

Electronic Supplementary Information

Revisiting indeno[1,2-*b*]fluorene by steric promoted synthesis while isolating the second stable $4n\pi$ indeno[2,1-*a*]fluorene

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1. EXPERIMENTAL SECTION

1.1 General Information. All reagents and chemicals were obtained from commercial sources and used as received. Silica gel (100-200 mesh) was used for column chromatography. NMR spectra, in CDCl₃ solution, were recorded on JEOL JNM ECS-400 spectrometer at 298 K. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. ¹H and ¹³C (proton-decoupled: ¹³C{¹H}) chemical shifts (δ) are reported in ppm relative to the residual CHCl₃ (¹H: 7.26 ppm, ¹³C: 77.16 ppm) reference. High resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on Waters (XEVO G2-XS QTOF) mass spectrometer. UV-Vis absorption spectra were recorded on a JASCO V-770 spectrophotometer in dichloromethane. Cyclic voltammetry (CV) measurements were performed in dry dichloromethane at room temperature under nitrogen atmosphere on CHI-1110C instrument electrochemical analyzer with a three-electrode cell setup (Ag wire as pseudoreference electrode, Pt disk as working electrode, Pt wire as counter electrode), using Bu₄NPF₆ as supporting electrolyte at 50 mV/s scan rate. The potential was externally calibrated against the ferrocene/ferrocenium couple (half-wave potential = 0.45 V). Melting points were determined using BIBBY-SMP30 melting point analyzer.

1.2 Synthetic procedures

4'-bromo-[1,1'-biphenyl]-2-carbaldehyde (9): Commercially available **7** (6 g, 21.21 mmol), 2-formylphenylboronic acid **8** (4.14 g, 27.6 mmol), and K₂CO₃ (8.8 g, 63.6 mmol) were added to 1,4-dioxane (25 mL) and water (7 mL) in an oven-dried thick-walled glass tube. The mixture was degassed with nitrogen for 10 mins. Catalyst PdCl₂(dppf)·DCM complex (260 mg, 0.42 mmol) was added. After sealing the glass vial, the reaction mixture was heated with stirring at 100 °C for 12 h. After being cooled to room temperature, water was added and the crude mixture was extracted with dichloromethane (DCM) (3 x 100 mL). The organic layer was dried

over anhydrous Na₂SO₄, filtered, and evaporated under reduced pressure and crude residue was purified by silica gel column chromatography (hexanes:EtOAc, 96:4) to give compound **9** as yellow solid (4.38 g, 79% yield). **R_f** = 0.62 (hexanes:EtOAc = 95:5). **mp**: 68-69 °C. **¹H NMR** (400 MHz, CDCl₃): δ 9.97 (d, *J* = 0.9 Hz, 1H), 8.02 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.41 (ddd, *J* = 7.6, 1.3, 0.5 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 192.1, 192.0, 144.6, 136.8, 133.8, 133.7, 131.7, 131.7, 130.7, 128.3, 128.0, 122.7. **HRMS** (ESI) *m/z*: [M + H]⁺ Calcd for C₁₃H₁₀OBr 260.9915, found 260.9911.

2-bromo-9-mesityl-9H-fluorene (11): To compound **9** (4 g, 15.32 mmol) in dry THF (35 mL) was added dropwise 2-mesitylmagnesium bromide (1M solution in THF, 30.64 mL, 30.64 mmol) under N₂ atmosphere. After stirring at room temperature for 24 h, the reaction mixture was quenched with saturated solution of ammonium chloride (50 mL), and extracted with DCM (3 x 100 mL). The combined organic phase was washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure to afford crude carbinol **10** as light-yellow solid (6.04 g). To a DCM solution of alcohol **10** (6.04 g), was added BF₃·Et₂O (0.4 mL) dropwise under nitrogen. After stirring the reaction mixture for 10 min at room temperature, a saturated aqueous NH₄Cl solution was added to the reaction mixture and it was extracted with DCM (3 x 100 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and removed under reduced pressure to afford a residue which was purified by silica gel column chromatography (hexanes) to give **11** as white solid (4.06 g, 73% yield in two steps). **R_f** = 0.65 (hexanes). **mp**: 130-131 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.80 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.51 (m, 1H), 7.39 (tt, *J* = 7.5, 1.1 Hz, 1H), 7.34 (t, *J* = 1.6 Hz, 1H), 7.28-7.25 (m, 1H), 7.23 – 7.18 (m, 1H), 7.02 (s, 1H), 6.67 (s, 1H), 5.46 (s, 1H), 2.66 (s, 3H), 2.29 (s, 3H), 1.10 (s, 3H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 149.3, 147.0, 140.0, 139.9,

137.9, 137.8, 136.7, 133.1, 130.7, 130.1, 129.0, 127.7, 127.4, 127.1, 124.3, 121.4, 121.2, 120.2, 49.8, 21.8, 20.9, 18.8. **HRMS** (ESI) m/z : $[M + H]^+$ Calcd for $C_{22}H_{20}Br$ 363.0748, found 363.0748.

2-(9-mesityl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13): To an oven-dried glass tube was added **11** (3.6 g, 9.91 mmol), bis(pinacolatodiboron) **12** (5.03 g, 19.82 mmol), $PdCl_2(dppf) \cdot DCM$ (809 mg, 10 mol%), KOAc (2.92 g, 29.73 mmol) and dioxane (20 mL). The glass tube was sealed and the reaction mixture was heated at 85 °C for 4 h. After cooling to room temperature, volatile organics were removed under reduced pressure and water was added. The reaction mixture was extracted with DCM (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 purified on a silica gel column chromatography (hexanes:EtOAc, 97:3) to give 3.03 g of compound **13** in 75% yield as a white solid. $R_f = 0.65$ (hexanes:EtOAc = 95:5). **mp**: 170-171 °C. **1H NMR** (400 MHz, $CDCl_3$): δ 7.88 – 7.83 (m, 3H), 7.68 (s, 1H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.27-7.25 (m, 1H), 7.20 (d, $J = 7.4$ Hz, 1H), 7.02 (s, 1H), 6.64 (s, 1H), 5.49 (s, 1H), 2.68 (s, 3H), 2.28 (s, 3H), 1.33 (s, 12H), 1.07 (s, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 147.9, 146.5, 143.9, 140.8, 138.0, 137.9, 136.2, 133.9, 133.8, 130.5, 130.3, 128.9, 127.8, 126.9, 124.3, 120.5, 119.5, 83.8, 49.7, 25.1, 24.9, 21.9, 20.9, 18.7. **HRMS** (ESI) m/z : $[M + H]^+$ Calcd for $C_{28}H_{32}O_2B$ 411.2495, found 411.2496.

2-(9-mesityl-9H-fluoren-2-yl)benzaldehyde (15): A solution of **13** (990 mg, 5.35 mmol), 2-bromobenzaldehyde **14** (2.22 g, 5.40 mmol), Na_2CO_3 (3.40 g, 32.10 mmol) and $Pd(PPh_3)_4$ (186 mg, 3 mol%) in toluene:EtOH:H₂O (2:1:1) were added to the solution, and the resulting mixture was refluxed for 3 h. After being cooled to room temperature, the mixture was washed with water and extracted with DCM (3 x 50 mL). The DCM layer was dried over anhydrous Na_2SO_4 , filtered, and removed under vacuum. The obtained material was subjected to column chromatography (hexanes:EtOAc, 97:3) to afford aldehyde **15** as yellow solid (1.79 g, 86%

yield). $R_f = 0.59$ (hexanes:EtOAc = 95:5). **mp**: 137-138 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.97 (m, 1H), 7.99 (ddd, $J = 7.9, 1.5, 0.6$ Hz, 1H), 7.92 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.89 (dt, $J = 7.7, 1.0$ Hz, 1H), 7.59 (td, $J = 7.5, 1.5$ Hz, 1H), 7.47 (dt, $J = 7.6, 1.1$ Hz, 1H), 7.45 – 7.42 (m, 2H), 7.41 – 7.37 (m, 2H), 7.30 (td, $J = 7.3, 1.1$ Hz, 1H), 7.26 – 7.23 (m, 1H), 7.00 (s, 1H), 6.66 (s, 1H), 5.56 (s, 1H), 2.67 (s, 3H), 2.26 (s, 3H), 1.14 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 192.5, 147.8, 147.6, 146.3, 141.0, 140.2, 137.8, 137.7, 136.8, 136.5, 1133.8, 133.5, 133.4, 131.0, 130.7, 129.3, 129.0, 127.8, 127.7, 127.6, 127.1, 125.7, 124.3, 120.4, 119.9, 49.9, 21.9, 20.9, 18.9. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{29}\text{H}_{25}\text{O}$ 389.1905, found 389.1900.

6,12-dimesityl-6,12-dihydroindeno[1,2-b]fluorene (16): 2-Mesitylmagnesium bromide (1.0 M in THF, 1.1 mL, 1.1 mmol) was added dropwise to the dry THF solution of **15** (200 mg, 0.51 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h, and then quenched by saturated aqueous NH_4Cl solution and extracted with DCM (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to afford crude product as yellow solid (365 mg, **HRMS** m/z : $[\text{M}]^+$ Calcd for $\text{C}_{38}\text{H}_{34}$ 490.2661, found 490.2661). The crude alcohol (319 mg) was then subjected to Friedel-Crafts cyclization with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.1 mL) in anhydrous DCM (10 mL) at room temperature. Once the starting material disappeared, a saturated aqueous NH_4Cl solution was added to the reaction mixture and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and the solvent was subsequently removed under reduced pressure. The residue was purified by silica gel column chromatography (hexanes) to afford dihydro precursor **16** as pink-white solid (165 mg, 65% yield in two steps). $R_f = 0.40$ (hexanes). **mp**: 270-271 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.72 (d, $J = 7.3$ Hz, 2H), 7.66 (d, $J = 9.1$ Hz, 2H), 7.36 – 7.30 (m, 2H), 7.21 (d, $J = 4.7$ Hz, 4H), 7.09 (s, 2H), 6.68 (d, $J = 10.2$ Hz, 2H), 5.58 (s, 2H), 2.76 (s, 6H), 2.32 – 2.31 (m, 6H), 1.17 – 1.09 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.6, 146.6, 146.5, 141.0, 140.7, 140.6, 138.1, 138.0, 137.9, 137.9, 136.4, 136.3, 134.4,

134.3, 130.7, 130.6, 128.9, 127.0, 126.9, 126.8, 124.1, 120.1, 120.1, 115.9, 115.9, 49.6, 49.5, 22.0, 21.0, 18.8, 18.6. **HRMS** (ESI) m/z : $[M]^+$ Calcd for $C_{38}H_{34}$ 490.2661, found 490.2661.

6,12-dimesitylindeno[1,2-b]fluorene (1): DDQ (41 mg, 0.18 mmol, 1.3 equiv) was added to dihydro precursor **16** (69 mg, 0.14 mmol) in dry 1,2-dichloroethane (3 mL) under N_2 , and the reaction mixture was warmed to 80 °C for 2 h. Once the starting material was consumed (monitored by TLC), the 1,2 dichloroethane was removed in vacuo and the crude material was purified by silica gel column chromatography (hexanes) to afford the desired product **1** as red solid (65 mg, 95% yield). R_f = 0.46 (hexanes). **mp**: 212-213 °C. **1H NMR** (400 MHz, $CDCl_3$): δ 7.30 (d, J = 7.0 Hz, 2H), 7.02 (s, 4H), 6.99 (td, J = 7.4, 1.4 Hz, 2H), 6.94 (td, J = 7.3, 1.3 Hz, 2H), 6.84 (s, 2H), 6.67 (d, J = 8.1 Hz, 2H), 2.39 (s, 6H), 2.18 (s, 12H). **HRMS** (ESI) m/z : $[M]^+$ Calcd for $C_{38}H_{32}$ 488.2504, found 488.2504.

3-(9-mesityl-9H-fluoren-2-yl)-2-naphthaldehyde (18): An oven-dried thick-walled glass tube was charged with **13** (470 mg, 1.15 mmol), pre-synthesized **17**¹ (401 mg, 1.15 mmol), K_2CO_3 (780 mg, 5.65 mmol). These solids were then placed under N_2 atmosphere and dissolved in THF (5 ml)/water (1 ml), and had been sparged with nitrogen for 25 mins. After sparging, catalyst $Pd(PPh_3)_4$ (40 mg, 0.03 mmol) was added, and the suspension was heated at 90 °C for 12 h under sealed condition. The reaction mixture was cooled to room temperature, water was added and the resultant mixture was extracted with EtOAc (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under reduced pressure to afford a crude residue which was column chromatographed on silica gel (hexanes:EtOAc, 97:3) to afford the title product **18** as yellow solid (340 mg, 68% yield). R_f = 0.44 (hexanes:EtOAc = 95:5). **mp**: 74-75 °C. **1H NMR** (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.54 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.91 (s, 1H), 7.89 (d, J = 3.7 Hz, 1H), 7.86 (s, 1H), 7.62 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.36 – 7.33 (m, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.27– 7.25 (m, 1H), 7.00 (d, J = 1.9 Hz, 1H), 6.68 (d, J = 1.9 Hz, 1H), 5.59 (s, 1H),

2.69 (s, 3H), 2.26 (s, 3H), 1.18 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 192.7, 192.7, 147.8, 147.5, 140.9, 140.7, 140.3, 137.2, 136.5, 135.6, 133.5, 131.9, 131.8, 130.7, 129.9, 129.9, 129.8, 129.4, 129.2, 129.0, 127.9, 127.7, 127.1, 127.0, 125.7, 124.3, 120.4, 120.0, 49.9, 21.9, 20.9, 18.9. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{38}\text{H}_{34}$ 439.2062, found 439.2060.

6,14-dimesitylbenzo[b]indeno[2,1-h]fluorene (2): 2-Mesitylmagnesium bromide (1.0 M in THF, 0.7 mL, 0.7 mmol) was added dropwise to the dry THF solution of **18** (152 mg, 0.34 mmol) under nitrogen atmosphere. The mixture was stirred at room temperature for 24 h. After complete disappearance of carbonyl **18**, the reaction mixture was quenched with saturated aqueous solution of saturated ammonium chloride (20 mL) and diluted with ethyl acetate (30 mL). The layers were separated and the organic layer was washed with brine. The extracts were dried over sodium sulfate, filtered, and was concentrated in vacuo to afford crude alcohol (183 mg, HRMS (ESI) m/z : $[\text{M} - \text{H}]^+$ Calcd for $\text{C}_{42}\text{H}_{37}\text{O}$ 557.2844, found 557.2845). Under nitrogen condition, a DCM solution of alcohol (136 mg, 0.24 mmol) was reacted with 0.1 ml of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at room temperature. Completion of Friedel-craft reaction and formation of compound **19** (97 mg, HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{42}\text{H}_{37}$ 541.2895, found 541.2894) was monitored by TLC (a partial conversion of **19** to **2** was also observed in TLC, likely by air oxidation). The obtained reaction mixture was filtered through short silica plug. Afterwards, crude precursor **19** (30 mg, 0.05 mmol) was dissolved in 1,2-dichloroethane (2 mL) and treated with DDQ (16 mg, 0.07 mmol, 1.3 equiv) for 15 mins at room temperature. After removing 1,2-dichloroethane in vacuo, the final compound **2** was obtained as red solid (27 mg, 63% yield over three steps) after purification of the crude reaction residue by silica gel (hexanes) column chromatography. R_f = 0.46 (hexanes). mp: >350 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.77 (s, 1H), 7.69 – 7.62 (m, 1H), 7.58 – 7.51 (m, 1H), 7.44 – 7.37 (m, 1H), 7.29 (ddd, J = 6.7, 4.0, 2.0 Hz, 2H), 7.10 (s, 1H), 7.08 (s, 2H), 7.04 (s, 2H), 7.03 – 6.98 (m, 4H), 6.77 – 6.71 (m, 1H), 2.44-2.41 (m, 6H), 2.19 (m, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ

145.0, 144.6, 142.9, 142.4, 140.8, 138.0, 137.9, 137.8, 137.6, 137.4, 137.4, 136.9, 135.7, 134.7, 134.1, 133.6, 130.2, 130.1, 128.8, 128.4, 128.3, 128.2, 126.5, 126.1, 121.6, 120.7, 120.6, 119.4, 118.3, 116.9, 21.4, 21.3, 20.5. **HRMS** (ESI) m/z : $[M + H]^+$ Calcd for $C_{42}H_{34}$ 538.2661, found 538.2659.

1-(9-mesityl-9H-fluoren-2-yl)-2-naphthaldehyde (21): An oven-dried thick-walled glass tube was charged with **13** (700 mg, 1.71 mmol), commercially available **20** (401 mg, 1.71 mmol), K_2CO_3 (1.16 g, 8.41 mmol), THF (5 ml), water (1 ml), and purged with nitrogen for 25 mins. After purging, catalyst $Pd(PPh_3)_4$ (59 mg, 0.05 mmol) was added. The mixture was heated at 90 °C for 12 h after sealing the glass tube. After being cooled to room temperature, water was added and the resultant mixture was extracted with EtOAc (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under reduced pressure to afford a crude residue which was column chromatographed on silica gel (hexanes:EtOAc, 97:3) to afford the title product **21** as yellow solid (626 mg, 84% yield). R_f = 0.5 (hexanes:EtOAc = 95:5). **mp**: 168-169 °C. **1H NMR** (400 MHz, $CDCl_3$): δ 10.19 – 9.82 (m, 1H), 8.37 – 7.87 (m, 6H), 7.78 – 7.54 (m, 2H), 7.51 – 7.36 (m, 3H), 7.31 (dd, J = 7.3, 1.1 Hz, 1H), 7.28-7.25 (m, 1H), 6.94 (t, J = 2.7 Hz, 1H), 6.65 (t, J = 2.8 Hz, 1H), 5.60 (d, J = 10.1 Hz, 1H), 2.64 (d, J = 4.9 Hz, 3H), 2.22 (d, J = 5.6 Hz, 3H), 1.27-1.18 (m, 3H). **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 193.0, 192.6, 192.4, 147.6, 147.6, 147.5, 147.5, 147.0, 146.9, 141.2, 141.2, 140.2, 137.9, 137.6, 136.6, 136.5, 136.1, 134.7, 134.1, 134.0, 133.4, 133.3, 132.7, 132.6, 131.4, 131.2, 130.8, 130.6, 130.0, 129.8, 129.6, 129.2, 129.0, 128.9, 128.8, 128.8, 128.3, 128.3, 128.2, 127.9, 127.8, 127.6, 127.2, 127.0, 126.9, 126.9, 126.6, 124.4, 122.9, 122.2, 120.4, 119.9, 49.94, 21.8, 20.9, 18.9, 18.8. **HRMS** (ESI) m/z : $[M + H]^+$ Calcd for $C_{33}H_{27}O$ 439.2062, found 439.2062.

