Electronic Supplementary Information

Unveiling two antiaromatic *s*-indacenodicarbazole isomers with tunable paratropicity

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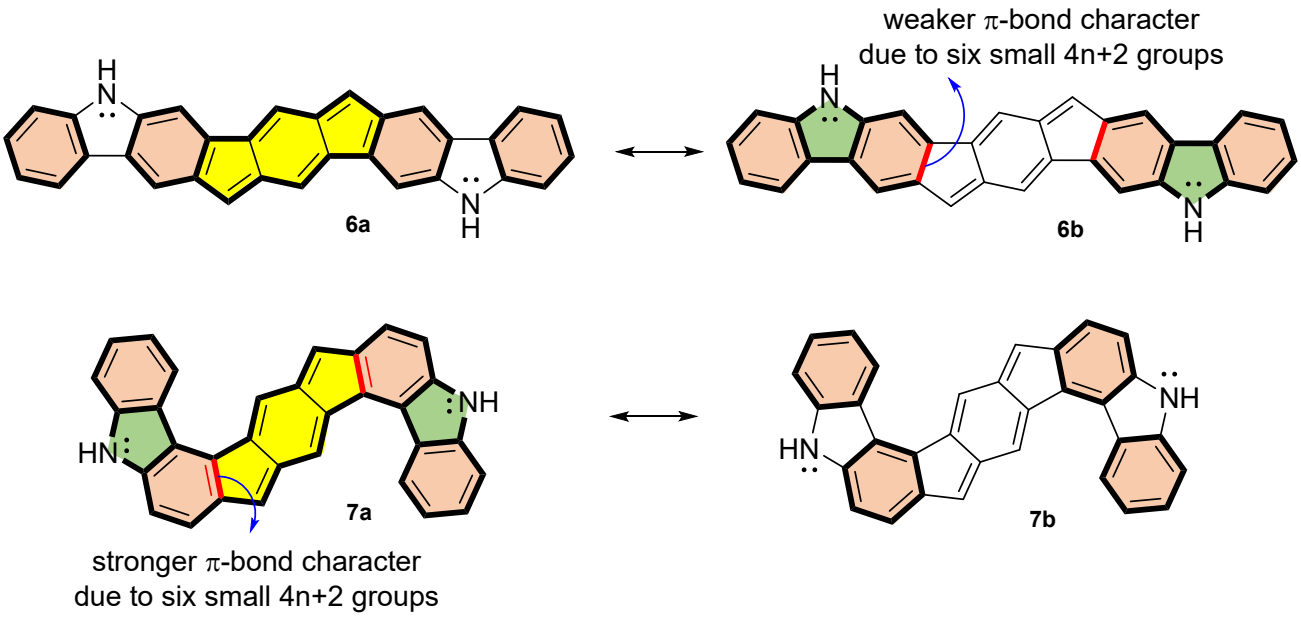
1. Glidewell-Lloyd (GL) rule and (anti)aromaticity of 6 and 7: According to GL rule, total population of π-electrons in conjugated polycyclic hydrocarbons tends to form the smallest 4n+2 groups and avoid the formation of the smallest 4n groups. M. Solà *et al.* modified the rule by stating that conjugated polycyclic hydrocarbons avoid the formation of the smallest 4n group except in the case that avoiding formation of the smallest 4n groups results in the formation of a greater number of large 4n groups.



Parent **6** (shown in above figure, and Fig. 1e in manuscript) can be written in two different closed-shell forms, **6a** and **6b**. Form **6a** has four 4n+2 groups (four benzene rings in orange shades) and **6b** has six 4n+2 groups (four benzene rings in orange shades and two pyrrole rings in green shades). Similarly, parent **7** (shown in above figure, and Fig. 1f in manuscript) can be written in two different forms (four benzene rings and two pyrrole rings) with **7a** having the maximum six 4n+2 groups than the four 4n+2 groups for **7b**. The driving force to gain six small aromatic 4n+2 groups would contribute less to the *s*-indacene (4n group) paratorpicity in the form **6b** for compound **6**, whereas the tendency to gain six small aromatic 4n+2 groups would contribute more to the formation of *s*-indacene in the form of **7a** for compound **7**. Therefore, **7** was expected to show a greater degree of antiaromaticity (stronger paratorpicity for the *s*-indacene unit) than **6** in the ground state, with structures **7a** and **6b** as the most relevant ground state contributors for **7** and **6**, respectively.

2. General information and syntheses: All reagents and chemicals were obtained from commercial sources and used as received. THF was dried over sodium/benzophenone prior using it. Silica gel (100-200 mesh) was used for column chromatography. NMR spectra, in solution, were recorded on JEOL JNM ECS-400 spectrometer at 298 K. Chloroform-D ($CDCl_3$) was passed through short alumina pad before using it for NMR sample preparation. Chemical shifts (δ) are given in ppm relative to residual solvent (chloroform δ = 7.26 for ^1H (400 MHz) and chloroform δ = 77.16 for proton decoupled ^{13}C NMR (100 MHz)) and coupling constants

(*J*) in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. UltraViolet-visible (UV-vis) absorption spectra were recorded on a JASCO V-770 spectrophotometer. Cyclic voltammetry (CV) measurements were performed in dry dichloromethane at 25 °C under nitrogen atmosphere using CHI-1110C Instruments electrochemical analyzer with a three-electrode cell set-up and Bu_4NPF_6 as supporting electrolyte, non-aqueous Ag/Ag+ as reference electrode, glassy carbon as working electrode, and Pt wire as counter electrode, by using 50 mV/s scan rate. The potential was externally calibrated against the ferrocene/ferrocenium couple. Melting points were determined using BIBBY-SMP30 melting point analyzer. High resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on Waters (XEVO G2-XS QTOF) mass spectrometer.

Compound 9: Sodium hydride (146 mg, 6.09 mmol) was added to dry THF (10 mL) solution of **8** (500.00 mg, 2.03 mmol) portion wise. After stirring for 15 min under nitrogen atmosphere, 1-bromobutane (303 mg, 2.21 mmol) was added to reaction mixture. The solution was stirred for 18 h at room temperature. Once the starting material was consumed (monitored by TLC), cold water was slowly added to the reaction mixture. The reaction mixture was then transferred to a 100 ml round-bottomed flask and concentrated by rotary evaporation to afford a solid residue, which was extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography with hexane as eluent to obtain **9** as a colorless viscous oil in 92% yield (570 mg). R_f = 0.9 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.06 (m, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.28 – 7.74 (m, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.46 – 1.36 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.4, 140.7, 126.2, 122.4, 122.0, 121.9, 121.6, 120.5, 119.4, 119.3, 111.9, 109.0, 43.1, 31.1, 20.7, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}BrN$ 302.0544, found 302.0540.

Compound 10: An oven-dried glass tube was charged with **9** (1 g, 3.31 mmol), bis(pinacolatodiboron) (1.09 g, 4.30 mmol), KOAc (974.23 mg, 9.39 mmol), dry 1,4-dioxane (5 mL). The suspension was purged with N_2 for 30 mins before adding $Pd(PPh_3)_4$ (191 mg, 5 mol%), and the glass tube was sealed. The reaction mixture was stirred at 85 °C for 4 h. After being cooled to room temperature, volatile organics were removed under reduced pressure and water was added. The mixture was extracted with EtOAc (5 x 60 mL), dried over anhydrous Na_2SO_4, and filtered. The organic layer was removed under reduced pressure, and the crude obtained was quickly column chromatographed on short silica gel pad (hexanes:EtOAc, 85:15) to afford the compound **10** as white solid (808 mg, 70% yield). R_f = 0.5 (hexanes:EtOAc = 9:1). mp: 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.12 (m, 1H), 8.11 (d, *J* = 4.0 Hz, 1H), 7.88 (s, 1H), 7.69 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 4.36 (t, *J* = 7.3 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.41 (s, 12H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 140.1, 126.3,

125.5, 125.1, 122.7, 120.9, 119.7, 118.8, 115.2, 109.0, 83.9, 42.9, 31.4, 25.1, 20.7, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{28}O_2BN$ 350.2291, found 350.2291.

Compound 11: An oven-dried glass tube was charged with compound **10** (300 mg, 0.859 mmol), 2,5-dibromophenyl-1,4-dialdehyde or dibromoterephthalaldehyde (100 mg, 0. 342 mmol), K_2CO_3 (142 mg, 1.06 mmol), tetrahydrofuran (10 mL) and water (1 mL), and the mixture was purged with nitrogen for 30 mins. Catalyst $Pd(PPh_3)_4$ (20 mg, 5 mol%) was subsequently added under nitrogen, and the glass tube was sealed and heated to 100 °C. After 12 h, the THF was evaporated under reduced pressure, and water was added. The mixture was extracted with EtOAc (4 x 50 mL), and the organic layer was washed with saturated brine solution, and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and removed under vacuum. The residue was purified by silica gel column chromatography (hexanes:EtOAc, 85:15) to afford **11** as yellow solid (150 mg, 75% yield). R_f = 0.45 (hexanes:EtOAc = 9:1). mp: 238-240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 2H), 8.30 (s, 2H), 8.23 (d, *J* = 7.9 Hz, 2H), 8.18 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.49 – 7.47 (m, 4H), 7.33 – 7.28 (m, 4H), 4.38 (t, *J* = 7.2 Hz, 4H), 1.94 – 1.86 (m, 4H), 1.49 – 1.39 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H).^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$): δ 192.6, 145.4, 141.2, 140.5, 136.8, 133.9, 130.4, 126.4, 123.2, 122.3, 121.3, 120.8, 120.6, 119.4, 110.3, 109.1, 43.1, 31.2, 20.7, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{36}N_2O_2$ 577.2855, found 577.2857.

Compound 13: 2-Mesitylmagnesium bromide (1.0 M in THF, 0.6 mL, 0.6 mmol) was added to the dry THF (5 mL) solution of **11** (85 mg, 0.147 mmol) under N_2. The mixture was stirred at room temperature for 12 h, and quenched with saturated aq. NH_4Cl solution. The volatile organics were evaporated, and the mixture was extracted with DCM (4 x 50 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered, and removed under reduced pressure to afford crude **12**. The crude material **12** was transferred to a dry 50 ml round bottomed flask and dissolved in 10 ml anhydrous DCM. To the solution of crude **12** (249 mg), $BF_3{\cdot}Et_2O$ (0.1 mL) was added dropwise under nitrogen and the reaction mixture was stirred for 10 min at room temperature. Once starting material **12** was consumed, (as monitored by TLC), the mixture was carefully quenched by addition of a saturated $NaHCO_3$ solution (5 ml). The aqueous layer was extracted with DCM (3 x 30 ml) and the resulting combined organic phases were dried over Na_2SO_4, filtered and all volatiles were removed under reduced pressure. Column chromatographic purification of residue was difficult due to compound's sticky nature on silica surface, and presence of diastereomers. However, the obtained residue was quickly filtered over a short silica gel pad (DCM: hexane: 1:9) to give dihydro precursor **13** (70 mg) as light green solid, as a mixture of stereoisomers (70 mg, 60% yield over two steps). R_f = 0.5 (hexanes:EtOAc = 95:5). mp: 198 - 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 8.09 (m, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.86 – 7.69 (m, 6H), 7.42 – 7.38 (m, 3H), 7.23 – 7.15 (m, 4H), 6.84 – 6.70 (m, 3H), 6.00 – 5.73 (m, 2H), 4.39 – 4.34 (m, 4H), 2.92 – 2.86 (m, 6H), 2.39 – 2.34 (m, 6H), 1.95 – 1.90 (m, 4H), 1.53 – 1.47 (m, 4H), 1.29 – 1.15 (m, 6H), 1.00 (t, *J* = 7.4

Hz, 6H).$^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$): δ 149.3, 143.1, 142.5, 141.6, 140.8, 140.6, 140.2, 138.4, 137.8, 137.7, 132.8, 130.8, 127.4, 127.3, 124.9, 124.7, 122.3, 120.7, 117.7, 110.6, 101.9, 50.9, 45.2, 33.3, 24.1, 23.1, 22.8, 20.8, 16.1. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{58}H_{56}N_2$ 781.4522, found 781.4523.

Compound 6 (5,14-dibutyl-8,17-dimesityl-*s*-indaceno[1,2-*b*:5,6-*b*']dicarbazole): In a 10 ml dry sealed tube, compound **13** (60 mg, 0.077 mmol) and oxidizing agent DDQ (45 mg, 0.2 mmol) were dissolved in dry toluene (3 ml) and the reaction mixture was heated at 80 °C. After two hours, the starting material was consumed (as monitored by TLC), and the reaction mixture was allowed to cool to room temperature. Afterwards, toluene was removed in vacuo and the crude material was purified by silica gel column chromatography (hexanes:DCM, 90:10) to afford the desired product **6** as blue solid (20 mg, 33%). R_f = 0.5 (hexanes:DCM = 10:1). mp: > 350 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.41 (s, 2H), 7.36 – 7.32 (m, 2H), 7.30 (s, 2H), 7.28 (s, 2H), 7.13 (s, 4H), 7.12 – 7.08 (m, 2H), 7.01 (s, 2H), 4.23 (t, *J* = 7.3 Hz, 4H), 2.48 (s, 6H), 2.28 (s, 12H), 1.88 – 1.81 (m, 4H), 1.47 – 1.40 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 6H). $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$): δ 143.9, 141.2, 140.7, 138.2, 137.9, 137.5, 137.0, 134.5, 131.2, 128.6, 128.3, 125.3, 123.6, 122.8, 120.3, 119.2, 117.5, 113.7, 108.9, 102.0, 43.2, 31.5, 21.5, 20.8, 20.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{58}H_{54}N_2$ 779.4365, found 779.4361.

Compound 15: It was synthesized by analogous procedure to that of **9**, by adding NaH (146 mg, 6.09 mmol) portion wise (in 20 mins) to a THF (10 mL) solution of **14** (500.00 mg, 2.03 mmol), under nitrogen. 1-bromobutane (303 mg, 2.21 mmol) was added to the solution after stirring for 15 min. Afterwards, the mixture was stirred for 18 h at room temperature. Once the starting material was consumed (monitored by TLC), cold water was slowly added to the reaction mixture to quench the remaining NaH carefully. The solution was then transferred to a 100 ml round-bottomed flask and concentrated to afford a solid residue, which was extracted with DCM (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by silica gel column chromatography with hexane to afford compound **15** as a colorless viscous oil in 91% yield (560 mg). R_f = 0.9 (hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ 8.82 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.56 - 7.52 (m, 1H), 7.44 - 7.40 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 2H), 4.30 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.45 – 1.36 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6, 140.6, 126.4, 126.1, 123.0, 122.9, 122.5, 121.5, 119.1, 117.0, 108.7, 107.7, 43.0, 31.1, 20.7, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}BrN$ 302.0544, found 302.0544.

Compound 16: An oven-dried glass tube was charged with **15** (1 g, 3.31 mmol), bis(pinacolatodiboron) (1.09 g, 4.30 mmol), KOAc (974.23 mg, 9.39 mmol) dry 1,4-dioxane (5 mL). The suspension was purged with N_2 for 30 mins before adding $Pd(PPh_3)_4$ (191 mg, 5 mol%), and the glass tube was sealed. The reaction mixture

was stirred at 85 °C for 4 h. After being cooled to room temperature, volatile organics were removed under reduced pressure and water was added. The mixture was extracted with EtOAc (5 x 60 mL), dried over anhydrous Na_2SO_4, and filtered. The organic layer was removed under reduced pressure, and the crude obtained was quickly column chromatographed on short silica gel pad (hexanes:EtOAc, 85:15) to afford the product **16** as colorless viscous oil (785 mg, 68% yield). R_f = 0.5 (hexanes:EtOAc = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.20 (m, 1H), 4.32 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.48 (s, 12H), 1.41 – 1.36 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ 140.9, 140.2, 127.7, 126.6, 125.7, 124.6, 124.4, 123.7, 118.7, 111.7, 108.3, 84.0, 42.7, 31.14, 25.2, 20.7, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{29}O_2BN$ 350.2291, found 350.2291.

Compound 17: An oven-dried glass tube was charged with compound **16** (300 mg, 0.859 mmol), dibromoterephthalaldehyde (100 mg, 0.342 mmol), K_2CO_3 (142 mg, 1.06 mmol), tetrahydrofuran (10 mL) and water (1 mL), and the mixture was purged with nitrogen for 30 mins. Catalyst $Pd(PPh_3)_4$ (20 mg, 5 mol%) was subsequently added under nitrogen, and the glass tube was sealed before being warmed to 100 °C. After 12 h, the THF was evaporated under reduced pressure, and water was added. The mixture was extracted with EtOAc (4 x 50 mL), and the organic layer washed with saturated brine solution, and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and removed under vacuum. The residue was purified by silica gel column chromatography (hexanes:EtOAc, 85:15) to afford the product **17** as yellow solid (140 mg, 70% yield). R_f = 0.45 (hexanes:EtOAc = 9:1). mp: 238-240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (d, *J* = 1.6 Hz, 2H), 8.36 (d, *J* = 4.6 Hz, 2H), 7.65 -7.56 (m, 4H), 7.50 – 7.41 (m, 4H), 7.31 (dd, *J* = 7.3, 3.3 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 2H), 7.13 – 6.98 (m, 2H), 4.48 – 4.39 (m, 4H), 1.98 – 1.91 (m, 4H), 1.53 – 1.44 (m, 4H), 1.01 (t, *J* = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$): δ 191.8, 144.6, 141.0, 140.5, 137.6, 131.4, 130.1, 126.2, 125.6, 122.1, 122.0, 121.8, 121.6, 121.4, 119.4, 109.2, 43.2, 31.3, 20.8, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{40}H_{36}N_2O_2$ 577.2855, found 577.2851.

Compound 19: 2-Mesitylmagnesium bromide (1.0 M in THF, 0.6 mL, 0.6 mmol) was added to the dry THF (5 mL) solution of **17** (85 mg, 0.15 mmol) under nitrogen. The mixture was stirred at room temperature for 12 h, and quenched with saturated aq. NH_4Cl solution. The volatile organics were evaporated, and the mixture was extracted with dichloromethane (4 x 50 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered, and removed under reduced pressure to afford crude **18**. To the dry DCM solution of crude **18** (90 mg, 0.11 mmol), $BF_3{\cdot}Et_2O$ (0.1 mL) was added dropwise under nitrogen and the reaction mixture was stirred for 10 min at room temperature. Once **18** was completely consumed (as monitored by TLC), the solution was carefully quenched by addition of a saturated $NaHCO_3$ solution (5 ml). Afterwards, the aqueous layer was extracted with DCM (3 x 30 ml) and the resulting combined organic phases were dried over Na_2SO_4, filtered

and all volatiles were removed under reduced pressure. The obtained residue was column chromatographed over a short silica gel pad (DCM: hexane: 1:9) to afford **19** (75 mg) as light green solid as a mixture of stereoisomers (75 mg, 65% yield over two steps). R_f = 0.5 (hexanes:EtOAc = 95:5). mp: 202 - 204 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 – 8.45 (m, 4H), 7.51 – 7.46 (m, 3H), 7.42 – 7.30 (m, 4H), 7.23 – 7.13 (m, 3H), 7.00 – 6.79 (m, 2H), 6.67 – 6.54 (m, 2H), 5.89 – 5.82 (m, 2H), 4.43 – 4.31 (m, 4H), 2.96 – 2.89 (m, 4H), 2.34 – 2.21 (m, 8H), 1.90 – 1.81 (m, 4H), 1.47 – 1.37 (m, 4H), 1.05 – 0.91 (m, 12H).^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$): δ 148.0, 147.8, 140.9, 140.8, 140.6, 138.0, 137.8, 136.1, 135.1, 130.9, 128.7, 125.3, 123.8, 122.4, 121.5, 121.4, 119.1, 118.5, 117.7, 108.8, 107.6, 50.0, 43.1, 31.1, 22.0, 20.7, 19.1, 18.7, 14.1. HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{58}H_{57}N_2$ 781.4522, found 781.4525.

Compound 7 (5,14-dibutyl-8,17-dimesityl-*s*-indaceno[2,1-*c*:6,5-*c*']dicarbazole): Compound **19** (70 mg, 0.09 mmol) was subjected to oxidative dehydrogenation reaction with DDQ (40.7 mg, 0.18 mmol,) in dry toluene (3 ml) at 80 °C. After 2 h, the starting material was completely consumed (as confirmed by TLC), and the reaction mixture was allowed to cool to room temperature. Afterwards, the toluene was removed in vacuo and the crude was purified by silica gel column chromatography (hexanes:DCM, 90:10) to afford the title product **7** as blue-green solid (40 mg, 57% yield). R_f = 0.5 (hexanes:DCM = 10:1). mp: 302 - 305 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.54 (s, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 2H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 4H), 2.45 (s, 6H), 2.31 (s, 12H), 1.85 – 1.78 (m,4H), 1.43 -1.37 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$): δ 147.1, 142.3, 141.6, 137.4, 137.3, 137.3, 136.7, 133.9, 133.7, 130.7, 128.3, 125.7, 124.8, 123.7, 122.3, 121.0, 119.2, 119.1, 108.8, 107.1, 43.0, 31.1, 21.4, 20.7, 20.7, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{58}H_{55}N_2$ 779.4365, found 779.4362.

3. NMR spectra:

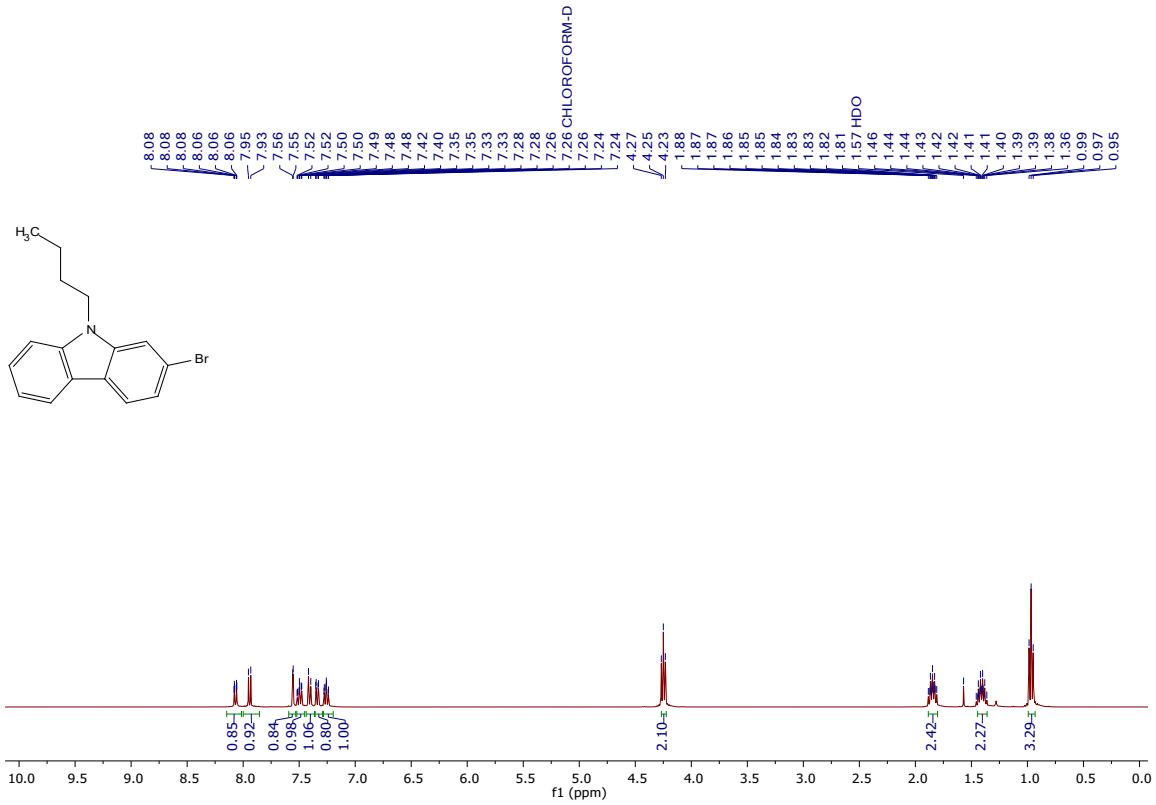


Fig. S1 ^{1}H NMR spectrum of **9**.

