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

Supporting Information

Diversity-Oriented Approach to Indolocarbazoles *via* Fischer Indolization and Olefin Metathesis: Total Synthesis of Tjipanazole D and I

Sambasivarao Kotha*, Mohammad Saifuddin and Vikas R. Aswar

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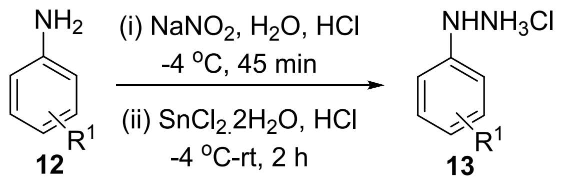
Experimental section

All commercially accessible reagents were used without further purification and the reactions involving air sensitive catalysts or reagents were performed in degassed solvents. The reactions were maintained under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on (7.5×2.5 cm) glass plates coated with Acme's silica gel GF 254 (containing 13% calcium sulfate as a binder) by using a suitable mixture of EtOAc and petroleum ether for development. Column chromatography was performed by using Acme's silica gel (100-200 mesh) with an appropriate mixture of EtOAc and petroleum ether. The coupling constants (*J*) are given in hertz (Hz) and chemical shifts are denoted in parts per million (ppm) downfield from internal standard, tetramethylsilane (TMS). The abbreviations, s, d, t, q, m, and dd refer to singlet, doublet, triplet, quartet, multiplet, and doublet of doublets respectively. Infrared (IR) spectra were recorded on Nicolet Impact-400 FT IR spectrometer. Proton nuclear magnetic resonance (^{1}H NMR, 400 MHz and 500 MHz) spectra and carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz and 125 MHz) spectra were recorded on a Bruker spectrometer. The high-resolution mass measurements were carried out by using electrospray ionization (ESI) spectrometer. Melting points were recorded on a Veego melting point apparatus.

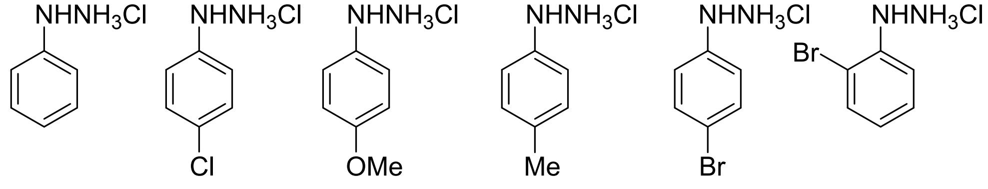
Preparation of Phenylhydrazine hydrochloride derivatives

Modified literature procedure,[1] to a suspension of *p*-methoxyaniline (0.02 mol, 2 g) in water (20 mL) and HCl (7 mL) was cooled at -4 ˚C. Further in the resulting cooled solution was added sodium nitrite (0.02 mol, 1.23 g in 3 mL water) drop wise under stirring at same temperature and stirred for 45 min. Subsequently, solution of $SnCl_2.2H_2O$ (0.03 mol, 7.3 g in 5 mL HCl) was added drop wise. Then, resulting suspension was stirred at -4 ˚C to rt for 2 h. The resulting residue was filtered, washed with diethyl ether (2 × 15 mL), and dried. Crude product was used for further reaction.

Similarly, compounds **13a-f** were prepared by using above procedure and they have been used directly in the following synthetic steps.



R^1 = H, 4-Cl, 4-Br, 4-OMe, 4-Me, 2-Br



13a, 87% **13b**, 85% **13c**, 91% **13d**, 88% **13e**, 86% **13f**, 80%

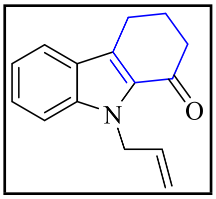
Compounds **16a-g** were prepared according to the literature procedure[2]

Compounds **17a-c** were prepared according to the literature procedure[3]

Compounds **18a** and **18b** were prepared according to the literature procedure[4]

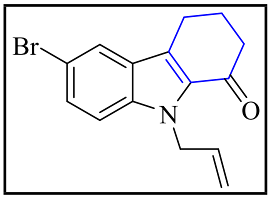
Synthesis of compounds 19a and **19b**

To the solution of **17a** (500 mg, 2.85 mmol) in dry acetone (10 mL), was added NaH (5.71 mmol) at 0 °C under a nitrogen atmosphere. Later, allyl bromide (0.34 mL, 4.28 mmol) was added to the reaction mixture dropwise, and stirring was continued at room temperature for further 2 h. After completion of the reaction (TLC monitoring), the reaction mixture was diluted with EtOAc (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product obtained was purified by silica gel column chromatography (2% EtOAc/petroleum ether) to give compound **19a**.



9-Allyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (**19a**): White liquid; yield 76% (463 mg, starting from 500 mg of **17a**); R_f = 0.65 (silica gel, 10% EtOAc-petroleum ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.40-7.33 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.03-5.95 (m, 1H), 5.22 (d, *J* = 5.0 Hz, 2H), 5.10 (d, *J* = 10.5 Hz, 1H), 4.96 (d, *J* = 17.5 Hz, 1H), 3.02 (t, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.25-2.20 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.9, 139.2, 134.1, 129.8, 129.7, 126.8, 125.0, 121.4, 120.2, 116.1, 110.8, 46.8, 40.0, 24.8, 21.9 ppm; **HRMS** (ESI) calcd for $C_{15}H_{16}NO$ [M + H] 226.1232 found 226.1232. **IR** (neat) 2912, 1714, 1120, 918 cm^{-1}.

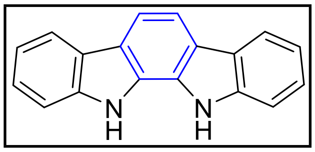


9-Allyl-6-bromo-2,3,4,9-tetrahydro-1H-carbazol-1-one (**19b**): White liquid; yield 79% (455 mg, starting from 500 mg of **17b**); R_f = 0.65 (silica gel, 10% EtOAc-petroleum ether).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.79 (t, J = 0.4 Hz, 1H), 7.43 (dd, J = 2.0, J = 8.8 Hz, 1H), 7.21 (d, J = 9.2 Hz, 1H), 5.99-5.90 (m, 1H), 5.20-5.18 (m, 2H), 5.10-5.07 (m, 1H), 4.92-4.86 (m, 1H), 2.97 (t, J = 6.0 Hz, 2H), 2.66-2.63 (m, 2H), 2.25-2.18 (m, 2H); ^{13}**C NMR** (125 MHz, $CDCl_3$) δ 192.1, 137.8, 133.8, 130.6, 129.7, 128.8, 126.7, 123.9, 116.4, 113.4, 112.5, 47.1, 40.1, 24.7, 21.8 ppm. **HRMS** (ESI) calcd for $C_{15}H_{15}BrNO$ [M + H] 304.0332 found 304.0334. **IR** (neat) 2923, 1722, 1420, 1125, 918 cm^{-1}.

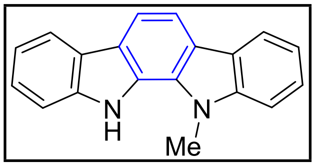
General procedure for the synthesis of 21a-o and **24** ***via*** **FI**

In a typical procedure, 2.0 g of a mixture of *N*,*N'*-dimethylurea/L-(+)-tartaric acid (70:30) was heated to 80 °C to obtain a clear melt. To this clear melt, 1.5 eq of aromatic hydrazine and 1.0 eq of corresponding ketones were added at 80 °C. After completion of the reaction (TLC monitoring by mini work up), the reaction mixture was quenched with water while it was still hot. The reaction mixture was cooled to rt and the solid was filtered through a sintered glass funnel and washed with water (3 × 5 mL). The crude products were dried under vacuum, purified by silica gel column chromatography to give the compounds **21a-o** and **24**.



11,12-Dihydroindolo[2,3-a]carbazole (**21**): Light yellow solid; yield 73% (504 mg, starting from 500 mg of **17a**); Mp> 300 °C; R_f = 0.51(silica gel, 20% EtOAc-petroleum ether)

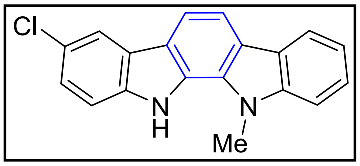
Spectral data matched with reported compound.[5]



11-Methyl-11,12-dihydroindolo[2,3-a]carbazole (**21b**): Light yellow solid; yield 77% (224 mg, starting from 200 mg of **17a**); Mp 230-234 °C; R_f = 0.57(silica gel, 20% EtOAc-petroleum ether).

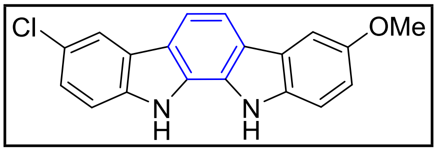
^{1}**H NMR** (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 7.93 (s, 2H), 7.70-7.65 (m, 2H), 7.47-7.40 (m, 2H), 7.24-7.20 (m, 2H), 4.34 (s, 3H); ^{13}**C NMR** (100 MHz, DMSO-d_6) δ 140.2, 139.8, 127.4, 125.3, 124.8, 124.7, 123.3, 123.2, 121.4, 120.0, 119.7, 119.6, 119.1, 119.0, 111.9, 111.8, 111.7, 109.3, 31.7 ppm; **HRMS** (ESI) calcd for $C_{19}H_{15}N_2$[M + H] 271.1235 found 271.1235.**IR** (neat) 3415, 2912, 1410, 925 cm^{-1}.

3-Chloro-11-methyl-11,12-dihydroindolo[2,3-a]carbazole (**21c**): Light yellow solid; yield 69% (191 mg, starting from 200 mg of **17c**); Mp 240-244 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).



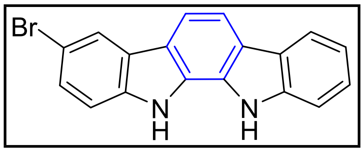
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.74 (s, 1H), 8.24-8.16 (m, 2H), 7.94 (s, 2H), 7.66 (s, 2H), 7.42-7.22 (m, 3H), 4.32 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 140.2, 138.2, 129.1, 127.2, 126.1, 124.9, 124.7, 124.6, 123.5, 123.1, 120.5, 119.8, 119.2, 119.1, 113.1, 112.3, 112.1, 109.4, 31.7 ppm; **HRMS** (ESI) calcd for $C_{19}H_{14}ClN_2$[M + H] 305.0840 found 305.0844. **IR** (neat) 3420, 2928, 1459, 874 cm^{-1}.

3-Chloro-8-methoxy-11,12-dihydroindolo[2,3-a]carbazole (**21d**): Light yellow solid; yield 78% (227 mg, starting from 200 mg of **17c**); Mp> 300 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).



^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1H), 10.93 (s, 1H), 8.21 (d, *J* = 1.6 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 2H), 7.71-7.68 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.4,2.0 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.4Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.5, 137.5, 134.0, 126.6, 126.3, 125.2, 124.3, 124.2, 123.4, 120.8, 119.3, 119.2, 114.3, 113.1, 112.5, 112.3, 111.5, 102.5, 55.7 ppm; **HRMS** (ESI) calcd for $C_{19}H_{14}ClN_2O$ [M + H] 321.0780 found 321.0789. **IR** (neat) 3411, 2938, 1632, 1453, 1028 cm^{-1}.

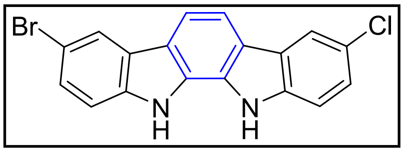
3-Bromo-11,12-dihydroindolo[2,3-a]carbazole (**21e**): Brown solid; yield 63% (160 mg, starting from 200 mg of **17b**); Mp> 300 °C; R_f = 0.49 (silica gel, 20% EtOAc-petroleum ether).



^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 11.13 (s, 1H), 8.37 (d, *J* = 1.6 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 1H), 7.94-7.90 (m, 2H), 7.69-7.65 (m, 2H), 7.51-7.48 (m, 1H), 7.41-7.38 (m, 1H), 7.23-7.18 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 137.8, 126.9, 126.3, 125.8, 125.5, 124.8, 123.7, 122.3, 120.7, 119.9, 119.2, 119.1, 113.6, 112.2, 111.9, 111.7, 111.2 ppm. **IR** (Neat) 3393, 2941, 1639, 1449, 1324, 1149, 1136, 912 cm^{-1};

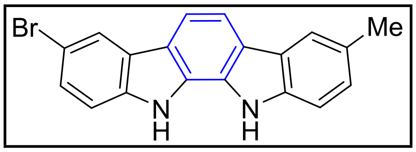
HRMS matched with reported compound.[6]

3-Bromo-8-chloro-11,12-dihydroindolo[2,3-a]carbazole (**21f**): Yellow solid; yield 46% (128 mg, starting from 200 mg



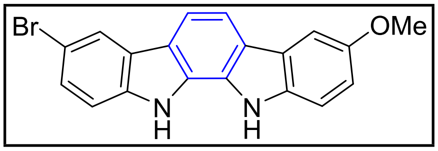
of **17b**); Mp> 300 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.59 (s, 1H), 11.59 (s, 1H), 8.40 (s, 1H), 8.26 (s, 1H), 7.97 (s, 2H), 7.74-7.68 (m, 2H),7.54-7.41 (m, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 137.8, 137.5, 127.1, 126.3, 126.2, 125.7, 125.0, 124.6, 123.5, 122.4, 119.9, 119.7, 119.4, 113.7, 113.2, 112.4, 112.3, 111.3 ppm; **HRMS** (ESI) calcd for $C_{18}H_{11}BrClN_2$ [M + H] 368.9789 found 368.9789. **IR** (neat) 3432, 2922, 1460, 1114 cm^{-1}.



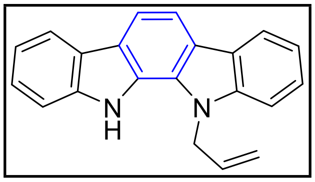
3-Bromo-8-methyl-11,12-dihydroindolo[2,3-a]carbazole (**21g**): Light yellow solid; yield 61% (161 mg, starting from 200 mg of **17b**); Mp> 300 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.21 (s, 1H), 10.97 (s, 1H), 8.35 (d, J = 2.0 Hz, 1H), 7.93-7.85 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.49-7.47 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 137.7, 137.4, 127.8, 126.8, 126.3, 126.2, 125.8, 125.7, 123.8, 122.2, 120.5, 119.6, 119.1, 113.5, 112.1, 111.7, 111.4, 111.1, 21.2 ppm; **HRMS** (ESI) calcd for $C_{19}H_{14}BrN_2$ [M + H] 349.0335 found 349.0336. **IR** (neat) 3402, 2930. 1640, 1093 cm^{-1}.



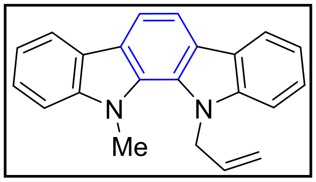
3-Bromo-8-methoxy-11,12-dihydroindolo[2,3-a]carbazole (**21h**): tan solid; yield 77% (213 mg, starting from 200 mg of **17b**); Mp> 300 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1H), 10.91 (s, 1H), 8.35 (d, J = 2.0 Hz, 1H), 7.89 (d, J = 0.8 Hz, 2H), 7.70 (d, J = 2.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H),7.48 (dd, J = 8.8, 2.0Hz, 1H), 7.03 (dd, J = 8.8,2.4Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.5, 137.7, 134.0, 126.8, 126.4, 126.2, 125.9, 124.2, 122.2, 120.8, 119.0, 114.3, 113.6, 112.5, 112.4, 111.5, 111.1, 102.5, 55.7 ppm; **HRMS** (ESI) calcd for $C_{19}H_{14}N_2BrO$ [M + H] 365.0293 found 365.0284. **IR** (neat) 3410, 2934, 1647, 1462, 1028 cm^{-1}.



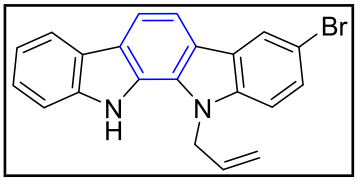
11-Allyl-11,12-dihydroindolo[2,3-a]carbazole (**21i**): White solid; yield = 53% (140 mg, starting from 200 mg of **19a**); Mp 236-238 °C; R_f = 0.45 (silica gel, 10% EtOAc-petroleum ether).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.35 (s, 1H), 8.19-8.15 (m 2H), 8.01-7.95 (m, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.49-7.42 (m, 3H), 7.32-7.29 (m, 2H), 6.40-6.34 (m, 1H), 5.36-5.34 (m, 1H), 5.24-5.21 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.4, 139.6, 134.5, 127.4, 125.5, 125.2, 125.1, 124.6, 124.3, 122.6, 122.5, 120.3, 120.2, 120.1, 119.7, 117.5, 112.8, 112.4, 111.2, 108.7, 47.1 ppm; **HRMS** (ESI) calcd for $C_{21}H_{17}N_2$ [M + H] 297.1387 found 297.1386. **IR** (neat) 3402, 2924, 1642, 1027 cm^{-1}.



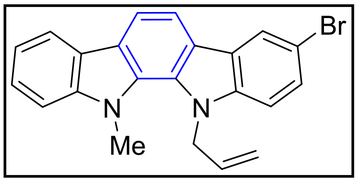
11-Allyl-12-methyl-11,12-dihydroindolo[2,3-a]carbazole (21j): White solid; yield 70% (192 mg, starting from 200 mg of **19a**); Mp 178-182 °C; R_f = 0.43(silica gel, 10% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 3.6 Hz, 2H), 8.01 (s, 2H), 7.50-7.38 (m, 6H), 6.24-6.18 (m, 1H), 5.49-5.45 (m, 2H), 5.04 (s, 2H), 4.03 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 133.9 (2C), 129.7, 125.6 (2C), 125.4, 124.9, 123.9, 123.7, 120.4, 120.0, 119.8 (2C), 117.4, 113.0, 112.7, 113.3, 110.1, 51.2, 36.0 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_2$ [M + H] 311.1549 found 311.1543. **IR** (neat) 2921, 1444, 1194, 930 cm^{-1}.



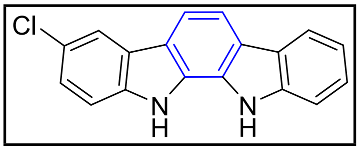
12-Allyl-3-bromo-11,12-dihydroindolo[2,3-a]carbazole (21k): Light yellow solid; yield 60% (148 mg, starting from 200 mg of **19b**); Mp 234-238 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.42 (s, 1H), 8.41 (s, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.00-7.95 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 1H), 6.14-6.06 (m, 1H), 5.46 (s, 2H), 5.01 (d, *J* = 10.2 Hz, 1H), 4.70 (d, *J* = 17.1 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 140.1, 138.8, 135.0, 134.6, 127.6, 127.5, 125.9, 125.4, 125.1, 123.4, 122.7, 122.4, 120.1, 119.6, 119.1, 116.0, 112.9, 112.5, 112.1, 111.9, 46.7 ppm; **HRMS** (ESI) calcd for $C_{21}H_{16}BrN_2$ [M + H] 375.0496 found 375.0491.**IR** (neat) 3410, 3019, 1620, 1068 cm^{-1}.



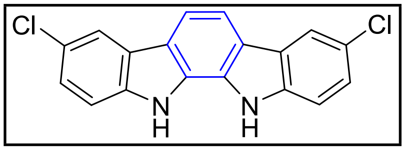
12-Allyl-3-bromo-11-methyl-11,12-dihydroindolo[2,3-a]carbazole (21l): Light yellow solid; yield 67% (171 mg, starting from 200 mg of **19b**); Mp 182-184 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.41 (d, *J* = 1.6 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 8.03-7.98 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54-7.52 (m, 1H), 7.48-7.43 (m, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.22-6.13 (m, 1H), 5.27-5.04 (m, 4H), 4.06 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 142.7, 141.0, 134.3, 129.1, 128.6, 127.7, 126.5, 125.7, 123.7, 123.4, 122.2, 121.9, 119.8, 119.7, 116.4, 113.3, 113.2, 112.9, 112.4, 110.6, 50.4, 35.5 ppm; **HRMS** (ESI) calcd for $C_{22}H_{18}BrN_2$ [M + H] 389.0648 found 389.0643. **IR** (neat) 2928, 1610, 1430, 1034 cm^{-1}.



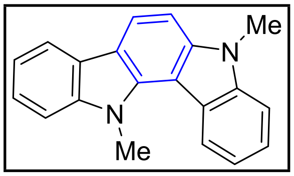
3-Chloro-11,12-dihydroindolo[2,3-a]carbazole (**21n**): Light brown solid; yield 75% (198 mg, starting from 200 mg of **17c**); Mp > 300 °C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (s, 1H), 11.18 (s, 1H), 8.27 (d, *J* = 1.9 Hz, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.98-7.94 (m, 2H), 7.73 (t, *J* = 8.3 Hz, 2H), 7.45-7.41 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.1, 137.5, 126.6, 125.5, 125.2, 124.9, 124.4, 123.7, 123.4, 120.7, 119.9, 119.4, 119.3, 119.2, 113.1, 112.2, 111.9, 111.7 ppm; **HRMS** (ESI) calcd for $C_{18}H_{12}ClN_2$[M + H] 291.0687 found 291.0684. **IR** (neat) 3400, 2913, 1641, 1096 cm^{-1}.



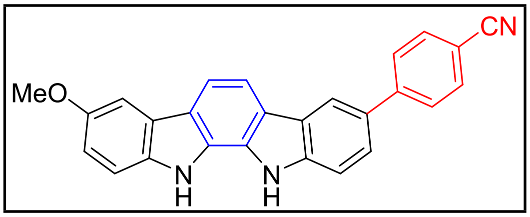
3,8-Dichloro-11,12-dihydroindolo[2,3-a]carbazole (**21o**): tan solid; yield 72% (213 mg, starting from 200 mg of **17c**); Mp> 300°C; R_f = 0.57 (silica gel, 20% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.30 (s, 2H), 8.24 (s, 2H),7.95 (s, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.0 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 137.6, 126.4, 125.1, 124.6, 123.6, 119.9, 119.4, 113.3, 112.4 ppm; **HRMS** (ESI) calcd for $C_{18}H_{11}Cl_2N_2$[M + H] 325.0294 found 325.0296. **IR** (neat) 3402, 2923, 1452, 1034 cm^{-1}.



5,12-Dimethyl-5,12-dihydroindolo[3,2-a]carbazole (**24**): White solid; yield 51% (72 mg, starting from 100 mg of **18b**); Mp 124-126 °C; R_f = 0.62 (silica gel, 10% EtOAc-petroleum ether).

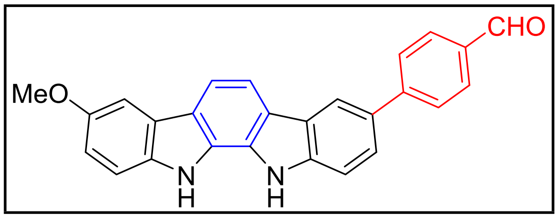
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.50-7.46 (m, 4H), 7.32-7.27 (m, 3H), 4.50 (s, 3H), 3.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 141.1, 140.4, 137.8, 124.4, 124.3, 124.0, 122.8, 121.2, 119.5, 119.1, 118.9, 118.7, 116.3, 109.0, 108.9, 107.2, 101.7, 34.9, 29.7 ppm; **HRMS** (ESI) calcd for $C_{20}H_{17}N_2$ [M + H] 285.1384 found 285.1386. **IR** (neat) 2918, 1645, 1250, 1038 cm^{-1}.