7,13-dimesitylbenzo[g]indeno[1,2-b]fluorene (3): Under nitrogen atmosphere, 2-mesitylmagnesium bromide (1.0 M in THF, 2.25 mL, 2.25 mmol) was added dropwise to the dry THF solution of aldehyde **21** (493 mg, 1.12 mmol). Then the mixture was stirred at room

temperature for 24 h. After complete conversion of **21** to intermediate alcohol, the reaction mixture was quenched with saturated aqueous ammonium chloride (30 mL) and diluted with ethyl acetate (50 mL). The layers were separated and the organic layer was washed with brine. The extracts were dried over sodium sulfate, filtered, and was concentrated in vacuo to afford crude product (706 mg, HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{42}H_{37}O$ 557.2844, found 557.2844). To the solution of crude alcohol (609 mg, 1.09 mmol) in anhydrous DCM (10 mL) at room temperature, $BF_3 \cdot Et_2O$ (0.1 mL) was added dropwise under nitrogen, and the reaction mixture was stirred for 10 min at room temperature. Completion of the reaction and formation of compound **22** (456 mg, HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{37}$ 541.2895, found 541.2892) was monitored by TLC (a partial conversion of **22** to **3** was also observed in TLC, likely by air oxidation). After filtration through short silica plug, a chloroform (5 mL) solution of crude dihydro intermediate **22** (150 mg, 0.27 mmol) was treated with DDQ (82 mg, 0.36 mmol, 1.3 equiv) for 15 mins at room temperature. After evaporation of solvent, the obtained material was subjected to silica gel column chromatography (hexanes) to afford pure **3** as red solid (133 mg, 77% yield over three steps). R_f = 0.46 (hexanes). mp: 285-286 °C. 1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.34 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 0.9 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.04 (d, J = 5.2 Hz, 4H), 6.96 (t, J = 7.4 Hz, 1H), 6.88 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.75 (s, 1H), 6.62 (d, J = 7.3 Hz, 1H), 2.43-2.41 (m, 6H), 2.23-2.22 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.3, 146.0, 144.3, 143.4, 140.5, 138.4, 137.7, 137.5, 137.3, 137.1, 135.4, 134.9, 134.2, 132.1, 130.1, 130.0, 129.8, 129.5, 128.5, 128.5, 128.3, 127.8, 127.7, 127.3, 125.0, 124.4, 123.6, 122.5, 120.5, 120.4, 119.8, 21.3, 20.6, 20.5. HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{42}H_{34}$ 538.2661, found 538.2659.

6-(3,5-bis(trifluoromethyl)phenyl)-12-mesityl-6,12-dihydroindeno[1,2-b]fluorene (23): A Grignard reagent mixture was prepared from 1-bromo-3,5-bis(trifluoromethyl)benzene (0.76

mL, 4.41 mmol), magnesium (129 mg, 5.30 mmol) and I₂ (one pellet) in freshly distilled dry THF (5 mL). To a THF solution of aldehyde **15** (343 mg, 0.88 mmol) was added the freshly prepared Grignard reagent at room temperature under N₂ atmosphere. The resulting solution was stirred for overnight. After complete consumption of carbonyl, the reaction mixture was quenched with saturated solution of ammonium chloride (50 mL), and the volatile organics were evaporated in vacuo. The residue was extracted with DCM (3 x 50 mL), washed with water, and dried over sodium sulfate. The organic layer was filtered, and the filtrate was removed under reduced pressure to afford intermediate alcohol (657 mg, **HRMS** m/z: [M - H]⁺ Calcd for C₃₇H₂₅F₆ 583.1860, found 583.1860). To the solution of crude alcohol (608 mg, 1.01 mmol) in anhydrous DCM (5 mL) at room temperature, BF₃·Et₂O (0.2 mL) was added dropwise under nitrogen, and the reaction mixture was stirred for 10 min at room temperature to perform an intra-molecular ring-closure reaction. After 10 min, a saturated aqueous NH₄Cl solution was added to the reaction mixture and it was extracted with DCM (3 x 30 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and removed under reduced pressure to afford a residue which was purified by silica gel column chromatography (hexanes) to give **23** as white/pink solid (303 mg, 59% yield over two steps. **R_f** = 0.46 (hexanes). **mp**: 89-90 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.78 (s, 1H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 4.7 Hz, 2H), 7.56 (d, *J* = 1.5 Hz, 2H), 7.43 – 7.27 (m, 3H), 7.26 – 7.21 (m, 3H), 7.08 (d, *J* = 2.1 Hz, 1H), 6.69 (d, *J* = 1.9 Hz, 1H), 5.57 (s, 1H), 5.23 (s, 1H), 2.75 (s, 3H), 2.31 (s, 3H), 1.10 (m, 3H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): δ 147.9, 147.6, 146.7, 146.6, 145.7, 145.6, 145.1, 14.2, 141.1, 140.7, 138.1, 138.0, 137.8, 136.6, 136.6, 133.9, 132.3, 132.0, 130.8, 130.7, 129.0, 129.0, 128.6, 128.2, 127.6, 127.4, 127.0, 125.2, 124.3, 124.3, 120.4, 120.1, 120.0, 116.8, 116.8, 116.2, 116.2, 53.7, 53.6, 49.7, 49.7, 22.0, 21.9, 21.0, 21.0, 18.9, 18.71. **HRMS** (ESI) m/z: [M - H]⁺ Calcd for C₃₇H₂₅F₆ 583.1860, found 583.1860.

6-(3,5-bis(trifluoromethyl)phenyl)-12-mesitylindeno[1,2-b]fluorene (4): DDQ (25 mg, 0.11 mmol, 1.3 equiv) was added to degassed solution of 1,2-dichloroethane (2 ml) of **23** (50 mg, 0.08 mmol) under N₂, and the reaction mixture was warmed to 80 °C for 2 h in a sealed tube. Once the starting material was consumed (monitored by TLC), the 1,2-dichloroethane was removed in vacuo and the crude was purified by silica gel column chromatography (hexanes) to afford title product **12** (46 mg, 92% yield) as deep red solid. **R_f** = 0.59 (hexanes). **mp:** 225-226 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.03 (s, 2H), 7.96 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.15 (s, 1H), 7.14 – 7.05 (m, 4H), 7.03 (s, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.70 (d, *J* = 7.4 Hz, 1H), 2.40 (s, 3H), 2.18 (s, 6H). **¹³C{¹H} NMR** (100 MHz, CDCl₃): 148.5, 144.2, 142.4, 140.9, 139.8, 138.9, 138.0, 137.9, 137.5, 137.0, 136.5, 135.0, 134.8, 132.9, 132.6, 132.2, 131.9, 129.6, 129.0, 128.5, 128.4, 128.2, 128.1, 127.7, 127.4, 124.7, 122.7, 122.0, 121.8, 121.2, 121.0, 120.7, 120.6, 119.3, 117.4, 21.3, 20.4. δ. **HRMS** (ESI) *m/z*: [M]⁺ Calcd for C₃₇H₂₄F₆ 582.1782, found 582.1782.

6-mesityl-12-(perfluorophenyl)indeno[1,2-b]fluorene (5) & 11-mesityl-12-(perfluorophenyl)indeno[2,1-a]fluorene (6): Under nitrogen atmosphere, in 10 mL dry THF solution of **15** (346 mg, 0.89 mmol), (perfluorophenyl)magnesium bromide (0.5 M solution in diethylether, 5.34 mL, 2.67 mmol) was added dropwise. The mixture was stirred at room temperature for 24 h. After removal of the solvent, the crude compound was quenched with NH₄Cl (20 mL) and extracted into DCM (3 x 50 mL), washed with brine, and dried over anhydrous sodium sulfate. The starting material **15** was consumed, so the crude (713 mg, HRMS *m/z*: [M - H⁺] Calcd for C₃₅H₂₄OF₅ 555.1747, found 555.1745) was used for next step without purification. To the solution of crude solid (668 mg) in anhydrous DCM (10 mL) at room temperature, 0.1 mL of BF₃·Et₂O was added dropwise under nitrogen, and the reaction mixture was stirred for 16 h at room temperature. Once the reaction was complete, as monitored by thin layer chromatography (TLC), a saturated aqueous NH₄Cl (10 mL) solution was added

to the reaction mixture and extracted with DCM (3 x 30mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give crude precursor (305 mg, **HRMS** (ESI) m/z: [M - H]⁺ Calcd for C₃₅H₂₂F₅ 537.1642, found 537.1642). DDQ (211 mg, 0.93 mmol, 10 equiv) was added to the mixture of crude dihydro precursor (50 mg, 0.09 mmol) in dry 1,2-dichloroethane (5 mL) under N₂, and the reaction mixture was heated at 80 °C for overnight. Once the starting material was consumed (monitored by TLC), the 1,2-dichloroethane was removed in vacuo and the crude was purified by silica gel column chromatography in pure hexanes to afford the product **5** (26 mg, 36% yield over three steps) and **6** (19 mg, 26% in three steps) as red and purple solid, respectively.

Analytical data of compound 5: R_f = 0.68 (hexanes). mp: 243-244 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.30 (m, 2H), 7.07 – 7.00 (m, 5H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 4.1 Hz, 3H), 6.67 (d, *J* = 7.4 Hz, 1H), 2.39 (s, 3H), 2.18 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.9, 144.3, 142.2, 140.8, 138.9, 138.1, 137.3, 136.9, 134.9, 129.5, 128.6, 128.4, 128.3, 128.1, 127.4, 122.8, 121.7, 120.8, 120.8, 120.7, 117.9, 21.3, 20.4. **HRMS** (ESI) m/z: [M]⁺ Calcd for C₃₅H₂₁F₅ 536.1563, found 536.1563.

Analytical data of compound 6: R_f = 0.56 (hexanes). mp: 212-213 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 6.6 Hz, 1H), 7.06 – 6.95 (m, 4H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.72 (s, 2H), 6.53 (d, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 7.4 Hz, 1H), 2.27 (s, 3H), 2.01 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.9, 144.7, 143.6, 143.5, 142.7, 138.0, 136.5, 136.3, 135.4, 132.9, 131.7, 129.1, 128.6, 128.5, 128.0, 127.8, 127.0, 123.0, 122.8, 120.7, 120.6, 120.4, 120.2, 20.8, 19.9. **HRMS** (ESI) m/z: [M]⁺ Calcd for C₃₅H₂₁F₅ 536.1563, found 536.1565.

1.3 NMR spectra

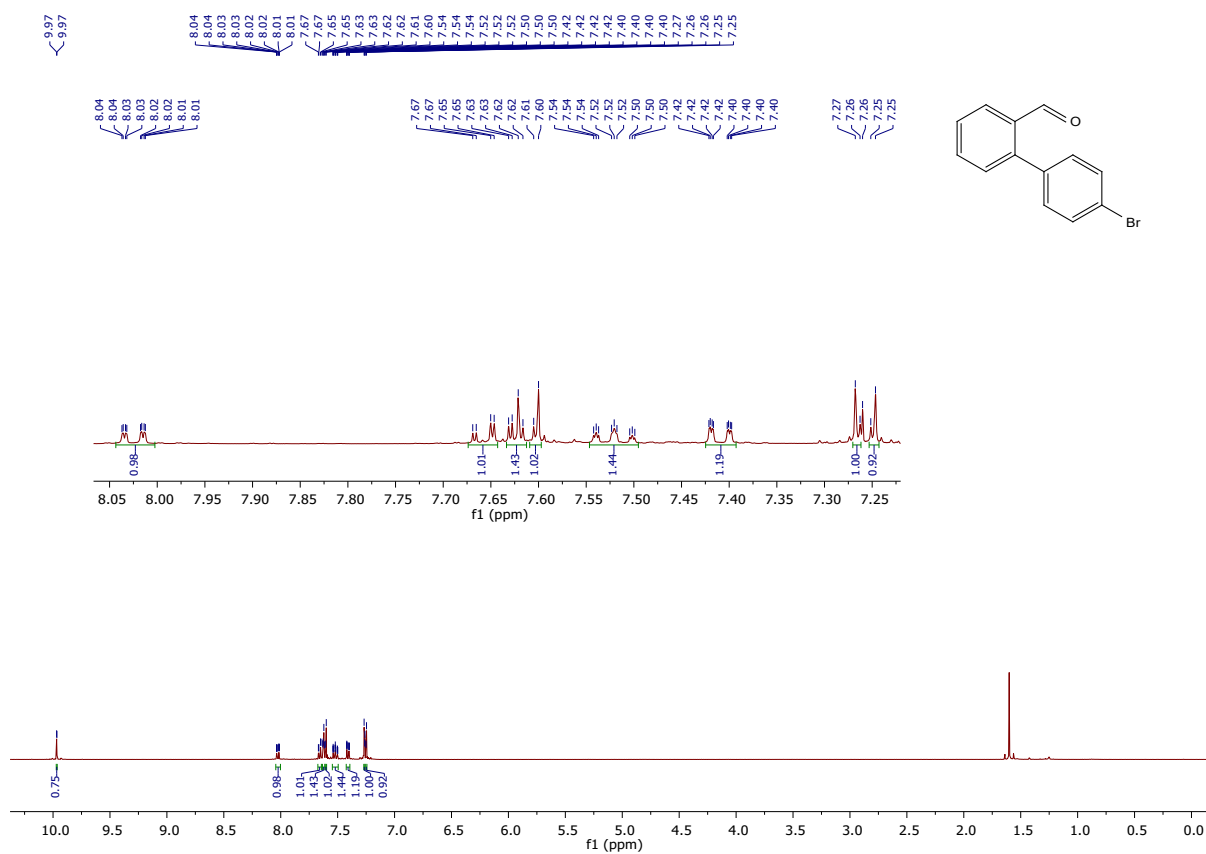


Fig. S1 ¹H NMR spectrum of **9** (in CDCl₃, 400 MHz).

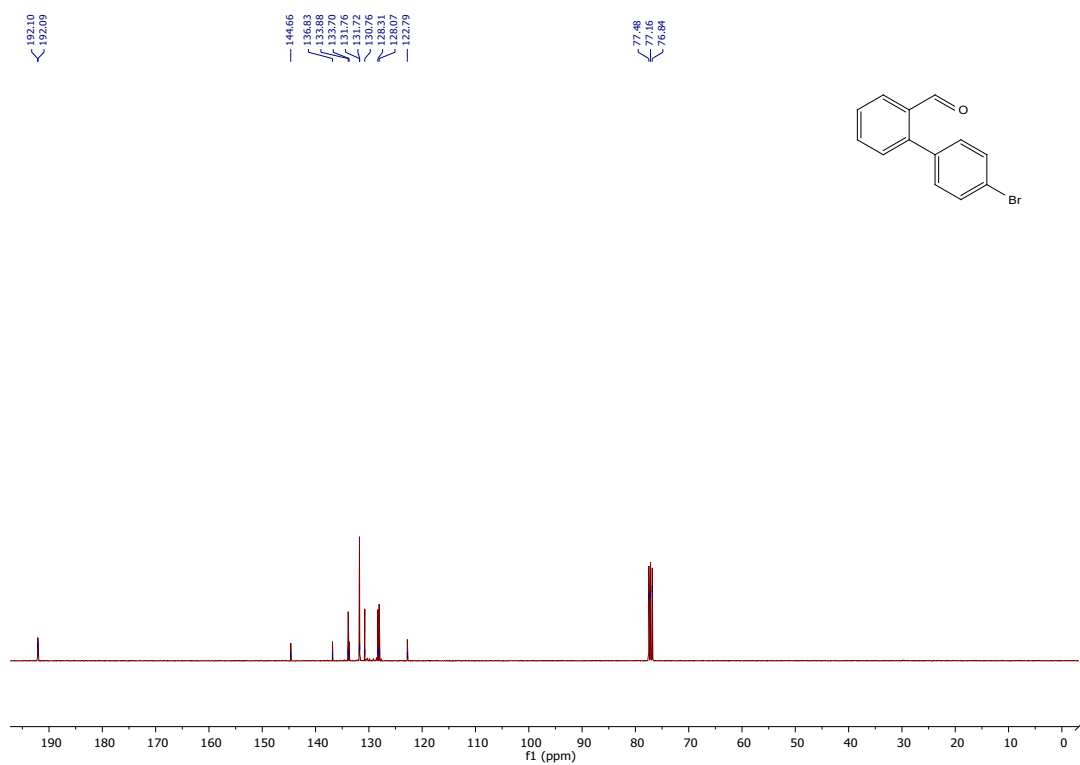


Fig. S2 ¹³C NMR spectrum of **9** (in CDCl₃, 100 MHz).

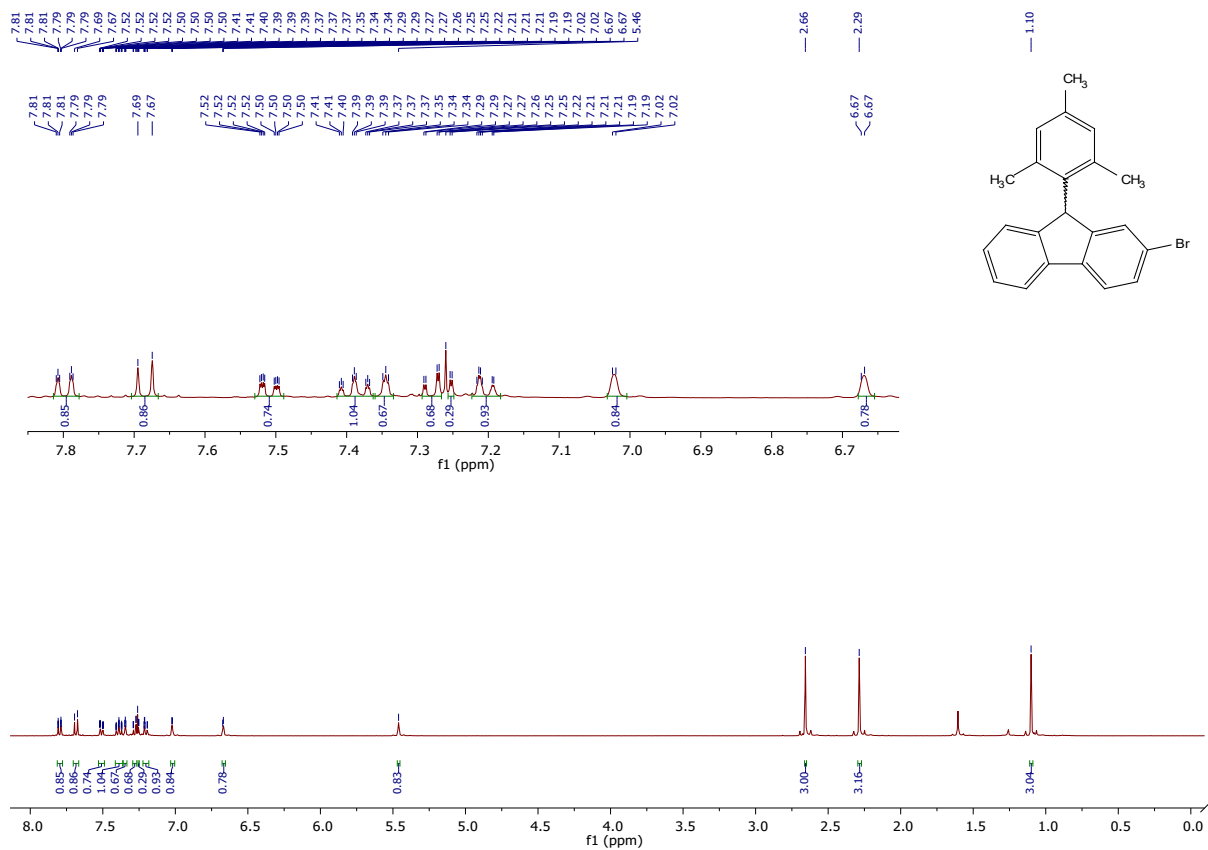


Fig. S3 ¹H NMR spectrum of **11** (in CDCl₃, 400 MHz).