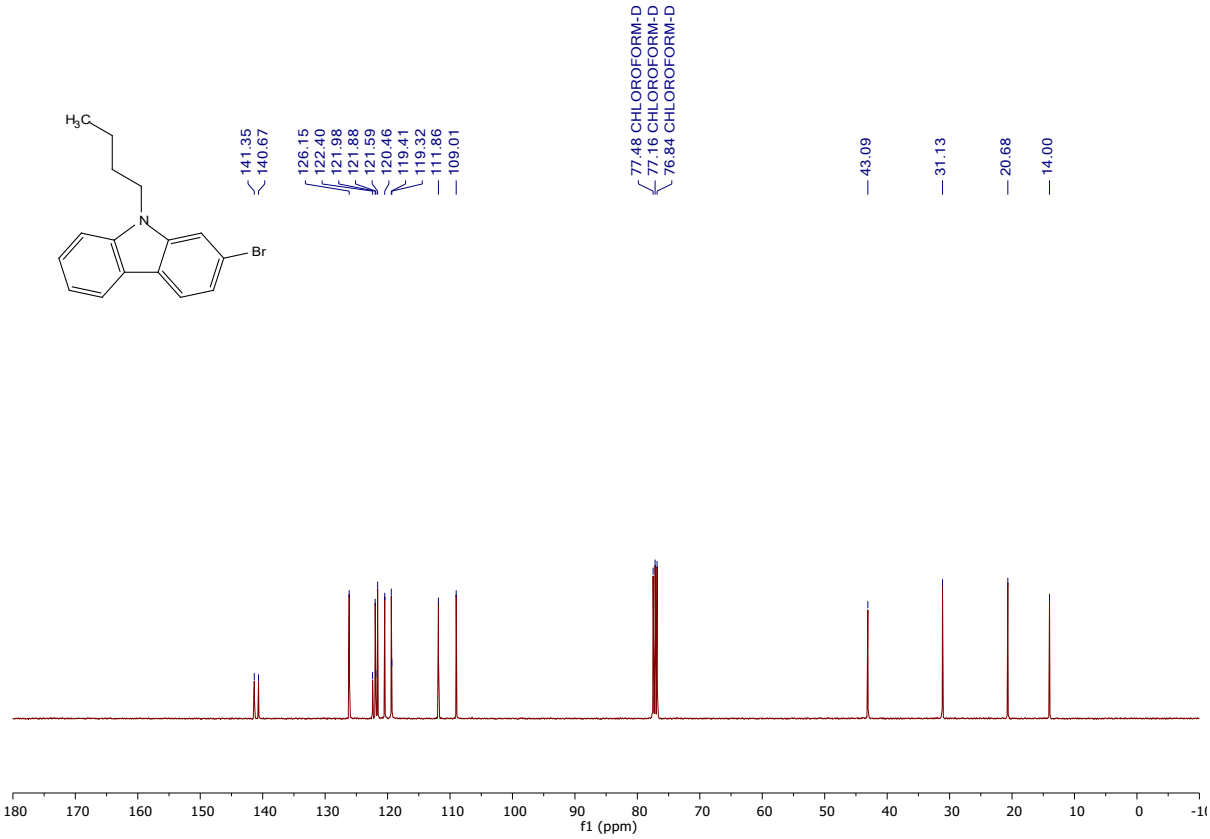


Fig. S2 ^{13}C NMR spectrum of **9**.

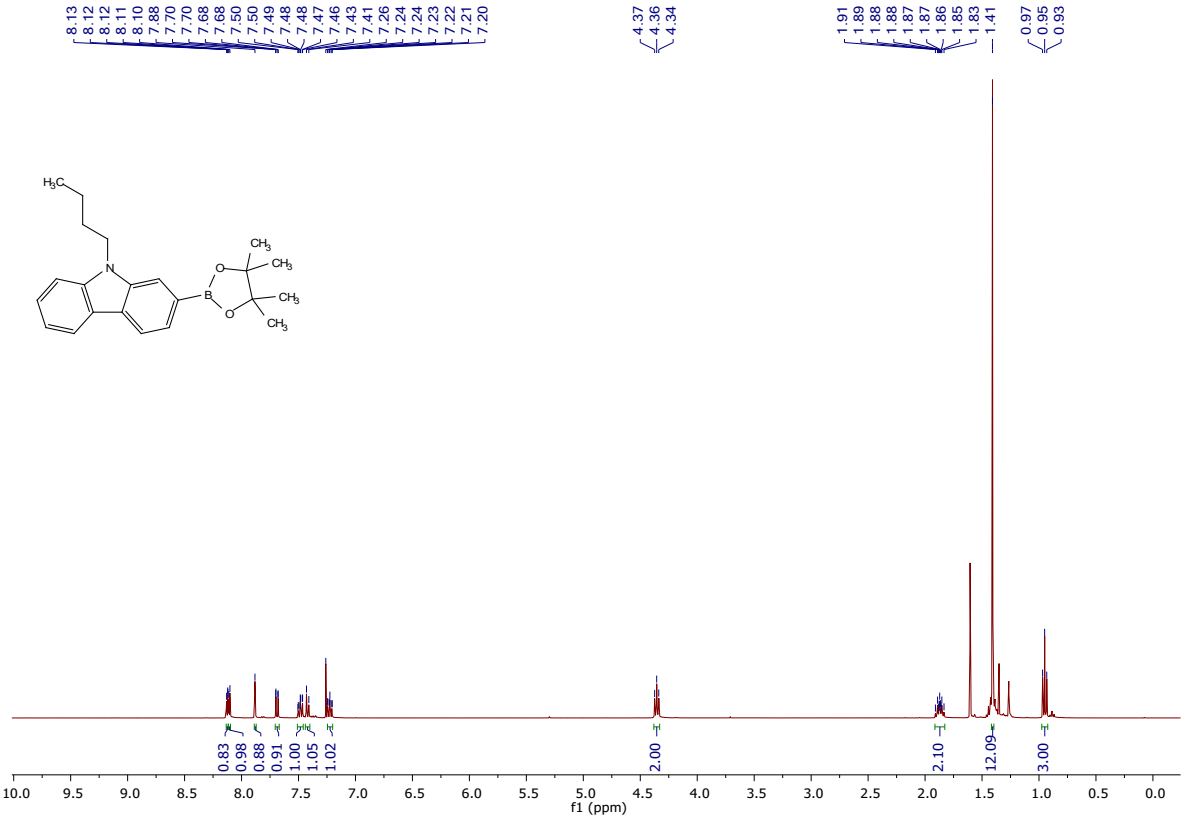


Fig. S3 ^{1}H NMR spectrum of **10**.

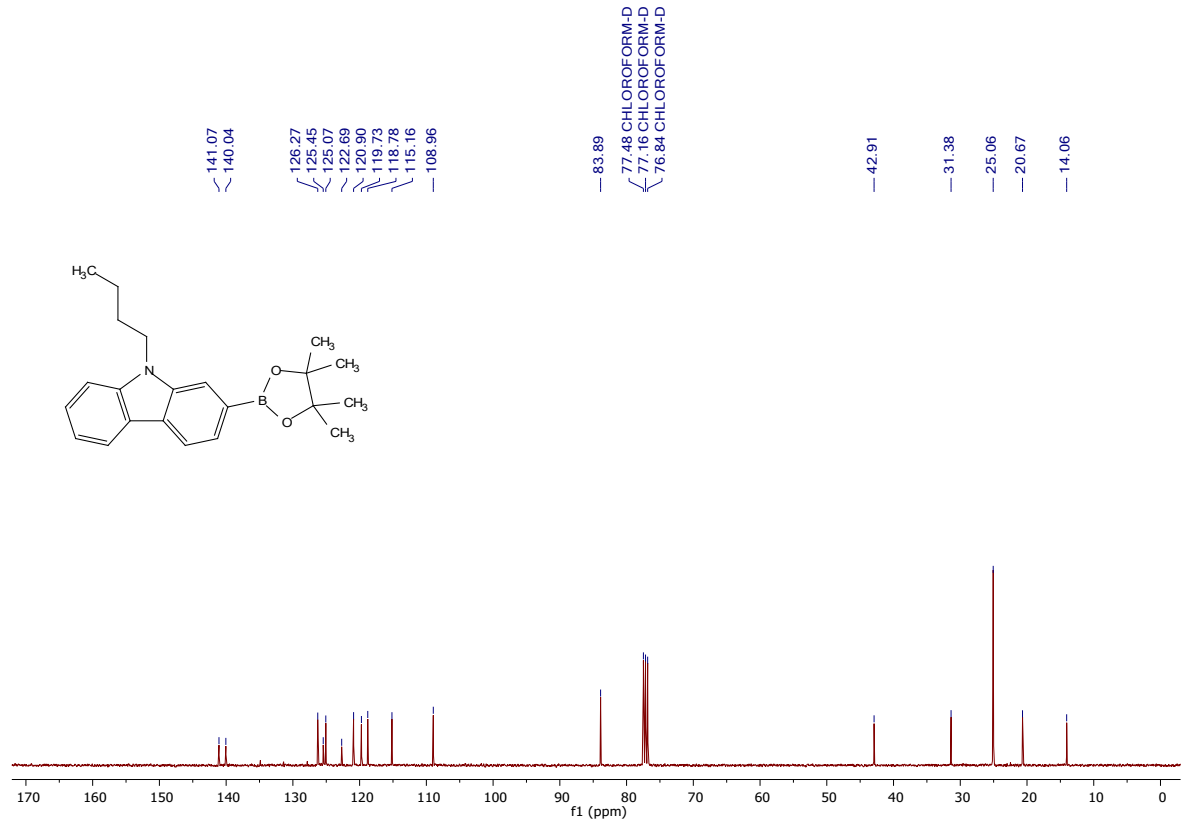


Fig. S4 ^{13}C NMR spectrum of **10**.

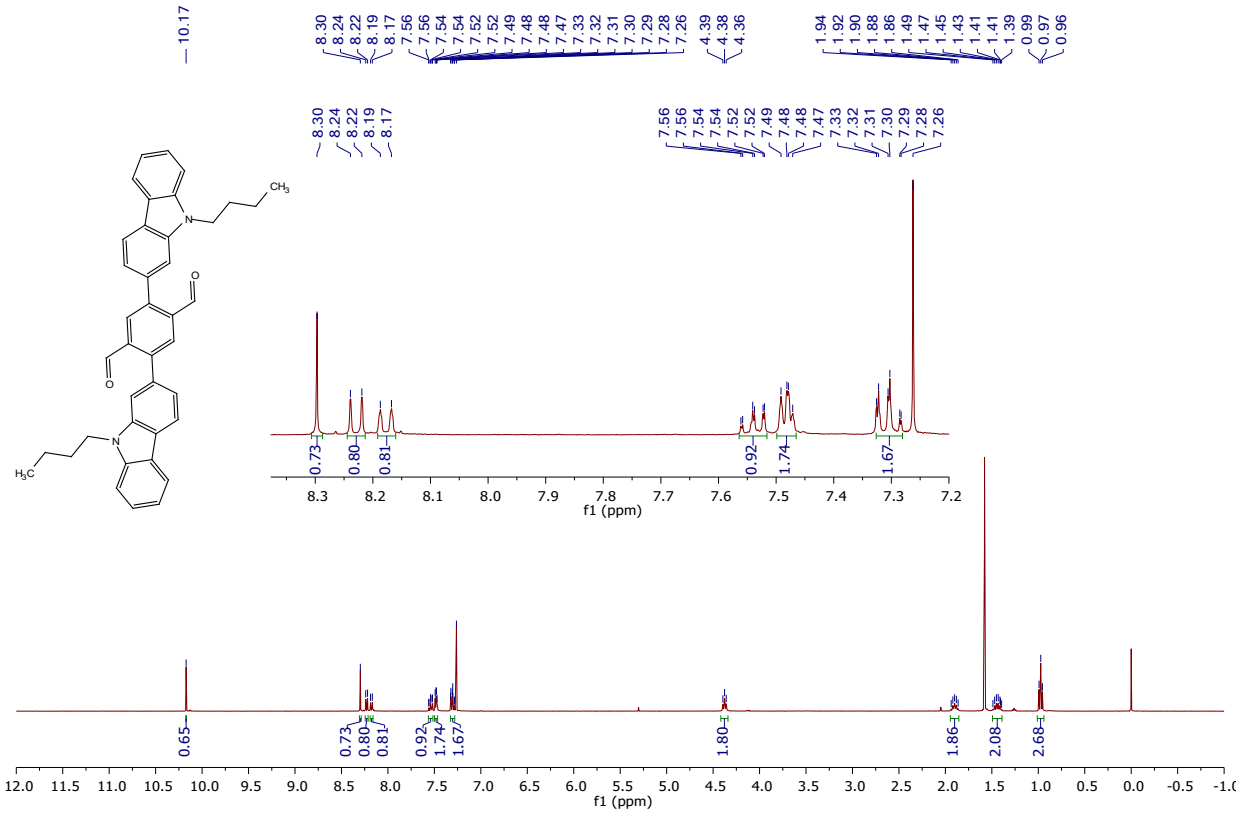


Fig. S5 ^{1}H NMR spectrum of **11**.

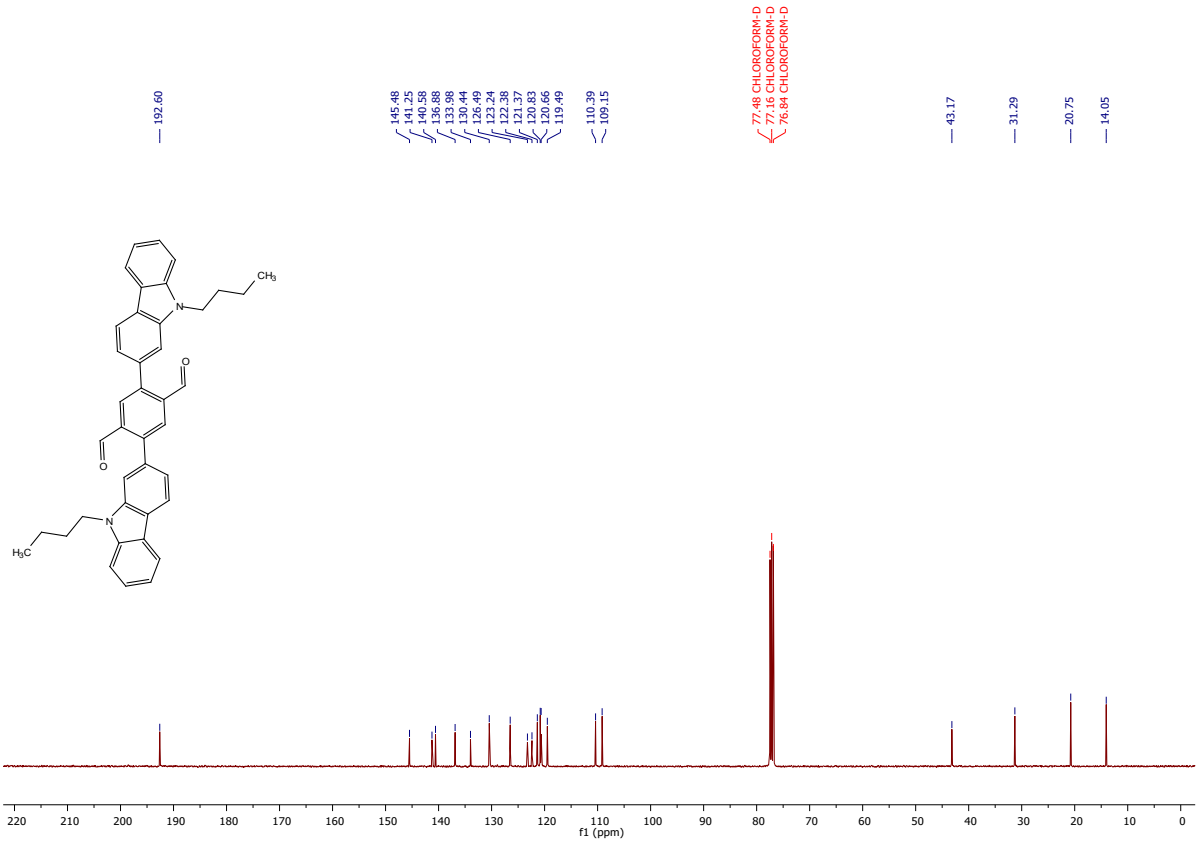


Fig. S6 ^{13}C NMR spectrum of **11**.

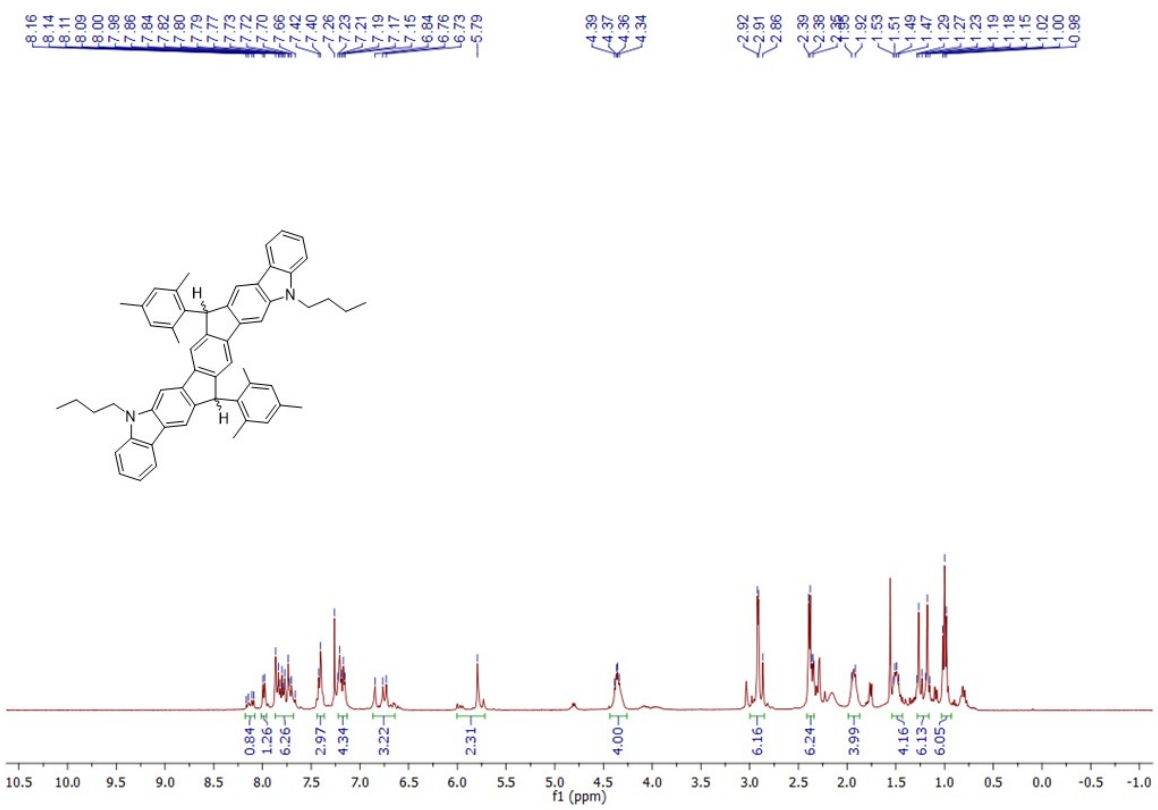


Fig. S7 ^{1}H NMR spectrum of **13**.

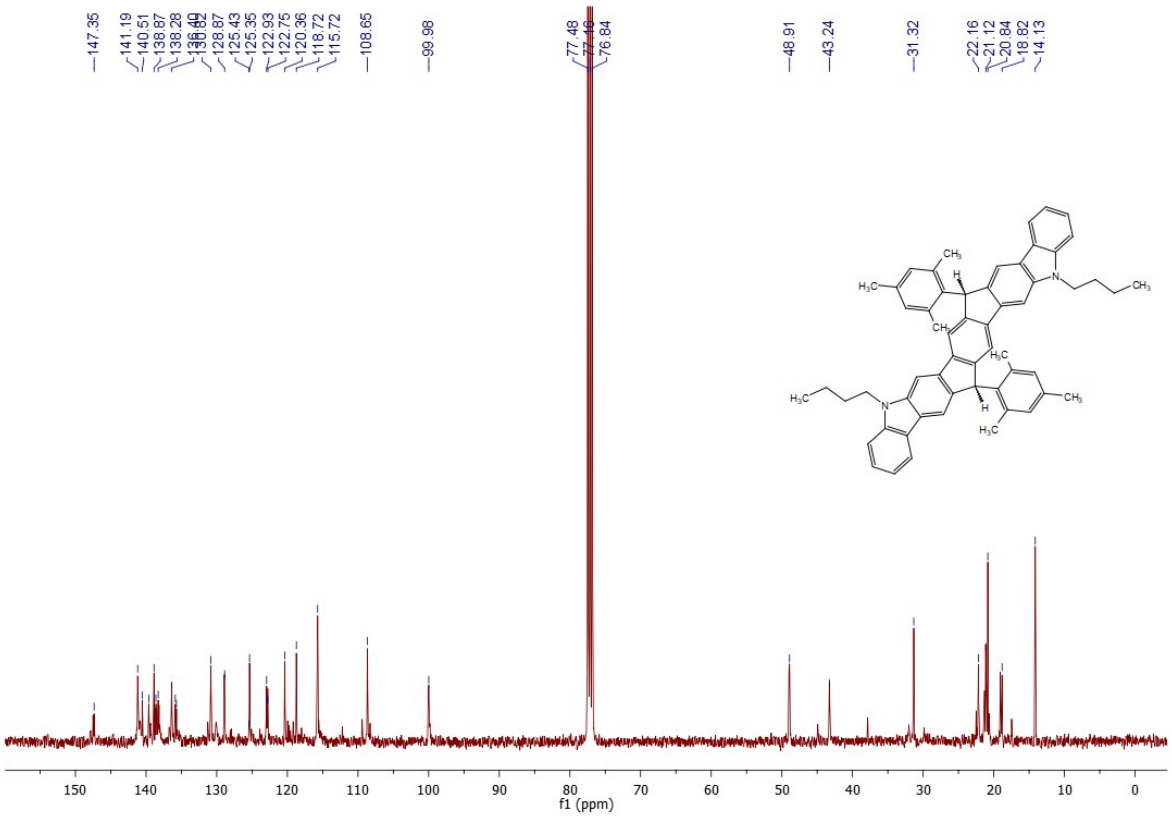


Fig. S8 ^{13}C NMR spectrum of **13**.

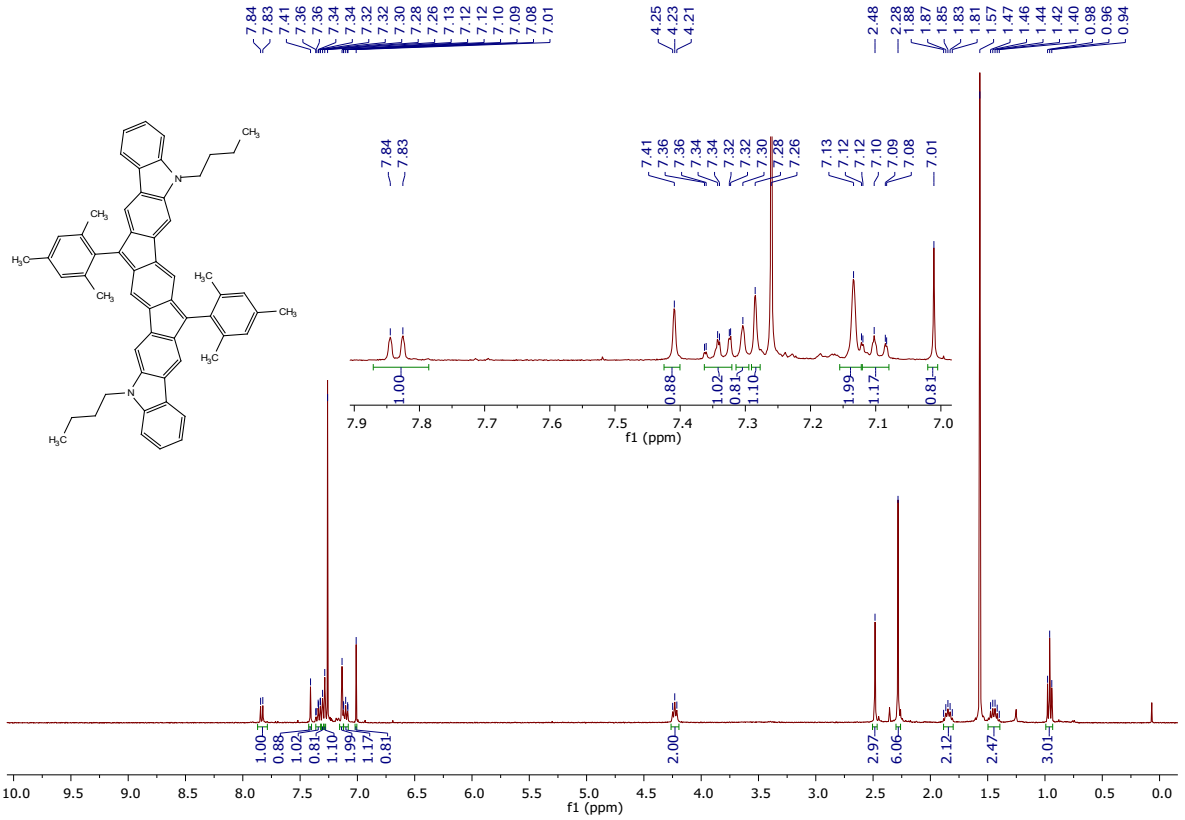


Fig. S9 ^{1}H NMR spectrum of **6**.

