Supporting Information

Synthesis of novel 2,8-disubstituted-5,11-dihydroindolo[3,2-*b*]carbazoles

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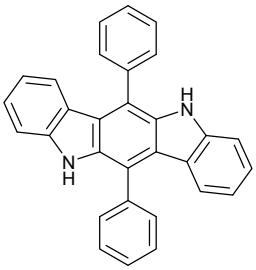
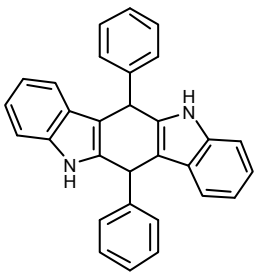
General Remarks

All chemicals were used as received from commercial sources without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz, ^{1}H; 75 MHz ^{13}C) or 400 (400 MHz, ^{1}H; 100 MHz ^{13}C) instruments. The chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) or the internal solvent signal of deuterated solvents (^{13}C and ^{1}H). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), m (multiplet) and dd (double doublet). Coupling constants, *J*, are reported in Hertz. Melting points (uncorrected) were measured using a Bruker ALPHA-P spectrometer. High resolution mass spectra were recorded on a Kratos MS50TC instrument. The ion source temperature was 150-250 °C as required. The low resolution spectra were recorded with a HP5989A MS instrument. Column chromatography was carried out using 70-230 mesh silica 60 (E.M. Merck) as stationary phase. For thin layer chromatography, analytical TLC plates (Alugram SIL G/UV_{254} and 70-230 mesh silica gel (Macherey-Nagel) were used. Visualization was accomplished with UV (254).



6,12-Diphenyl-5,11-dihydroindolo[3,2-b]carbazole (1)

This compound was obtained according to the previously reported procedure.[1] Experimental data was in full agreement with previously obtained data.



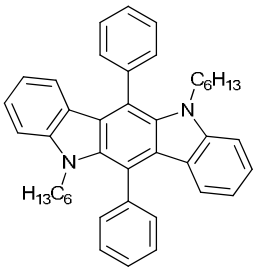
6,12-Diphenyl-5,6,11,12-tetrahydroindolo[3,2-*b*]carbazole (2)

A round-bottomed flask was charged with indole (5 g, 42.7 mmol), CH_3CN (85 mL) and benzaldehyde (4.334 mL, 42.7 mmol). While stirring, HI (561 μL, 4.27 mmol, 57%w/w) was

added dropwise at room temperature. The reaction mixture was placed in the dark and stirred for 17 hours at room temperature. The resulting precipitate was filtered off, washed with cold CH_3CN (20 mL) and dried *in vacuo*, yielding a mixture of *cis*- and *trans*-ICZ **2** (1:2) (97% yield) mp: >300 °C; δ_H (300 MHz; DMSO-d_6; Me_4Si) 5.59 (2 H, s), 5.69 (2 H, s), 6.76-7.51 (36 H, m), 10.69 (2 H, s, NH), 10.80 (2 H, s, NH); δ_C (75 MHz; DMSO-d_6; Me_4Si) 109.3, 109.9, 111.1, 118.2, 118.3, 118.5, 120.6, 120.7, 125.7, 126.4, 126.6, 128.3, 128.4, 128.5, 136.6, 137.1, 143.7, 144.2;[2] HRMS (EI): calcd. for $C_{30}H_{22}N_2$ $[M]^+$: 410.1783; found: 410.1784.

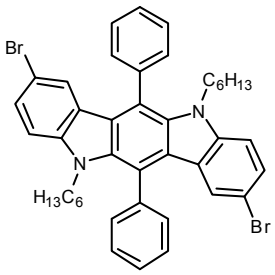
General procedure for the alkylation of ICZs

A round-bottomed flask containing **2** (1g, 2.44 mmol) in DMSO (36 mL) was charged with benzyltriethylammoniumchloride (5.5 mg, 0.02 mmol). A solution of NaOH (2.4 mL, 50% w/w) was added dropwise under Ar atmosphere, followed by the immediate addition of the appropriate alkylating reagent (9.74 mmol). The reaction mixture was stirred for 4 hours at room temperature and then poured into water (250 mL). The resulting precipitate was stirred for another 30 minutes, then filtered and washed with water (200 mL). Crystallization from ethyl acetate yielded the alkylated compound as a solid in 50-86% yield.



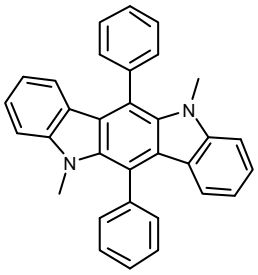
5,11-Dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (3)

The compound was synthesized according to the general procedure for the alkylation of ICZs and was obtained as a yellow solid (59% yield) mp: 204.6 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.82-0.91 (10 H, m), 1.08-1.25 (8 H, m), 1.52 (4 H, m), 3.78 (4 H, t, J 8.4), 6.51 (2 H, d, J 7.7), 6.80 (2 H, t, J 7.7), 7.24-7.34 (4 H, m), 7.66 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.1, 22.7, 26.5, 28.8, 31.6, 44.6, 108.3, 118.0, 122.5, 122.7, 123.1, 125.4, 128.2, 129.1, 130.7, 132.5, 139.1, 142.6; HRMS (EI): calcd. for $C_{42}H_{44}N_2$: 576.3504; found: 576.3533.



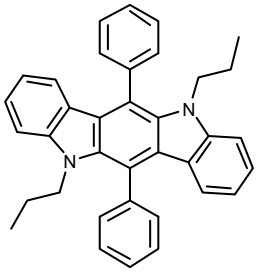
2,8-Dibromo-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (4)

A round-bottomed flask containing **6a** (2 g, 2.44 mmol) was flushed with Ar and charged with a solution of N-bromosuccinimide (2.5 g, 13.8 mmol) in HOAc (28 mL). The reaction mixture was stirred for 4 hours at room temperature. The resulting black solution was poured into water (200 mL) and extracted with CH_2Cl_2 (3 x 75 mL). The organic layers were combined, washed firstly with a saturated $NaHCO_3$ solution until no more CO_2 evolved and secondly with brine (100 mL). The organic layer was then dried on anhydrous $MgSO_4$ and concentrated under reduced pressure, resulting in a black powder, which was purified by crystallization from ethyl acetate. Compound **4** was obtained as a bright yellow solid (82% yield) mp: 275.6 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.82-0.90 (10 H, m), 1.05-1.24 (8 H, m), 1.48 (4 H, m), 3.76 (4 H, t, J 8.3), 6.50 (2 H, d, J 1.7), 7.12 (2 H, d, J 8.6), 7.39 (2 H, dd, J 8.6 and 1.7), 7.64 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.1, 22.7, 26.4, 28.8, 31.5, 109.7, 110.7, 118.3, 122.4, 124.6, 125.3, 128.2, 128.7, 129.3, 130.4, 132.7, 138.1, 141.3; HRMS (EI): calcd. for $C_{42}H_{42}Br_2N_2$ $[M]^+$: 732.1715; found: 732.1719.



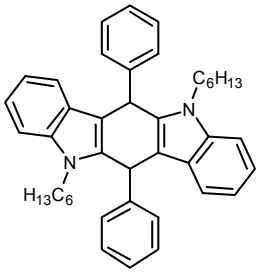
5,11-Dimethyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (5a)

The compound was synthesized according to the general procedure for the alkylation of ICZs and was obtained as a yellow solid (59% yield) mp: >300 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 3.36 (6 H, s), 6.67 (2 H, m), 6.84 (2 H, m), 7.26-7.34 (4 H, m), 7.63 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 32.4, 108.1, 118.0, 122.3, 122.4, 122.9, 125.5, 128.2, 128.8, 128.9, 129.6, 130.3, 131.1, 133.5, 138.9, 143.4; HRMS (EI): calcd. for $C_{32}H_{24}N_2$ $[M]^+$: 436.1939; found: 436.1939.



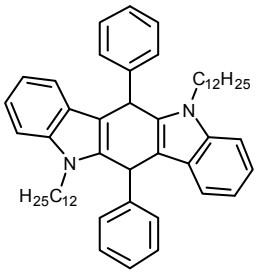
5,11-Dipropyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (5b)

The compound was synthesized according to the general procedure for the alkylation of ICZs and was obtained as a yellow solid (86% yield) mp: 278.0 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.55 (6 H, t, J 7.1), 1.53-1.58 (4 H, m), 3.73 (4 H, t, J 7.8), 6.53 (2 H, d, J 7.9), 6.80 (2 H, t, J 7.1), 7.24-7.34 (4 H, m), 7.64 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 11.0, 22.1, 46.0, 108.4, 118.0, 122.5, 122.6, 123.1, 125.4, 128.2, 129.1, 130.7, 132.5, 139.1, 142.6; HRMS (EI): calcd. for $C_{36}H_{32}N_2$ $[M]^+$: 492.2565; found: 492.2563.



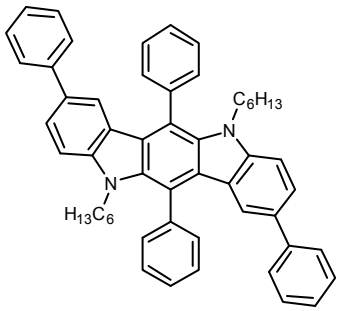
5,11-Dihexyl-6,12-diphenyl-5,6,11,12-tetrahydroindolo-[3,2-*b*]carbazole (6a)

The compound was synthesized according to the general procedure for the alkylation of ICZs and was obtained as a white solid, composed of a mixture of *cis*- and *trans*-ICZ **6a** (1:3) (67% yield) mp: 240.4 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.65 (2 H, m), 0.85 (12 H, t, J 6.4), 1.12-1.20 (26 H, m), 1.53 (4 H, m), 3.78-4.00 (8 H, m), 5.64 (2 H, s), 5.75 (2 H, s), 6.91-7.46 (36 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.2, 22.7, 26.9, 29.2, 31.6, 40.5, 44.4, 109.4, 111.8, 118.9, 119.3, 121.1, 125.9, 126.7, 128.7, 129.2, 135.8, 137.4, 143.6, 144.1; HRMS (EI): calcd. for $C_{42}H_{46}N_2$ $[M]^+$: 578.3661; found: 578.3661.



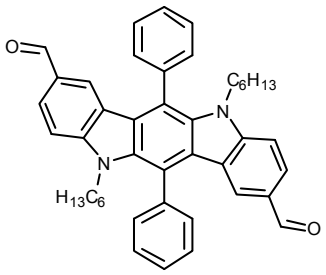
5,11-Didodecyl-6,12-diphenyl-5,6,11,12-tetrahydroindolo-[3,2-*b*]carbazole (6b)

The compound was synthesized according to the general procedure for the alkylation of ICZs and was obtained as a white solid (50% yield, only *trans*-isomer) mp: 192.3 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.65 (2 H, m), 0.88 (6 H, m), 1.14-1.26 (36 H, m), 1.53 (2 H, m), 3.78-4.01 (4 H, m), 5.75 (2 H, s), 6.93 (2 H, t, J 7.3), 7.05-7.23 (10 H, m), 7.32-7.34 (4 H, m), 7.43 (2 H, d, J 7.5); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.3, 22.8, 27.3, 29.3, 29.5, 29.7, 29.8, 32.1, 40.5, 44.4, 109.4, 111.7, 118.9, 119.3, 121.1, 125.9, 126.7, 128.7, 129.1, 135.9, 137.4, 144.2; HRMS (EI): calcd. for $C_{54}H_{70}N_2$ $[M]^+$: 746.5539; found: 746.5549.