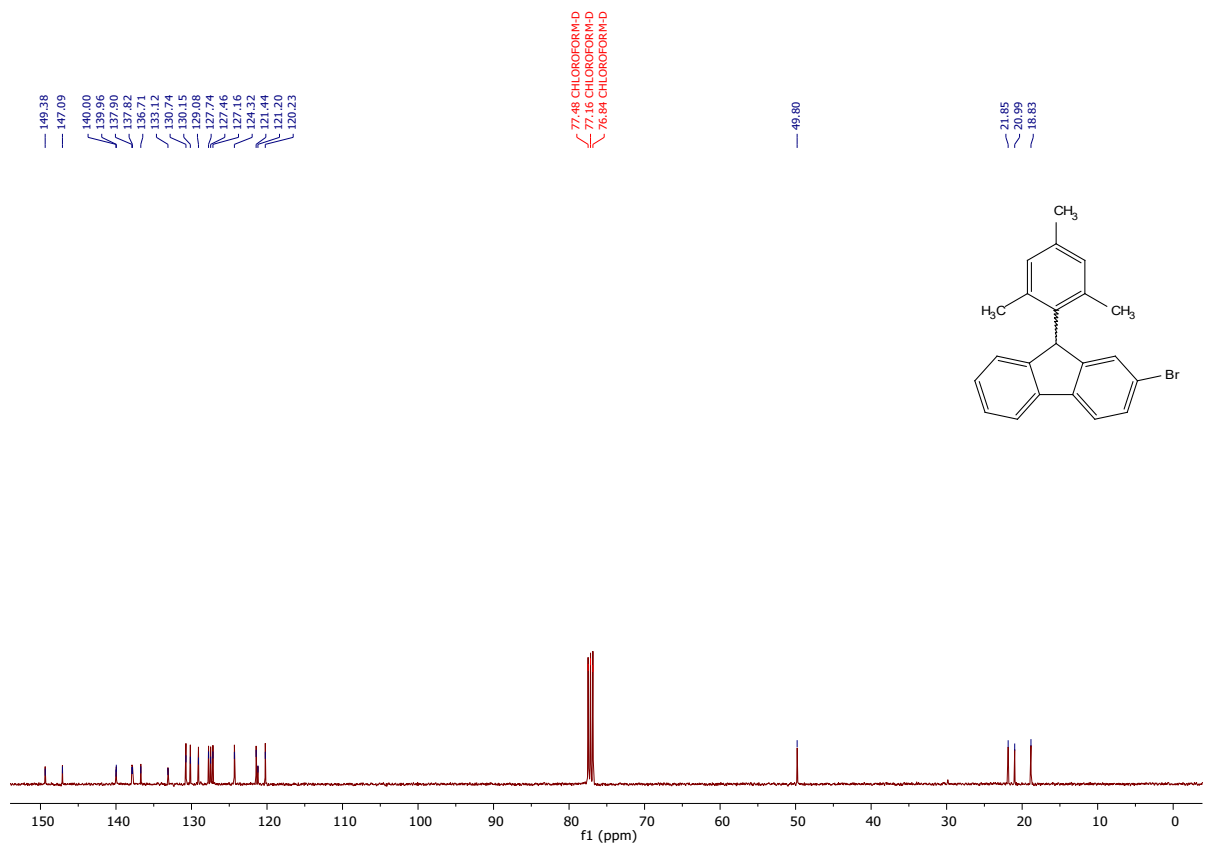


Fig. S4 ¹³C NMR spectrum of **11** (in CDCl₃, 100 MHz).

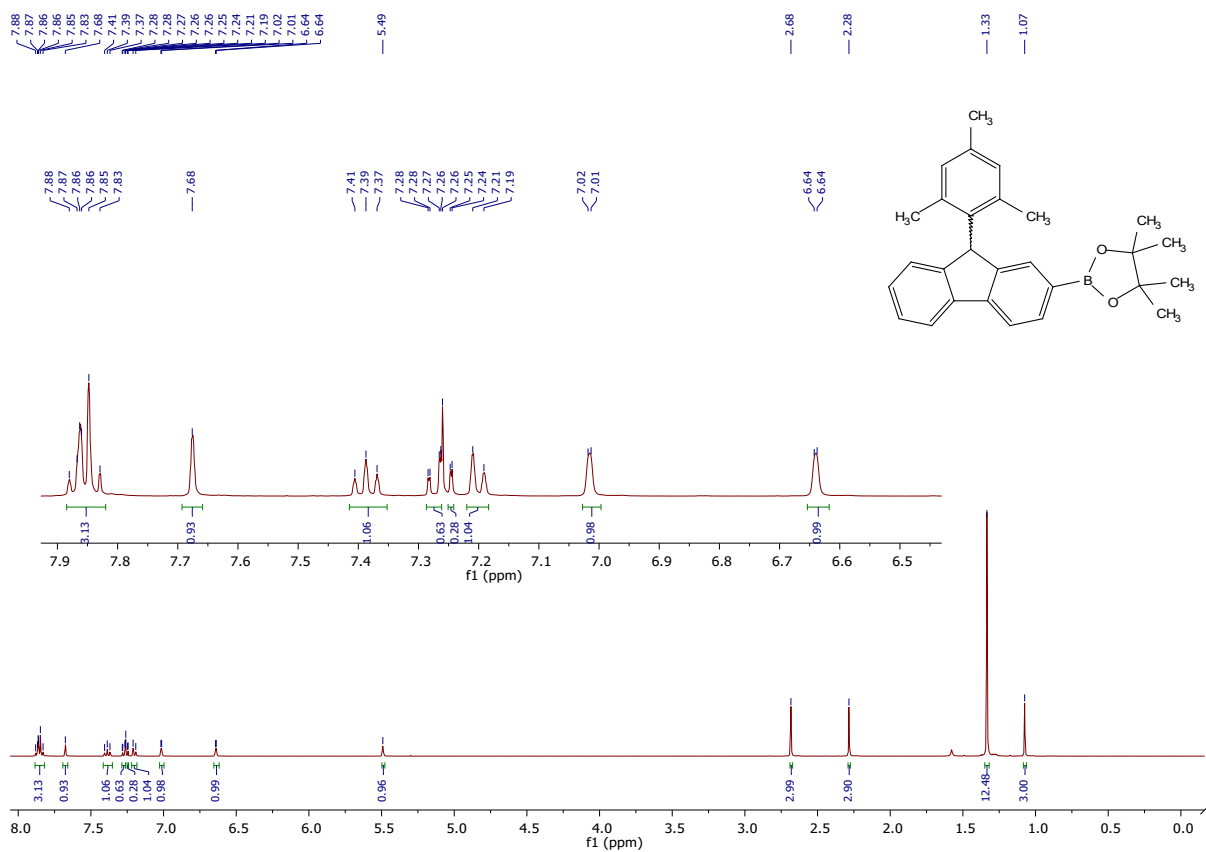


Fig. S5 ¹H NMR spectrum of **13** (in CDCl₃, 400 MHz).

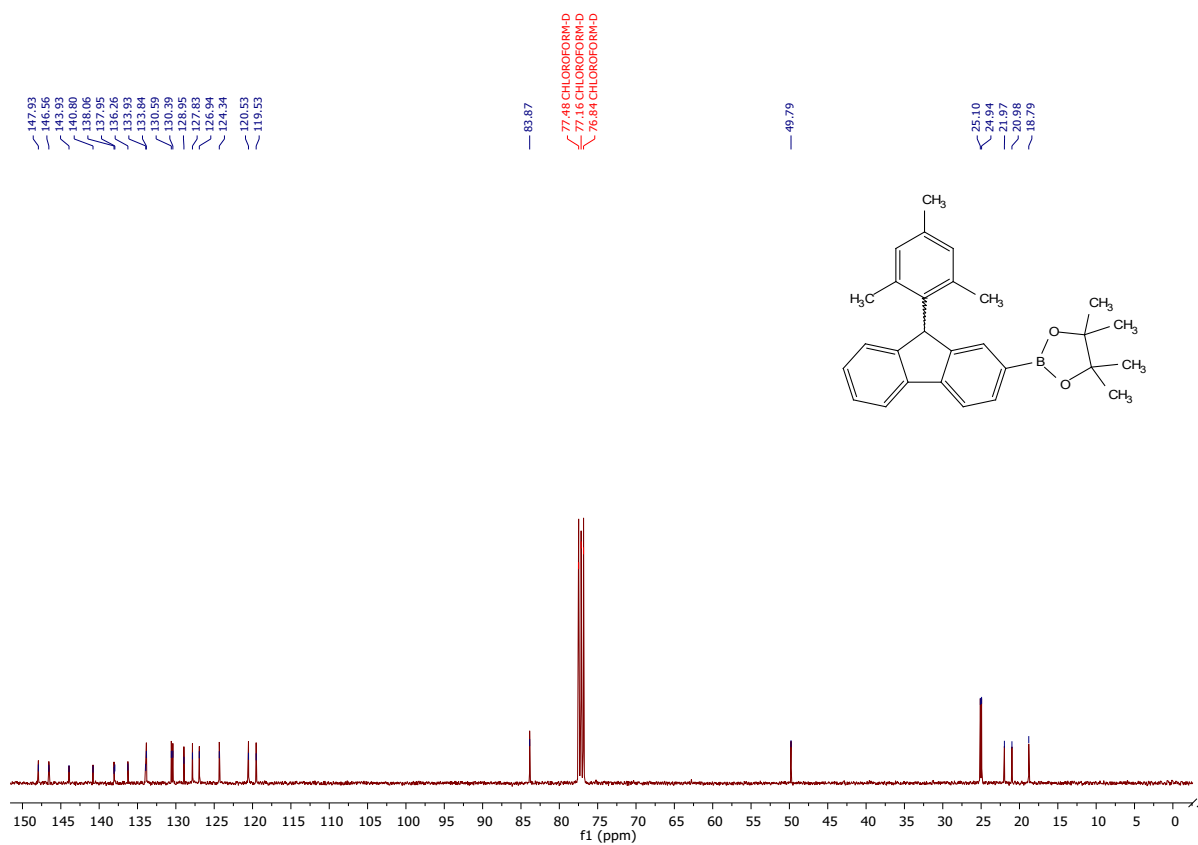


Fig. S6 ¹³C NMR spectrum of **13** (in CDCl₃, 100 MHz).

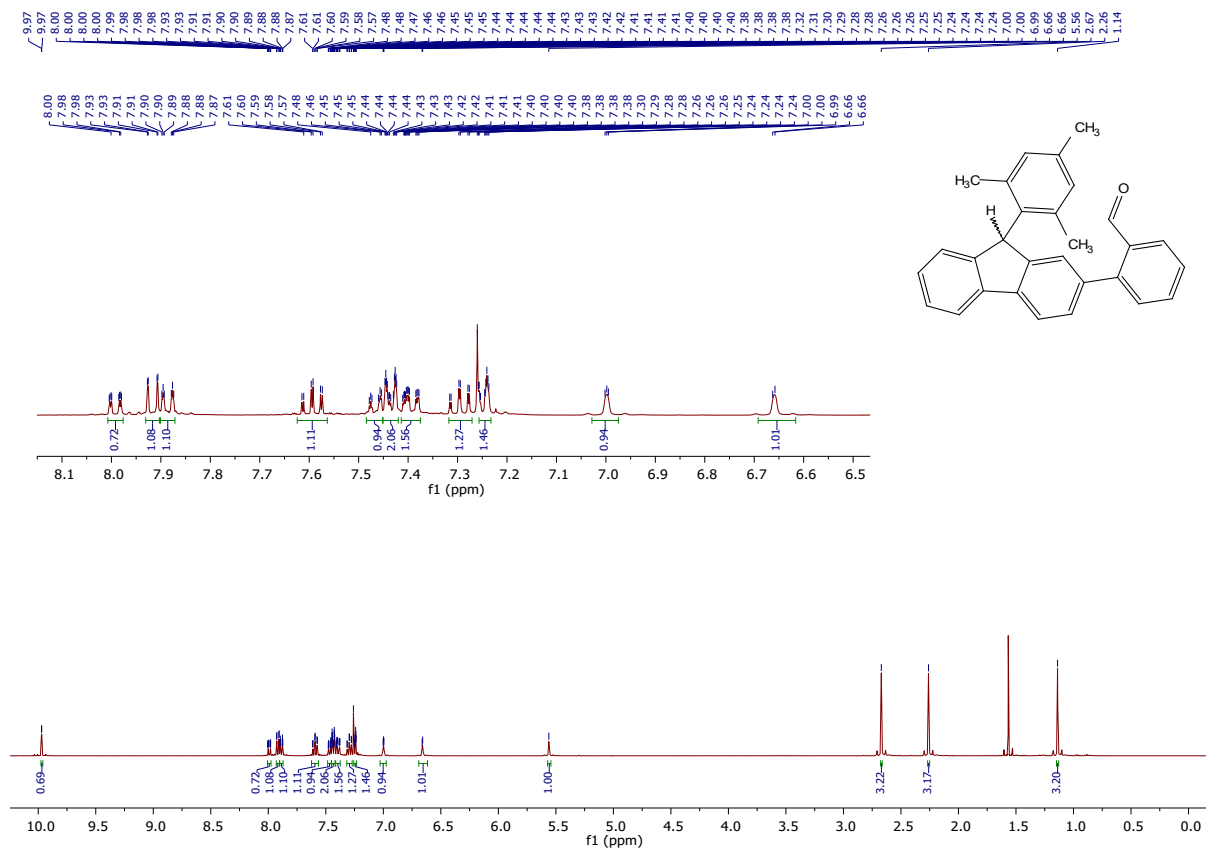


Fig. S7 ¹H NMR spectrum of **15** (in CDCl₃, 400 MHz).

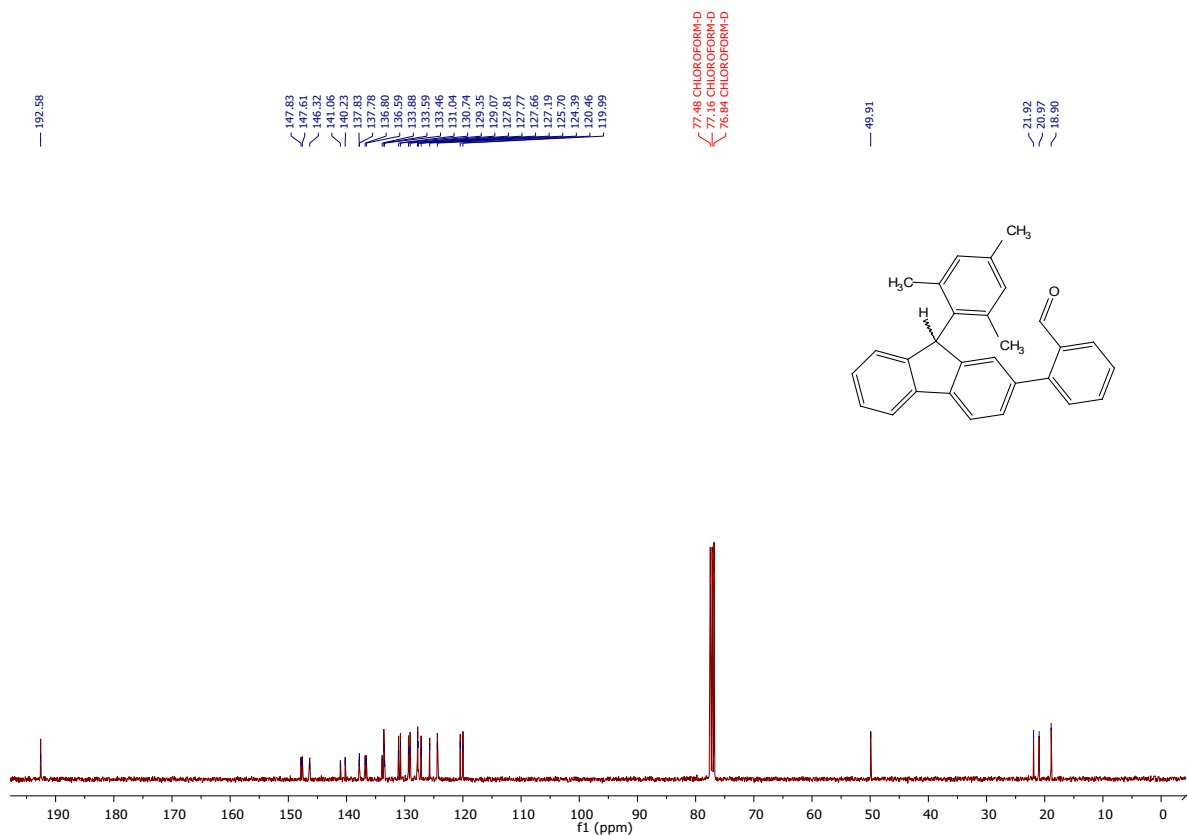


Fig. S8 ¹³C NMR spectrum of **15** (in CDCl₃, 100 MHz).

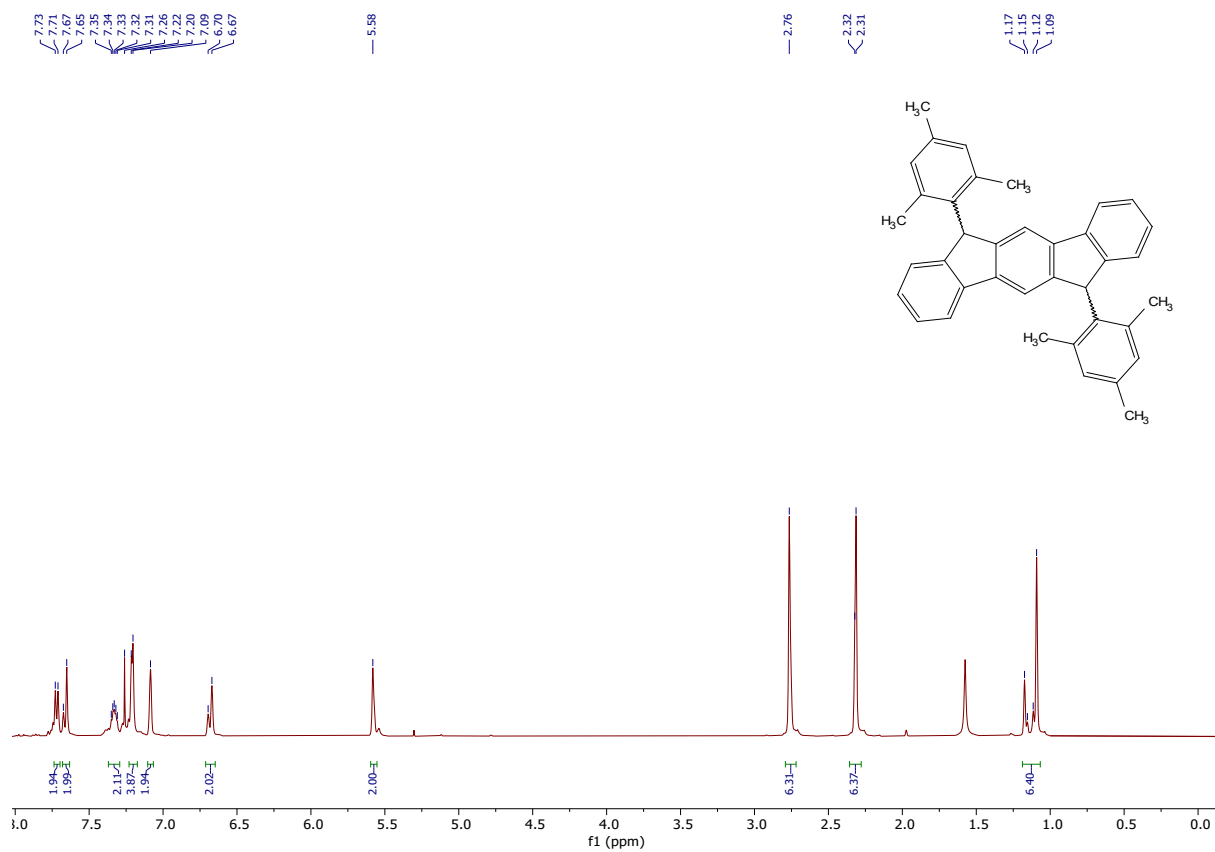


Fig. S9 ¹H NMR spectrum of **16** (in CDCl₃, 400 MHz).