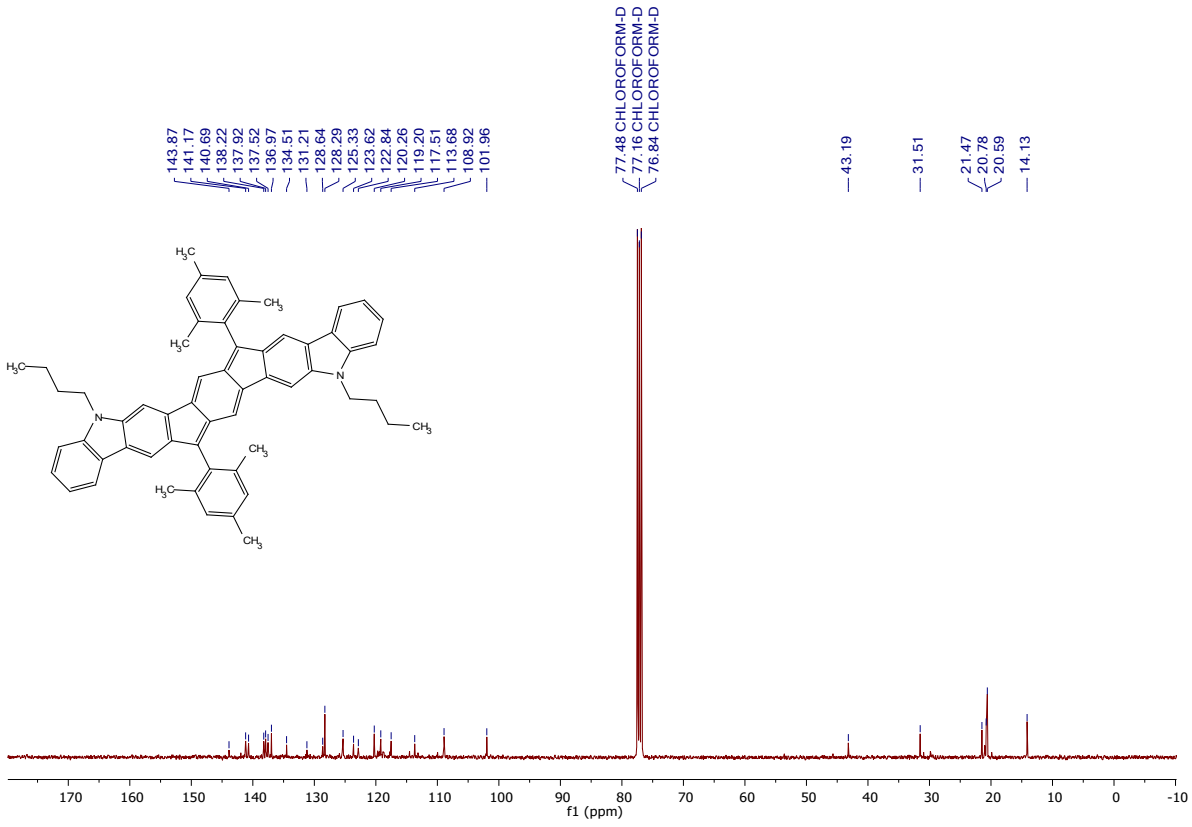


Fig. S10 ^{13}C NMR spectrum of **6**.

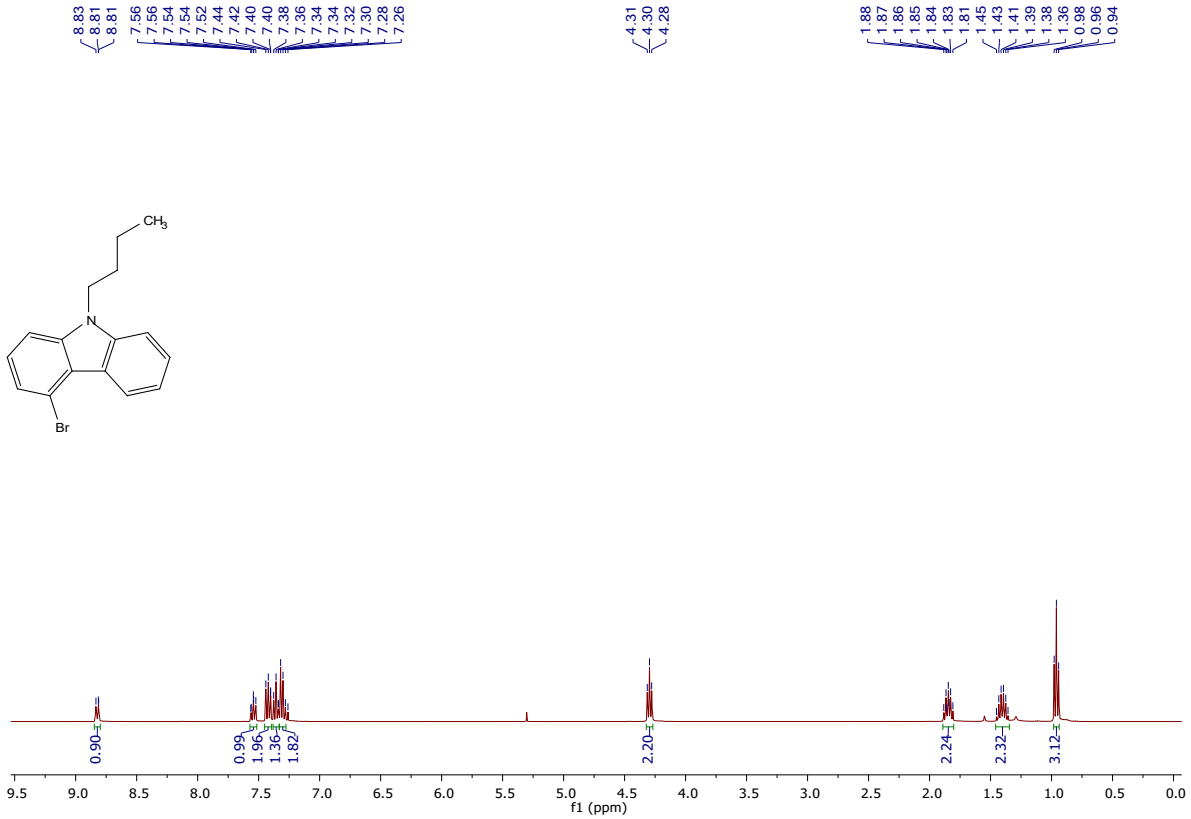


Fig. S11 ^{1}H NMR spectrum of **15**.

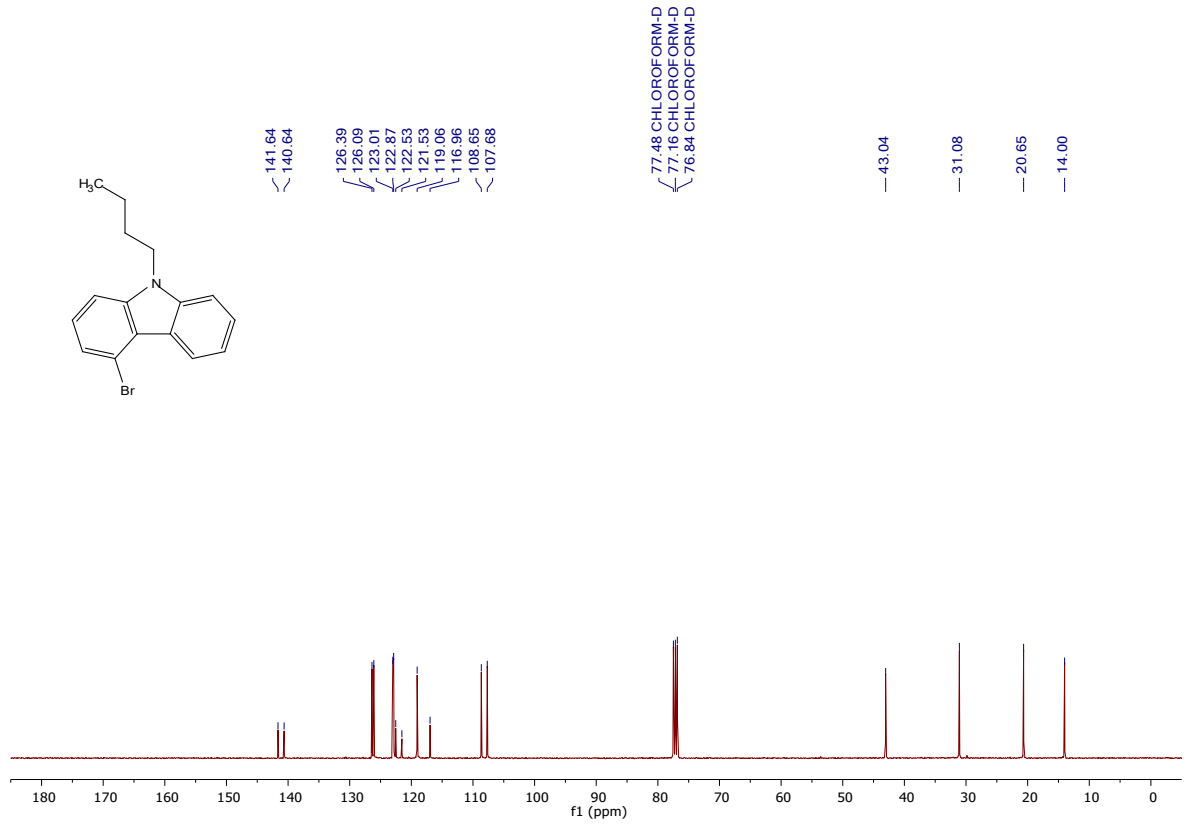


Fig. S12 ^{13}C NMR spectrum of **15**.

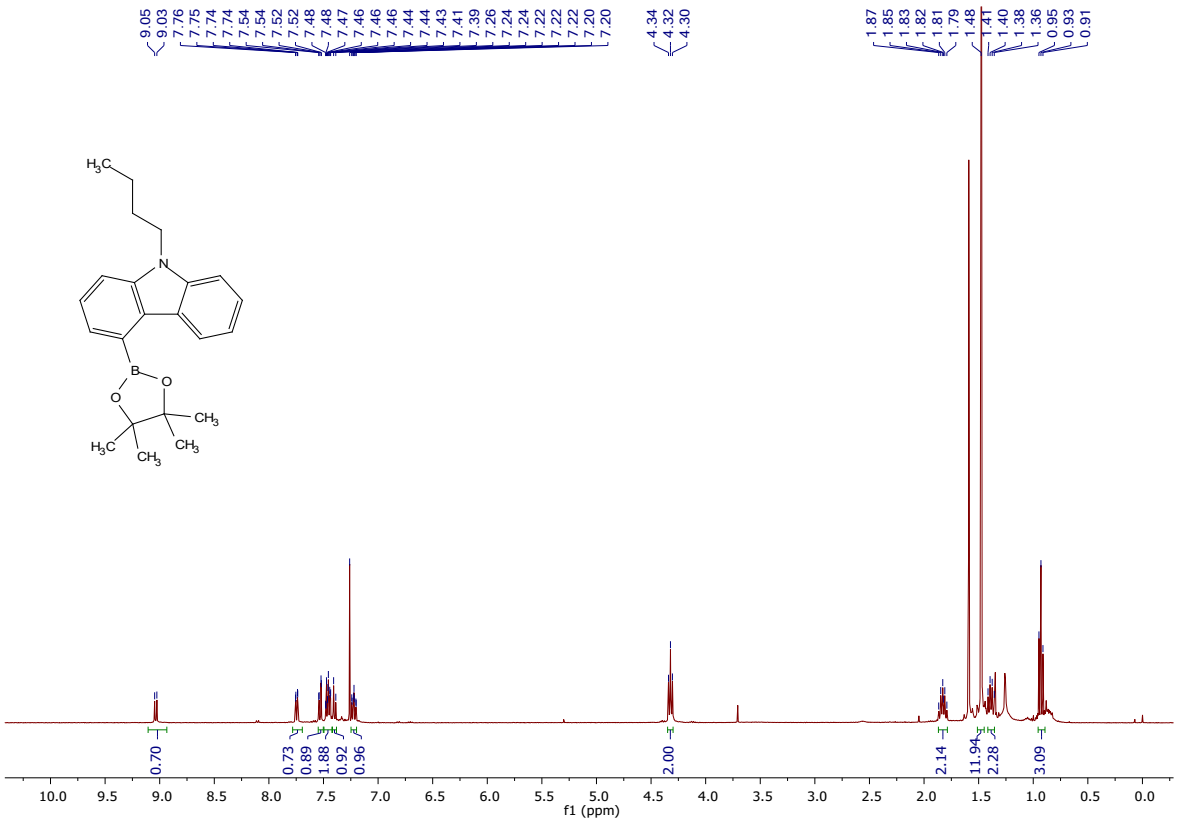


Fig. S13 ^{1}H NMR spectrum of **16**.

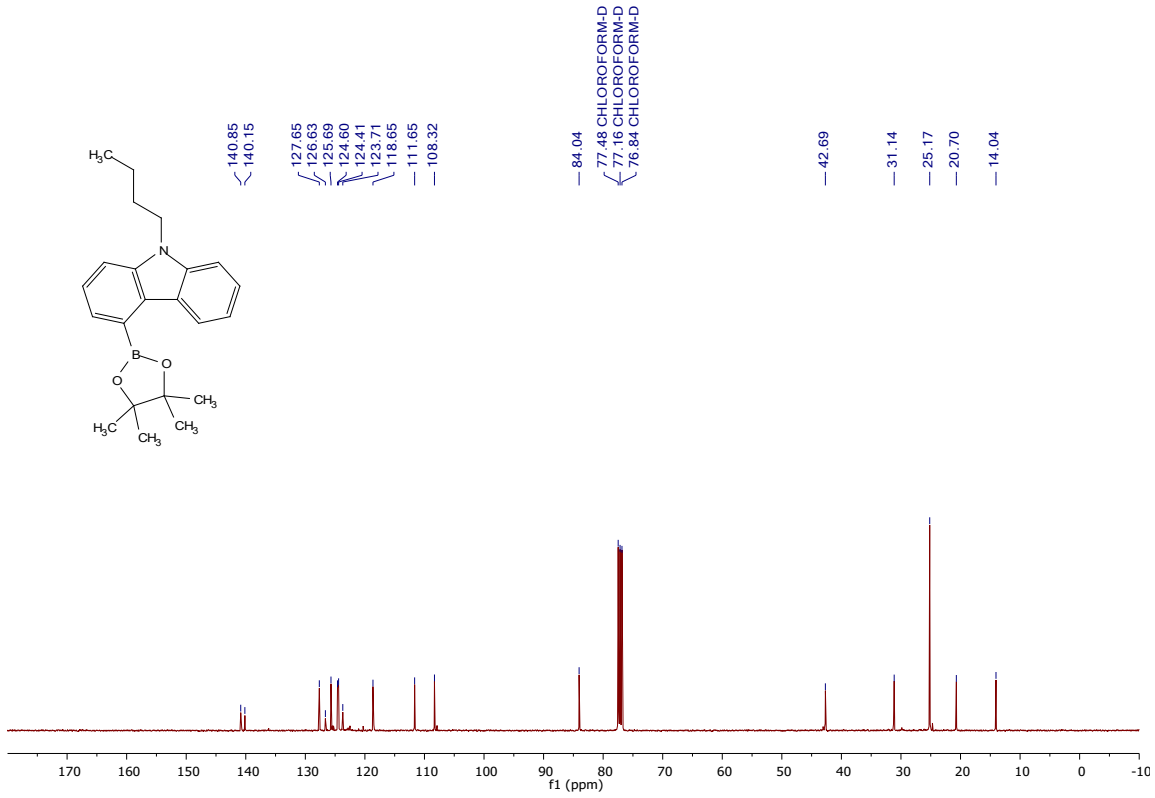


Fig. S14 ^{13}C NMR spectrum of **16**.

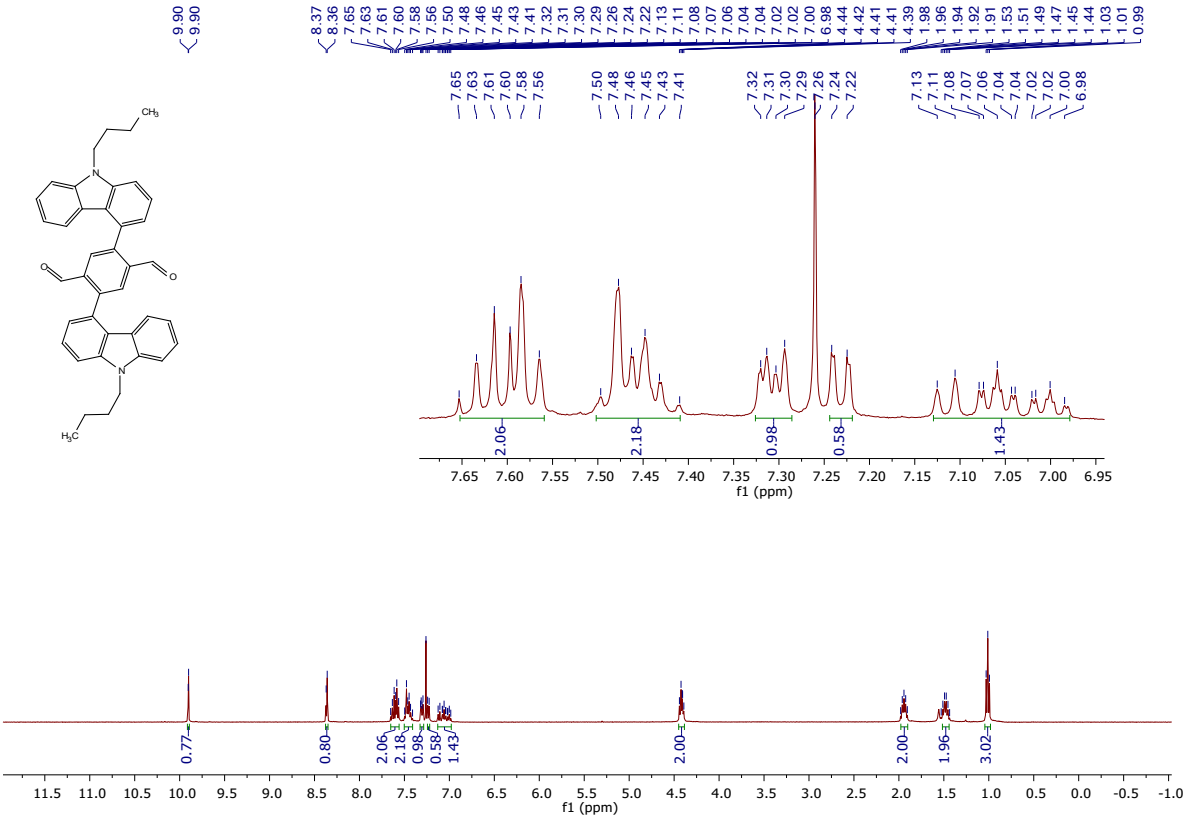


Fig. S15 ^{1}H NMR spectrum of **17**.

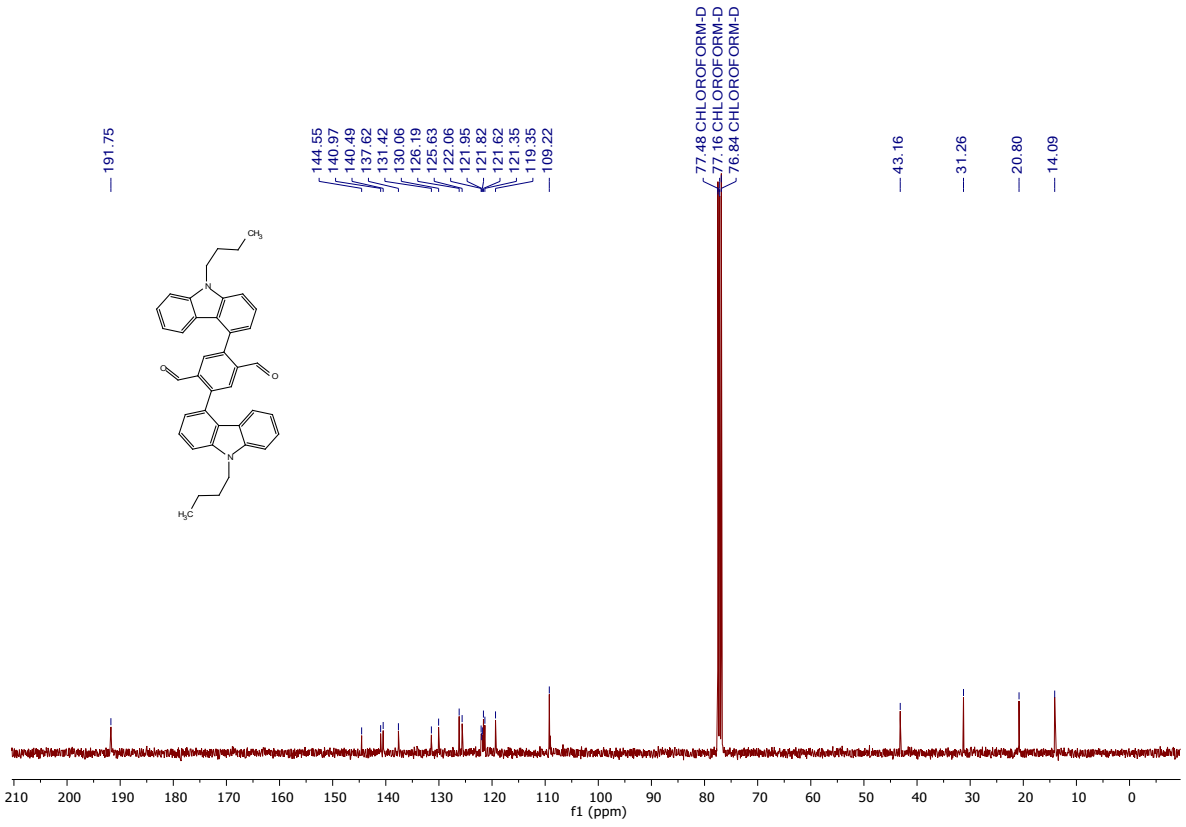


Fig. S16 ^{13}C NMR spectrum of **17**.

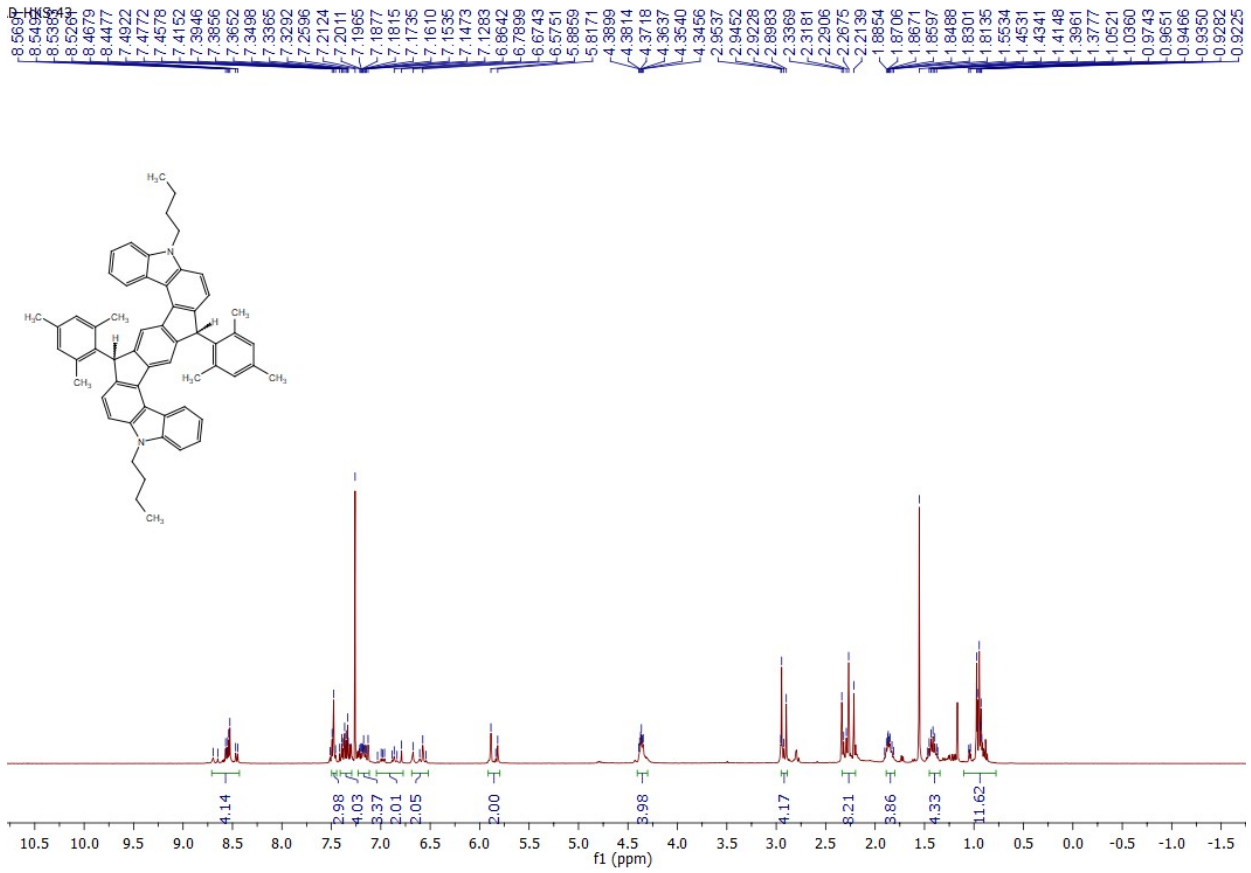


Fig. S17 ^{1}H NMR spectrum of **19**.