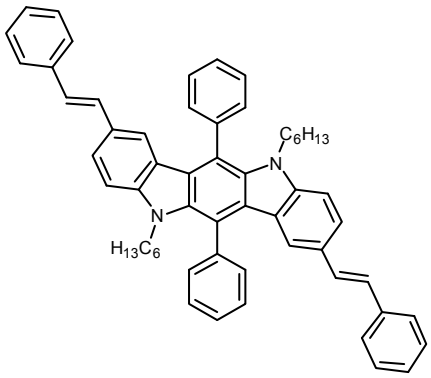
5,11-Dihexyl-2,6,8,12-tetraphenyl-5,11-dihydroindolo-[3,2-*b*]carbazole (7)

A round-bottomed flask containing **6** (100 mg, 0.14 mmol), benzeneboronic acid (0.34 mmol) and $Pd(PPh_3)_4$ (0.007 mmol) in THF (5 mL) was flushed with Ar. A solution of potassium *tert*-butoxide (76.4 mg, 0.68 mmol) in water (1.5 mL) was added. The resulting reaction mixture was heated to reflux and stirred for 30 minutes, subsequently poured into water (20 mL) and extracted with diethyl ether (3 x 30 mL). The organic layers were combined, dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica using petroleum ether/ethyl acetate 9/1 as eluent yielded the expected compound as a yellow solid (92 % yield) mp: 260.3 °C; δ_H (300 MHz; CD_2Cl_2) 0.83-0.96 (10 H, m), 1.11-1.26 (8 H, m), 1.56 (4 H, m), 3.89 (4 H, t, J 7.7), 6.72 (2 H, s), 7.23-7.26 (2 H, m), 7.34-7.36 (10 H, m), 7.61-7.72 (12 H, m); δ_C (75 MHz; CD_2Cl_2) 14.2, 22.9, 26.7, 29.1, 31.8, 44.9, 108.9, 118.7, 121.1, 123.2, 123.7, 124.7, 126.3, 126.9, 128.6, 128.9, 129.5, 130.7, 130.9, 133.1 139.1, 142.1, 142.4; HRMS (EI): calcd. for $C_{54}H_{52}N_2$ $[M]^+$: 728.4130; found: 728.4153.



2,8-Diformyl-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (8)

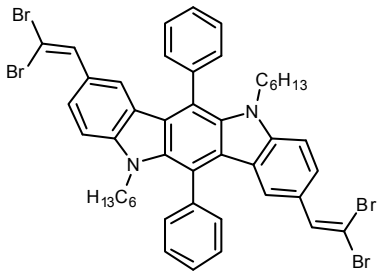
A round-bottomed flask was charged with **6** (1980 mg, 2.69 mmol) and dry THF (97 mL), flushed with Ar and cooled to –78 °C. At –78 °C *n*-BuLi (4.31 mL, 10.78 mmol, 2.5 M in hexane) was added dropwise. The mixture was stirred for 60 minutes at –78 °C, followed by the dropwise addition of dry DMF (1 mL, 13 mmol). The reaction mixture was allowed to warm up to room temperature over the course of 30 minutes. The reaction mixture was then quenched with HCl (5 mL, 2M) and extracted with diethyl ether (3 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting orange precipitate was purified by crystallization from ethyl acetate. Compound **8** was obtained as an yellow solid (81% yield) mp: 279.2 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.83-0.94 (10 H, m), 1.10-1.26 (8 H, m), 1.58 (4 H, m), 3.90 (4 H, t, J 8.1), 6.85 (2 H, s), 7.34 (2 H, d, J 8.5), 7.69-7.73 (10 H, m), 7.93 (2 H, d, J 7.7), 9.58 (2 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.1, 22.6, 26.4, 29.0, 31.5, 44.9, 108.9, 119.2, 122.8, 123.3, 125.9, 128.0, 129.0, 129.6, 130.3, 133.2, 137.7, 146.1, 191.7; HRMS (EI): calcd. for $C_{44}H_{44}N_2O_2$ $[M]^+$: 632.3403; found: 632.3404.



2,8-Bis(2-phenylethenyl)-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (9)

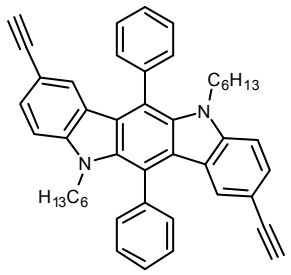
A round bottom flask was charged with potassium *tert*-butoxide (70.9 mg, 0.632 mmol) and dry THF (10 mL) under Ar. The solution was cooled to 0 °C, followed by the addition of diethylbenzyl phosphonate (132 µL, 0.632 mmol) and a solution of **8** (100 mg, 0.158 mmol) in THF (5 mL). The reaction mixture was stirred for 60 minutes at room temperature and then

quenched with a saturated NH_4Cl solution (10 mL) and extracted with diethyl ether (3 x 30 mL). The organic layers were combined, washed with brine, dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting yellow solid was purified by column chromatography on silica using petroleum ether/ethyl acetate 8/2 as eluent yielding **9** (74% yield) mp: 260.9 °C; δ_H (300 MHz; CD_2Cl_2) 0.84-0.98 (10 H, m), 1.09-1.26 (8 H, m), 1.55 (4 H, m), 3.87 (4 H, t, J 7.7), 6.62-6.67 (4 H, m), 6.96 (2H, d, J 16.2), 7.20-7.49 (14 H, m), 7.76 (10 H, m); δ_C (75 MHz; CD_2Cl_2) 14.2, 22.9, 26.7, 29.2, 31.8, 44.9, 108.7, 118.8, 120.4, 123.0, 123.6, 125.3, 125.4, 126.3, 127.2, 127.5, 128.7, 128.9, 129.6, 129.8, 130.9, 133.1, 138.4, 139.0, 142.7; MS (ESI): *m/z* 781 ([M^+], 100%), 782 ([M+H]$^+$, 52).



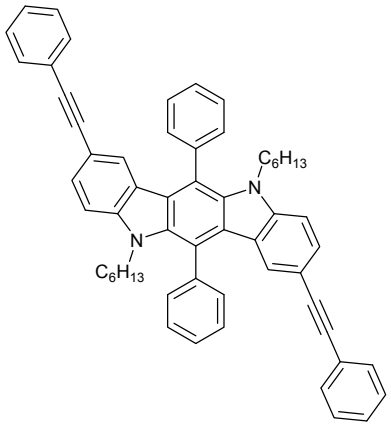
2,8-Bis(2,2-dibromovinyl)-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (10)

A solution of PPh_3 (305 mg, 1.264 mmol) in CH_2Cl_2 (1 mL) was added at 0 °C and under Ar to a mixture of CBr_4 (193 mg, 0.632 mmol) and CH_2Cl_2 (2 mL) in a round-bottomed flask. The reaction mixture was stirred at 0 °C for 30 minutes, followed by the addition of a solution of **8** (100 mg, 0.158 mmol) in CH_2Cl_2 (2 mL). The resulting reaction mixture was stirred at room temperature for another 30 minutes, followed by aqueous work-up and extraction with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica using heptane/toluene 9/1 as eluent yielded **10** as a yellow solid (83% yield) mp: 196.9 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.83-0.90 (10 H, m), 1.09-1.26 (8 H, m), 1.48 (4 H, m), 3.69 (4 H, t, J 8.4), 7.07 (2 H, s), 7.21 (2 H, d, J 8.5), 7.29 (2 H, s), 7.47 (2 H, d, J 8.5), 7.64 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.1, 22.7, 26.4, 28.9, 31.6, 44.7, 85.3, 108.2, 118.6, 122.6, 122.8, 125.2, 126.8, 128.6, 129.4, 130.5, 133.1, 137.6, 138.4, 142.5; MS (ESI): *m/z* 944 ([M^+], 100%), 946 ([M^+], 66), 942 ([M^+], 47).



2,8-Diethynyl-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (11)

A glass vial was charged with **10** (100 mg, 0.106 mmol), THF (3 mL), flushed with Ar and cooled to –78 °C. At –78 °C *n*-BuLi (254 µL, 0.635 mmol, 2.5 M in hexane) was added dropwise. The reaction mixture was stirred for 90 minutes at –78 °C and another 30 minutes at room temperature. The reaction was then quenched with a saturated NH_4Cl solution (2 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined, dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting yellow precipitate was further purified by column chromatography on silica using heptane/toluene 8/2 as eluent yielding **11** as a yellow solid (65% yield) mp: 238.0 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.82-0.90 (10 H, m), 1.05-1.25 (8 H, m), 1.47 (4 H, m), 2.87 (2 H, s), 3.78 (4 H, t, J 8.1), 6.60 (2 H, s), 7.18 (2 H, d, J 8.5), 7.45 (2 H, d, J 8.5), 7.65 (10 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 14.1, 22.7, 26.4, 28.8, 31.5, 44.7, 74.4, 85.5, 108.3, 111.0, 118.5, 122.6, 122.8, 127.0, 128.6, 129.3, 129.6, 130.4, 132.9, 138.2, 142.5; HRMS (EI): calcd. for $C_{46}H_{44}N_2$ $[M]^+$: 624.3504; found: 624.3518.



2,8-Bis(phenylethynyl)-5,11-dihexyl-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (12)

A round-bottomed flask was charged with **11** (150 mg, 0.24 mmol), $Pd(PPh_3)_4$ (0.024 mmol) and CuI (0.012 mmol) and flushed with Ar. A 1:1 mixture of THF: iPr_2NH (10 mL) was added, followed by the addition of bromobenzene (152 µL, 1.44 mmol). The reaction mixture was heated to reflux and stirred for 30 minutes. The reaction mixture was poured into water

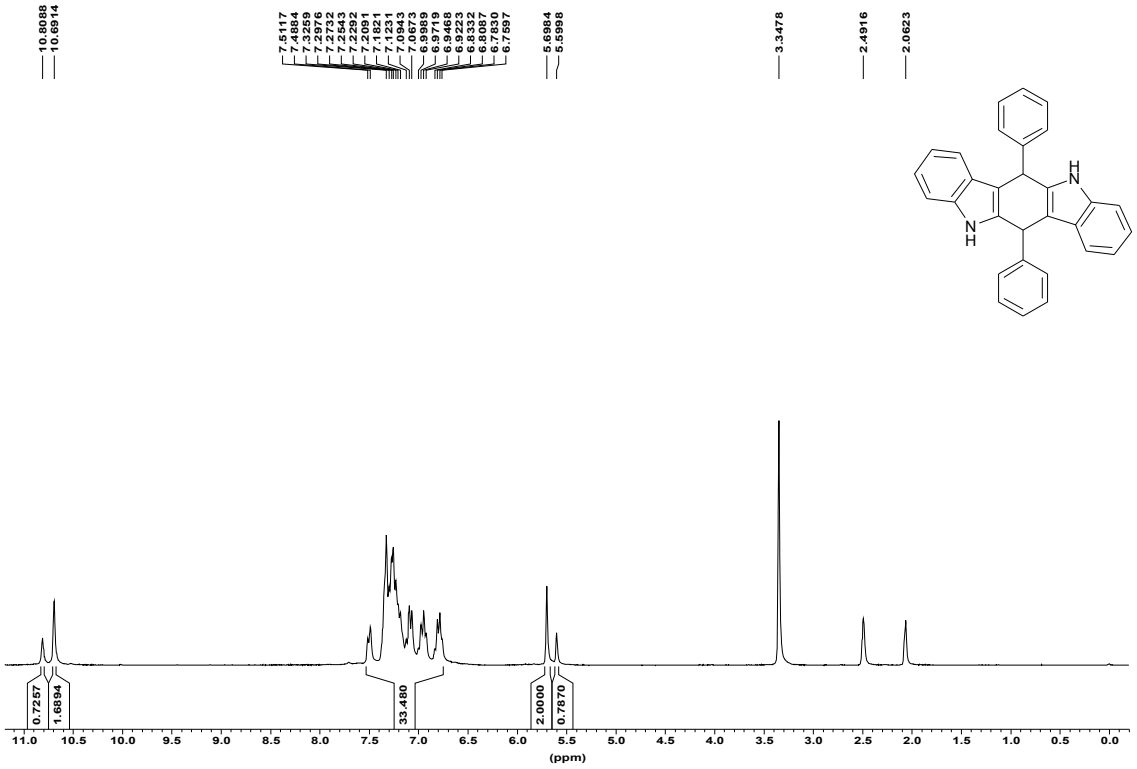
(50 mL), extracted with diethyl ether (3 x 50 mL) and washed with brine (50 mL). The organic layers were combined, dried on anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography on silica using petroleum ether/ethyl acetate 8/2 as eluent yielded **12** as a yellow solid (57% yield) mp: 233.2 °C; δ_H (300 MHz; CD_2Cl_2) 0.84-0.93 (10 H, m), 1.11-1.26 (8 H, m), 1.53 (4 H, m), 3.83 (4 H, t, J 8.1), 6.61 (2 H, s), 7.25-7.51 (14 H, m), 7.70 (10 H, m); δ_C (75 MHz; CD_2Cl_2) 14.1, 22.9, 26.6, 29.1, 31.8, 44.9, 87.1, 91.5, 108.8, 112.3, 118.9, 122.8, 123.2, 124.3, 126.5, 128.0, 128.7, 128.8, 129.2, 129.6, 130.7, 131.6, 133.1, 138.5, 142.6; MS (ESI): *m/z* 944 ($[M]^+$, 100%), 946 ($[M]^+$, 66), 942 ($[M]^+$, 47).