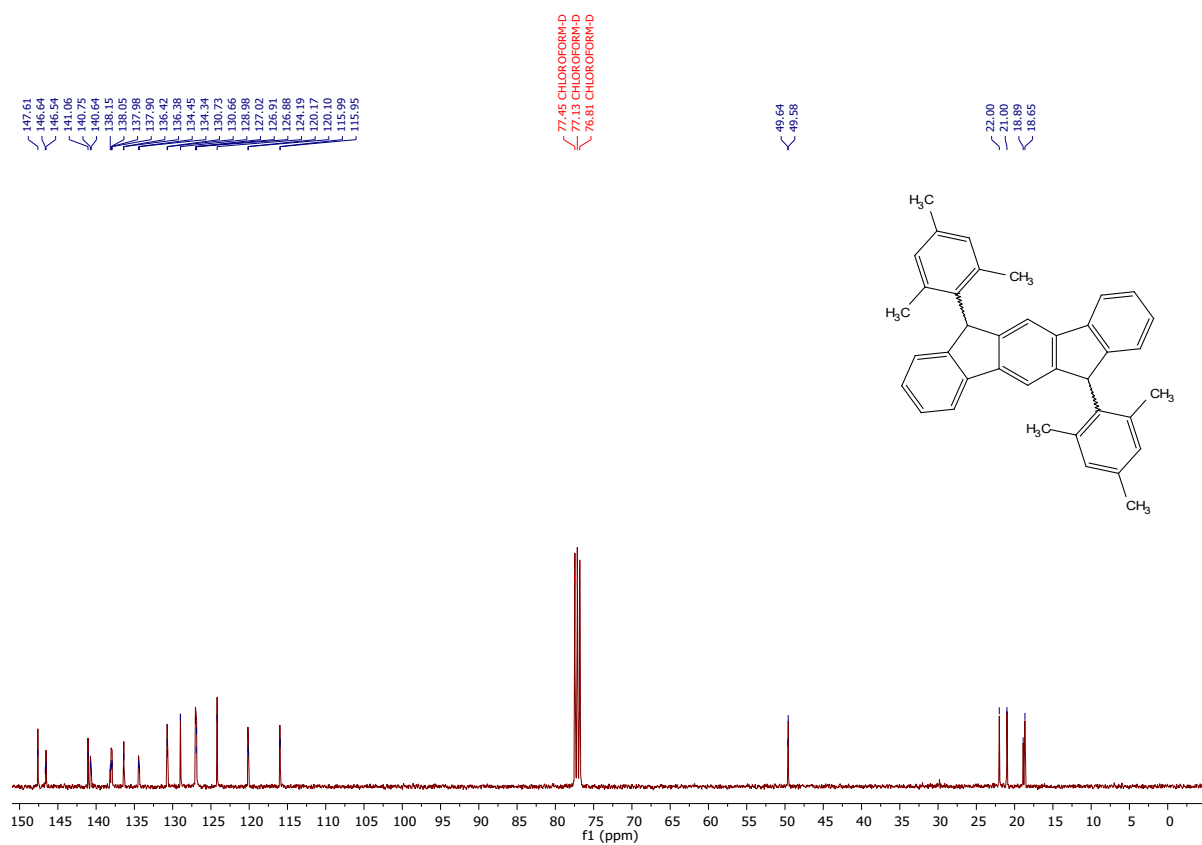


Fig. S10 ¹³C NMR spectrum of **16** (in CDCl₃, 100 MHz).

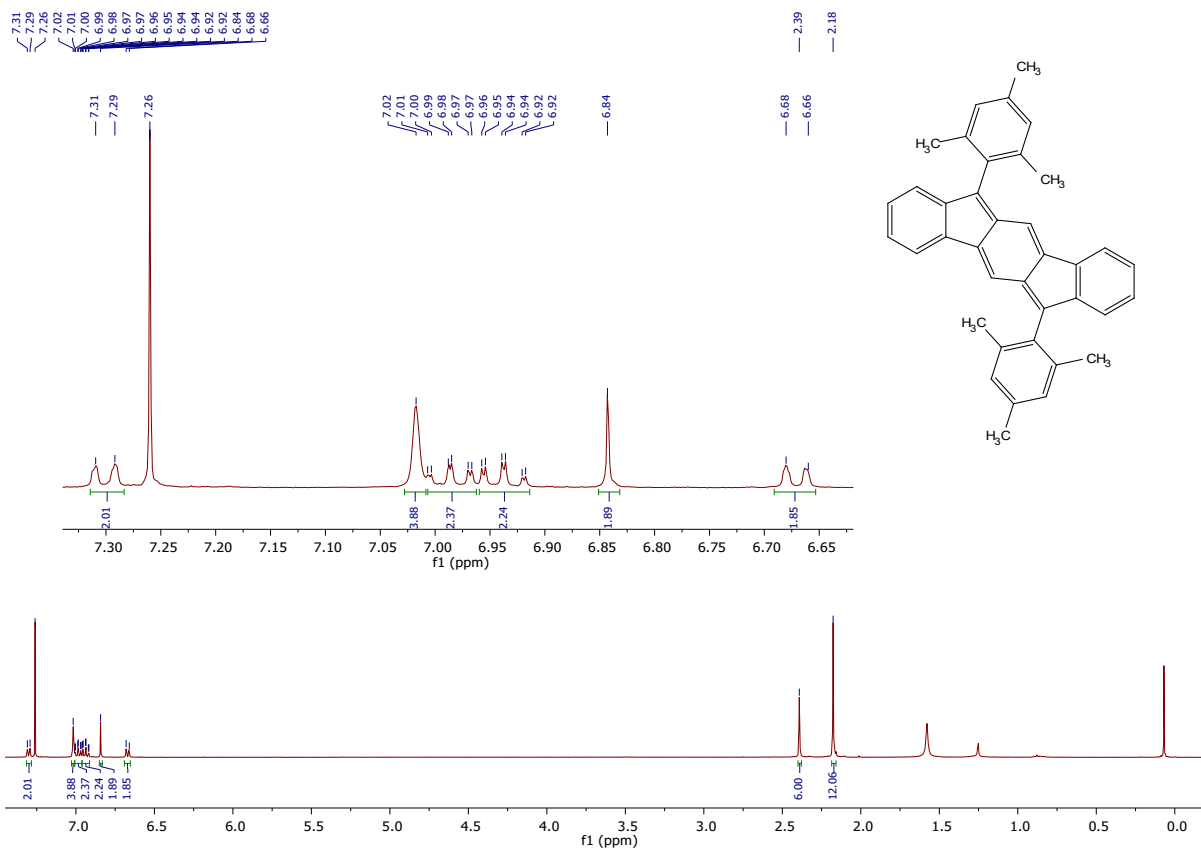


Fig. S11 ^1H NMR spectrum of **1** (in CDCl_3 , 400 MHz).

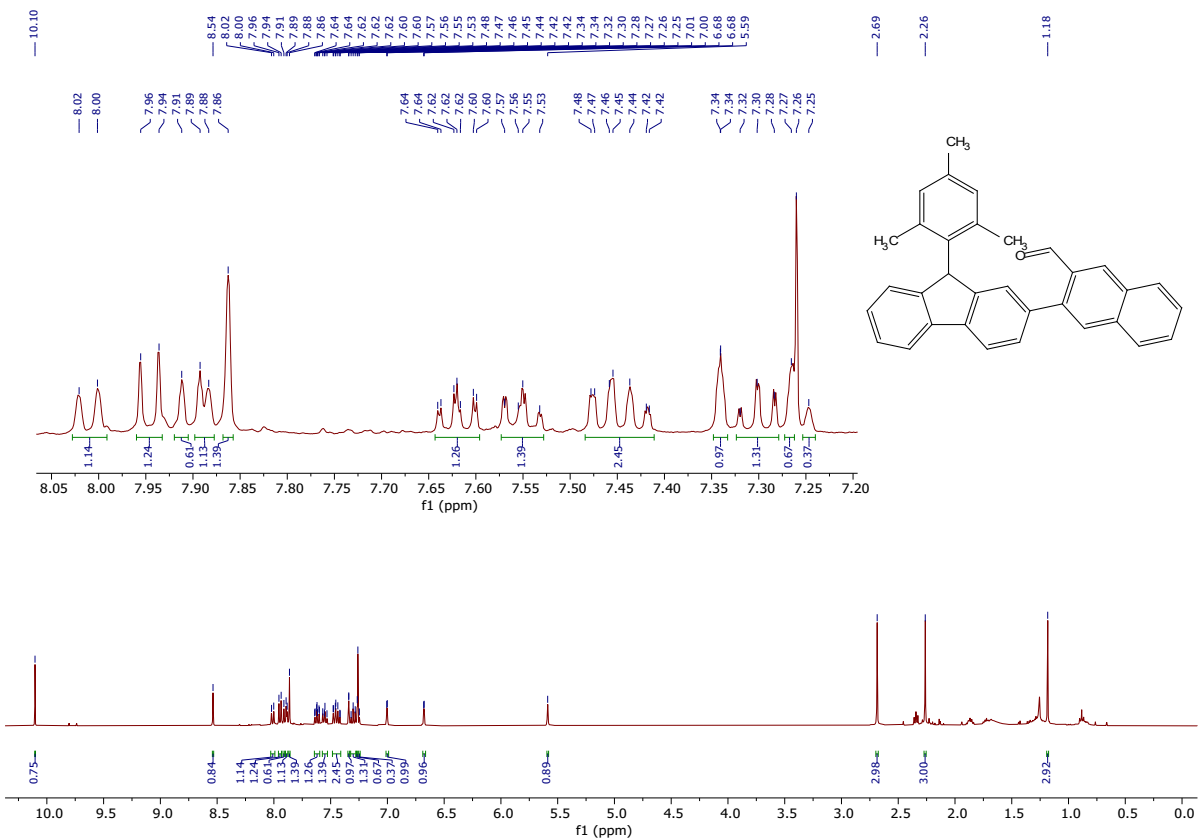


Fig. S12 ^1H NMR spectrum of **18** (in CDCl_3 , 400 MHz).

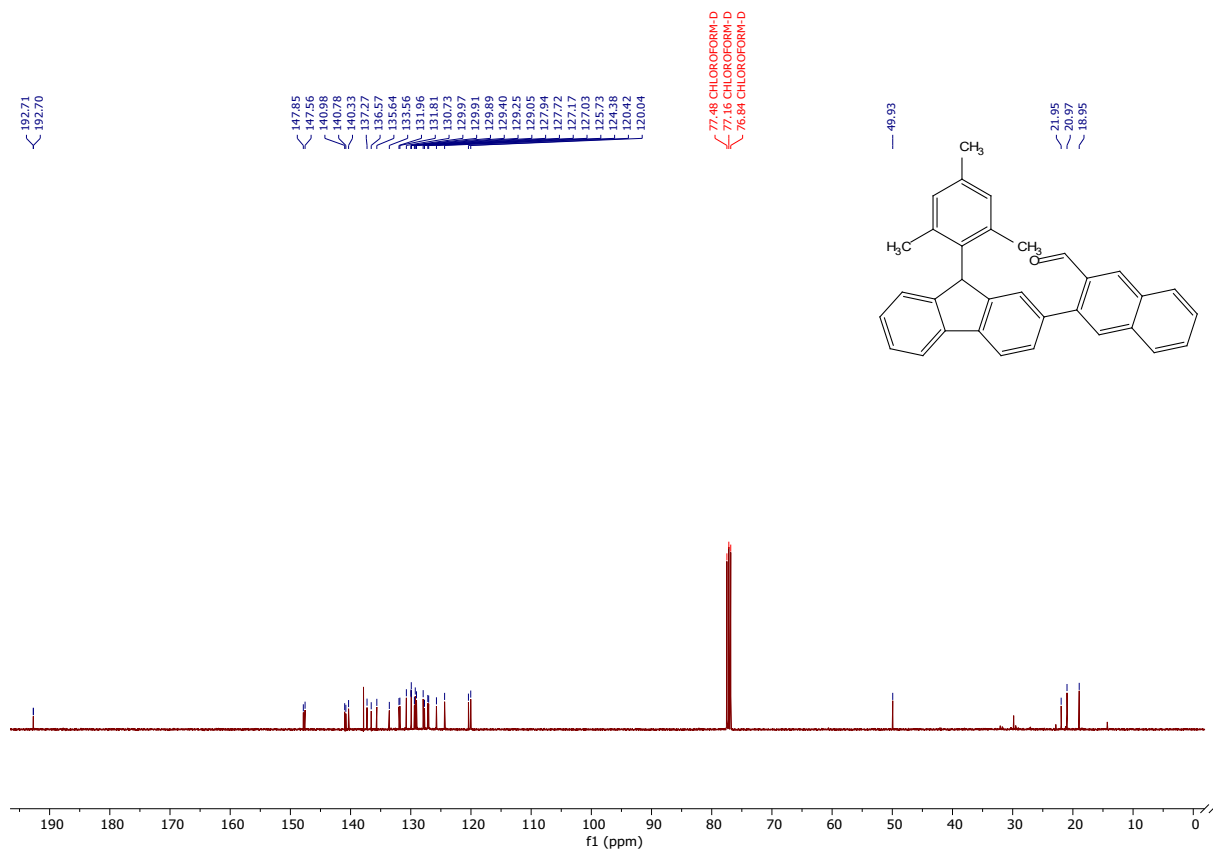


Fig. S13 ¹³C NMR spectrum of **18** (in CDCl₃, 100 MHz).

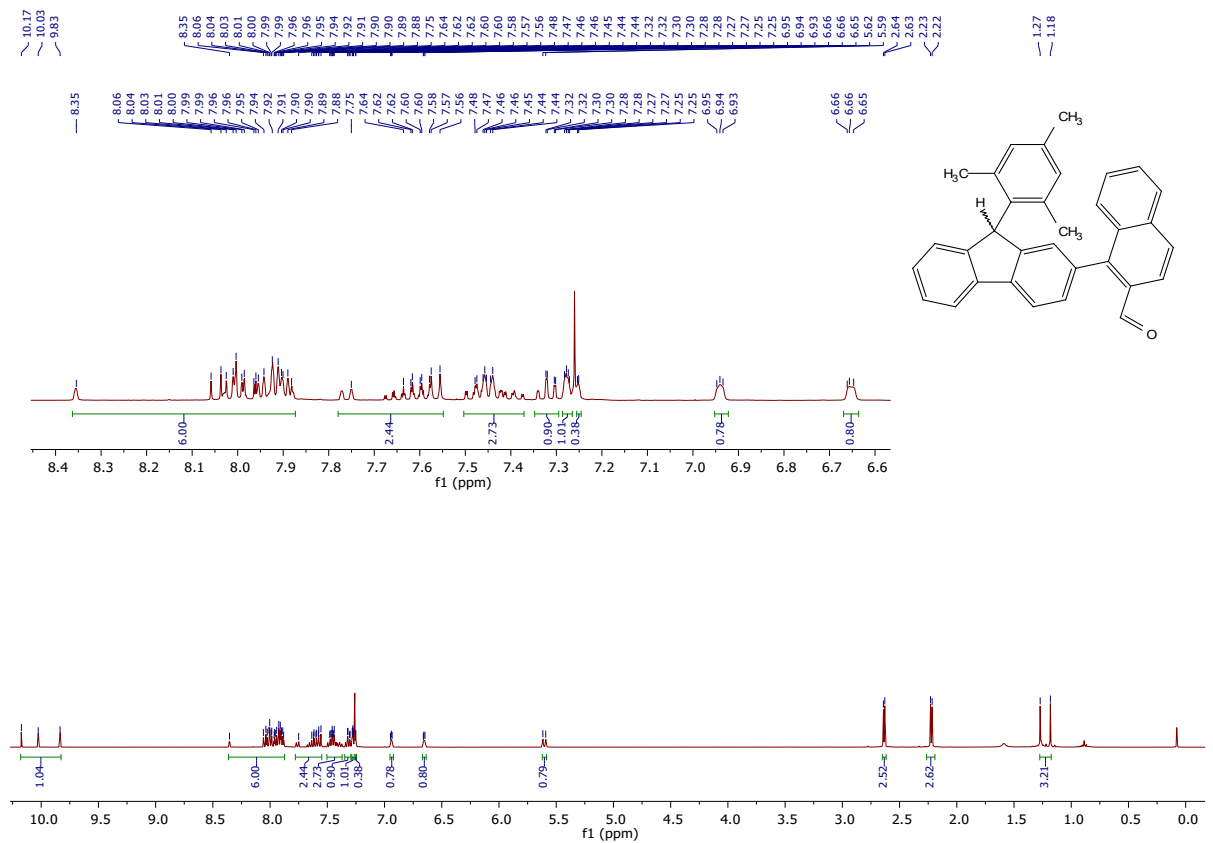


Fig. S14 ¹H NMR spectrum of **21** (in CDCl₃, 400 MHz).

