.44 (m, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 4.23 (s, 3H), 2.94 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.4, 135.9, 132.7, 131.6, 129.4, 128.9, 128.4, 125.9, 125.9, 124.3, 124.2, 124.1, 123.6, 123.5, 123.1, 123.0, 120.3, 119.0, 113.4, 109.2, 34.4, 24.1; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}N]H^+$: 296.1434; Found 296.1441.

1-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3ah): white solid, isolated yield 75% (67.3 mg); mp 182.2-184.1 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.68 (d, J = 8.5 Hz, 1H), 8.65-8.63 (m, 1H), 8.47-8.45 (m, 1H), 8.42 (d, J = 8.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.46-7.30 (m, 5H), 4.18 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 158.5 (d, J = 245.9 Hz), 141.1, 135.3, 130.2, 129.6 (d, J = 7.0 Hz), 126.4, 125.9, 124.6 (d, J = 36.3 Hz), 124.3, 123.9 (d, J = 1.4 Hz), 123.7, 123.6 (d, J = 9.1 Hz),

123.2, 123.1, 120.1 (d, *J* = 5.6 Hz), 119.1 (d, *J* = 2.9 Hz), 118.3 (d, *J* = 18.0 Hz), 113.0 (d, *J* = 24.0 Hz), 110.6, 109.1, 34.9; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}FN]H^+$: 300.1183; Found 300.1189.

2,9-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole and **4,9-Dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3ai** and **3ai'** = **1.1 : 1)**: white solid, isolated yield 91% (80.5 mg); mp 179.6-181.5 °C (uncorrected); 1H NMR (CDCl3, 500 MHz) δ = 8.73 (d, *J* = 7.0 Hz, 0.5H), 8.67-8.62 (m, 1H), 8.50-8.42 (m, 3H), 7.56-7.44 (m, 2.5H), 7.39-7.27 (m, 4H), 4.10 (s, 1.4H), 4.07 (s, 1.6H), 3.04 (s, 1.4H), 2.60 (s, 1.6H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.1, 140.6, 136.8, 135.2, 134.7, 134.6, 131.7, 131.3, 130.8, 129.9, 129.0, 128.2, 127.5, 126.3, 125.5, 125.4, 125.3, 125.1, 124.6, 124.6, 124.0, 123.7, 123.5, 123.4, 123.4, 123.3, 123.2, 122.7, 122.6, 121.8, 121.7, 121.3, 120.2, 120.0, 113.8, 113.0, 109.5, 109.3, 34.3, 34.2, 27.2, 22.0; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}N]H^+$: 296.1434; Found 296.1440.

2-Fluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3aj): white solid, isolated yield 75% (67.3 mg); mp 187.5-188.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.23-9.20 (m, 1H), 8.52-8.47 (m, 2H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 3H), 7.44-7.42 (m, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.23-7.18 (m, 1H), 4.15 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 161.8 (d, *J* = 250.5 Hz), 140.9, 135.2, 132.4 (d, *J* = 4.4 Hz), 129.0 (d, *J* = 5.8 Hz), 128.8 (d, *J* = 28.5 Hz), 127.3 (d, J = 10.9 Hz), 126.1, 125.9, 124.0, 123.8, 123.1, 122.5, 121.7, 120.5, 119.3 (d, *J* = 3.3 Hz), 116.0 (d, *J* = 7.3 Hz), 112.9, 110.7 (d, *J* = 25.9 Hz), 109.6, 34.5; HRMS (ESI, m/z) calcd for $[C_{21}H_{14}FN]H^+$: 300.1183; Found 300.1190.

9-methyl-2-(trifluoromethyl)-9*H*-dibenzo[*a*,*c*]carbazole (3ak): white solid, isolated yield 30% (31.3 mg); mp 203.8-204.6 °C(uncorrected); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ = 8.81 (s, 1H), 8.61-8.57 (m, 2H), 8.41-8.38 (m, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.58-7.56 (m, 2H), 7.47-7.42 (m, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 4.06 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ = 140.5, 134.7, 129.8, 129.1, 128.6 (d, *J* = 31.8Hz), 128.6, 127.0, 126.1, 125.8, 124.3, 124.2, 124.0, 123.9, 123.4, 122.8, 121.4, 120.6, 120.4 (q, *J* = 4.3 Hz), 119.2 (q, *J* = 3.3 Hz), 112.7, 109.5, 34.2.

2,4,9-trimethyl-9*H*-dibenzo[*a*,*c*]carbazole (3al): white solid, isolated yield 93% (86.2 mg); mp 179.5-180.9 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.68-

8.67 (m, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.43 (s, 1H), 8.38-8.36 (m, 1H), 7.45-7.31 (m, 6H), 4.03 (s, 3H), 2.97 (s, 3H), 2.55 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.0, 135.8, 135.0, 134.8, 131.7, 131.4, 129.8, 128.6, 125.2, 124.9, 124.2, 124.0, 123.4, 123.4, 122.6, 121.8, 121.4, 120.0, 113.5, 109.4, 34.2, 27.1, 21.6; HRMS (ESI, m/z) calcd for $[C_{23}H_{19}N]H^+$: 310.1590; Found 310.1596.

2,4-Difluoro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3am): white solid, isolated yield 78% (74.2 mg); mp 172.8-173.9 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.84-8.81(m, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 10.0 Hz, 1H), 7.42-7.34 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22-7.16 (m, 2H), 6.77-6.72 (m, 1H), 3.78 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 162.3 (d, *J* = 143.1 Hz), 162.2 (d, *J* = 145.4 Hz), 160.3 (d, *J* = 134.5 Hz), 160.2 (d, *J* = 136.4 Hz), 140.4, 135.2, 132.4-132.3 (m, 1C), 128.4 (d, *J* = 5.6 Hz), 127.9, 127.7, 125.9 (d, *J* = 1.6 Hz), 125.7, 123.8, 123.1, 122.5, 122.4, 121.0, 120.5, 112.2 (d, *J* = 7.2 Hz), 112.0, 104.3 (d, *J* = 3.5 Hz), 104.1 (d, *J* = 3.5 Hz), 100.1 (d, *J* = 30.0 Hz), 99.9 (d, *J* = 30.0 Hz), 34.1; HRMS (ESI, m/z) calcd for $[C_{21}H_{13}F_2N]H^+$: 318.1089; Found 318.1097.

9-Methyl-3-phenyl-9*H*-dibenzo[*a*,*c*]carbazole (3an): white solid, isolated yield 85% (91.0 mg); mp 186.5-187.5 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.79 (s, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.70 (d, *J* = 8.5 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 2H), 7.55-7.49 (m, 4H), 7.41-7.37 (m, 3H), 7.34-7.31 (m, 1H), 4.07 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 141.7, 140.6, 135.8, 134.4, 130.7, 128.9, 127.3, 127.0, 126.2, 126.0, 125.4, 123.9, 123.9, 123.8, 123.6, 123.2, 122.8, 121.7, 120.2, 113.0, 109.4, 34.2; HRMS (ESI, m/z) calcd for $[C_{27}H_{19}N]H^+$: 358.1590; Found 358.1596.

11-Methyl-11*H*-benzo[*a*]naphtho[2,1-*c*]carbazole (3ao): white solid, isolated yield 72% (71.5 mg); mp 191.5-192.8 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 9.07 (d, *J* = 8.5 Hz, 1H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.52-8.47 (m, 3H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.60-7.53 (m, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44-7.38 (m, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 4.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.7, 136.2, 132.9, 130.8, 129.0, 128.9, 127.4, 126.9, 126.3, 125.8, 125.5, 124.7, 124.4, 124.2, 124.0, 123.9, 123.1, 123.0, 122.9, 121.1, 118.8, 114.0, 109.3, 34.3; HRMS (ESI, m/z) calcd for $[C_{25}H_{17}N]H^+$: 332.1434; Found 332.1444.

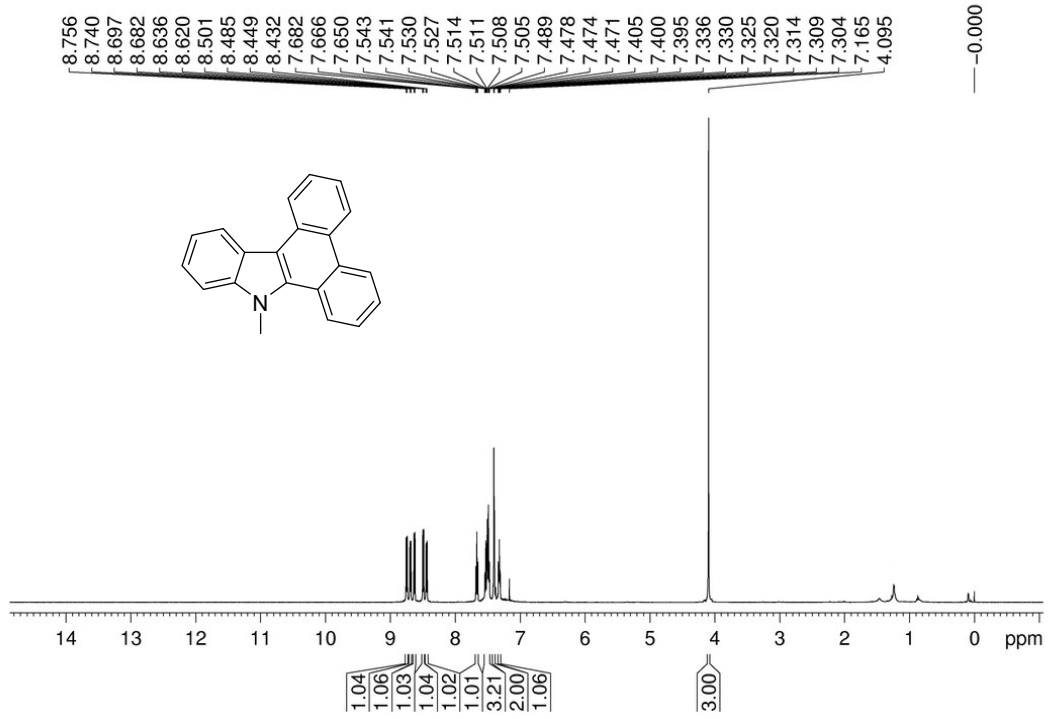
8-Methyl-8*H*-benzo[a]thieno[2,3-*c*]carbazole (3ap): white solid, isolated yield 23% (19.8 mg); mp 169.3-171.1 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.58 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 5.0 Hz, 1H), 7.53-7.45 (m, 2H), 7.43-7.40 (m, 3H), 7.32-7.29 (m, 1H), 4.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.4, 133.6, 132.1, 130.7, 129.1, 125.1, 125.0, 124.6, 124.4, 122.7, 122.1, 122.0, 121.7, 121.6, 120.9, 119.9, 113.4, 109.1, 34.1; HRMS (ESI, m/z) calcd for $[C_{19}H_{13}NS]H^+$: 288.0841; Found 288.0848.

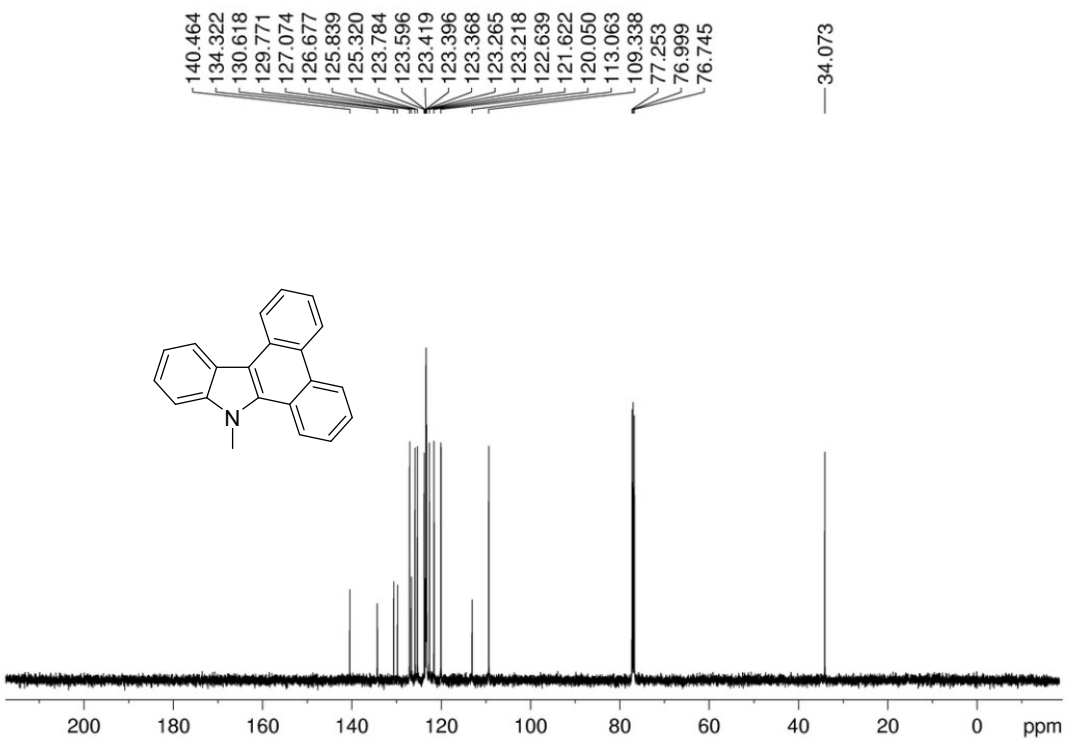
7-Methoxy-9-methyl-9*H*-dibenzo[a,c]carbazole (3na): white solid, isolated yield 51% (47.6 mg); mp 152.9-154.1 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.74 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 9.0 Hz, 1H), 8.52-8.50 (m, 2H), 7.80 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43-7.39 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.11 (dd, *J* = 8.5 Hz, 2.5Hz, 1H), 4.07 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 157.6, 140.6, 134.1, 128.8, 127.0, 126.2, 125.4, 124.9, 124.8, 123.6, 123.6, 123.4, 123.3, 122.8, 121.8, 120.1, 113.9, 113.7, 109.4, 105.5, 55.2, 34.0; HRMS (ESI, m/z) calcd for $[C_{22}H_{17}NO]H^+$: 312.1383; Found 312.1390.

7-Chloro-9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (3oa): white solid, isolated yield 52% (49.5 mg); mp 167.8-169.1 °C (uncorrected); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 8.66 (d, *J* = 8.0 Hz, 1H), 8.49 (t, *J* = 9.0 Hz, 2H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.30 (s, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.44-7.41 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 4.04 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ = 140.6, 133.0, 131.8, 129.6, 128.8, 127.4, 126.1, 125.5, 125.3, 124.5, 124.0, 123.7, 123.5, 123.2, 123.0, 122.0, 121.8, 120.3, 114.0, 109.4, 34.0; HRMS (ESI, m/z) calcd for $[C_{21}H_{15}NCl]H^+$: 316.0888; Found 316.0893.

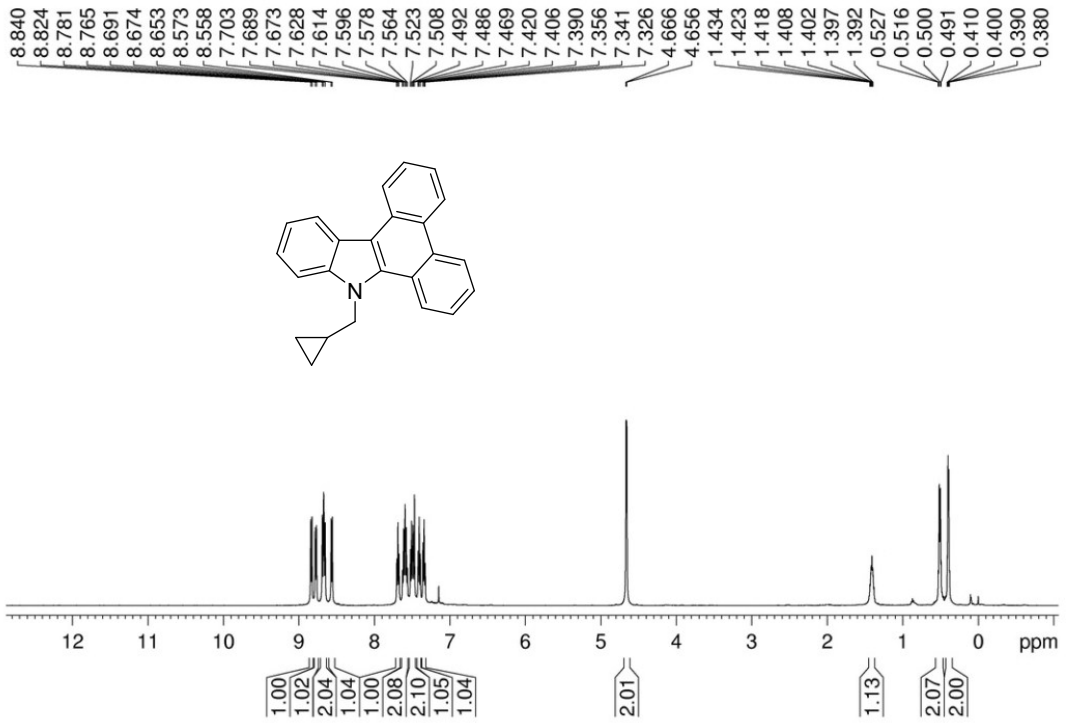
5) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All New Compounds

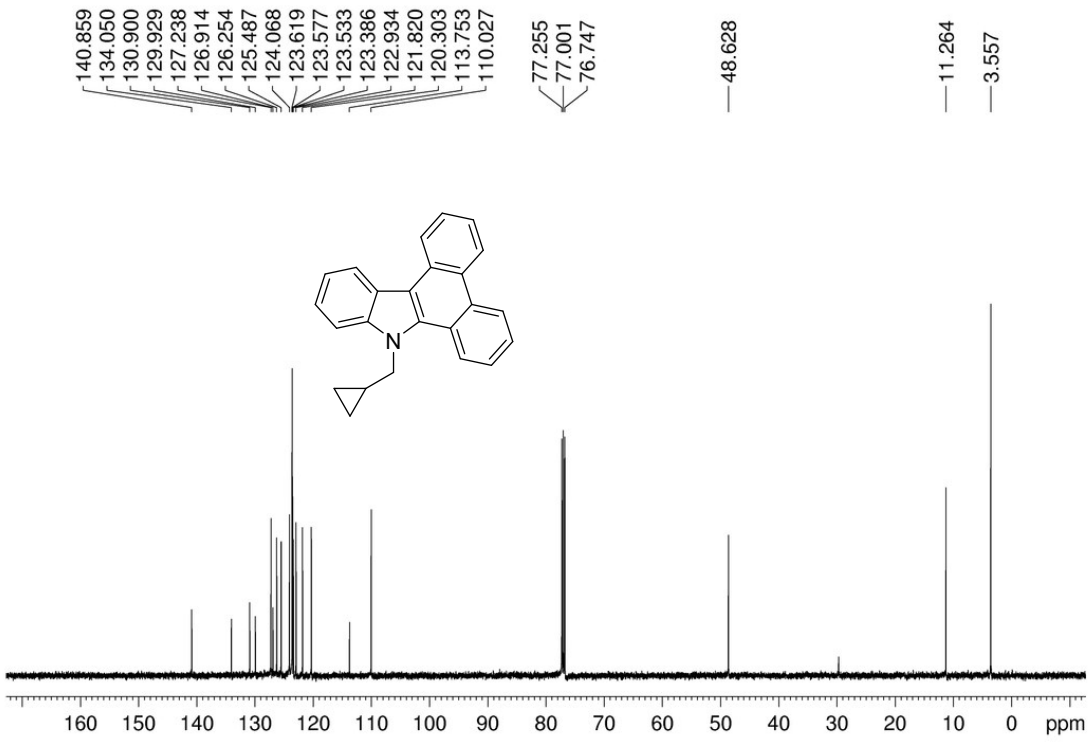
^{1}H and ^{13}C Spectrum of Compound **3aa**[1]