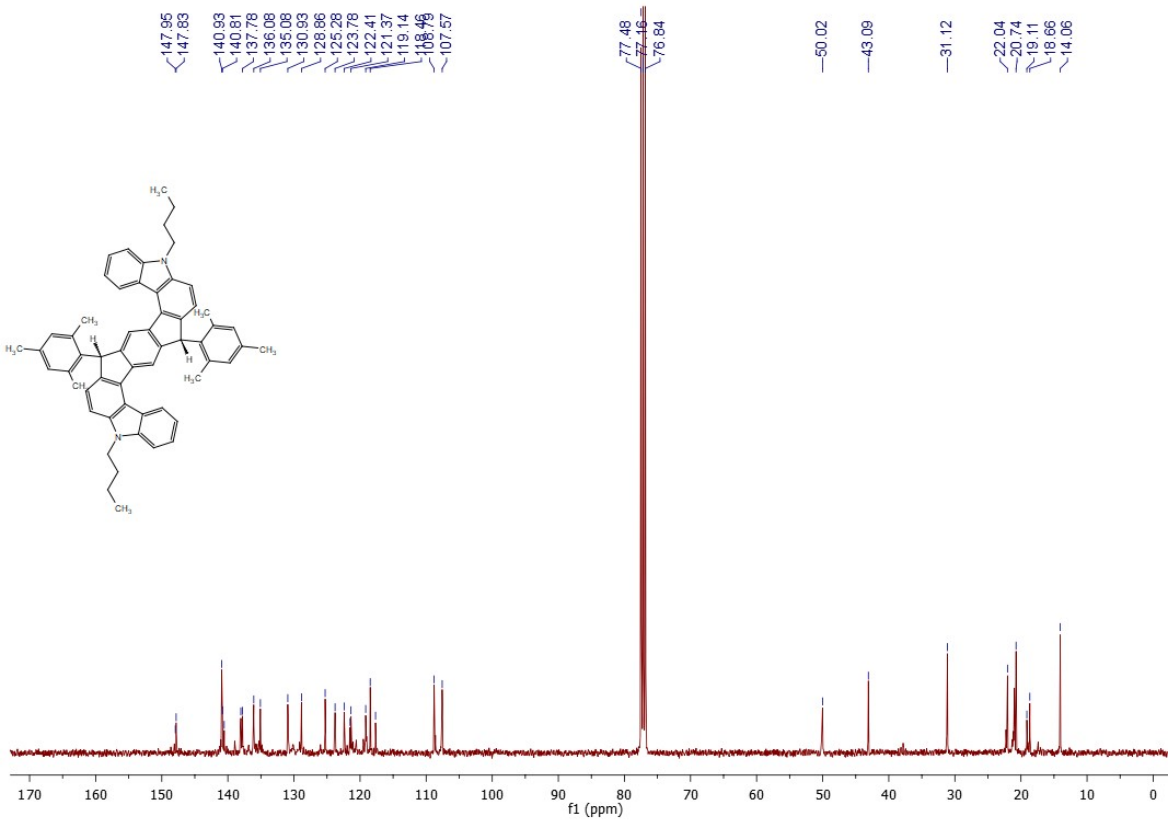


Fig. S18 ^{13}C NMR spectrum of **19**.

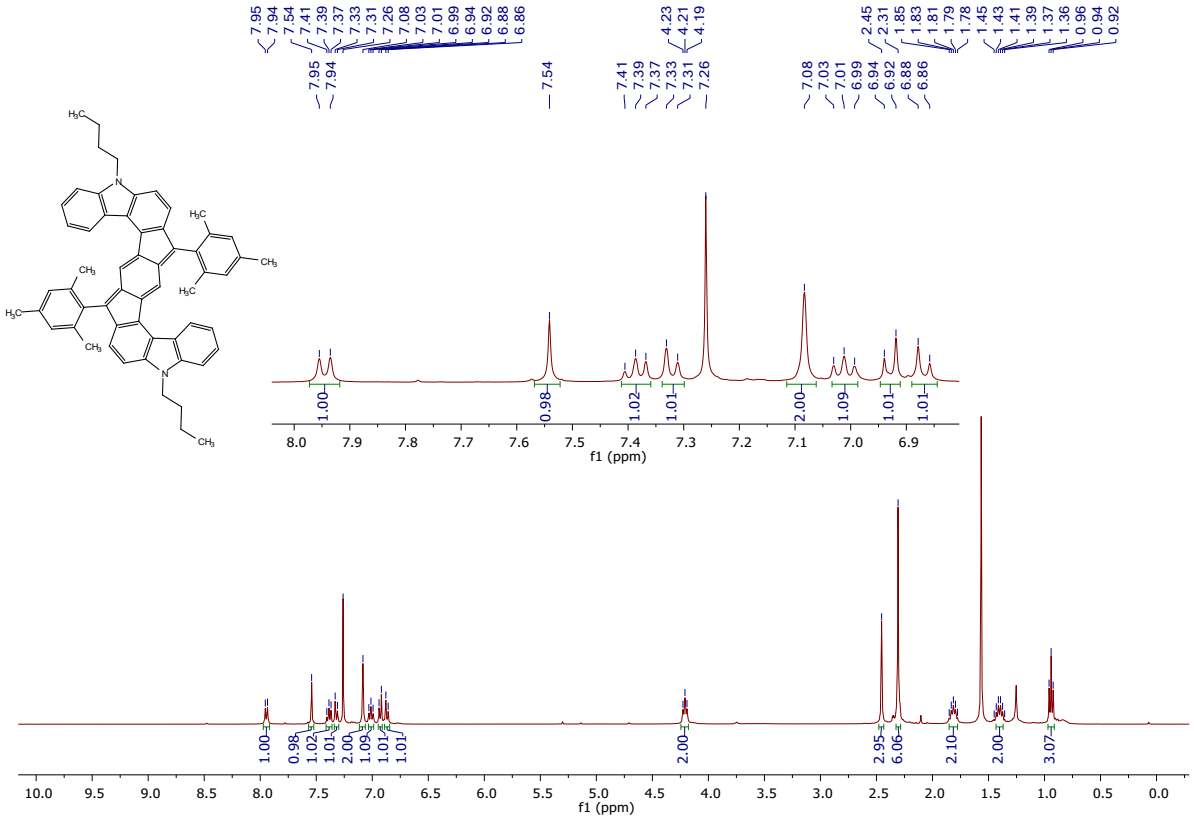


Fig. S19 ^{1}H NMR spectrum of **7**.

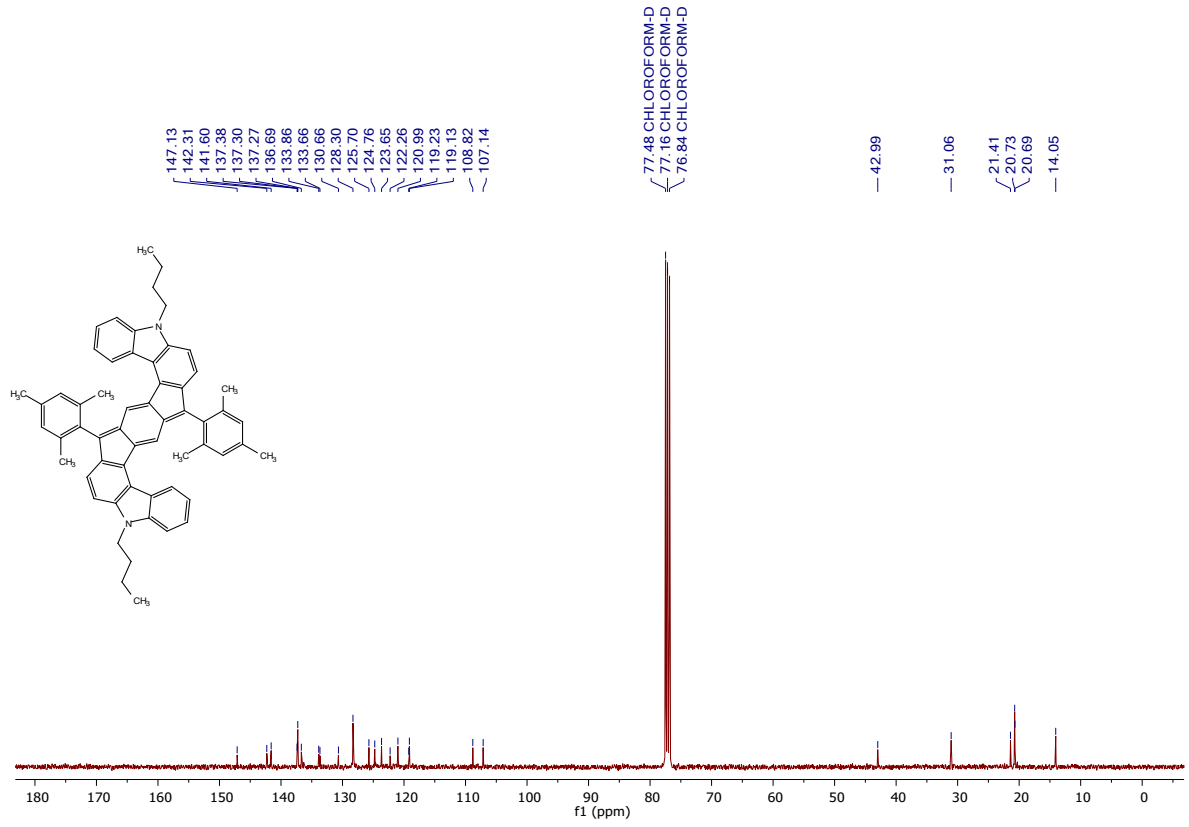


Fig. S20 ^{13}C NMR spectrum of **7**.

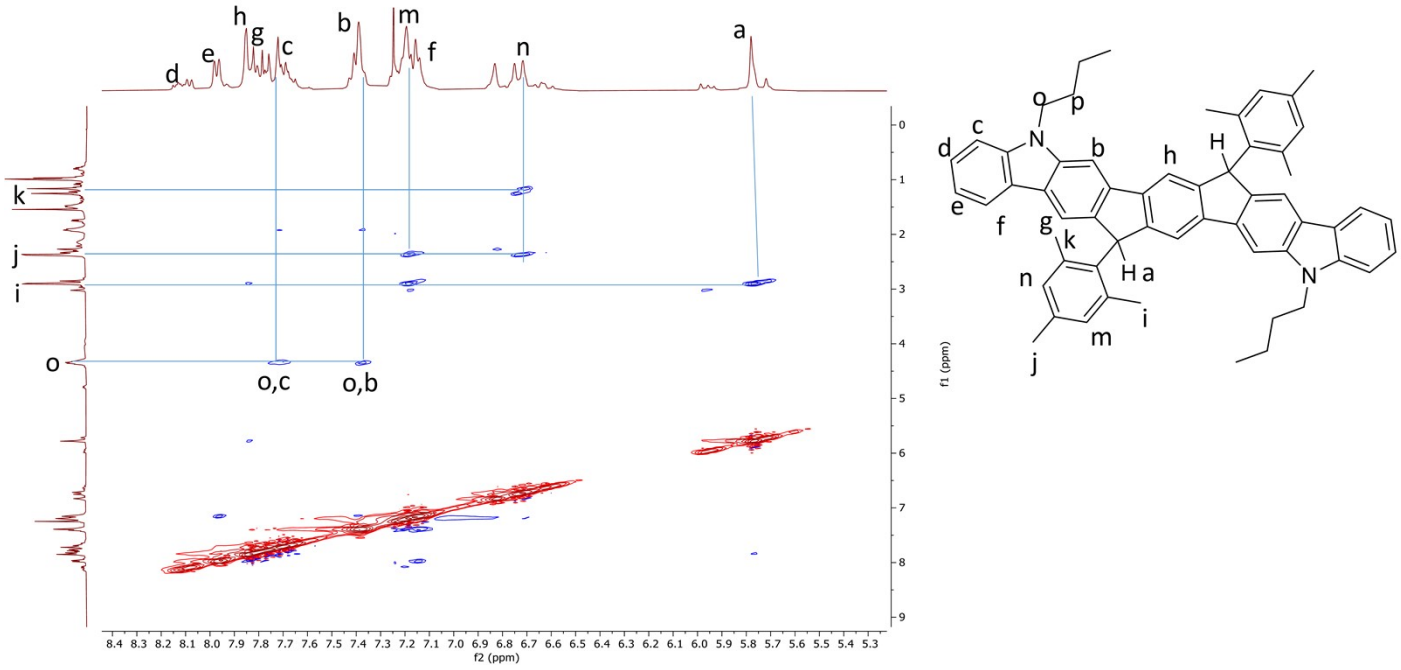
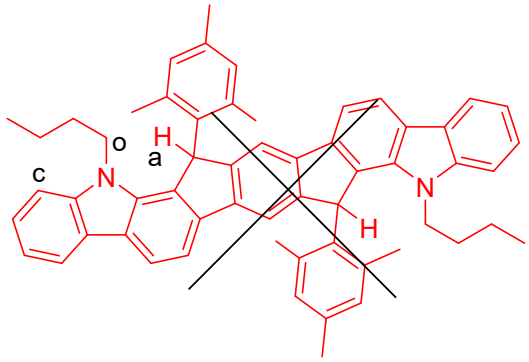


Fig. S21 ^{1}H-^{1}H NOESY spectrum of **13** in $CDCl_3$.

The NOESY correlations among NCH_2 protons "o" and outer phenyl proton "c" (o,c in Fig. S21), and NCH_2 protons "o" and other phenyl proton "b" (o,b in Fig. S21) suggest the formation of the desired *para*-isomer **13**.



another isomer (*ortho*-isomer)

not observed

Fig. S22 Another plausible isomer, for the conversion of **12** to **13** using $BF_3{\cdot}Et_2O$, which was not observed.

Had there been the formation of the another *ortho*-isomer (Fig. S22), the NCH_2 protons "o" should have shown NOESY correlations with the hydrogens "a", which is clearly absent in the above NOESY spectrum (Fig. S21). The NOESY analysis confirmed the regioselective formation of *para*-isomer **13**.

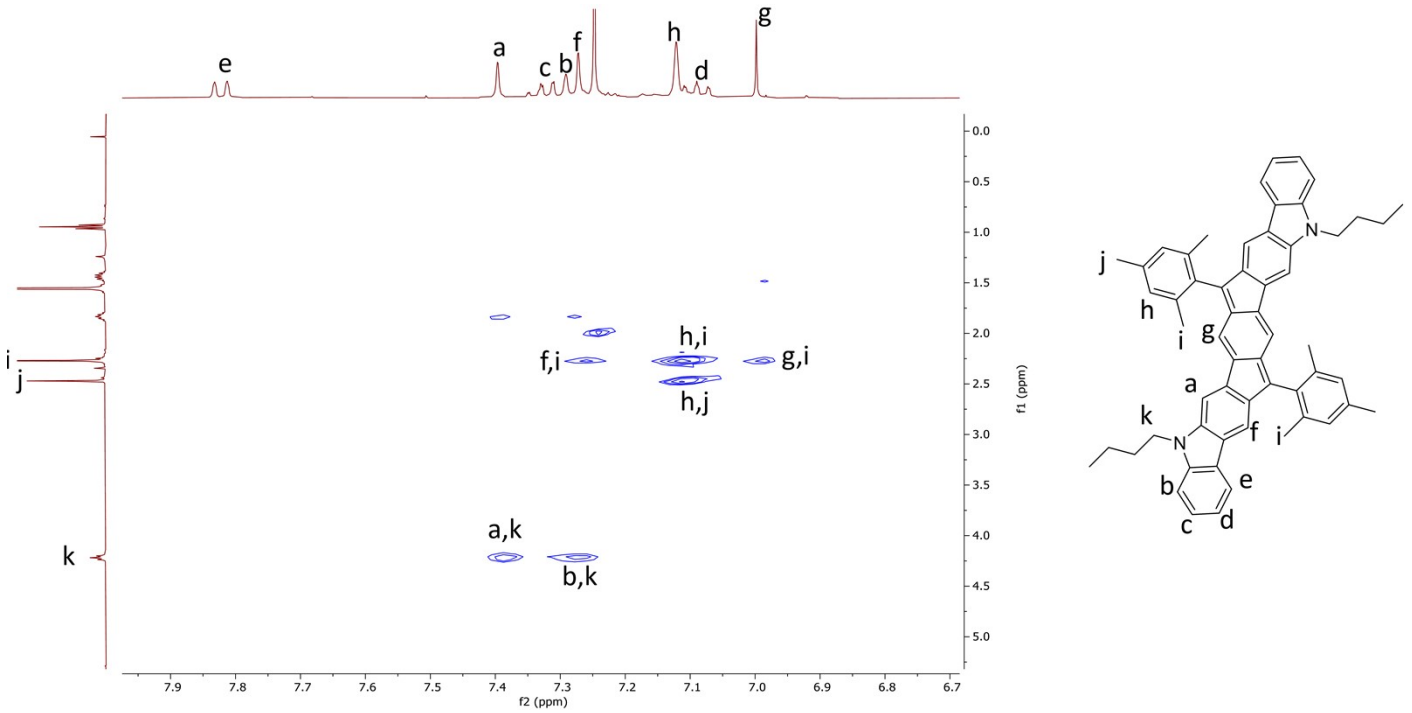


Fig. S23 ^{1}H-^{1}H NOESY spectrum of **6** in $CDCl_3$ showing the aliphatic *vs* aromatic region.

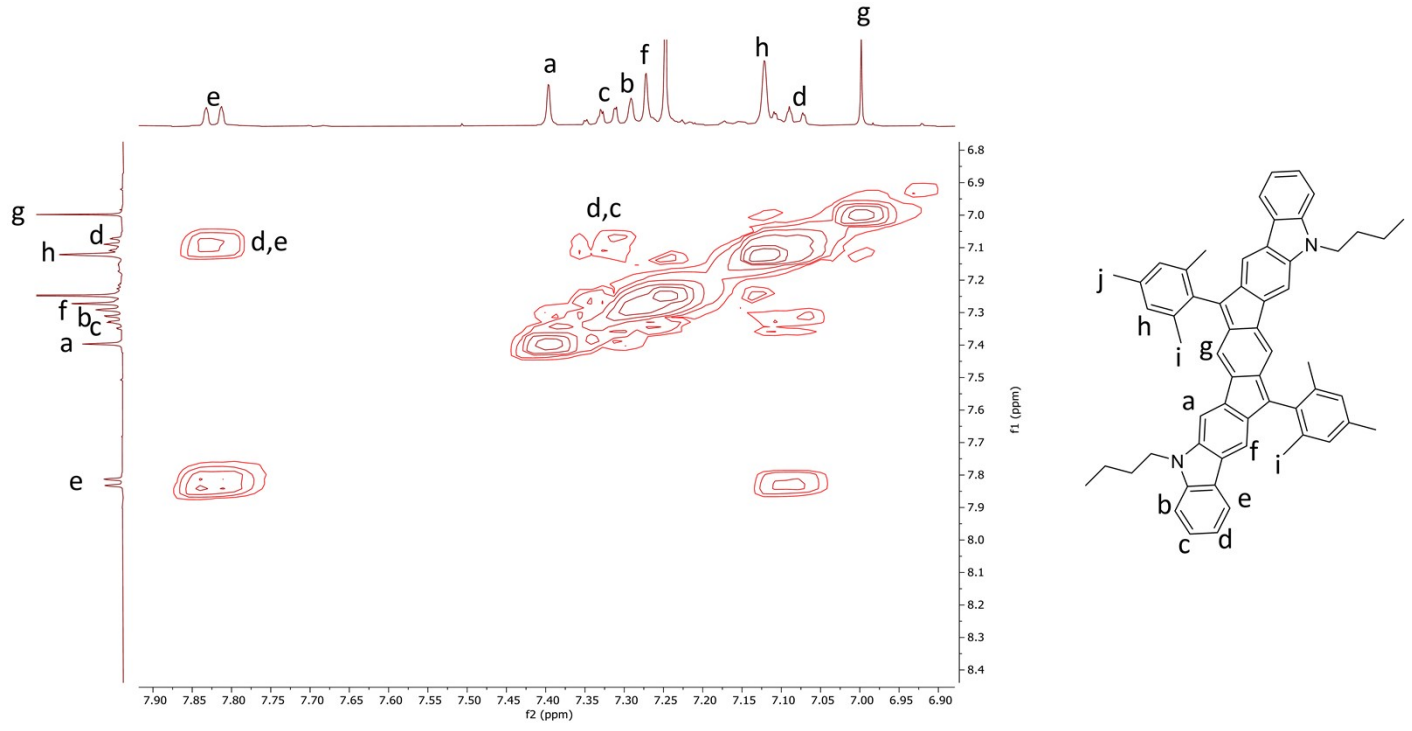


Fig. S24 ^{1}H-^{1}H COSY spectrum of **6** in $CDCl_3$ for the aromatic region.

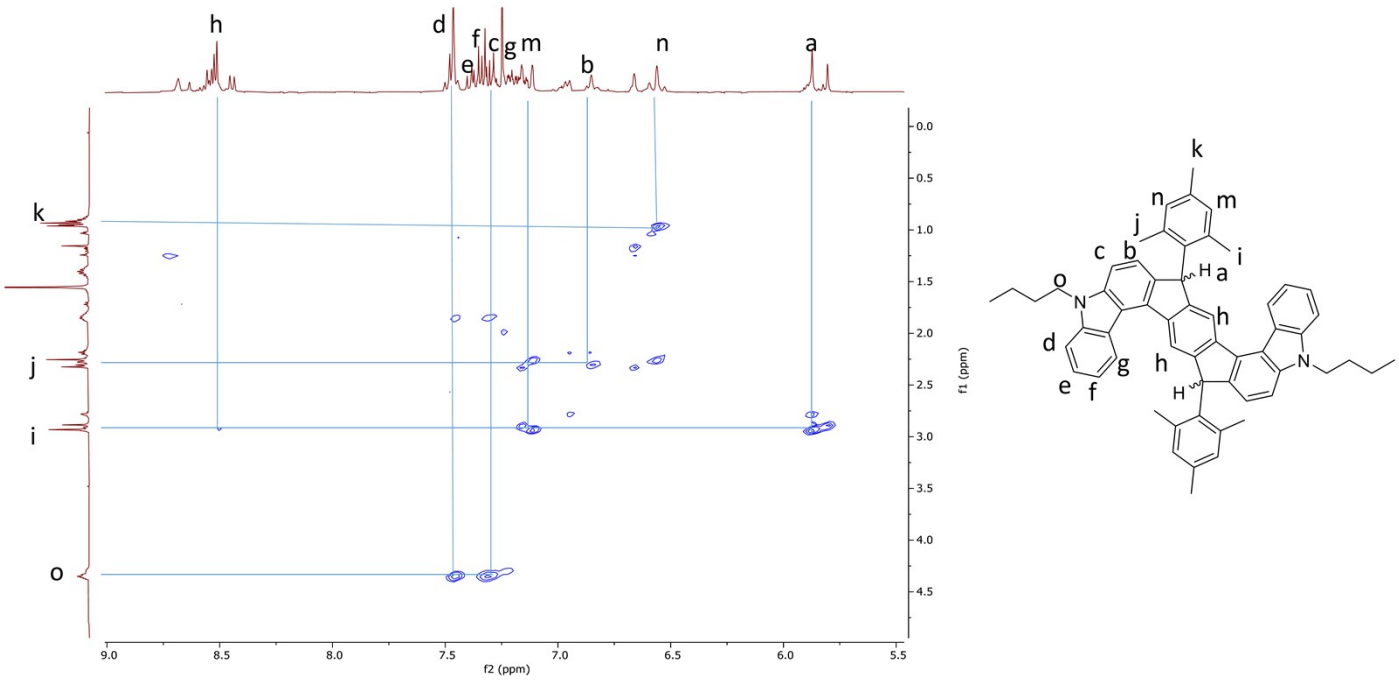


Fig. S25 ^{1}H-^{1}H NOESY spectrum of **19** in $CDCl_3$ for the aliphatic *vs* aromatic region.