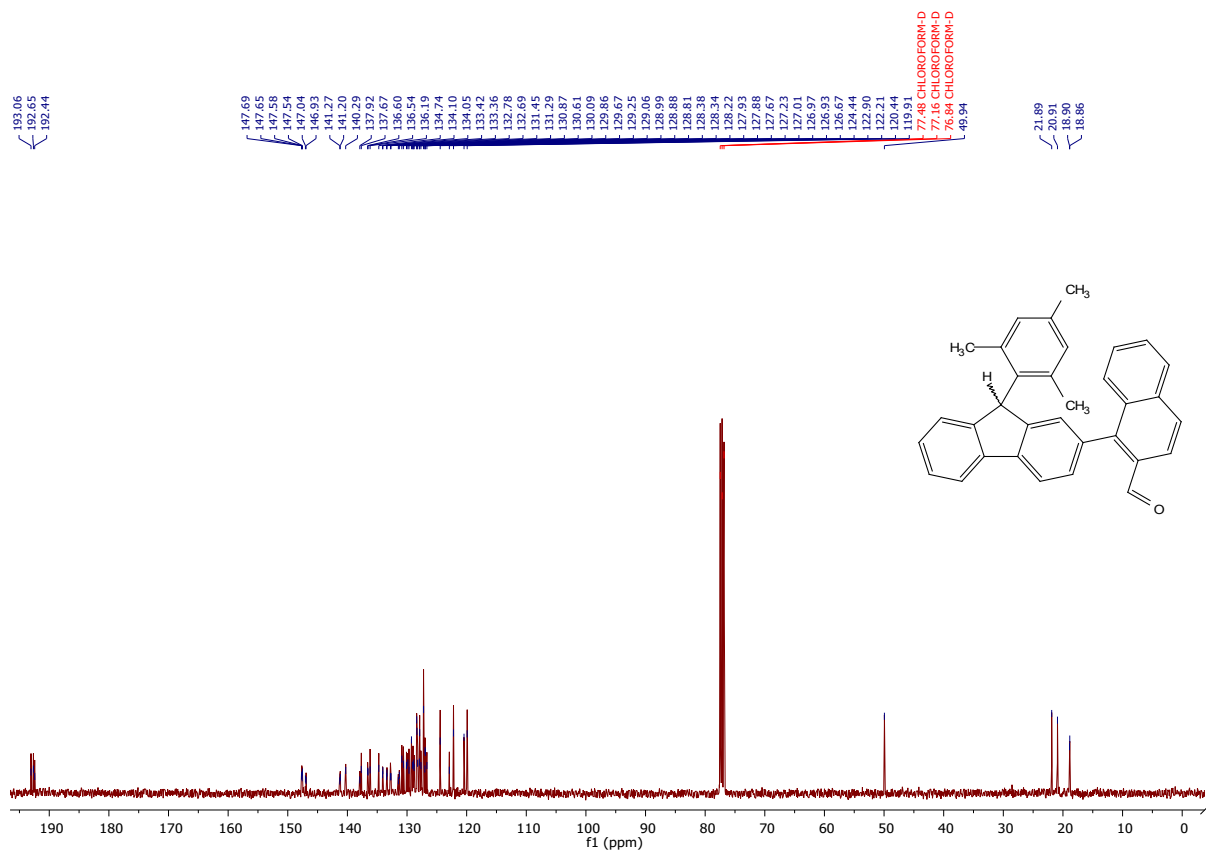


Fig. S15 ¹³C NMR spectrum of **21** (in CDCl₃, 100 MHz).

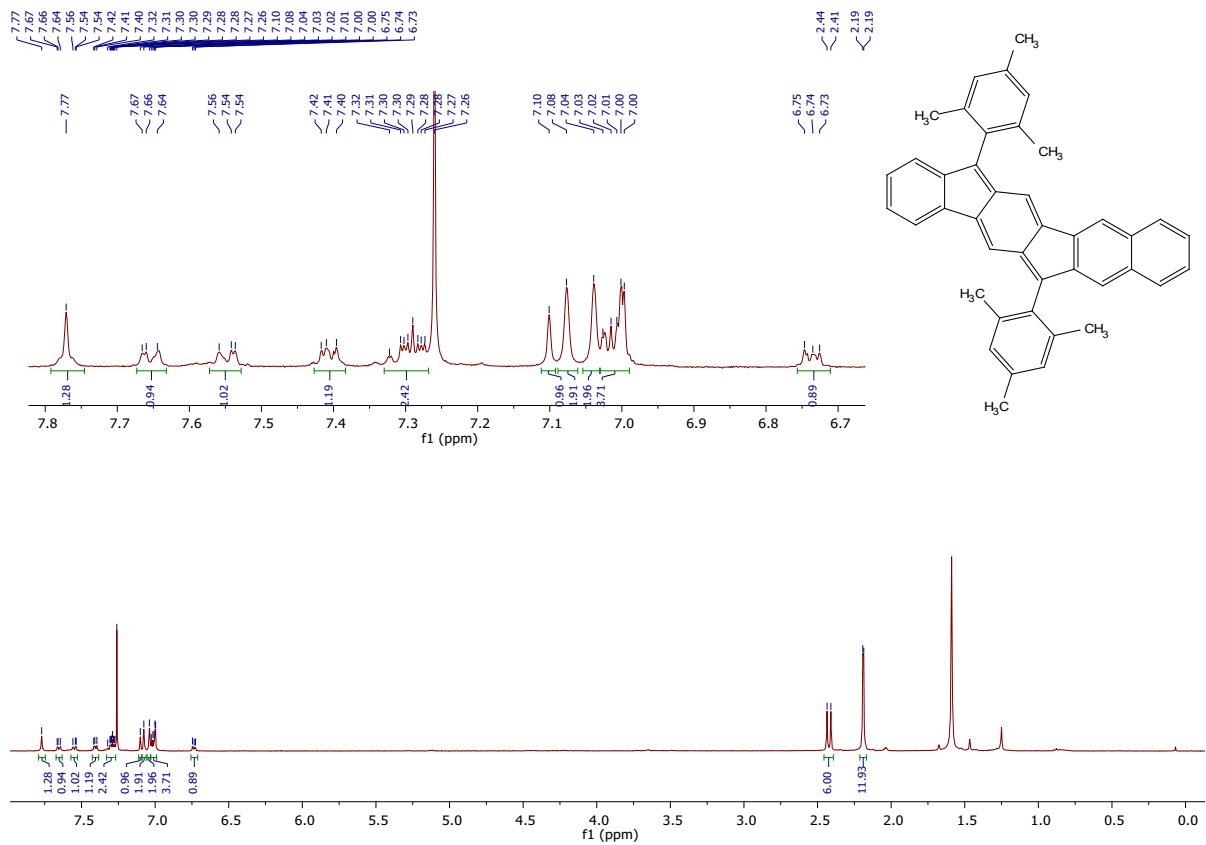


Fig. S16 ¹H NMR spectrum of **2** (in CDCl₃, 400 MHz).

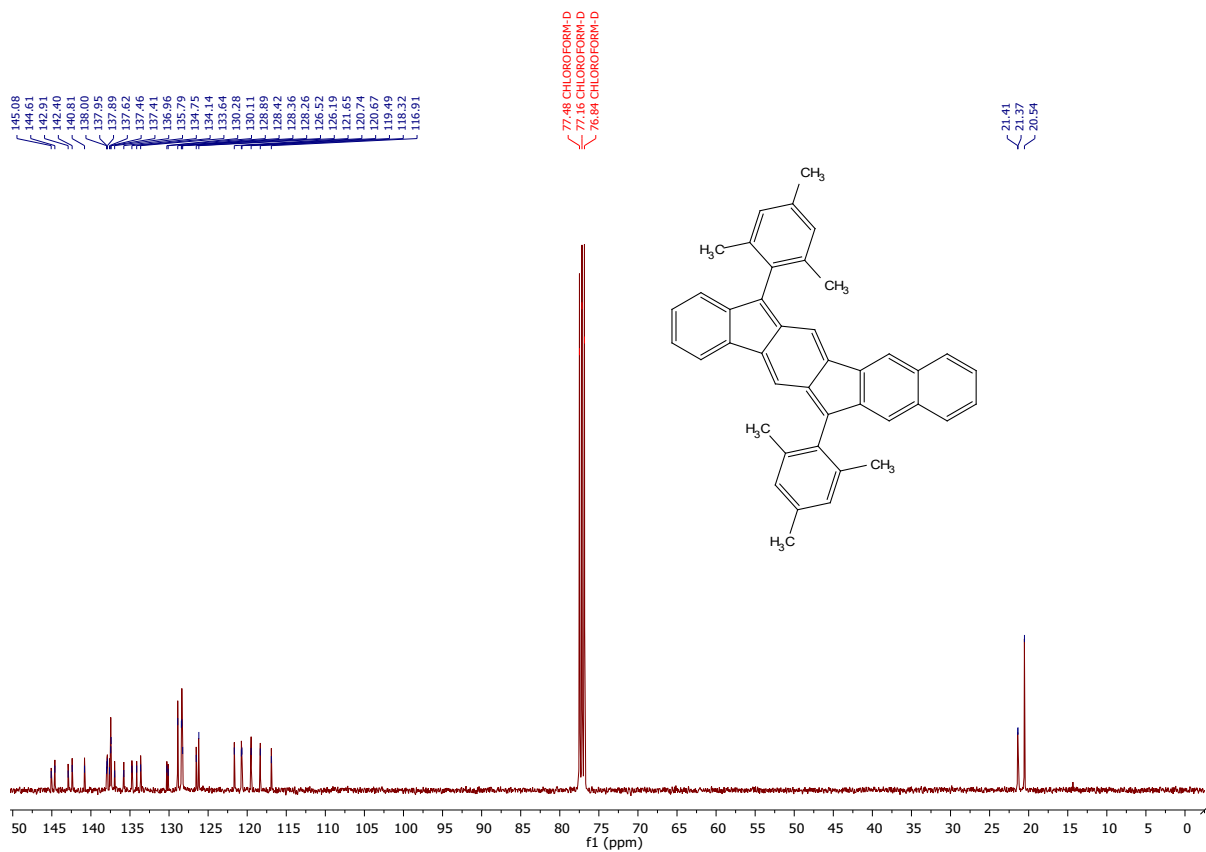


Fig. S17 ^{13}C NMR spectrum of **2** (in CDCl_3 , 100 MHz).

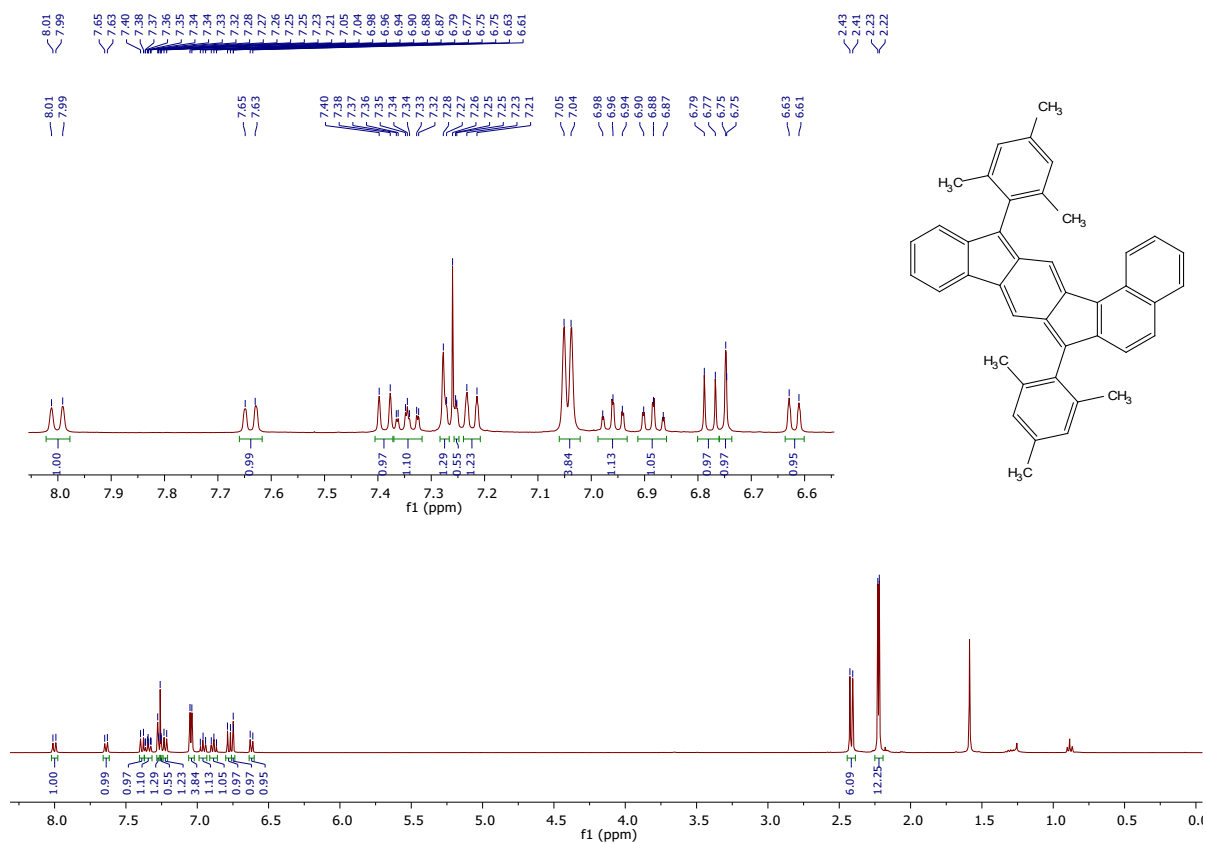
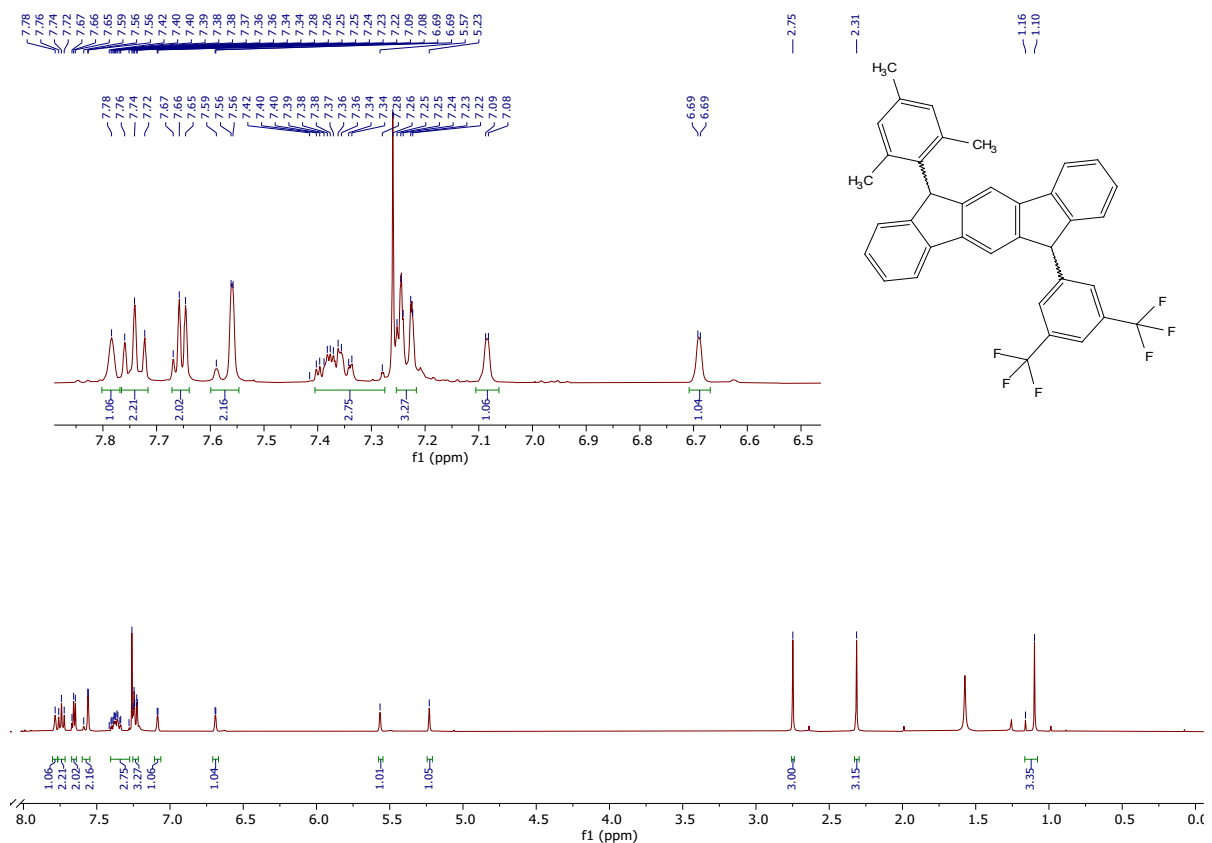
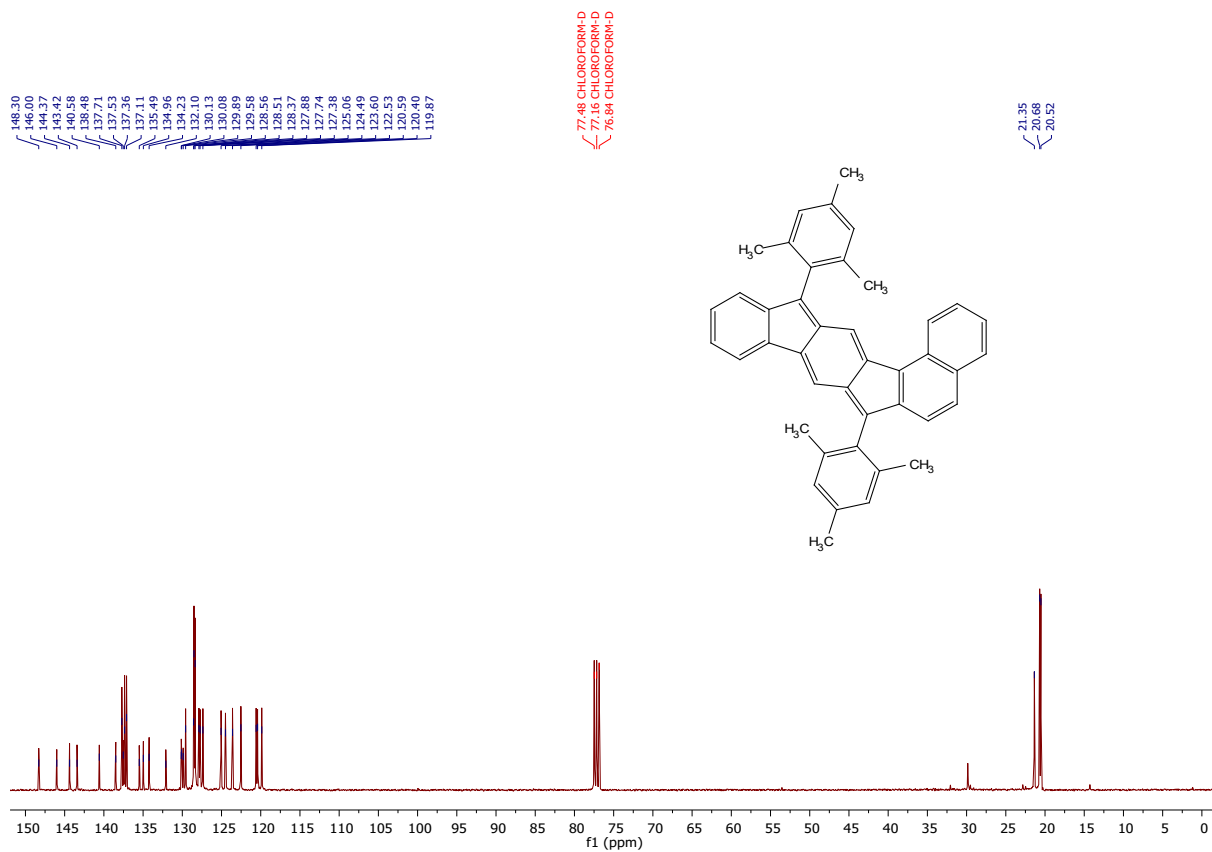


Fig. S18 ^1H NMR spectrum of **3** (in CDCl_3 , 400 MHz).