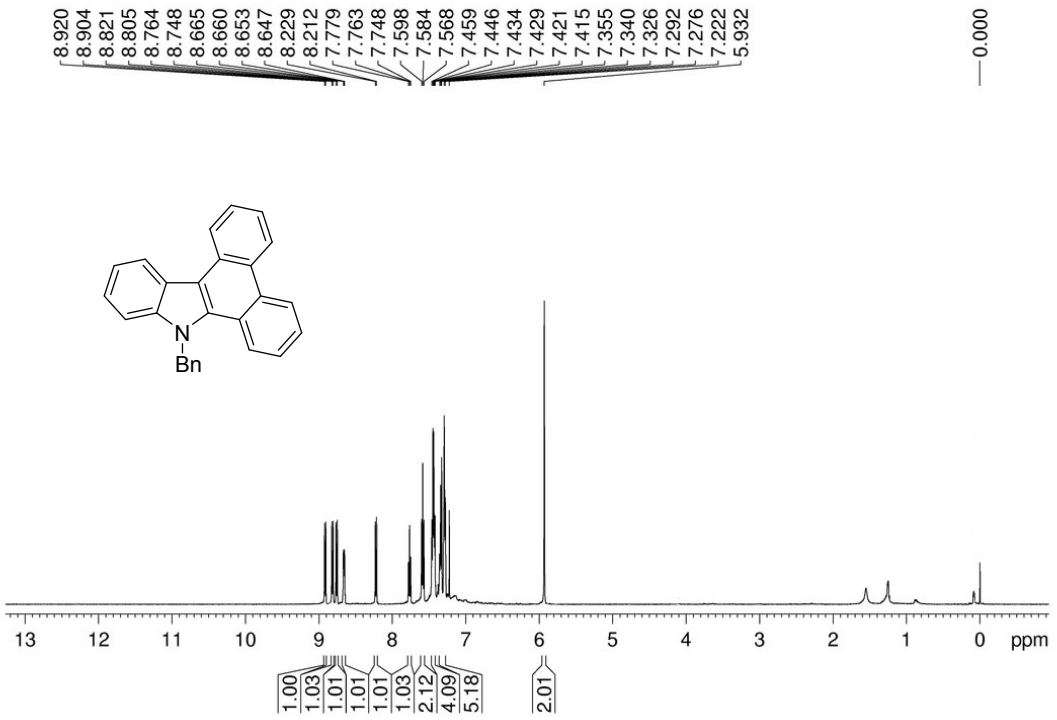


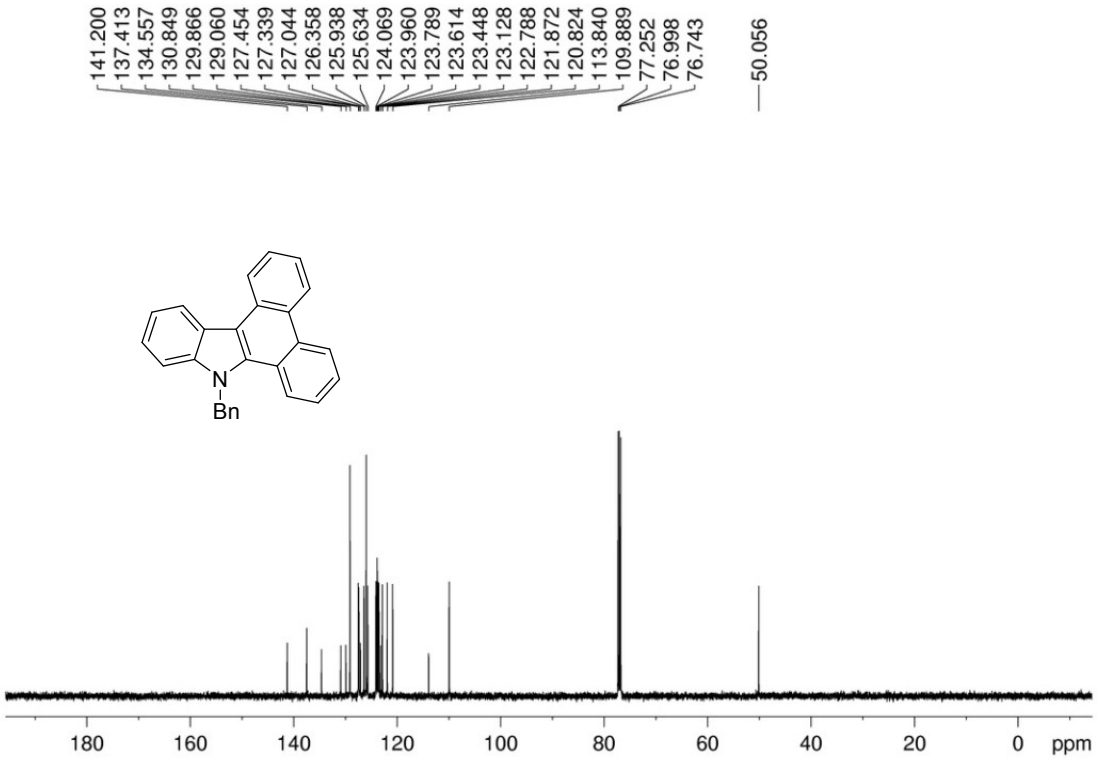
^{1}H and ^{13}C Spectrum of Compound **3ba**[1]



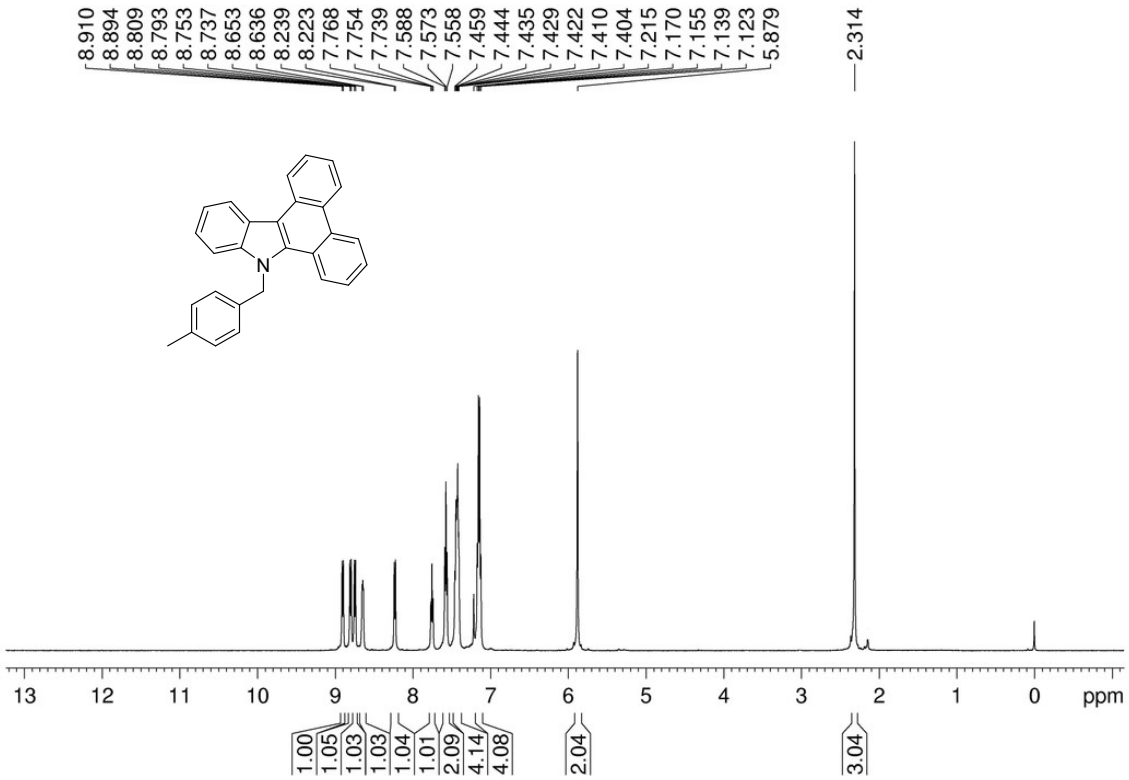


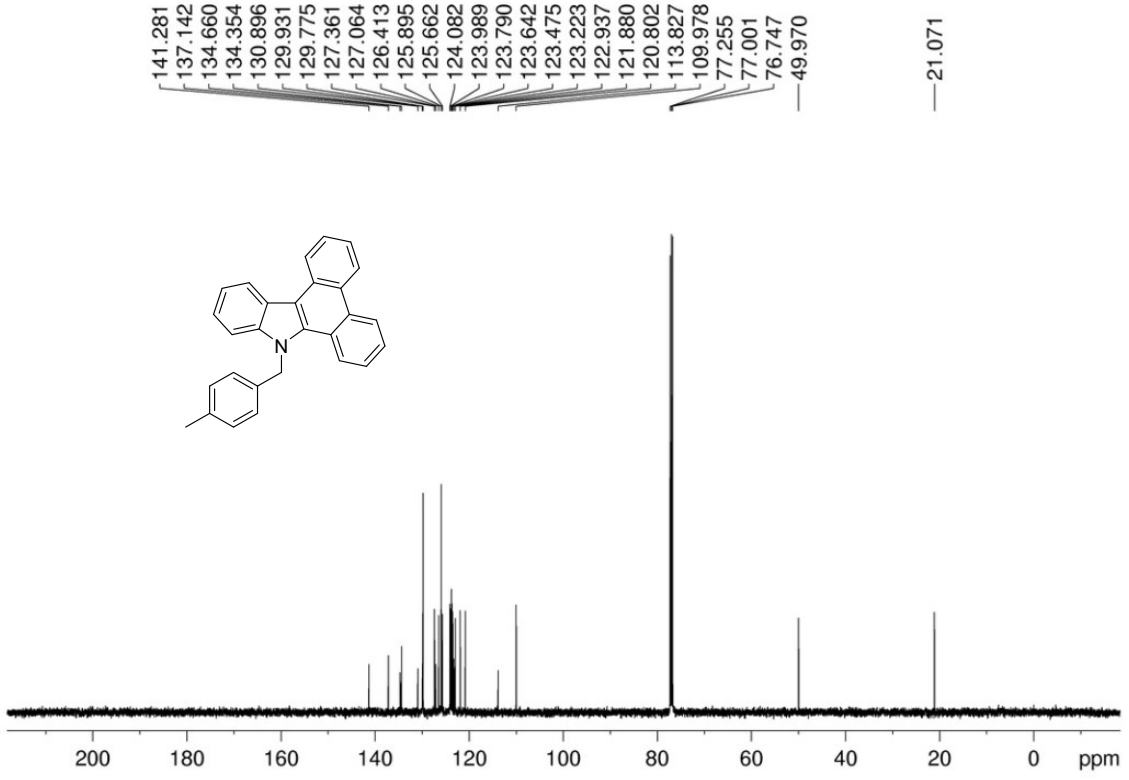
^{1}H and ^{13}C Spectrum of Compound **3ca**



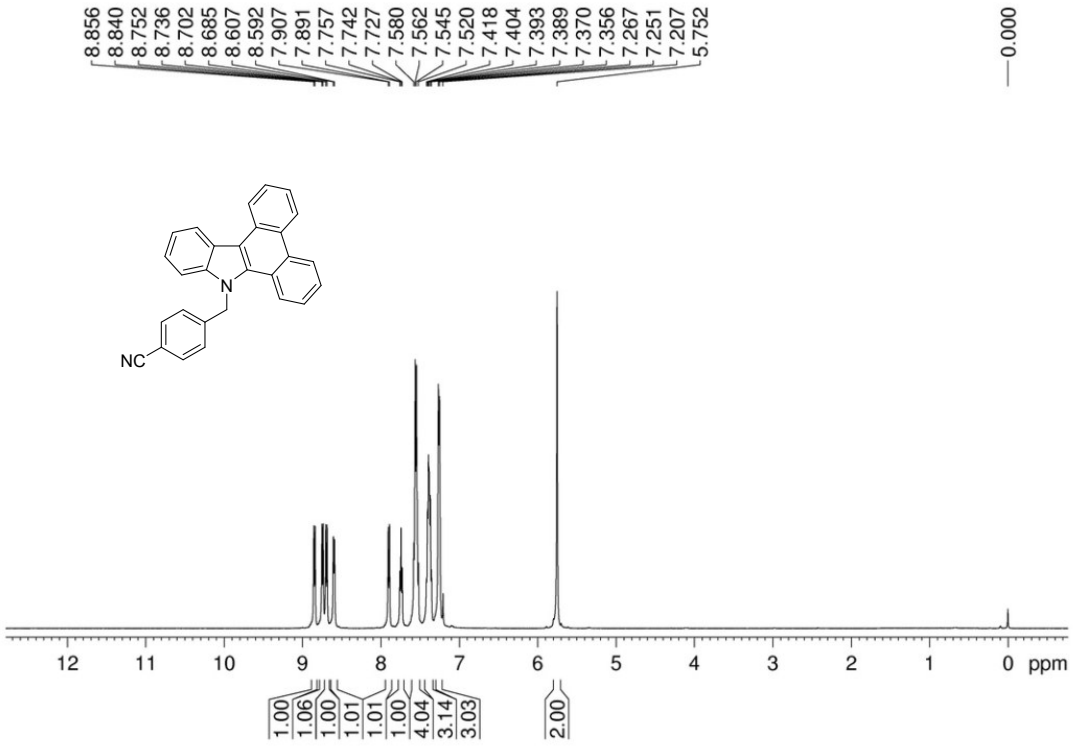


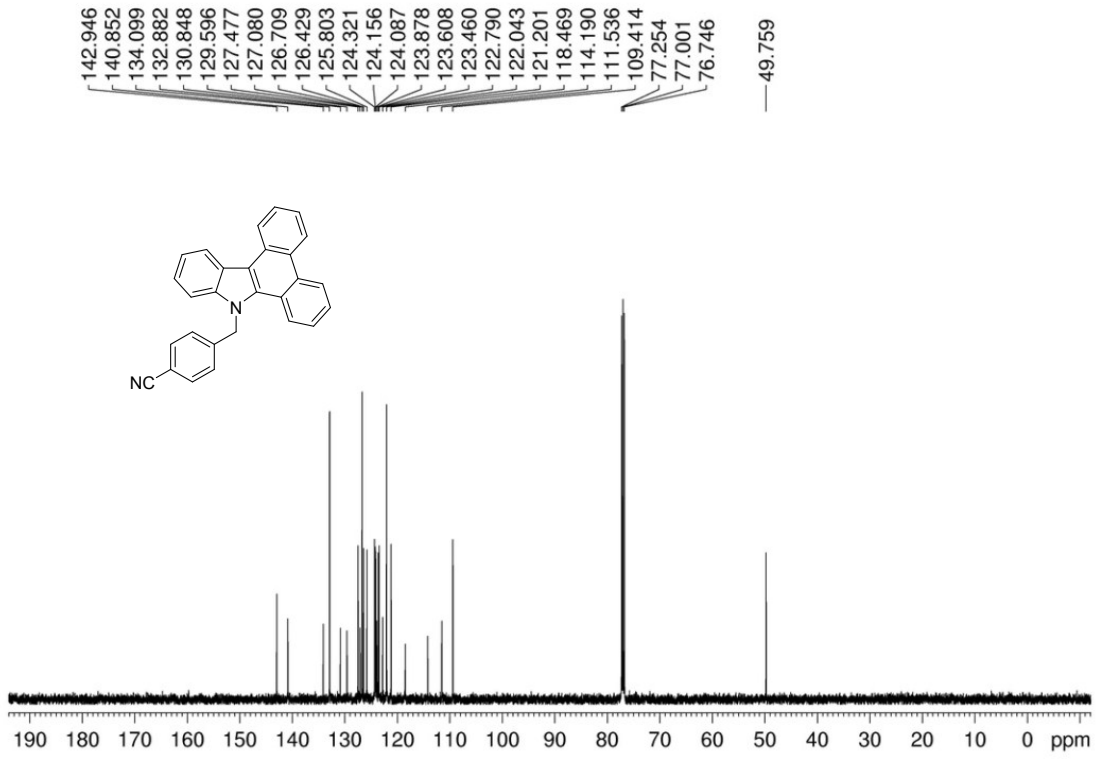
^{1}H and ^{13}C Spectrum of Compound **3da**