Notes and References

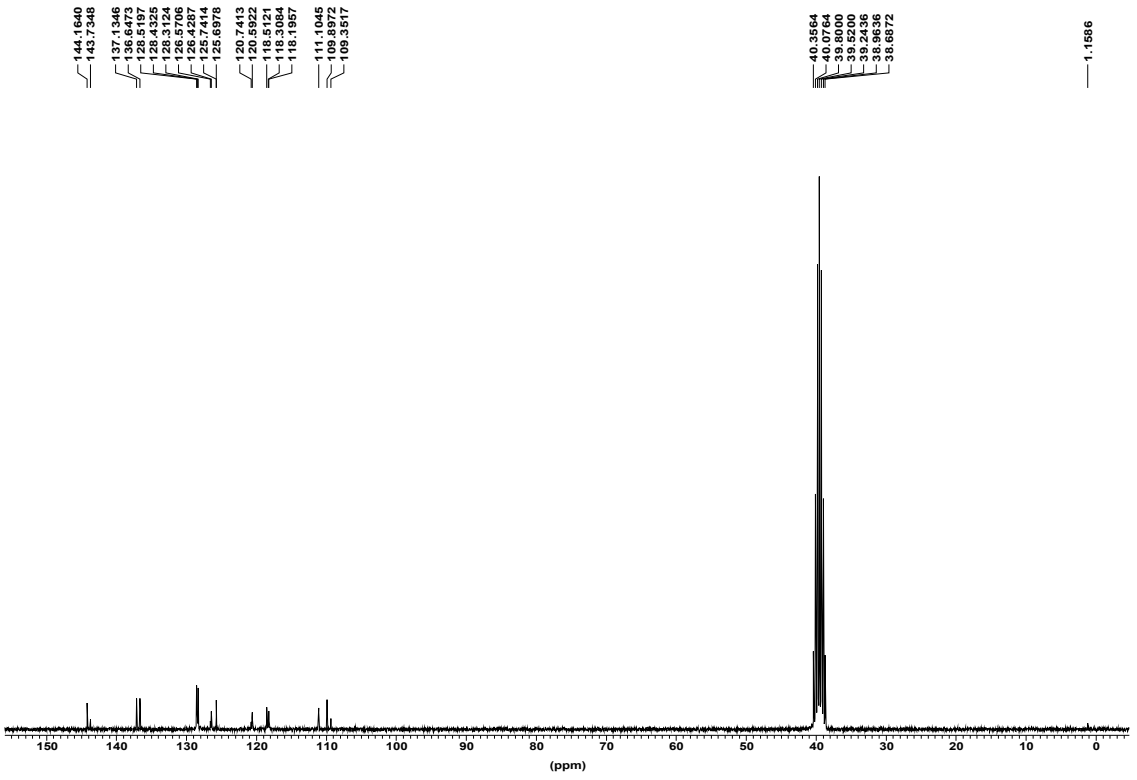
1. R. Gu, S. Van Snick, K. Robeyns, L. Van Meervelt and W. Dehaen, *Org. Biomol. Chem.*, 2009, **7**, 380-385.

2. Benzylic carbon signal is masked by the DMSO residual signal.

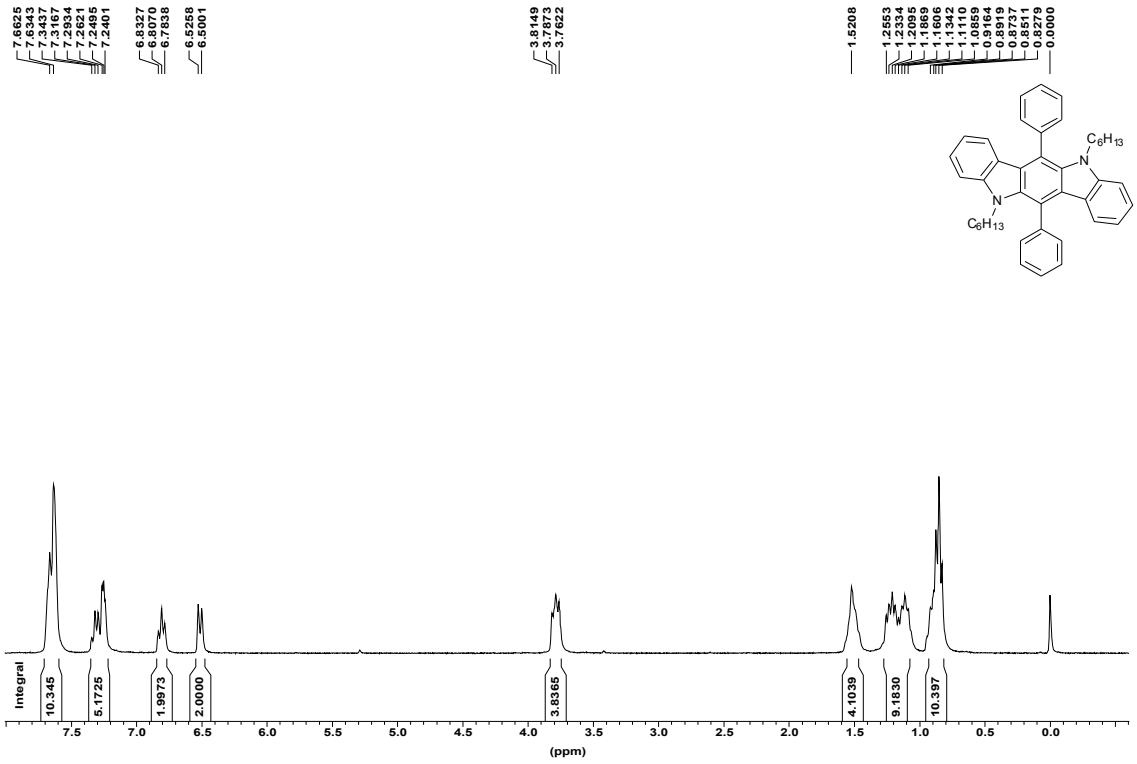
^{1}H NMR of compound **2** in DMSO-d_6



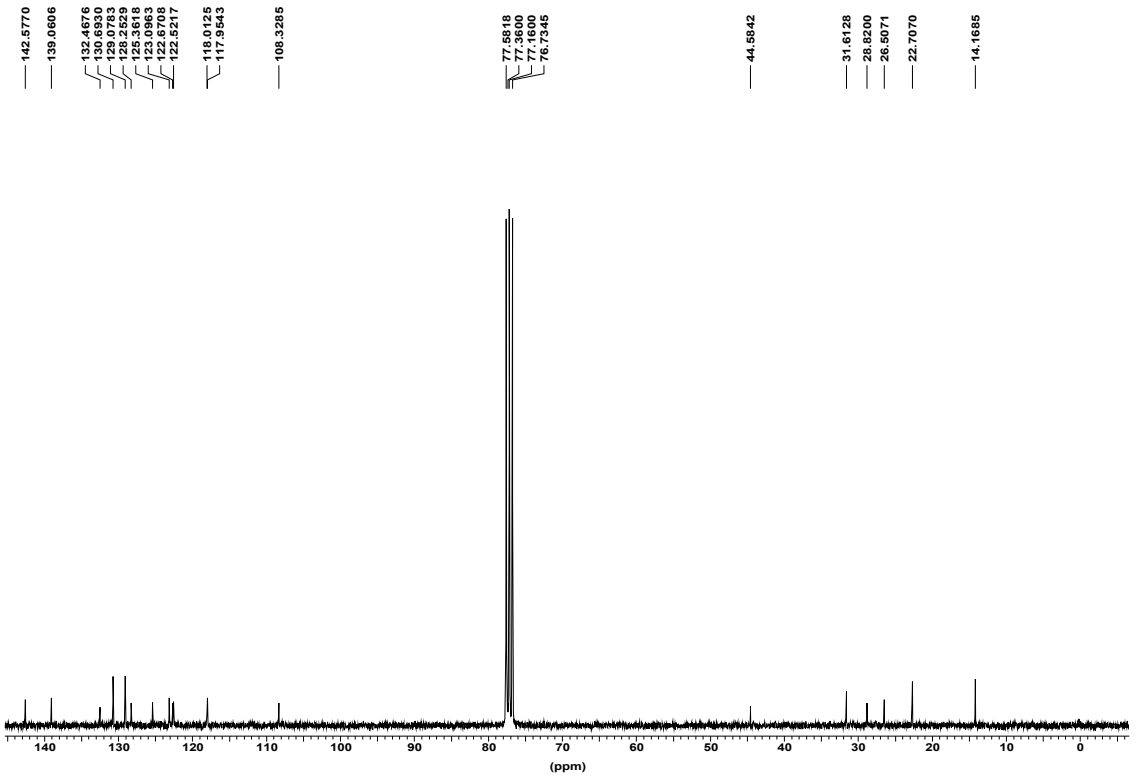
^{13}C spectrum of compound **2** in DMSO-d_6