4-(8-Methoxy-11,12-dihydroindolo[2,3-a]carbazol-3-yl)benzonitrile (**26a**): tan solid; yield 75% (159 mg, starting from 200 mg of **21h**); Mp> 300 °C; R_f = 0.51 (silica gel, 20% EtOAc-petroleum ether).

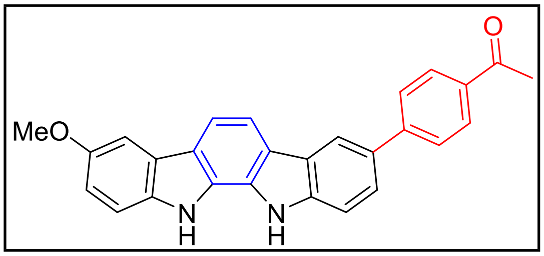
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.28 (s, 1H), 10.92 (s, 1H), 8.58 (s, 1H), 8.01-7.97 (m, 3H), 7.93-7.88 (m, 3H), 7.76-7.71 (m, 3H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.05-7.03 (m, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.5, 146.1, 139.4, 134.1, 132.9, 129.3, 127.4, 126.5, 126.4, 124.8, 124.3, 123.8, 120.8, 120.2, 119.4, 118.6, 114.2, 112.5, 112.4, 112.3, 111.6, 108.8, 102.5, 55.5 ppm; **HRMS** (ESI) calcd for $C_{26}H_{18}N_3O$ [M + H] 388.1444 found 388.1444. **IR** (neat) 3402, 2923, 1639, 1454, 992 cm^{-1}.

4-(8-Methoxy-11,12-dihydroindolo[2,3-a]carbazol-3-yl)benzaldehyde (**26b**): Yellow solid; yield 67% (143 mg, starting from 200 mg of **21h**); Mp> 300 °C; R_f = 0.52 (silica gel, 20% EtOAc-petroleum ether).

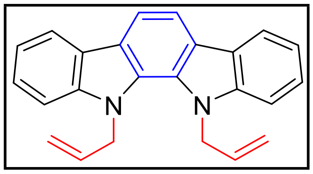


^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 10.89 (s, 1H), 10.04 (s, 1H), 8.61 (s, 1H), 8.06-7.98 (m, 5H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.82-7.76 (m, 2H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.8,2.4 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 192.7, 153.5, 147.3, 139.3, 134.2, 134.0, 130.3, 129.7, 127.1, 126.4, 126.3, 124.7, 124.2, 123.9, 120.7, 120.2, 118.6, 114.1, 112.4, 112.3, 112.2, 111.5, 102.5, 55.7 ppm; **HRMS** (ESI) calcd for $C_{26}H_{19}N_2O_2$ [M + H] 391.1443 found 391.1441. **IR** (neat) 3392, 2925, 2851, 1732, 1461, 1028 cm^{-1}.

1-(4-(8-methoxy-11,12-dihydroindolo[2,3-a]carbazol-3-yl)phenyl)ethan-1-one (**26c**): Light yellow solid; yield 69% (153 mg, starting from 200 mg of **21h**); Mp> 300 °C; R_f = 0.52 (silica gel, 20% EtOAc-petroleum ether).



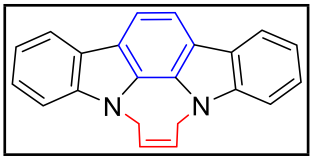
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23 (s, 1H), 10.89 (s, 1H), 8.58 (s, 1H), 8.07-7.91 (m, 6H), 7.78 (d, *J* = 3.2 Hz, 2H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.87 (s, 3H), 2.62 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 197.7, 153.5, 146.0, 139.2, 134.7, 134.0, 129.9, 129.1, 126.7, 126.4, 126.3, 124.7, 124.3, 123.8, 120.7, 120.2, 118.4, 114.1, 112.4, 112.3, 112.2, 111.6, 102.5, 55.7, 26.8 ppm; **HRMS** (ESI) calcd for $C_{27}H_{21}N_2O_2$ [M + H] 405.1592 found 405.1598. **IR** (neat) 3335, 2926, 1733, 1445, 1028 cm^{-1}.



11,12-Diallyl-11,12-dihydroindolo[2,3-a]carbazole (**27**): To the suspension of NaH (2.0 mmol) in THF was added compound **21i** and stirred for 20 min at room temperature then allyl bromide (1.0 mmol) was added to the suspension at 0 °C. Futher, reaction mixture was stirred for 1h at 0 °C to rt. After copletion of reaction (TLC monitoring), reaction mixture was quenched with sat. NH_4Cl and extacted by EtOAc, dried over Na2SO4 and purfied by silica gel as a column chromatoghraphy afford **27** as a colurless liquid; yield 88% (198 mg, starting from 200 mg of **21i**); R_f = 0.40 (silica gel, 10% EtOAc-petroleum ether).

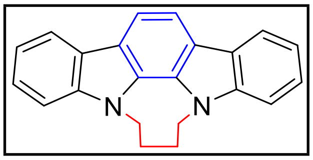
Alternatively, Using above procedure, yield 84% (220 mg, starting from 200 mg of **21a**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, J= 7.5, 0.5 Hz, 2H), 8.00 (s, 2H), 7.48 (d, J = 4.0 Hz, 4H), 7.37-7.33 (m, 2H), 6.25-6.18 (m, 2H), 4.99-4.98 (m, 4H), 5.51-5.45 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.7, 133.6, 129.7, 125.5, 124.1 (2C), 120.4, 119.8, 117.0, 113.0, 111.3, 50.3 ppm; **HRMS** (ESI) calcd for $C_{24}H_{21}N_2$ [M + H] 337.1699 found 337.1696. **IR** (neat) 2924, 1625, 1440, 1038 cm^{-1}.



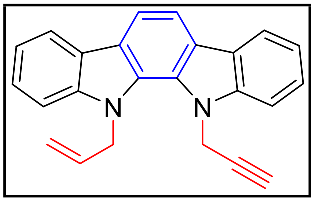
(Z)-11,14-Dihydro-10b,14a-diazadibenzo[b,h]cycloocta[jkl]-as-indacene (**28**): To a stirred solution of **31** (50 mg, 0.59 mmol) in dry toluene (20 mL) degassed with nitrogen for 15 min was added G-II (5mol%) catalyst and the reaction mixture was stirred at refluxing condition for 12 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude products was purified by column chromatography (100–200 silica gel) using appropriate mixtures of EtOAc-petroleum ether as eluent to afford the RCM product **28**.White solid; yield 76% (35 mg, starting from 50 mg of **27**); Mp 160-162 °C; R_f = 0.37 (silica gel, 10% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 2H), 8.03 (s, 2H), 7.54-7.46 (m, 4H), 7.30-7.26 (m, 2H), 6.43-6.41 (m, 2H), 5.14 (t, J = 5.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.6, 132.0, 126.6, 125.0, 123.9, 122.7, 120.0, 119.3, 112.2, 108.5, 39.5 ppm; **HRMS** (ESI) calcd for $C_{22}H_{17}N_2$ [M + H] 309.1386 found 309.1381. **IR** (neat) 2932, 1623, 1438, 1027 cm^{-1}.



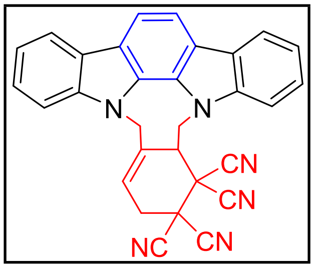
11,12,13,14-Tetrahydro-10b,14a-diazadibenzo[b,h]cycloocta[jkl]-as-indacene (**29**): To a stirred solution of **32** (40 mg, 0.59 mmol) in dry EtOAc (10 mL) degassed with nitrogen for 15 min was added 10% Pd/C (23 mg, 0.59 mmol) under the H_2 atmosphere (1 atm) and the reaction mixture was stirred at room temperature for 24 h. At the conclusion of the reaction (TLC monitoring), the reaction mixture was filtered through celite-pad and washed with EtOAc (10 mL). Evaporation of the solvent in vacuo gave the crude product. Further purification by silica gel column chromatography (100–200 silica gel) using appropriate mixtures of EtOAc-petroleum ether as an eluent afforded the hydrogenated product **33**.White solid; yield 70% (28 mg, starting from 40 mg of **28**); Mp 160-162 ^{o}C; R_f = 0.52 (silica gel, 10% EtOAc-petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19-8.17 (m, 2H), 8.00 (s, 2H),7.51-7.47 (m, 4H), 7.31-7.28 (m, 2H), 4.58 (s, 4H), 2.22 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.4, 127.6, 125.1, 124.2, 122.5, 120.0, 119.5, 112.2, 109.1, 43.7, 26.4 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_2$ [M + H] 311.1540 found 311.1543. **IR** (neat) 2912, 1624, 1038 cm^{-1}.



11-Allyl-12-(prop-2-yn-1-yl)-11,12-dihydroindolo[2,3-a]carbazole (**30**):To a suspension of sodium hydride (2.0 mmol) in dry THF (5 mL), was added the compounds **21i** and the reaction mixture was stirred at room temperature for 10 min. Later, propargyl bromide (1.0 mmol) was added and the stirring was continued for 2 h at the same temperature. At the conclusion of the reaction (TLC monitoring), the reaction mixture was quenched with saturated aq. NH_4Cl (5 mL) solution. Aqueous layer was then extracted with EtOAc and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using appropriate mixtures of EtOAc-petroleum ether to afford the desired compound **30**. White liquid; yield 88% (198 mg, starting from 200 mg of **21i**); R_f = 0.52 (silica gel, 10% EtOAc-petroleum ether).

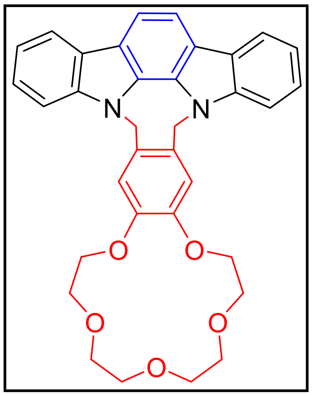
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 8.00-7.93 (m, 2H), 7.75 (d, J = 8.1 Hz, 1H), 7.55-7.46 (m, 3H), 7.38-7.32 (m, 2H), 6.45-6.36 (m, 1H), 5.56-5.47 (m, 2H), 5.18-5.16 (m, 2H), 5.05 (d, J = 2.4 Hz, 2H), 2.54 (t, J = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 143.6, 133.6, 129.5, 128.6, 125.8, 125.7, 125.4, 124.3, 124.1, 120.9, 120.5, 120.0, 119.9, 117.0, 113.5, 113.0, 111.3, 110.9, 79.3, 73.9, 73.9, 50.5, 38.6 ppm; **HRMS** (ESI) calcd for $C_{24}H_{18}N_2Na$ [M + Na] 357.1362 found 357.1367. **IR** (neat) 3326, 2915, 2126, 1624, 1039 cm^{-1}.



(R)-11,11a,14,16-Tetrahydro-10b,16a-diazadibenzo[b,h]benzo[6,7]cycloocta[1,2,3,4-jkl]-as-indacene-12,12,13,13-tetracarbonitrile (**32**):The solution of enyne **34** (0.14 mmol) in CH_2Cl_2 (20 mL) was degassed with nitrogen for 10 min. After that, G-II (10 mol %) and titanium isopropoxide (20 mol %)

was added and the reaction vessel was kept under ethylene atmosphere. The reaction mixture was stirred at rt for 16 h. After completion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and without isolating the intermediate, it was subjected for the Diels-Alder reaction using tetracyanoethylene (0.14 mmol) in dry toluene (20 mL) under N_2 atmosphere at refluxing condition for 24 h. At the conclusion of the reaction (TLC monitoring), the solvent was removed under reduced pressure and the crude products was purified by column chromatography (100–200 silica gel) using appropriate mixtures of EtOAc-petroleum ether as eluent to afford the DA product **32**.White solid; yield 72% (99 mg, starting from 100 mg of **30**); Mp 184-186 °C; R_f = 0.49 (silica gel, 50% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29-8.25 (m, 2H), 8.14-8.09 (m, 2H), 7.96 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.36-7.30 (m, 2H), 6.02 (s, 1H), 5.62 (d, J = 14.8 Hz, 1H), 5.50-5.44 (m, 2H), 5.14 (d, J = 14.4 Hz, 1H), 4.41 (s, 1H), 3.74-3.69 (m, 1H), 2.87 (d, J = 19.6 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 141.0, 140.1, 130.1, 126.3, 126.0, 125.5, 125.4, 124.8, 123.7, 122.6, 122.3, 120.0, 119.6, 119.5, 112.8, 112.3, 112.1, 112.0, 111.1, 109.6, 109.0, 108.3, 44.3, 43.0, 42.6, 41.6, 31.1 ppm; **HRMS** (ESI) calcd for $C_{30}H_{18}N_6Na$ [M + Na] 485.1485 found 485.1482. **IR** (neat) 3018, 1438, 1215, 1044, 912 cm^{-1}.



11,14,15,17,18,20,21,23,24,27-Decahydro-13,16,19,22,25-pentaoxa-10b,27a-diazadibenzo[b,h]cyclopentadeca[4',5']benzo[1',2':6,7]cycloocta[1,2,3,4-jkl]-as-indacene (**34**): To a suspension of sodium hydride (0.58 mmol) in dry DMF (5 mL), was added the compound **21a** and the reaction mixture was stirred at room temperature for 10 min. Later, compound **33** (0.21 mmol) was added and the stirring was continued for 12 h at the same temperature. After completion of the reaction (TLC monitoring), the reaction mixture was quenched with saturated aq. NH_4Cl (5 mL) solution. Aqueous layer was then extracted with EtOAc and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using appropriate mixtures of EtOAc-petroleum ether to afford the desired compound **34**. Yellow solid; yield 90% (96 mg, starting from 50 mg of **21a**); Mp 196-200°C; R_f = 0.51(silica gel, 50% EtOAc-petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 2H), 7.96 (s, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.53-7.49 (m, 2H), 7.30-7.25 (m, 2H), 6.80 (s, 2H), 5.41 (s, 4H), 3.95-3.93 (m, 4H), 3.75-3.73 (m, 4H), 3.63 (s, 8H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.7, 139.5, 129.2, 126.1, 125.0, 123.8, 122.5, 120.0, 119.3, 115.3, 112.0, 108.4, 71.1, 70.5, 69.5, 69.2, 45.8 ppm; **HRMS** (ESI) calcd for $C_{34}H_{32}N_2NaO_5$ [M + Na] 571.2203 found 571.2207. **IR** (neat) 2924, 1625, 1139, 1024 cm^{-1}.

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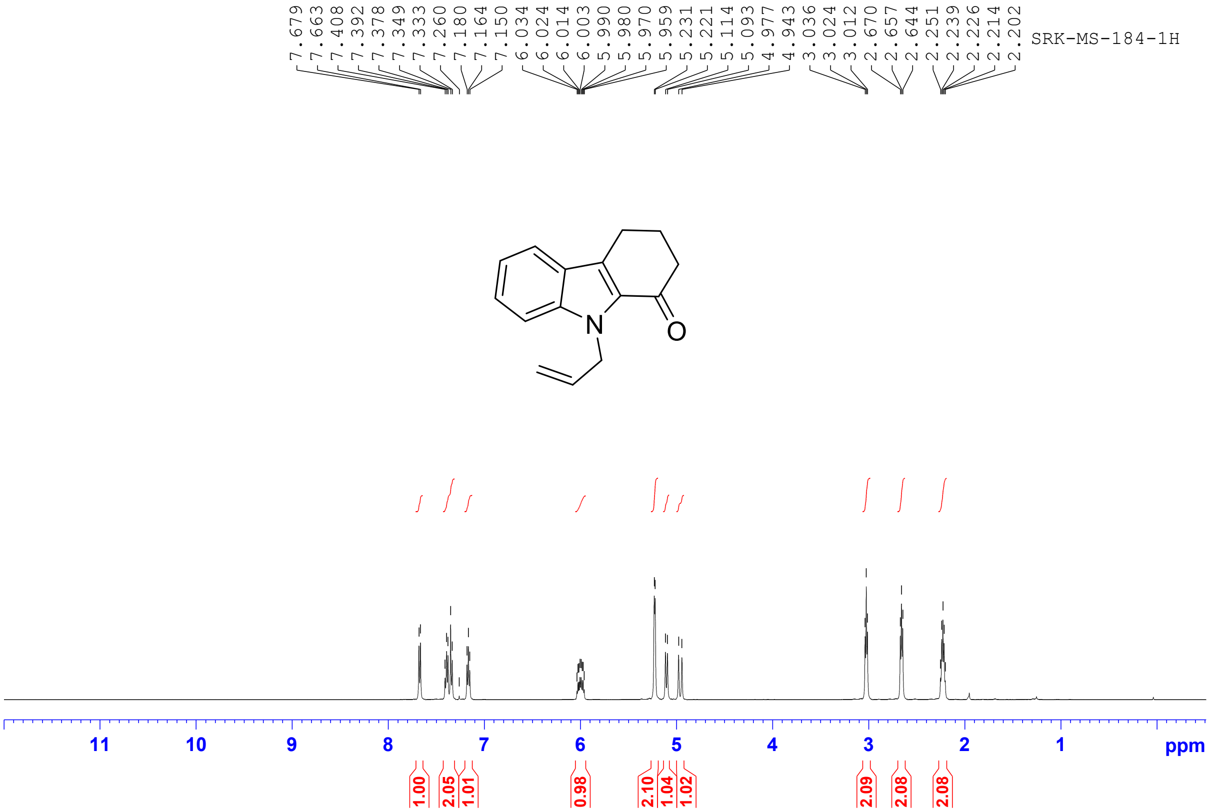
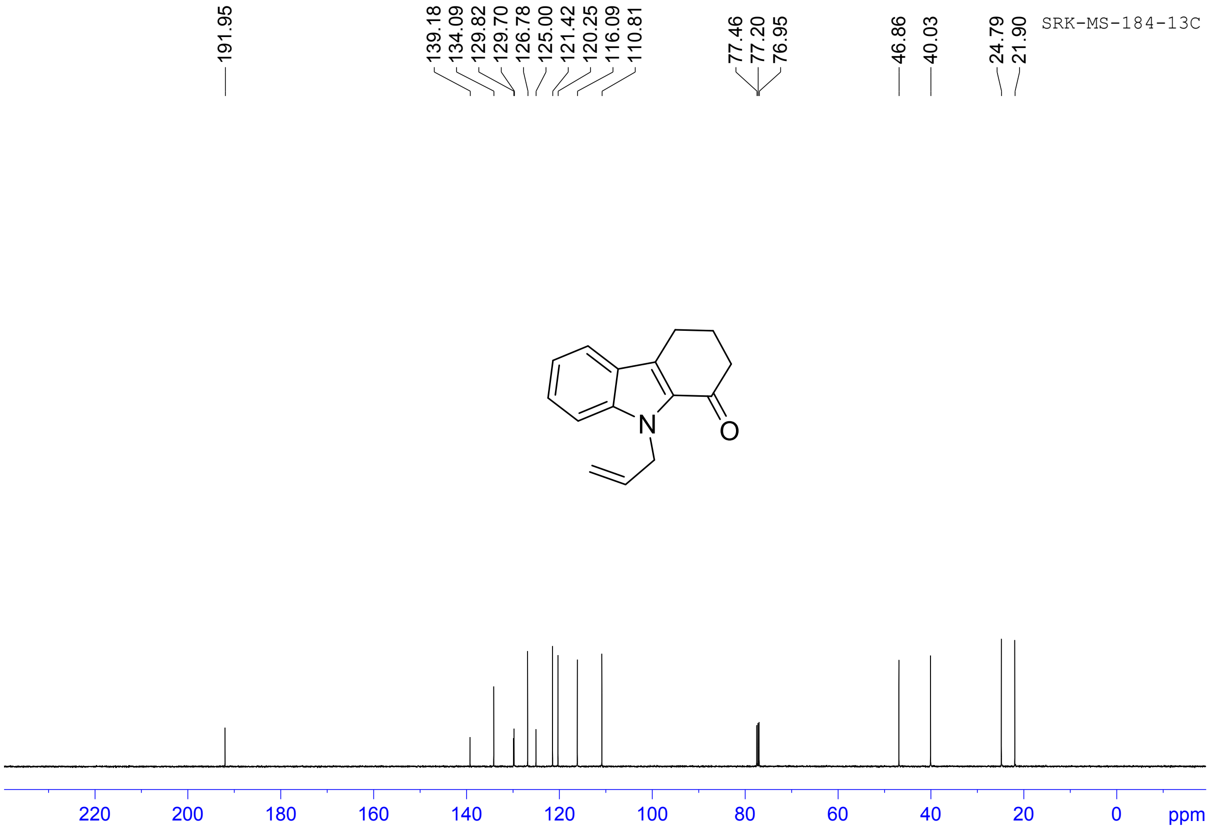
^{1}H and ^{13}C NMR of compound 19a