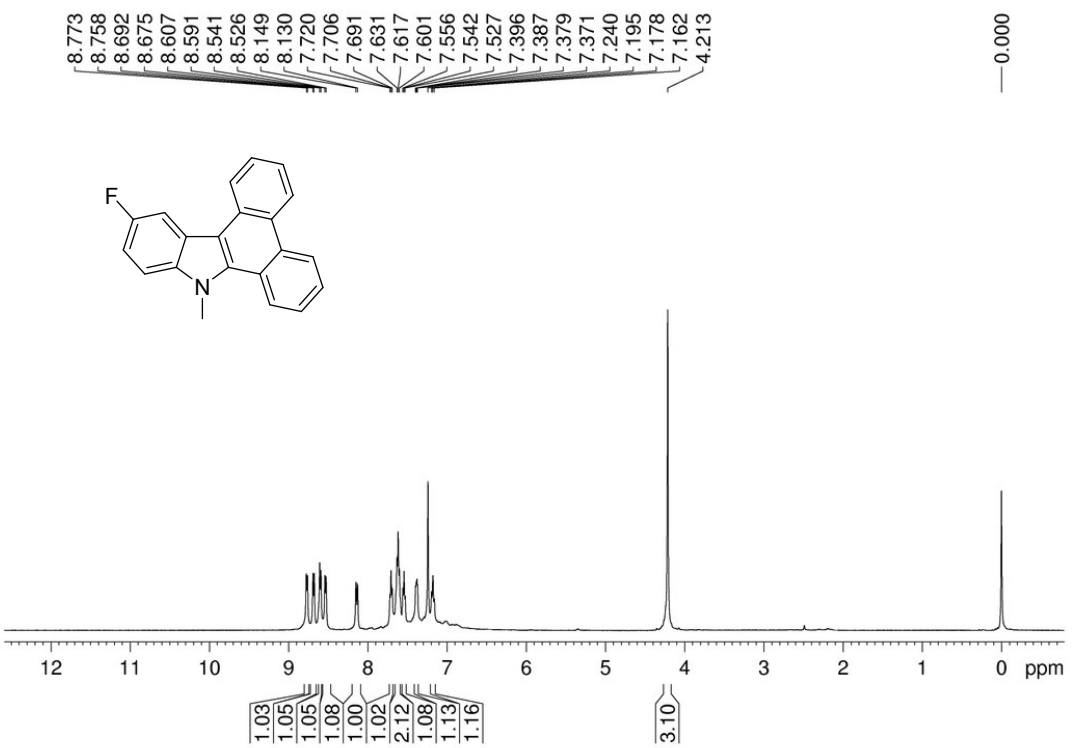


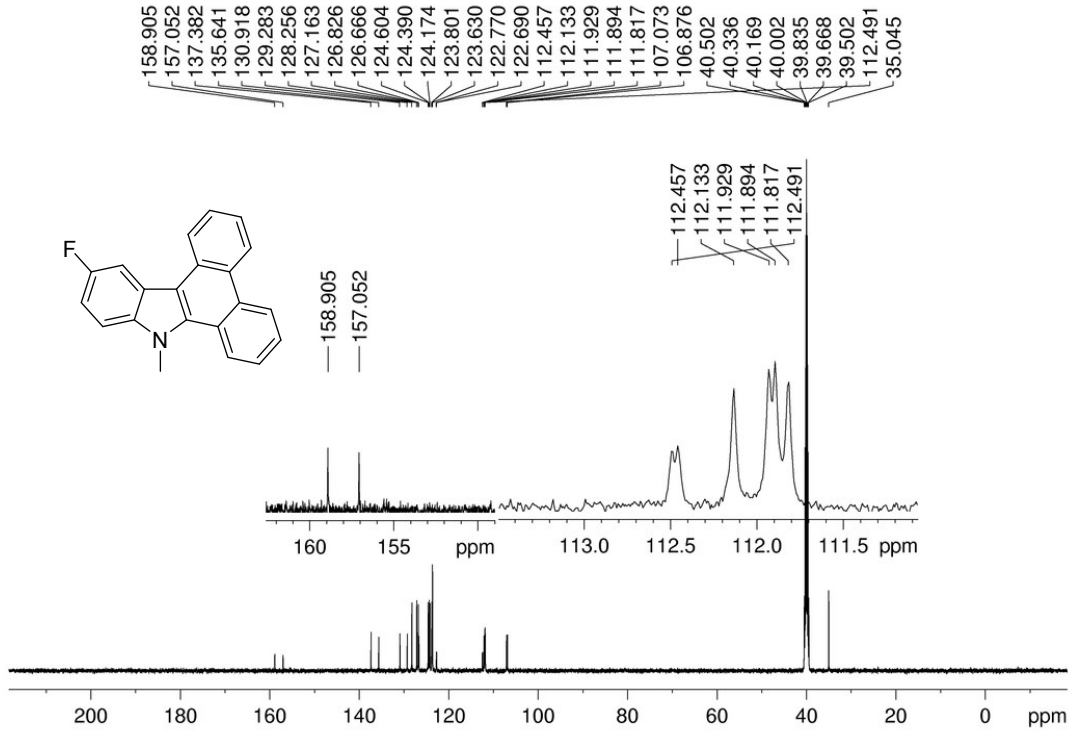
^{1}H and ^{13}C Spectrum of Compound **3ea**



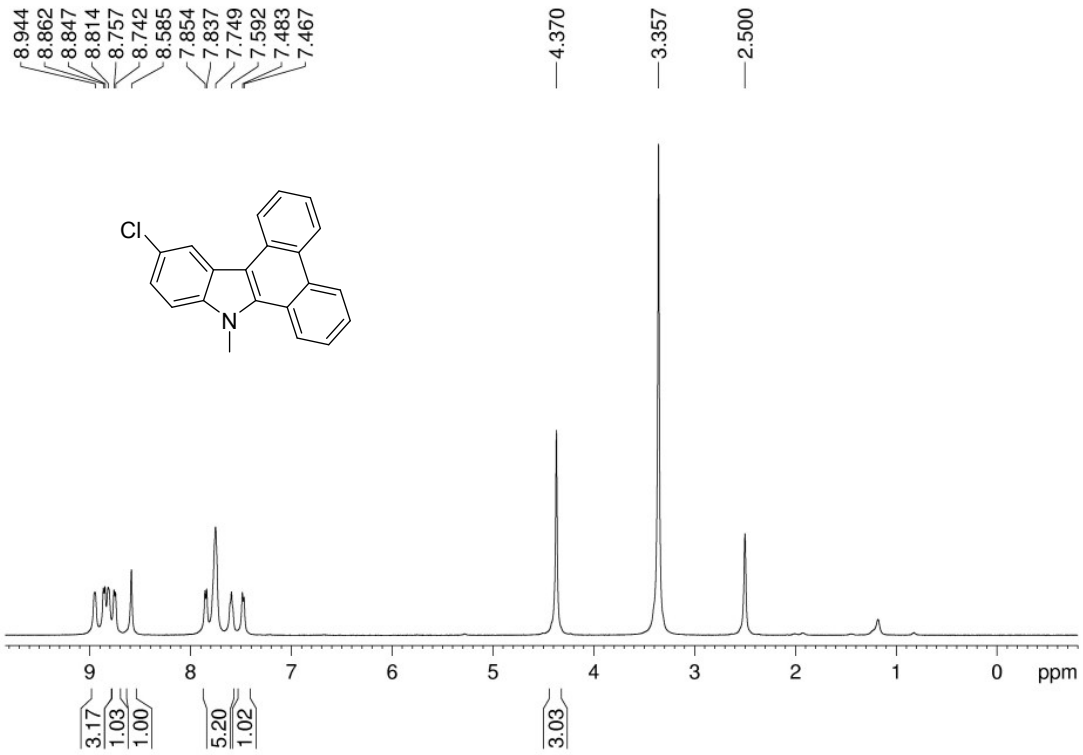


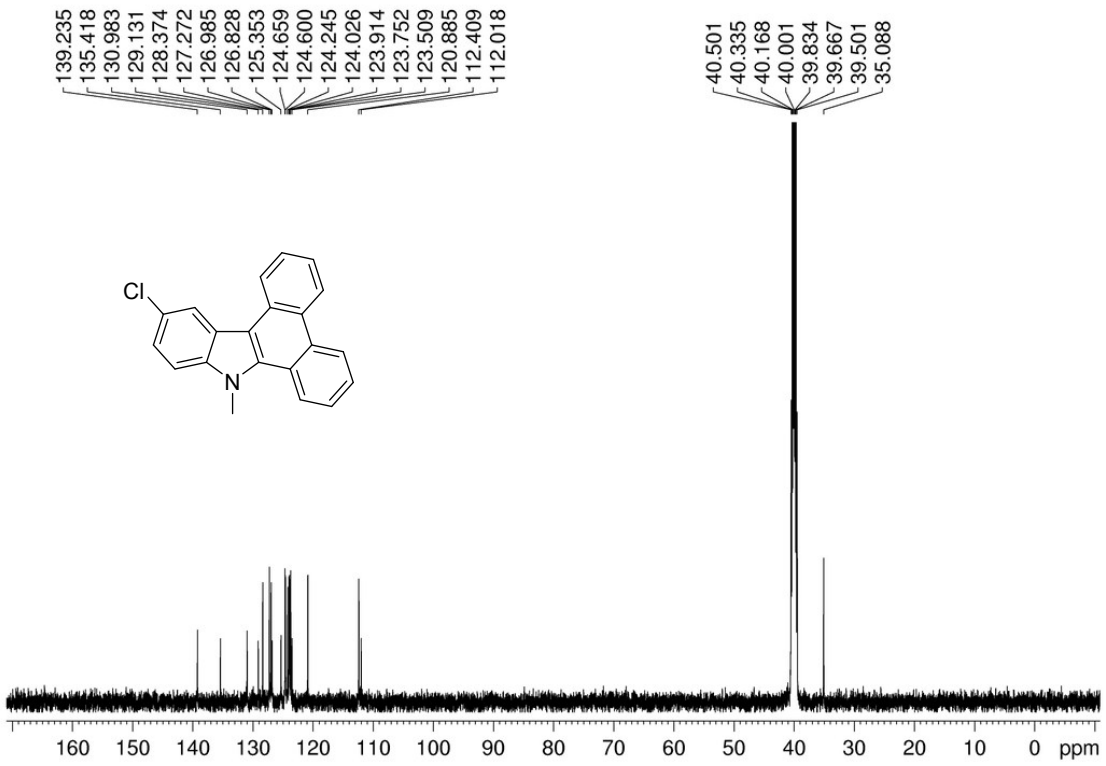
^{1}H and ^{13}C Spectrum of Compound **3ia**



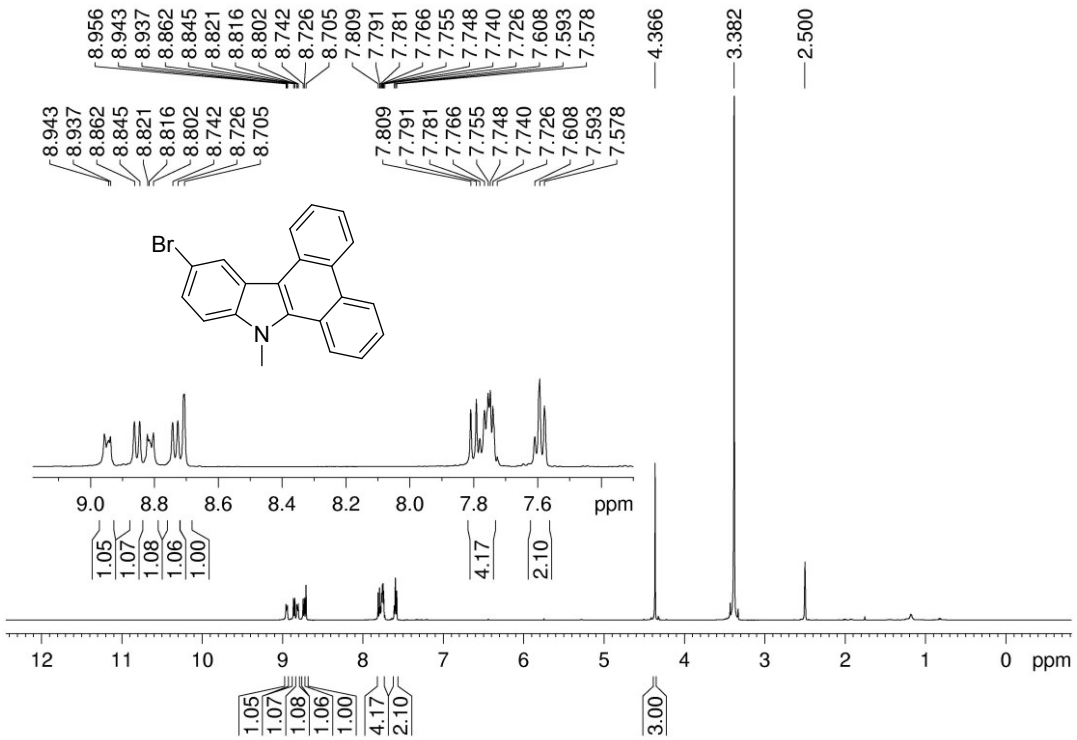


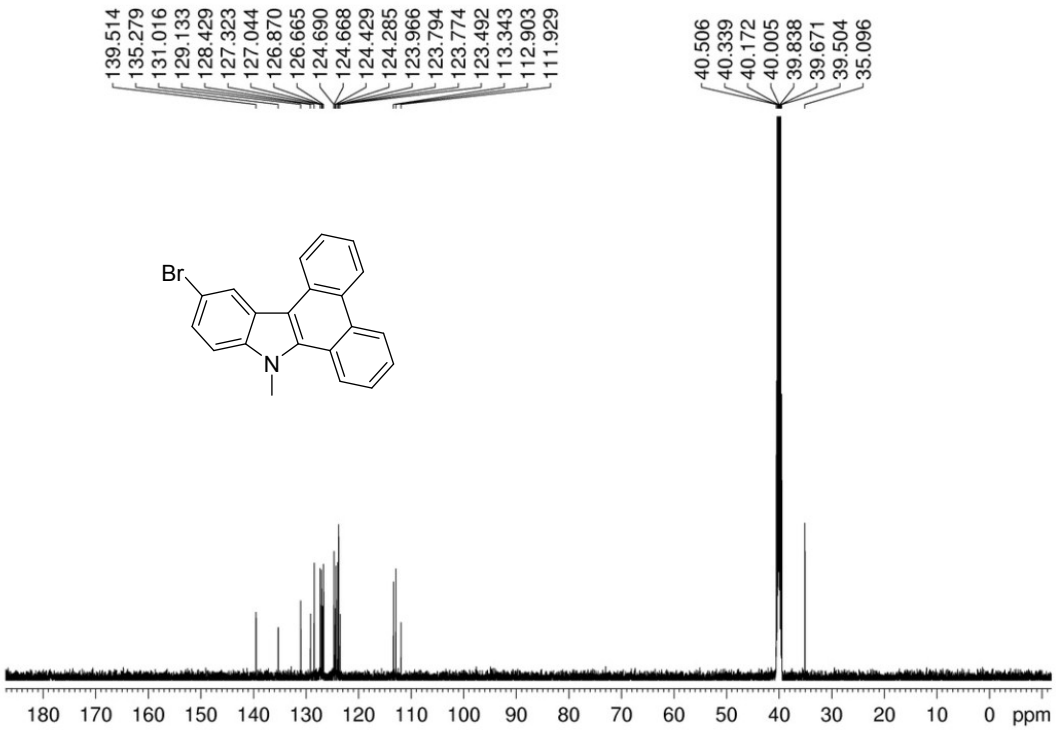
^{1}H and ^{13}C Spectrum of Compound **3ja**



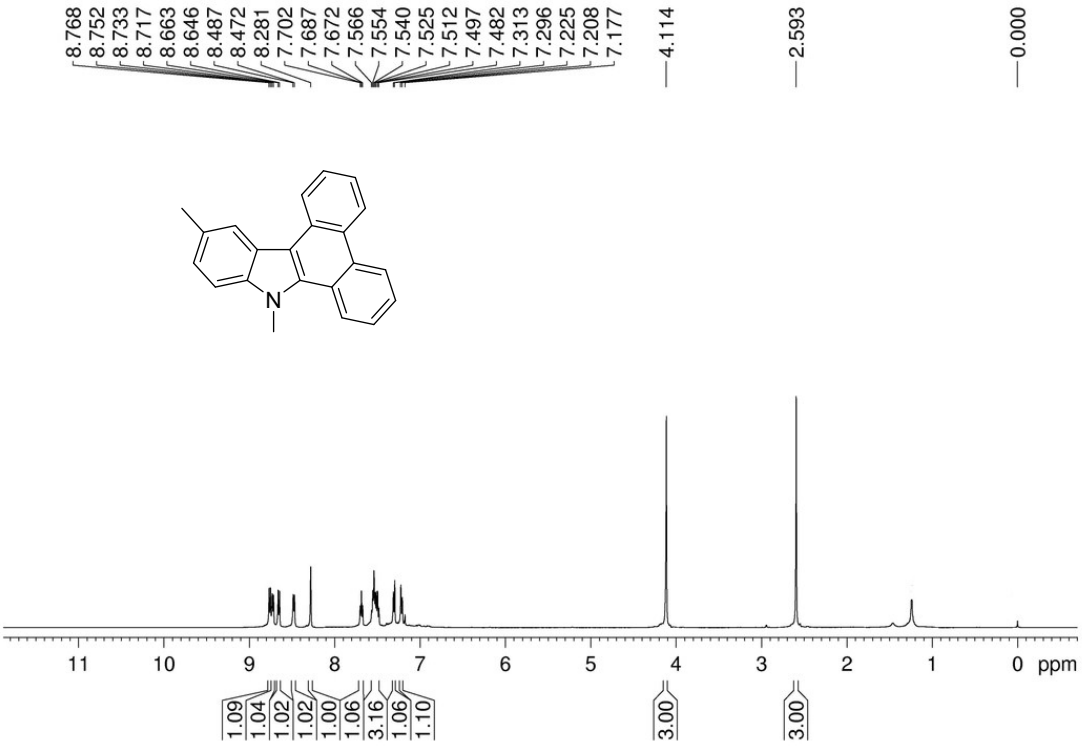


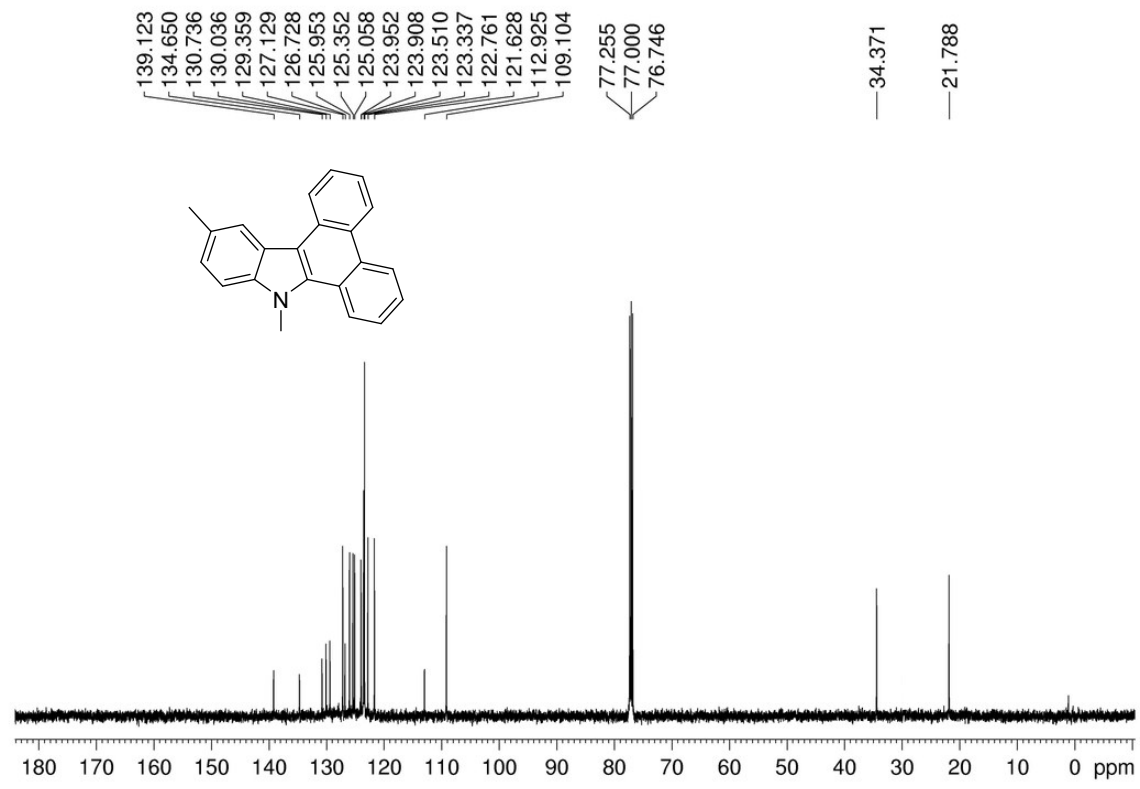
^{1}H and ^{13}C Spectrum of Compound **3ka**