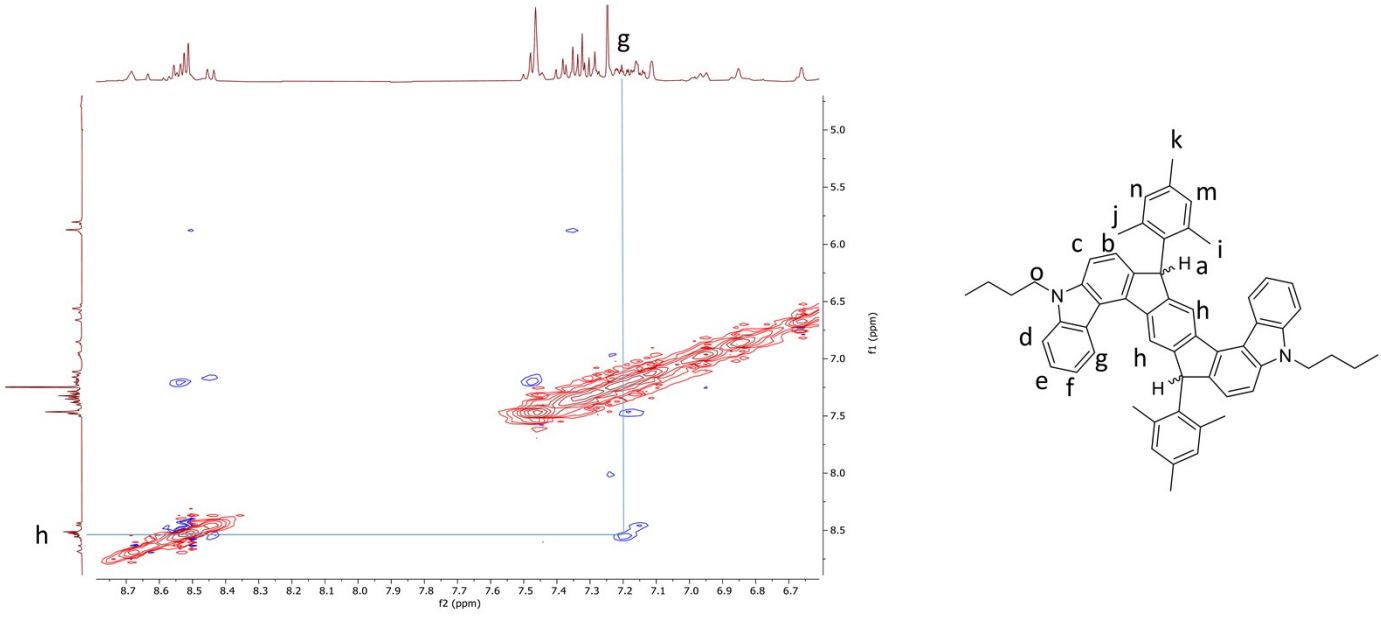


Fig. S26 ^{1}H-^{1}H NOESY spectrum of **19** in $CDCl_3$ for the aromatic region.

The above Fig. S26 clearly suggested the NOESY correlation between "g" and "h" protons in space, confirming the formation of **19**. Notably, the chemical shift of "h" protons for **19** is quite downfield shifted (8.57 ppm) in comparison to that of **13** (7.86 ppm), due to the deshielding ring-current effect of outer phenyl rings of carbazole and the mesityl rings which are now much closer to the "h" hydrogens in space.

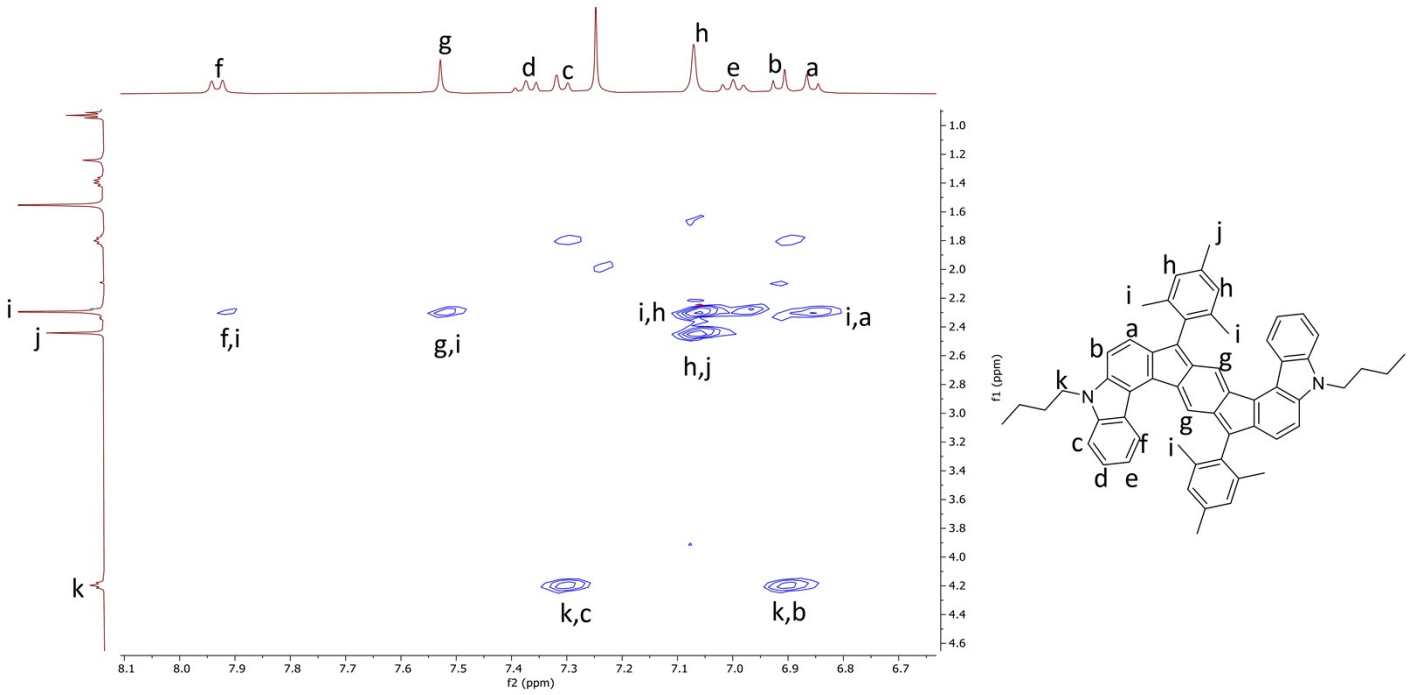


Fig. S27 ^{1}H-^{1}H NOESY spectrum of **7** in $CDCl_3$ showing the aliphatic *vs* aromatic region.

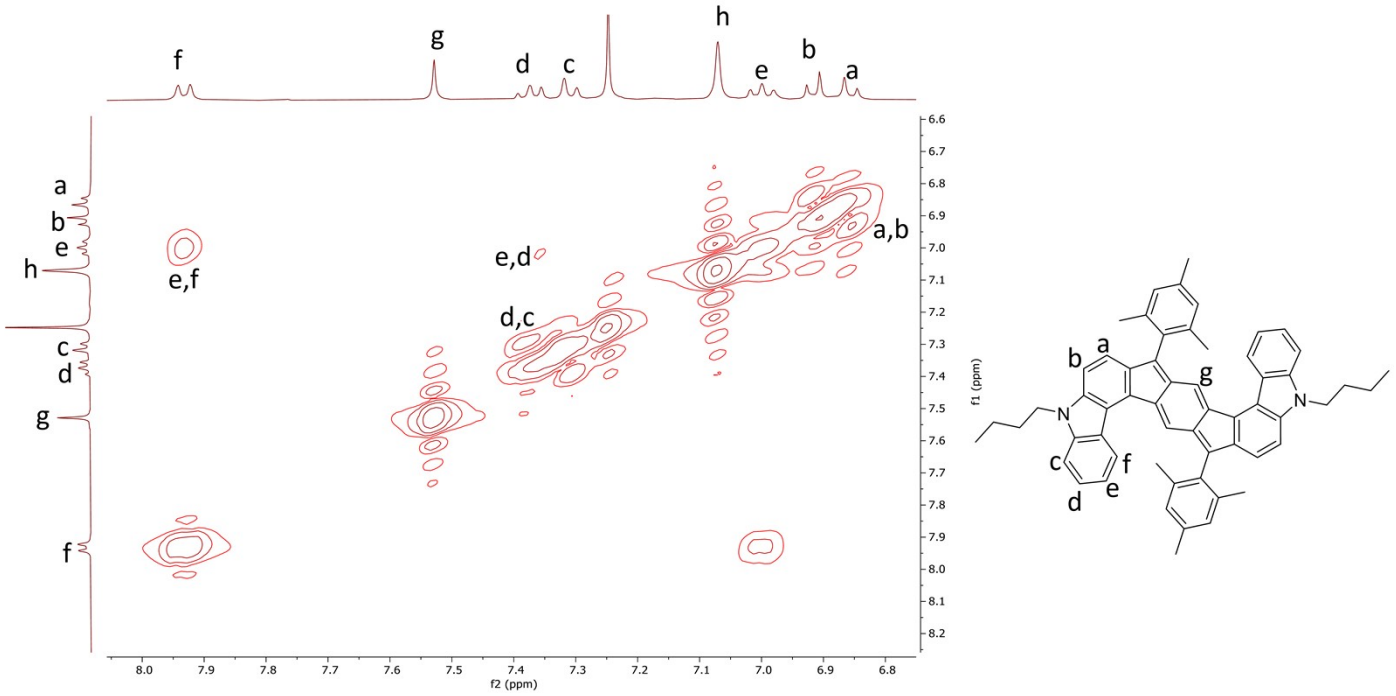


Fig. S28 ^{1}H-^{1}H COSY spectrum of **7** in $CDCl_3$ for the aromatic region.

4. X-ray crystallographic analyses:

Suitable single crystals of **6** and **7** were selected using paratone oil and mounted on glass fiber with the help of gum. The intensity data and geometric parameters of these crystals were garnered with the help of Bruker D8 Venture X-ray diffractometer having a micro-focus sealed X-ray tube Mo-Kα (λ = 0.71073 Å) source of X-rays along with a PHOTON 100 detector with inclining Phi and Omega (width of 0.5 for one frame) working at a scan speed of 10 s per frame. The crystal was kept at 298 K during data collection. For each sample, three sets of frames of data were collected with 0.30° steps in ω and an exposure time of 10 s within a randomly oriented region of reciprocal space surveyed to the extent of 1.3 hemispheres to a resolution of 0.85 Å. Data acquisition as well as extraction of data was accomplished by utilizing Bruker Apex-3 and Bruker SAINT software packages using a narrow -frame algorithm.[1] By utilizing OLex2,[2] the crystal structure was solved with the help of olex2.solve[3] structure solution program by employing intrinsic Phasing methods and crystal structure refinement was done with the SHELXL[4] refinement package by putting into use Least Squares minimization. Refinement of all non-hydrogen atoms was completed with the help of anisotropic thermal parameters.

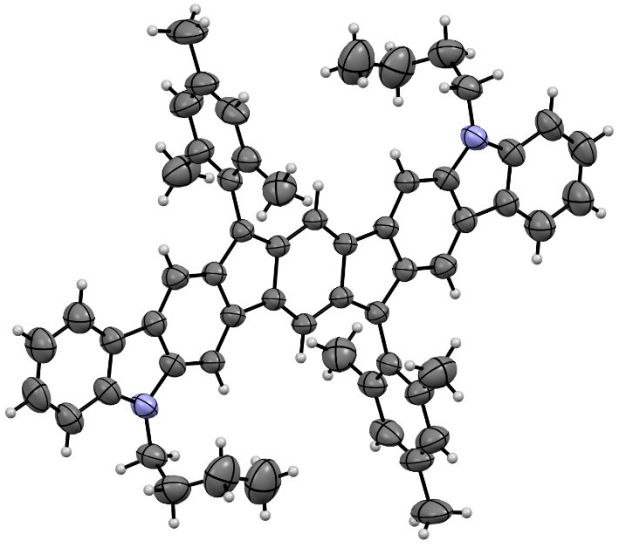


Fig. S29. ORTEP drawing of **6** showing the thermal ellipsoids at 50% probability level.

Table S1. Crystal data and structure refinement for **6**.

CCDC number	2150266
Crystallization solvents	Recrystallization from toluene/methanol,[5] by slow evaporation
Empirical formula	$C_{58}H_{54}N_2$
Formula weight	857.14
Temperature/K	298.15
Crystal system	triclinic
Space group	P-1
a/Å	10.460(4)
b/Å	10.508(4)

c/Å	12.714(5)
α/°	66.725(10)
β/°	88.452(11)
γ/°	69.973(10)
Volume/Å^3	1196.7(8)
Z	1
ρ_{calc}g/cm^3	1.189
μ/mm^{-1}	0.068
F(000)	458.0
Crystal size/mm^3	0.256 × 0.204 × 0.078
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.446 to 50.358
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	22192
Independent reflections	4261 [R_{int} = 0.0982, R_{sigma} = 0.0802]
Data/restraints/parameters	4261/0/276
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0642, wR_2 = 0.1658
Final R indexes [all data]	R_1 = 0.1410, wR_2 = 0.2109
Largest diff. peak/hole / e Å^{-3}	0.23/-0.18

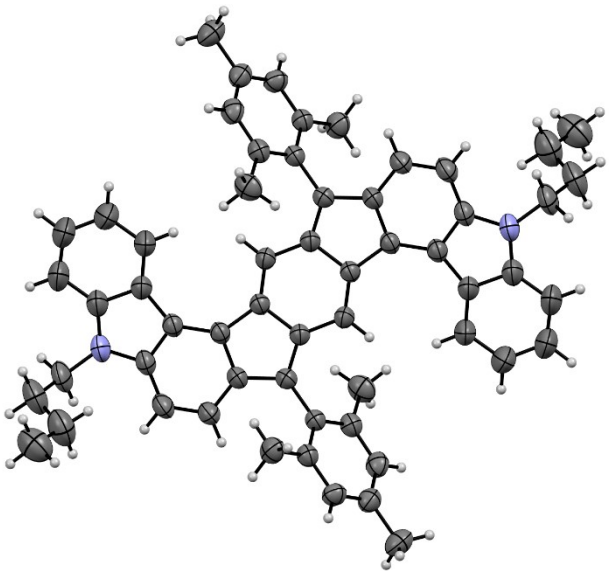


Fig. S30. ORTEP drawing of **7** showing the thermal ellipsoids at 50% probability level.

Table S2. Crystal data and structure refinement for **7**.

CCDC number	2150267
Crystallization solvents	Recrystallization from dichloromethane/hexane, by slow evaporation
Empirical formula	$C_{58}H_{54}N_2$

Formula weight	779.03
Temperature/K	298.(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	18.6226(10)
b/Å	9.5211(6)
c/Å	24.5141(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4346.5(4)
Z	4
ρ_{calc}g/cm^3	1.190
μ/mm^{-1}	0.068
F(000)	1664.0
Crystal size/mm^3	0.356 × 0.289 × 0.215
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.38 to 50.1
Index ranges	-22 ≤ h ≤ 22, -11 ≤ k ≤ 11, -29 ≤ l ≤ 29
Reflections collected	75152
Independent reflections	3844 [R_{int} = 0.1190, R_{sigma} = 0.0399]
Data/restraints/parameters	3844/0/275
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0582, wR_2 = 0.1425
Final R indexes [all data]	R_1 = 0.1172, wR_2 = 0.1916
Largest diff. peak/hole / e Å^{-3}	0.27/-0.30

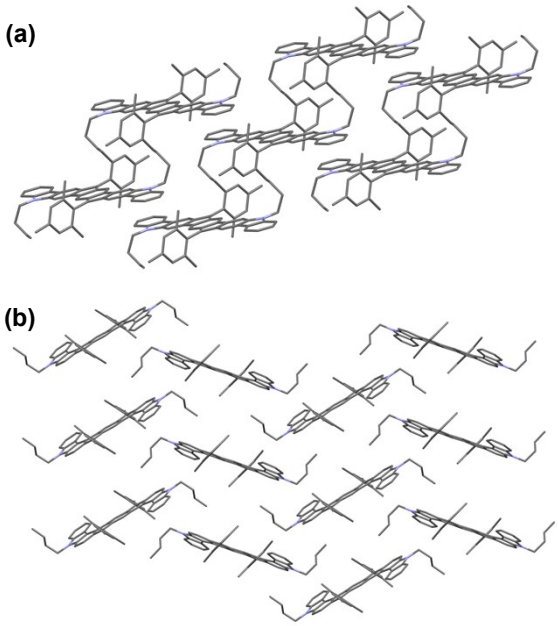


Fig. S31. Packing arrangement of (a) **6** and (b) **7**.

5. DFT calculations:

Density functional theory (DFT) calculations were performed with Gaussian 09 package using a high-performance computing cluster facility of IIT Ropar in gas phase using the B3LYP (restricted and unrestricted) level of theory with basis set 6-31G(d,p).[6] NICS (standard GIAO method) and HOMA[7] indices were calculated for the optimized closed-shell structures for **6** and **7**. Excitation energies were computed using time dependent density functional theory (TDDFT) for the optimized closed-shell structures of **6** and **7** in gas-phase and solvation (PCM) model. Molecular orbital contributions were determined using GaussSum 3.0 package.[8] Anisotropy of the induced current density (ACID) plots were generated following Herges's protocol.[9]

Table S3. Relative energies for the optimized structure **6** at B3LYP/6-31G(d,p) level.

State	Hartree	kcal/mol
Singlet Closed-Shell	-2352.398687	-1476130.176
Singlet Open-Shell	-2352.398687	-1476130.176
Triplet Open-Shell	-2352.372734	-1476113.89

$\Delta E_{\text{Triplet-Singlet}}$ = 16.28 kcal/mol.

Table S4. Relative energies for the optimized structure **7** at B3LYP/6-31G(d,p) level.

State	Hartree	kcal/mol
Singlet Closed-Shell	-2352.39093	-1476125.309
Singlet Open-Shell	-2352.39093	-1476125.309
Triplet Open-Shell	-2352.36407	-1476108.454

$\Delta E_{\text{Triplet-Singlet}}$ = 16.85 kcal/mol.

Experimental UV-vis absorption and TDDFT calculated spectra:

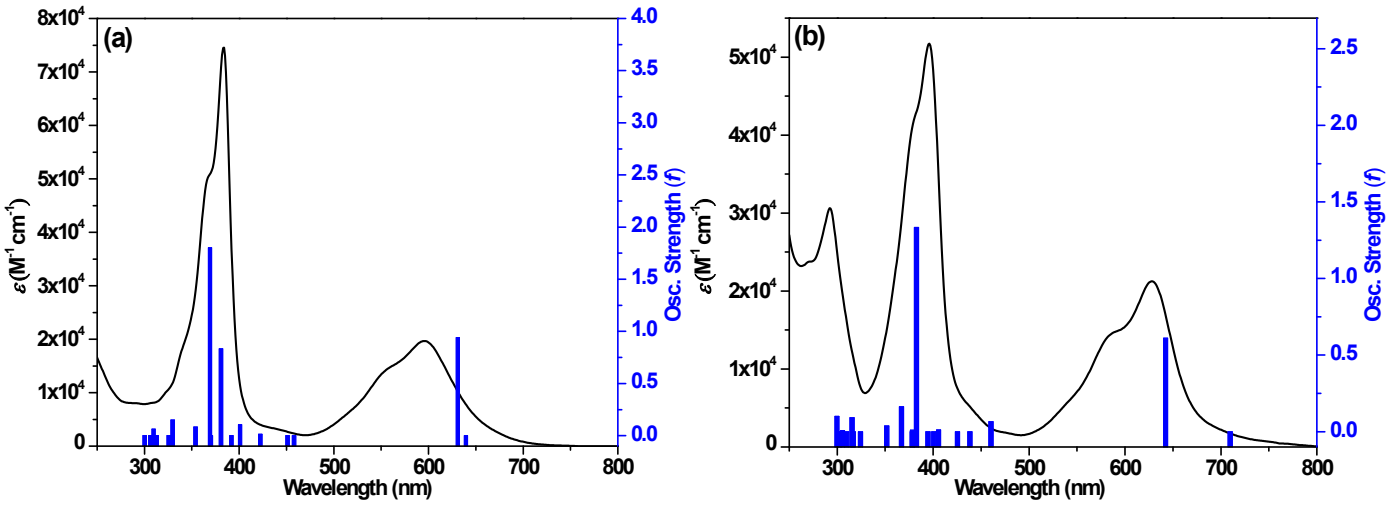


Fig. S32. Experimental UV-vis spectrum (black) in DCM (dichloromethane), against the TDDFT calculated oscillator strength shown as stick diagram (blue) in DCM, for (a) **6** and (b) **7**.

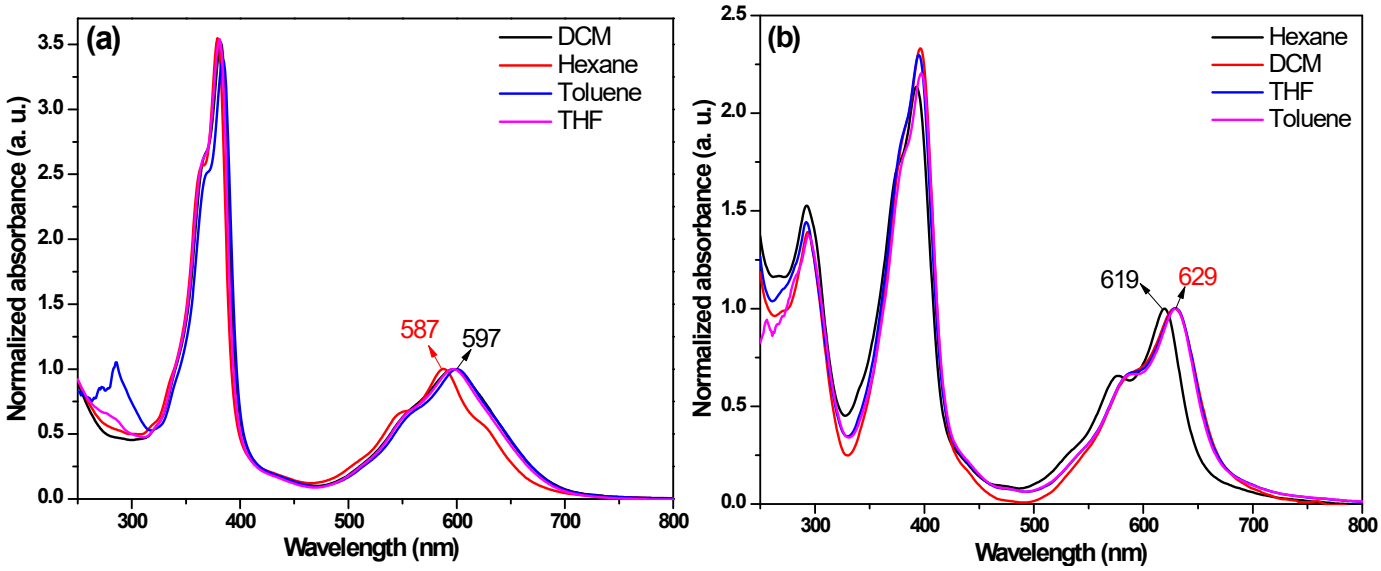


Fig. S33. UV-vis absorption spectra of (a) **6** and (b) **7** in solvents (DCM, THF, hexane, Toluene) with different polarity indices, recorded in JASCO V-770 spectrophotometer. The λ_{max} for the HOMO→LUMO transition is shown.

5.1 Summary of TDDFT calculations

Table S5. Summary of low energy transitions in different solvents by TDDFT calculations

Solvent	λ (HOMO→LUMO)	λ (HOMO-1→LUMO)
Dichloromethane	**6**: 631 nm **7**: 642 nm	**6**: 639 nm **7**: 709 nm
Tetrahydrofuran	**6**: 630 nm **7**: 641 nm	**6**: 639 nm **7**: 709 nm
Toluene	**6**: 631 nm **7**: 641 nm	**6**: 641 nm **7**: 706 nm
Hexane	**6**: 625 nm **7**: 636 nm	**6**: 642 nm **7**: 705 nm
Gas phase	**6**: 604 nm **7**: 616 nm	**6**: 643 nm **7**: 702 nm

The HOMO→LUMO transition is predicted to be almost unaffected in THF/DCM/toluene solvents for **6** and **7**, while a blue-shift (by 6 nm) was predicted in hexane by TDDFT calculations, which is in line with the experimental observations. The forbidden HOMO-1→LUMO transition of **6** is slightly red-shifted (by 2 to 3 nm) when changing solvents from polar THF/DCM to comparatively non-polar toluene/hexane. In contrast, the HOMO-1→LUMO transition for **7** is blue-shifted (by 3 to 4 nm) when changing from polar to non-polar solvents. These observations clearly imply some charge transfer character of **6** and **7**, for the lower energy electronic transitions.