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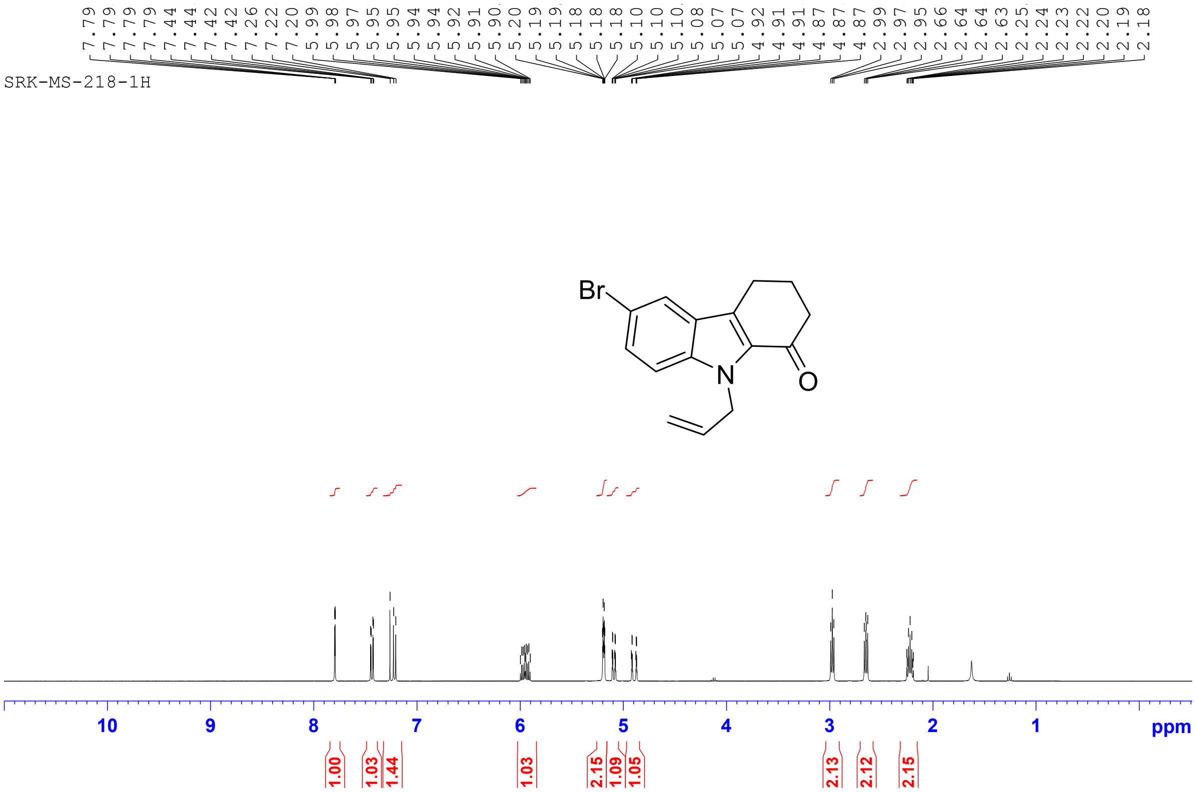
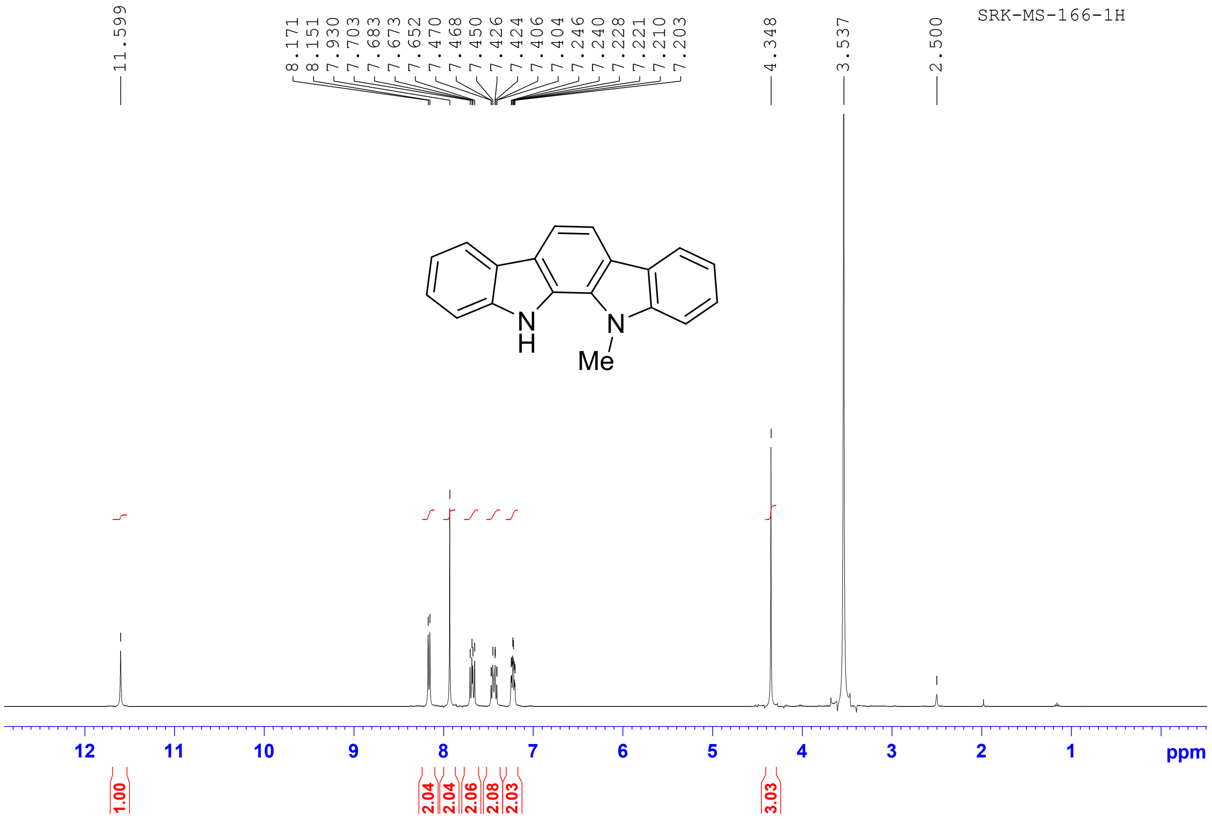
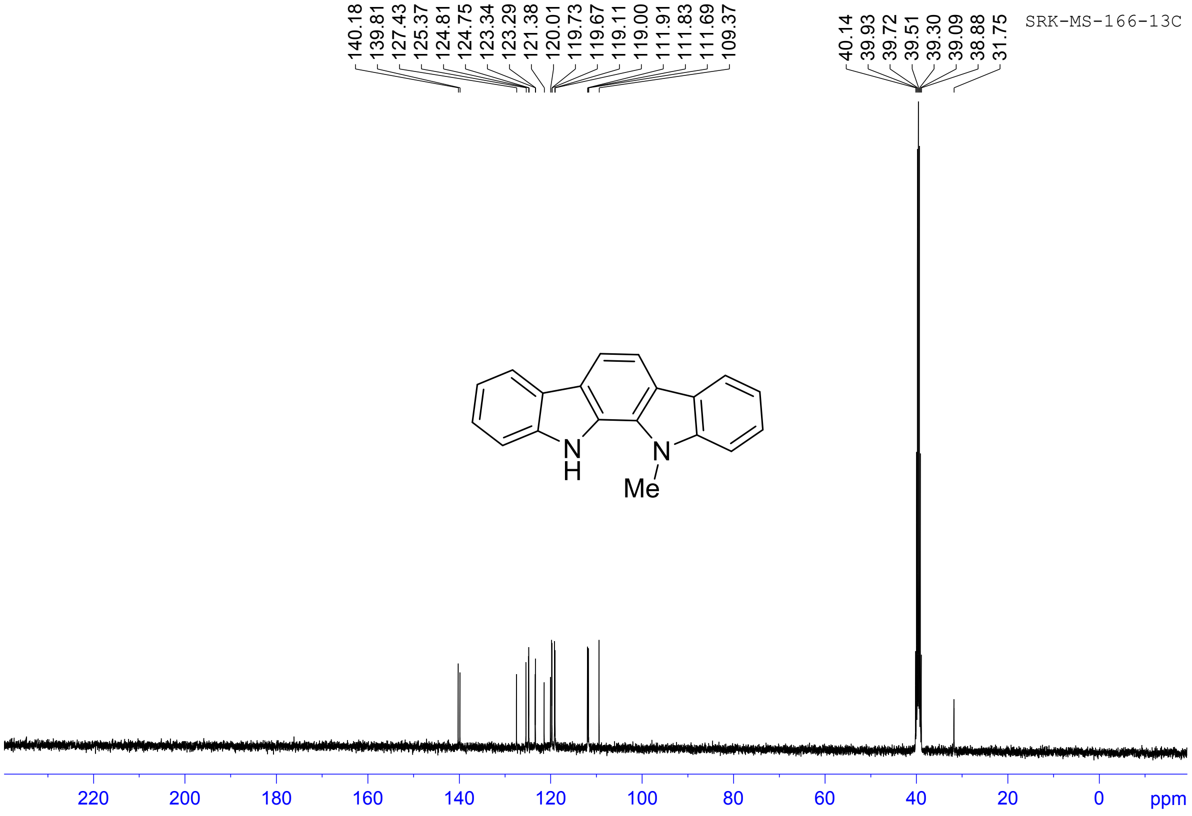
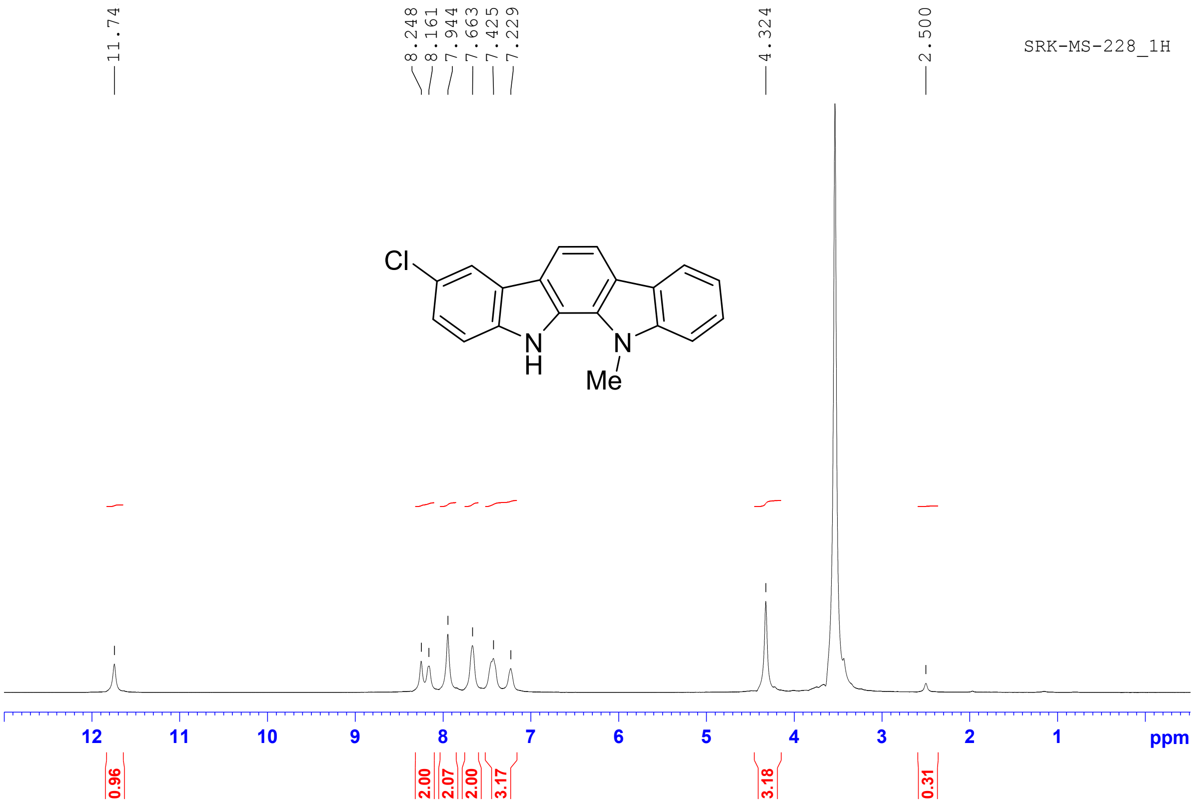