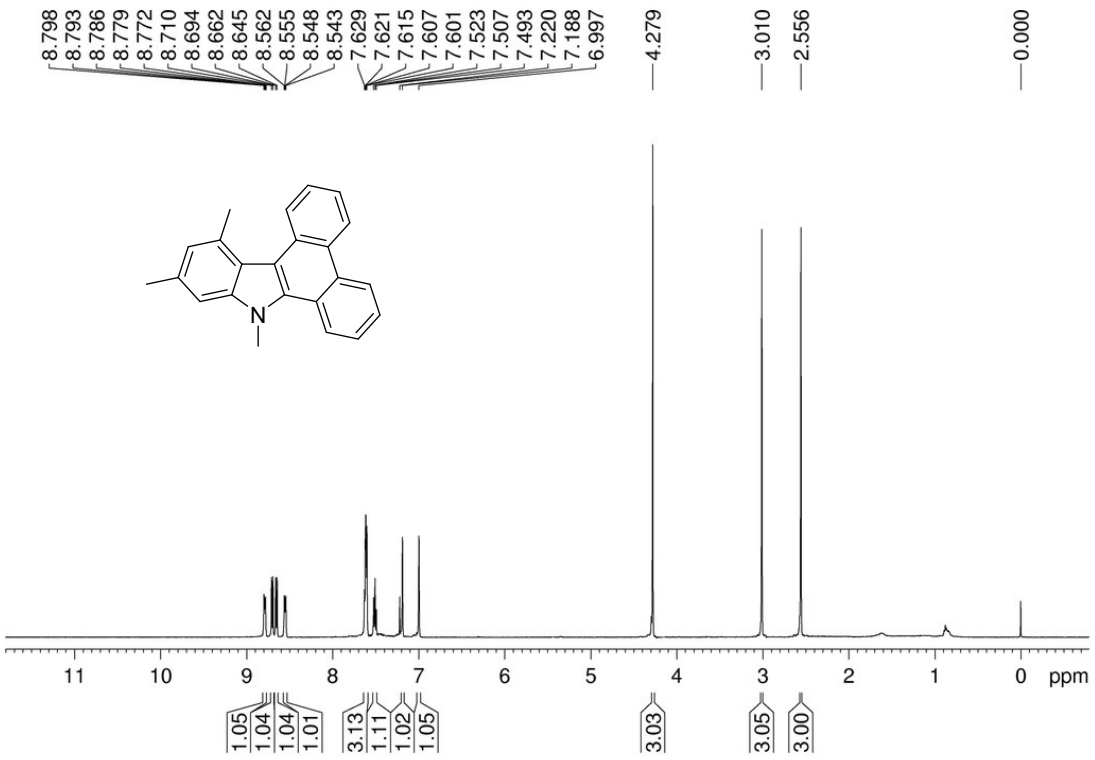


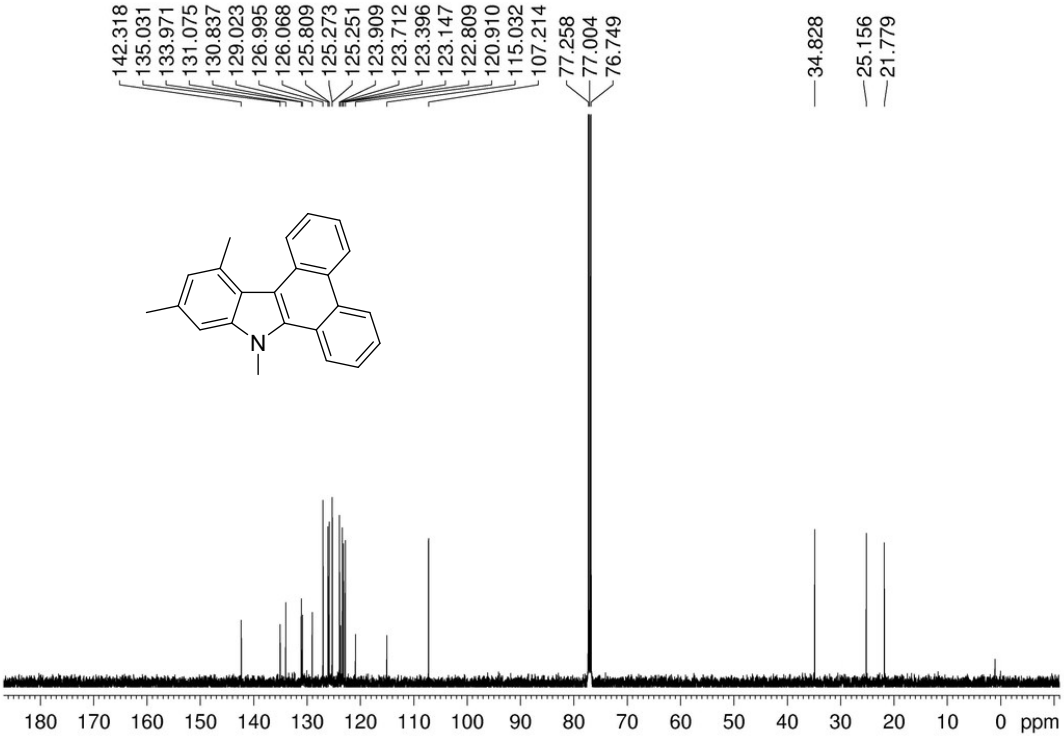
^{1}H and ^{13}C Spectrum of Compound **3la**



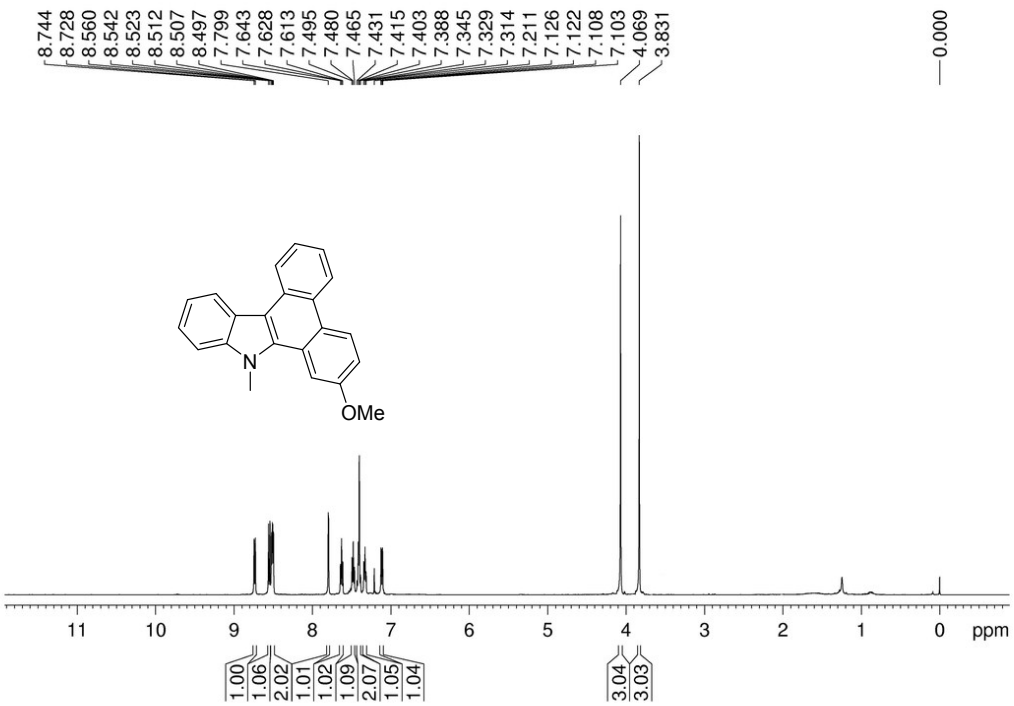


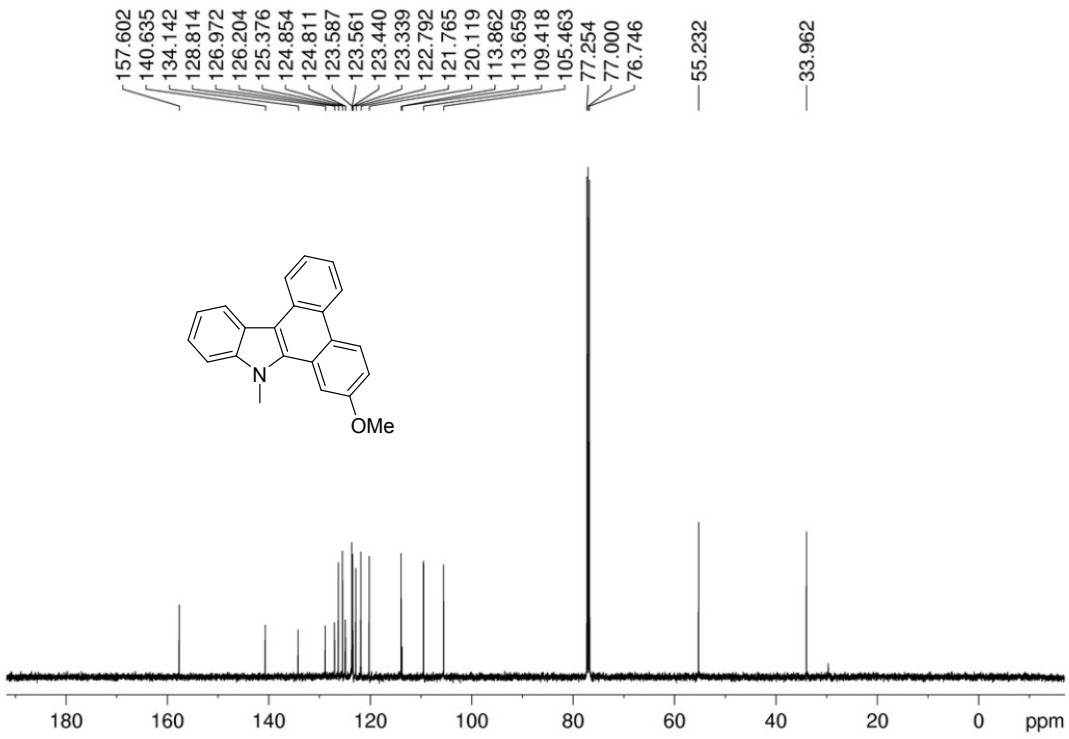
^{1}H and ^{13}C Spectrum of Compound **3ma**



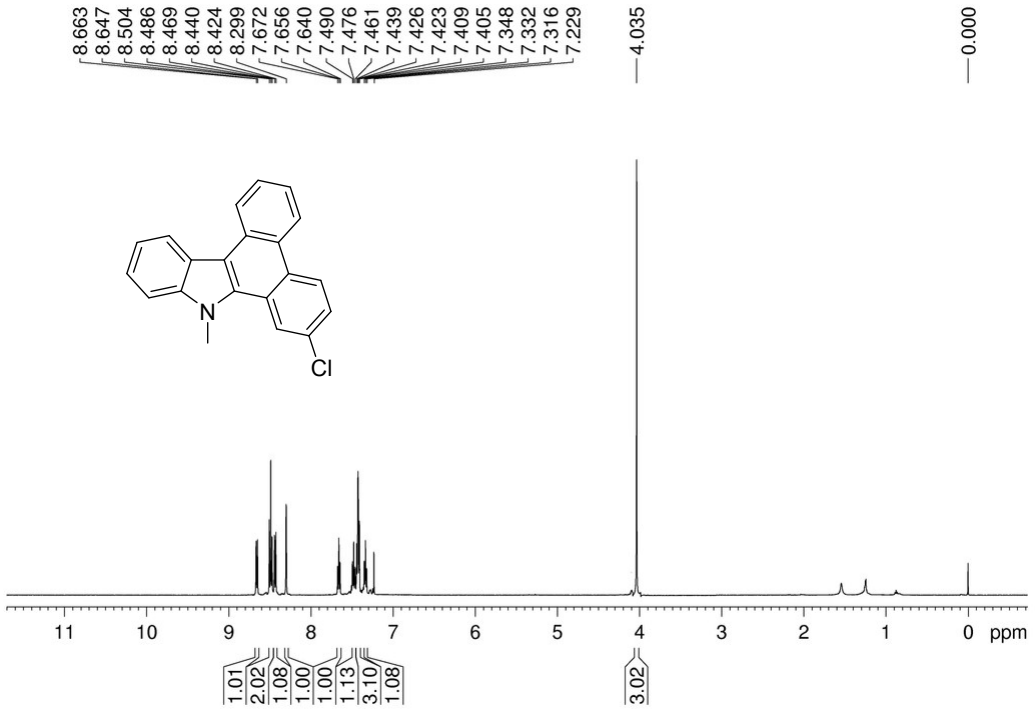


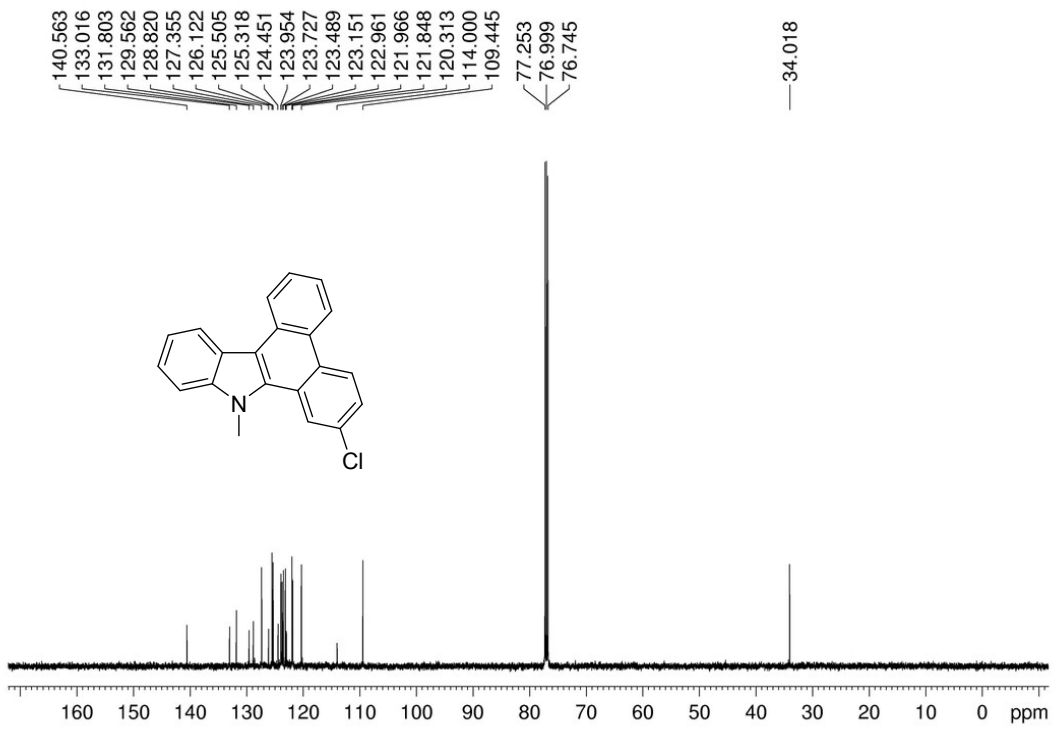
^{1}H and ^{13}C Spectrum of Compound **3na**