Table S6. Calculated electronic transitions for **6** in dichloromethane.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
639.5839	**0**	**H-1->LUMO (99%)**
630.9906	**0.9397**	**HOMO->LUMO (97%)**
457.9255	0	H-2->LUMO (38%), HOMO->L+1 (59%)
451.1766	0	H-2->LUMO (59%), HOMO->L+1 (38%)
422.3441	0.0146	H-3->LUMO (96%)
400.8903	0.1058	H-6->LUMO (46%), H-4->LUMO (52%)
391.8192	0	H-5->LUMO (99%)
380.8076	0.8337	H-6->LUMO (33%), H-4->LUMO (23%), H-1->L+1 (41%)
370.1879	0	H-7->LUMO (100%)
370.1437	0.0017	H-8->LUMO (100%)
369.1408	1.8032	H-6->LUMO (20%), H-4->LUMO (20%), H-1->L+1 (54%)
353.8741	0.0832	HOMO->L+2 (93%)
329.7166	0.15	H-2->L+1 (94%)
325.6207	0	H-9->LUMO (86%)
312.9154	0	H-10->LUMO (76%), H-1->L+2 (13%)
310.6184	0	H-10->LUMO (12%), H-4->L+1 (19%), H-3->L+1 (10%), H-1->L+2 (34%)
309.5868	0.0631	HOMO->L+3 (98%)
307.7502	0	H-3->L+1 (10%), HOMO->L+4 (69%)
305.9126	0	H-4->L+1 (18%), H-3->L+1 (13%), H-1->L+2 (17%), HOMO->L+4 (26%), HOMO->L+9 (10%)
300.1146	0	H-4->L+1 (32%), H-3->L+1 (43%), H-1->L+2 (11%)

Table S7. Calculated electronic transitions for **6** in THF.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
639.7819	**0**	**H-1->LUMO (99%)**
629.9646	**0.9305**	**HOMO->LUMO (97%)**
457.7227	0	H-2->LUMO (36%), HOMO->L+1 (62%)
450.8813	0	H-2->LUMO (61%), HOMO->L+1 (36%)
422.2722	0.0144	H-3->LUMO (96%)
400.5147	0.1051	H-6->LUMO (46%), H-4->LUMO (52%)
391.448	0	H-5->LUMO (99%)
380.5738	0.8343	H-6->LUMO (33%), H-4->LUMO (23%), H-1->L+1 (41%)
369.8566	0	H-7->LUMO (100%)
369.8235	0.0013	H-8->LUMO (100%)
368.8443	1.7963	H-6->LUMO (20%), H-4->LUMO (20%), H-1->L+1 (54%)
353.8539	0.0844	HOMO->L+2 (93%)
329.5326	0.1493	H-2->L+1 (94%)
325.5523	0	H-9->LUMO (86%)
312.8759	0	H-10->LUMO (75%), H-1->L+2 (14%)
310.5873	0	H-10->LUMO (13%), H-4->L+1 (17%), H-1->L+2 (34%)
309.7802	0.0631	HOMO->L+3 (98%)
307.8649	0	HOMO->L+4 (75%)
305.9126	0	H-4->L+1 (20%), H-3->L+1 (14%), H-1->L+2 (17%), HOMO->L+4

		(20%), HOMO->L+9 (11%)
300.1073	0	H-4->L+1 (32%), H-3->L+1 (43%), H-1->L+2 (10%)

Table S8. Calculated electronic transitions for **6** in toluene.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
641.8354	**0**	**H-1->LUMO (99%)**
631.2154	**0.9596**	**HOMO->LUMO (97%)**
456.7278	0	H-2->LUMO (26%), HOMO->L+1 (72%)
448.8897	0	H-2->LUMO (71%), HOMO->L+1 (26%)
422.2147	0.0163	H-3->LUMO (96%)
398.0331	0.1151	H-6->LUMO (44%), H-4->LUMO (54%)
388.6625	0	H-5->LUMO (99%)
380.5505	1.2673	H-6->LUMO (26%), H-4->LUMO (15%), H-1->L+1 (57%)
369.5369	1.3972	H-6->LUMO (29%), H-4->LUMO (26%), H-1->L+1 (38%)
367.456	0	H-7->LUMO (100%)
367.4234	0.0012	H-8->LUMO (100%)
353.9853	0.0839	HOMO->L+2 (94%)
328.1806	0.1371	H-2->L+1 (94%)
325.2022	0	H-9->LUMO (85%)
312.9549	0	H-10->LUMO (62%), H-1->L+2 (23%)
311.3751	0.0631	HOMO->L+3 (98%)
310.7508	0	H-10->LUMO (26%), H-1->L+2 (30%), HOMO->L+4 (11%)
309.0698	0	HOMO->L+4 (81%)
305.8447	0	H-4->L+1 (30%), H-3->L+1 (24%), H-1->L+2 (11%), HOMO->L+9 (12%)
300.1582	0	H-4->L+1 (32%), H-3->L+1 (41%), H-1->L+2 (10%), HOMO->L+5 (10%)

Table S9. Calculated electronic transitions for **6** in hexane.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
642.2676	**0**	**H-1->LUMO (99%)**
625.8624	**0.9069**	**HOMO->LUMO (96%)**
456.0894	0	H-2->LUMO (22%), HOMO->L+1 (75%)
447.8681	0	H-2->LUMO (74%), HOMO->L+1 (23%)
422.1428	0.0147	H-3->LUMO (96%)
397.2552	0.1081	H-6->LUMO (44%), H-4->LUMO (54%)
388.0664	0	H-5->LUMO (99%)
379.4556	1.1046	H-6->LUMO (29%), H-4->LUMO (17%), H-1->L+1 (51%)
368.0669	1.5193	H-6->LUMO (25%), H-4->LUMO (24%), H-1->L+1 (44%)
367.0101	0	H-7->LUMO (100%)
366.9775	0.0023	H-8->LUMO (100%)
353.6823	0.0901	HOMO->L+2 (93%)
327.6515	0.1357	H-2->L+1 (94%)

325.1169	0	H-9->LUMO (85%)
312.8128	0	H-10->LUMO (63%), H-1->L+2 (23%)
311.649	0.0635	HOMO->L+3 (98%)
310.6807	0	H-10->LUMO (25%), H-1->L+2 (29%), HOMO->L+4 (17%)
309.2625	0	HOMO->L+4 (77%)
305.5207	0	H-4->L+1 (31%), H-3->L+1 (25%), H-1->L+2 (10%), HOMO->L+9 (13%)
300.1001	0	H-4->L+1 (32%), H-3->L+1 (40%), H-1->L+2 (10%), HOMO->L+5 (11%)

Table S10. Calculated electronic transitions for **6** in gas phase.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
643.5009947	**0**	**H-1->LUMO (99%)**
604.6198022	**0.6842**	**HOMO->LUMO (94%)**
453.8854028	0	H-2->LUMO (14%), HOMO->L+1 (83%)
444.3847191	0	H-2->LUMO (82%), HOMO->L+1 (14%)
421.9560176	0.0092	H-3->LUMO (95%)
395.0275175	0.0785	H-6->LUMO (48%), H-4->LUMO (50%)
386.7228217	0	H-5->LUMO (99%)
375.684312	0.47	H-6->LUMO (39%), H-4->LUMO (31%), H-1->L+1 (27%)
366.1970542	0	H-7->LUMO (100%)
366.1646091	0.0006	H-8->LUMO (100%)
360.4061994	1.8143	H-6->LUMO (10%), H-4->LUMO (12%), H-1->L+1 (63%)
352.1553573	0.2256	HOMO->L+2 (87%)
325.8603255	0.14	H-2->L+1 (94%)
324.9805684	0	H-9->LUMO (85%)
312.2769983	0	H-10->LUMO (67%), H-1->L+2 (20%)
312.0726337	0.0691	HOMO->L+3 (97%)
310.4939437	0	H-10->LUMO (15%), H-1->L+2 (19%), HOMO->L+4 (50%)
309.4786497	0	H-1->L+2 (19%), HOMO->L+4 (46%)
304.3133293	0	H-4->L+1 (34%), H-3->L+1 (25%), HOMO->L+9 (14%)
299.860538	0	H-4->L+1 (32%), H-3->L+1 (38%), HOMO->L+5 (14%)

Table S11. Calculated electronic transitions for **7** in dichloromethane.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
709.571	**0**	**H-1->LUMO (98%)**
642.3674	**0.6112**	**HOMO->LUMO (96%)**
460.2715	0.0653	H-2->LUMO (94%)
438.2585	0	HOMO->L+1 (89%)
425.3871	0	H-3->LUMO (86%)
405.6781	0.0114	H-4->LUMO (92%)
400.6959	0	H-6->LUMO (97%)
394.6629	0	H-5->LUMO (94%)

382.6528	1.3339	H-1->L+1 (93%)
378.3209	0.0099	H-8->LUMO (94%)
378.0787	0	H-9->LUMO (100%)
366.9666	0.1624	H-7->LUMO (78%)
351.5861	0.0373	HOMO->L+2 (95%)
324.1903	0	H-1->L+2 (82%)
316.6071	0	H-2->L+1 (78%), H-1->L+2 (10%)
315.4953	0.0918	H-10->LUMO (92%)
309.7647	0	H-2->L+1 (10%), HOMO->L+3 (81%)
305.5282	0.0073	HOMO->L+4 (98%)
302.2362	0	HOMO->L+5 (97%)
299.7156	0.1006	H-3->L+1 (91%)

Table S12. Calculated electronic transitions for **7** in THF.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
709.2057	**0**	**H-1->LUMO (98%)**
641.3042	**0.606**	**HOMO->LUMO (96%)**
459.8277	0.064	H-2->LUMO (94%)
438.2121	0	HOMO->L+1 (89%)
425.1829	0	H-3->LUMO (86%)
405.1346	0.0114	H-4->LUMO (91%)
400.1657	0	H-6->LUMO (97%)
394.3741	0	H-5->LUMO (94%)
382.3578	1.331	H-1->L+1 (93%)
377.8482	0.0093	H-8->LUMO (94%)
377.6181	0	H-9->LUMO (100%)
366.8146	0.1607	H-7->LUMO (78%)
351.6659	0.0369	HOMO->L+2 (95%)
324.1649	0	H-1->L+2 (82%)
316.4859	0	H-2->L+1 (78%), H-1->L+2 (10%)
315.3749	0.0906	H-10->LUMO (92%)
309.7493	0	H-2->L+1 (10%), HOMO->L+3 (81%)
305.8146	0.0073	HOMO->L+4 (98%)
302.5164	0	HOMO->L+5 (97%)
299.6649	0.1	H-3->L+1 (91%)

Table S13. Calculated electronic transitions for **7** in toluene.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
706.498	**0**	**H-1->LUMO (98%)**
641.4037	**0.6306**	**HOMO->LUMO (96%)**
456.7783	0.0632	H-2->LUMO (95%)
438.274	0	HOMO->L+1 (90%)
424.2808	0	H-3->LUMO (87%)
400.8514	0.0136	H-7->LUMO (13%), H-4->LUMO (86%)

395.9105	0	H-6->LUMO (98%)
392.1414	0	H-5->LUMO (95%)
383.2205	1.3599	H-1->L+1 (94%)
374.2102	0.0042	H-8->LUMO (96%)
373.9732	0	H-9->LUMO (100%)
366.2187	0.1709	H-7->LUMO (75%), H-4->LUMO (11%)
352.5559	0.0387	HOMO->L+2 (95%)
324.7082	0	H-1->L+2 (84%)
315.6399	0	H-2->L+1 (74%), HOMO->L+3 (14%)
314.7744	0.0938	H-10->LUMO (92%)
309.8964	0	H-2->L+1 (15%), HOMO->L+3 (76%)
308.125	0.0078	HOMO->L+4 (98%)
304.7996	0	HOMO->L+5 (97%)
299.6431	0.0971	H-3->L+1 (91%)

Table S14. Calculated electronic transitions for **7** in hexane.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
705.6134	**0**	**H-1->LUMO (98%)**
636.3668	**0.5983**	**HOMO->LUMO (96%)**
455.7373	0.0575	H-2->LUMO (94%)
437.9334	0	HOMO->L+1 (90%)
423.7298	0	H-3->LUMO (87%)
399.8689	0.013	H-7->LUMO (15%), H-4->LUMO (84%)
394.9646	0	H-6->LUMO (98%)
391.5593	0	H-5->LUMO (95%)
381.4989	1.3362	H-1->L+1 (93%)
373.4213	0.0047	H-8->LUMO (96%)
373.1965	0	H-9->LUMO (100%)
365.7865	0.1586	H-7->LUMO (74%), H-4->LUMO (12%)
352.5559	0.0371	HOMO->L+2 (95%)
324.3854	0	H-1->L+2 (85%)
315.3428	0	H-2->L+1 (72%), HOMO->L+3 (17%)
314.479	0.0871	H-10->LUMO (92%)
309.6487	0	H-2->L+1 (18%), HOMO->L+3 (72%)
308.6466	0.0075	HOMO->L+4 (98%)
305.3175	0	HOMO->L+5 (97%)
299.4405	0.0947	H-3->L+1 (90%)

Table S15. Calculated electronic transitions for **7** in gas phase.

Wavelength (nm)	Oscillator Strength (*f*)	Major contributions
702.8135403	**0**	**H-1->LUMO (98%)**
616.5871128	**0.4629**	**HOMO->LUMO (94%)**
452.6921887	0.0386	H-2->LUMO (93%)
436.607165	0	HOMO->L+1 (91%)
421.884227	0	H-3->LUMO (88%)

397.4971519	0.0098	H-7->LUMO (21%), H-4->LUMO (78%)
392.7002934	0	H-6->LUMO (98%)
389.9582834	0	H-5->LUMO (95%)
373.5225398	1.1656	H-1->L+1 (88%)
371.5969928	0.0498	H-8->LUMO (93%)
371.4522639	0	H-9->LUMO (100%)
364.3139887	0.1128	H-7->LUMO (68%), H-4->LUMO (17%)
352.2153821	0.0342	HOMO->L+2 (94%)
323.1257145	0	H-1->L+2 (85%)
314.4789769	0	H-2->L+1 (62%), HOMO->L+3 (30%)
313.5088291	0.0635	H-10->LUMO (91%)
309.8731265	0.0064	HOMO->L+4 (98%)
308.3702349	0	H-2->L+1 (29%), HOMO->L+3 (58%)
306.540416	0	HOMO->L+5 (97%)
298.5751635	0.0889	H-3->L+1 (89%)

5.2 Cartesian coordinates

Singlet closed-shell **6**: `-2352.3986874 hartree`

Atom	x	y	z
C	-0.52475900	1.34079300	-0.15349500
H	-0.88192300	2.36105900	-0.27079200
N	6.30706400	-1.49749500	0.49566500
C	0.88217600	1.09311800	-0.05189600
C	1.38001000	-0.27787200	0.10063400
C	2.83918300	-0.19040400	0.17128300
C	6.81603900	-3.68403600	-0.63556000
H	7.74627700	-3.23348900	-0.99993600
H	7.06008900	-4.71945000	-0.36054800
C	6.39569700	-2.94378700	0.64751500
H	5.42888100	-3.30318700	1.00979500
H	7.11931400	-3.15205100	1.44429000
C	5.14828400	-0.74143900	0.35157600
C	3.81184500	-1.16933900	0.31732700
H	3.54511000	-2.21766600	0.40116200
C	5.77166800	-3.68614800	-1.76354300
H	6.26688900	-3.99477300	-2.69219100
H	5.41970300	-2.66197700	-1.93646700
C	7.40270800	-0.63851300	0.49090300
C	4.57861300	-4.61442900	-1.51057600
H	4.02845300	-4.34723500	-0.60168700
H	4.90504100	-5.65499000	-1.40058100
H	3.86661800	-4.57516000	-2.34079000
C	8.76260200	-0.93608500	0.62333400
H	9.11257300	-1.95622300	0.74248500
C	7.87482100	1.74431400	0.31207600
H	7.54165500	2.77169900	0.19563500
C	9.22996500	1.45228200	0.44171200
H	9.95938200	2.25618500	0.42345500
C	9.66540100	0.12544700	0.59765200

H	10.72698000	-0.08025000	0.69879900
C	6.94608900	0.69774300	0.33695400
C	5.50403500	0.63619800	0.24735200
C	3.18272000	1.19868700	0.05928800
C	4.51158200	1.61362200	0.10112400
H	4.76796400	2.66670800	0.02657900
C	1.95369700	1.97324600	-0.07687600
C	1.89161400	3.45146400	-0.21115600
C	2.12753300	4.05754100	-1.46525700
C	2.42113900	3.22000600	-2.68921400
H	2.54152400	3.85025100	-3.57437100
H	1.61489500	2.50545400	-2.88652800
H	3.33667600	2.63207100	-2.56433400
C	2.06825700	5.45018600	-1.57044700
H	2.24320600	5.91016500	-2.54079900
C	1.78838200	6.26378900	-0.46884400
C	1.55759100	5.64515200	0.76232000
H	1.33758500	6.25945900	1.63290900
C	1.76524500	7.76848300	-0.60077400
H	2.76950800	8.19353300	-0.47850600
H	1.12443900	8.22727200	0.15808100
H	1.40134700	8.07904000	-1.58509000
C	1.60507500	4.25540500	0.91359800
C	1.35853200	3.63751100	2.27159400
H	2.17557000	2.96793800	2.55975000
H	0.44256700	3.03716900	2.28344100
H	1.26460500	4.41017700	3.03943300
C	0.52477400	-1.34080500	0.15348900
H	0.88193700	-2.36107100	0.27078500
N	-6.30705100	1.49748500	-0.49566800
C	-0.88216100	-1.09313000	0.05189100
C	-1.37999500	0.27786000	-0.10064000
C	-2.83916800	0.19039200	-0.17128900
C	-6.81609200	3.68401900	0.63555300
H	-7.74630900	3.23342200	0.99991900
H	-7.06019900	4.71941600	0.36052600
C	-6.39569300	2.94377800	-0.64751000
H	-5.42887500	3.30319800	-1.00976900
H	-7.11929500	3.15202900	-1.44430100
C	-5.14827000	0.74142900	-0.35157900
C	-3.81183000	1.16932700	-0.31733400
H	-3.54509400	2.21765300	-0.40117300
C	-5.77174300	3.68621100	1.76355600
H	-6.26701400	3.99477200	2.69219800
H	-5.41968200	2.66207100	1.93647200
C	-7.40269300	0.63850100	-0.49091200
C	-4.57877500	4.61461900	1.51063800
H	-4.02856700	4.34750300	0.60175700
H	-4.90530600	5.65515000	1.40066000
H	-3.86679600	4.57540300	2.34086800
C	-8.76258700	0.93607100	-0.62334700
H	-9.11255800	1.95620900	-0.74249700
C	-7.87480400	-1.74432700	-0.31208700
H	-7.54163800	-2.77171100	-0.19564400
C	-9.22994800	-1.45229600	-0.44172600

H	-9.95936500	-2.25619900	-0.42347200
C	-9.66538500	-0.12546100	-0.59766800
H	-10.72696400	0.08023500	-0.69881700
C	-6.94607400	-0.69775500	-0.33696100
C	-5.50402000	-0.63620900	-0.24735400
C	-3.18270500	-1.19869900	-0.05929100
C	-4.51156800	-1.61363200	-0.10112600
H	-4.76795000	-2.66671800	-0.02658100
C	-1.95368300	-1.97325800	0.07687200
C	-1.89160000	-3.45147500	0.21115500
C	-2.12751300	-4.05754900	1.46525900
C	-2.42111000	-3.22001100	2.68921500
H	-2.54150300	-3.85025500	3.57437200
H	-1.61485900	-2.50546800	2.88652900
H	-3.33664100	-2.63206600	2.56433400
C	-2.06823900	-5.45019400	1.57045100
H	-2.24318300	-5.91017100	2.54080500
C	-1.78837100	-6.26380000	0.46884700
C	-1.55758600	-5.64516600	-0.76231900
H	-1.33758600	-6.25947400	-1.63290700
C	-1.76523500	-7.76849300	0.60078300
H	-2.76951700	-8.19353300	0.47863900
H	-1.12452300	-8.22729400	-0.15814400
H	-1.40122400	-8.07904900	1.58505900
C	-1.60506900	-4.25541800	-0.91359900
C	-1.35853200	-3.63752800	-2.27159800
H	-2.17557200	-2.96795600	-2.55975200
H	-0.44256800	-3.03718500	-2.28345000
H	-1.26460700	-4.41019500	-3.03943500

Singlet open-shell **6**: `-2352.3986874 hartree`

Atom	x	y	z
C	-0.52475900	1.34079300	-0.15349500
H	-0.88192200	2.36105900	-0.27079200
N	6.30706400	-1.49749500	0.49566500
C	0.88217600	1.09311800	-0.05189600
C	1.38001000	-0.27787300	0.10063400
C	2.83918300	-0.19040400	0.17128300
C	6.81603900	-3.68403700	-0.63556000
H	7.74627700	-3.23349000	-0.99993600
H	7.06008900	-4.71945100	-0.36054800
C	6.39569700	-2.94378700	0.64751500
H	5.42888000	-3.30318800	1.00979500
H	7.11931400	-3.15205100	1.44429100
C	5.14828400	-0.74143900	0.35157600
C	3.81184500	-1.16933900	0.31732700
H	3.54511000	-2.21766600	0.40116200
C	5.77166800	-3.68614800	-1.76354300
H	6.26688900	-3.99477300	-2.69219100
H	5.41970400	-2.66197700	-1.93646700
C	7.40270800	-0.63851400	0.49090300
C	4.57861200	-4.61442800	-1.51057600

H	4.02845200	-4.34723400	-0.60168700
H	4.90504000	-5.65498900	-1.40058100
H	3.86661800	-4.57515900	-2.34079000
C	8.76260200	-0.93608500	0.62333400
H	9.11257300	-1.95622300	0.74248500
C	7.87482100	1.74431400	0.31207600
H	7.54165500	2.77169800	0.19563500
C	9.22996500	1.45228200	0.44171200
H	9.95938200	2.25618400	0.42345500
C	9.66540100	0.12544700	0.59765200
H	10.72698000	-0.08025000	0.69879900
C	6.94608900	0.69774300	0.33695400
C	5.50403500	0.63619800	0.24735200
C	3.18272000	1.19868700	0.05928800
C	4.51158200	1.61362100	0.10112400
H	4.76796400	2.66670700	0.02657900
C	1.95369800	1.97324600	-0.07687600
C	1.89161500	3.45146400	-0.21115600
C	2.12753300	4.05754000	-1.46525800
C	2.42113900	3.22000600	-2.68921400
H	2.54152400	3.85025100	-3.57437100
H	1.61489400	2.50545400	-2.88652800
H	3.33667500	2.63207000	-2.56433400
C	2.06825800	5.45018600	-1.57044700
H	2.24320700	5.91016500	-2.54079900
C	1.78838300	6.26378900	-0.46884400
C	1.55759300	5.64515200	0.76232100
H	1.33758700	6.25945800	1.63290900
C	1.76524700	7.76848200	-0.60077400
H	2.76951000	8.19353300	-0.47850600
H	1.12444100	8.22727200	0.15808100
H	1.40134900	8.07904000	-1.58509000
C	1.60507600	4.25540400	0.91359800
C	1.35853300	3.63751100	2.27159400
H	2.17557000	2.96793700	2.55974900
H	0.44256800	3.03717000	2.28344200
H	1.26460700	4.41017700	3.03943300
C	0.52477400	-1.34080500	0.15348900
H	0.88193700	-2.36107100	0.27078500
N	-6.30705100	1.49748500	-0.49566800
C	-0.88216100	-1.09313000	0.05189100
C	-1.37999500	0.27786000	-0.10064000
C	-2.83916800	0.19039300	-0.17128900
C	-6.81609200	3.68402000	0.63555300
H	-7.74630900	3.23342300	0.99991900
H	-7.06019900	4.71941700	0.36052600
C	-6.39569200	2.94377800	-0.64751000
H	-5.42887500	3.30319800	-1.00976800
H	-7.11929500	3.15203000	-1.44430100
C	-5.14827000	0.74143000	-0.35157900
C	-3.81183000	1.16932800	-0.31733400
H	-3.54509300	2.21765300	-0.40117300
C	-5.77174300	3.68621200	1.76355600
H	-6.26701500	3.99477300	2.69219800
H	-5.41968300	2.66207200	1.93647200