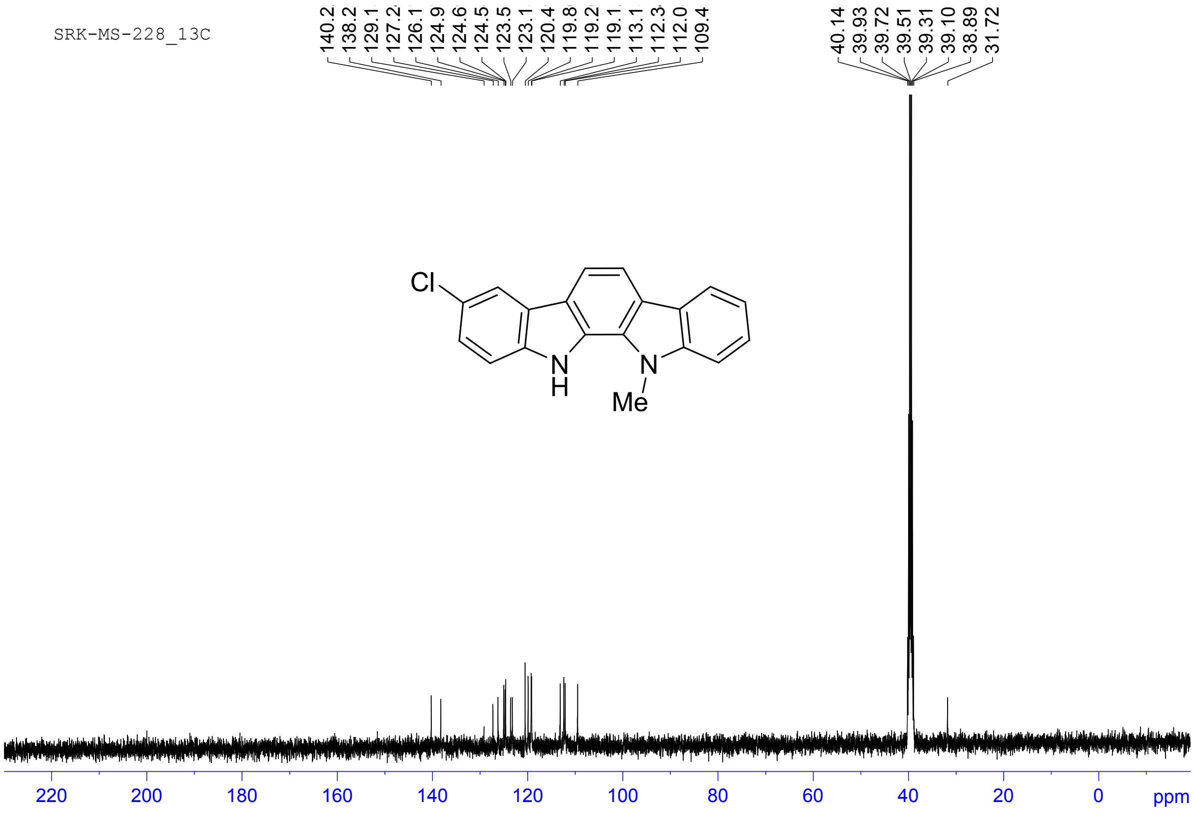
^{1}H and ^{13}C NMR of compound 21b



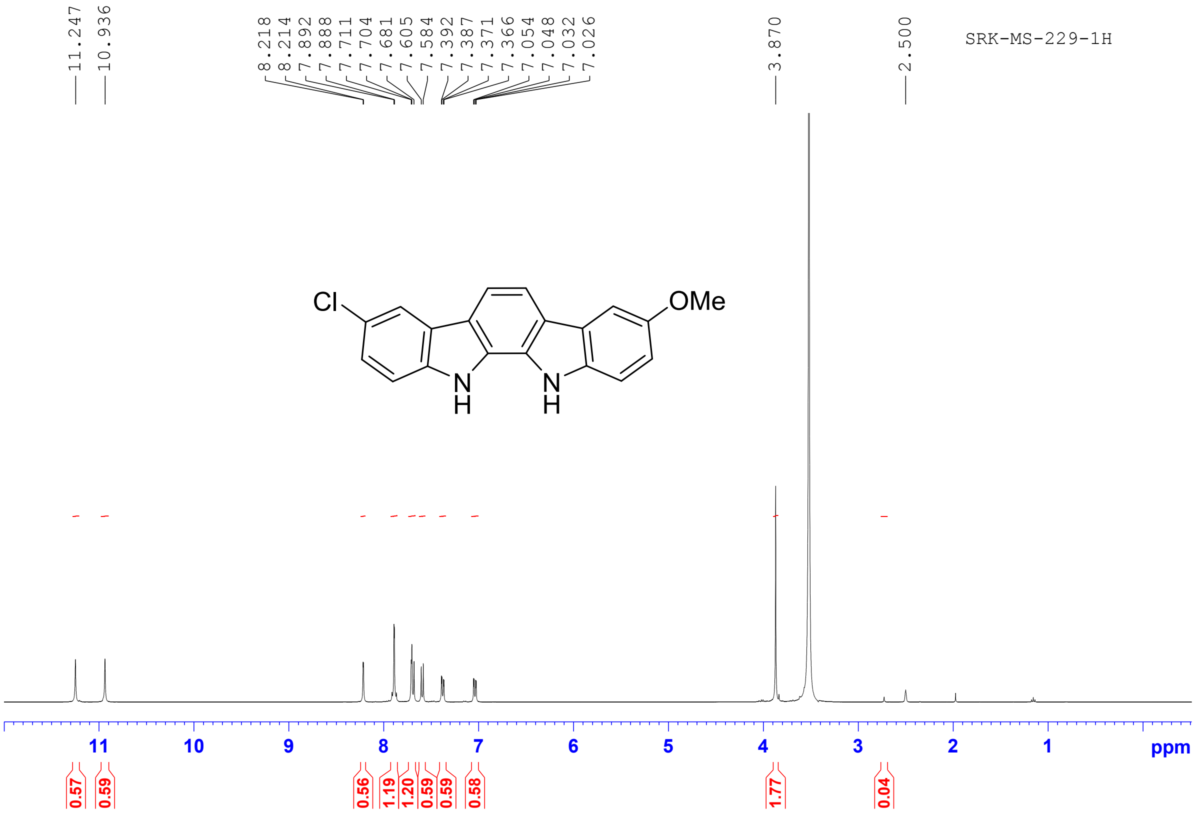


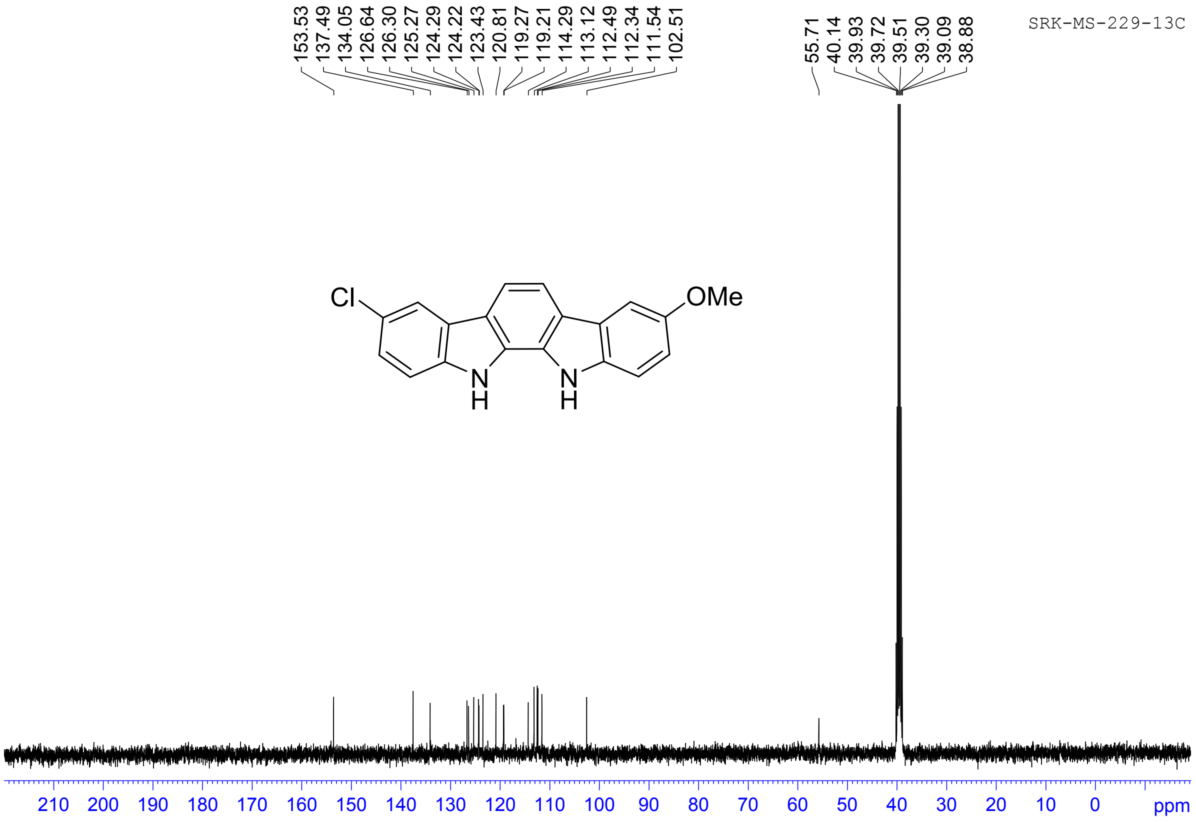
^{1}H and ^{13}C NMR of compound 21c



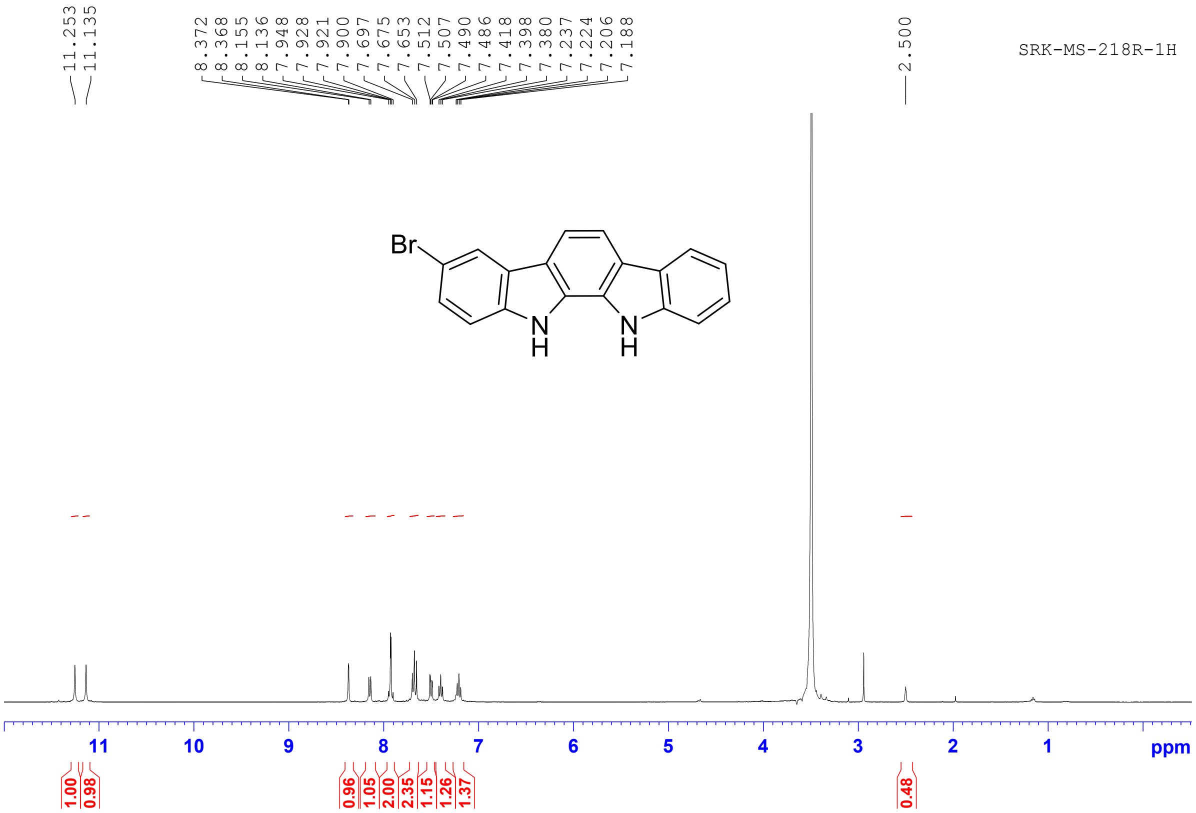


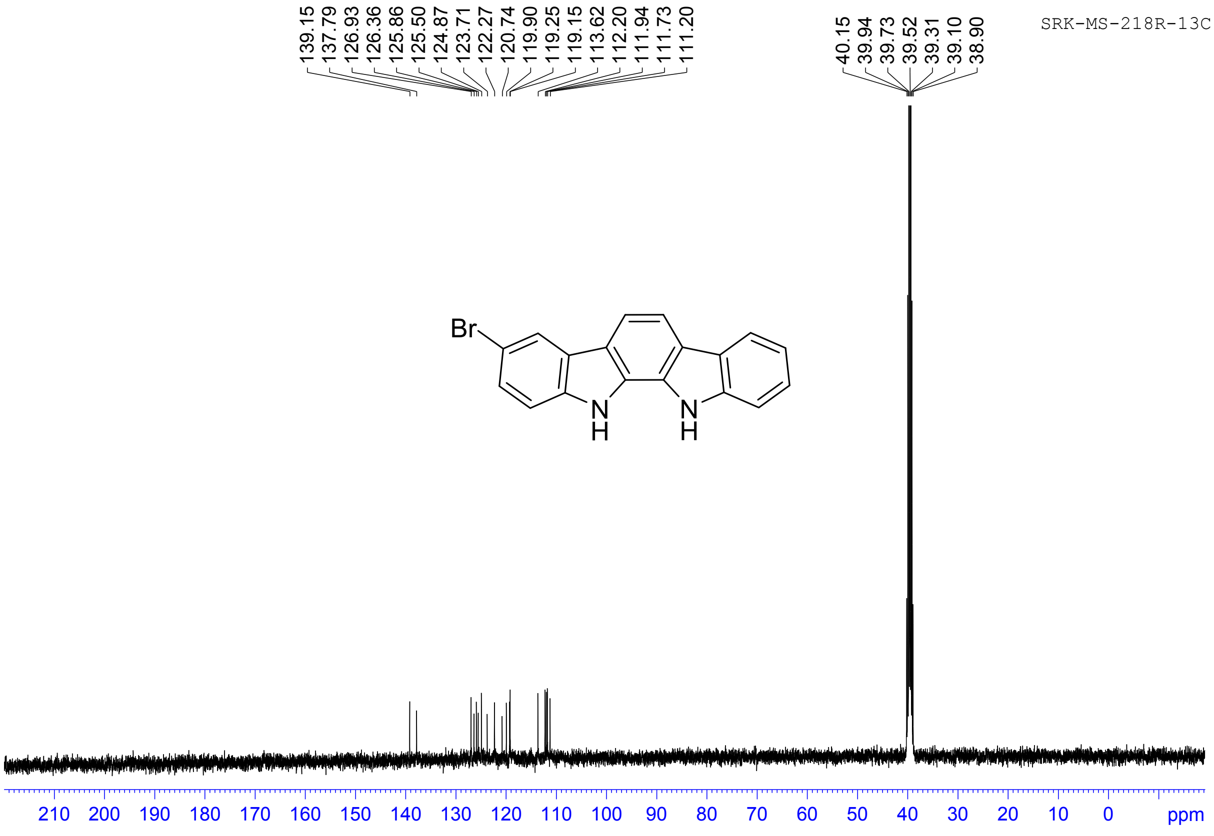
^{1}H and ^{13}C NMR of compound 21d



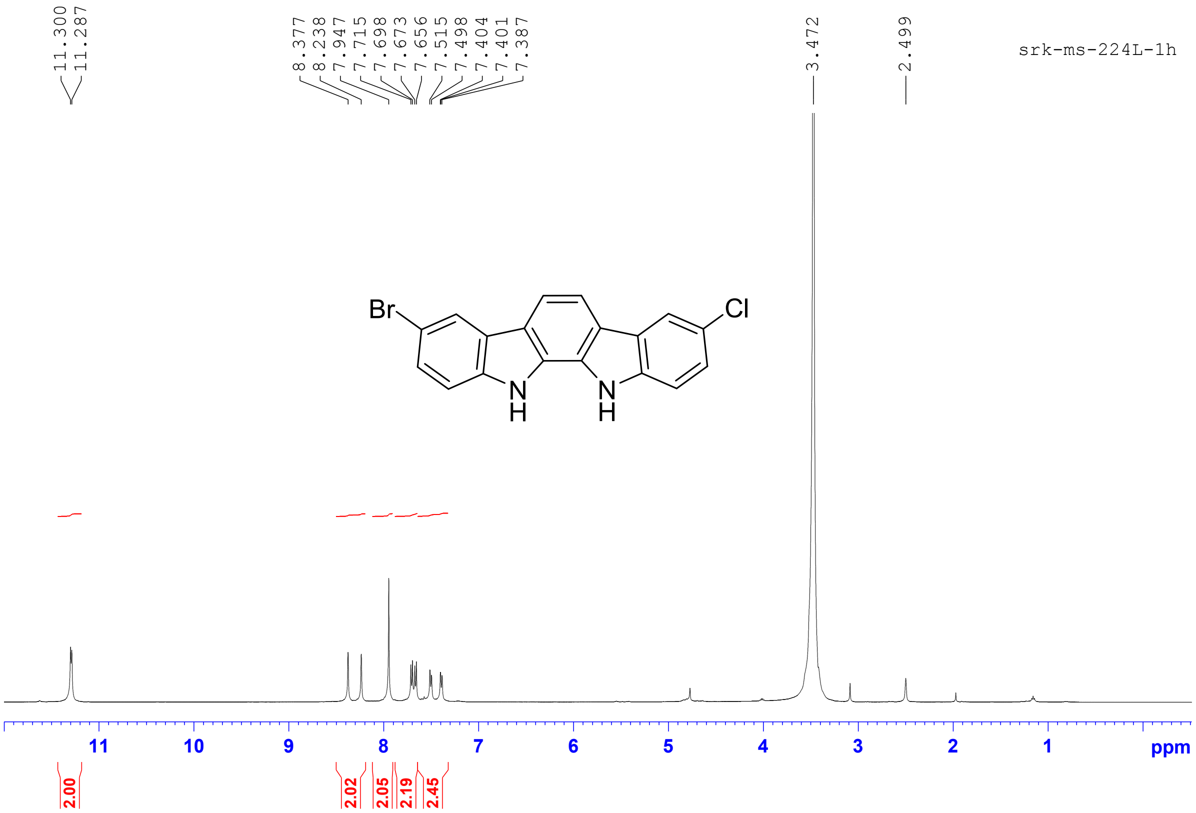


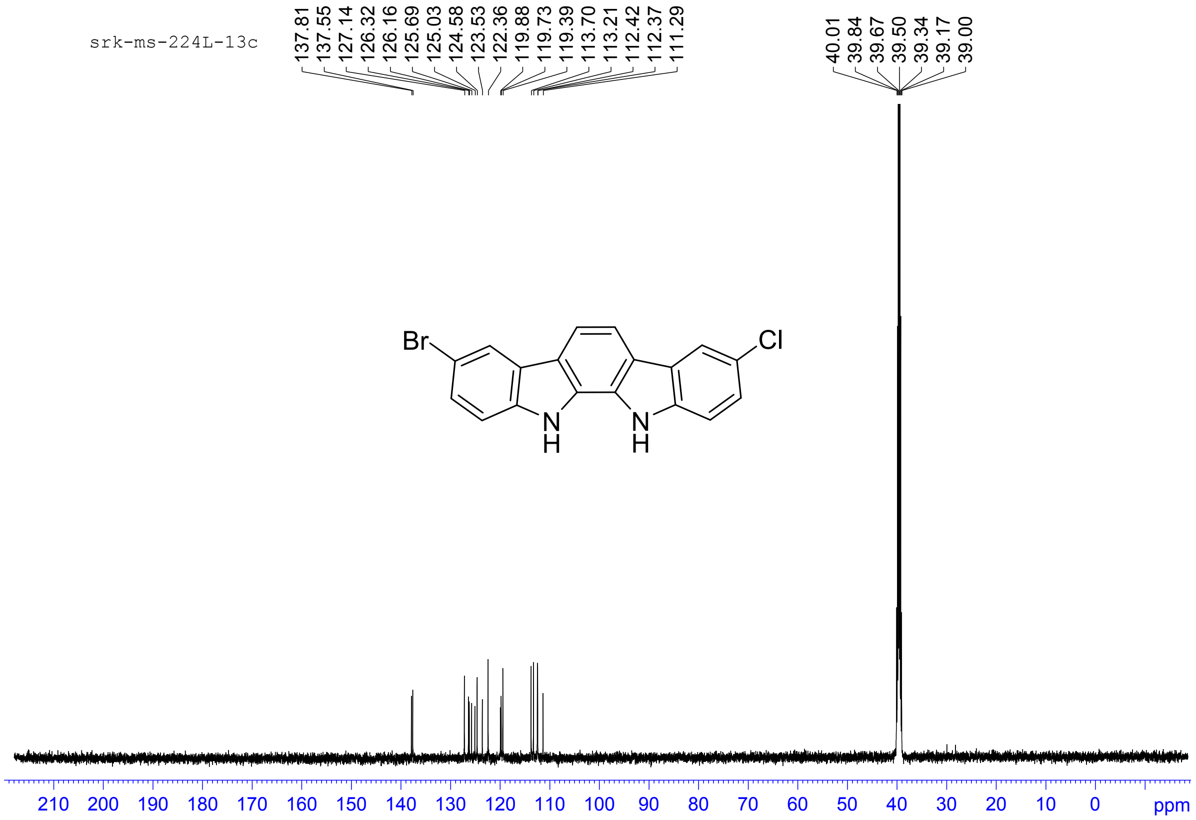
^{1}H and ^{13}C NMR of compound 21e



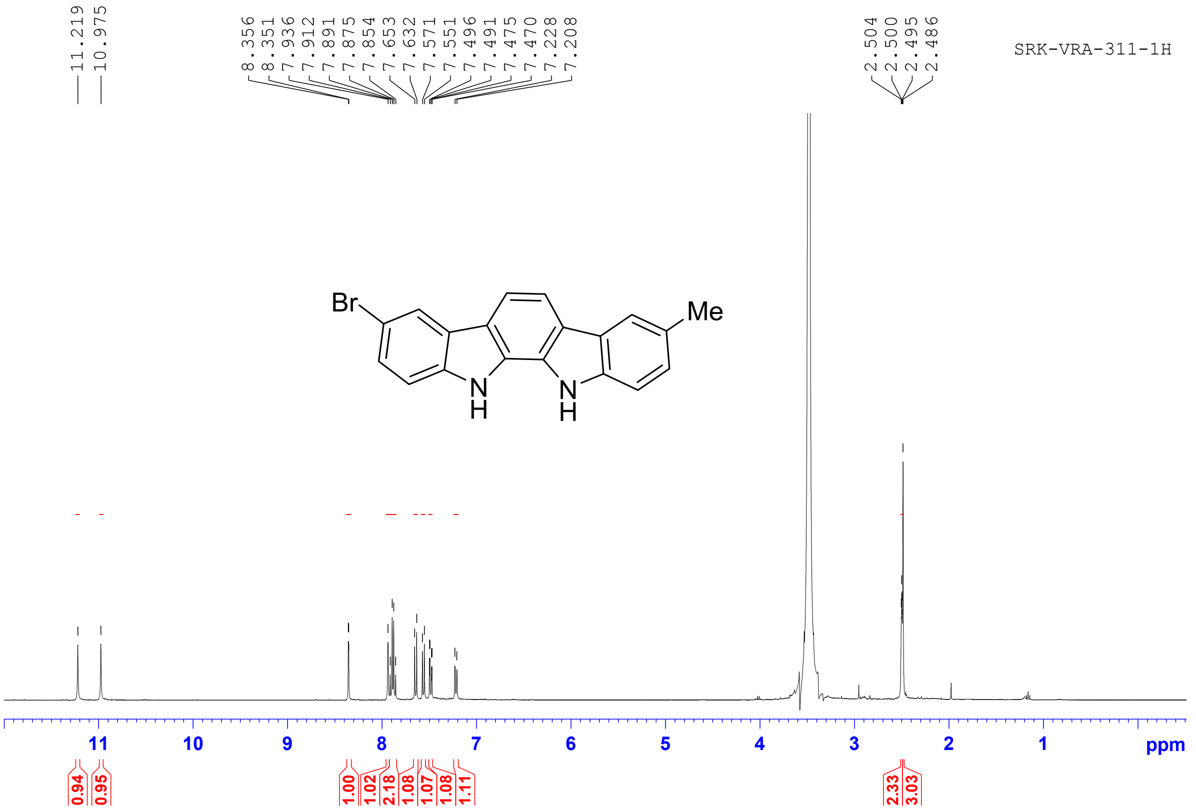


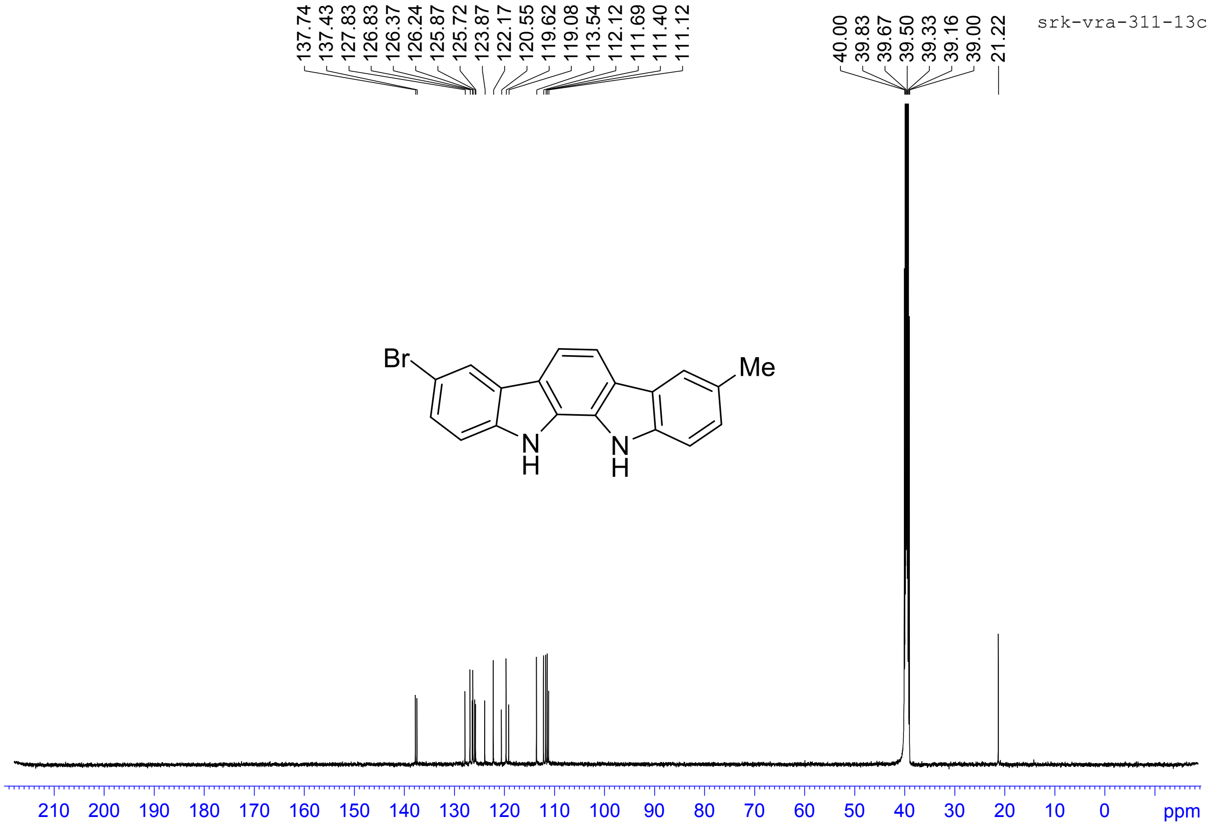