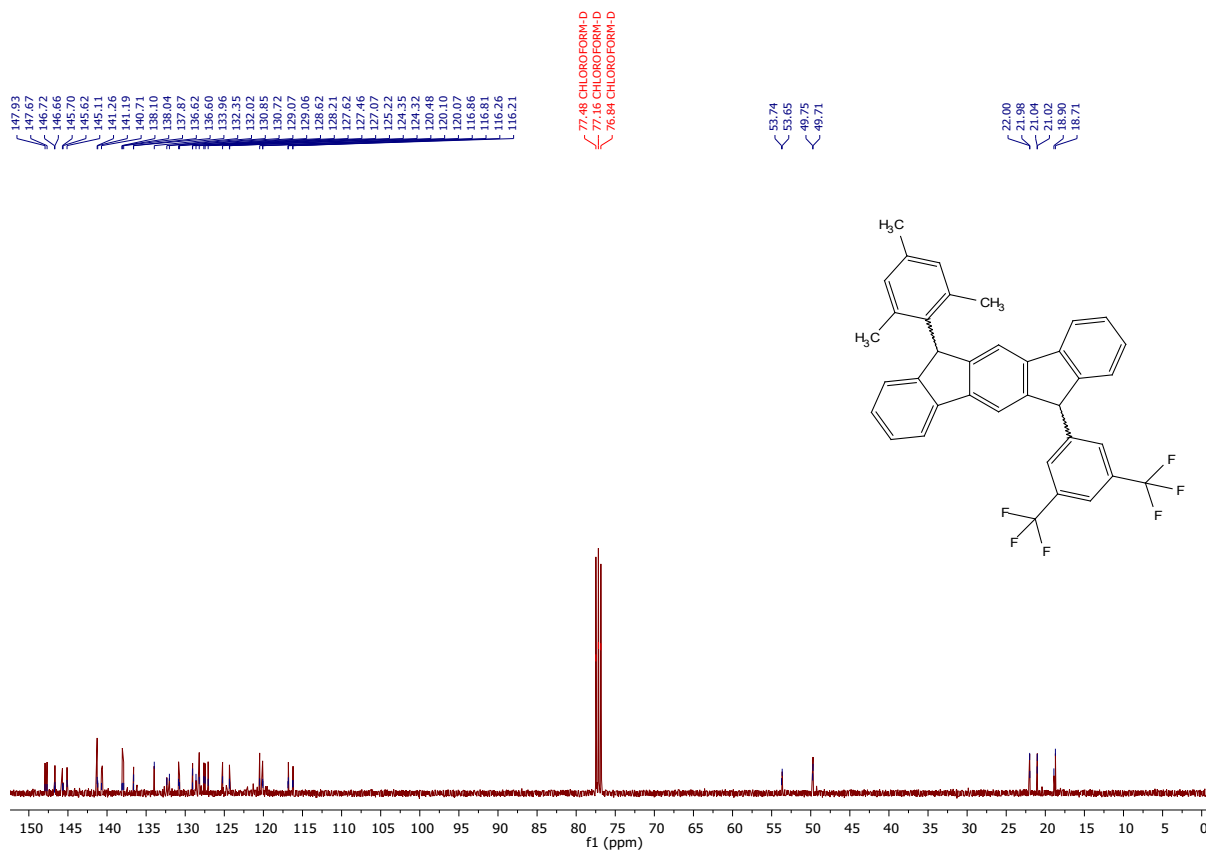


Fig. S21 ¹³C NMR spectrum of **23** (in CDCl₃, 100 MHz).

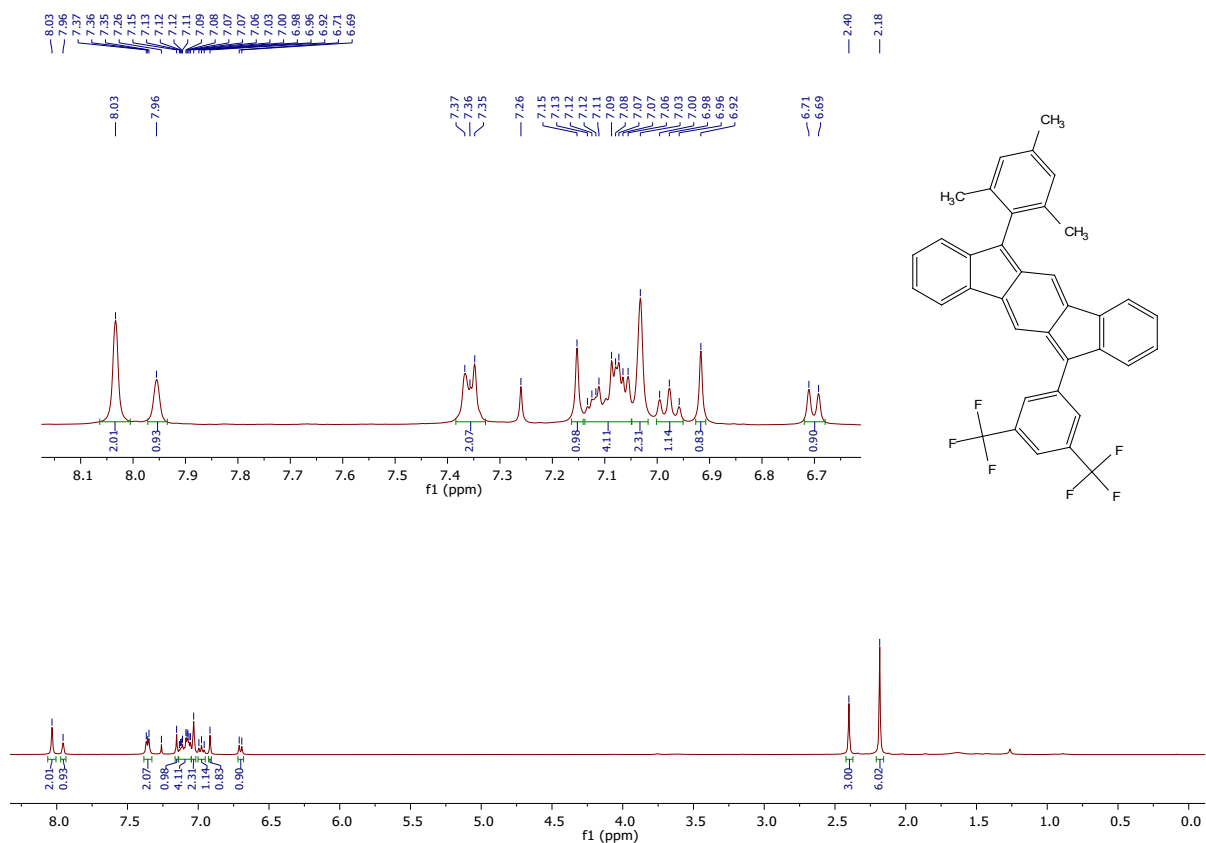


Fig. S22 ¹H NMR spectrum of **4** (in CDCl₃, 400 MHz).

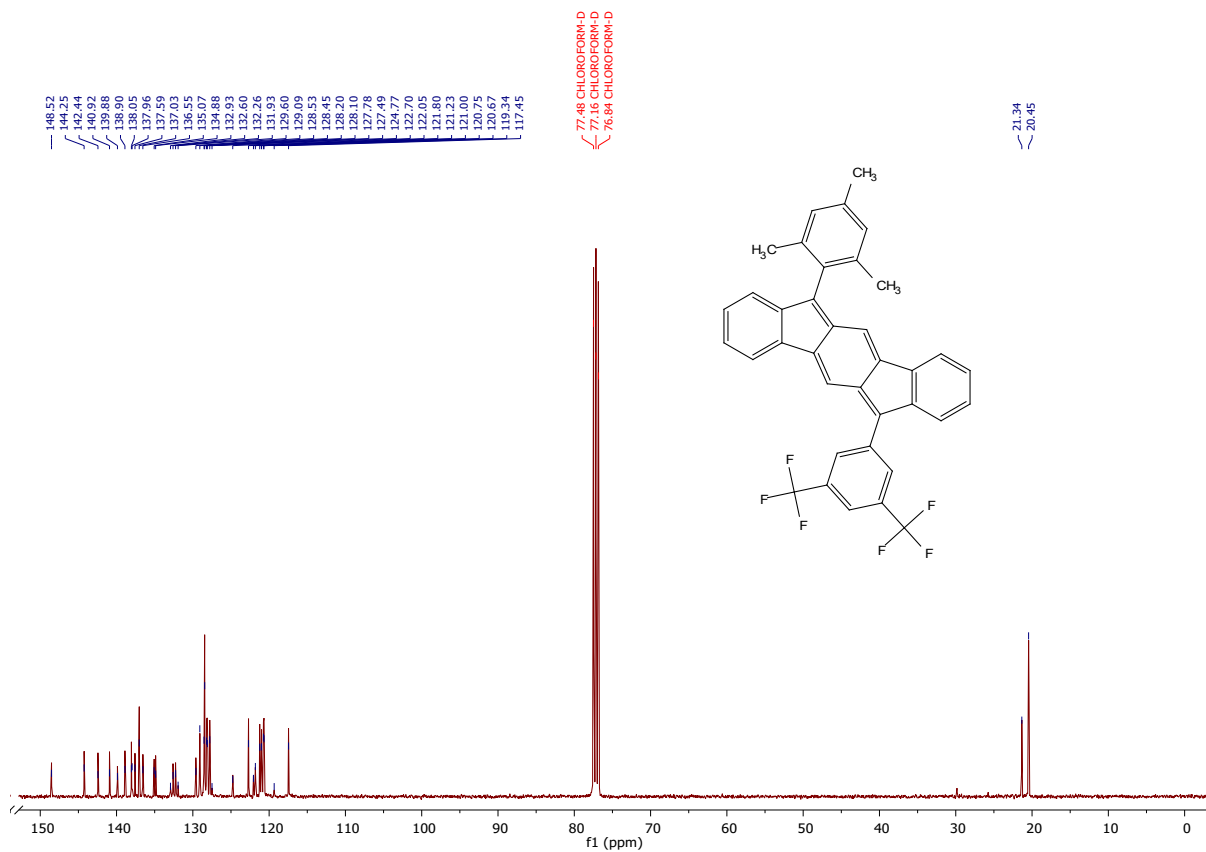


Fig. S23 ¹H NMR spectrum of 4 (in CDCl₃, 100 MHz).

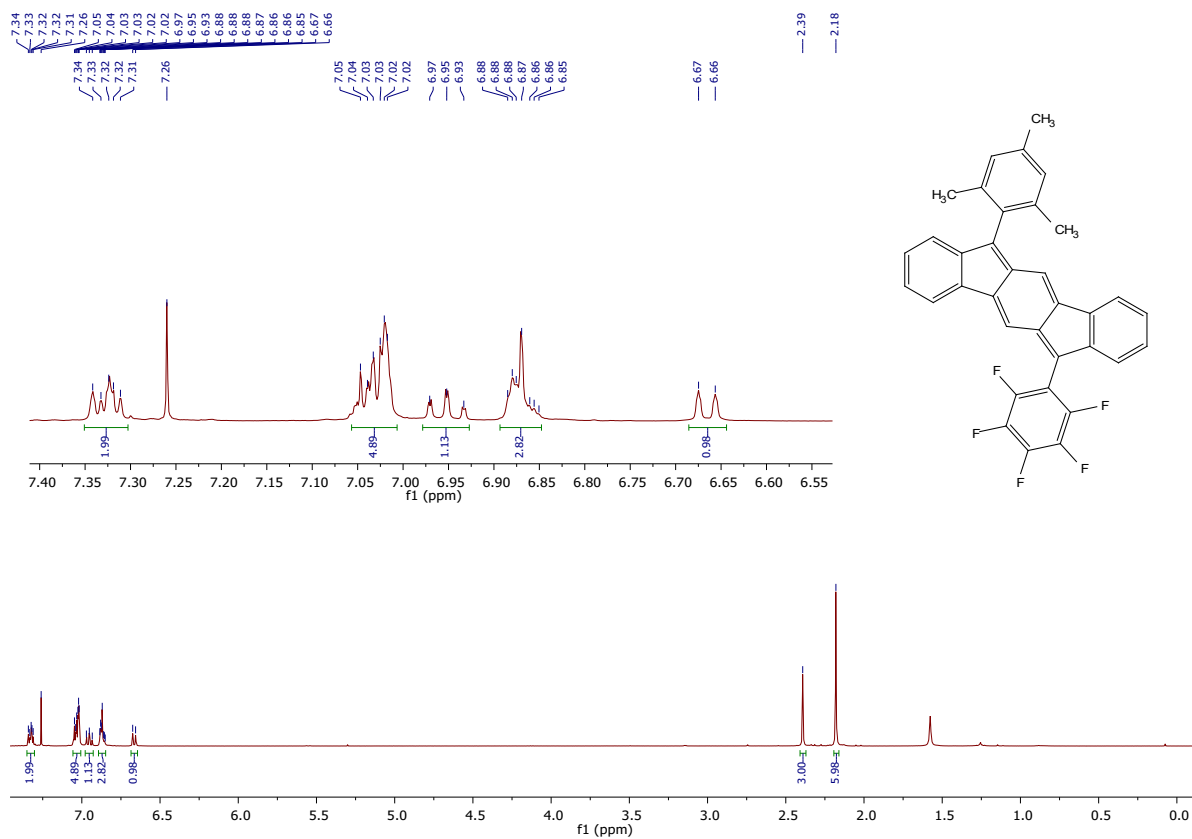


Figure S24 ¹H NMR spectrum of 5 (in CDCl₃, 400 MHz).

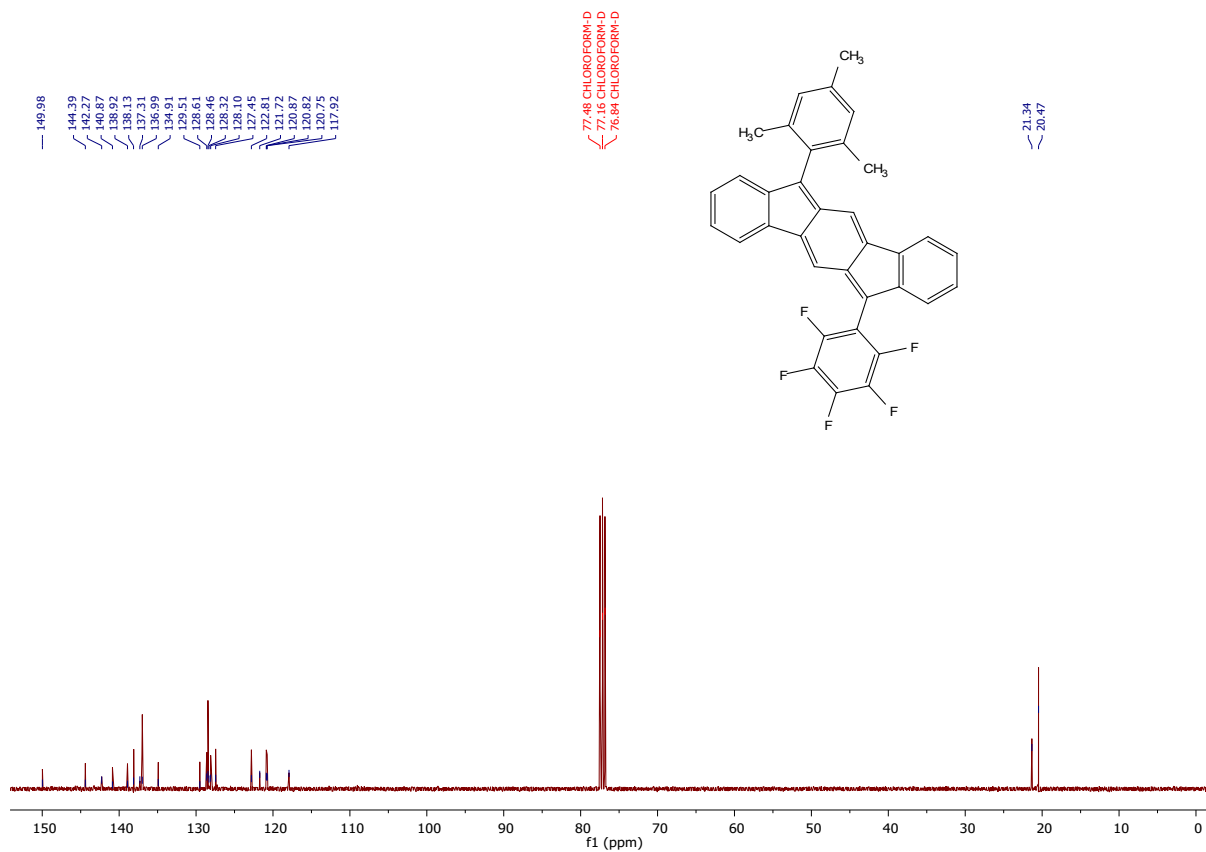


Fig. S25 ^{13}C NMR spectrum of **5** (in CDCl_3 , 100 MHz).

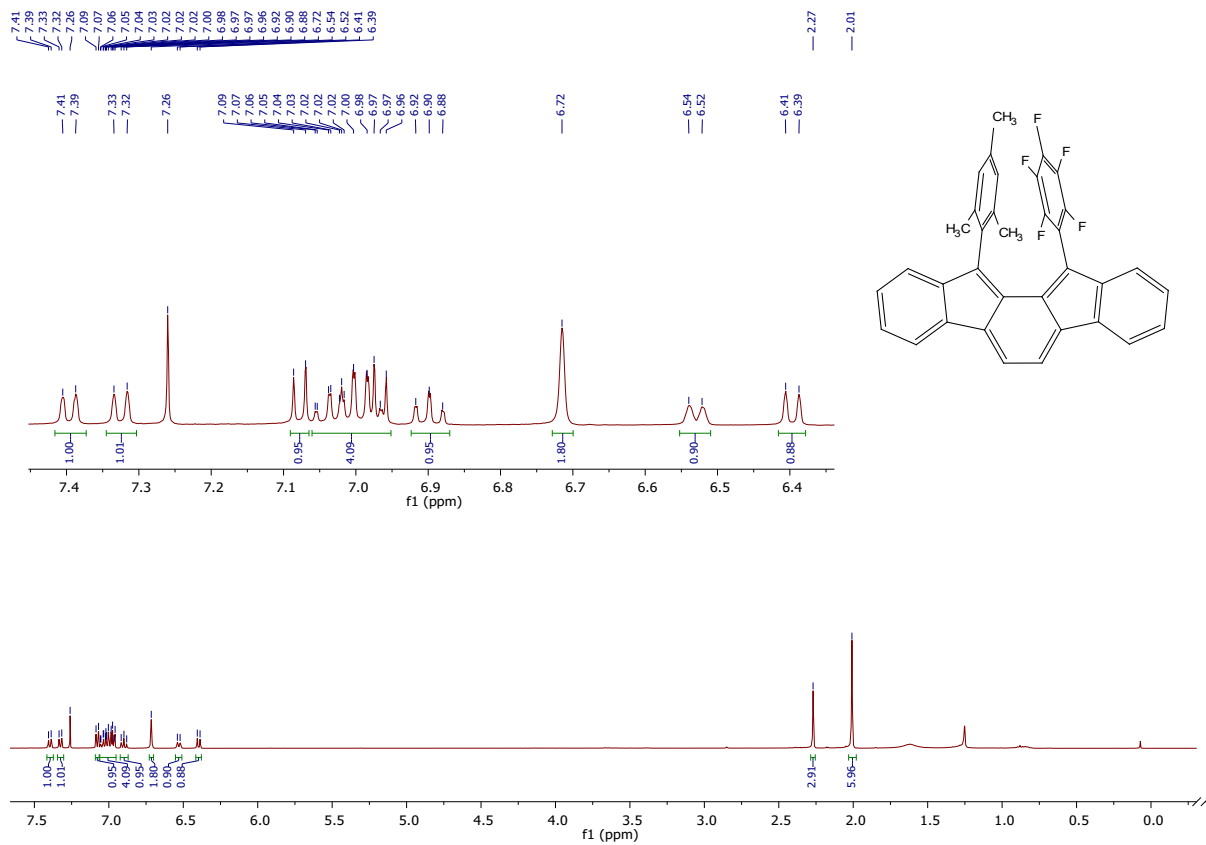


Fig. S26 ^1H NMR spectrum of **6** (in CDCl_3 , 400 MHz).