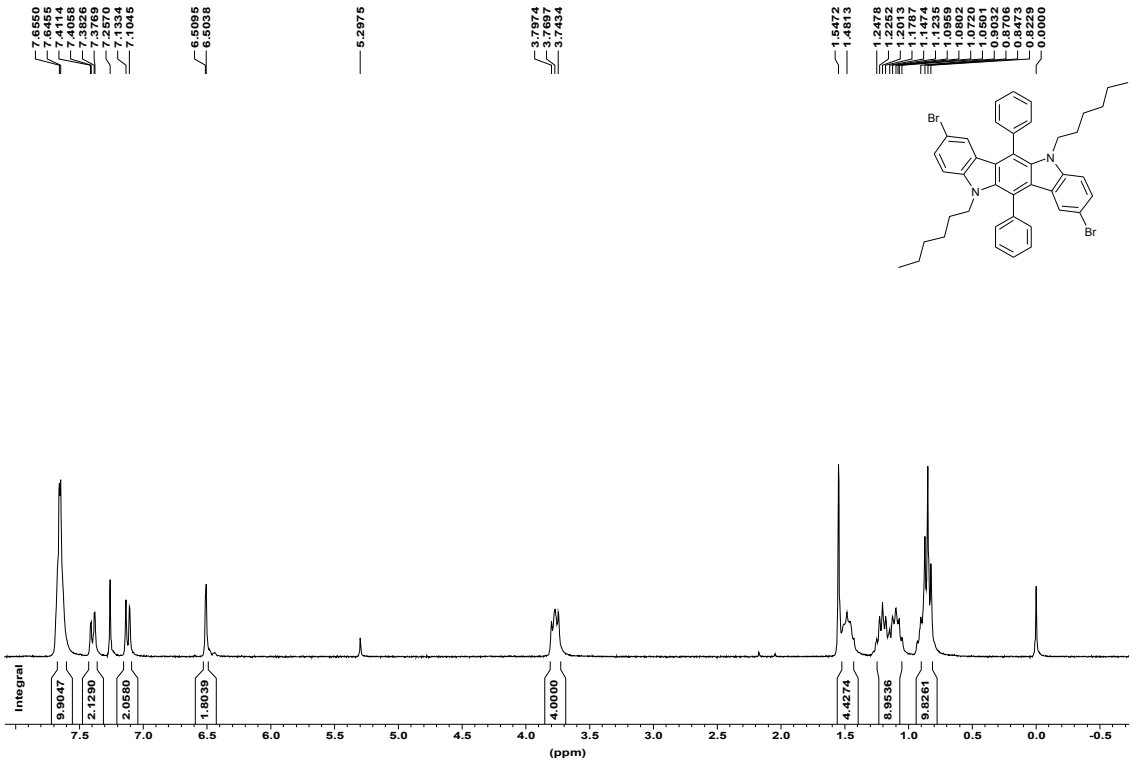
^{1}H NMR of compound **3** in $CDCl_3$



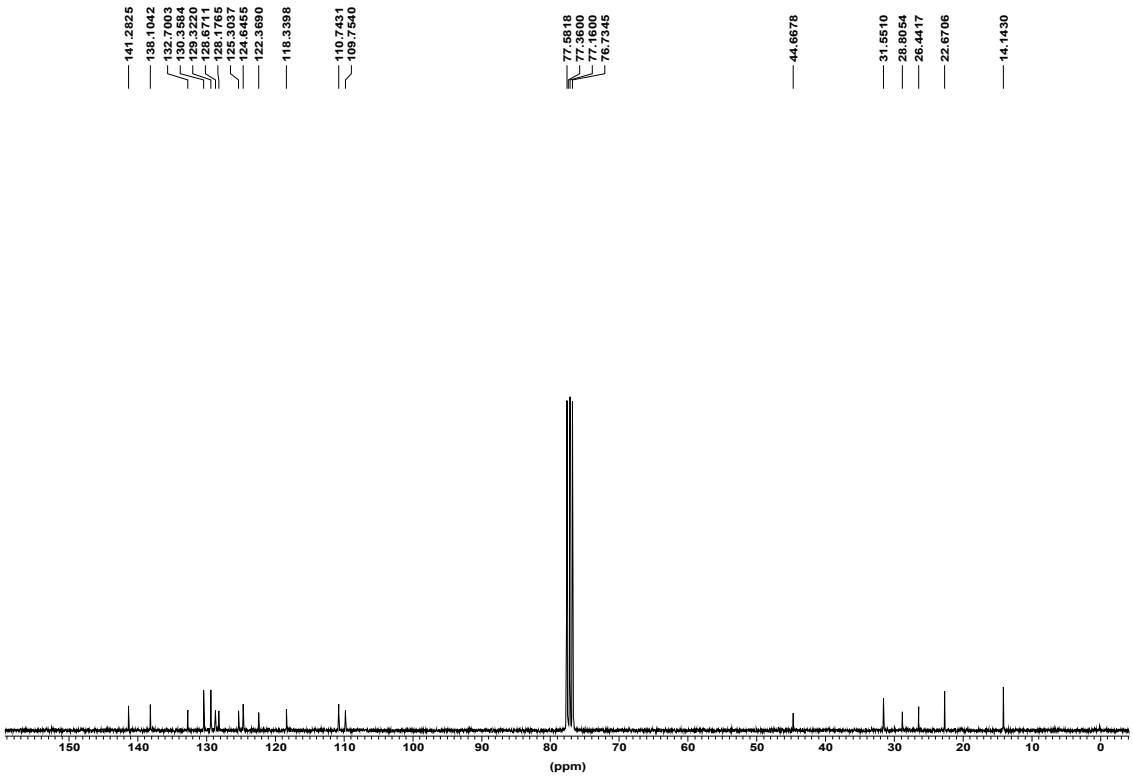
^{13}C spectrum of compound **3** in $CDCl_3$



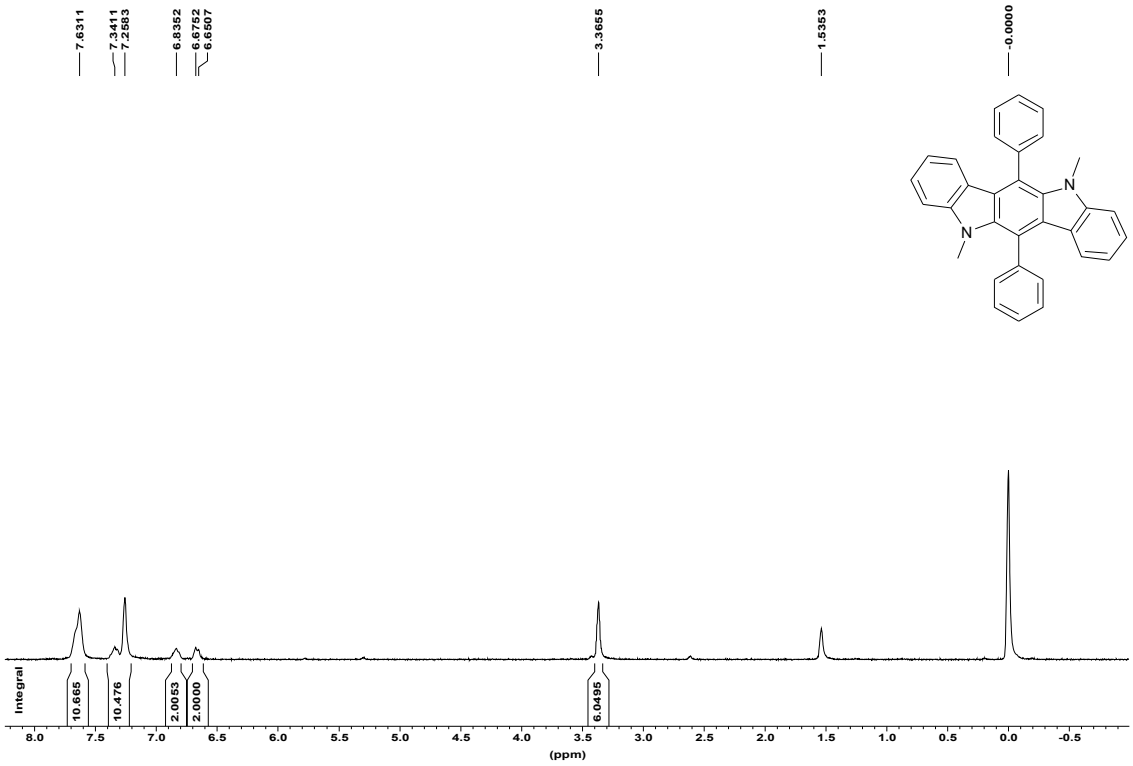
^{1}H NMR of compound **4** in $CDCl_3$



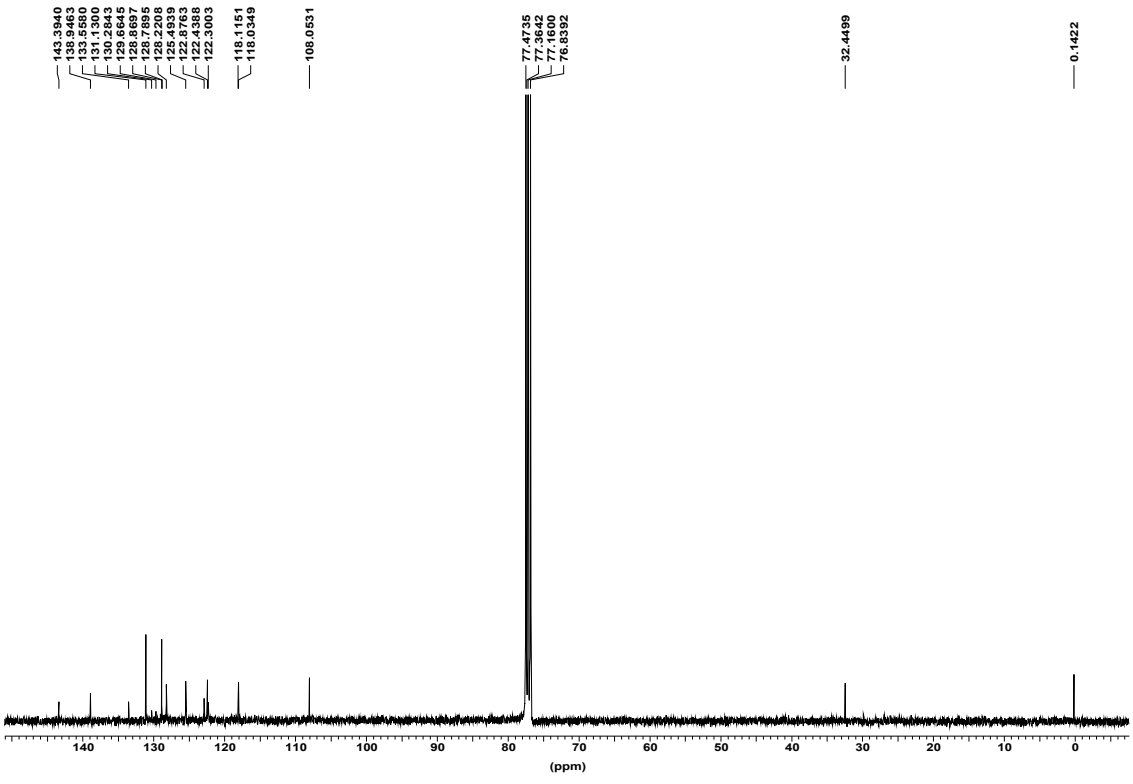
^{13}C spectrum of compound **4** $CDCl_3$



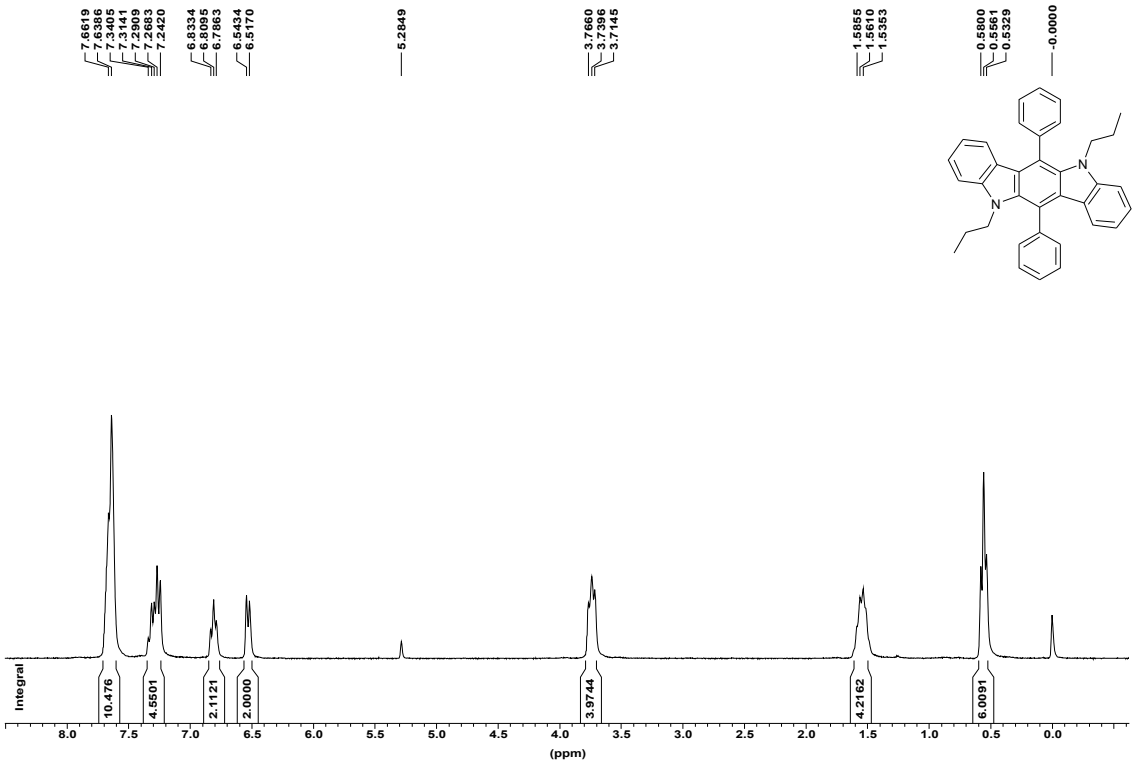
^{1}H NMR of compound **5a** in $CDCl_3$



