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Supporting Information

for

Introducing Indole Fused Heterocycles as Novel Donor Units in Dye-Sensitized Solar Cells

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Experimental Section

General Methods

All the chemicals and solvents used in this study were of the highest commercially available quality and were employed without further refinement. Gravity column chromatography was performed using silica, and mixtures of hexane-ethyl acetate were used for elution. The melting points were determined using a Buchi melting point apparatus and were uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AMX 500 spectrophotometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C{1H} NMR) at 300 K unless otherwise specified. Chemical shifts δ are given in parts per million (ppm) and referenced to the external standard TMS or internal solvent standard. ^{1}H NMR coupling constants (J) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublets). Mass spectra were recorded under ESI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. To investigate the electrochemical properties of these dyes, cyclic voltammetry (CV) was carried out using an electrochemical workstation (model: HI6211B, M/s. Shanghai Chen Hua Co. Ltd., China) with 0.1 M of Bu4NPF6 as a supporting electrolyte in DCM at a scan rate of 50 mV s−1. The setup included an Ag/AgCl reference electrode, a glassy carbon working electrode, a platinum counter electrode, and ferrocene as the internal standard. The oxidation potentials of the dyes were calculated with respect to ferrocene and were converted to NHE using the equation, EHOMO = [Eox(Fc/Fc+) + 0.63 V]. The lowest unoccupied molecular orbital (LUMO) level (ELUMO) was calculated as the difference EHOMO - E0−0. E0−0 (band gap) was determined from the tangent intercept of absorption edges. The UV-visible absorbance studies were studied in THF using a SCHIMADZU UV-1800 UV-Visible spectrophotometer, using commercially available 1 cm quartz cuvette purchased from Sigma-Aldrich.

Synthesis of 5-bromo-2-(2-nitrophenyl)-1H-indole (3): To a 100 mL Schlenk flask, 5-bromoaniline **1** (2 g, 10.2 mmol), 1-iodo-2-nitrobenzene **2** (3 g, 12.2 mmol), Pd(OAc)$_2$ (114 mg, 5 mol%), K_2CO_3 (2.8 g, 20.2 mmol), and norbornene (1.9 g, 20.2 mmol) were added. The reaction vessel was degassed using a vacuum pump and backfilled with argon. This procedure was repeated three times, followed by the addition of a 0.5 M solution of H_2O in DMA under an argon atmosphere. The reaction mixture was then stirred at 70 °C for 48 h. After completion, the crude reaction mixture was filtered through celite and extracted using ethyl acetate. The organic layer was washed successively with water and brine and then dried over anhydrous Na_2SO_4. The solvent removal was followed by column purification on silica gel to obtain 3 as a red solid (2.2 g, 69%). m.p. 134-136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.78 (d, J = 8 Hz, 1H), 7.70 (s, 1H), 7.62-7.57 (m, 2H), 7.46 (t, J = 7 Hz, 1H), 7.25 (d, J = 9 Hz, 1H), 7.19 (d, J = 4.5 Hz, 1H), 6.57 (s, 1H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 149.0, 135.5, 133.7, 132.5, 131.8, 129.9, 129.1, 126.5, 126.1, 124.5, 123.5, 113.7, 112.7, 103.9 ppm. HRMS (ESI-Orbitrap) m/z: $(M-H)^+$ calcd for $C_{14}H_8BrN_2O_2$: 314.9775, found: 314.9765.

Synthesis of 3-bromo-10-dodecyl-5,10-dihydroindolo[3,2-*b*]indole (4): To a stirred solution of **3** (2 g, 6.30 mmol) in dry DMF, NaH (2.26 g, 9.45 mmol) was added under a nitrogen atmosphere at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was cooled again to 0 °C, and 1-bromododecane (1.8 g, 7.56 mmol) was added dropwise and stirred at room temperature for 8 h. Upon completion, the reaction mixture was quenched by slowly adding water and then extracted with ethyl acetate. The organic layer was washed successively with water and brine and then dried over anhydrous Na_2SO_4. After removal of the solvent, column purification of the crude was performed on silica gel to isolate the alkylated product **4** as a red-coloured viscous oil (2.9 g, 95%). Rf: 0.48 (5% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.5 Hz, 1H), 7.66 (s, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.18-7.16 (m, 1H), 6.32 (s, 1H), 3.83 (t, J = 7 Hz, 2H), 1.54-1.51 (m, 2H), 1.22-1.04 (m, 18H), 0.80 (t, J = 7 Hz, 3H)) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 149.6, 136.3, 135.6, 133.4, 132.6, 129.9, 129.5, 127.3, 124.8, 124.4, 123.3, 113.0, 111.5, 102.3, 44.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.4, 29.0, 26.8, 22.7, 14.2 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{26}H_{34}BrN_2O_2$: 485.1804, found: 485.1802.

Synthesis of 3-bromo-10-dodecyl-5,10-dihydroindolo[3,2-*b*]indole (5): To the alkylated intermediate **4** (2.9 g, 5.90 mmol) in DMA, PPh_3 (3.86 g, 14.7 mmol) was added and stirred the reaction mixture for 24 h at 165 °C. After completion of the reaction, the mixture was extracted with ethyl acetate and washed successively with water and brine. After solvent removal, column purification of the crude was performed on silica gel to isolate **5** as a colourless solid (2.4 g, 89%). m.p. 74-76 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 10.38 (s, 1H), 7.95-7.93 (m, 2H), 7.59-7.57 (m, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 4.62 (t, J = 7 Hz, 2H), 2.01-1.96 (m, 2H), 1.44-1.39 (m, 2H) 1.35-1.22 (m, 16H), 0.88 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 141.3, 139.2, 127.9, 123.7, 123.6, 122.4, 120.2, 118.6, 117.7, 116.1, 114.8, 112.4, 111.6, 110.3, 44.9, 31.7, 30.2, 26.7, 22.4, 13.5 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{26}H_{33}BrN_2$: 452.1827, found: 452.1839.