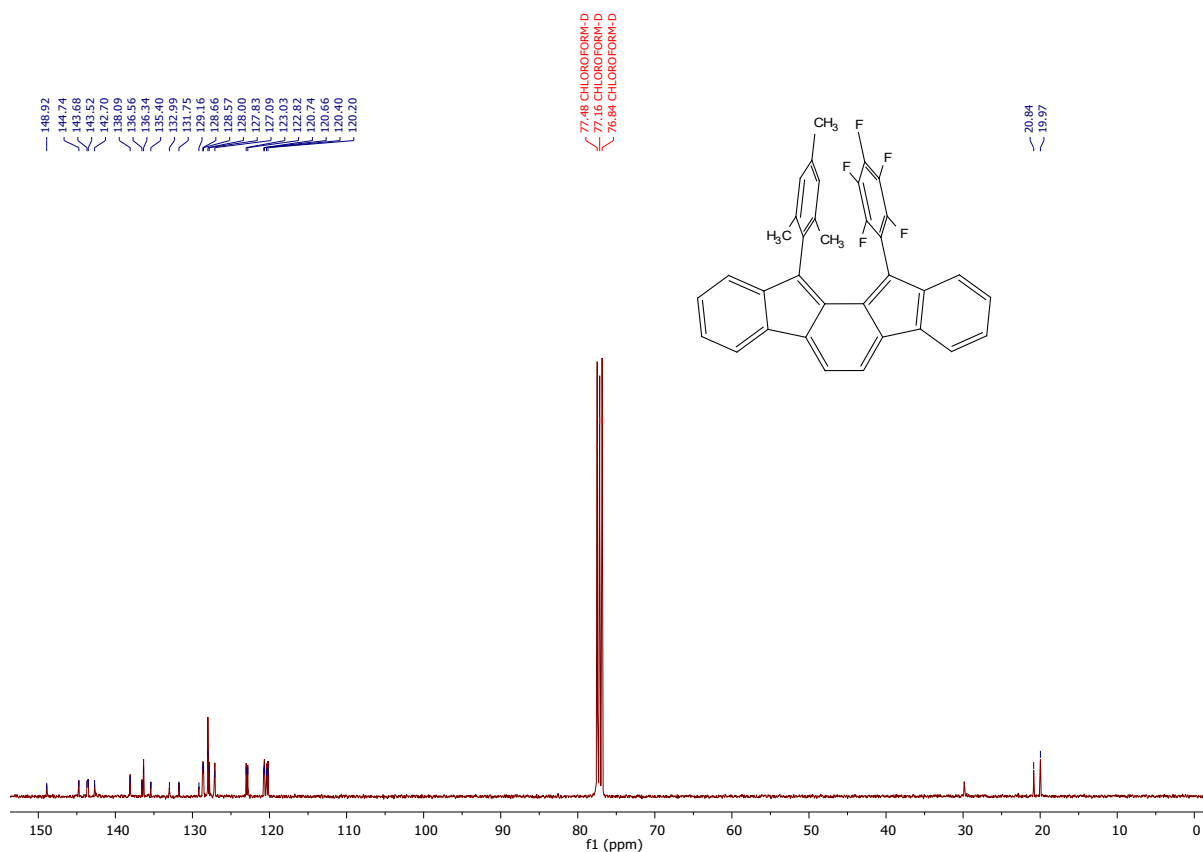


Fig. S27 ¹³C NMR spectrum of **6** (in CDCl₃, 100 MHz).

2. 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).² NICS (standard GIAO method) and HOMA³ indices were calculated for the optimized closed-shell structures for **5** and **6**. The NICS indices were averaged by two positions (above and below the plane) for each molecule. Charge analysis was performed for the singlet closed-shell structures using natural population analysis (NPA) as implemented in G09.

Table S1. Relative energies for the optimized structure **5** at B3LYP/6-31G(d) level.

State	Hartree	kcal/mol
Singlet Closed-Shell	-1845.548217	-1158081.507
Singlet Open-Shell	-1845.548217	-1158081.507
Triplet Open-Shell	-1845.521241	-1158064.579

$$\Delta E_{\text{Triplet-Singlet}} = 16.92 \text{ kcal/mol.}$$

Table S2. Relative energies for the optimized structure **6** at B3LYP/6-31G(d) level.

State	Hartree	kcal/mol
Singlet Closed-Shell	-1845.536124	-1158073.918
Singlet Open-Shell	-1845.536124	-1158073.918
Triplet Open-Shell	-1845.513937	-1158059.996

$$\Delta E_{\text{Triplet-Singlet}} = 13.92 \text{ kcal/mol.}$$

2.1 NPA analyses

Compound 5.

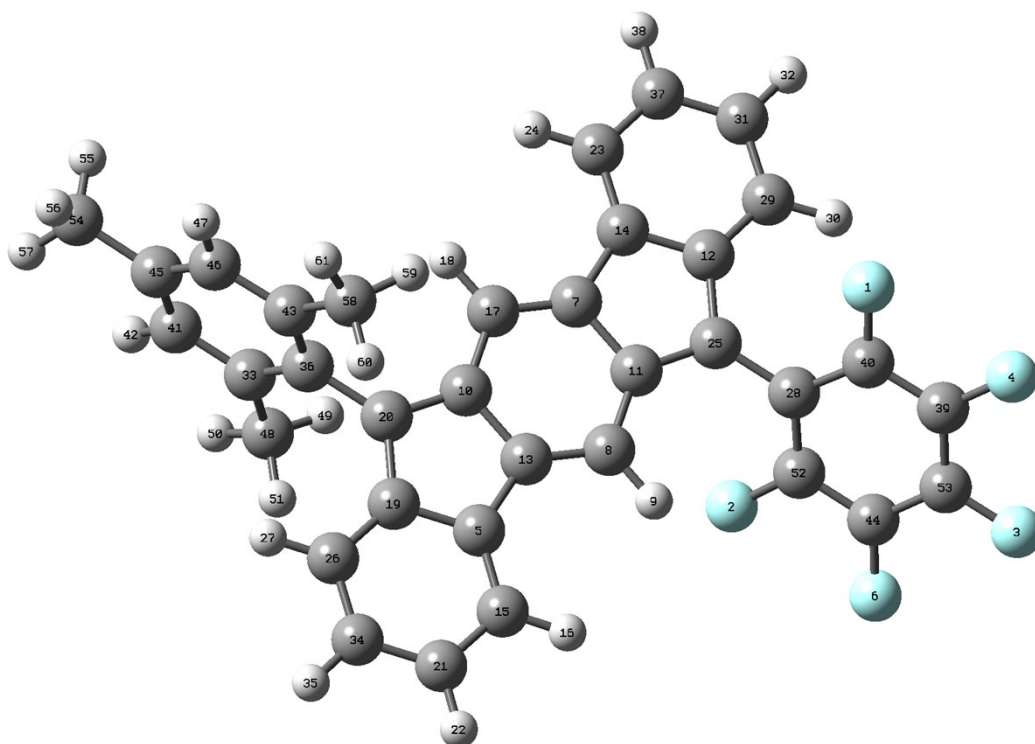


Fig. S28 Optimized closed-shell structure of **5**.

Table S3. Natural Population of **5**

Natural -----						
Atom No	Charge	Core	Valence	Rydberg	Total	
F 1	-0.31041	1.99994	7.30414	0.00633	9.31041	
F 2	-0.31175	1.99994	7.30551	0.00631	9.31175	
F 3	-0.30274	1.99994	7.29588	0.00692	9.30274	
F 4	-0.30653	1.99994	7.29977	0.00681	9.30653	
C 5	-0.03283	1.99899	4.01919	0.01465	6.03283	
F 6	-0.30687	1.99994	7.30012	0.00681	9.30687	
C 7	-0.04327	1.99903	4.02911	0.01513	6.04327	
C 8	-0.15425	1.99895	4.14275	0.01255	6.15425	
H 9	0.24112	0.00000	0.75756	0.00133	0.75888	
C 10	-0.06845	1.99894	4.05473	0.01478	6.06845	
C 11	-0.03858	1.99898	4.02465	0.01496	6.03858	

C	12	-0.04368	1.99899	4.02978	0.01491	6.04368
C	13	-0.03369	1.99903	4.01947	0.01519	6.03369
C	14	-0.03651	1.99899	4.02296	0.01456	6.03651
C	15	-0.20847	1.99902	4.19697	0.01248	6.20847
H	16	0.23726	0.00000	0.76179	0.00095	0.76274
C	17	-0.14709	1.99895	4.13640	0.01175	6.14709
H	18	0.24629	0.00000	0.75261	0.00110	0.75371
C	19	-0.05615	1.99898	4.04240	0.01478	6.05615
C	20	0.05022	1.99897	3.93319	0.01763	5.94978
C	21	-0.22647	1.99912	4.21360	0.01374	6.22647
H	22	0.23808	0.00000	0.76115	0.00077	0.76192
C	23	-0.20909	1.99902	4.19761	0.01247	6.20909
H	24	0.23627	0.00000	0.76279	0.00094	0.76373
C	25	-0.00760	1.99894	3.98977	0.01890	6.00760
C	26	-0.21022	1.99902	4.19851	0.01269	6.21022
H	27	0.24472	0.00000	0.75425	0.00103	0.75528
C	28	-0.17298	1.99886	4.15932	0.01480	6.17298
C	29	-0.20930	1.99902	4.19696	0.01331	6.20930
H	30	0.23821	0.00000	0.76058	0.00121	0.76179
C	31	-0.23393	1.99912	4.22103	0.01379	6.23393
H	32	0.23802	0.00000	0.76121	0.00077	0.76198
C	33	0.00373	1.99898	3.98351	0.01378	5.99627
C	34	-0.23567	1.99912	4.22271	0.01384	6.23567
H	35	0.23851	0.00000	0.76072	0.00077	0.76149
C	36	-0.08043	1.99889	4.06718	0.01436	6.08043
C	37	-0.23015	1.99912	4.21726	0.01377	6.23015
H	38	0.23727	0.00000	0.76196	0.00077	0.76273
C	39	0.29721	1.99837	3.67672	0.02770	5.70279
C	40	0.38044	1.99840	3.59432	0.02685	5.61956
C	41	-0.23231	1.99896	4.22165	0.01170	6.23231
H	42	0.22994	0.00000	0.76889	0.00117	0.77006
C	43	0.00291	1.99897	3.98432	0.01379	5.99709
C	44	0.29667	1.99837	3.67728	0.02768	5.70333
C	45	-0.01743	1.99902	4.00417	0.01424	6.01743
C	46	-0.23225	1.99896	4.22161	0.01169	6.23225
H	47	0.22989	0.00000	0.76894	0.00117	0.77011
C	48	-0.69126	1.99939	4.68473	0.00714	6.69126
H	49	0.24803	0.00000	0.75102	0.00095	0.75197
H	50	0.23685	0.00000	0.76236	0.00079	0.76315
H	51	0.24802	0.00000	0.75095	0.00103	0.75198
C	52	0.37873	1.99840	3.59601	0.02686	5.62127
C	53	0.31526	1.99841	3.65873	0.02759	5.68474
C	54	-0.68696	1.99939	4.68027	0.00730	6.68696
H	55	0.24447	0.00000	0.75458	0.00095	0.75553
H	56	0.23922	0.00000	0.75991	0.00088	0.76078
H	57	0.23872	0.00000	0.76041	0.00087	0.76128
C	58	-0.69044	1.99939	4.68388	0.00716	6.69044
H	59	0.24718	0.00000	0.75184	0.00097	0.75282
H	60	0.24765	0.00000	0.75139	0.00097	0.75235
H	61	0.23690	0.00000	0.76230	0.00080	0.76310

* Total * 0.00000 79.96274 195.44537 0.59190 276.00000

Compound 6.

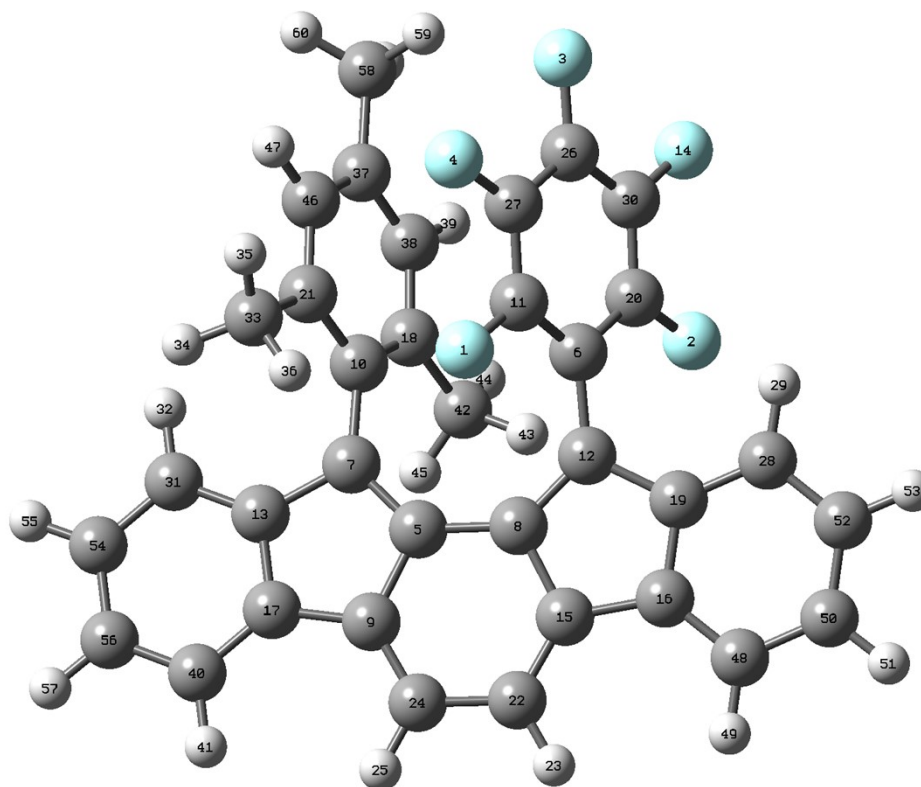


Fig. S29 Optimized closed-shell structure of **6**.

Table S4. Natural Population of **6**

Natural -----						
Atom No	Charge	Core	Valence	Rydberg	Total	
F 1	-0.31228	1.99993	7.30605	0.00630	9.31228	
F 2	-0.31343	1.99994	7.30723	0.00626	9.31343	
F 3	-0.30764	1.99994	7.30091	0.00679	9.30764	
F 4	-0.30823	1.99994	7.30151	0.00678	9.30823	
C 5	-0.05530	1.99894	4.04137	0.01499	6.05530	
C 6	-0.17014	1.99885	4.15580	0.01549	6.17014	
C 7	0.04877	1.99899	3.93578	0.01646	5.95123	
C 8	-0.02592	1.99896	4.01200	0.01495	6.02592	
C 9	-0.00667	1.99903	3.99290	0.01474	6.00667	
C 10	-0.08224	1.99889	4.06835	0.01500	6.08224	
C 11	0.39444	1.99836	3.57963	0.02757	5.60556	
C 12	-0.01019	1.99896	3.99250	0.01874	6.01019	
C 13	-0.04716	1.99897	4.03350	0.01468	6.04716	
F 14	-0.30912	1.99994	7.30246	0.00672	9.30912	
C 15	-0.01369	1.99903	3.99998	0.01468	6.01369	
C 16	-0.04836	1.99898	4.03466	0.01472	6.04836	
C 17	-0.04445	1.99897	4.03063	0.01485	6.04445	
C 18	0.00717	1.99897	3.97964	0.01422	5.99283	
C 19	-0.03865	1.99898	4.02486	0.01481	6.03865	
C 20	0.37696	1.99838	3.59744	0.02722	5.62304	
C 21	-0.00344	1.99899	3.98948	0.01497	6.00344	
C 22	-0.18067	1.99899	4.16882	0.01286	6.18067	

H 23	0.24001	0.00000	0.75910	0.00090	0.75999
C 24	-0.19142	1.99899	4.17952	0.01291	6.19142
H 25	0.23976	0.00000	0.75934	0.00090	0.76024
C 26	0.31688	1.99840	3.65712	0.02760	5.68312
C 27	0.30460	1.99834	3.66895	0.02811	5.69540
C 28	-0.21214	1.99902	4.19975	0.01337	6.21214
H 29	0.23779	0.00000	0.76112	0.00109	0.76221
C 30	0.29917	1.99835	3.67466	0.02783	5.70083
C 31	-0.21340	1.99902	4.20136	0.01302	6.21340
H 32	0.24544	0.00000	0.75360	0.00096	0.75456
C 33	-0.69252	1.99938	4.68509	0.00806	6.69252
H 34	0.24453	0.00000	0.75434	0.00113	0.75547
H 35	0.24023	0.00000	0.75877	0.00099	0.75977
H 36	0.25152	0.00000	0.74719	0.00128	0.74848
C 37	-0.01769	1.99902	4.00406	0.01461	6.01769
C 38	-0.23630	1.99895	4.22542	0.01193	6.23630
H 39	0.23235	0.00000	0.76648	0.00117	0.76765
C 40	-0.20530	1.99902	4.19386	0.01242	6.20530
H 41	0.23481	0.00000	0.76423	0.00096	0.76519
C 42	-0.69013	1.99938	4.68325	0.00749	6.69013
H 43	0.24754	0.00000	0.75068	0.00178	0.75246
H 44	0.23779	0.00000	0.76139	0.00082	0.76221
H 45	0.24760	0.00000	0.75150	0.00090	0.75240
C 46	-0.23581	1.99895	4.22436	0.01250	6.23581
H 47	0.23369	0.00000	0.76511	0.00120	0.76631
C 48	-0.20385	1.99902	4.19241	0.01241	6.20385
H 49	0.23424	0.00000	0.76480	0.00096	0.76576
C 50	-0.23511	1.99912	4.22219	0.01380	6.23511
H 51	0.23733	0.00000	0.76190	0.00077	0.76267
C 52	-0.22959	1.99912	4.21668	0.01380	6.22959
H 53	0.23801	0.00000	0.76122	0.00077	0.76199
C 54	-0.23226	1.99911	4.21932	0.01382	6.23226
H 55	0.23822	0.00000	0.76100	0.00077	0.76178
C 56	-0.23080	1.99912	4.21789	0.01379	6.23080
H 57	0.23755	0.00000	0.76168	0.00077	0.76245
C 58	-0.68912	1.99938	4.68222	0.00752	6.68912
H 59	0.24785	0.00000	0.75026	0.00188	0.75215
H 60	0.24003	0.00000	0.75908	0.00088	0.75997
H 61	0.23876	0.00000	0.76038	0.00085	0.76124

* Total * 0.00000 79.96262 195.43682 0.60056 276.00000

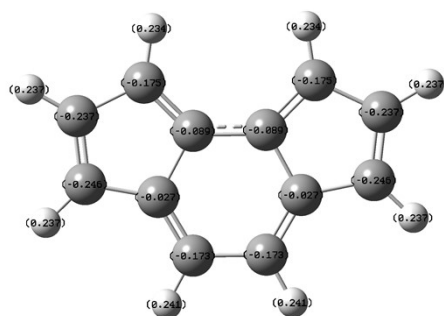
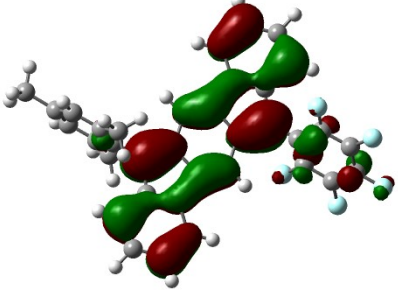
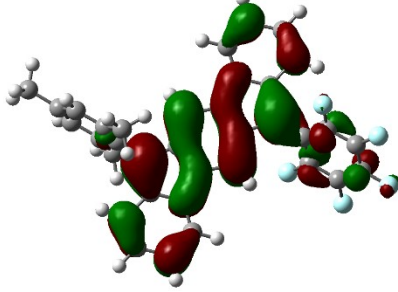
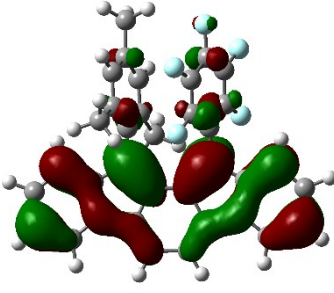
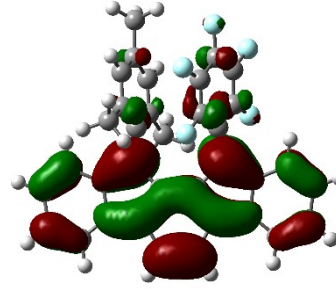


Fig. S30 NPA charges of parent *as*-Indacene

2.2 Frontier molecular orbital profiles

Table S5.