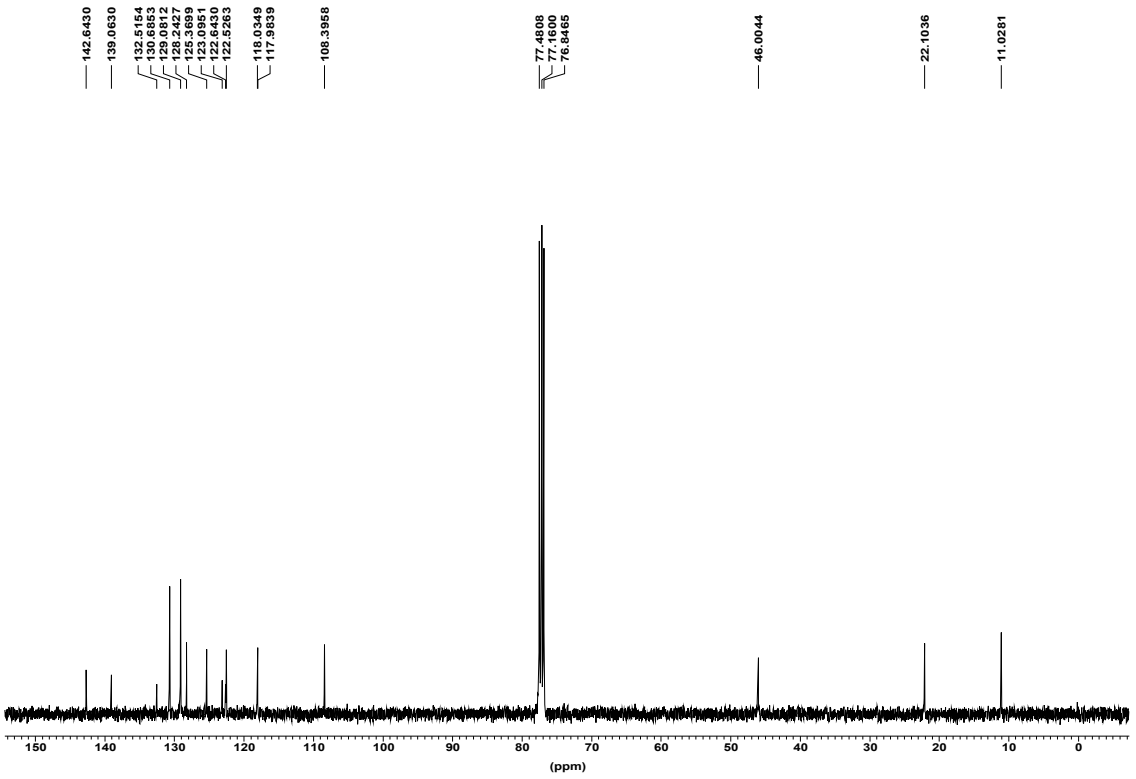
^{13}C spectrum of compound **5a** in $CDCl_3$



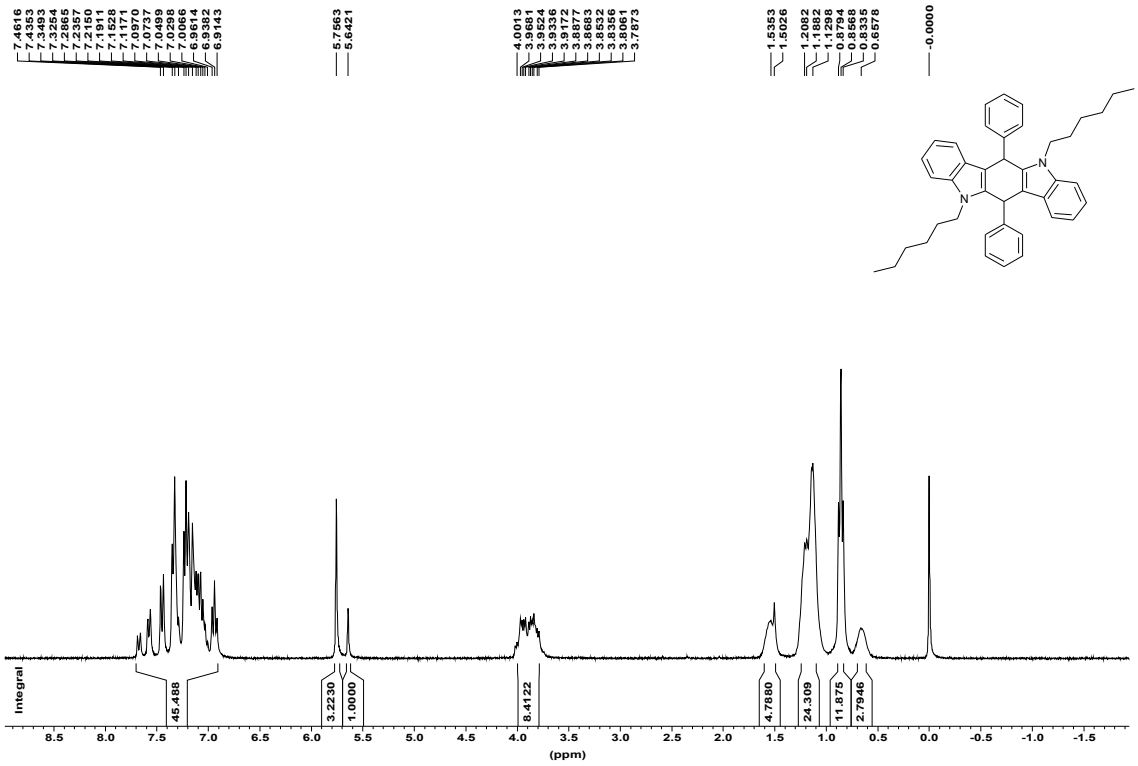
^{1}H NMR of compound **5b** in $CDCl_3$



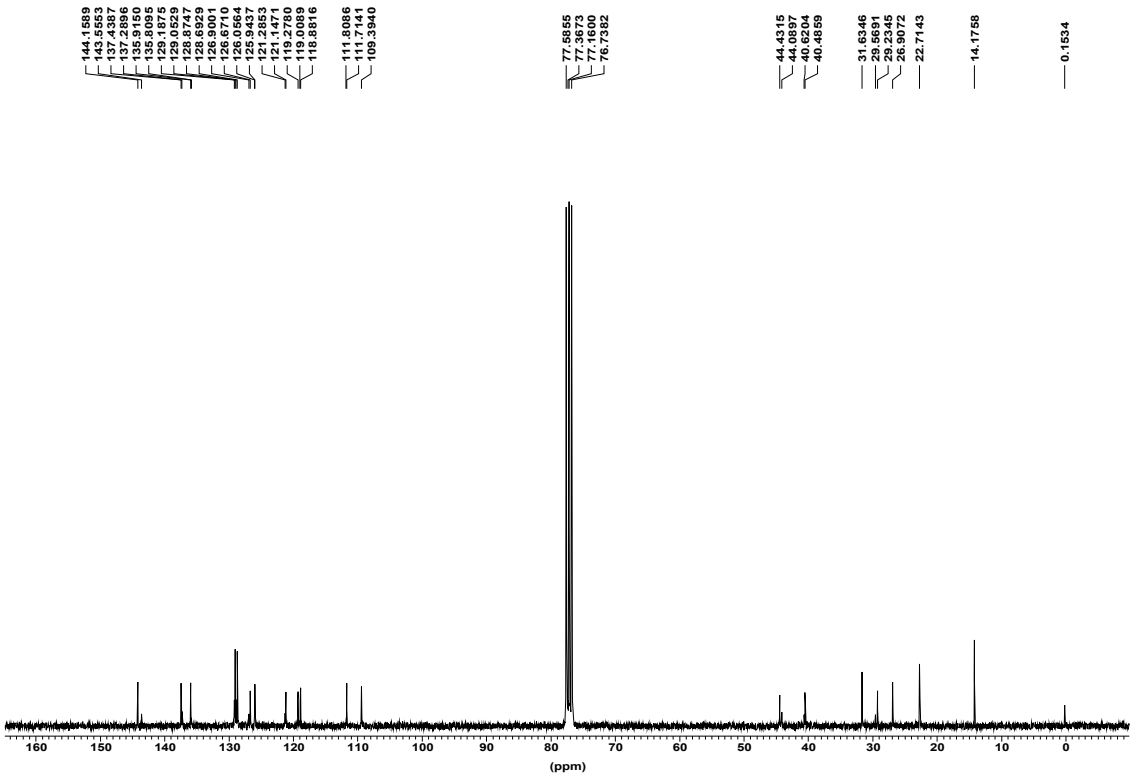
^{13}C spectrum of compound **5b** in $CDCl_3$



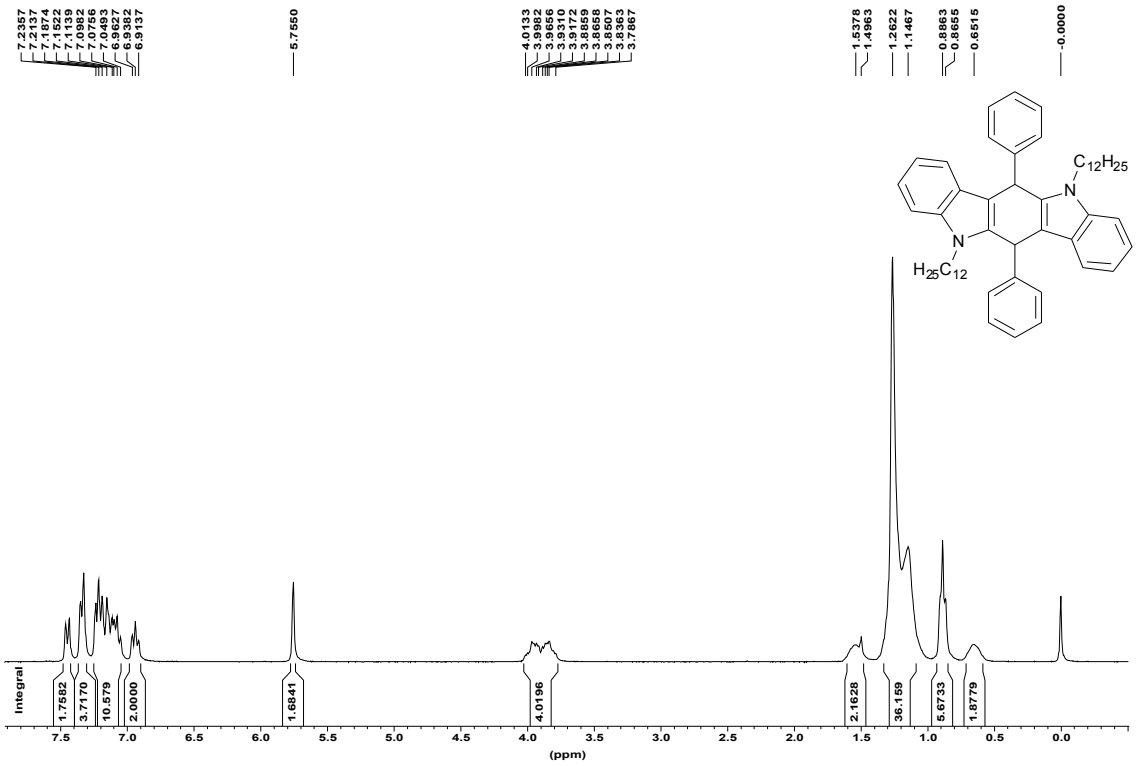
^{1}H NMR of compound **6a** in $CDCl_3$