Synthesis of 3-bromo-5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indole (6): NaH (182 mg, 7.6 mmol) was added to a stirred solution of **5** (2.3 g, 5.07 mmol) in dry DMF under a nitrogen atmosphere at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was cooled again to 0 °C, and 1-bromododecane (1.51 g, 6.08 mmol) was added dropwise and stirred at room temperature for 8 h. Upon completion, the reaction mixture was quenched by slowly adding water and then extracted with EtOAc. The organic layer was washed successively with water and brine and then dried over anhydrous Na_2SO_4. After solvent removal, column purification of the crude was performed on silica gel to isolate alkylated product **6** as a colourless solid (2.9 g, 92%). m.p. 80-84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.77 (d, J = 8 Hz, 1H), 7.41 (d, J = 8 Hz, 1H), 7.31-7.25 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 4.42-4.38 (m, 4H), 1.93-1.87 (m, 4H), 1.38-1.18 (m, 36H), 0.82 (t, J = 7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $(CDCl_3)$: δ 140.8, 139.0, 126.8, 124.8, 124.0, 122.2, 120.0, 118.2, 117.9, 115.8, 115.2, 114.3, 111.0, 110.8, 109.9, 45.4, 45.3, 31.9, 30.2, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.4, 29.3, 27.1, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{38}H_{57}BrN_2$: 620.3705, found: 620.3683.

Synthesis of 4-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)benzaldehyde (10): A mixture of **6** (100 mg, 0.16 mmol.), 4-formylphenylboronic acid **7** (28 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), and K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was subjected to silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielding product **10** as a yellow solid (72 mg, 70%). m.p. 75-77 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.07 (s, 1H), 8.08 (s, 1H), 7.98 (d, J = 8.5 Hz, 2H), 7.88-7.84 (m, 3H), 7.60-7.58 (m, 1H), 7.54 (d, J = 9 Hz, 1H), 7.49 (d, J = 8 Hz, 1H), 7.32 (t, J = 8 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.56-4.50 (m, 4H), 2.02-1.97 (m, 14H), 1.46-1.40 (m, 4H), 1.38-1.33 (m, 4H), 1.28-1.20 (m, 28H), 0.88-0.84 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 192.0, 148.7, 140.8, 140.5, 134.4, 130.4, 129.8, 127.6, 126.8, 126.0, 122.0, 121.0, 118.3, 117.8, 116.6, 115.2, 114.5, 110.2, 109.9, 45.5, 45.4. 31.9, 31.9, 30.3, 30.3, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 27.2, 27.2, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{45}H_{62}N_2O$: 646.4862, found: 646.4881.

Synthesis of 2-cyano-3-(4-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)phenyl)acrylic acid (IID-4): A mixture of aldehyde **10** (50 mg, 0.077 mmol), cyanoacetic acid (20 mg, 0.23 mmol), and ammonium acetate (30 mg, 0.38 mmol) in acetic acid was heated under reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-4** was obtained as an orange solid (44 mg, 80% yield). m.p. 98-100 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.08 (d, J = 8.5 Hz, 2H), 8.04 (s, 1H), 7.82-7.77 (m, 3H), 7.54 (d, J = 8.5 Hz, 1H), 7.48 (d, J = 9 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.26 (t, J = 8 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.49-4.43 (m, 4H), 1.97-1.93 (m, 4H), 1.38-1.34 (m, 4H), 1.30-1.13 (m, 32H), 0.81-0.77 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 166.7, 156.2, 148.2, 140.8, 140.6, 132.3, 129.2, 129.0, 127.7, 126.8, 125.9, 122.0, 120.9, 118.3, 117.8, 116.6, 115.6, 115.2, 114.5, 110.3, 109.9, 100.1, 45.6, 45.4, 31.9, 30.3, 29.6, 29.5, 29.5, 29.4, 29.3, 27.2, 27.2, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{48}H_{63}N_3O_2$: 713.4920, found: 713.4953.

Synthesis of 5-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)thiophene-2-carbaldehyde (11): A mixture of **6** (100 mg, 0.16 mmol.), 5-formyl-2-thiopheneboronic acid **8** (30 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), and K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. The solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielding product **11** as a yellow solid (57 mg, 55%). m.p. 58-60 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (s, 1H), 8.06 (s, 1H), 7.76 (d, J = 8 Hz, 1H), 7.69 (d, J = 4 Hz, 1H), 7.54-7.52 (m, 1H), 7.41-7.39 (m, 2H), 7.35 (d, J = 4 Hz, 1H), 7.23 (t, J = 8 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 4.46-4.41 (m, 4H), 1.95-1.89 (m, 4H), 1.39-1.14 (m, 36H), 0.81-0.77 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 181.6, 155.9, 140.1, 139.9, 136.9, 128.2, 125.9, 124.7, 122.3, 121.6, 121.1, 119.1, 117.4, 116.8, 115.0, 113.9, 113.4, 109.2, 108.9, 44.5, 44.4, 30.8, 29.3, 29.2, 28.6, 28.5, 28.5, 28.4, 28.4, 28.3, 26.2, 26.1, 21.7, 13.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{43}H_{61}BrN_2OS$: 653.4505, found: 653.4517.

Synthesis of (2-cyano-3-(5-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)thiophen-2-yl)acrylic acid (IID-5): A mixture of aldehyde **11** (50 mg, 0.076 mmol), cyanoacetic acid (20 mg, 0.23 mmol), ammonium acetate (30 mg, 0.38 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-5** was obtained as red coloured solid (38 mg, 69%). m.p. 140-142 ^{o}C. ^{1}H NMR (500 MHz, $(CD_3)_2$ CO): δ 8.32 (s, 1H), 8.27 (s, 1H), 7.88 (d, J = 4 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.61-7.60 (m, 3H), 7.51 (d, J = 8 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7 Hz, 1H), 4.57-4.51 (m, 4H), 1.89-1.86 (m, 4H), 1.35-1.28 (m, 4H), 1.25-1.05 (m, 32H), 0.74-0.70 (m, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2$ CO): δ 165.3, 156.4, 146.5, 141.0, 140.7, 133.7, 126.8, 125.7, 123.4, 123.2, 122.2, 120.3, 118.4, 118.0, 116.0, 114.9, 114.4, 110.8, 110.1, 45.0, 44.8, 31.7, 30.1, 30.0, 29.7, 26.7, 26.7, 22.4, 13.5 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{46}H_{62}N_3O_2S$: 720.4563, found: 720.4572.