Compd.	HOMO (eV)	LUMO (eV)	E_g^{DFT}
5	 -5.24	 -2.91	2.33 eV
6	 -5.22	 -3.00	2.22 eV

2.3 TDDFT calculations in gas-phase

Table S6. Summary of TDDFT calculations of compound 5.

Wavelength (nm)	Osc. Strength (<i>f</i>)	Major contribution
642.8337	0.0002	H-1->LUMO (100%)
538.3792	0.5377	HOMO->LUMO (95%)
439.6572	0.0038	H-2->LUMO (99%)
414.2997	0.0008	H-3->LUMO (100%)
368.4169	0.0292	H-5->LUMO (22%), H-4->LUMO (74%)
362.9808	0.0096	H-5->LUMO (62%), H-4->LUMO (16%), HOMO->L+1 (17%)
356.3456	0.0023	H-5->LUMO (10%), HOMO->L+1 (78%)
351.1381	0.0019	H-6->LUMO (95%)
338.2901	0.0928	H-7->LUMO (89%)
312.8522	0.3305	H-1->L+1 (18%), HOMO->L+2 (74%)
294.7072	0.3767	H-8->LUMO (53%), H-1->L+1 (29%)
292.4825	0.019	HOMO->L+3 (93%)
286.8988	0.0097	H-1->L+2 (94%)
284.9406	0.9618	H-8->LUMO (32%), H-1->L+1 (40%), HOMO->L+2 (12%)
277.1259	0.0291	HOMO->L+4 (95%)
272.5208	0.04	H-9->LUMO (92%)

266.3502	0.0008	H-1->L+3 (97%)
263.7831	0.0004	HOMO->L+5 (35%), HOMO->L+6 (36%)
261.9053	0.0076	H-2->L+1 (83%), HOMO->L+5 (14%)
261.6731	0.0233	HOMO->L+5 (39%), HOMO->L+6 (44%)

Table S7. Summary of TDDFT calculations of compound **6**.

<i>Wavelength (nm)</i>	<i>Osc. Strength (f)</i>	<i>Major contribution</i>
708.9673	0.0369	H-1->LUMO (43%), HOMO->LUMO (57%)
558.739	0.2859	H-1->LUMO (56%), HOMO->LUMO (43%)
472.9153	0.049	H-2->LUMO (98%)
449.9517	0.0043	H-3->LUMO (99%)
413.515	0.0095	H-4->LUMO (97%)
373.4576	0.0002	H-6->LUMO (40%), H-5->LUMO (59%)
365.541	0.0007	H-6->LUMO (55%), H-5->LUMO (34%)
356.3481	0.0142	H-7->LUMO (90%)
329.281	0.1207	HOMO->L+1 (89%)
313.511	0.1094	HOMO->L+2 (85%)
310.038	0.021	H-8->LUMO (92%)
295.7779	0.0055	HOMO->L+3 (96%)
285.1129	0.2439	H-1->L+1 (60%), H-1->L+2 (10%), HOMO->L+4 (16%)
284.0742	0.037	H-1->L+2 (15%), HOMO->L+4 (72%)
278.1037	0.3915	H-1->L+1 (11%), H-1->L+2 (60%), HOMO->L+5 (11%)
268.847	0.1307	H-9->LUMO (12%), HOMO->L+5 (66%)
266.1519	0.1391	H-9->LUMO (24%), H-1->L+4 (21%), HOMO->L+5 (14%), HOMO->L+6 (24%)
262.3393	0.0206	H-2->L+1 (13%), HOMO->L+6 (28%), HOMO->L+7 (38%)
260.2468	0.0402	H-2->L+1 (65%)
259.8541	0.0029	H-1->L+3 (89%)

3. Electrochemistry

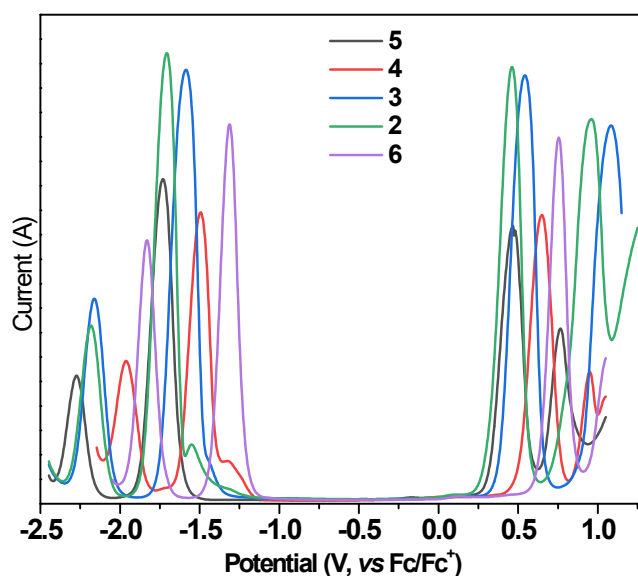


Fig. S31 Differential pulse voltammogram of **2-6** in CH_2Cl_2 .

4. X-ray crystallographic analyses

Suitable single crystal of **5** and **6** 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 $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) 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. 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.⁴ By utilizing OLex2,⁵ the crystal structure was solved with the help of olex2.solve⁶ structure solution program by employing intrinsic Phasing methods and crystal structure refinement was done with the SHELXL⁷ refinement package by putting into use Least Squares minimization. Refinement of all non-hydrogen atoms was completed with the help of anisotropic thermal parameters.

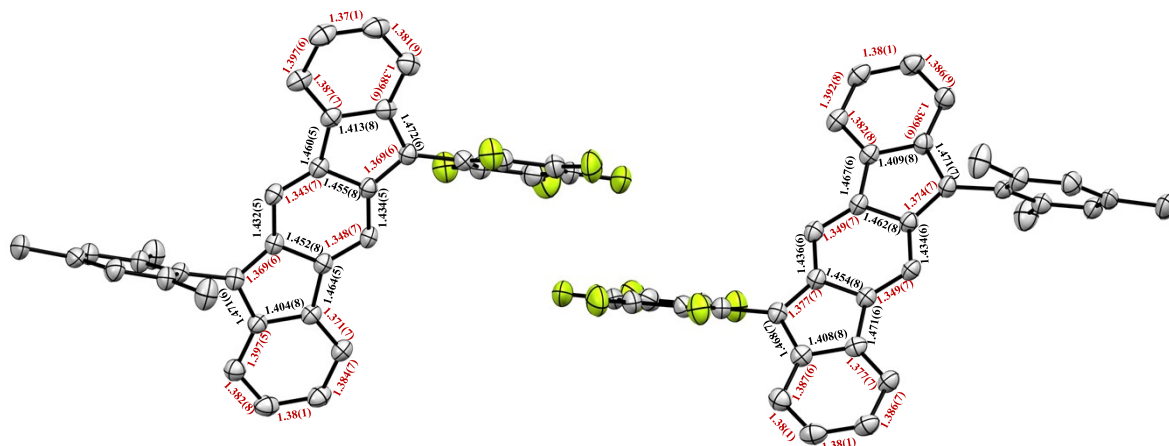


Fig. S32 ORTEP drawing of **5** with thermal ellipsoids at 30% probability level, showing the bond lengths with e.s.d values for the two crystallographically independent molecules.

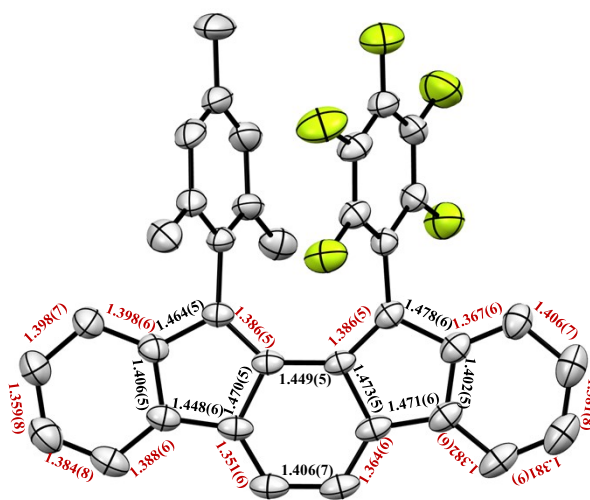


Fig. S33 ORTEP drawing of **6** showing with thermal ellipsoids at 30% probability level showing the bond lengths with e.s.d values.

Tables S8.

Compounds	5	6
CCDC numbers	2205894	2205895
Solvents, and conditions for recrystallization	Ethyl acetate/hexane, by evaporation at rt in dark	Acetonitrile/hexane, by evaporation at rt in dark
Empirical formula	C ₃₅ H ₂₁ F ₅	C ₃₅ H ₂₁ F ₅
Formula weight	536.52	536.52
Temperature/K	298.00	298
Crystal system	triclinic	Monoclinic
Space group	P-1	C2/c
a/Å	13.8434(14)	26.325(3)
b/Å	14.8766(13)	8.0202(10)

$c/\text{\AA}$	16.0001(16)	24.777(3)
$\alpha/^\circ$	117.393(3)	90
$\beta/^\circ$	111.710(3)	97.845(4)
$\gamma/^\circ$	93.822(3)	90
Volume/ \AA^3	2603.7(4)	5182.3(11)
Z	4	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.369	1.375
μ/mm^{-1}	0.103	0.104
F(000)	1104.0	2208.0
Crystal size/ mm^3	$0.256 \times 0.236 \times 0.198$	$0.236 \times 0.154 \times 0.059$
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.93 to 51.536	4.858 to 54.298
Index ranges	$-16 \leq h \leq 15, -18 \leq k \leq 16, 0 \leq l \leq 19$	$-33 \leq h \leq 33, -10 \leq k \leq 10, -31 \leq l \leq 31$
Reflections collected	9906	61587
Data/restraints/parameters	9906/0/729	5586/0/365
Goodness-of-fit on F^2	1.033	1.023
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0619, wR_2 = 0.1600$	$R_1 = 0.0827, wR_2 = 0.2053$
Final R indexes [all data]	$R_1 = 0.1234, wR_2 = 0.2111$	$R_1 = 0.1696, wR_2 = 0.2682$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.34/-0.24	0.60/-0.25

Crystal packing.

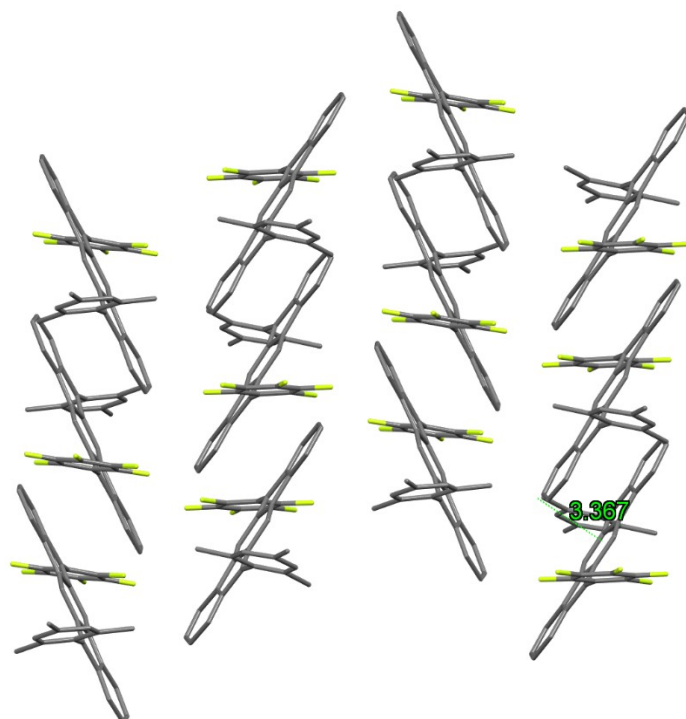


Fig. S34 Herringbone packing arrangement for **5** with two IF molecules cofacially stacked at an interplanar distance of 3.367 Å, implying strong π - π interaction.

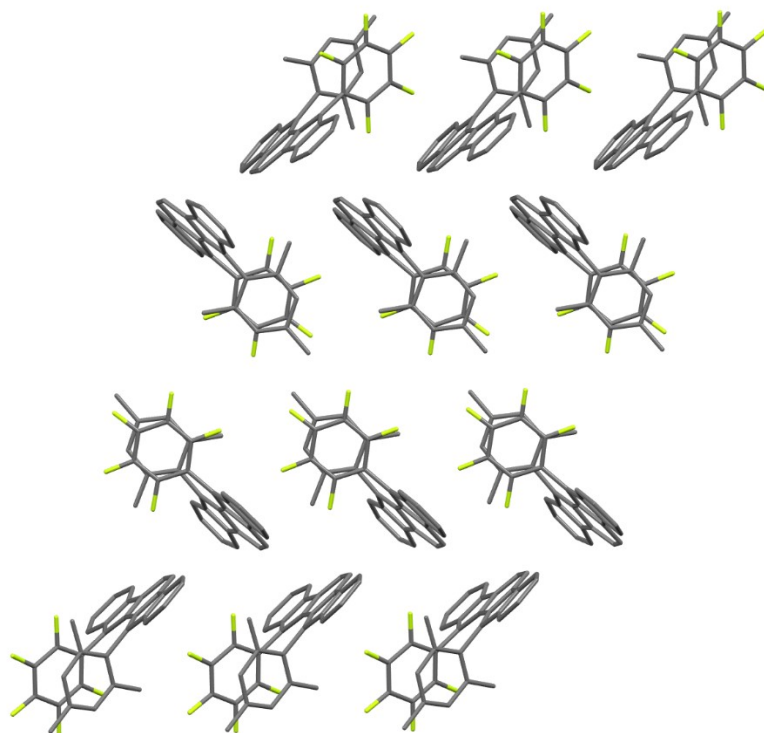


Fig. S35 Herringbone packing arrangement for **6** with two IF molecules forming T-shaped interaction in one-dimensional stack.

5. Appendix

Table S9. Summary of photophysical and electrochemical data for **2-6**.

IF	$E_{1/2}^{ox}$ [V]	$E_{1/2}^{red}$ [V]	$E_{1/2}^{ox}$ [V]	$E_{1/2}^{red}$ [V]	HOMO [eV]	LUMO [eV]	E_g^{calc} [eV]	λ_{abs}^{max} [nm]	ϵ [M ⁻¹ cm ⁻¹]	E_g^{exp} [eV]
1⁸	-1.56	-2.07	0.71	-	-5.41	-3.32	2.09	515	42640	2.21
2	-1.70	-2.18	0.46	0.95	-5.16	-3.22	1.94	529, 493, 334	27990, 21200, 60980	2.19
3	-1.58	-2.16	0.54	1.08	-5.23	-3.34	1.89	545, 511, 342	17770, 13750, 33080	2.16
4	-1.49	-1.96	0.65	0.95	-5.34	-3.5	1.84	531, 501	18380, 14640	2.17
5	-1.73	-2.27	0.47	0.76	-5.2	-3.22	1.98	527, 502	22940, 20590	2.19
6	-1.31	-1.83	0.75	-	-5.45	-3.63	1.82	537, 320 293	11100, 11540, 26990	1.55

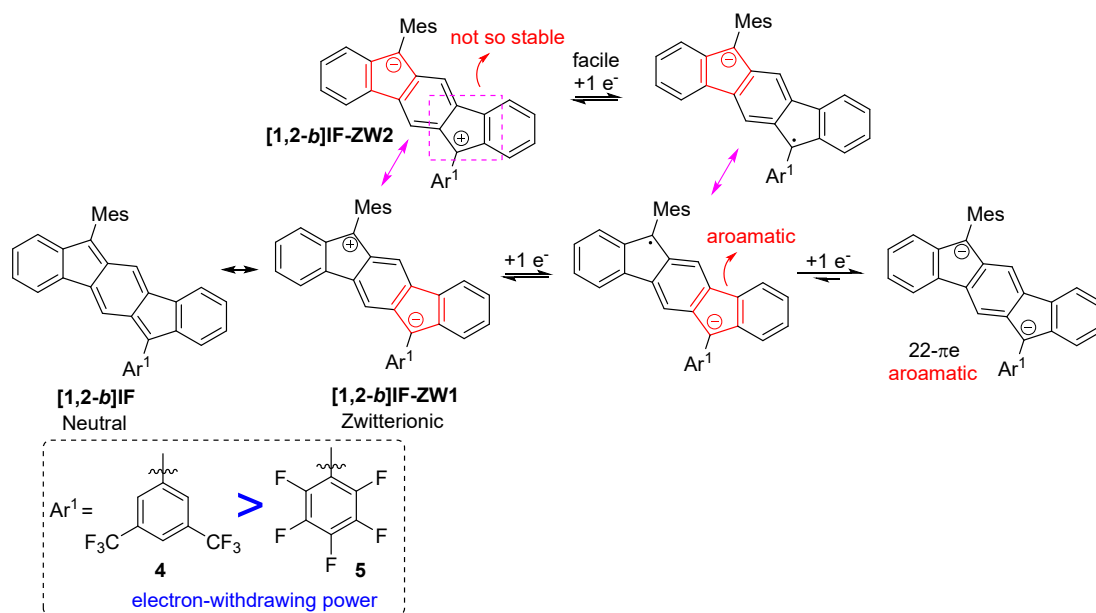


Fig. S36 Supporting figure that may explain the electron-withdrawing effect on **4** vs **5**. Stronger the electron-withdrawing ability of the apical substituent, easier is the one-electron reduction considering [1,2-*b*]IF-ZW2 substructure (Electron-donating power of mesityl group is not so strong).⁹

6. References

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