^{1}H and ^{13}C NMR of compound 21f



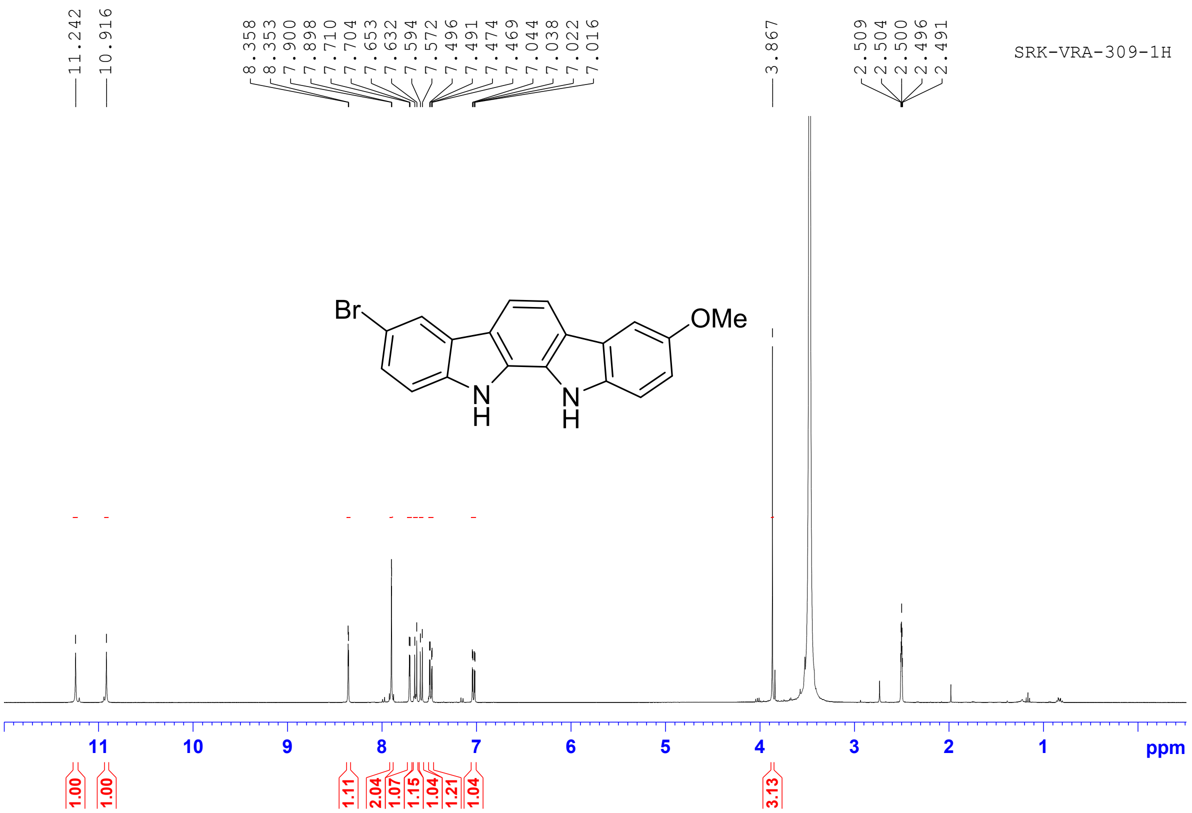


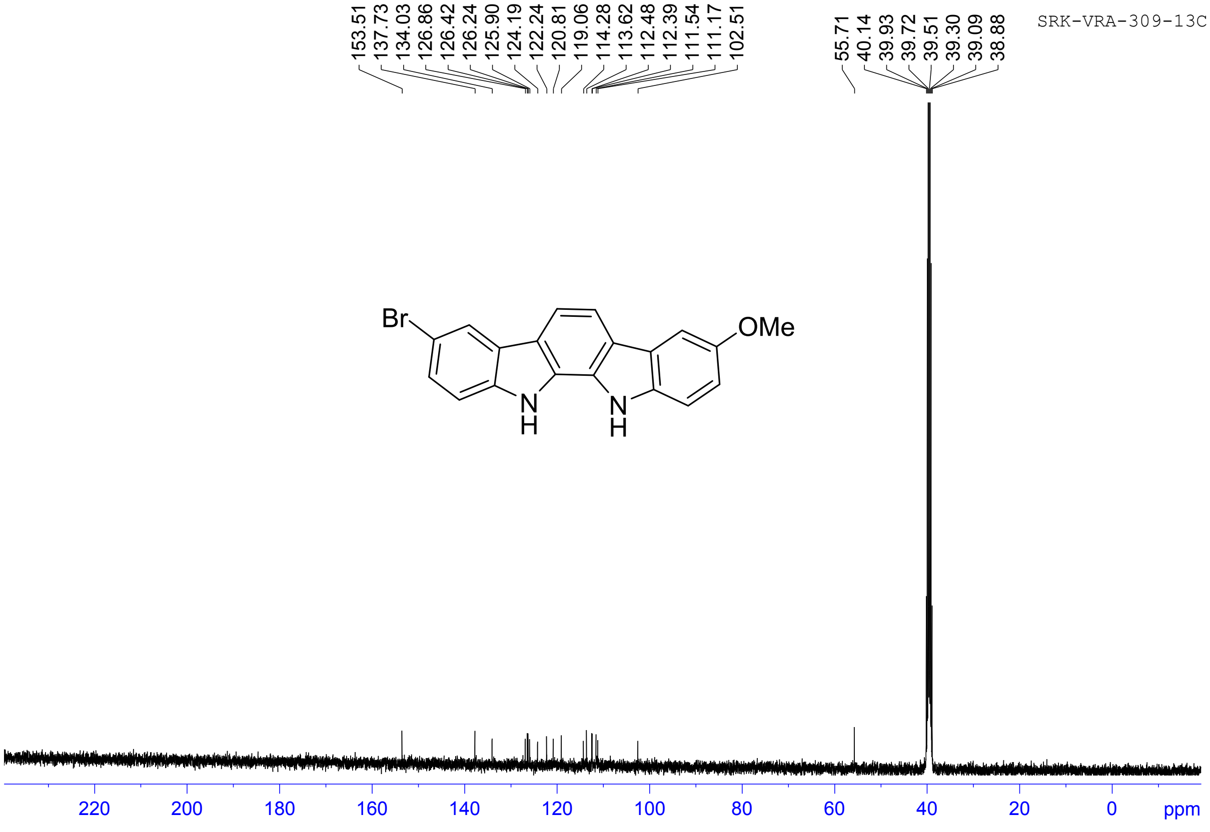
^{1}H and ^{13}C NMR of compound 21g



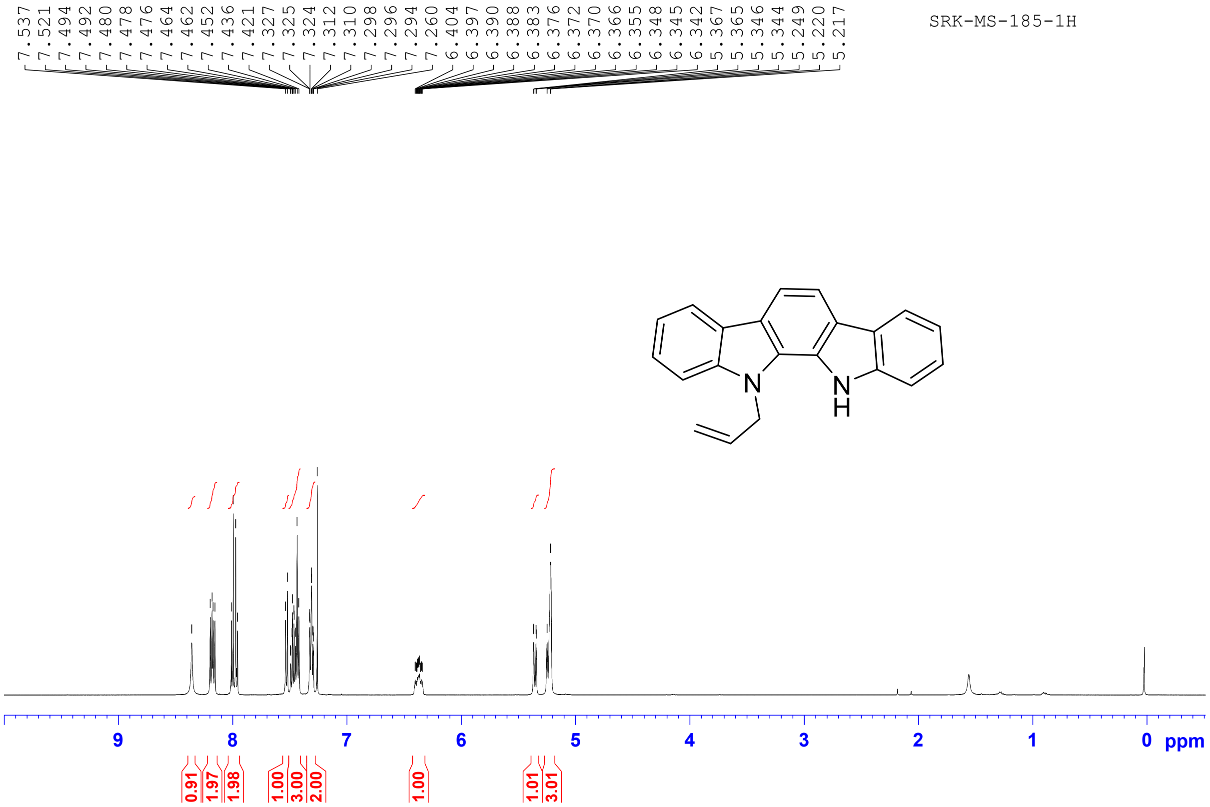


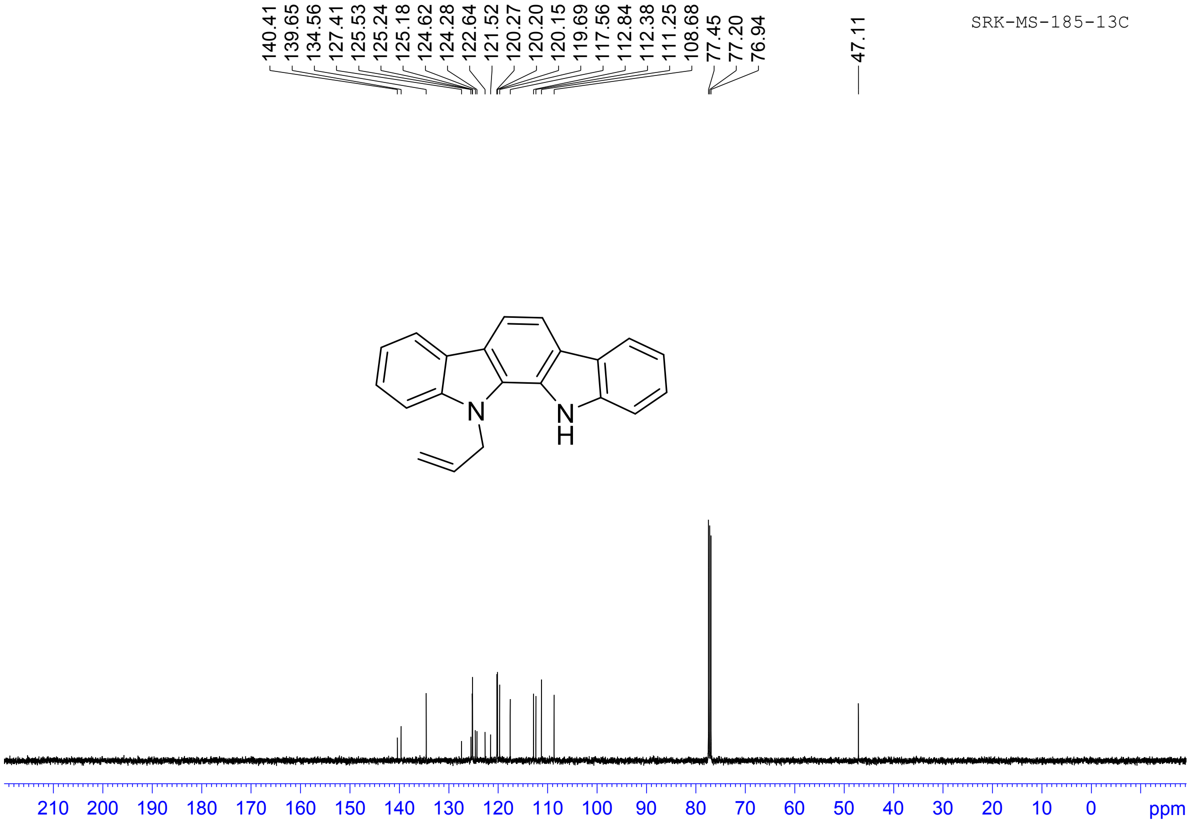
^{1}H and ^{13}C NMR of compound 21h



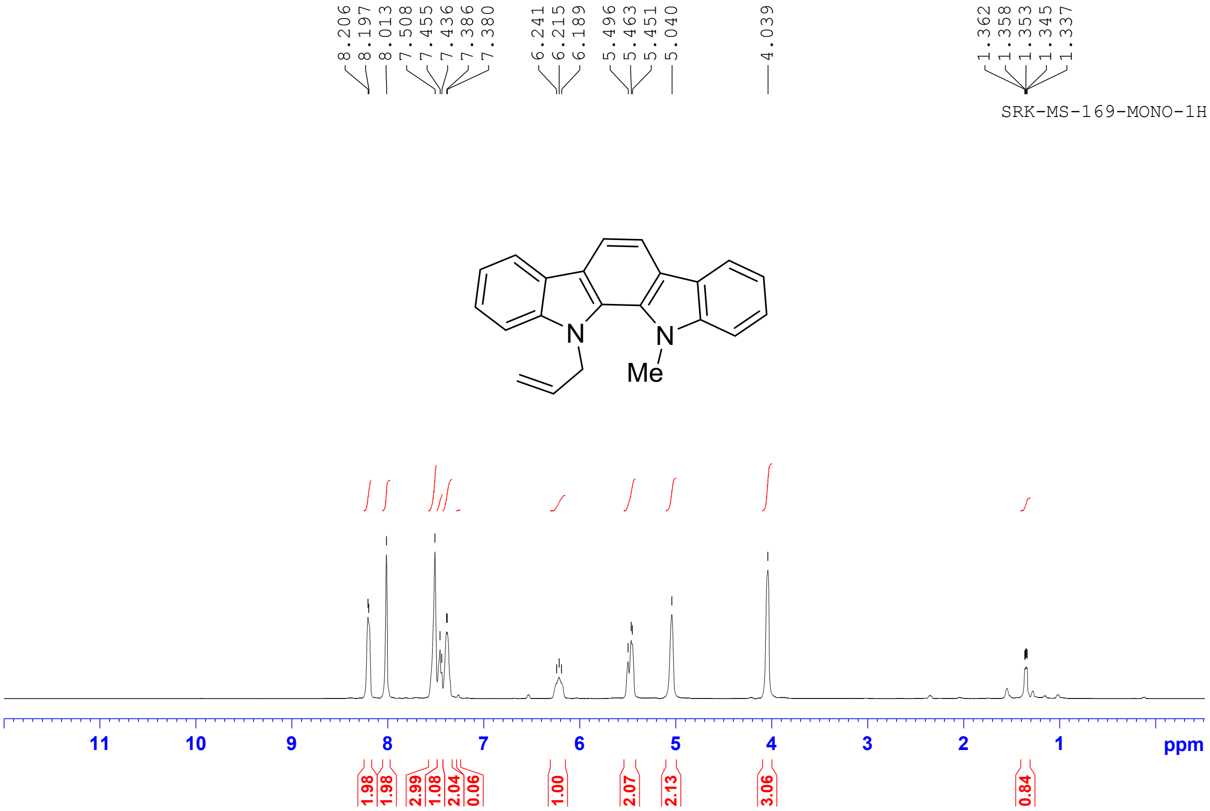


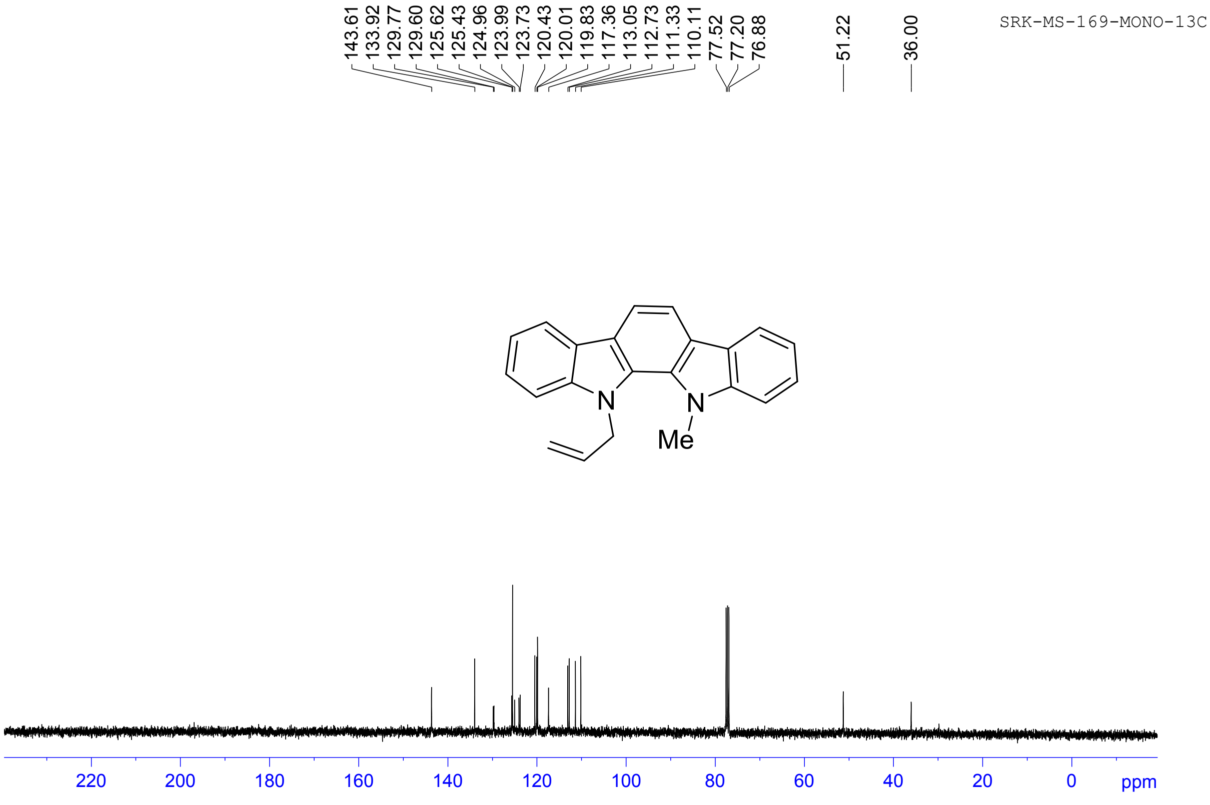
^1H and ^{13}C NMR of compound 21i



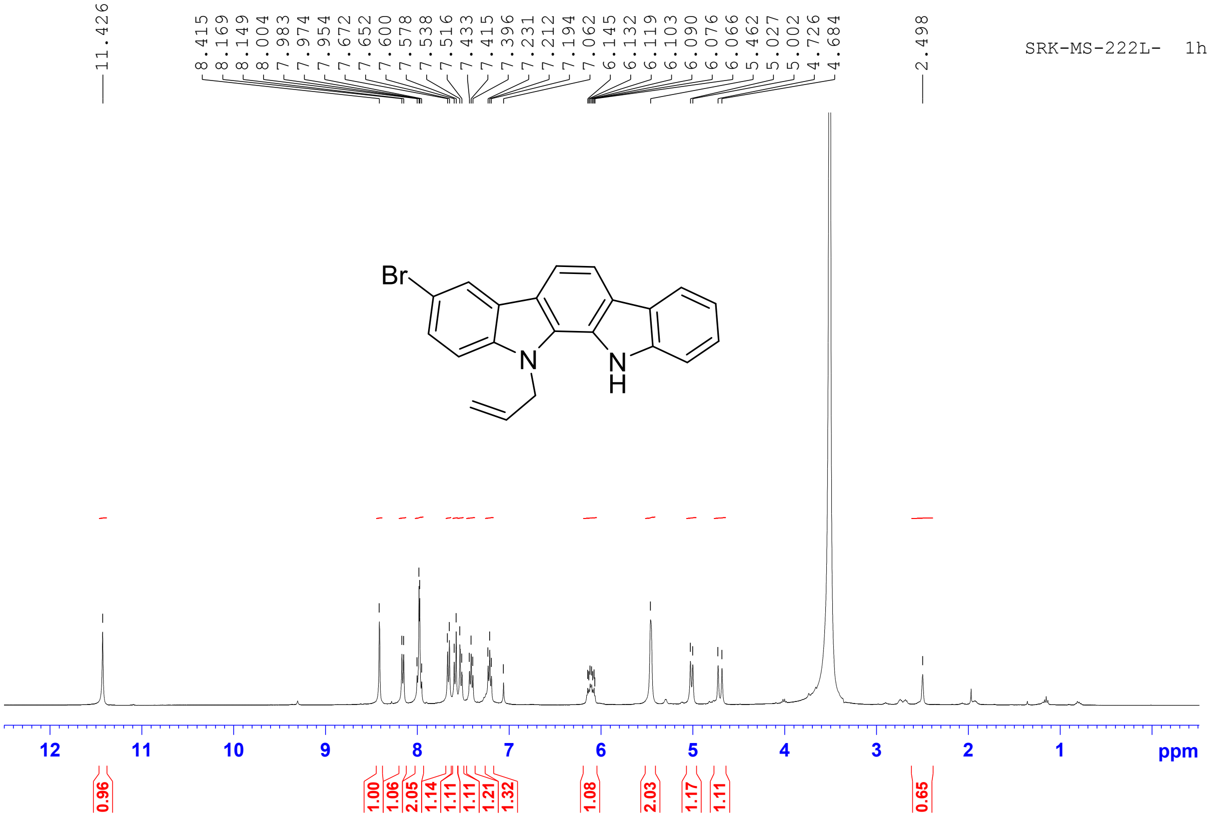


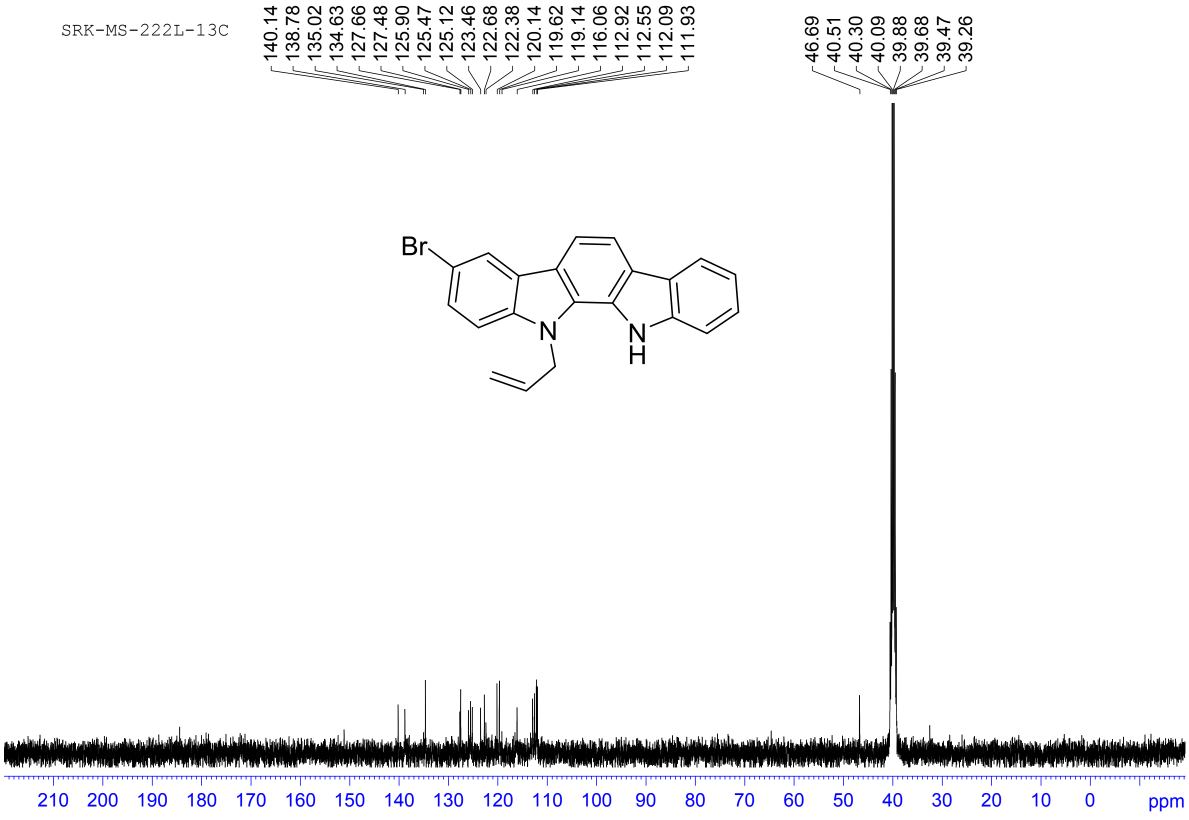
^{1}H and ^{13}C NMR of compound 21j