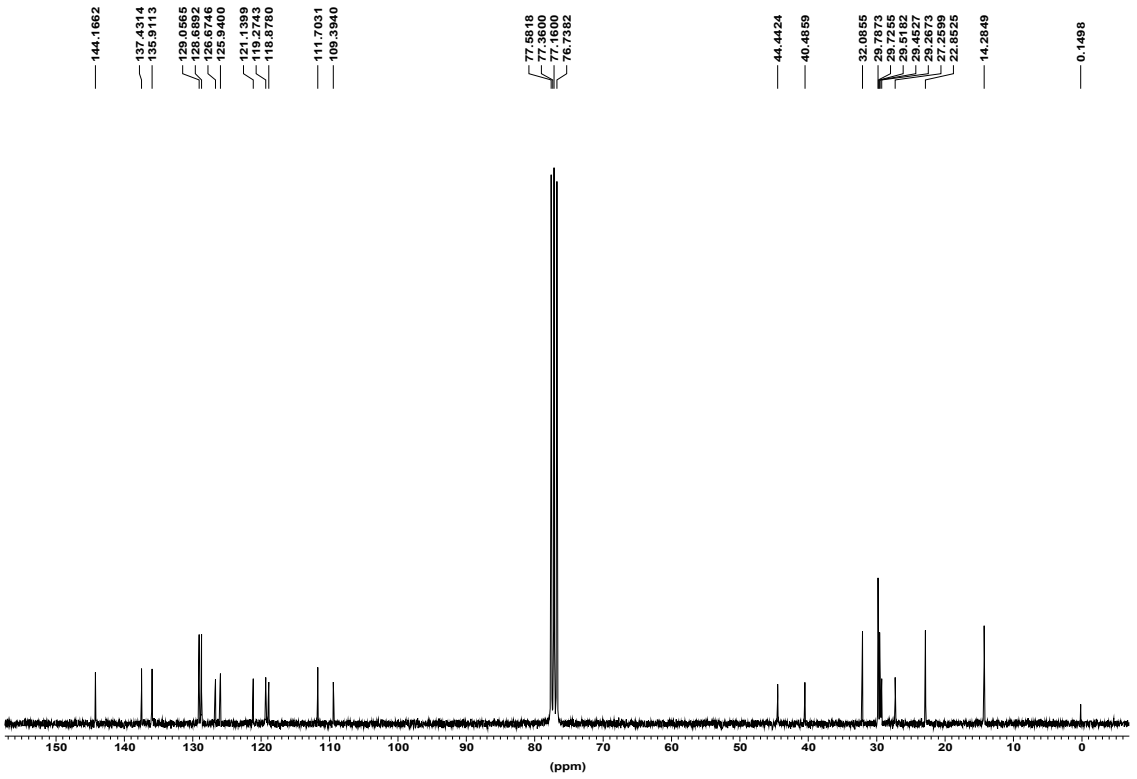
^{13}C spectrum of compound **6a** in $CDCl_3$



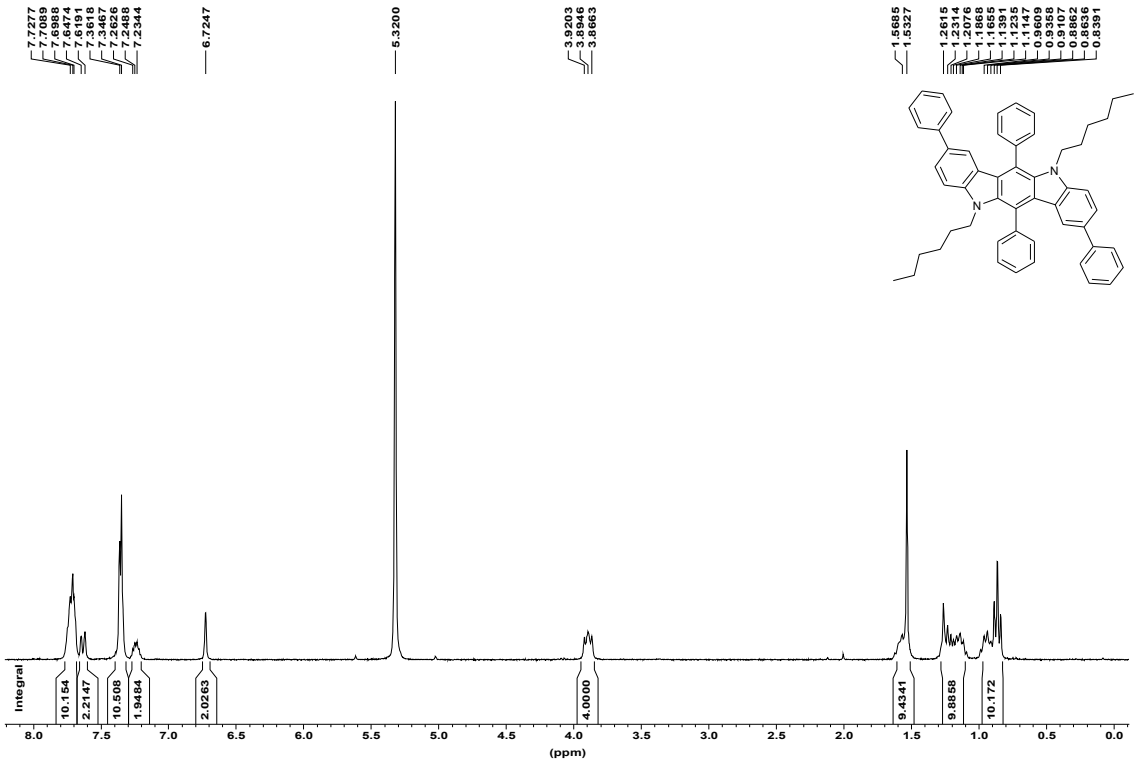
^{1}H NMR of compound **6b** in $CDCl_3$



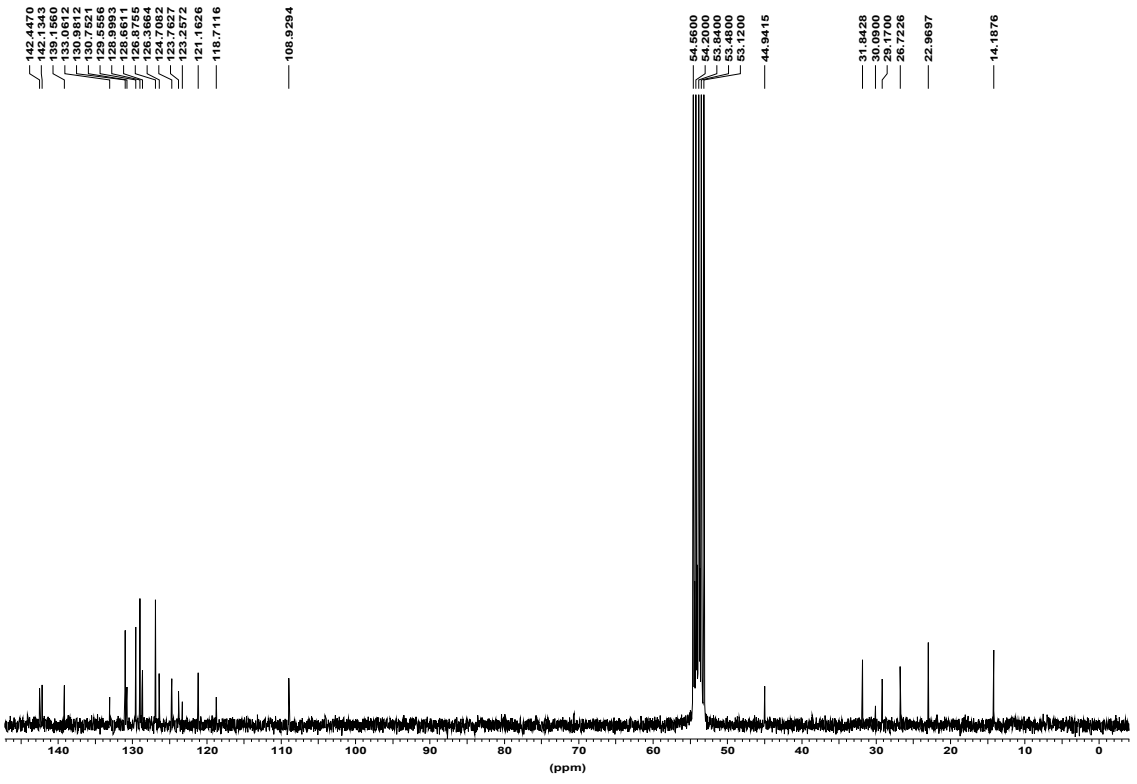
^{13}C spectrum of compound **6b** in $CDCl_3$