Synthesis of 5-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)furan-2-carbaldehyde (12): A mixture of **6** (100 mg, 0.16 mmol.), 5-formyl-2-furanylboronic acid **9** (22 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielding product **12** as a yellow solid (61 mg, 60%). m.p. 62-64 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.57 (s, 1H), 8.22 (s, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.67 (d, J = 9 Hz, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 3.5 Hz, 1H),7.26 (t, J = 8 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 4 Hz, 1H), 4.50-4.42 (m, 4H), 1.95-1.91 (m, 14H), 1.37-1.32 (m, 4H), 1.26-1.13 (m, 32H), 0.81-0.77 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 176.9, 161.8, 151.6, 140.8, 140.7, 126.8, 125.9, 122.1, 119.3, 118.4, 117.8, 115.2, 114.8, 114.4, 110.1, 110.0, 106.0, 45.5. 45.4, 31.9, 30.3, 0.2, 29.6, 29.5, 29.5, 29.5, 29.5, 29.4, 29.4, 29.3, 27.1, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{43}H_{61}N_2O_2$: 637.473, found: 637.4736.

Synthesis of 2-cyano-3-(5-(5,10-didodecyl-5,10-dihydroindolo[3,2-*b*]indol-3-yl)furan-2-yl)acrylic acid (IID-6): A mixture of aldehyde **12** (50 mg, 0.078 mmol), cyanoacetic acid (20 mg, 0.23 mmol), ammonium acetate (30 mg, 0.39 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-6** was obtained as a red solid (35 mg, 64%). m.p. 168-170 °C. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 8.56 (s, 1H), 8.05 (s, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 9 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.56 (d, J = 3 Hz, 1H), 7.34 (d, J = 3.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 4.60-4.58 (m, 4H), 1.88-1.82 (m, 4H), 1.25-1.05 (m, 36H), 0.82-0.79 (m, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2SO$): δ 164.8, 161.6, 147.2, 141.1, 140.9, 137.7, 126.6, 126.0, 122.5, 119.5, 119.2, 118.8, 118.3, 117.6, 115.6, 114.7, 114.4, 111.5, 110.9, 108.6, 45.2, 44.8, 31.7, 31.7, 30.1, 30.1, 29.4, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 29.0, 26.5, 26.3, 22.5, 14.4. ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{46}H_{61}N_3O_3$: 703.4713, found: 703.4704.

Synthesis of 5-bromo-3-(2-nitrophenyl)-1H-indole (13): A solution of 5-bromoindole **1** (2 g, 10.2 mmol), 2-iodonitrobenzene **2** (3 g, 12.24 mmol), $Pd(OAc)_2$ (229 mg., 10 mol%), K_2CO_3 (2.1 g, 15.3 mmol) in dioxane was degassed and the reaction mixture was stirred at 110 °C for 72 hours. After the completion of the reaction, it was then cooled, passed through celite, and extracted using ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated. The obtained residue was subjected to column chromatography to obtain

13 as a red solid (1.94 g, 60%). m.p. 100-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.68-7.63 (m, 3H), 7.51-7.48 (m, 1H), 7.37-7.32 (m, 3H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 150.0, 134.6, 132.5, 132.1, 128.3, 128.2, 127.7, 125.8, 124.5, 124.1, 121.6, 114.1, 113.0, 112.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{14}H_{10}BrN_2O_2$: 316.9926, found: 316.9935.

Synthesis of 2-bromo-5,6-dihydroindolo[2,3-*b*]indole (14): To compound **13** (1.5 g, 4.72 mmol) in DMA, PPh_3 (3.09 g, 11.82 mmol) was added and the reaction mixture was stirred for 24 h at 165 °C. After completion of the reaction, the mixture was extracted with ethyl acetate and washed successively with water and brine. After removal of the solvent, column purification of the residue was performed on silica gel to isolate **14** as a colourless solid (737 mg, 2.59 mmol, 55%). m.p. > 240 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 10.44 (s, 1H), 10.34 (s, 1H), 7.86 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 8 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.06-7.02 (m, 2H), 6.97 (t, J = 8 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 145.2, 139.2, 137.7, 124.2, 122.2, 121.6, 120.0, 119.9, 118.0, 113.0, 112.3, 111.6, 100.3 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{14}H_9BrN_2$: 283.9949, found: 283.9954.

Synthesis of 2-bromo-5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indole (15): NaH (88 mg, 3.69 mmol) was added to a stirred solution of **14** (700 mg, 2.46 mmol) in dry DMF under a nitrogen atmosphere at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was cooled again to 0 °C, and 1-bromododecane (735 mg, 2.95 mmol) was added dropwise and stirred at room temperature for 8 h. Upon completion, the reaction mixture was quenched by slowly adding water and then extracted with EtOAc. The organic layer was washed successively with water and brine and then dried over anhydrous Na_2SO_4. After removal of the solvent, column purification of the residue was performed on silica gel to isolate alkylated product **15** as a colourless solid (1.4 g, 93%). m.p. 68-70 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.86 (d, J = 7 Hz, 1H), 7.38 (d, J = 8 Hz, 1H), 7.29-7.22 (m, 4H), 4.36-4.32 (m, 4H), 1.46-1.27 (m, 36H), 1.93-1.84 (m, 4H), 1.46-1.27 (m, 36H), 0.92-0.89 (m, 6H) ppm.13C NMR (125 MHz, ($CDCl_3$): δ 144.6, 139.6, 138.2, 123.6, 121.8, 121.7, 120.7, 120.3, 119.9, 118.3, 113.1, 110.5, 109.3, 100.4, 44.4, 44.2, 31.9, 30.4, 30.4, 29.6, 29.6, 29.5, 29.5, 29.4, 27.1, 27.0, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M)^+$ calcd for $C_{38}H_{57}BrN_2$: 620.3705, found: 620.3714.