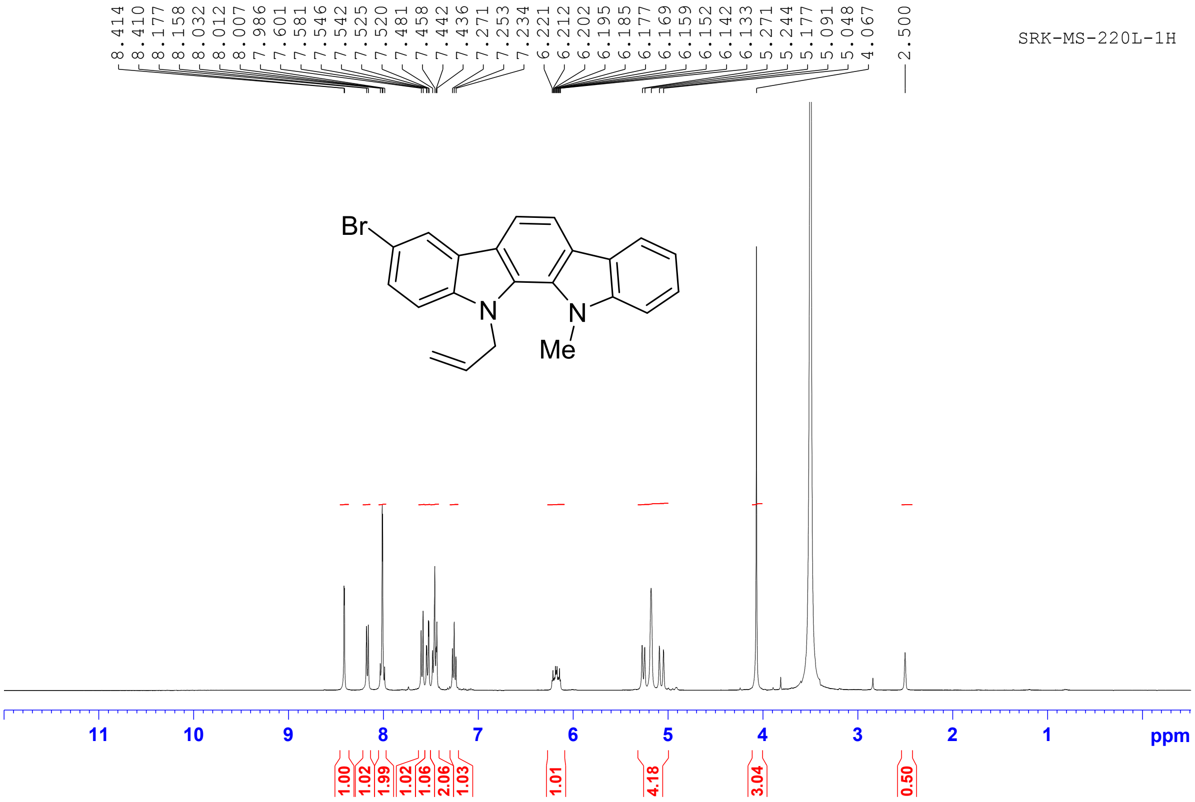


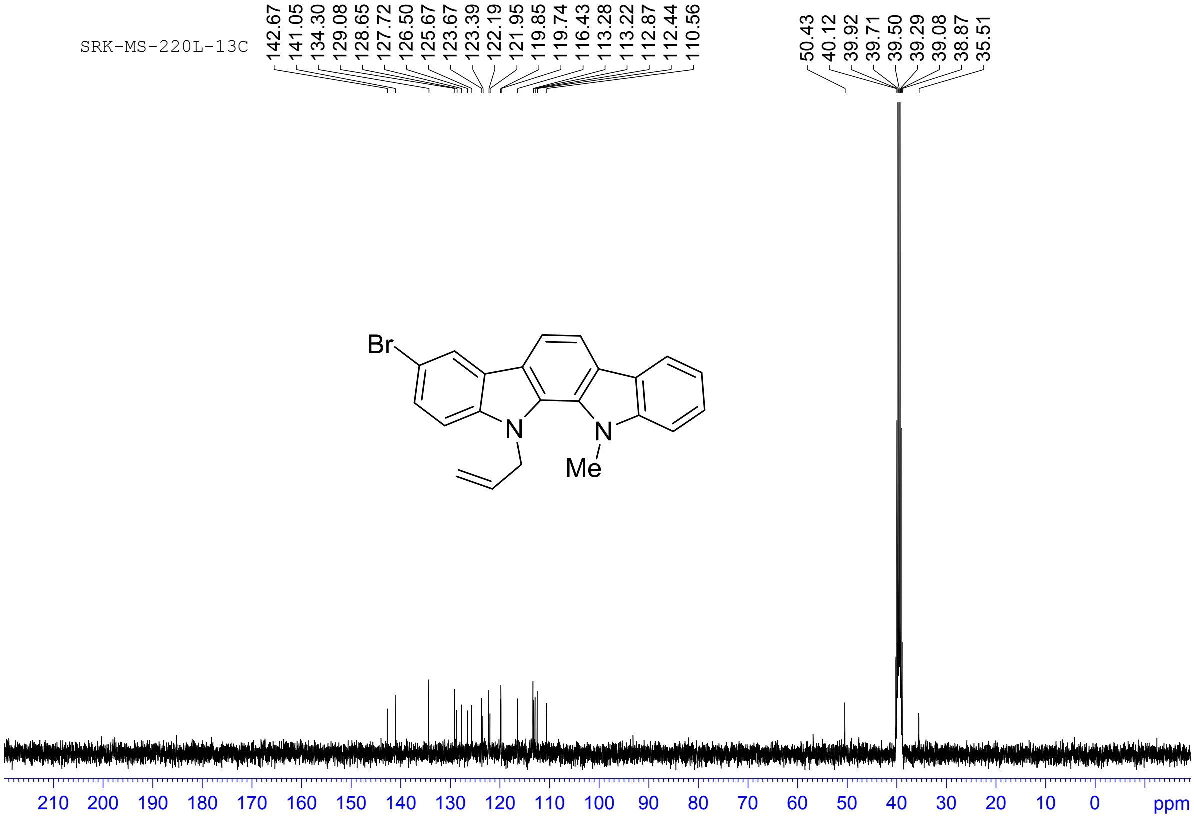
^{1}H and ^{13}C NMR of compound 21k



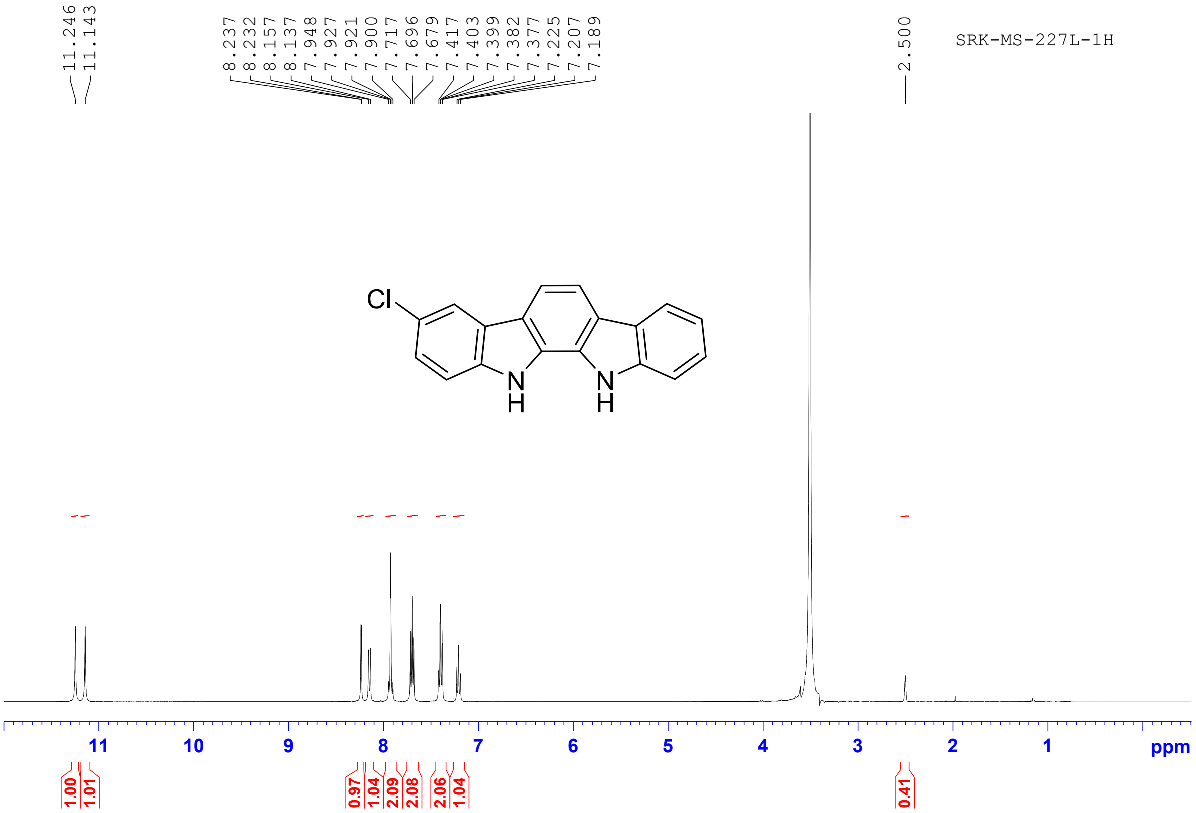


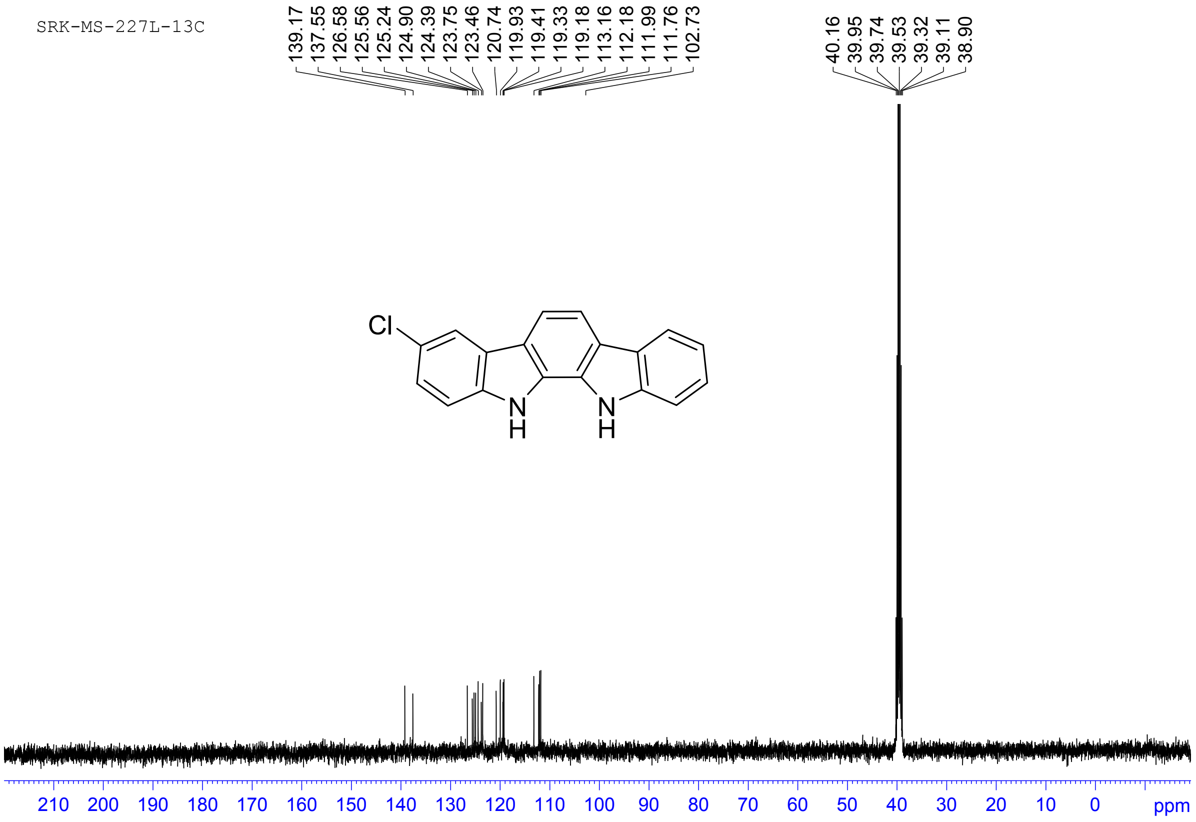
^{1}H and ^{13}C NMR of compound 21l



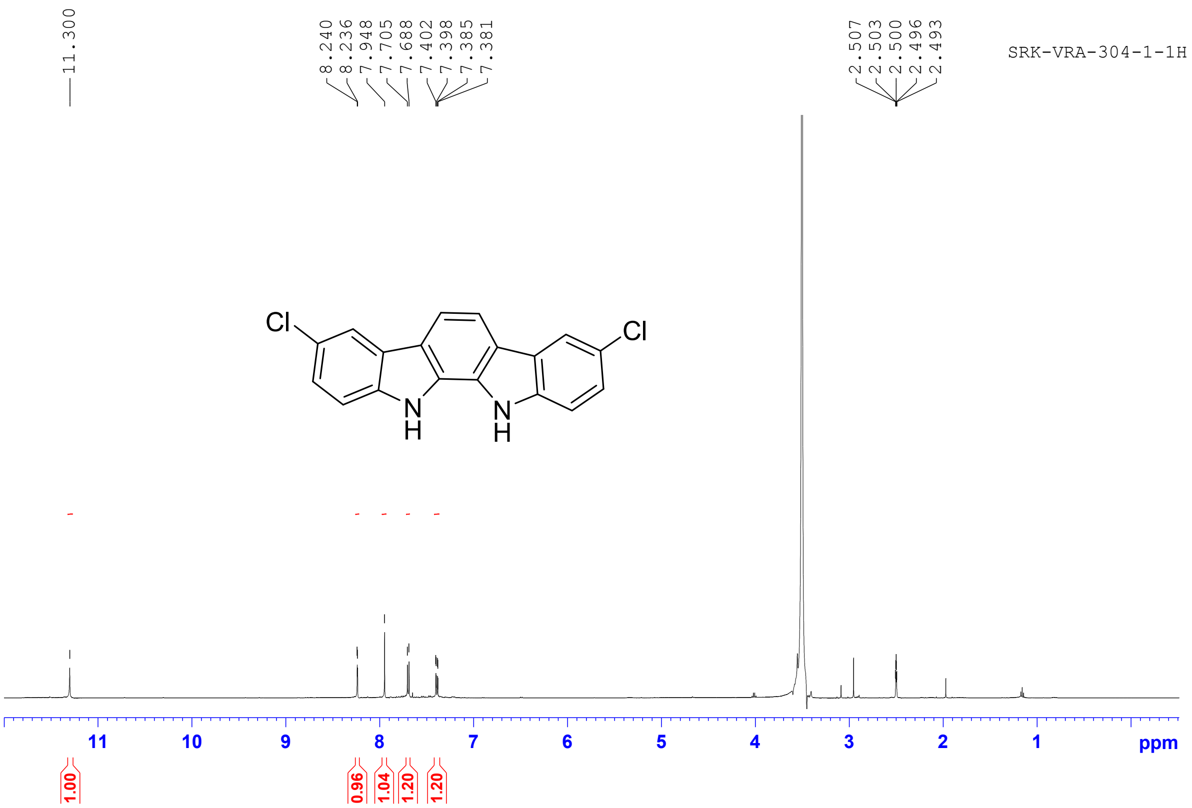


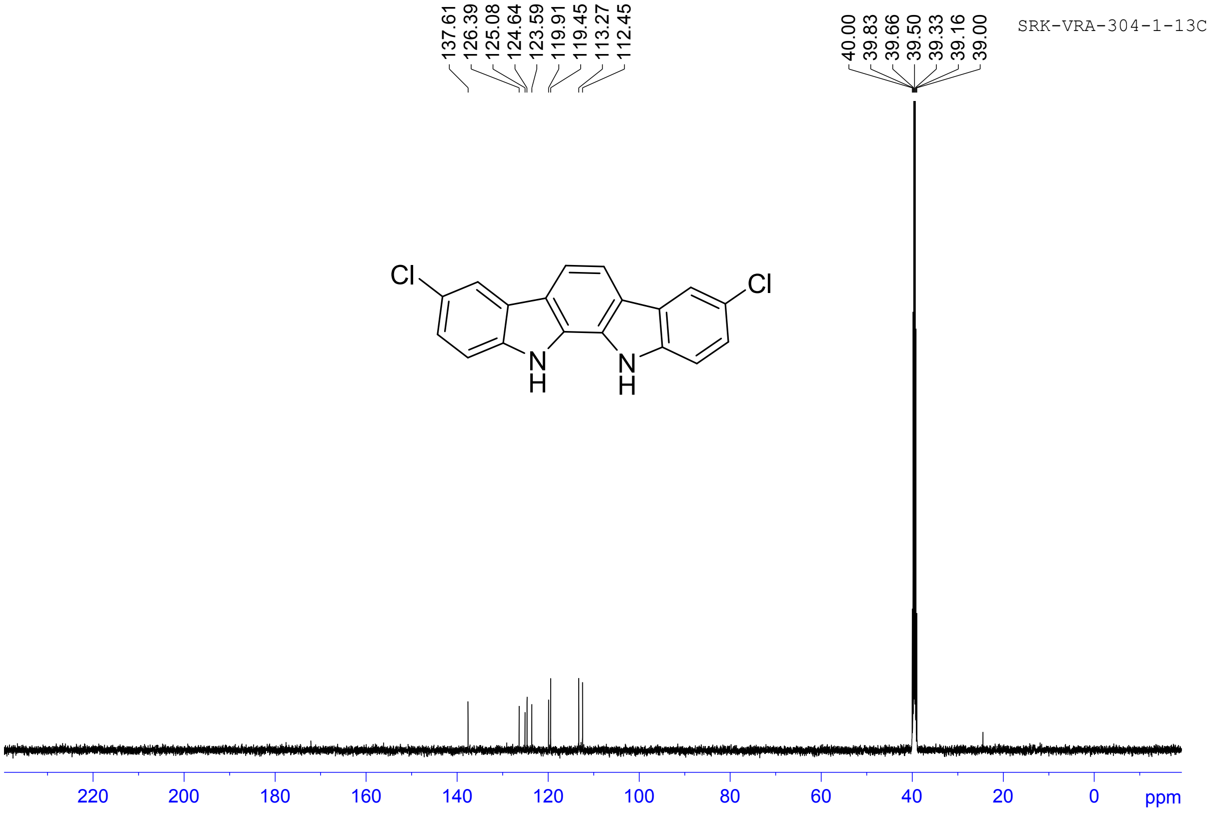
^{1}H and ^{13}C NMR of compound 21n



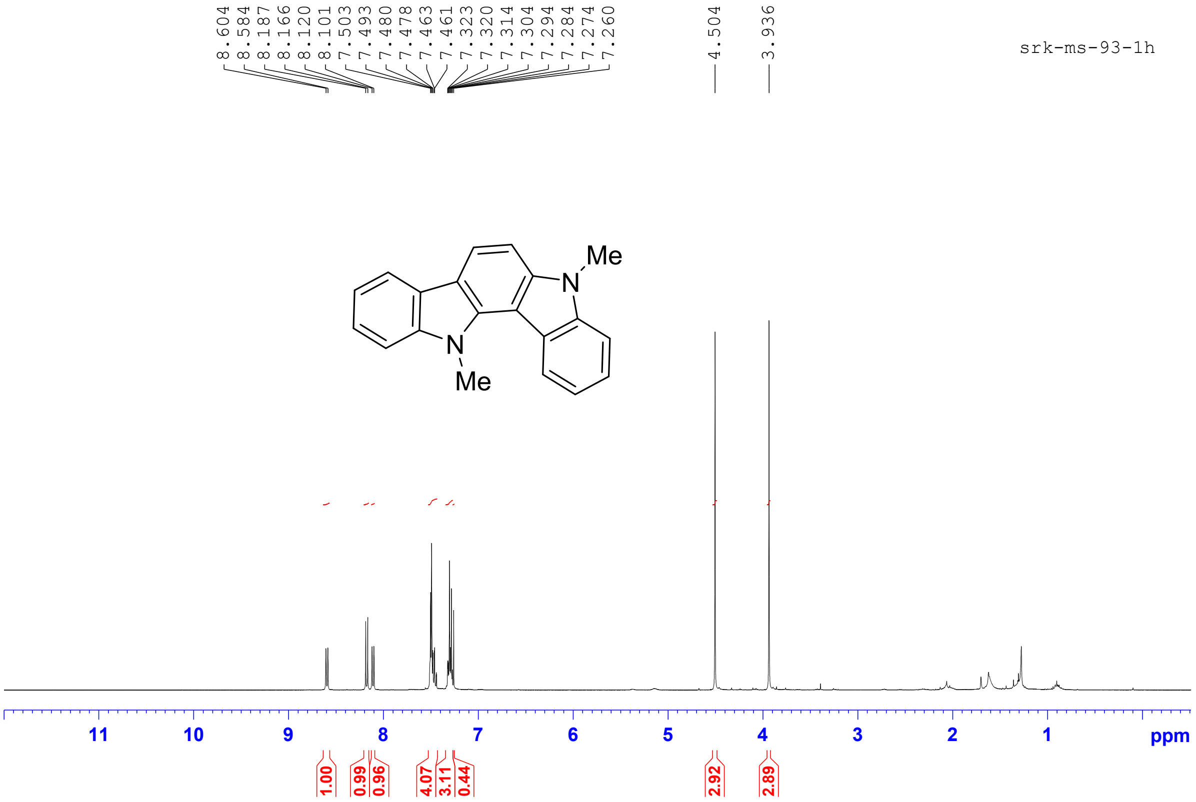


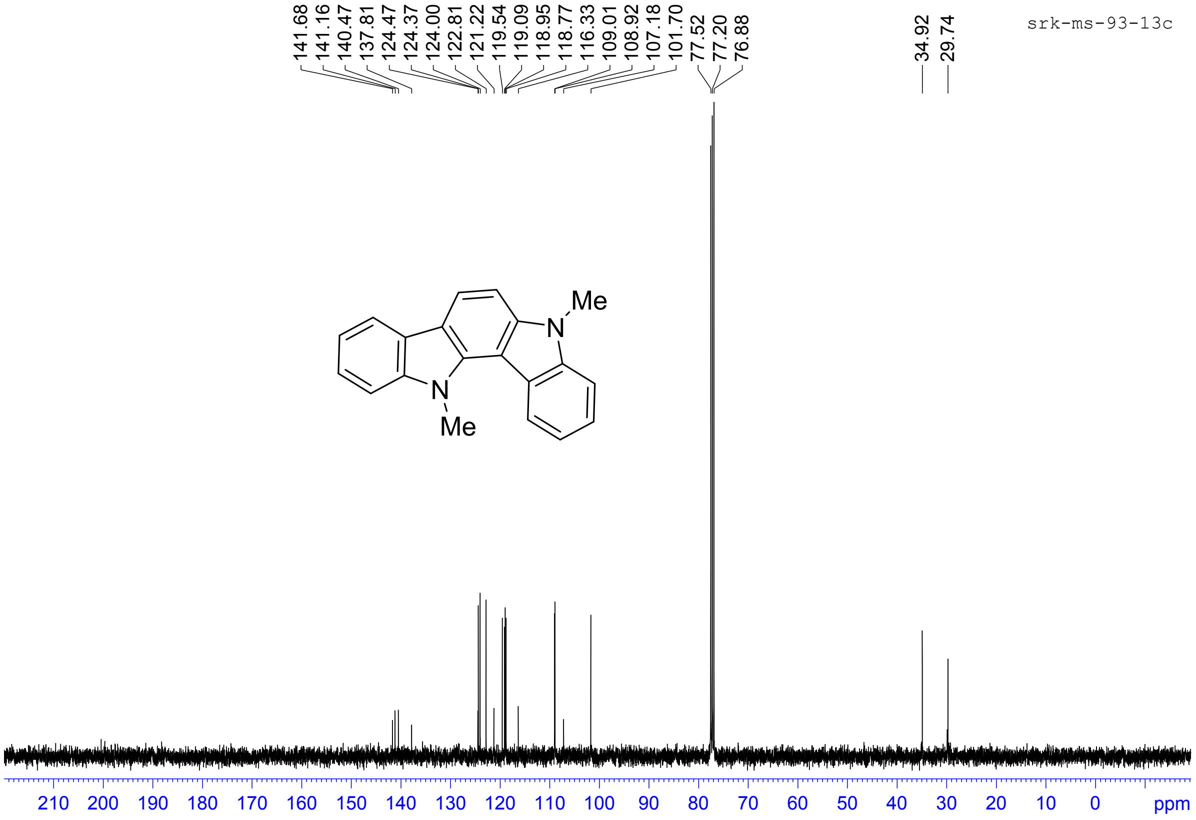
^{1}H and ^{13}C NMR of compound 21o