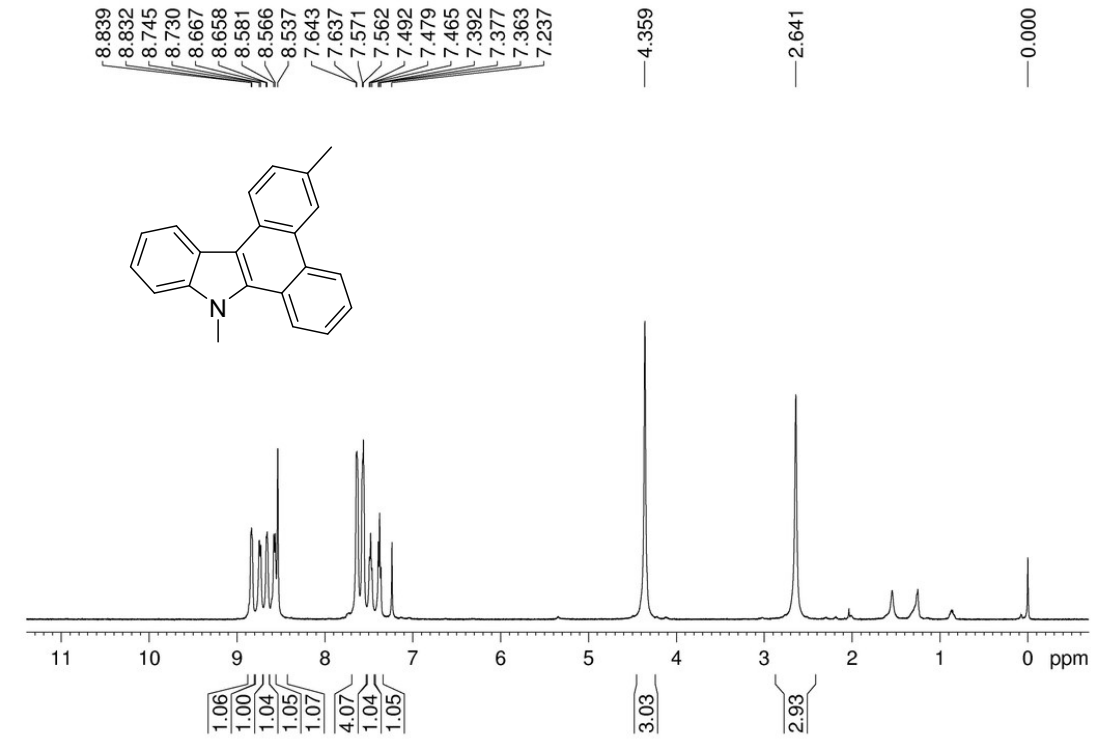


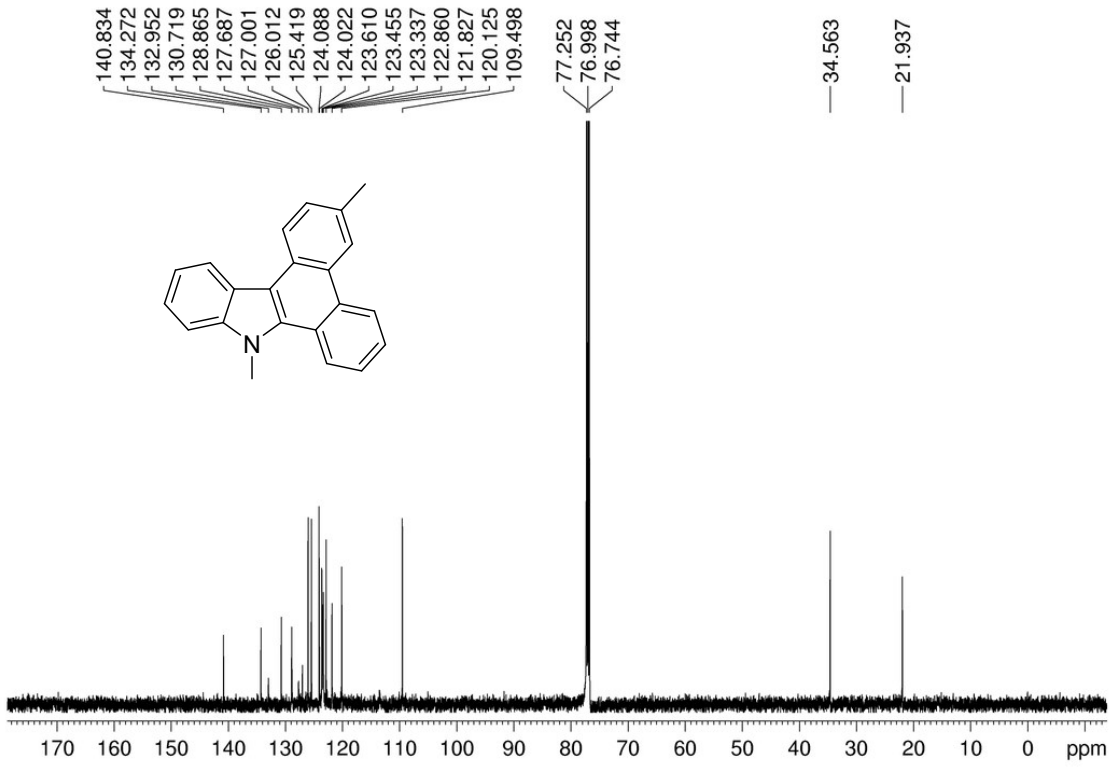
^{1}H and ^{13}C Spectrum of Compound **3oa**



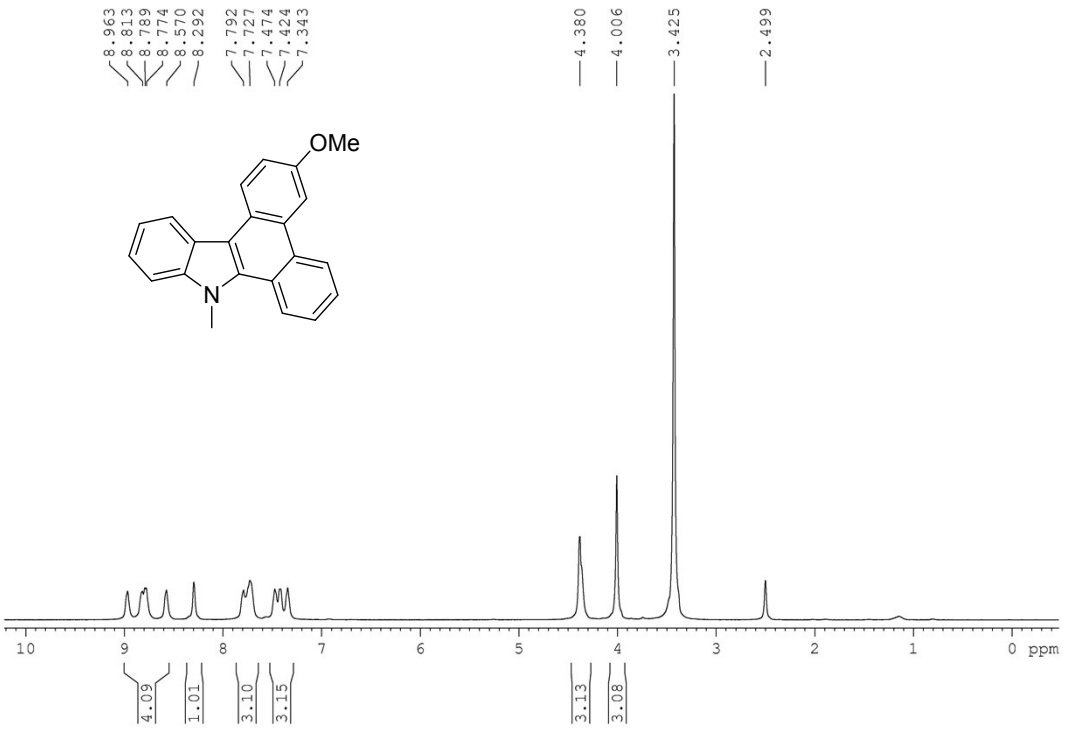


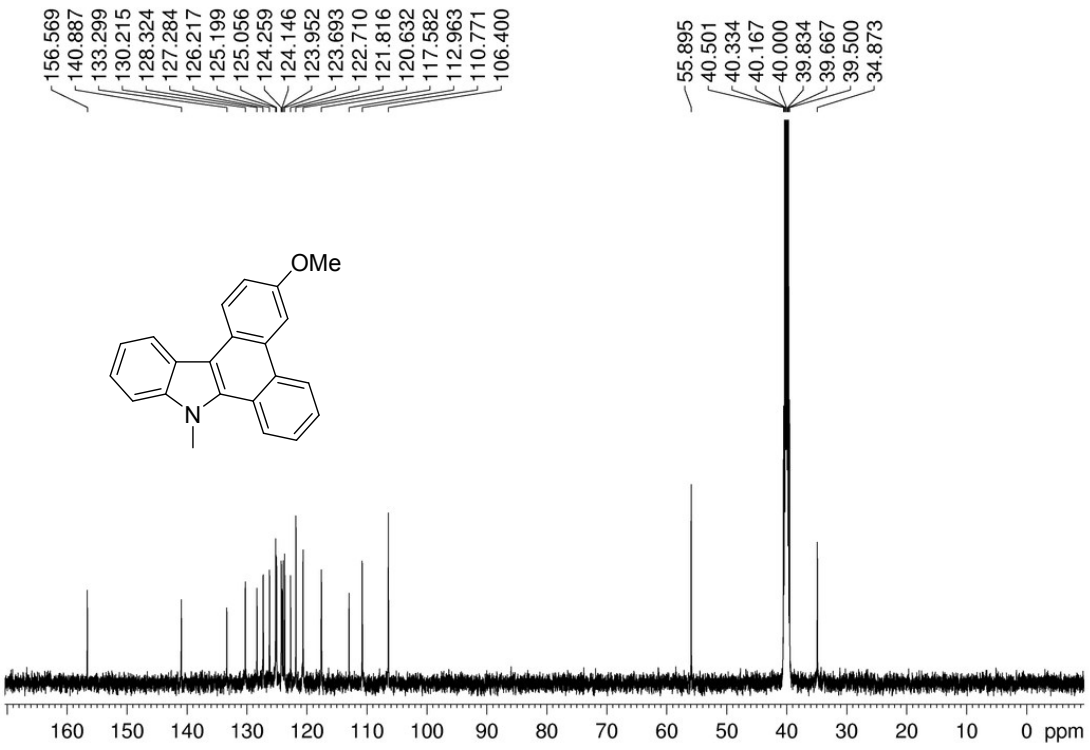
^{1}H and ^{13}C Spectrum of Compound **3ab**



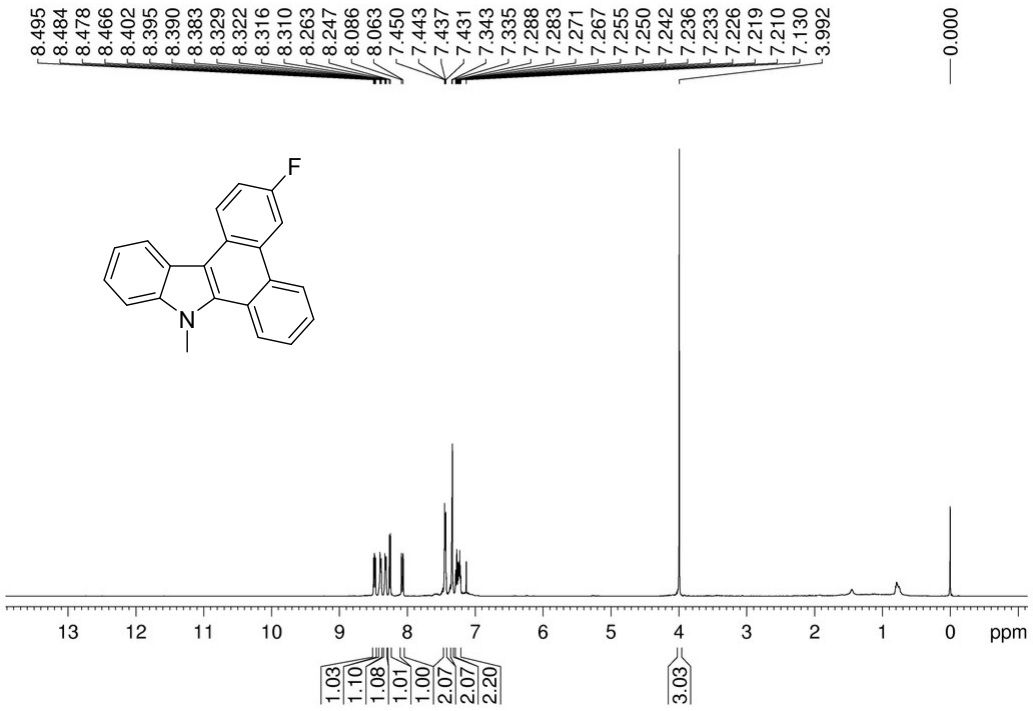


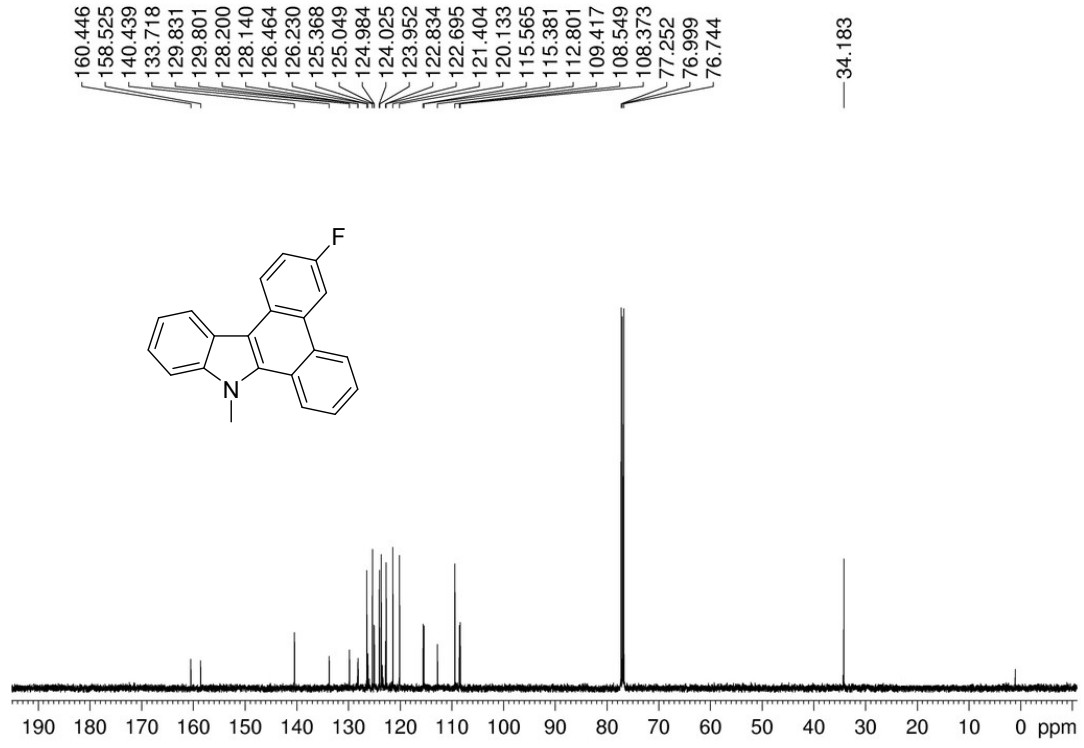
^{1}H and ^{13}C Spectrum of Compound **3ac**



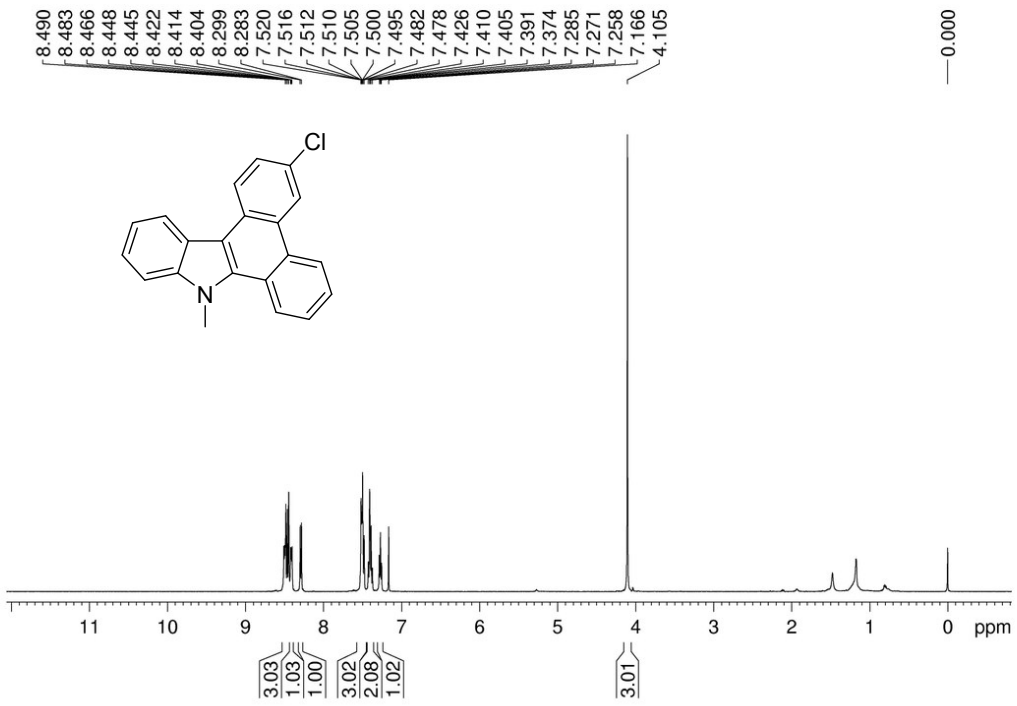


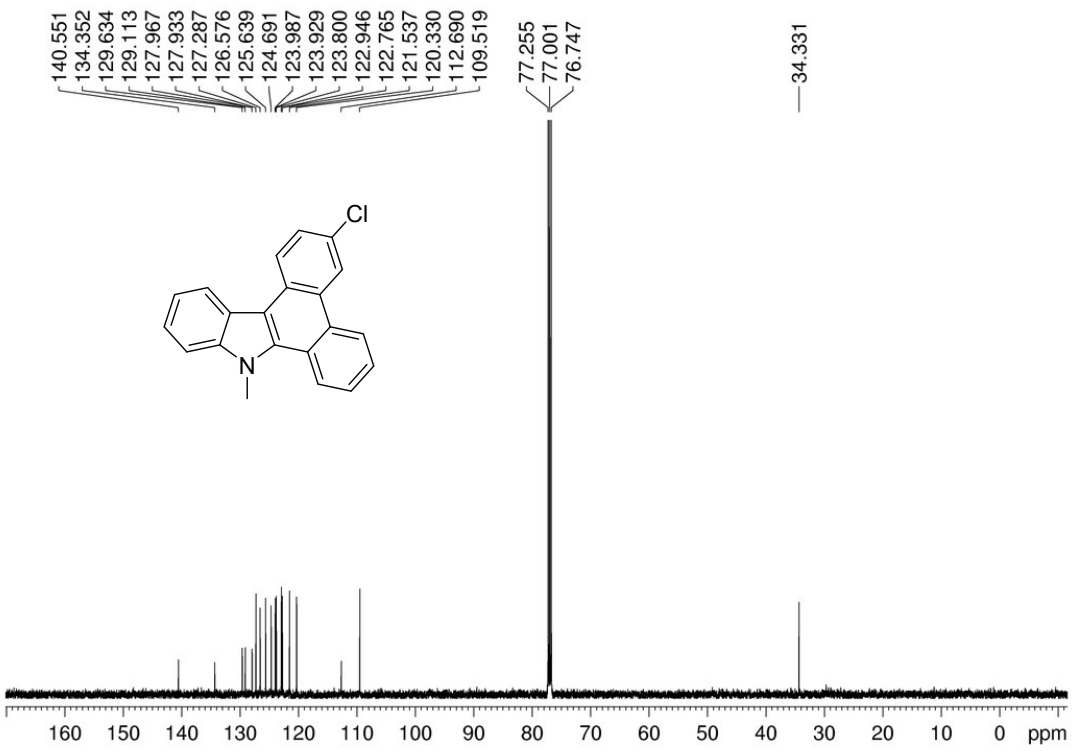
^{1}H and ^{13}C Spectrum of Compound **3ad**