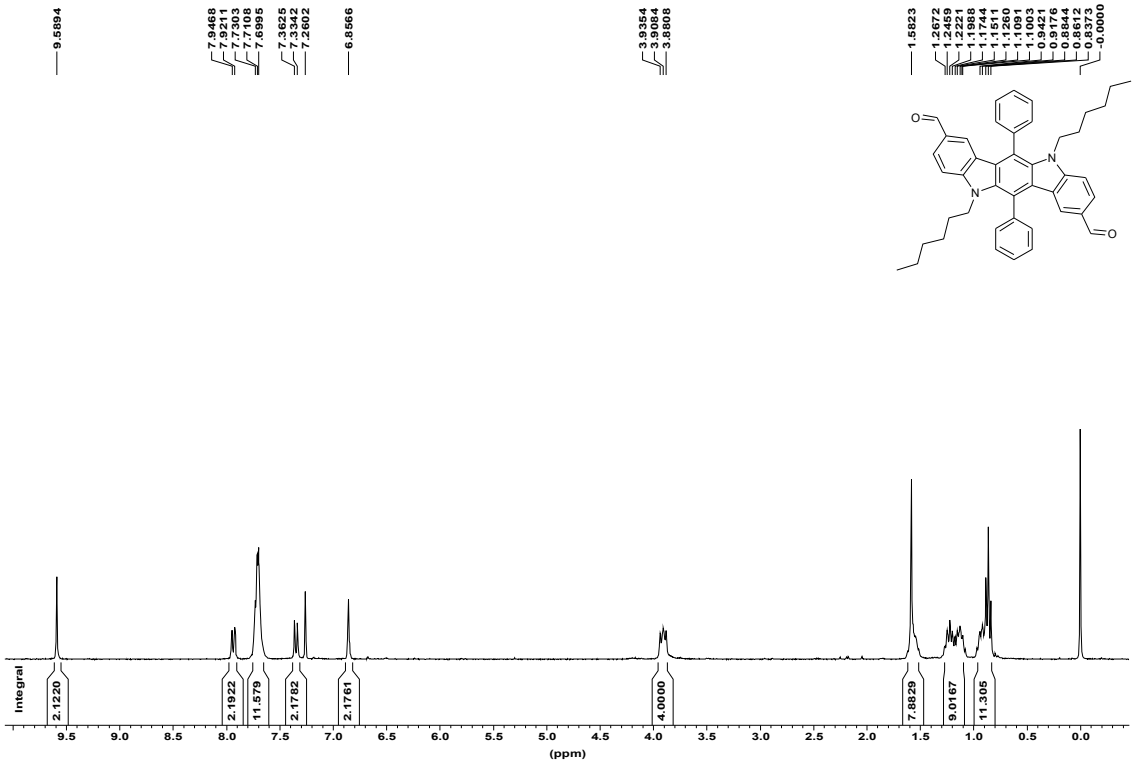
^{1}H NMR of compound **7** in CD_2Cl_2



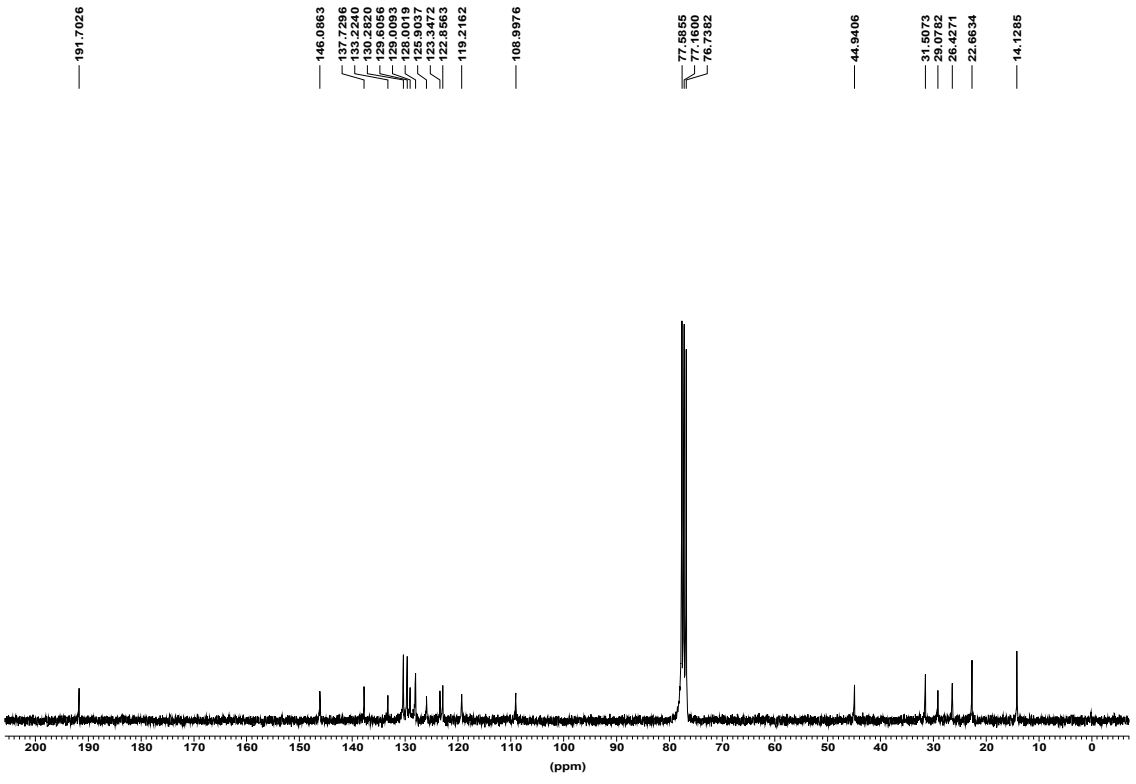
^{13}C NMR of compound **7** in CD_2Cl_2



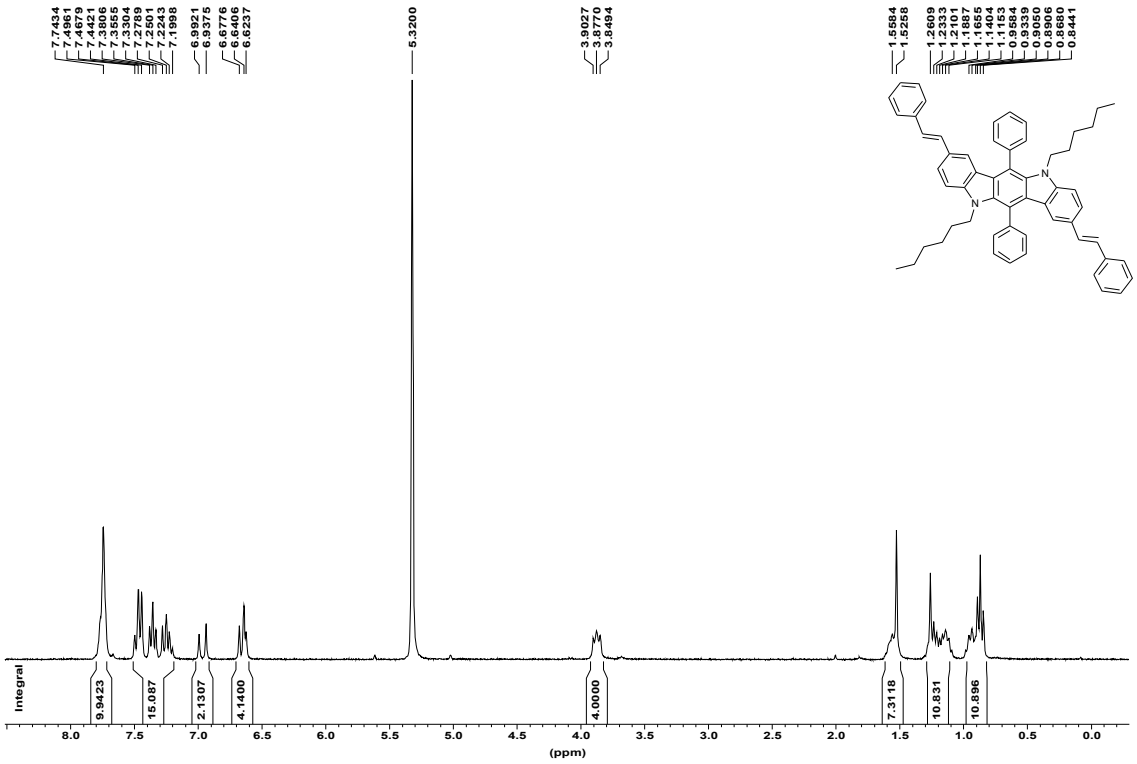
^{1}H NMR of compound **8** in $CDCl_3$



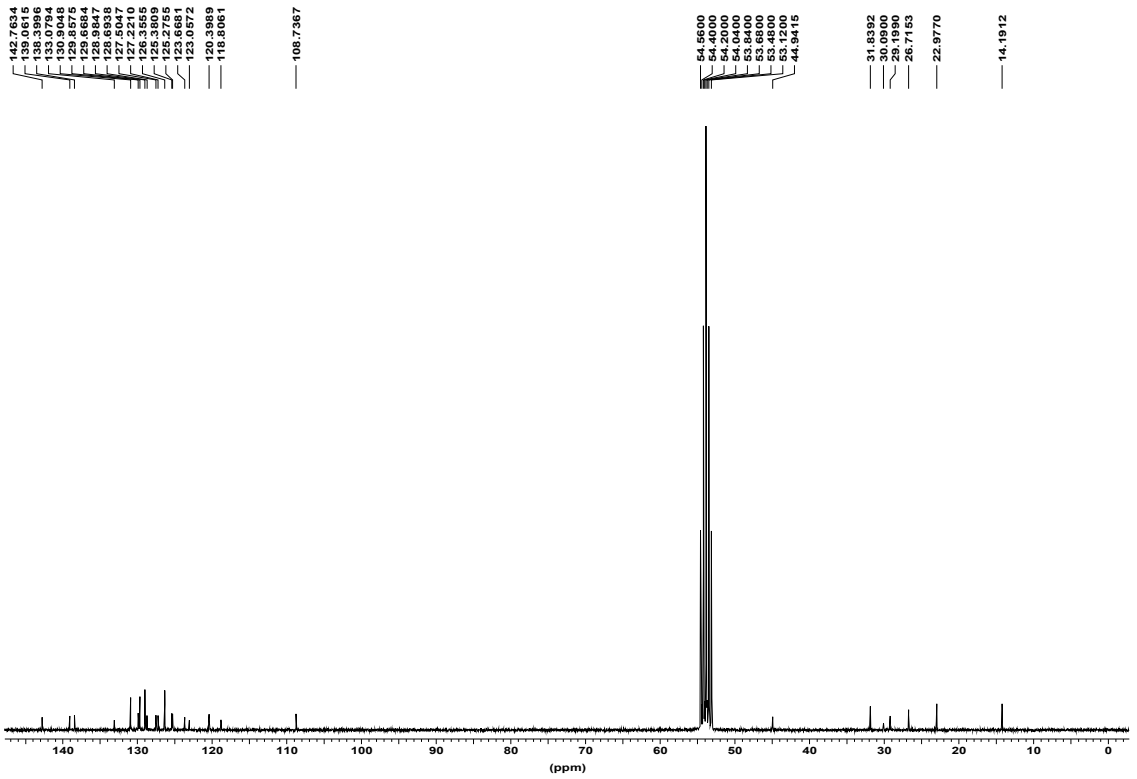
^{13}C spectrum of compound **8** in $CDCl_3$