C	-7.40269300	0.63850100	-0.49091200
C	-4.57877500	4.61462000	1.51063800
H	-4.02856700	4.34750400	0.60175700
H	-4.90530700	5.65515000	1.40066100
H	-3.86679700	4.57540400	2.34086800
C	-8.76258700	0.93607200	-0.62334700
H	-9.11255800	1.95621000	-0.74249800
C	-7.87480400	-1.74432700	-0.31208700
H	-7.54163800	-2.77171100	-0.19564400
C	-9.22994800	-1.45229500	-0.44172600
H	-9.95936500	-2.25619800	-0.42347200
C	-9.66538500	-0.12546100	-0.59766800
H	-10.72696400	0.08023500	-0.69881700
C	-6.94607400	-0.69775500	-0.33696100
C	-5.50402000	-0.63620800	-0.24735400
C	-3.18270500	-1.19869800	-0.05929100
C	-4.51156800	-1.61363200	-0.10112600
H	-4.76795000	-2.66671800	-0.02658100
C	-1.95368300	-1.97325700	0.07687200
C	-1.89160100	-3.45147500	0.21115500
C	-2.12751300	-4.05754900	1.46525900
C	-2.42111000	-3.22001100	2.68921500
H	-2.54150200	-3.85025400	3.57437200
H	-1.61485800	-2.50546800	2.88652900
H	-3.33664000	-2.63206600	2.56433500
C	-2.06823900	-5.45019400	1.57045100
H	-2.24318400	-5.91017100	2.54080500
C	-1.78837200	-6.26380000	0.46884700
C	-1.55758800	-5.64516600	-0.76231900
H	-1.33758800	-6.25947400	-1.63290700
C	-1.76523700	-7.76849300	0.60078300
H	-2.76951900	-8.19353300	0.47863900
H	-1.12452500	-8.22729400	-0.15814400
H	-1.40122500	-8.07904900	1.58505900
C	-1.60507000	-4.25541800	-0.91359900
C	-1.35853300	-3.63752800	-2.27159800
H	-2.17557200	-2.96795600	-2.55975100
H	-0.44256800	-3.03718500	-2.28345100
H	-1.26460900	-4.41019600	-3.03943500

Triplet open-shell **6**: `-2352.3727338 hartree`

Atom	x	y	z
C	-0.50778300	-1.33418500	0.14654700
H	-0.88055600	-2.34866800	0.26167200
N	6.28364400	1.48844100	-0.50432800
C	0.86837000	-1.09293200	0.04121200
C	1.37176800	0.23964000	-0.10141800
C	2.82873900	0.15167700	-0.17070700
C	6.77684100	3.67811100	0.62733200
H	7.71380900	3.23675300	0.98558900
H	7.00853300	4.71623800	0.35212900
C	6.35638000	2.93621800	-0.65475600
H	5.38376100	3.28601100	-1.01037400
H	7.07321300	3.15210900	-1.45548300

C	5.13551500	0.72116100	-0.35628300
C	3.79272300	1.13579200	-0.31835100
H	3.51689900	2.18171900	-0.40302600
C	5.73889100	3.66809300	1.76113100
H	6.23645600	3.98116200	2.68700300
H	5.39880400	2.64013500	1.93551300
C	7.39121700	0.64174300	-0.50613100
C	4.53460600	4.58383600	1.51592300
H	3.98127200	4.31108600	0.61066200
H	4.84936200	5.62779900	1.40424000
H	3.82840200	4.53675200	2.35059800
C	8.74568500	0.95693900	-0.64504900
H	9.08227800	1.98144600	-0.76480300
C	7.89204500	-1.73418300	-0.33354800
H	7.57227600	-2.76577700	-0.21727100
C	9.24360700	-1.42518400	-0.46953600
H	9.98250200	-2.22045900	-0.45625300
C	9.66224200	-0.09370600	-0.62550600
H	10.72059800	0.12525600	-0.73177300
C	6.95128000	-0.69940900	-0.35212300
C	5.50727700	-0.65526600	-0.25541800
C	3.18438800	-1.24497100	-0.05925200
C	4.53066900	-1.64131300	-0.10912900
H	4.79956500	-2.69179400	-0.04292300
C	1.99116300	-2.02026900	0.06842700
C	1.90173600	-3.49223900	0.20245200
C	2.22166000	-4.11744600	1.42901600
C	2.63788300	-3.30321500	2.63343900
H	2.72094300	-3.93595500	3.52129400
H	1.91485200	-2.50894700	2.84643700
H	3.60477600	-2.81275800	2.47819400
C	2.12458900	-5.50878100	1.53203900
H	2.36315100	-5.98145900	2.48254300
C	1.72261500	-6.30450800	0.45636200
C	1.40546200	-5.66876900	-0.74738400
H	1.08982300	-6.26877600	-1.59849500
C	1.65764300	-7.80851700	0.58106800
H	2.59564600	-8.27557400	0.25495300
H	0.85726400	-8.22787600	-0.03645500
H	1.48471800	-8.11764400	1.61625700
C	1.48774100	-4.28137200	-0.89571800
C	1.15844700	-3.64632100	-2.22764200
H	1.99650700	-3.04730900	-2.59976000
H	0.29959400	-2.97076900	-2.15427600
H	0.92641700	-4.40823200	-2.97675900
C	0.50777500	1.33417700	-0.14655000
H	0.88054900	2.34866000	-0.26167500
N	-6.28365100	-1.48844800	0.50433300
C	-0.86837700	1.09292500	-0.04121400
C	-1.37177500	-0.23964800	0.10141500
C	-2.82874600	-0.15168500	0.17070500
C	-6.77681500	-3.67811500	-0.62734100
H	-7.71379500	-3.23678400	-0.98559900
H	-7.00847300	-4.71625400	-0.35215200
C	-6.35638100	-2.93622500	0.65475600

H	-5.38376300	-3.28601000	1.01038100
H	-7.07322000	-3.15212800	1.45547600
C	-5.13552200	-0.72116800	0.35628400
C	-3.79273100	-1.13580000	0.31834900
H	-3.51690700	-2.18172800	0.40302200
C	-5.73885700	-3.66804500	-1.76113300
H	-6.23639600	-3.98114400	-2.68700900
H	-5.39882500	-2.64006900	-1.93551400
C	-7.39122400	-0.64175100	0.50613200
C	-4.53452200	-4.58371700	-1.51590700
H	-3.98121100	-4.31092800	-0.61064400
H	-4.84921900	-5.62769700	-1.40421900
H	-3.82831300	-4.53659900	-2.35057700
C	-8.74569200	-0.95694800	0.64505000
H	-9.08228500	-1.98145500	0.76480600
C	-7.89205300	1.73417400	0.33354800
H	-7.57228400	2.76576800	0.21727100
C	-9.24361600	1.42517500	0.46953600
H	-9.98251100	2.22044900	0.45625200
C	-9.66224900	0.09369600	0.62550600
H	-10.72060600	-0.12526600	0.73177400
C	-6.95128800	0.69940100	0.35212400
C	-5.50728500	0.65525900	0.25542000
C	-3.18439500	1.24496300	0.05925200
C	-4.53067600	1.64130500	0.10913100
H	-4.79957200	2.69178600	0.04292500
C	-1.99117000	2.02026200	-0.06842800
C	-1.90174300	3.49223200	-0.20245300
C	-2.22166600	4.11743900	-1.42901700
C	-2.63788700	3.30320900	-2.63344200
H	-2.72094700	3.93595000	-3.52129500
H	-1.91485500	2.50894200	-2.84644000
H	-3.60477900	2.81275000	-2.47819800
C	-2.12459500	5.50877400	-1.53204000
H	-2.36315600	5.98145300	-2.48254400
C	-1.72262200	6.30450100	-0.45636200
C	-1.40546900	5.66876100	0.74738400
H	-1.08983200	6.26876800	1.59849500
C	-1.65764900	7.80851000	-0.58106700
H	-2.59564800	8.27556800	-0.25494100
H	-0.85726300	8.22786700	0.03644700
H	-1.48473500	8.11763700	-1.61625800
C	-1.48774800	4.28136400	0.89571800
C	-1.15845700	3.64631400	2.22764200
H	-1.99651700	3.04730100	2.59975900
H	-0.29960300	2.97076200	2.15427800
H	-0.92642900	4.40822400	2.97676000

Singlet closed-shell **7**: `-2352.3909301 hartree`

Atom	x	y	z
N	-0.94231200	2.48063100	5.81160100
C	0.80866100	0.51932700	9.51782500
C	0.70349100	1.40804000	8.27472300

H	0.68994100	0.78117400	7.37566600
H	1.60142300	2.03616300	8.19715600
C	-0.54081800	2.30304200	8.29191500
H	-0.51100800	2.95768000	9.17396100
H	-1.43780200	1.68058300	8.40009800
C	-0.70330500	3.20152400	7.05422300
H	-1.54201000	3.89087000	7.20582000
H	0.18577000	3.82362100	6.91586900
C	-0.01044200	2.19745700	4.82274000
C	-0.65411100	1.49579100	3.74972800
C	0.12677500	1.16207700	2.62719500
C	-0.13265200	0.53592200	1.32400100
C	-1.26297900	0.11398300	0.67882100
H	-2.24901100	0.20247100	1.11550300
C	1.15665800	0.44344800	0.63317700
C	-2.16991100	1.95756700	5.42968100
C	-2.03865600	1.31992200	4.16390500
C	1.52419400	1.46753800	2.65409400
C	2.14566100	1.00200200	1.42664700
C	2.12365200	2.12929300	3.73512100
C	1.35507100	2.51362600	4.82598400
C	-3.38366100	2.00227800	6.12119400
C	-4.48640700	1.37574900	5.54636700
C	-4.37429600	0.70625100	4.31912500
C	-3.16371900	0.67347700	3.63175800
H	-3.10056700	0.11871600	2.70611700
C	3.58876400	1.13292700	1.09637000
C	4.07294100	2.31703100	0.49830800
C	3.13806700	3.45914000	0.17053200
C	5.43479700	2.42012000	0.19807500
C	6.33336200	1.38650400	0.47612300
C	5.83399200	0.22293300	1.06720200
C	4.47989100	0.07645400	1.38450900
C	3.98847800	-1.20230100	2.02434800
C	7.80596900	1.53433100	0.17305500
H	1.80990100	3.02957400	5.66389600
H	6.51567100	-0.59543600	1.28911000
H	5.80121300	3.33269500	-0.26742000
H	3.18787100	2.34407000	3.71159400
H	3.68601200	4.30134000	-0.26037900
H	-5.23926300	0.20283400	3.89886000
H	3.45842500	-1.00263200	2.96161500
H	7.97404100	2.19098600	-0.68597400
H	8.26941700	0.56701200	-0.04329500
H	0.85408500	1.11898600	10.43418000
H	-3.46799400	2.49999400	7.08155200
H	8.34546300	1.96931100	1.02395400
H	-5.44084400	1.39627400	6.06411500
H	3.28557600	-1.73367300	1.37383300
H	2.36819800	3.15303500	-0.54588200
H	4.82220000	-1.87541900	2.24118900
H	-0.05723900	-0.14688800	9.60154100
H	2.61197600	3.81542400	1.06244300
H	1.70625700	-0.10605300	9.48468900
N	0.94231200	-2.48063100	-5.81160100

C	-0.80866100	-0.51932700	-9.51782500
C	-0.70349100	-1.40804000	-8.27472300
H	-0.68994100	-0.78117400	-7.37566600
H	-1.60142300	-2.03616300	-8.19715600
C	0.54081800	-2.30304200	-8.29191500
H	0.51100800	-2.95768000	-9.17396100
H	1.43780200	-1.68058300	-8.40009800
C	0.70330500	-3.20152400	-7.05422300
H	1.54201000	-3.89087000	-7.20582000
H	-0.18577000	-3.82362100	-6.91586900
C	0.01044200	-2.19745700	-4.82274000
C	0.65411100	-1.49579100	-3.74972800
C	-0.12677500	-1.16207700	-2.62719500
C	0.13265200	-0.53592200	-1.32400100
C	1.26297900	-0.11398300	-0.67882100
H	2.24901100	-0.20247100	-1.11550300
C	-1.15665800	-0.44344800	-0.63317700
C	2.16991100	-1.95756700	-5.42968100
C	2.03865600	-1.31992200	-4.16390500
C	-1.52419400	-1.46753800	-2.65409400
C	-2.14566100	-1.00200200	-1.42664700
C	-2.12365200	-2.12929300	-3.73512100
C	-1.35507100	-2.51362600	-4.82598400
C	3.38366100	-2.00227800	-6.12119400
C	4.48640700	-1.37574900	-5.54636700
C	4.37429600	-0.70625100	-4.31912500
C	3.16371900	-0.67347700	-3.63175800
H	3.10056700	-0.11871600	-2.70611700
C	-3.58876400	-1.13292700	-1.09637000
C	-4.07294100	-2.31703100	-0.49830800
C	-3.13806700	-3.45914000	-0.17053200
C	-5.43479700	-2.42012000	-0.19807500
C	-6.33336200	-1.38650400	-0.47612300
C	-5.83399200	-0.22293300	-1.06720200
C	-4.47989100	-0.07645400	-1.38450900
C	-3.98847800	1.20230100	-2.02434800
C	-7.80596900	-1.53433100	-0.17305500
H	-1.80990100	-3.02957400	-5.66389600
H	-6.51567100	0.59543600	-1.28911000
H	-5.80121300	-3.33269500	0.26742000
H	-3.18787100	-2.34407000	-3.71159400
H	-3.68601200	-4.30134000	0.26037900
H	5.23926300	-0.20283400	-3.89886000
H	-3.45842500	1.00263200	-2.96161500
H	-7.97404100	-2.19098600	0.68597400
H	-8.26941700	-0.56701200	0.04329500
H	-0.85408500	-1.11898600	-10.43418000
H	3.46799400	-2.49999400	-7.08155200
H	-8.34546300	-1.96931100	-1.02395400
H	5.44084400	-1.39627400	-6.06411500
H	-3.28557600	1.73367300	-1.37383300
H	-2.36819800	-3.15303500	0.54588200
H	-4.82220000	1.87541900	-2.24118900
H	0.05723900	0.14688800	-9.60154100
H	-2.61197600	-3.81542400	-1.06244300

H	-1.70625700	0.10605300	-9.48468900

Singlet open-shell **7**: -2352.3909301 hartree

N	-0.94231200	2.48063100	5.81160100
C	0.80866100	0.51932700	9.51782500
C	0.70349100	1.40804000	8.27472300
H	0.68994100	0.78117400	7.37566600
H	1.60142300	2.03616300	8.19715600
C	-0.54081800	2.30304100	8.29191500
H	-0.51100800	2.95768000	9.17396100
H	-1.43780200	1.68058200	8.40009800
C	-0.70330500	3.20152400	7.05422300
H	-1.54201000	3.89087000	7.20582000
H	0.18577000	3.82362100	6.91586900
C	-0.01044200	2.19745700	4.82274000
C	-0.65411100	1.49579100	3.74972800
C	0.12677500	1.16207700	2.62719500
C	-0.13265200	0.53592200	1.32400100
C	-1.26297900	0.11398300	0.67882100
H	-2.24901100	0.20247100	1.11550300
C	1.15665800	0.44344800	0.63317700
C	-2.16991100	1.95756700	5.42968100
C	-2.03865600	1.31992200	4.16390500
C	1.52419400	1.46753800	2.65409400
C	2.14566100	1.00200200	1.42664700
C	2.12365200	2.12929300	3.73512100
C	1.35507100	2.51362600	4.82598400
C	-3.38366100	2.00227800	6.12119400
C	-4.48640700	1.37574900	5.54636700
C	-4.37429600	0.70625100	4.31912500
C	-3.16371900	0.67347700	3.63175800
H	-3.10056700	0.11871600	2.70611700
C	3.58876400	1.13292700	1.09637000
C	4.07294100	2.31703100	0.49830800
C	3.13806700	3.45914000	0.17053200
C	5.43479700	2.42012000	0.19807500
C	6.33336200	1.38650400	0.47612300
C	5.83399200	0.22293300	1.06720200
C	4.47989100	0.07645400	1.38450900
C	3.98847800	-1.20230100	2.02434800
C	7.80596900	1.53433100	0.17305500
H	1.80990100	3.02957400	5.66389600
H	6.51567100	-0.59543600	1.28911000
H	5.80121300	3.33269500	-0.26742000
H	3.18787100	2.34407000	3.71159400
H	3.68601200	4.30134000	-0.26037900
H	-5.23926300	0.20283400	3.89886000
H	3.45842500	-1.00263200	2.96161500
H	7.97404100	2.19098600	-0.68597400
H	8.26941700	0.56701200	-0.04329500
H	0.85408500	1.11898600	10.43418000
H	-3.46799400	2.49999400	7.08155200
H	8.34546300	1.96931100	1.02395400
H	-5.44084400	1.39627400	6.06411500

H	3.28557600	-1.73367300	1.37383300
H	2.36819800	3.15303500	-0.54588200
H	4.82220000	-1.87541900	2.24118900
H	-0.05723900	-0.14688800	9.60154100
H	2.61197600	3.81542400	1.06244300
H	1.70625700	-0.10605300	9.48468900
N	0.94231200	-2.48063100	-5.81160100
C	-0.80866100	-0.51932700	-9.51782500
C	-0.70349100	-1.40804000	-8.27472300
H	-0.68994100	-0.78117400	-7.37566600
H	-1.60142300	-2.03616300	-8.19715600
C	0.54081800	-2.30304100	-8.29191500
H	0.51100800	-2.95768000	-9.17396100
H	1.43780200	-1.68058200	-8.40009800
C	0.70330500	-3.20152400	-7.05422300
H	1.54201000	-3.89087000	-7.20582000
H	-0.18577000	-3.82362100	-6.91586900
C	0.01044200	-2.19745700	-4.82274000
C	0.65411100	-1.49579100	-3.74972800
C	-0.12677500	-1.16207700	-2.62719500
C	0.13265200	-0.53592200	-1.32400100
C	1.26297900	-0.11398300	-0.67882100
H	2.24901100	-0.20247100	-1.11550300
C	-1.15665800	-0.44344800	-0.63317700
C	2.16991100	-1.95756700	-5.42968100
C	2.03865600	-1.31992200	-4.16390500
C	-1.52419400	-1.46753800	-2.65409400
C	-2.14566100	-1.00200200	-1.42664700
C	-2.12365200	-2.12929300	-3.73512100
C	-1.35507100	-2.51362600	-4.82598400
C	3.38366100	-2.00227800	-6.12119400
C	4.48640700	-1.37574900	-5.54636700
C	4.37429600	-0.70625100	-4.31912500
C	3.16371900	-0.67347700	-3.63175800
H	3.10056700	-0.11871600	-2.70611700
C	-3.58876400	-1.13292700	-1.09637000
C	-4.07294100	-2.31703100	-0.49830800
C	-3.13806700	-3.45914000	-0.17053200
C	-5.43479700	-2.42012000	-0.19807500
C	-6.33336200	-1.38650400	-0.47612300
C	-5.83399200	-0.22293300	-1.06720200
C	-4.47989100	-0.07645400	-1.38450900
C	-3.98847800	1.20230100	-2.02434800
C	-7.80596900	-1.53433100	-0.17305500
H	-1.80990100	-3.02957400	-5.66389600
H	-6.51567100	0.59543600	-1.28911000
H	-5.80121300	-3.33269500	0.26742000
H	-3.18787100	-2.34407000	-3.71159400
H	-3.68601200	-4.30134000	0.26037900
H	5.23926300	-0.20283400	-3.89886000
H	-3.45842500	1.00263200	-2.96161500
H	-7.97404100	-2.19098600	0.68597400
H	-8.26941700	-0.56701200	0.04329500
H	-0.85408500	-1.11898600	-10.43418000
H	3.46799400	-2.49999400	-7.08155200

H	-8.34546300	-1.96931100	-1.02395400
H	5.44084400	-1.39627400	-6.06411500
H	-3.28557600	1.73367300	-1.37383300
H	-2.36819800	-3.15303500	0.54588200
H	-4.82220000	1.87541900	-2.24118900
H	0.05723900	0.14688800	-9.60154100
H	-2.61197600	-3.81542400	-1.06244300
H	-1.70625700	0.10605300	-9.48468900

Triplet open-shell **7**: `-2352.3640702 hartree`

N	-0.93337500	2.41008400	5.82452900
C	0.79585100	0.36393300	9.49487100
C	0.69819400	1.28055000	8.27154200
H	0.68973700	0.67391700	7.35864600
H	1.59663400	1.90998200	8.21332600
C	-0.54612800	2.17514800	8.30188600
H	-0.52178600	2.80913100	9.19897500
H	-1.44395400	1.55079100	8.38968500
C	-0.70049200	3.10298200	7.08476400
H	-1.53994100	3.78879300	7.24646100
H	0.18958500	3.72734000	6.96600500
C	0.00198300	2.14186500	4.83911300
C	-0.63462500	1.45682300	3.74841800
C	0.15205300	1.14022800	2.62658100
C	-0.10635600	0.53567200	1.31132900
C	-1.26031700	0.09643900	0.65903100
H	-2.24202700	0.18474700	1.10274100
C	1.14881800	0.44780500	0.62654600
C	-2.16117300	1.89424700	5.42842100
C	-2.02408700	1.27664700	4.15398500
C	1.56188400	1.44238100	2.67135400
C	2.18744100	1.00974100	1.46913700
C	2.14724600	2.09902900	3.77525600
C	1.37075700	2.46337600	4.85982000
C	-3.37585900	1.92978800	6.11763300
C	-4.47806900	1.31369300	5.53009400
C	-4.36177400	0.66432900	4.29307500
C	-3.14848000	0.64005200	3.60947100
H	-3.08524600	0.10103200	2.67516400
C	3.62350500	1.12162000	1.12237200
C	4.06140900	2.12090000	0.22287100
C	3.08684900	3.11179000	-0.37239700
C	5.41936400	2.20060000	-0.10011300
C	6.36184900	1.32217200	0.44208400
C	5.91019700	0.33962000	1.32681200
C	4.56164600	0.22248400	1.67786000
C	4.12222100	-0.87364000	2.62227300
C	7.82822100	1.44946800	0.10233300
H	1.81373600	2.97162500	5.70857400
H	6.62510300	-0.36218800	1.75111900
H	5.74861300	2.97444300	-0.79063600
H	3.20931700	2.32471800	3.75981800
H	3.60837000	3.85186200	-0.98525700
H	-5.22547200	0.16933100	3.86045300

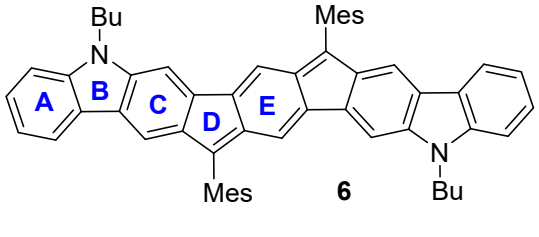
H	3.72241700	-0.46653500	3.55707500
H	7.97315300	1.80949500	-0.92095100
H	8.34672600	0.49108700	0.20089700
H	0.83529300	0.94271000	10.42481400
H	-3.46194700	2.41260200	7.08534600
H	8.33087100	2.16126900	0.76945500
H	-5.43399100	1.32694700	6.04522500
H	3.32734900	-1.48417000	2.18123900
H	2.33915100	2.61760000	-1.00169700
H	4.95856400	-1.53230500	2.87173900
H	-0.07025500	-0.30425200	9.55792200
H	2.53482400	3.64456400	0.40934600
H	1.69390900	-0.26021100	9.45313400
N	0.93337500	-2.41008400	-5.82452900
C	-0.79585100	-0.36393300	-9.49487100
C	-0.69819400	-1.28055000	-8.27154200
H	-0.68973700	-0.67391700	-7.35864600
H	-1.59663400	-1.90998200	-8.21332600
C	0.54612800	-2.17514800	-8.30188600
H	0.52178600	-2.80913100	-9.19897500
H	1.44395400	-1.55079100	-8.38968500
C	0.70049200	-3.10298200	-7.08476400
H	1.53994100	-3.78879300	-7.24646100
H	-0.18958500	-3.72734000	-6.96600500
C	-0.00198300	-2.14186500	-4.83911300
C	0.63462500	-1.45682300	-3.74841800
C	-0.15205300	-1.14022800	-2.62658100
C	0.10635600	-0.53567200	-1.31132900
C	1.26031700	-0.09643900	-0.65903100
H	2.24202700	-0.18474700	-1.10274100
C	-1.14881800	-0.44780500	-0.62654600
C	2.16117300	-1.89424700	-5.42842100
C	2.02408700	-1.27664700	-4.15398500
C	-1.56188400	-1.44238100	-2.67135400
C	-2.18744100	-1.00974100	-1.46913700
C	-2.14724600	-2.09902900	-3.77525600
C	-1.37075700	-2.46337600	-4.85982000
C	3.37585900	-1.92978800	-6.11763300
C	4.47806900	-1.31369300	-5.53009400
C	4.36177400	-0.66432900	-4.29307500
C	3.14848000	-0.64005200	-3.60947100
H	3.08524600	-0.10103200	-2.67516400
C	-3.62350500	-1.12162000	-1.12237200
C	-4.06140900	-2.12090000	-0.22287100
C	-3.08684900	-3.11179000	0.37239700
C	-5.41936400	-2.20060000	0.10011300
C	-6.36184900	-1.32217200	-0.44208400
C	-5.91019700	-0.33962000	-1.32681200
C	-4.56164600	-0.22248400	-1.67786000
C	-4.12222100	0.87364000	-2.62227300
C	-7.82822100	-1.44946800	-0.10233300
H	-1.81373600	-2.97162500	-5.70857400
H	-6.62510300	0.36218800	-1.75111900
H	-5.74861300	-2.97444300	0.79063600
H	-3.20931700	-2.32471800	-3.75981800

H	-3.60837000	-3.85186200	0.98525700
H	5.22547200	-0.16933100	-3.86045300
H	-3.72241700	0.46653500	-3.55707500
H	-7.97315300	-1.80949500	0.92095100
H	-8.34672600	-0.49108700	-0.20089700
H	-0.83529300	-0.94271000	-10.42481400
H	3.46194700	-2.41260200	-7.08534600
H	-8.33087100	-2.16126900	-0.76945500
H	5.43399100	-1.32694700	-6.04522500
H	-3.32734900	1.48417000	-2.18123900
H	-2.33915100	-2.61760000	1.00169700
H	-4.95856400	1.53230500	-2.87173900
H	0.07025500	0.30425200	-9.55792200
H	-2.53482400	-3.64456400	-0.40934600
H	-1.69390900	0.26021100	-9.45313400

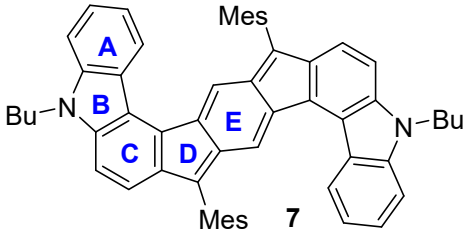
5.3 NICS(1)$_{zz}$ and ACID analyses:

B3LYP functional has been generally used for *s*-indacene based PHs for estimation of paratorpicity.[10] However, some reports[11] suggested that B3LYP functional may overestimate the paratropic ring current effect in 4nπ conjugated systems. Hence, BHandHLYP functional is also examined as it may give more reliable results. Interestingly, the NICS values for BHandHLYP functional (shown below in Table S16) have been found comparable to those of estimated by B3LYP functional. More importantly, the curved isomer **7** is found to show a stronger paratropic ring-current for the *s*-indacene unit as compared to **6**, corroborating the trend observed for B3LYP functional, and further confirming **7** to show a greater degree of antiaromaticity than **6**.