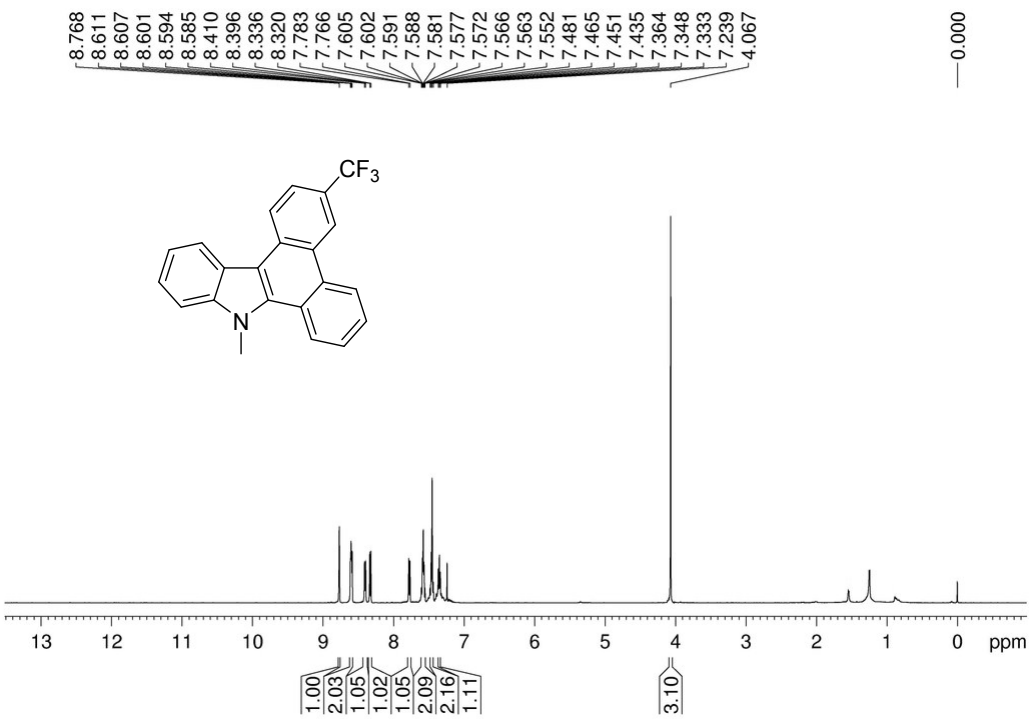


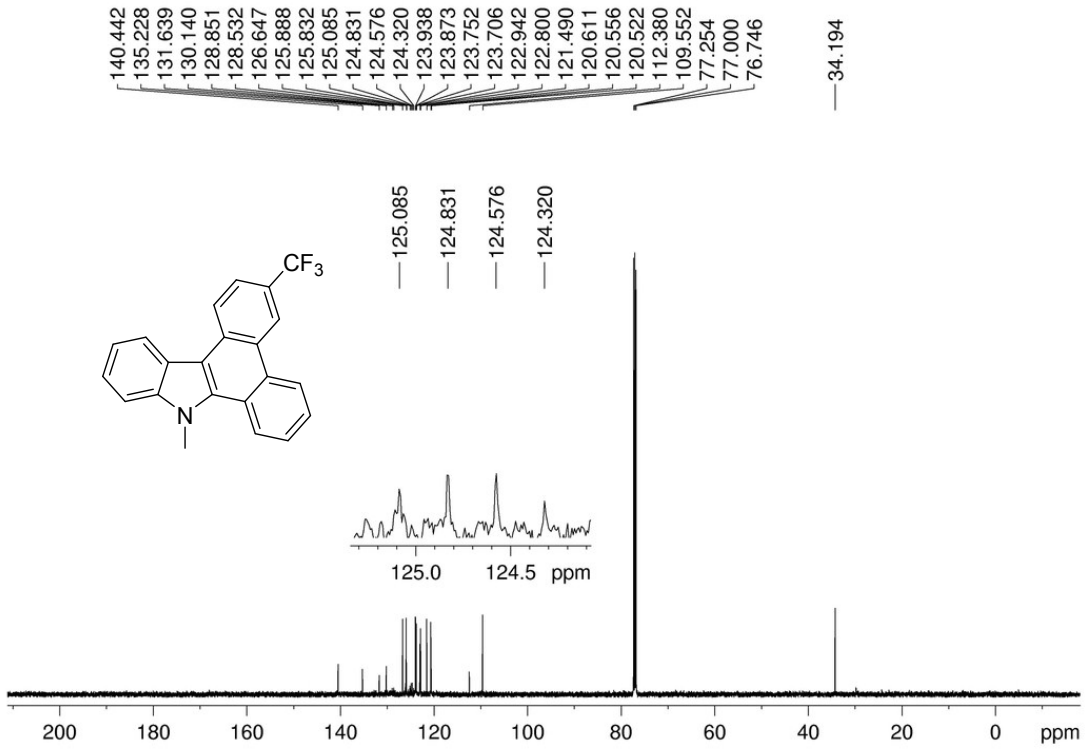
^{1}H and ^{13}C Spectrum of Compound **3ae**



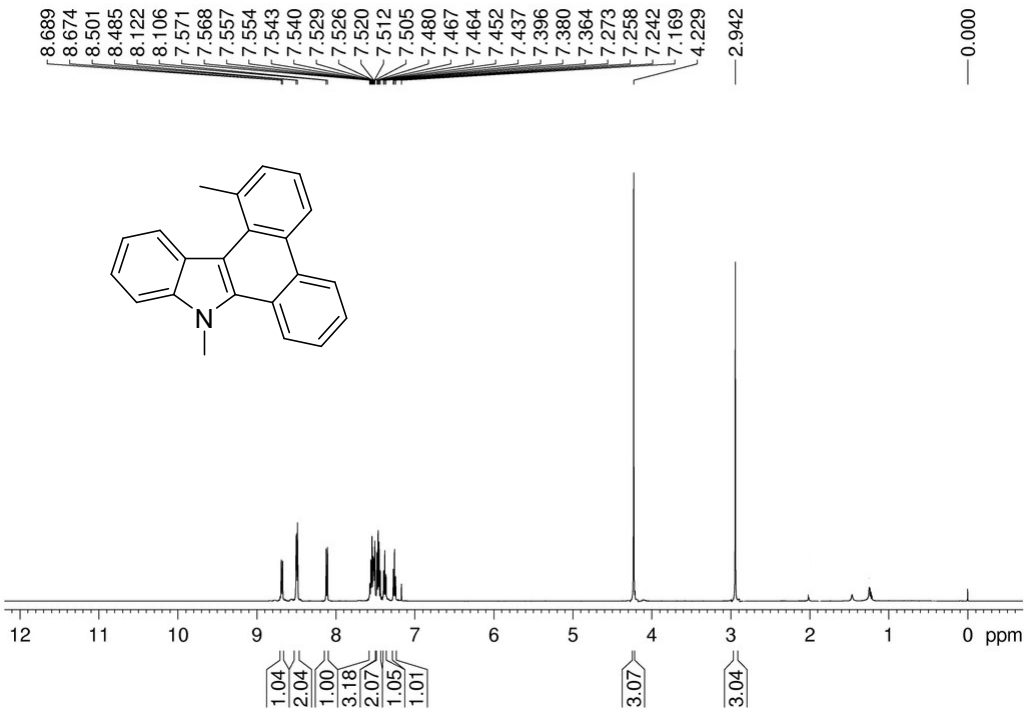


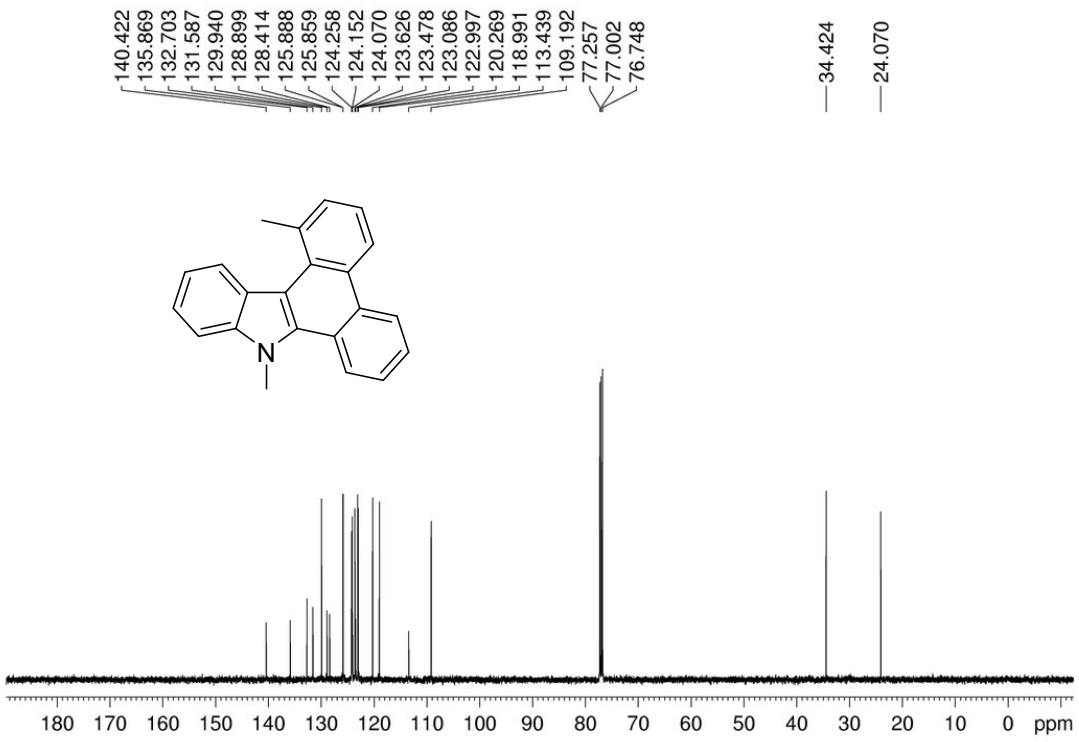
^{1}H and ^{13}C Spectrum of Compound **3af**



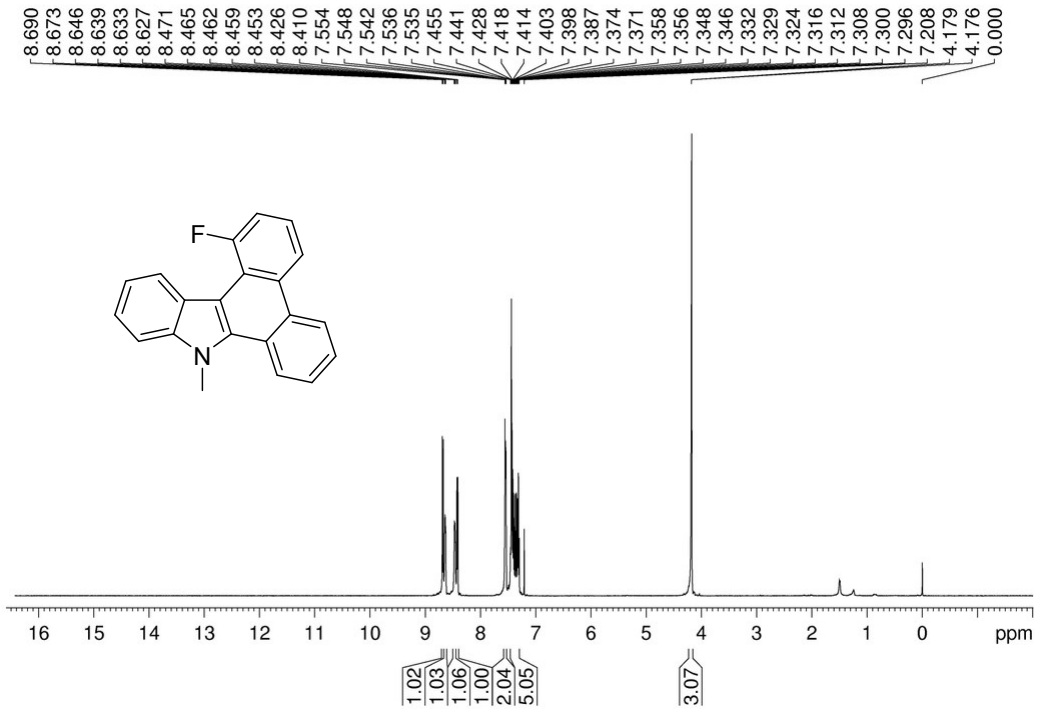


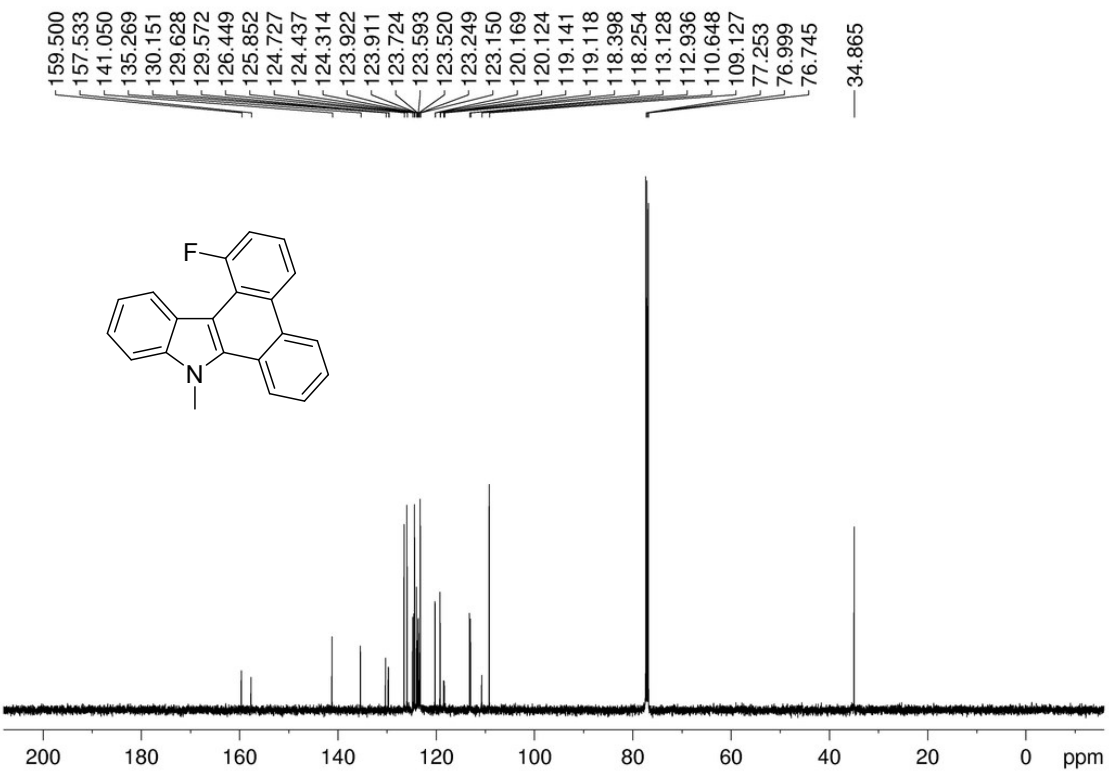
^{1}H and ^{13}C Spectrum of Compound **3ag**



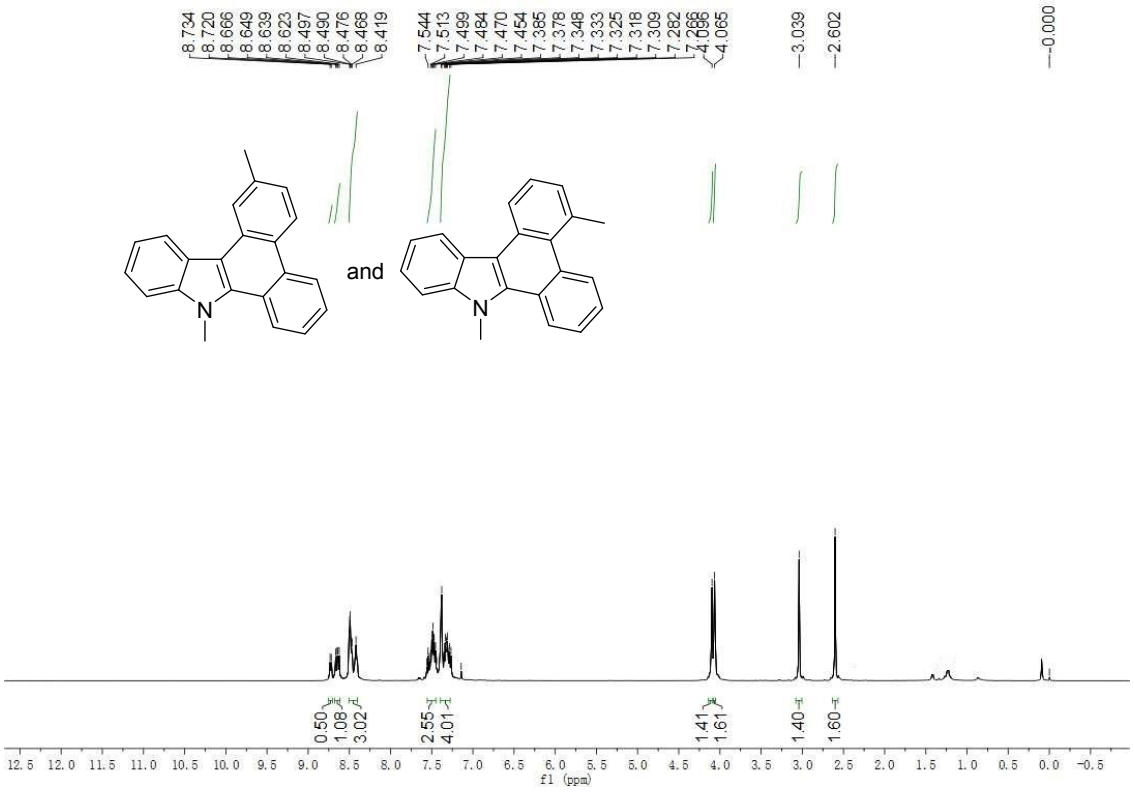


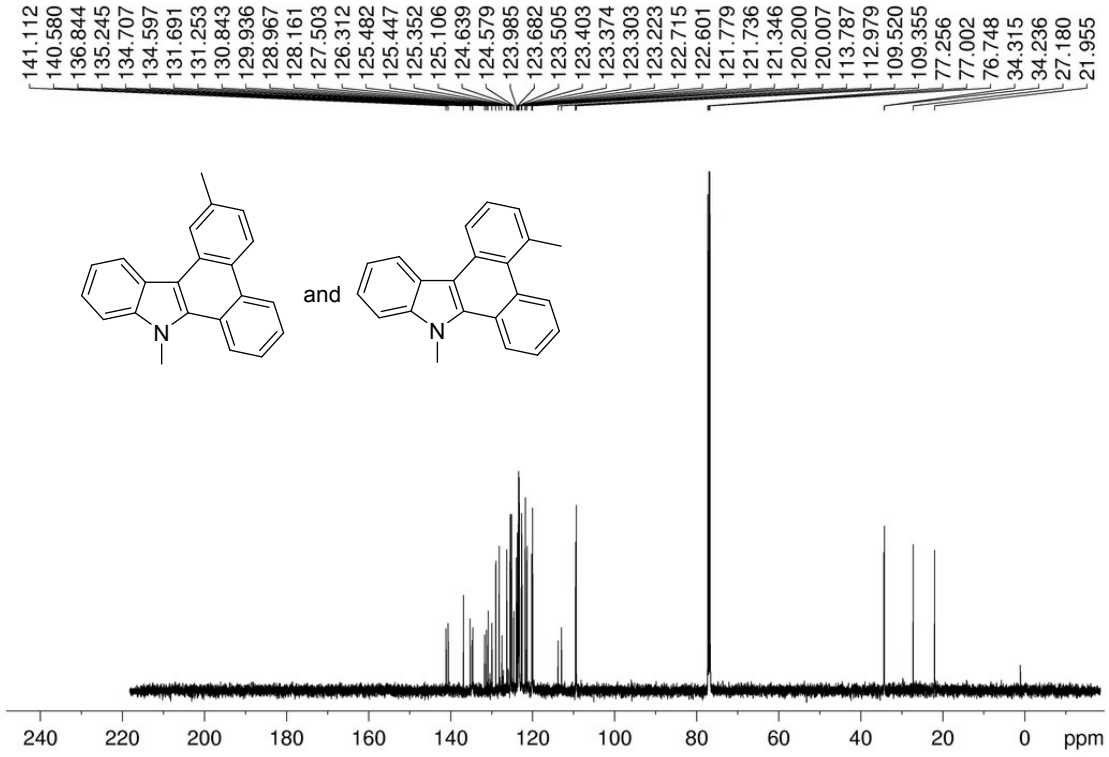
^{1}H and ^{13}C Spectrum of Compound **3ah**