Synthesis of 4-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)benzaldehyde (16): A mixture of **15** (100 mg, 0.16 mmol.), 4-formylphenylboronic acid **7** (28 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), and K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielding the product **16** as a yellow solid (68 mg, 65%). m.p. 64-66 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 10.0 (s, 1H), 8.06 (d, J = 1.5 Hz, 1H), 7.91 (d, J = 8 Hz, 2H), 7.86-7.83 (m, 3H), 7.41 (dd, J1 = 6.5 Hz, J2 = 2 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8 Hz, 1H), 7.21-7.14 (m, 2H), 4.33-4.28 (m, 4H), 1.86-1.81 (m, 4H), 1.38-1.18 (m, 36H), 0.82-0.79 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 192.2, 148.9, 144.7, 139.7, 139.6, 134.4, 131.8, 130.3, 127.8, 122.6, 121.9, 120.2, 119.8, 118.9, 118.3, 117.1, 109.6, 109.4, 101.1, 44.5, 44.3, 31.9, 30.5, 30.5, 29.6, 29.6, 29.5, 29.4, 29.4, 27.1, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{45}H_{63}N_2O$: 647.4940, found: 647.4943.

Synthesis of 2-cyano-3-(4-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)phenyl)acrylic acid (IID-7): A mixture of aldehyde **16** (50 mg, 0.077 mmol), cyanoacetic acid (20 mg, 0.23 mmol), ammonium acetate (30 mg, 0.38 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-7** was obtained as an orange solid (38 mg, 69% yield). m.p. 142-144 °C. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 8.25 (d, J = 10 Hz, 2H), 8.10 (d, J = 8 Hz, 2H), 7.94 (d, J = 8 Hz, 2H), 7.89 (d, J = 7 Hz, 1H), 7.53-7.48 (m, 2H), 7.40 (d, J = 8 Hz, 1H), 7.09-7.03 (m, 2H), 4.46-4.39 (m, 4H), 1.86-1.80 (m, 4H), 1.39-1.13 (m, 36H), 0.75-0,72 (m, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 154.3, 148.1, 147.4, 144.8, 140.1, 139.8, 131.7, 131.0, 129.6, 127.4, 122.7, 121.9, 119.9, 119.7, 118.6, 118.2, 116.6, 110.2, 109.7, 101.0, 44.1, 44.0, 31.7, 30.3, 30.2, 26.6, 22.4, 13.4 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{48}H_{64}N_3O_2$:714.4999, found: 714.5001.

Synthesis of 5-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)thiophene-2-carbaldehyde (17): A mixture of **15** (100 mg, 0.16 mmol.), 5-formyl-2-thiopheneboronic acid **8** (30 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained by silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielded product **17** as a yellow solid (58 mg, 55%). m.p. 88-90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H), 8.09 (s, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 3.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 3.5 Hz, 1H), 7.32-7.30 (m, 2H), 7.23-7.15 (m, 2H), 4.32-4.28 (m, 4H), 1.86-1.80 (m, 4H), 1.39-1.17 (m, 36 H), 0.82-0.79 (m, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 182.7, 157.2, 144.8, 141.2, 140.2, 139.6, 137.9, 125.2, 123.0, 122.5, 121.7, 120.3, 120.0, 118.4, 118.2, 116.2, 109.7, 109.4, 101.0, 44.5, 44.3, 31.9, 30.5, 29.6, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{43}H_{61}N_2OS$: 653.4505, found: 653.4506.

Synthesis of 2-cyano-3-(5-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)thiophen-2-yl)acrylic acid (IID-8): A mixture of aldehyde **17** (50 mg, 0.076 mmol), cyanoacetic acid (20 mg, 0.23 mmol), ammonium acetate (30 mg, 0.38 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-8** was obtained as a red solid (39 mg, 71%). m.p. 154-156 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.32 (s, 1H), 8.26 (s, 1H), 7.88-7.85 (m, 2H), 7.65 (d, J = 4 Hz, 1H), 7.52-7.47 (m, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.10-7.04 (m, 2H), 4.45-4.38 (m, 4H), 1.86-1.78 (m, 4H), 1.39-1.13 (m, 36H), 0.75-0.72 (m, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 157.1, 146.7, 145.0, 140.8, 140.7, 140.0, 133.7, 124.9, 123.5, 122.5, 121.7, 120.1, 120.0, 118.2, 118.2, 115.8, 110.5, 109.8, 100.8, 44.1, 43.9, 31.7, 30.3, 30.2, 26.7, 22.4, 13.4 ppm. HRMS (ESI-Orbitrap) m/z: (M+H)$^+$ calcd for $C_{46}H_{62}BrN_3O_2S$: 720.4563, found: 720.4581.

Synthesis of 5-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)furan-2-carbaldehyde (18): A mixture of **15** (100 mg, 0.16 mmol.), 5-formyl-2-furanylboronic acid **9** (22 mg, 0.19 mmol), $Pd(PPh_3)_4$ (18 mg, 10 mol%), and K_2CO_3 (110 mg, 0.8 mmol) were weighed into a Schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography (with mixtures of ethyl acetate in hexane as eluent) yielding product **18** as a yellow solid (41 mg, 40%). m.p. 74-76 ^oC. ^1H NMR (500 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.26 (s, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.33-7.30 (m, 3H), 7.23-7.15 (m, 2H), 6.81 (d, J = 3 Hz, 1H), 4.30 (q, J = 8.5 Hz, 4H), 1.84-1.81 (m, 4H), 1.38-1.17 (m, 36H), 0.80 (t, J = 7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, ($CDCl_3$): δ 176.9, 161.8, 151.6, 144.7, 140.3, 139.6, 122.2, 121.7, 121.1, 120.4, 120.0, 118.6, 117.3, 115.5, 109.5, 109.4, 106.3, 101.2, 44.5, 44.3, 31.9, 30.5, 29.6, 29.6, 29.5, 29.4, 29.3, 27.1, 27.1, 22.7, 14.1 ppm. HRMS (ESI-Orbitrap) m/z: (M+H)$^+$ calcd for $C_{43}H_{61}N_2O_2$: 637.4728, found: 637.4723.