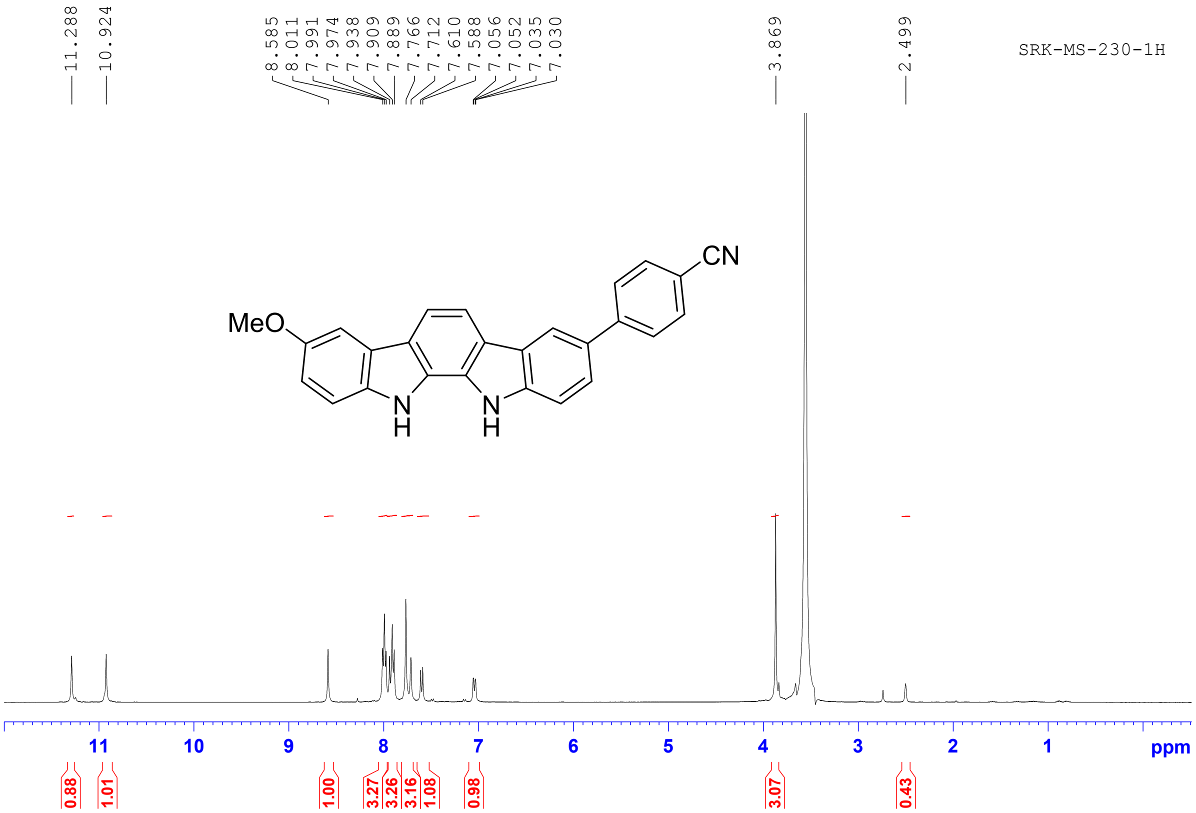


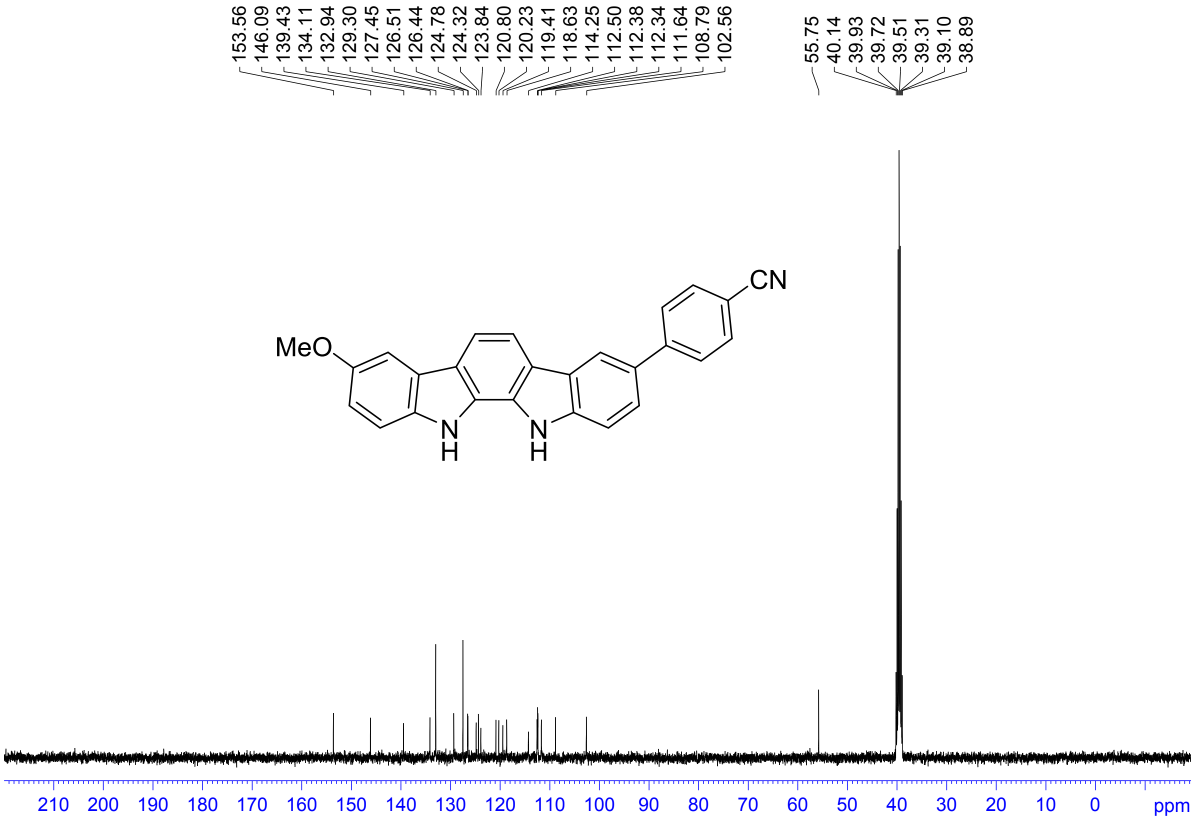
^{1}H and ^{13}C NMR of compound 24



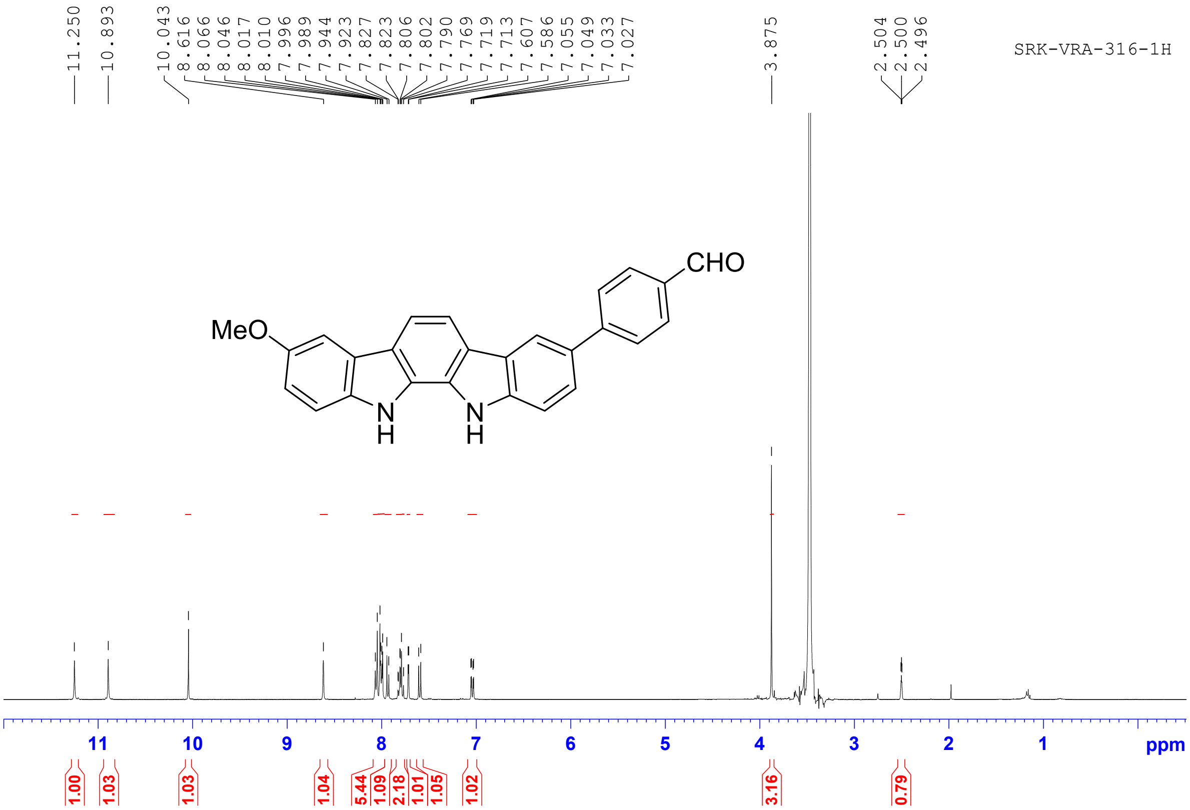


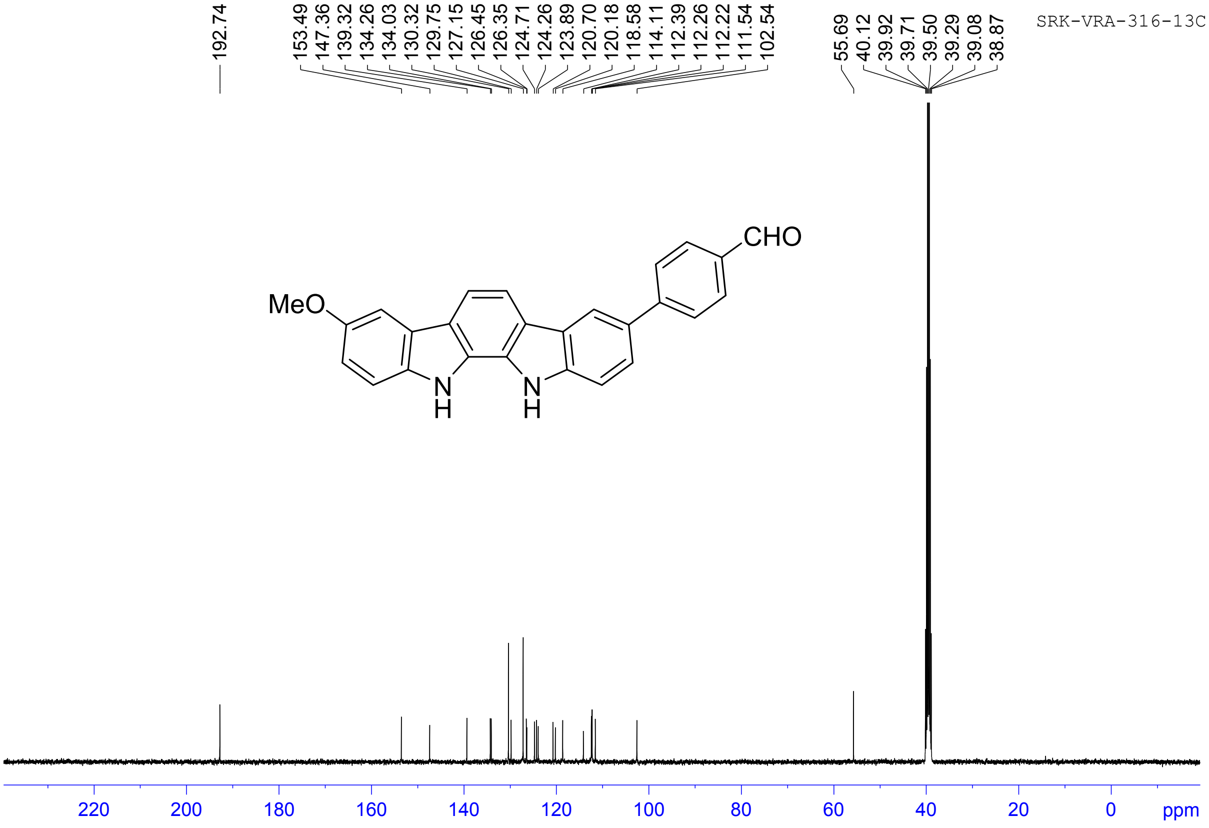
^{1}H and ^{13}C NMR of compound 26a



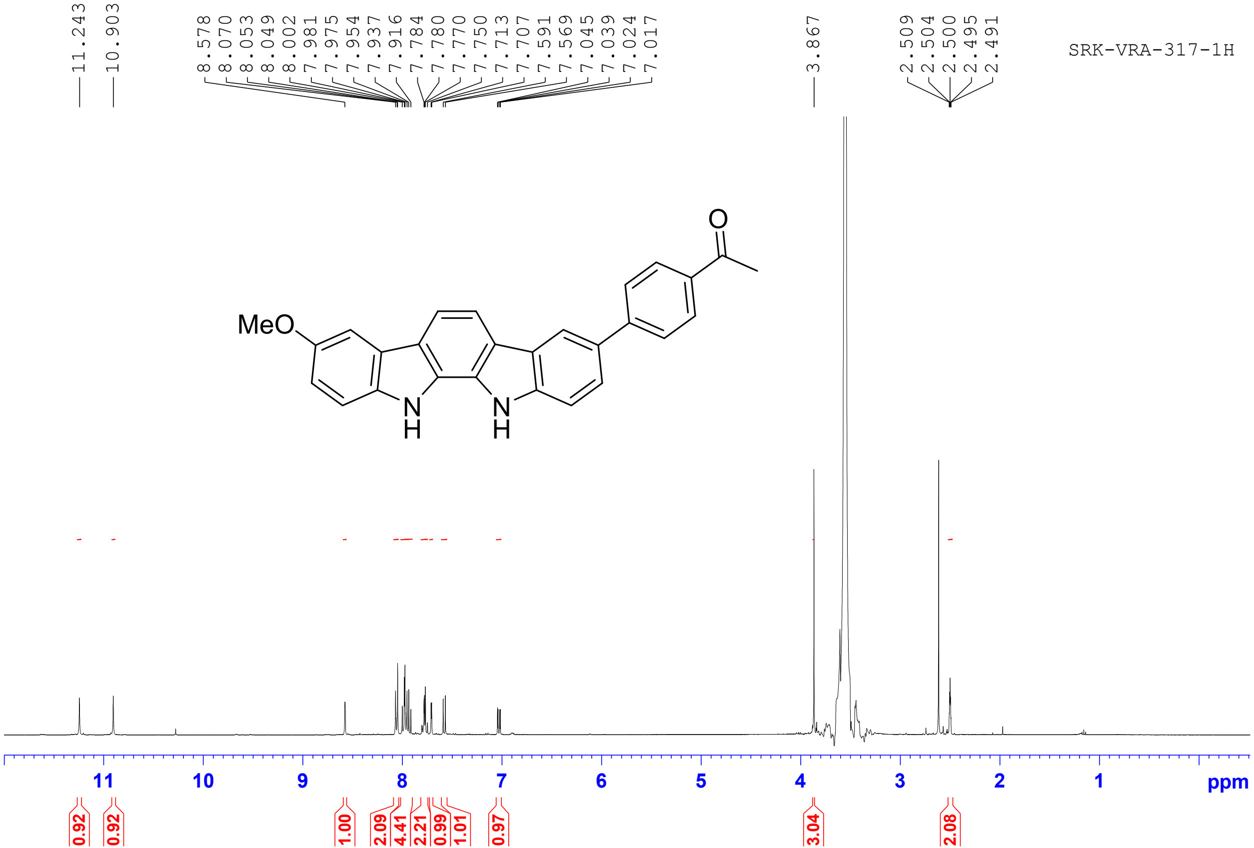


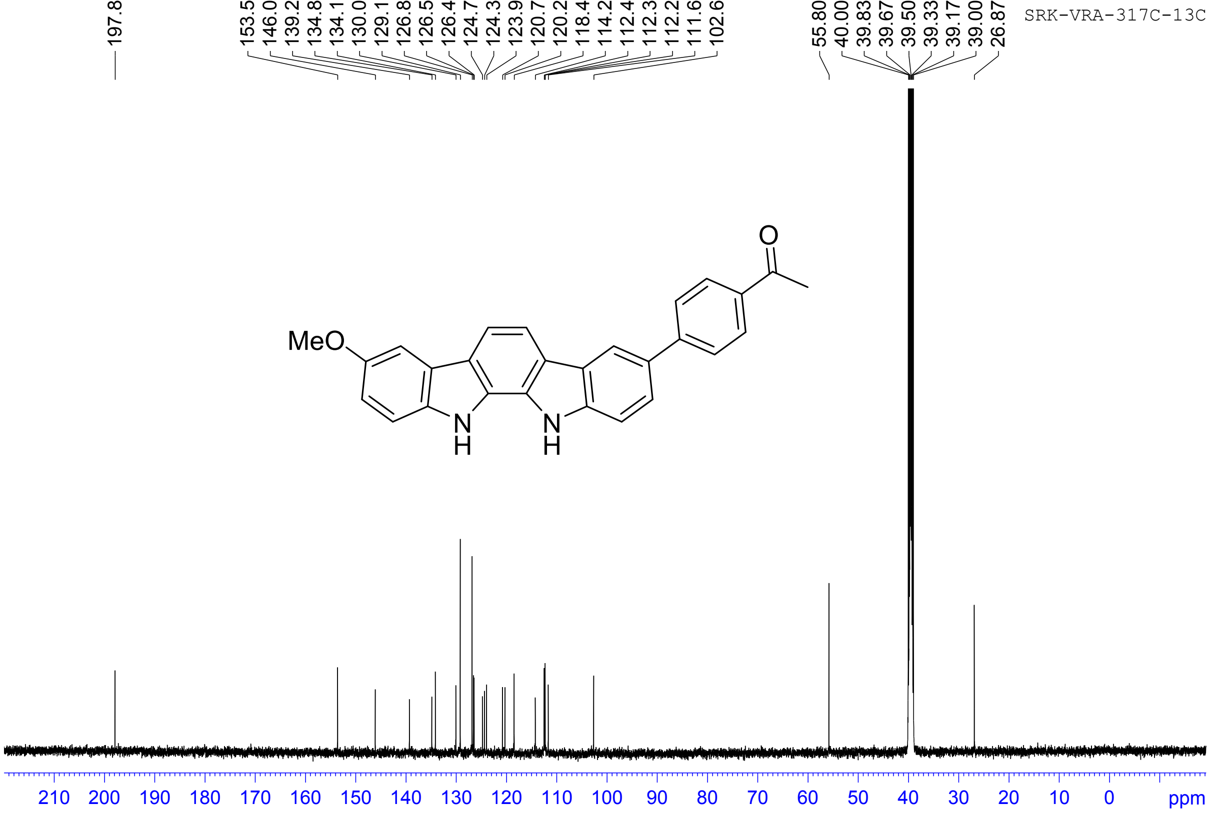
^{1}H and ^{13}C NMR of compound 26b



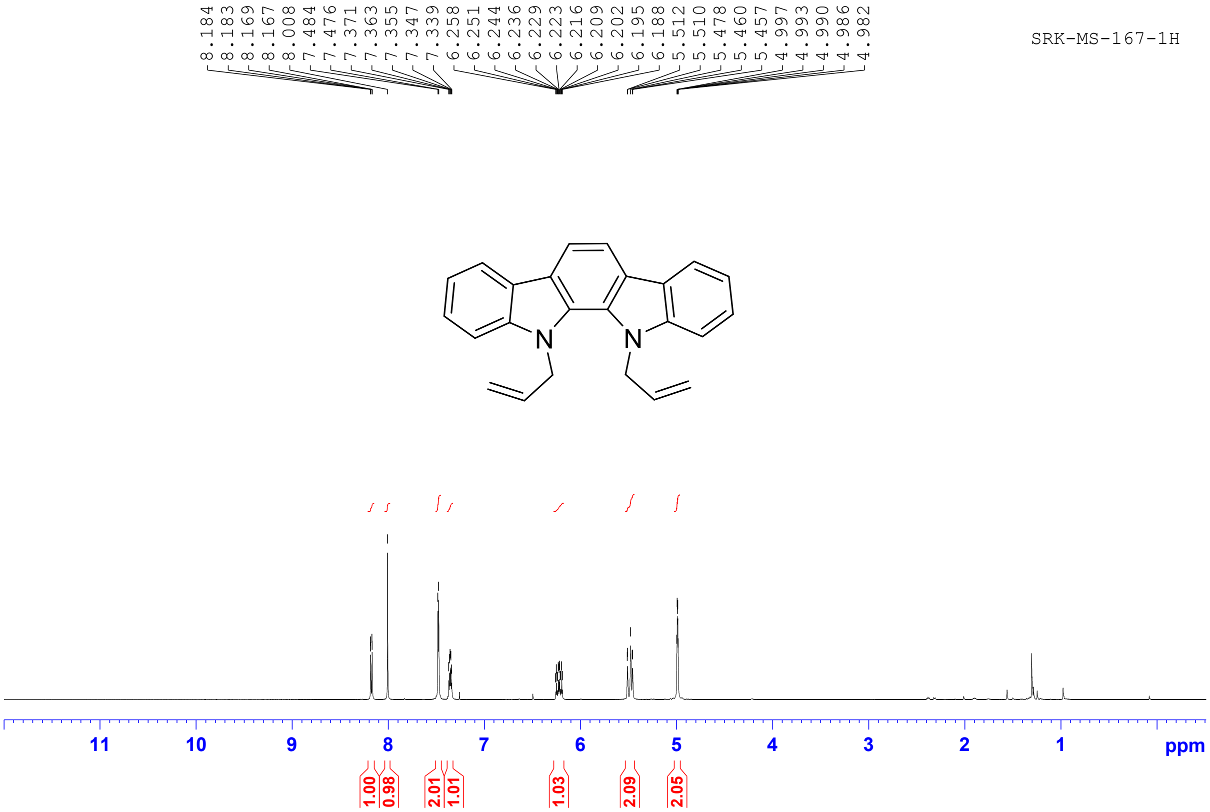


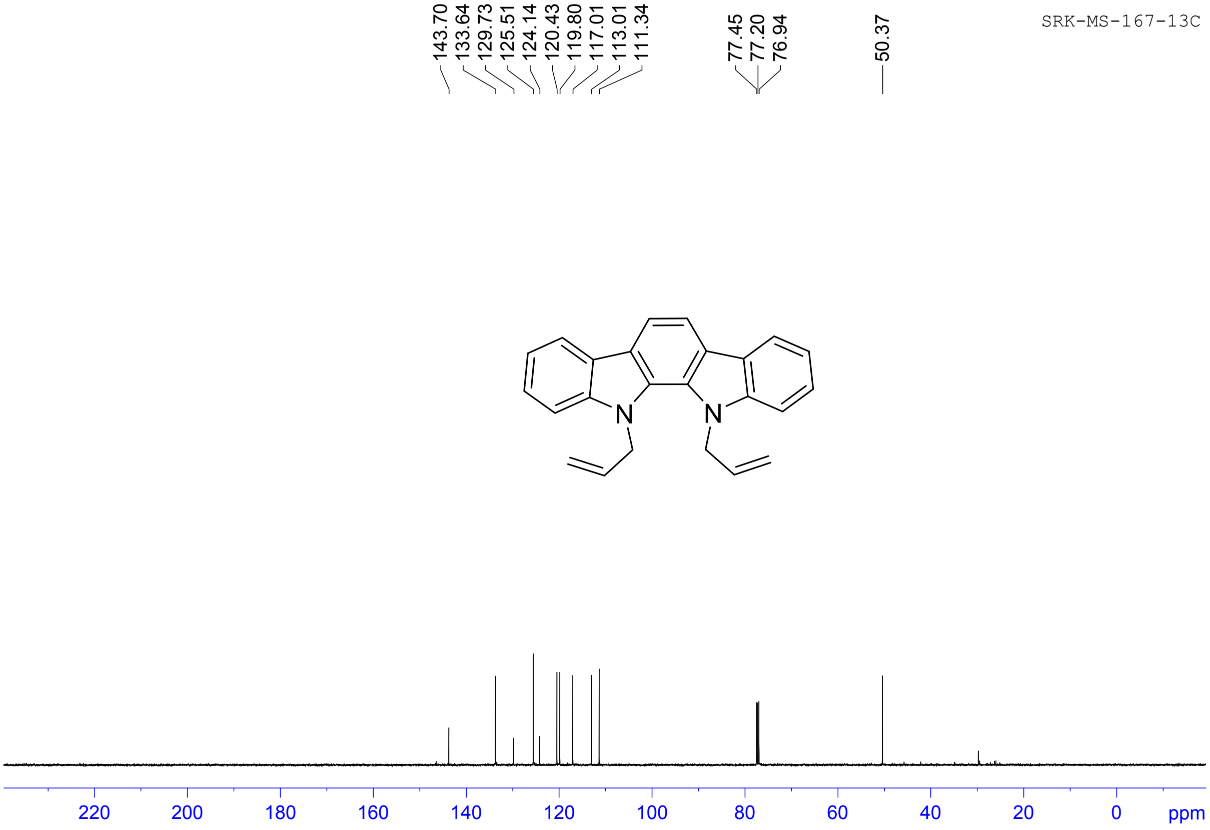
^{1}H and ^{13}C NMR of compound 26c



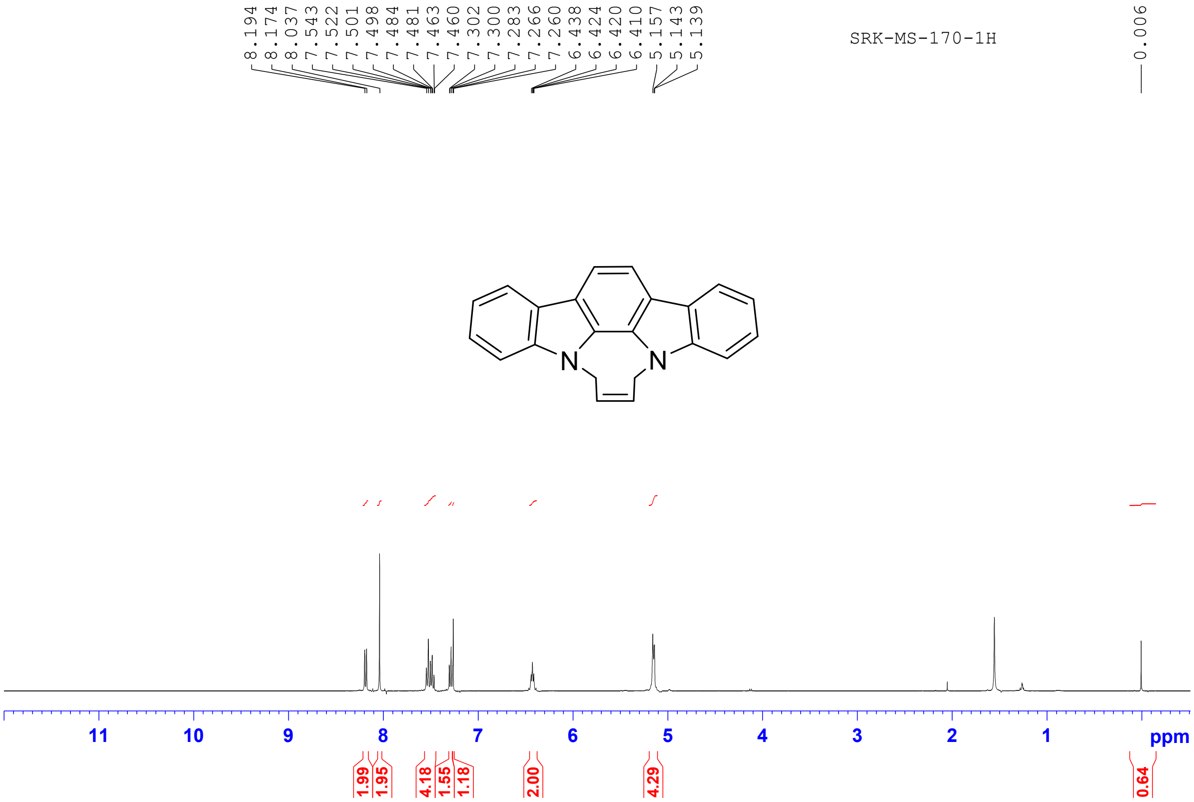