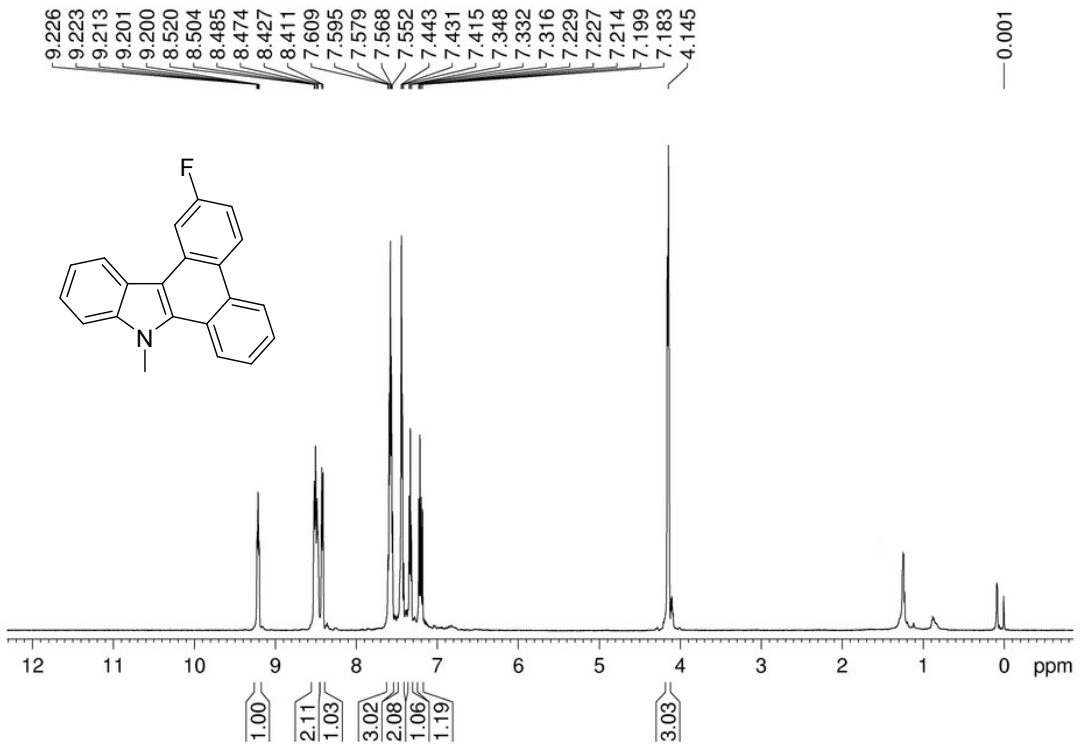


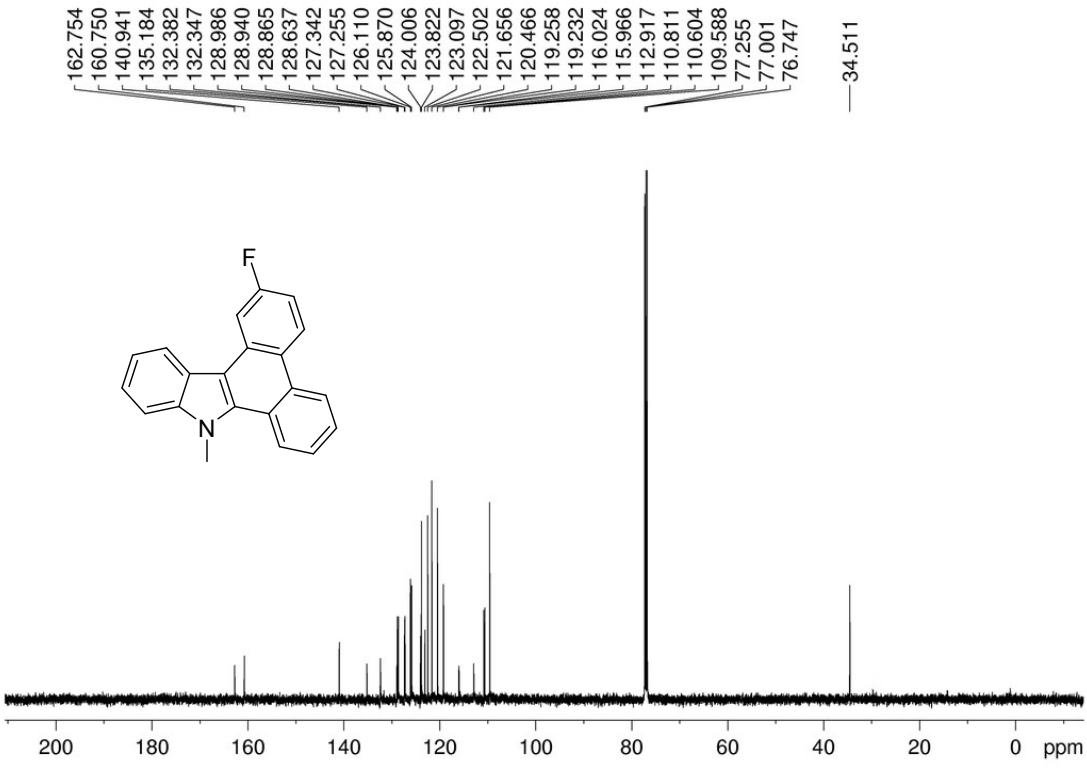
^{1}H and ^{13}C Spectrum of Compound **3ai and 3ai'**



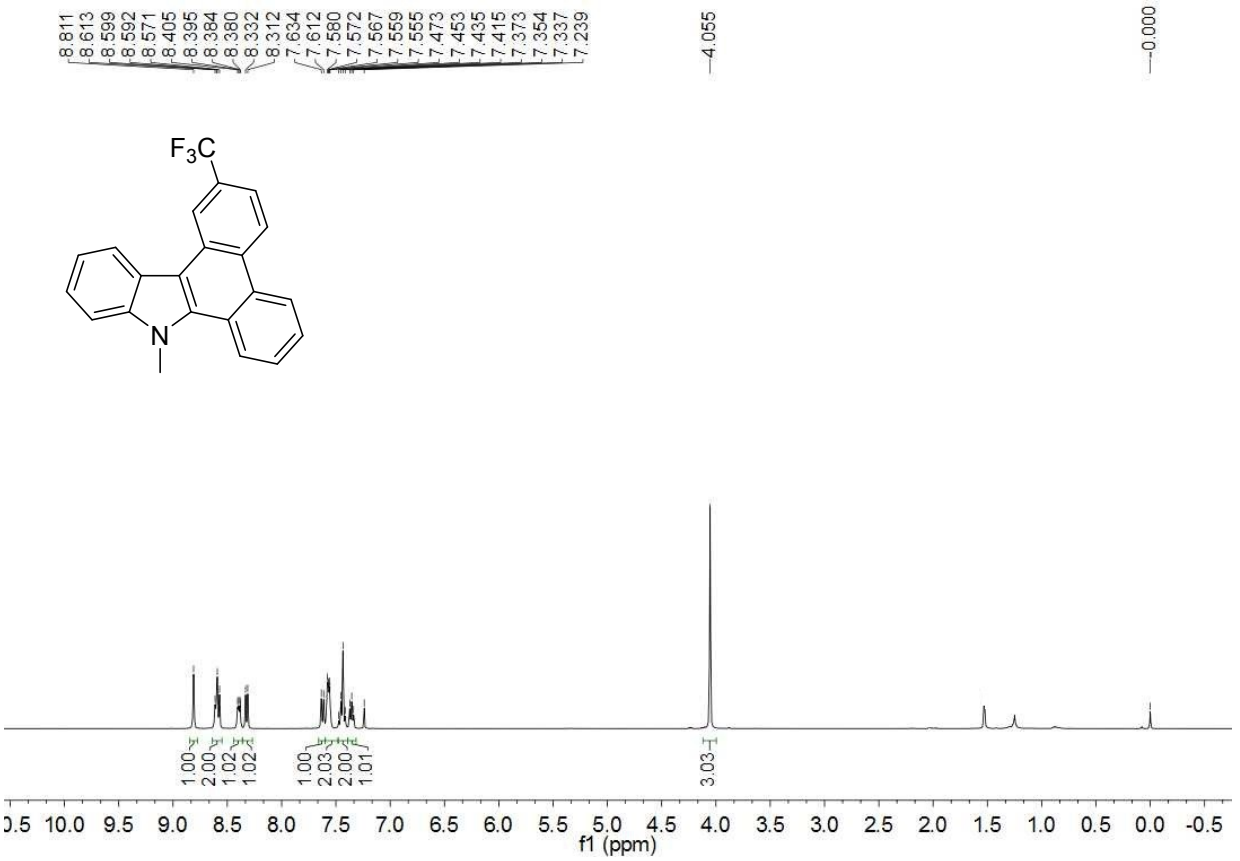


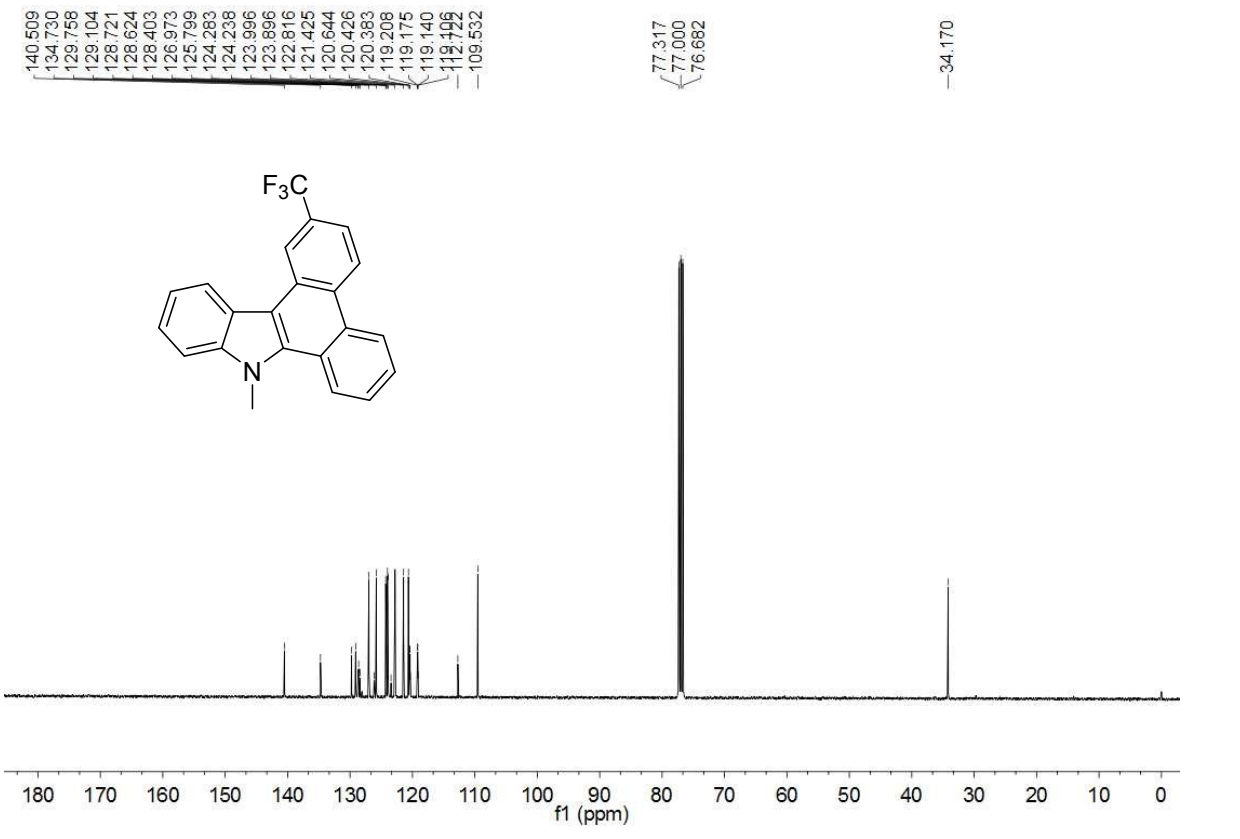
^{1}H and ^{13}C Spectrum of Compound **3aj**



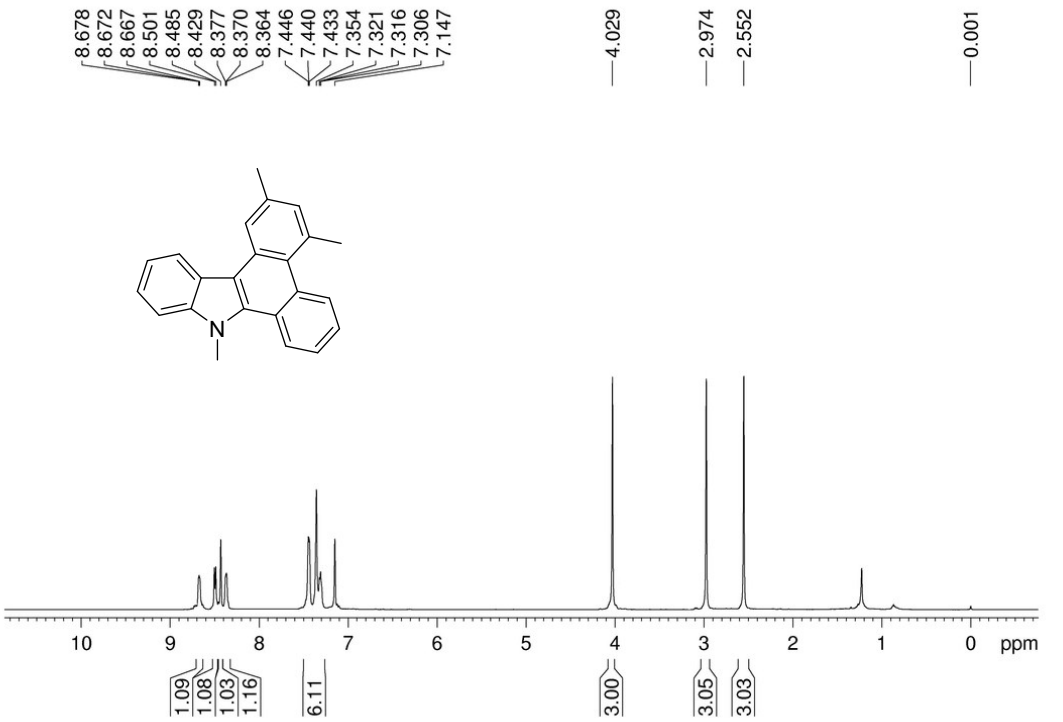


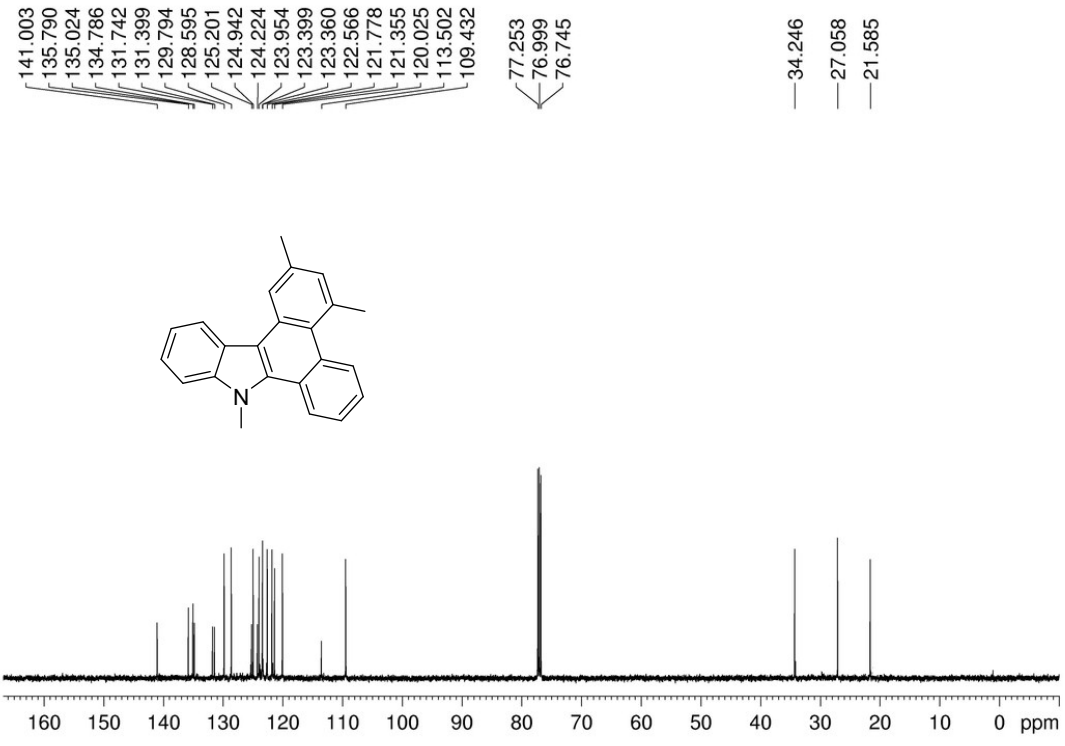
^{1}H and ^{13}C Spectrum of Compound **3ak**