Synthesis of (2-cyano-3-(5-(5,6-didodecyl-5,6-dihydroindolo[2,3-*b*]indol-2-yl)furan-2-yl)acrylic acid (IID-9): A mixture of aldehyde **18** (50 mg, 0.078 mmol), cyanoacetic acid (20 mg, 0.23 mmol), ammonium acetate (30 mg, 0.39 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **IID-9** was obtained as a red solid (41 mg, 74%). m.p. 190-192 ^oC. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ 8.52 (s, 1H), 7.94 (s, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.43-7.40 (m, 2H), 7.15 (d, J = 3 Hz, 1H), 7.10-7.04 (m, 2H), 4.46-4.39 (m, 4H), 1.86-1.80 (m, 4H), 1.38-1.13 (m, 36H), 0.74-0.72 (m, 6H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 163.6, 162.2, 147.1, 144.8, 140.6, 140.0, 137.5, 122.2, 121.7, 120.9, 120.2, 119.9, 118.2, 117.1, 116.5, 115.6, 110.3, 109.8, 107.8, 101.0, 95.3, 44.1, 43.9, 31.8, 30.3, 30.3, 26.7, 22.4, 13.5 ppm. HRMS (ESI-Orbitrap) m/z: $(M+H)^+$ calcd for $C_{46}H_{62}N_3O_3$: 704.4791, found: 704.4816.

Synthesis of 9-bromo-6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indole (21): 5-bromo-1-dodecyl-1H-indole **19** (2 g, 5.49 mmol), cyclohexanone **20** (568 μL, 5.49 mmol), iodine (1.39 g, 5.49 mmol) and sulfur powder (702 mg, 21.96 mmol) were weighed into a reaction tube and NMP was added to this. The sealed reaction vessel was stirred under an air atmosphere at 150 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed successively with water and saturated brine. The combined organic layers were dried over anhydrous sodium sulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel to yield the desired product **21** as a colourless viscous liquid (1.26 g, 49%). Rf: 0.4 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.96 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 8 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.31-7.30 (m, 1H), 7.22-7.20 (m, 2H), 4.15 (t, J = 7 Hz, 2H), 1.88-1.83(m, 2H), 1.25-1.15 (m, 18H), 0.80 (t, J = 6 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8, 139.9, 138.0, 132.7, 125.3, 124.1, 124.0, 123.7, 122.4, 121.5, 120.6, 116.2, 113.1, 110.8, 46.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 27.0, 22.7, 14.1 ppm. HRMS (ESI) m/z: $(M)^+$ calcd for $C_{26}H_{32}BrNS$ 469.1439, found 469.1443.

Synthesis of 4-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)benzaldehyde (22): A mixture of benzothienoindole **21** (100 mg, 0.21 mmol), 4-formylphenylboronic acid **7** (94 mg, 0.63 mmol), $Pd(PPh_3)_4$ (24 mg, 10 mol%), and K_2CO_3 (145 mg, 1.05 mmol) were weighed into a schlenk tube and degassed for 10 minutes. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography yielding the product as a yellow solid (80 mg, 77%). m.p. 82-84 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 10.08 (S, 1H), 8.27 (S, 1H), 8.15 (d, J = 8 Hz, 1H), 8.00 (d, J = 8 Hz, 2H), 7.90 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 8 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.52-7.49 (m, 2H), 7.30-7.27 (m, 1H), 4.49 (t, = 7 Hz, 2H), 2.00-1.97 (m, 2H), 1.41-1.23 (m, 18H), 0.87 (t, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.1, 148.5, 143,7, 141.3, 138.2, 134.6, 133.0, 131.8, 130.4, 127.9, 125.3, 123.7, 123.2, 122.3, 121.0, 120.6, 117.9, 117.1, 110.0, 46.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 27.0, 22.7, 14.1 ppm. HRMS (ESI) m/z: $(M+H)^+$ calcd for $C_{33}H_{38}NOS$ 496.2669, found 496.2681.

Synthesis 2-cyano-3-(4-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)phenyl)acrylic acid (BID-4): A mixture of aldehyde **22** (50 mg, 0.10 mmol), cyanoacetic acid (25 mg, 0.30 mmol) ammonium acetate (65 mg, 0.50 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **BID-4** was obtained as an orange solid (49 mg, 88%). m.p. 157-160 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.46 (S, 1H), 8.26-8.26 (m, 2H), 8.12 (d, J = 8 Hz, 2 H), 7.98 (d, J = 8 Hz, 2 H), 7.83 (d, J = 8 Hz, 1H), 7.64 (s, 2 H), 7.39 (t, J = 7 Hz,1 H), 7.18 (t, J = 7.5 Hz, 1 H), 4.32 (t, J = 7 Hz, 2H), 1.90-1.87(m, 2H), 1.31-1.23 (m, 4H), 1.15-1.10 (m, 14 H), 0.72 (t, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 163.0, 154.1, 146.7, 143.4, 141.7, 138.2, 133.0, 131.7, 131.3, 130.1, 127.7, 125.3, 123.8, 123.1, 122.4, 120.9, 117.6, 117.1, 115.9, 110.6, 46.1, 31.7, 26.6, 22.4, 13.5 ppm. HRMS (ESI) m/z: $(M+H)^+$ calcd for $C_{36}H_{39}N_2O_2S$ 563.2727, found 563.2736.

Synthesis of 5-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)thiophene-2-carbaldehyde (23): Benzothienoindole **21** (94 mg, 0.63 mmol.), (5-formylthiophene-2-yl)boronic acid **8** (98 mg, 0.63 mmol), $Pd(PPh_3)_4$ (24 mg, 10 mol%), and K_2CO_3 (145 mg, 1.05 mmol.) were weighed in a Schlenk tube and degassed for 10 min. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography yielding product **23** as a yellow solid (74 mg, 70%). m.p.82-84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (S, 1H), 8.31 (S, 1H), 8.13 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 8 Hz, 1H), 7.79 (d, J = 4 Hz, 1H), 7.54-7.49(m, 2H), 7.46 (d, J = 8.5 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 4.28 (t, J= 7 Hz, 2H), 1.98-1.95 (m, 2 H), 1.39-1.23 (m, 18 H), 0.87(t, J = 6 Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.6, 156.4, 141.7, 141.5, 138.2, 137.9, 132.8, 125.4, 124.7, 123.8, 123.3, 123.1, 122.6, 122.5, 120.7, 120.3, 117.1, 110.1, 46.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 27.0, 22.7, 14.1 ppm; HRMS (ESI) m/z: $(M+H)^+$ calcd for $C_{31}H_{36}NOS_2$ 563.2727, found 563.2736.