Table S16. NICS(1)$_{zz}$ values using B3LYP/6-31g(d,p) and BHandHLYP/6-31g(d,p) functionals



6

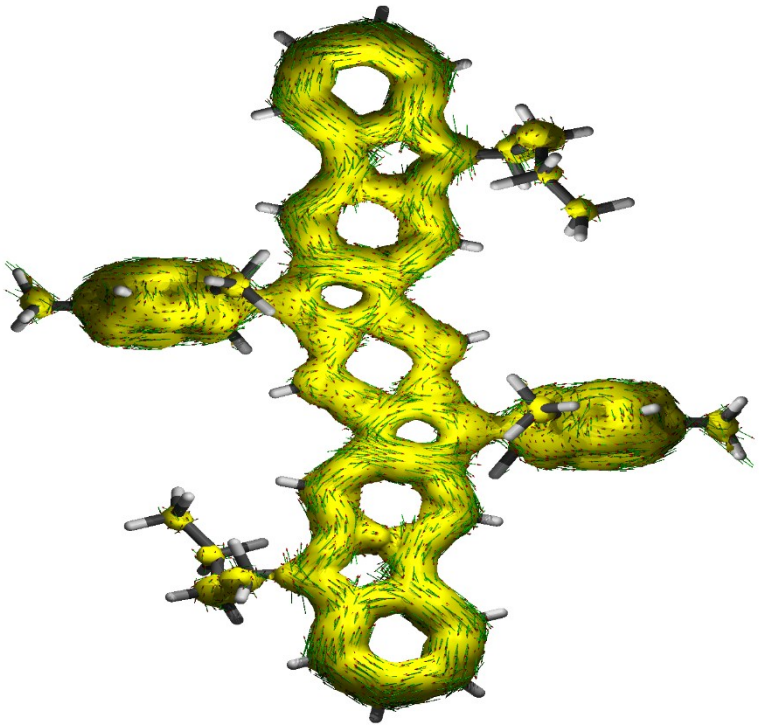


7

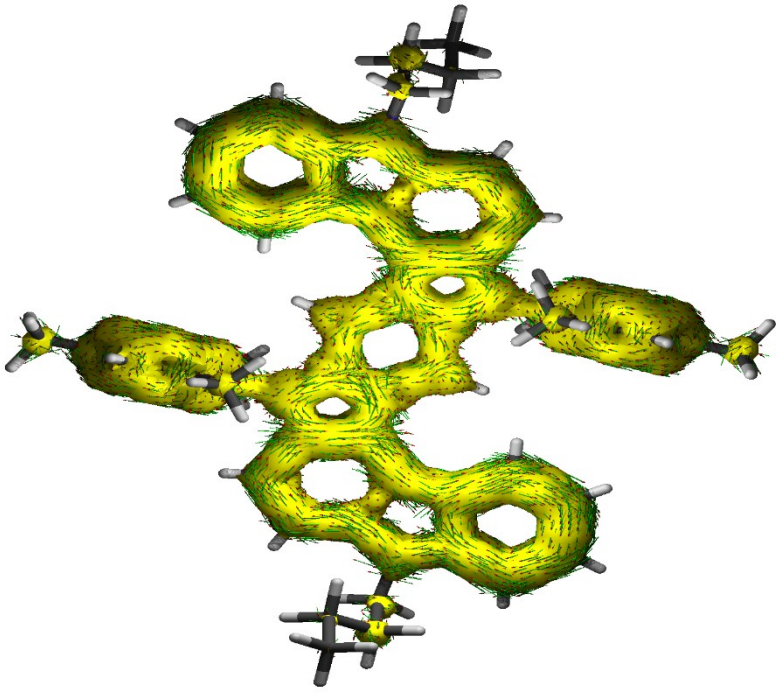
	A	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**
B3LYP	-26.04	-15.22	-13.26	15.56	10.07	-24.93	-14.86	-13.01	21.33	13.78
BHandHLYP	-27.76	-16.27	-16.78	14.69	10.17	-26.59	-15.96	-16.69	19.60	13.34

Using B3LYP functional

ACID plot of **6**

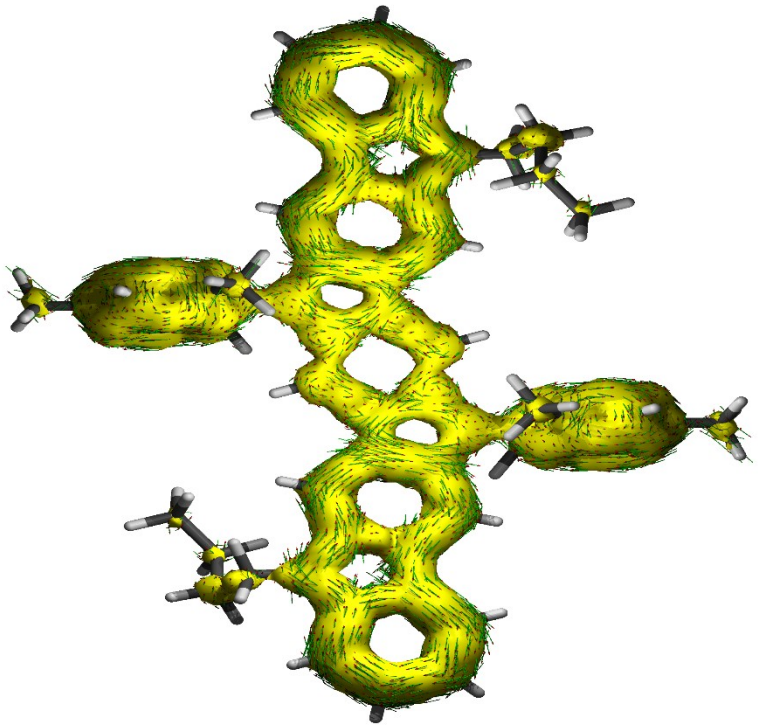


ACID plot of **7**

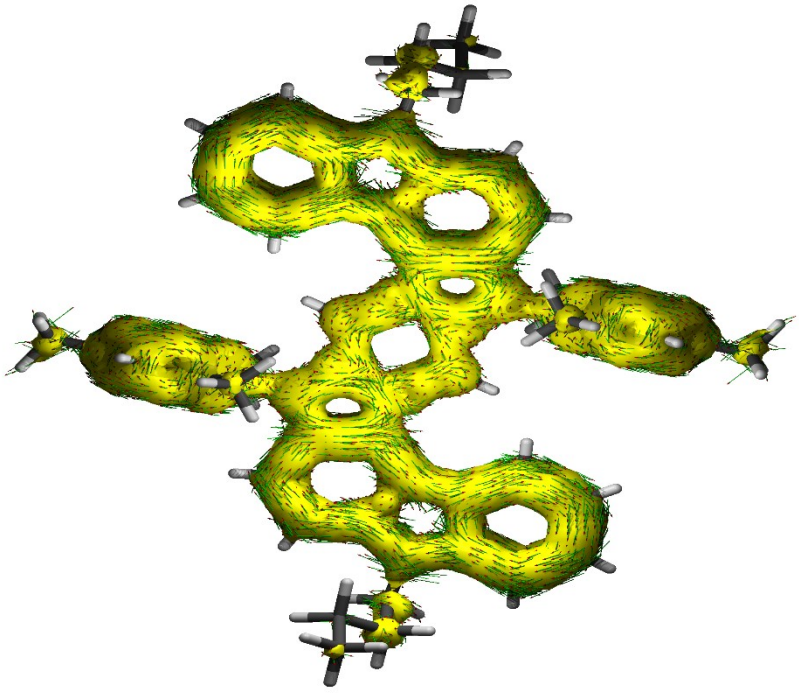


Using BHandHLYP functional

ACID plot of **6**

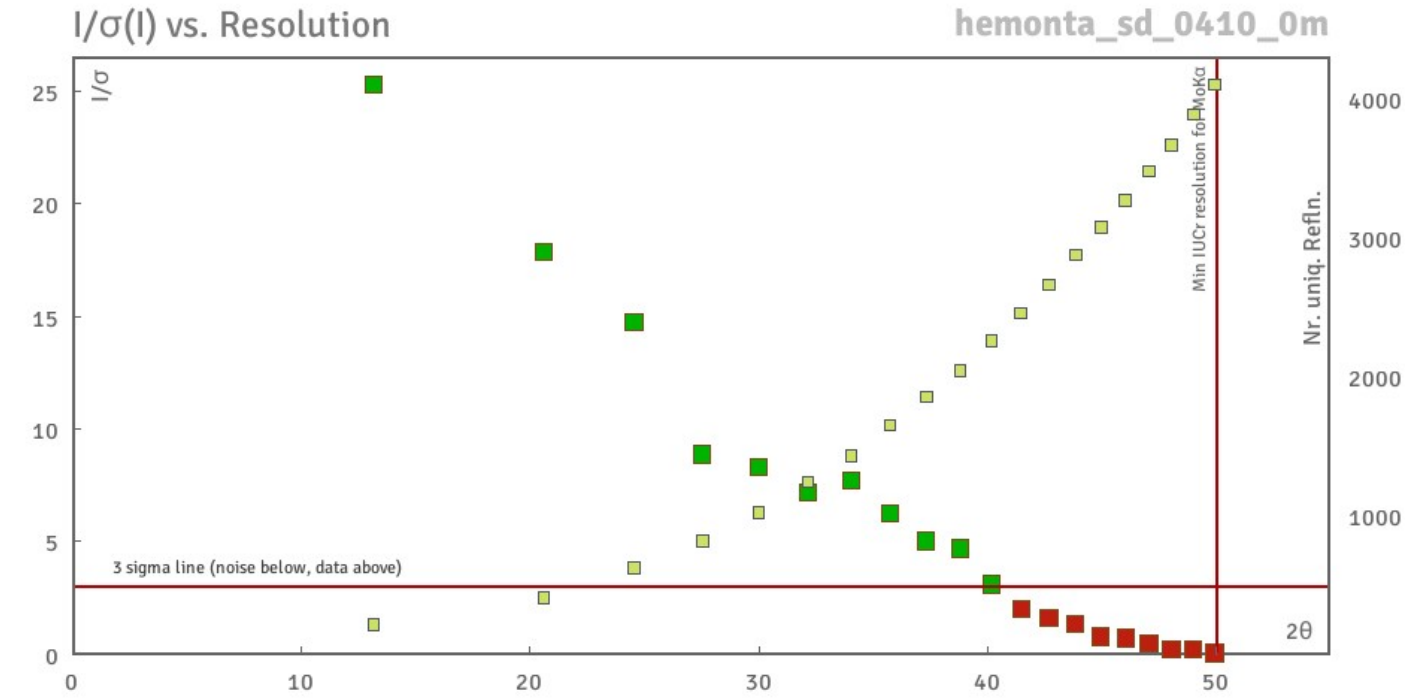


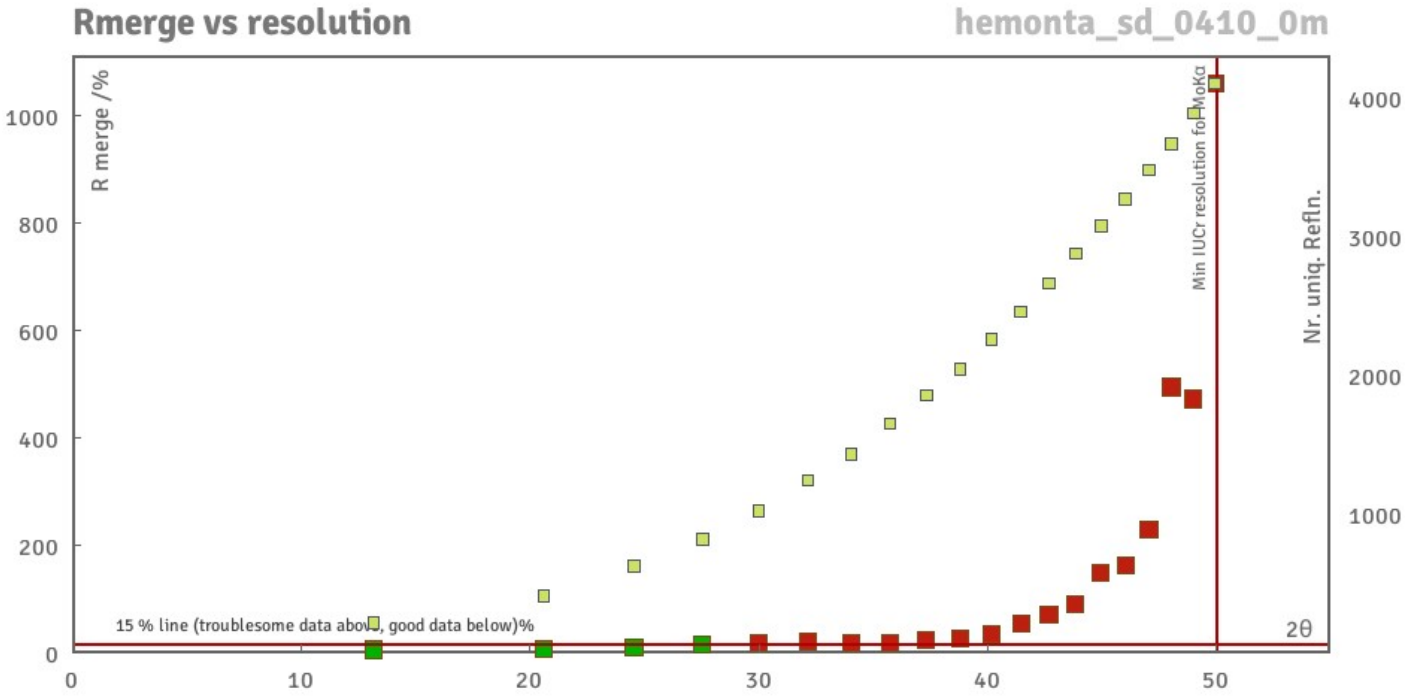
ACID plot of **7**



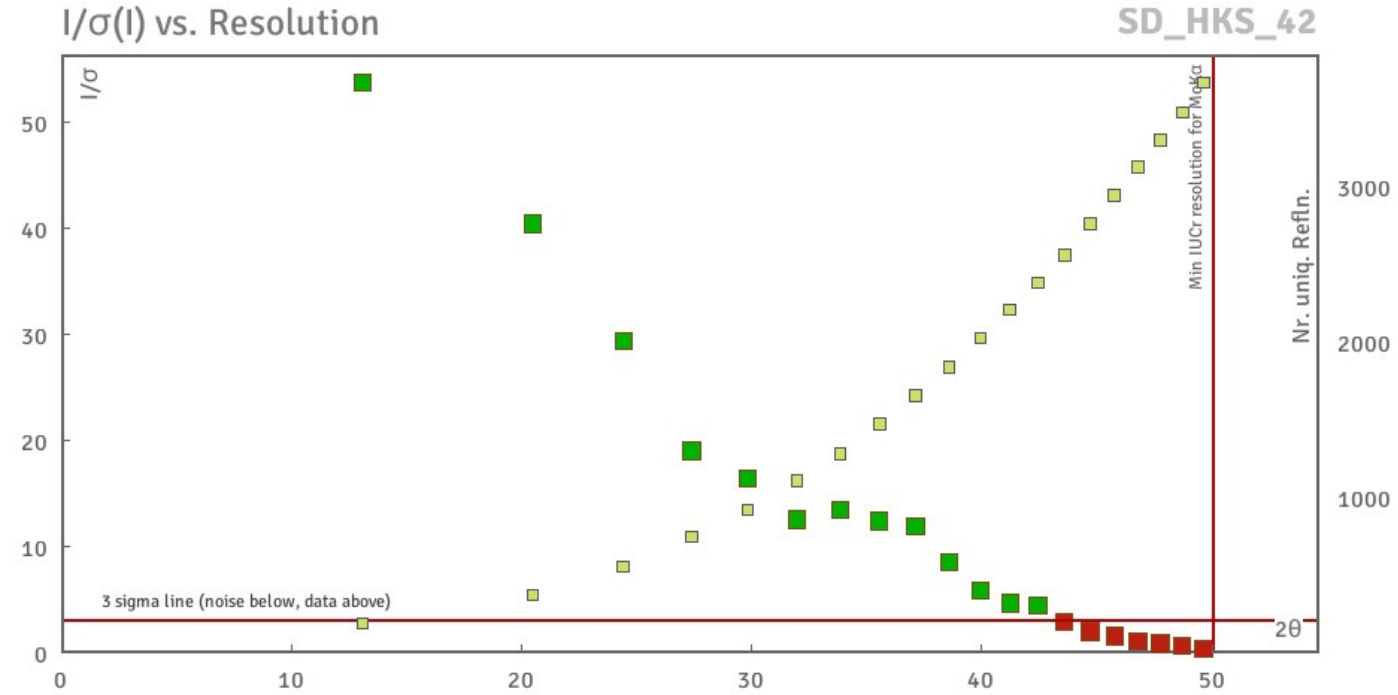
6. Appendix:

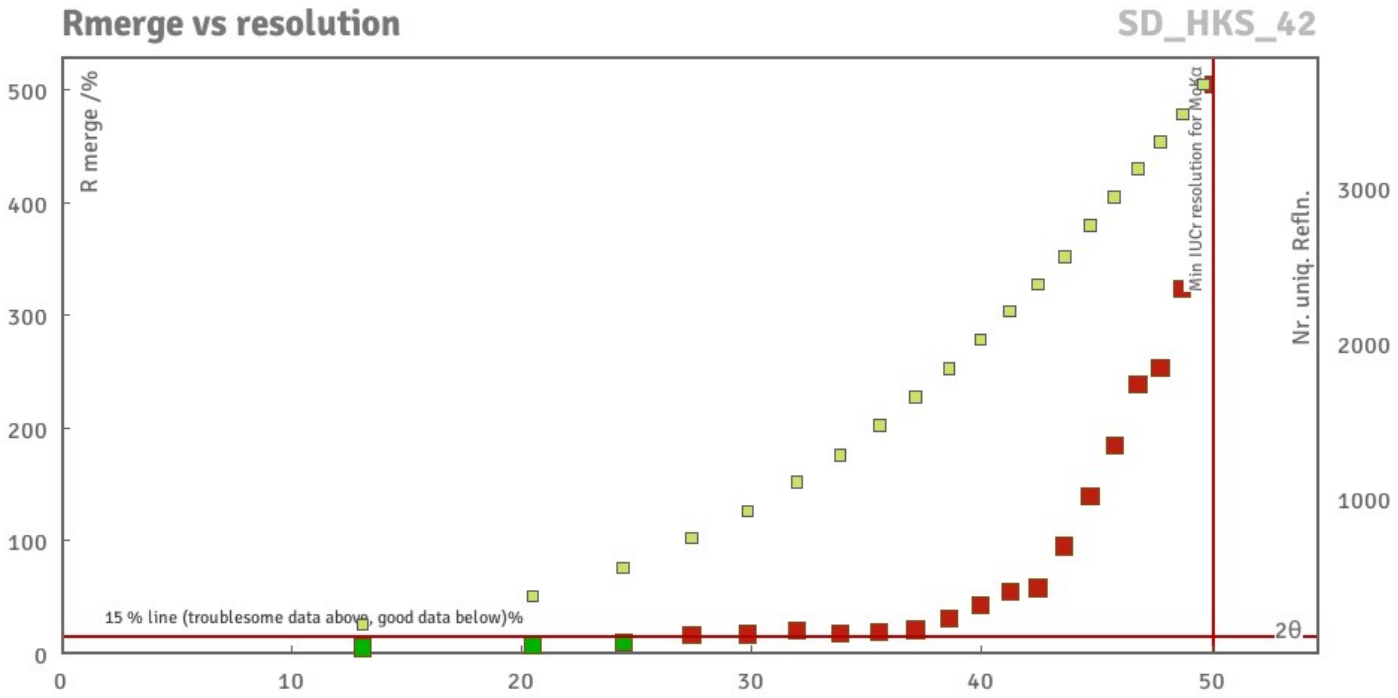
For single-crystal **6**:



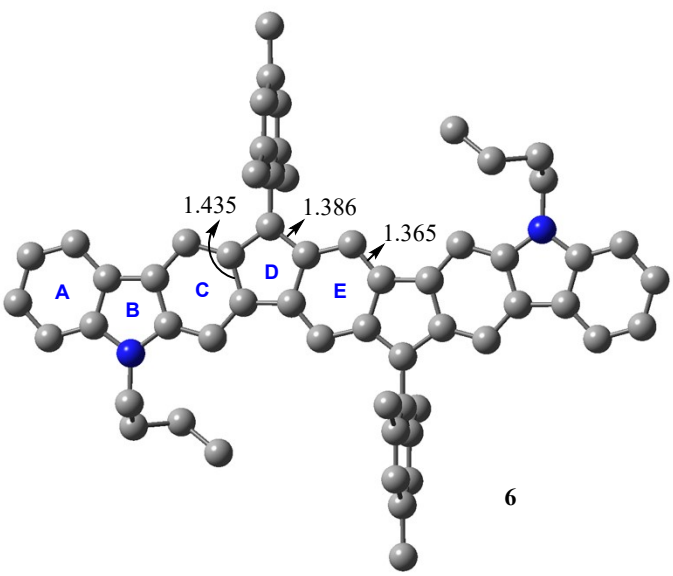


For single-crystal **7**:

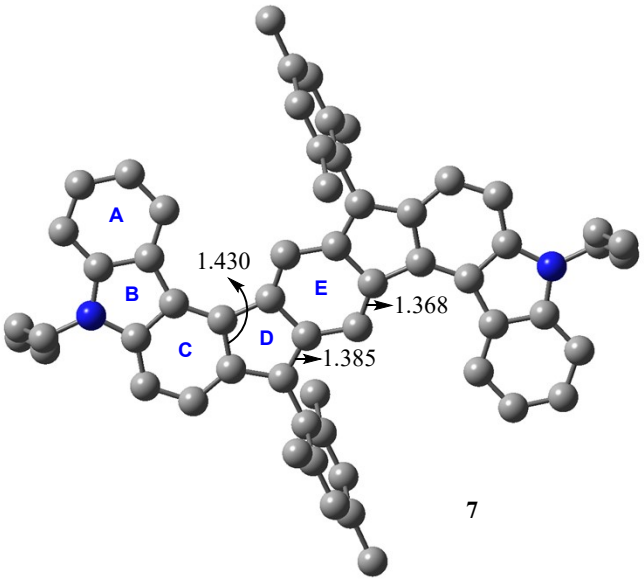




B3LYP/6-31G(d,p) optimized structures of **6** and **7**, and the $C(sp^2)=C(sp^2)$ bond lengths (in Å) for the *s*-indacene unit:



6



7

7. References:

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