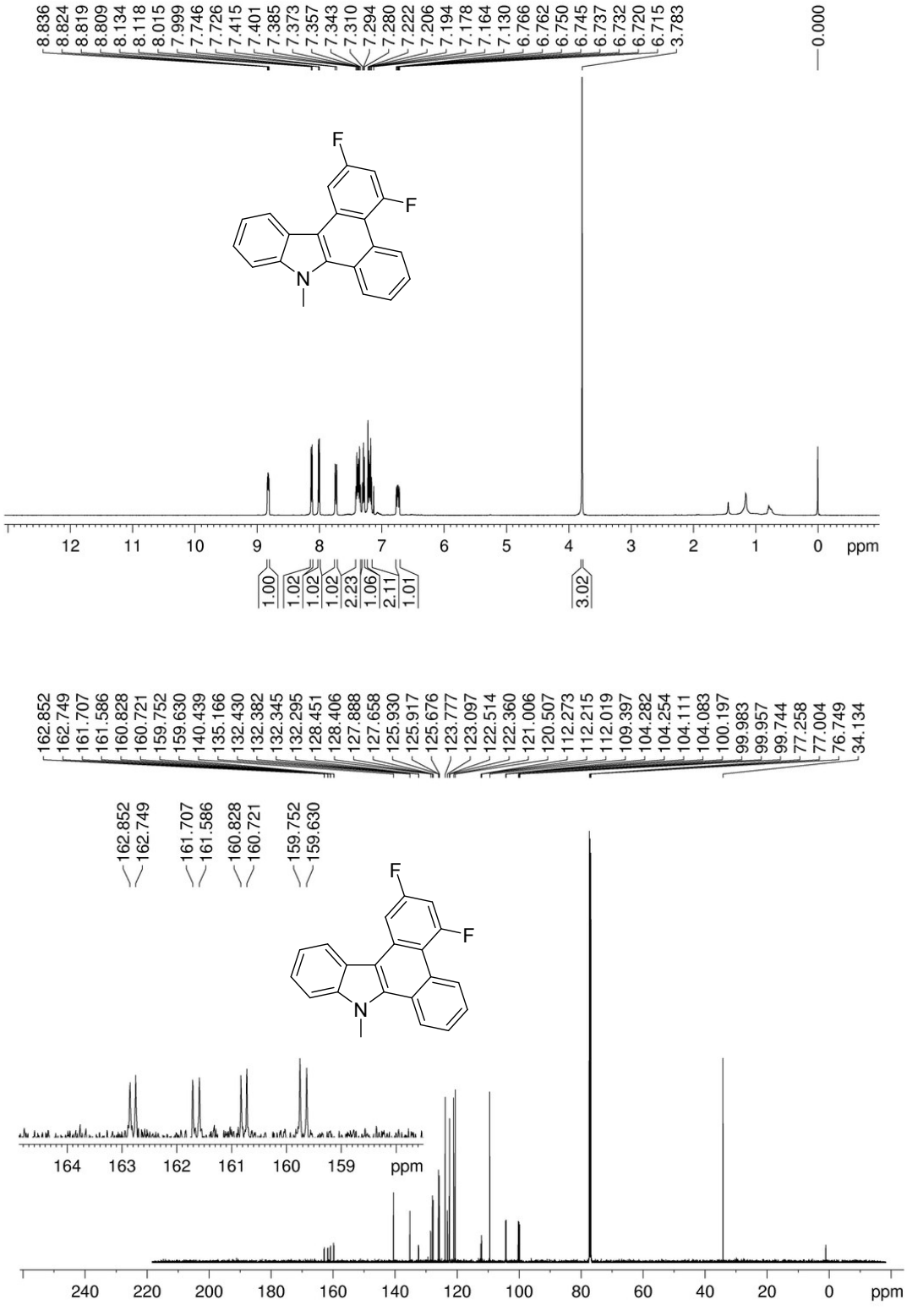


^{1}H and ^{13}C Spectrum of Compound **3al**

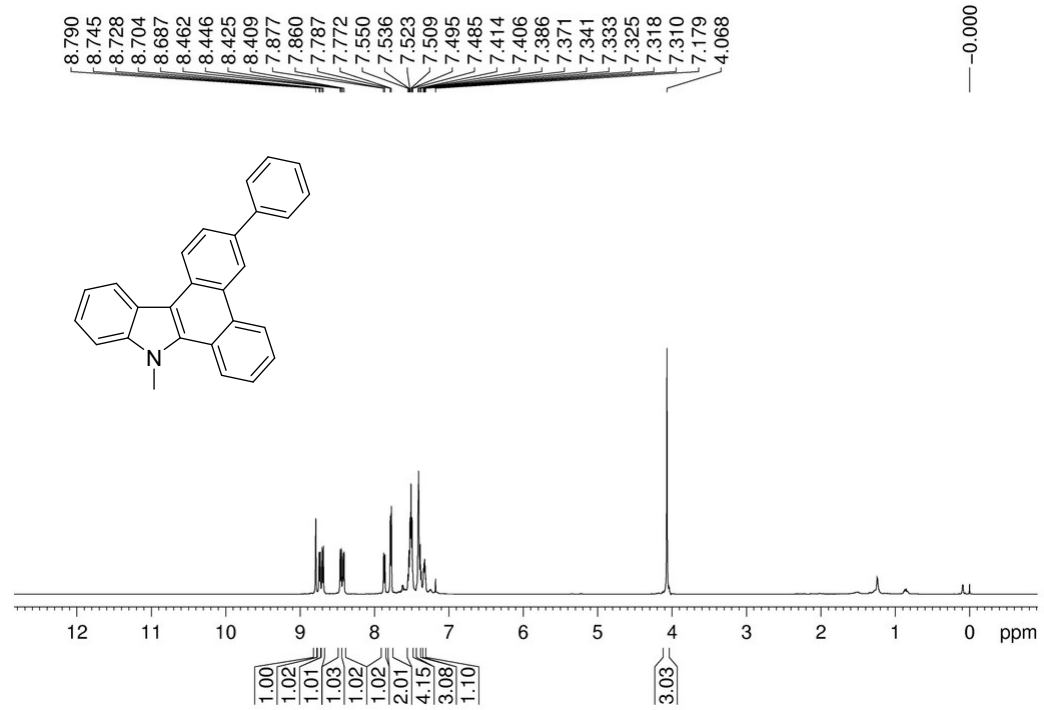


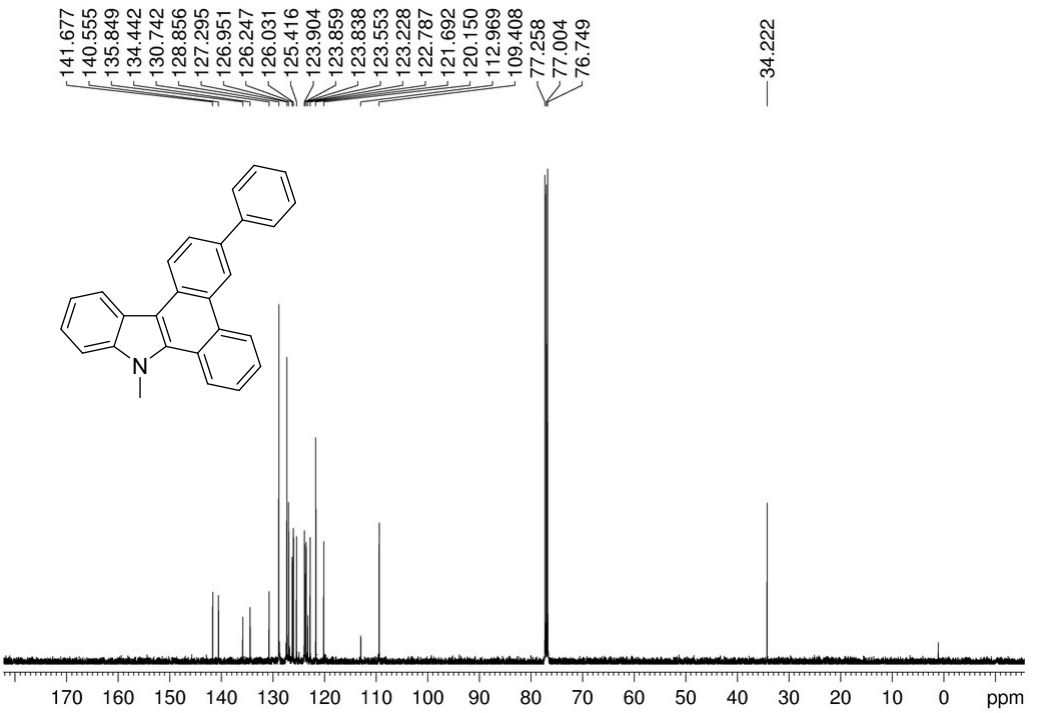


^{1}H and ^{13}C Spectrum of Compound **3am**

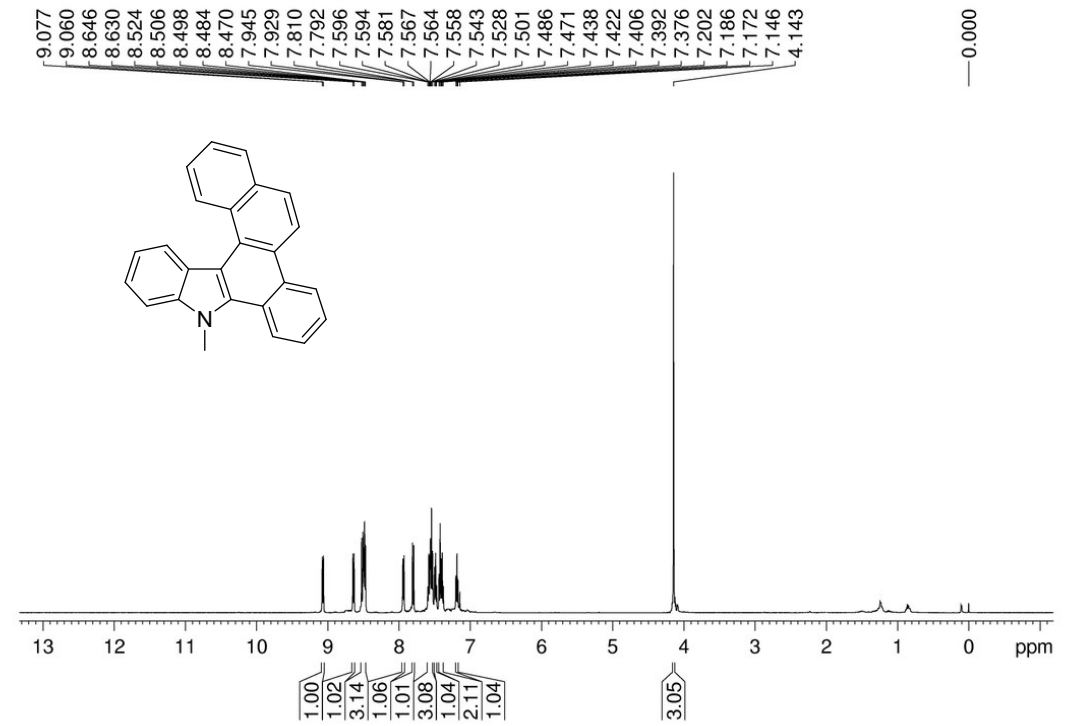


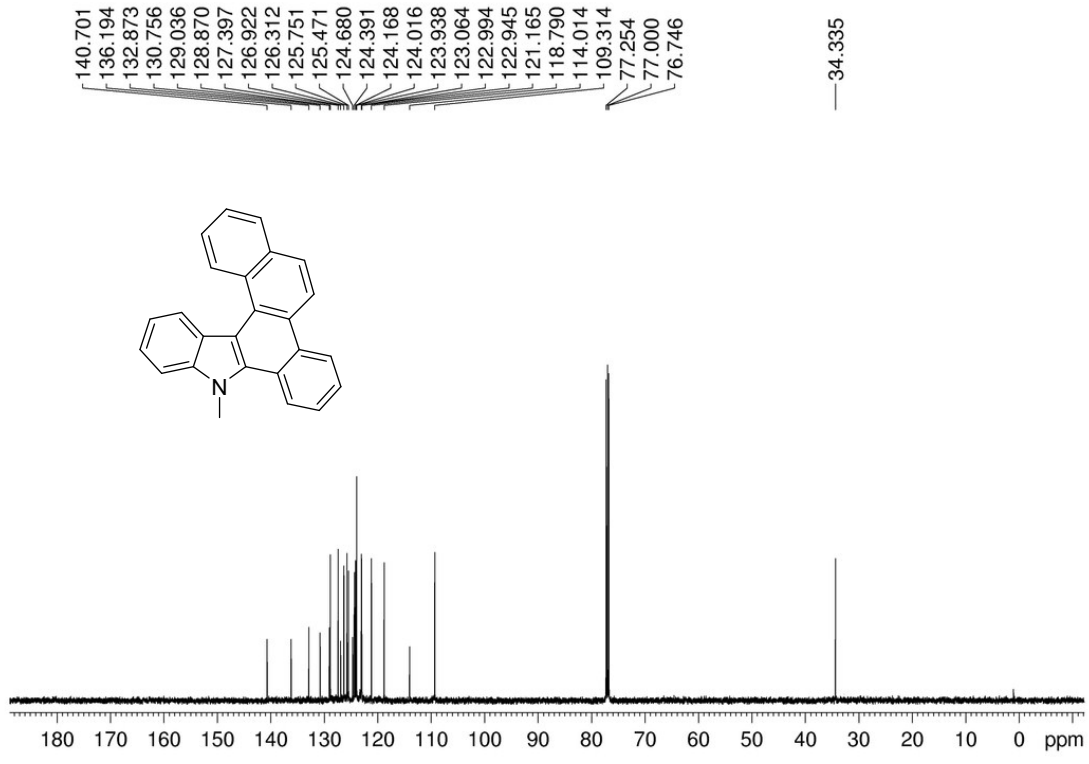
^{1}H and ^{13}C Spectrum of Compound **3an**



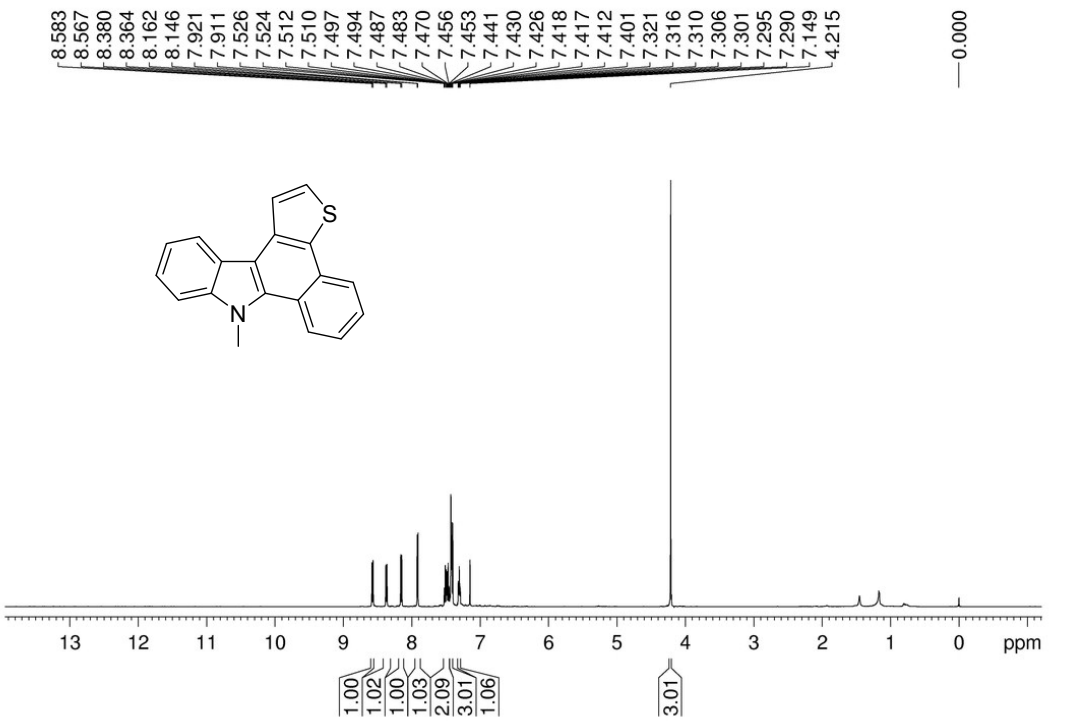


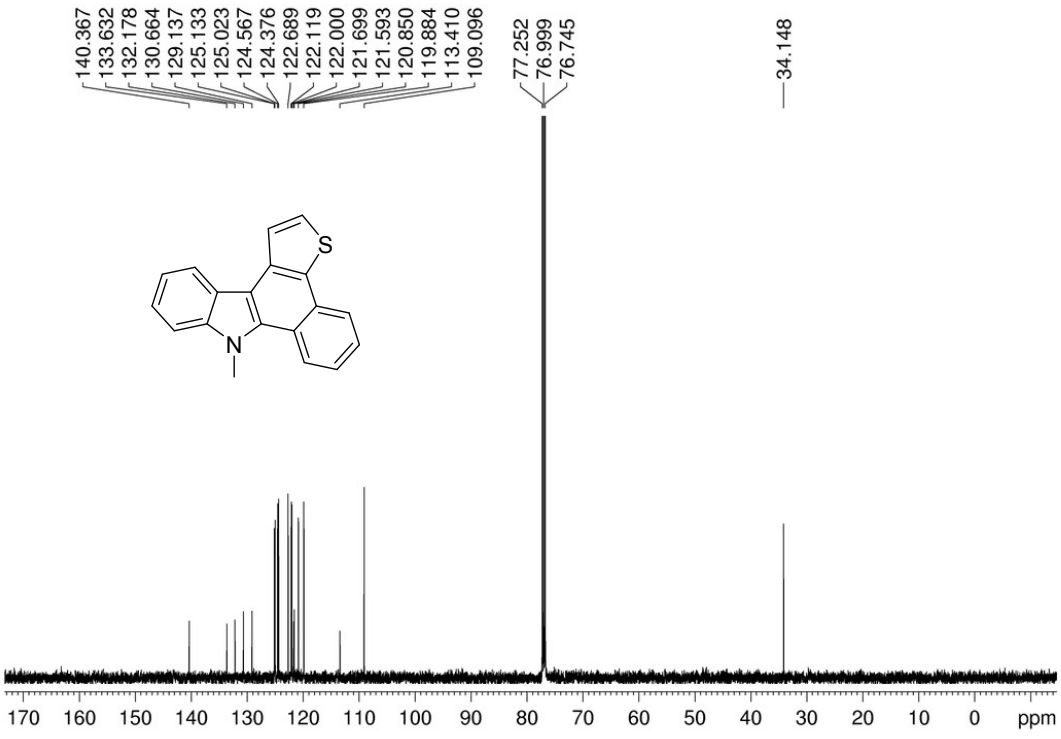
^{1}H and ^{13}C Spectrum of Compound **3ao**





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





6) References

Wu, Y.; Peng, X.; Luo, B.; Wu, F.; Liu, B.; Song, F.; Huang, P.; Wen, S. *Org. Biomol. Chem.* **2014**, *12*, 9777.