Synthesis of 2-cyano-3-(5-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)thiophen-2-yl)acrylic acid (BID-5): A mixture of aldehyde **23** (50 mg, 0.10 mmol), cyanoacetic acid (25 mg, 0.30 mmol) ammonium acetate (65 mg, 0.50 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **BID-5** was obtained as a red solid (44 mg, 80%). m.p. 210-212 ^{o}C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.49 (S, 1H), 8.34 (S, 1H), 8.22 (d, J = 8 Hz, 1H), 7.91(d, J = 4 Hz, 1 H), 7.84(d, J = 8 Hz, 1 H), 7.74 (d, J = 4 Hz, 1 H), 7.64 (s, 2H), 7.41 (t, J = 7.5 Hz, 1 H), 7.20 (t, J = 7.5 Hz, 1 H), 4.33(t, J = 7 Hz, 2 H), 1.88-1.87 (m, 2H), 1.31-1.10 (m, 18 H), 0.72 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 163.3, 156.0, 146.9, 143.8, 142.3, 141.0, 138.3, 134.1, 132.7, 125.4, 125.1, 124.1, 123.8, 122.9, 122.6, 120.9, 120.4, 117.0, 116.8, 116.1, 111.0, 97.1, 46.1, 31.7, 26.6, 22.4, 13.5 ppm. HRMS (ESI) m/z: $(M+H)^+$ calcd for $C_{34}H_{37}N_2O_2S_2$ 569.2291, found 569.2300.

Synthesis of 5-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)furan-2-carbaldehyde (24): Benzothienoindole **21** (100 mg, 0.21 mmol.), (5-formylfuran-2-yl)boronic acid **9** (88 mg, 0.63 mmol) $Pd(PPh_3)_4$ (24 mg, 10 mol%), and K_2CO_3 (145 mg, 1.05 mmol.) were weighed in a Schlenk tube and degassed for 10 min. Degassed THF and water were then added in a 3:1 ratio, and the reaction mixture was purged with argon and stirred at 70 °C for 24 h. After completion of the reaction, the solvent was evaporated under vacuum, and the residue obtained was purified by silica column chromatography yielding the product **24** as a yellow-coloured viscous liquid (61 mg, 60%). Rf: 0.44 (20 % ethyl acetate in hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.59 (s, 1H), 8.40 (s, 1H), 8.12 (d, J = 8 Hz, 1H), 7.75 (d, J = 8 Hz, 1 H), 7.69-7.67 (m, 1H), 7.45 (t, J =7 Hz, 1H), 7.38-7.37 (m, 1H), 7.30 (d, J = 4 Hz, 1 H), 7.22 (t, J = 7 Hz,1 H), 6.81(d, 3.5, J = Hz,1H), 4.18 (t, J = 7 Hz, 2 H), 1.91-1.86 (m, 2H), 1.32-1.26 (m, 4 H), 1.18-1.15 (m, 14 H), 0.79 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.8, 161.4, 151.7, 143.9, 141.8, 138.2, 132.8, 125.4, 123.7, 122.8, 122.5, 121.1, 120.9, 119.2, 117.3, 116.2, 109.9, 106.6, 46.6. 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 27.0, 22.7, 14.1 ppm; HRMS (ESI) m/z: $(M+H)^+$ calcd for $C_{34}H_{37}N_2O_3S$ 553.2539, found 553.2519

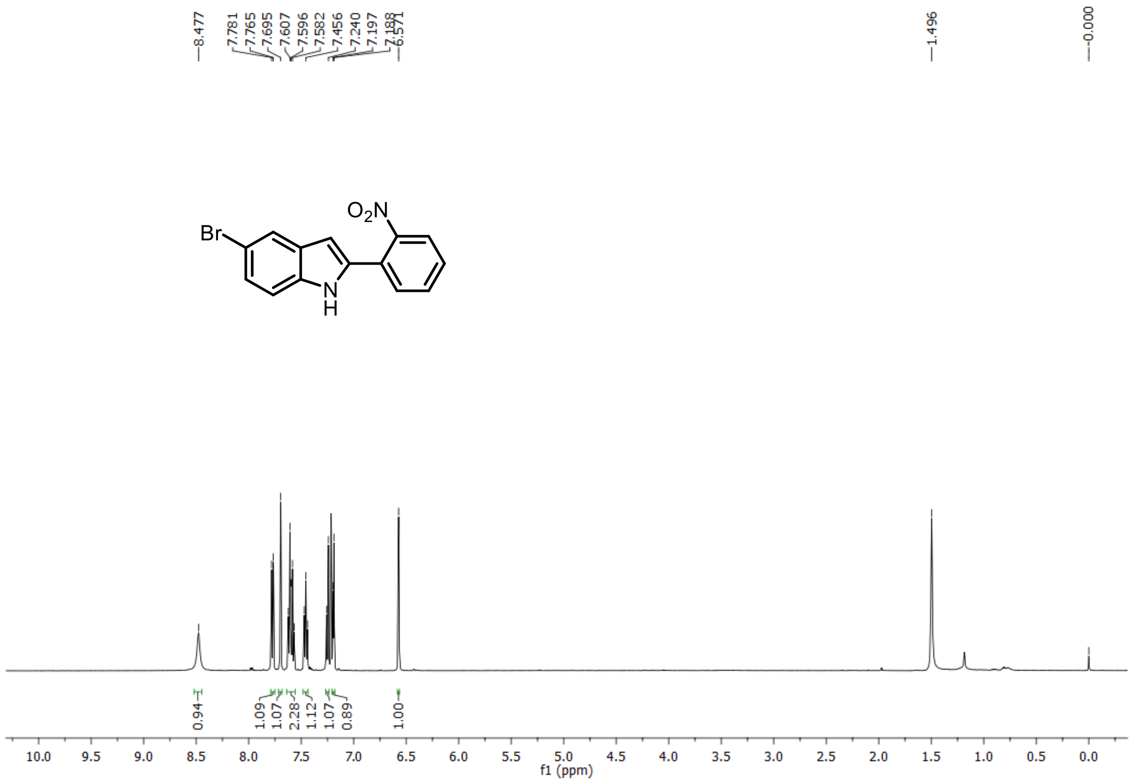
Synthesis of 2-cyano-3-(5-(6-dodecyl-6H-benzo[4,5]thieno[2,3-*b*]indol-9-yl)furan-2-yl) acrylic acid (BID-6): A mixture of aldehyde **24** (50 mg, 0.10 mmol), cyanoacetic acid (25 mg, 0.30 mmol) ammonium acetate (65 mg, 0.50 mmol) in acetic acid was heated at reflux overnight under argon atmosphere. After cooling the reaction mixture to room temperature, it was precipitated by pouring it into water. The precipitate was then washed with water and dried in a vacuum oven. The product **BID-6** was obtained as a red solid (41 mg,75%). m.p. 173-175 °C. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.72 (S, 1H), 8.24 (d, J = 7.5 Hz, 1H), 7.97(s, 1H), 7.82(t, J = 9 Hz, 2H), 7.62 (d, J = 9 Hz, 1H), 7.42-7.38 (m, 2H), 7.21-7.18 (m, 2H), 1.29-1.22 (m, 6.5 Hz, 4H), 1,15-1.09 (m, 14H), 0.72 (t, J = 6.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ 161.4, 147.4, 143.7, 142.0, 138.3, 137.6, 132.7, 125.5, 123.7, 122.7, 122.6, 121.2, 121.0, 119.1, 117.3, 116.5, 110.7, 108.1, 46.2, 31.5, 26.6, 22.4, 13.8 ppm; HRMS (ESI) m/z: $(M)^+$ calcd for $C_{34}H_{36}N_2O_3S$ 552.2446, found 552.2373**.**