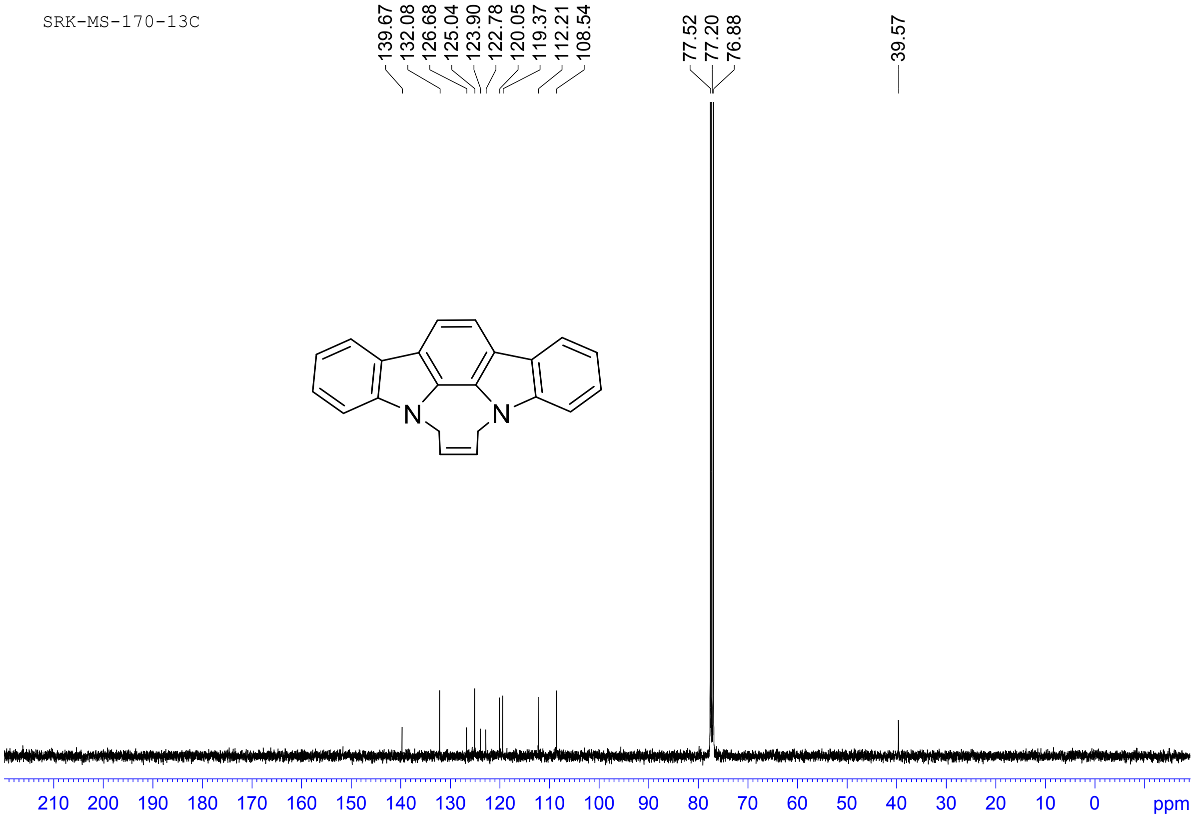
^{1}H and ^{13}C NMR of compound 27



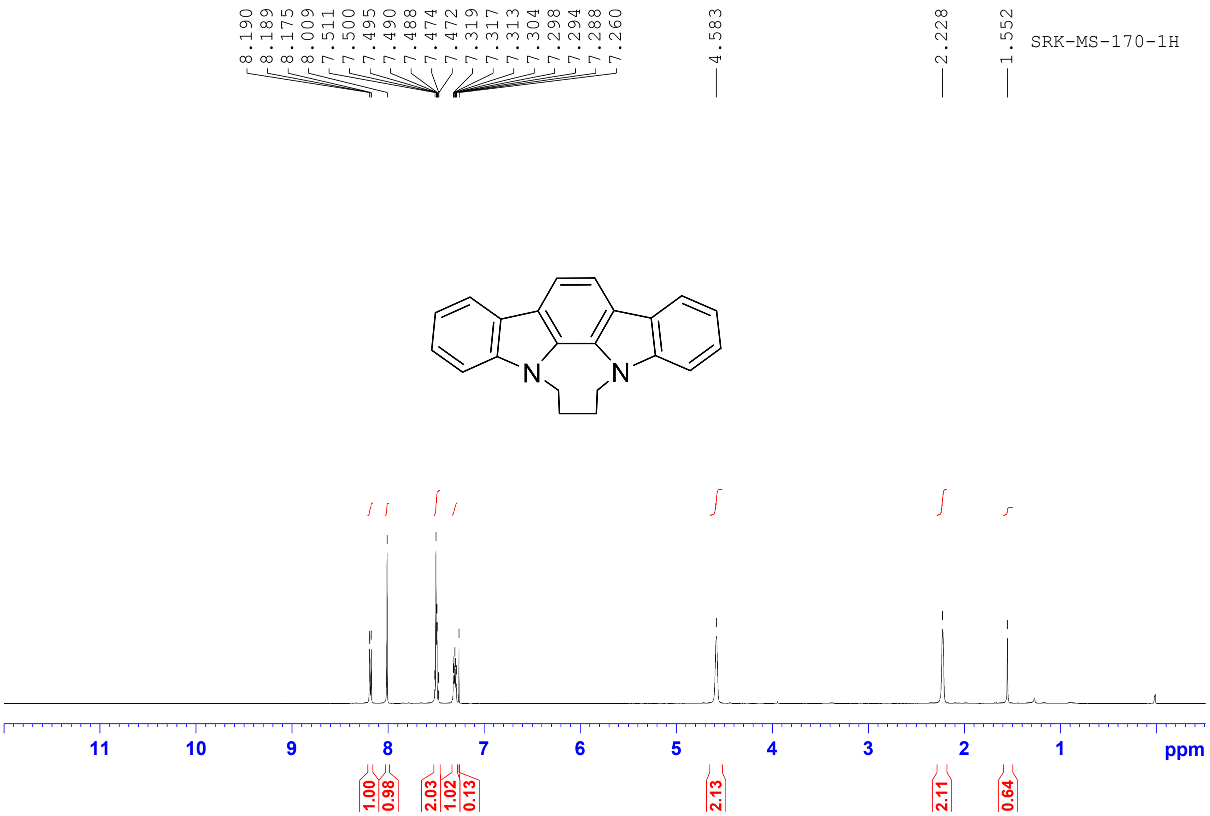


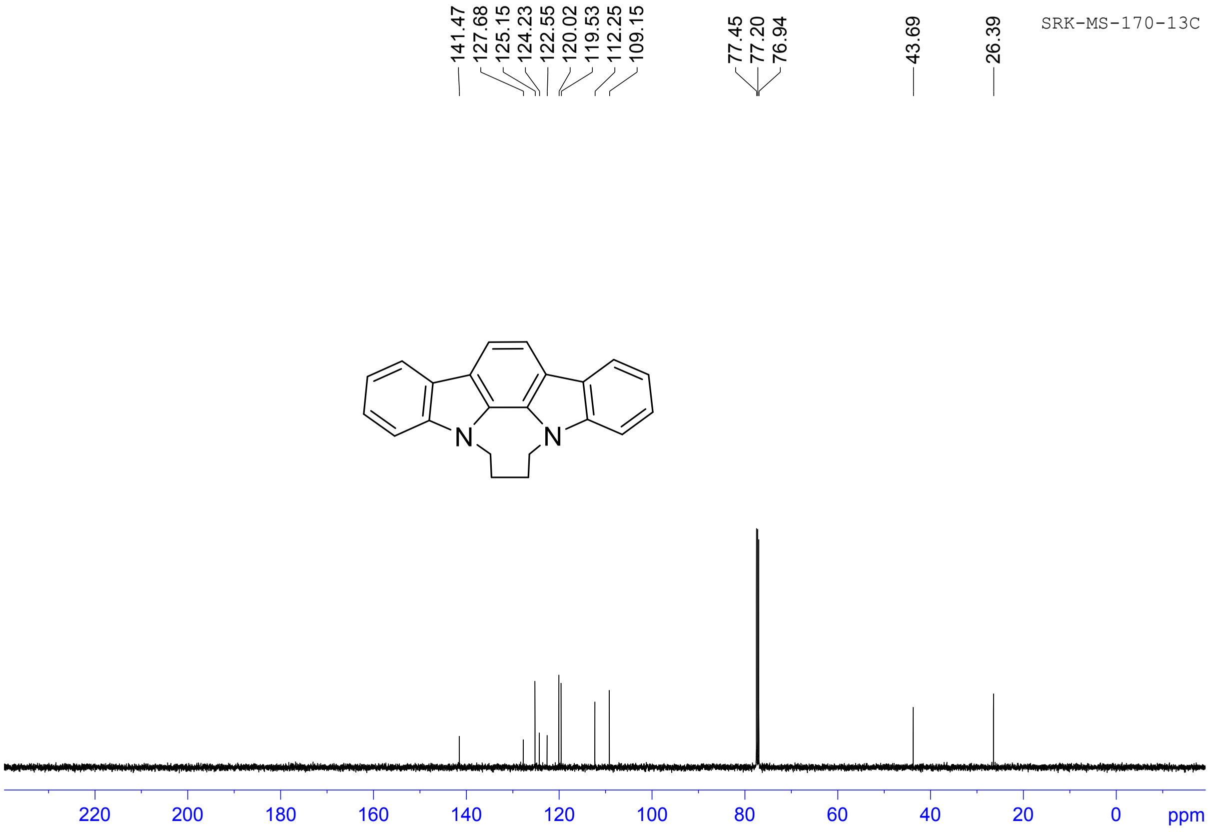
^{1}H and ^{13}C NMR of compound 28



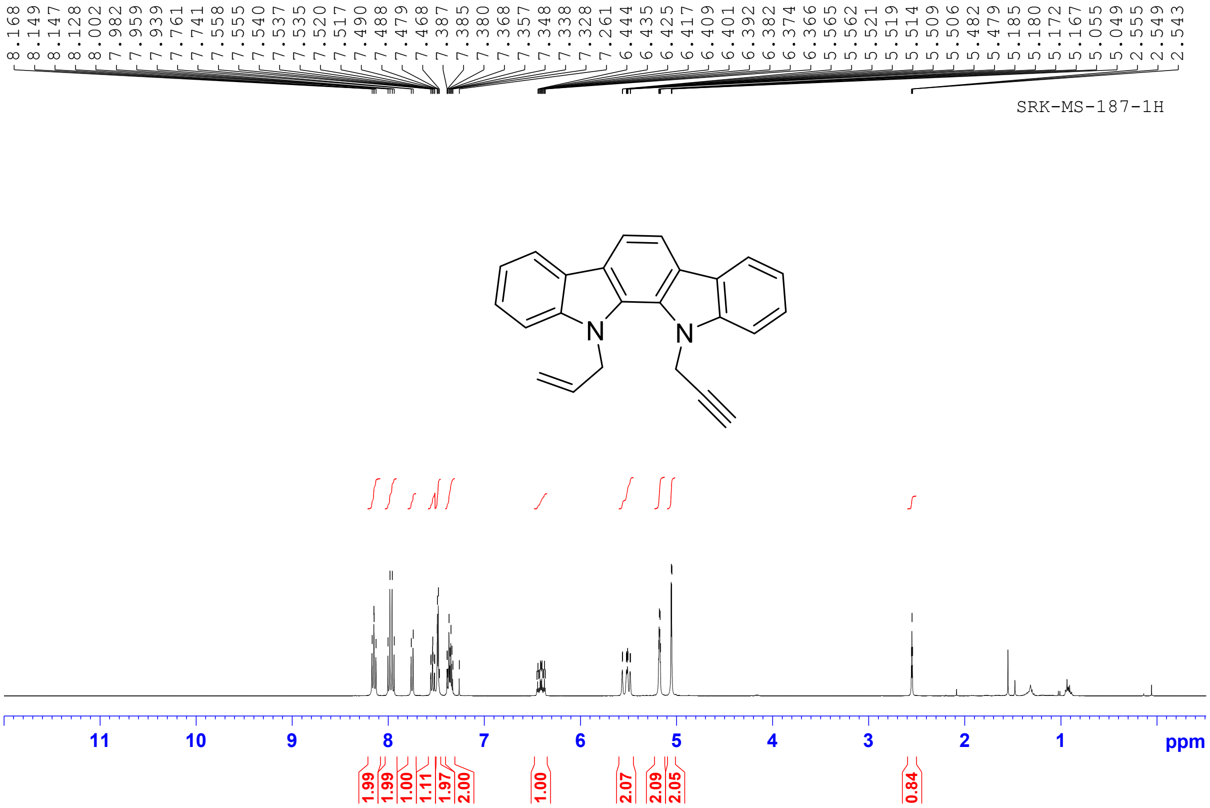


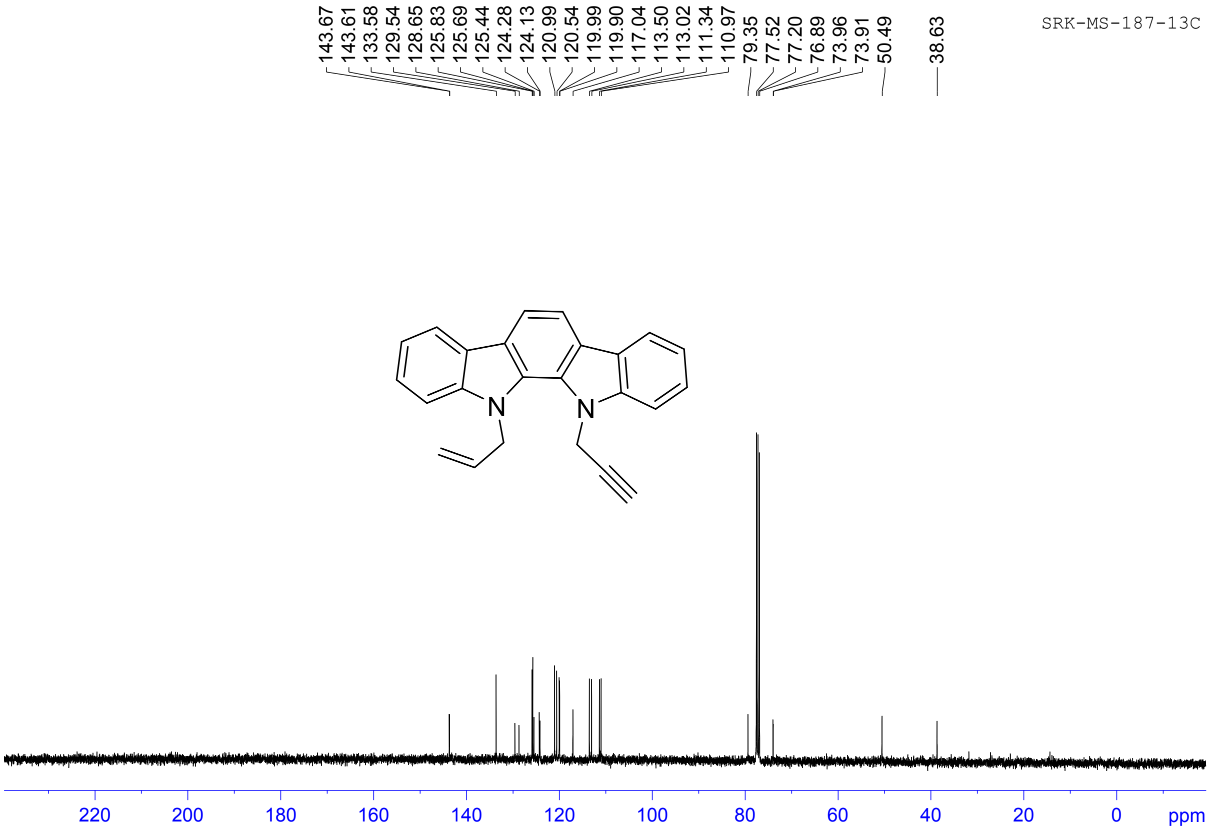
^{1}H and ^{13}C NMR of compound 29



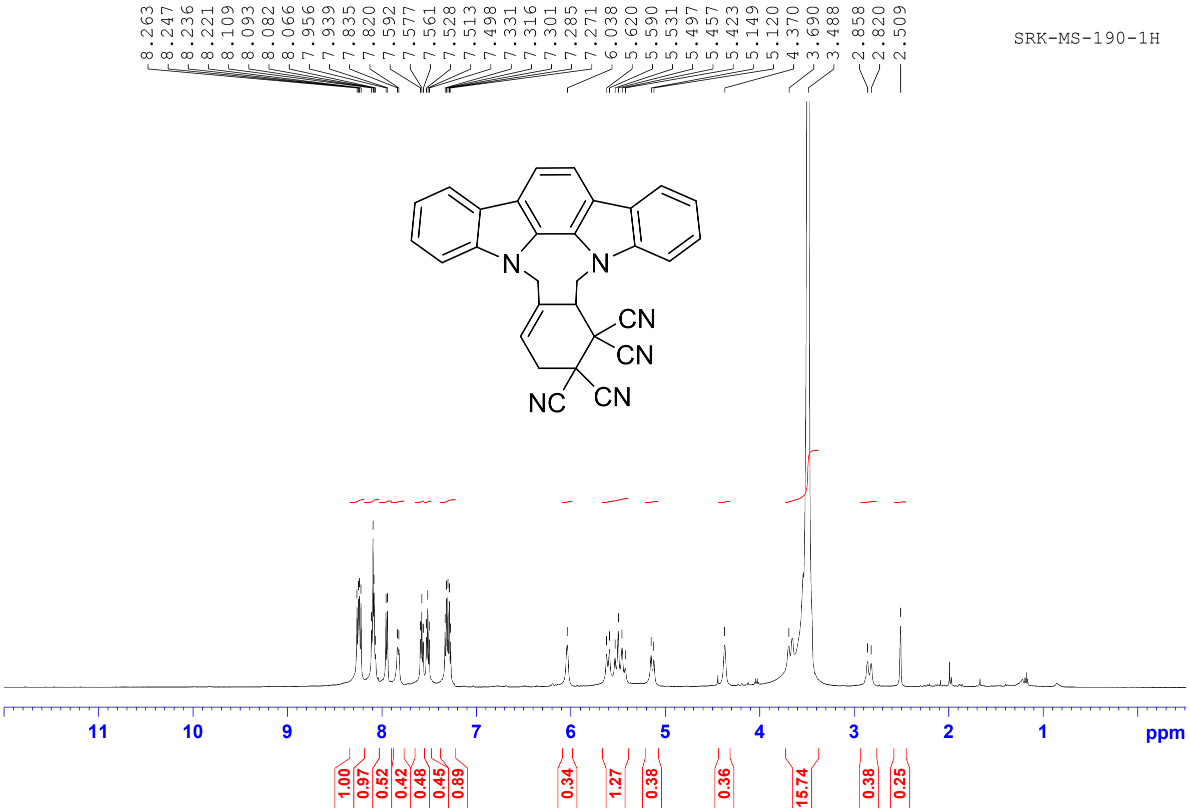


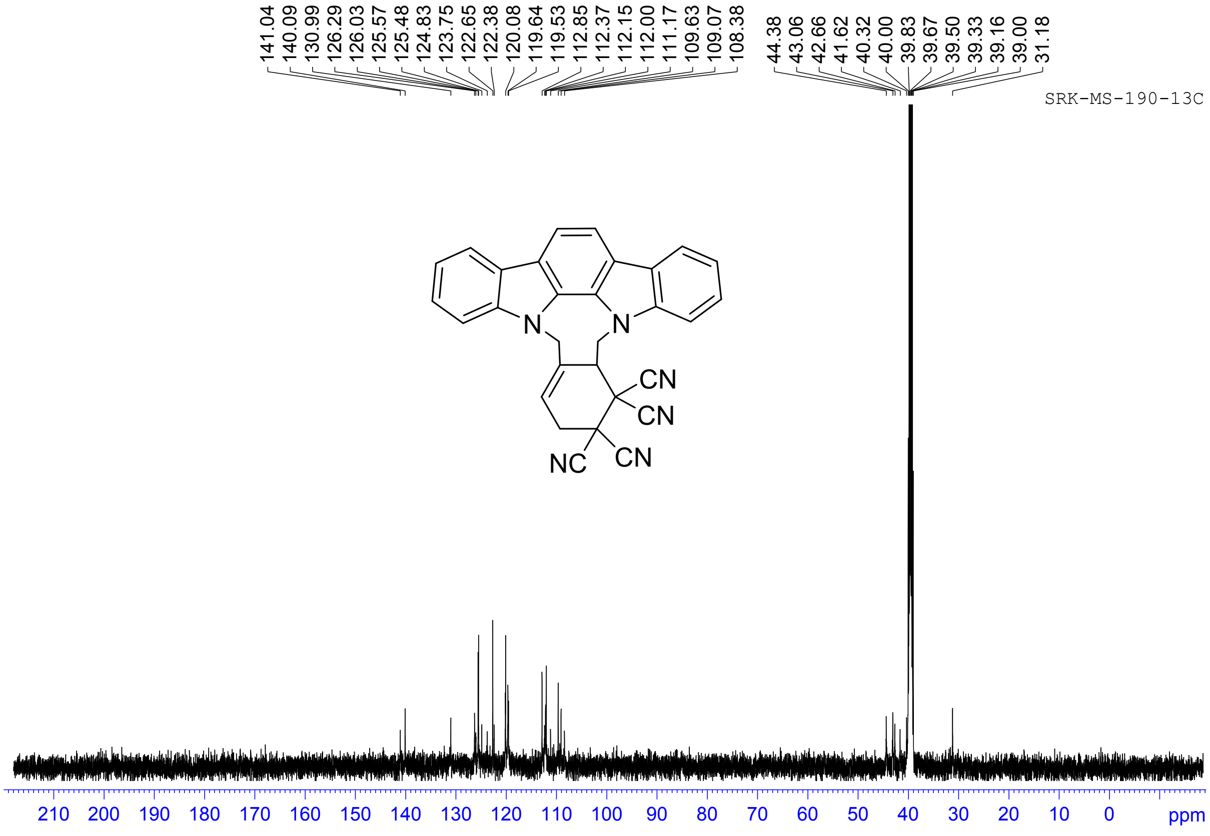
^{1}H and ^{13}C NMR of compound 30





^{1}H and ^{13}C NMR of compound 32





^{1}H and ^{13}C NMR of compound 34