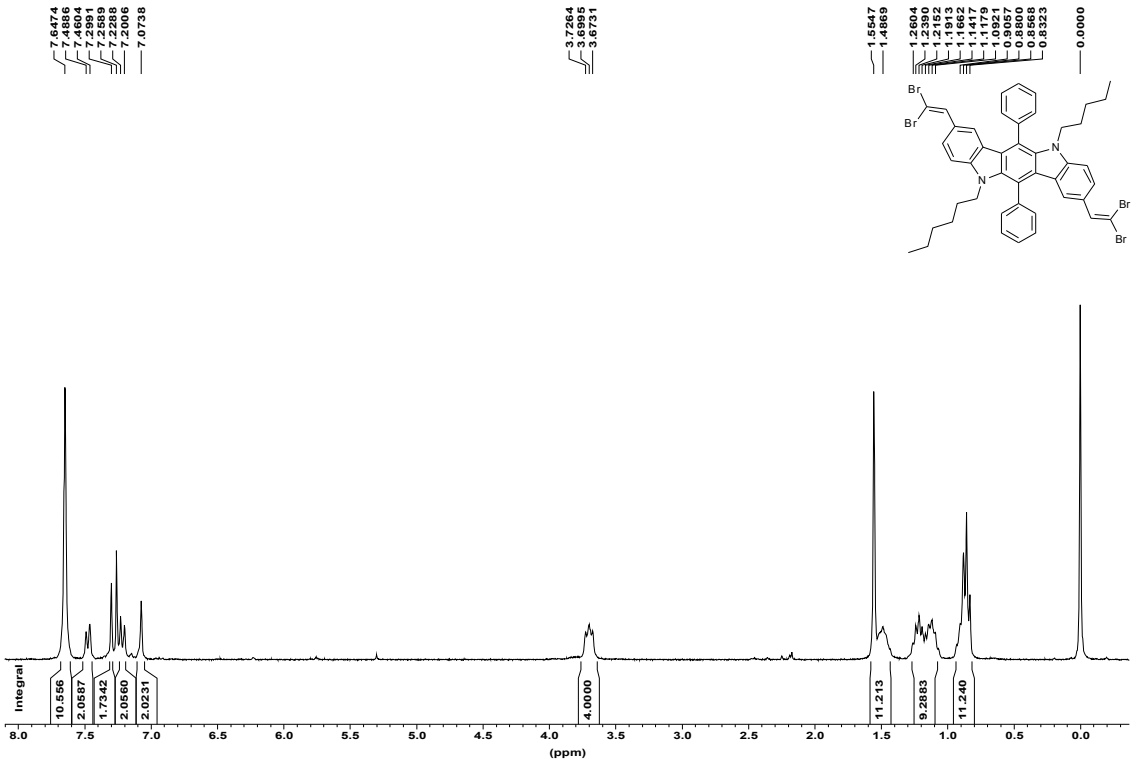
^{1}H NMR of compound **9** in CD_2Cl_2



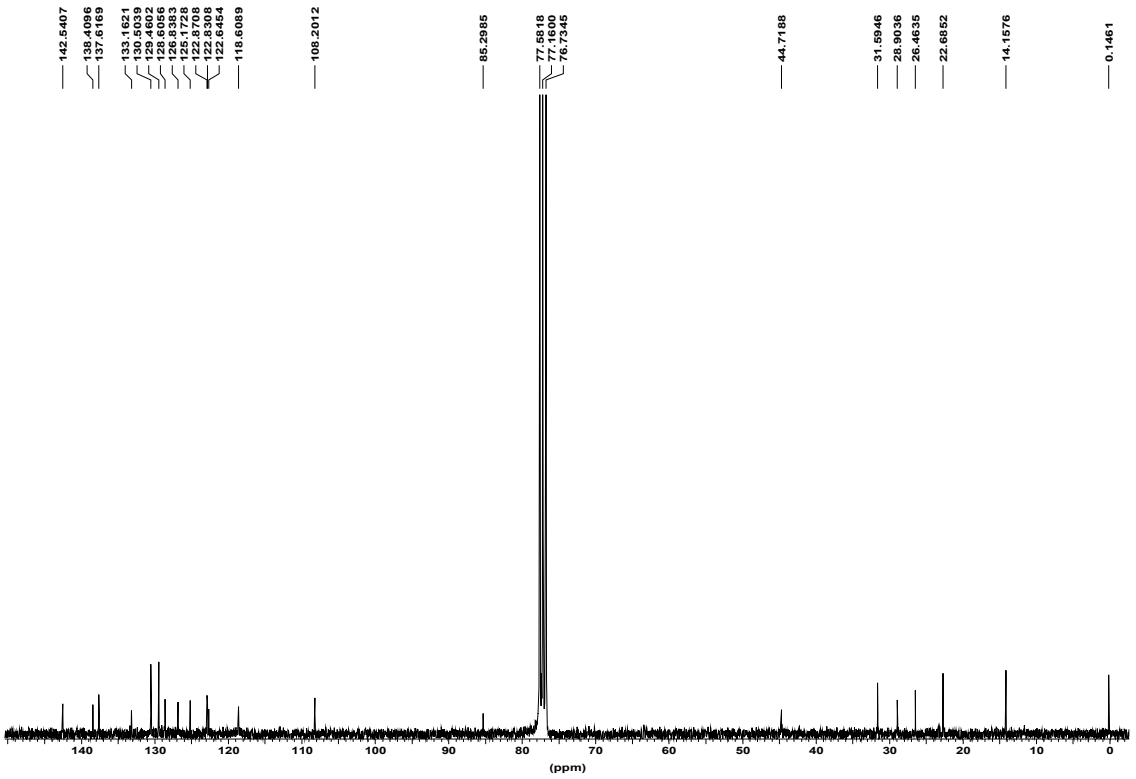
^{13}C spectrum of compound **9** in CD_2Cl_2



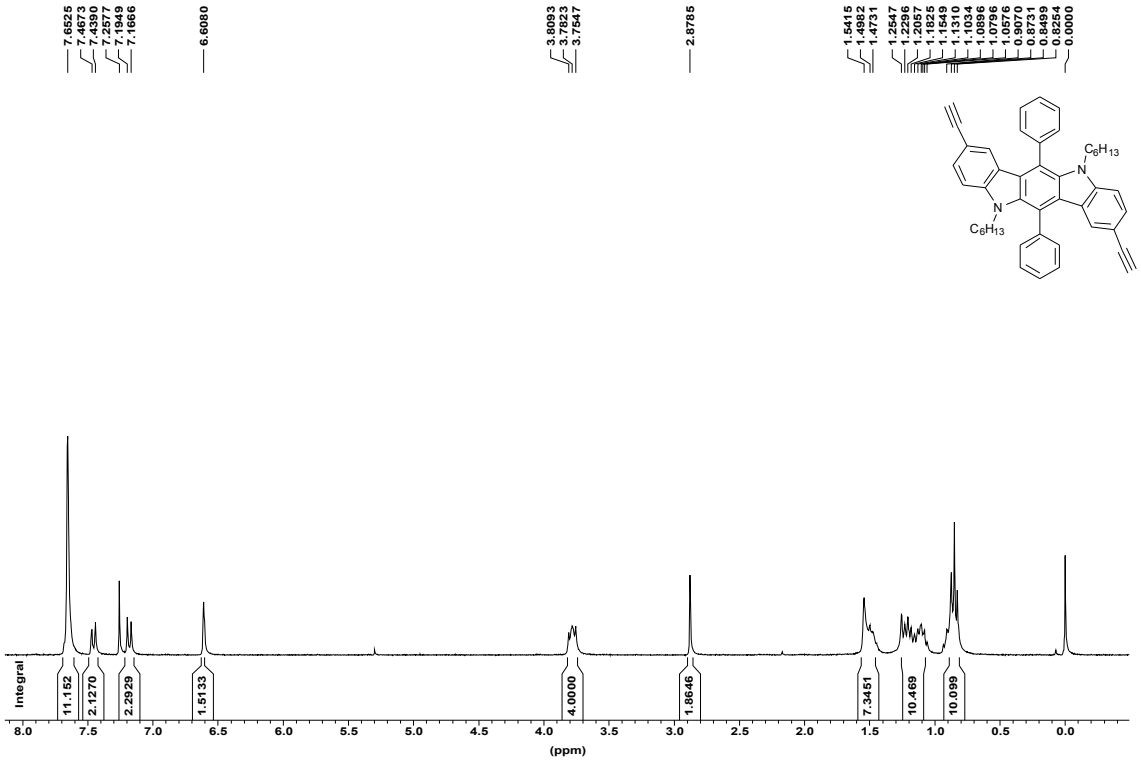
^{1}H NMR of compound **10** in $CDCl_3$



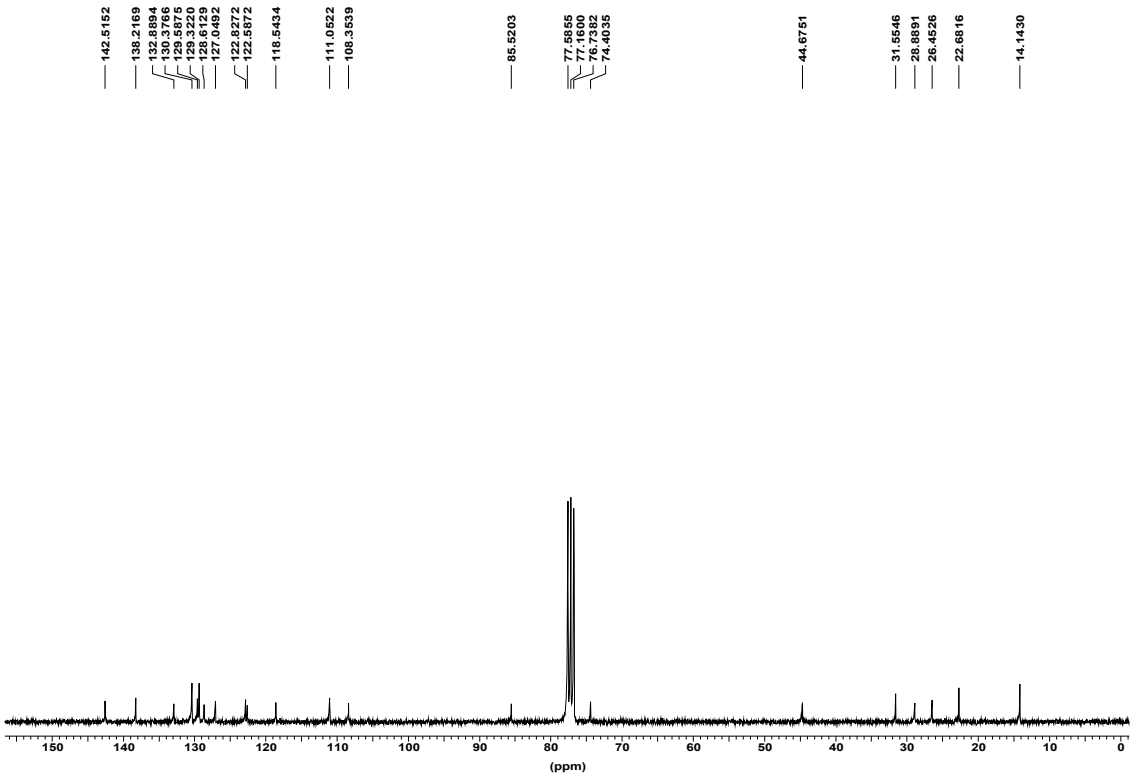
^{13}C spectrum of compound **10** in $CDCl_3$



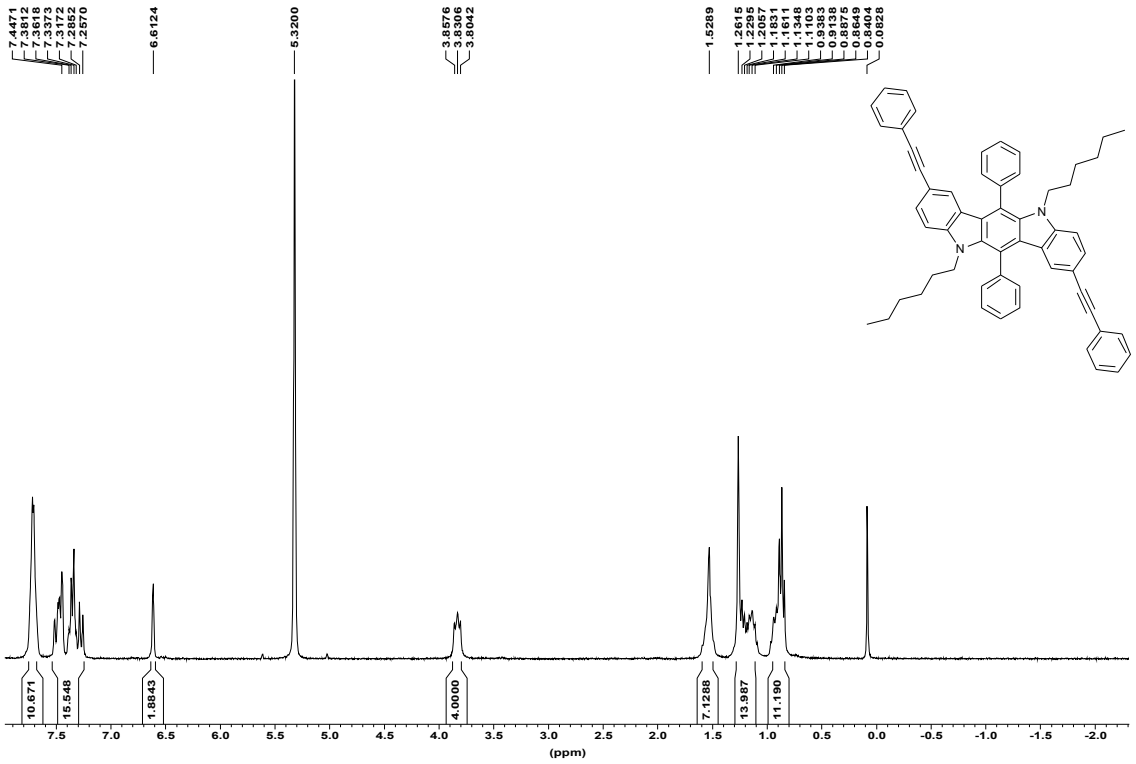
^{1}H NMR of compound **11** in $CDCl_3$



^{13}C spectrum of compound **11** in $CDCl_3$



^{1}H NMR of compound **12** in CD_2Cl_2



^{13}C spectrum of compound **12** in CD_2Cl_2