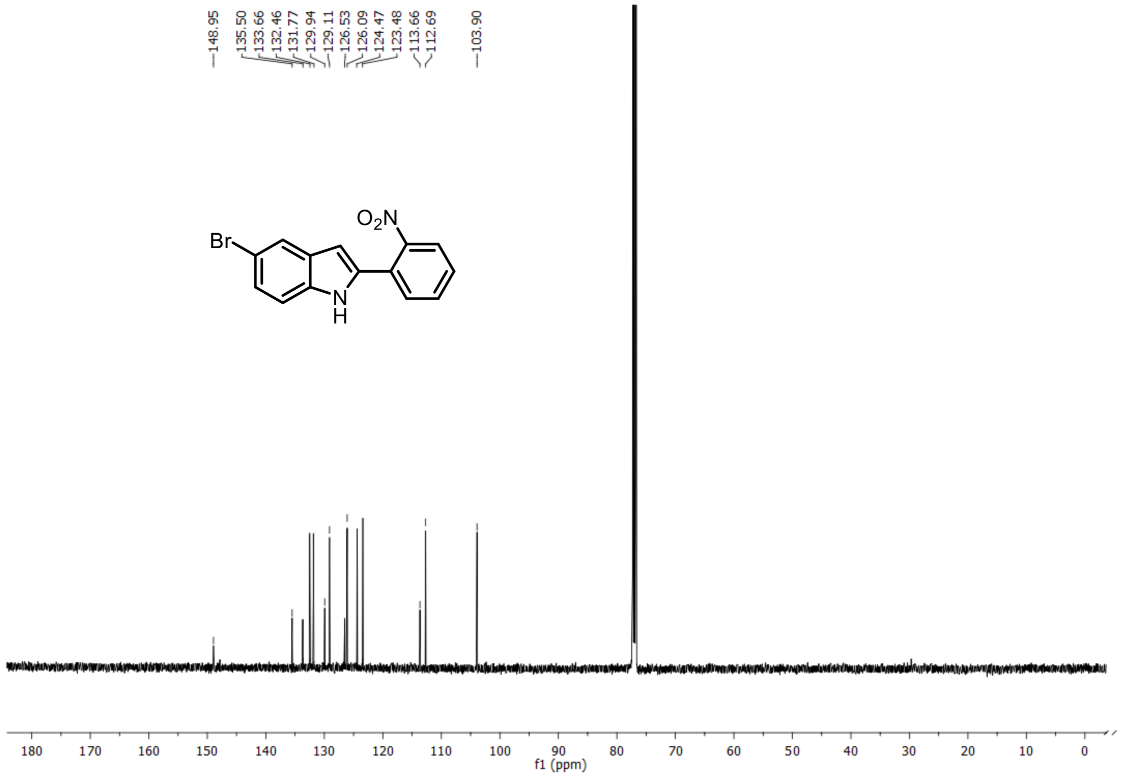
2.2 Device Fabrication

The fabrication and characterization procedures for the devices are detailed elsewhere.[18] The DSCs were fabricated by coating the photoanode with a 16μm thick layer of titanium dioxide, consisting of a 12μm transparent layer and a 4μm scattering layer, and subsequently immersing the electrodes in 0.2 mM dye solutions. A 25μm surlyn spacer was used to assemble the photoanode with a predrilled platinum-coated counter electrode. The iodide/triiodide electrolyte, composed of 0.5M BMII, 0.1M LiI, 0.03M I_2, and 0.5M TBP, is used as the redox mediator in the fabricated DSCs.

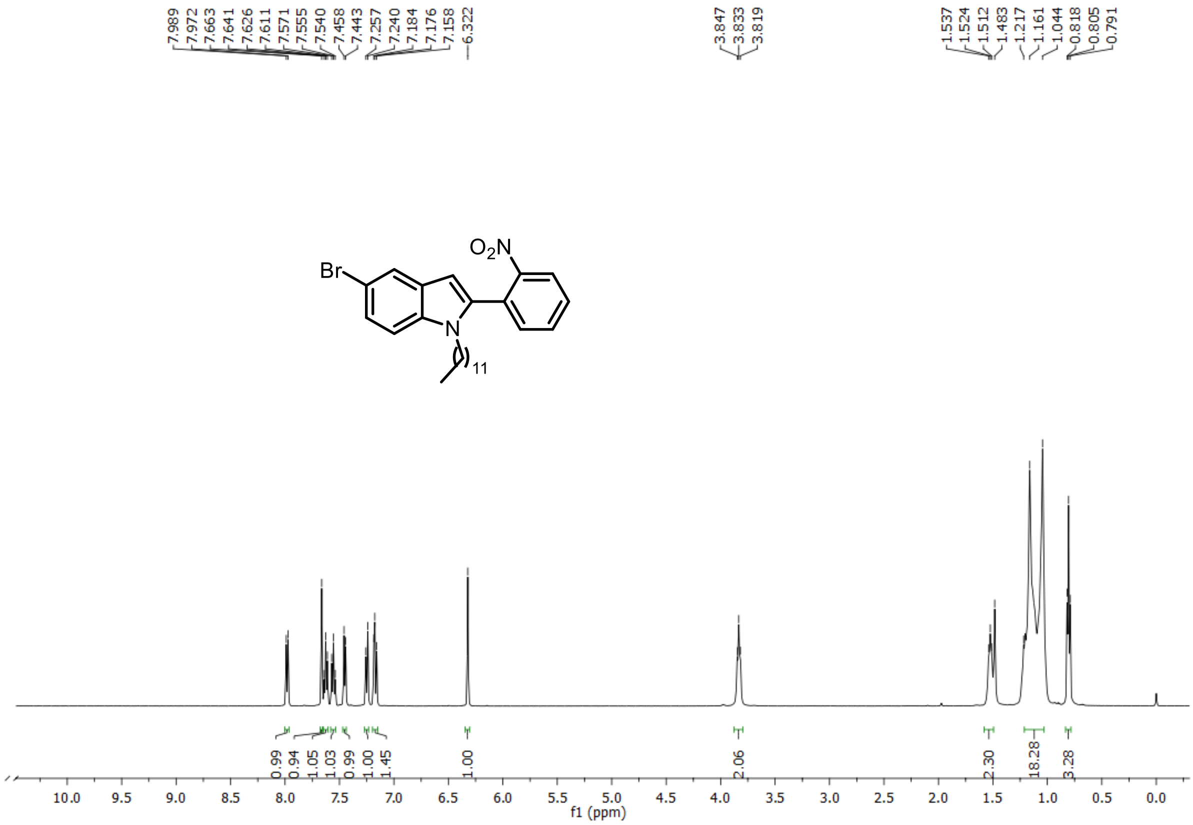
Current density-voltage (J-V) measurements were done using a Class AAA solar simulator (Newport, Sol3A-94023) under one sun illumination (AM 1.5G 100 $mWcm^{-2}$). The incident photon-to-current conversion efficiency (IPCE) was measured using a 350W xenon lamp with a monochromator (Newport). Charge Extraction (CE) measurements were done using an Autolab PGSTAT302N and toolbox setup (Dyenamo A.B., Sweden). Transient photovoltage and photocurrent decay were also measured using the toolbox (Dyenamo A.B., Sweden). The open-circuit photovoltage decay (OCVD) was measured using an Autolab PGSTAT302N workstation.

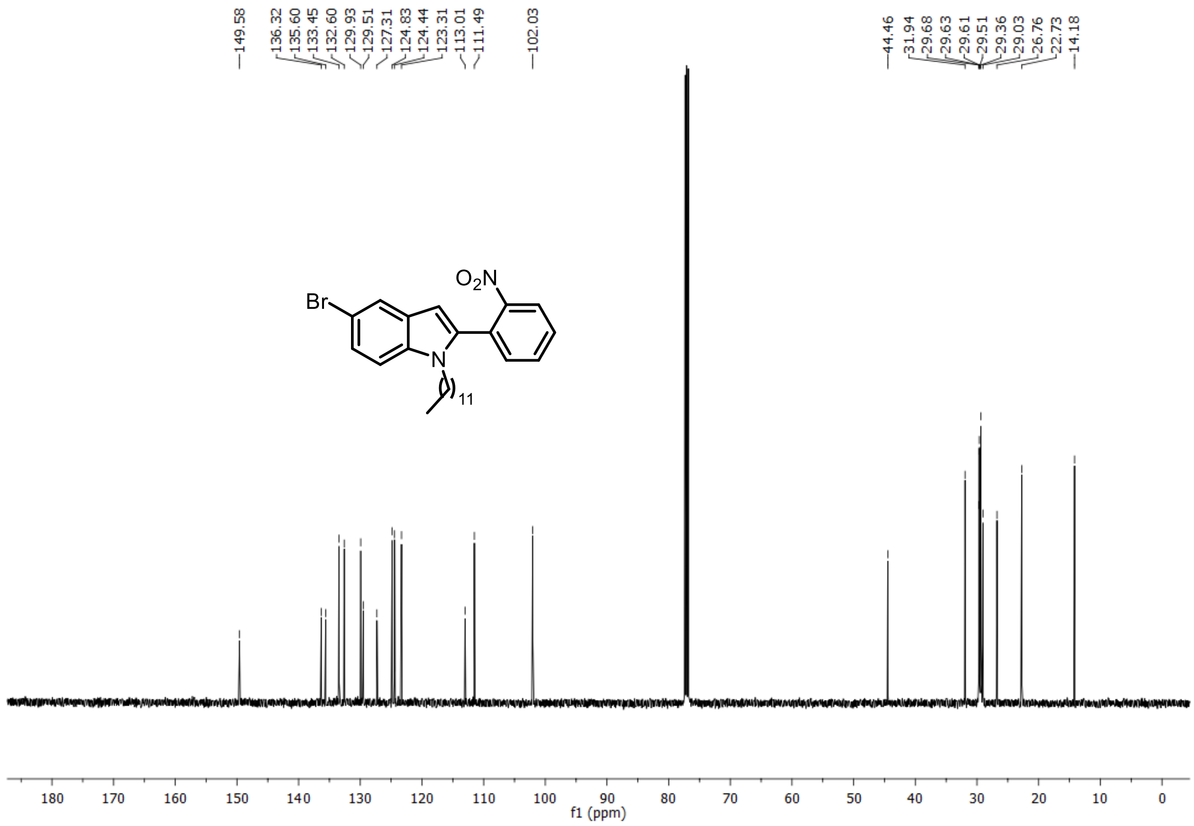
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **3**



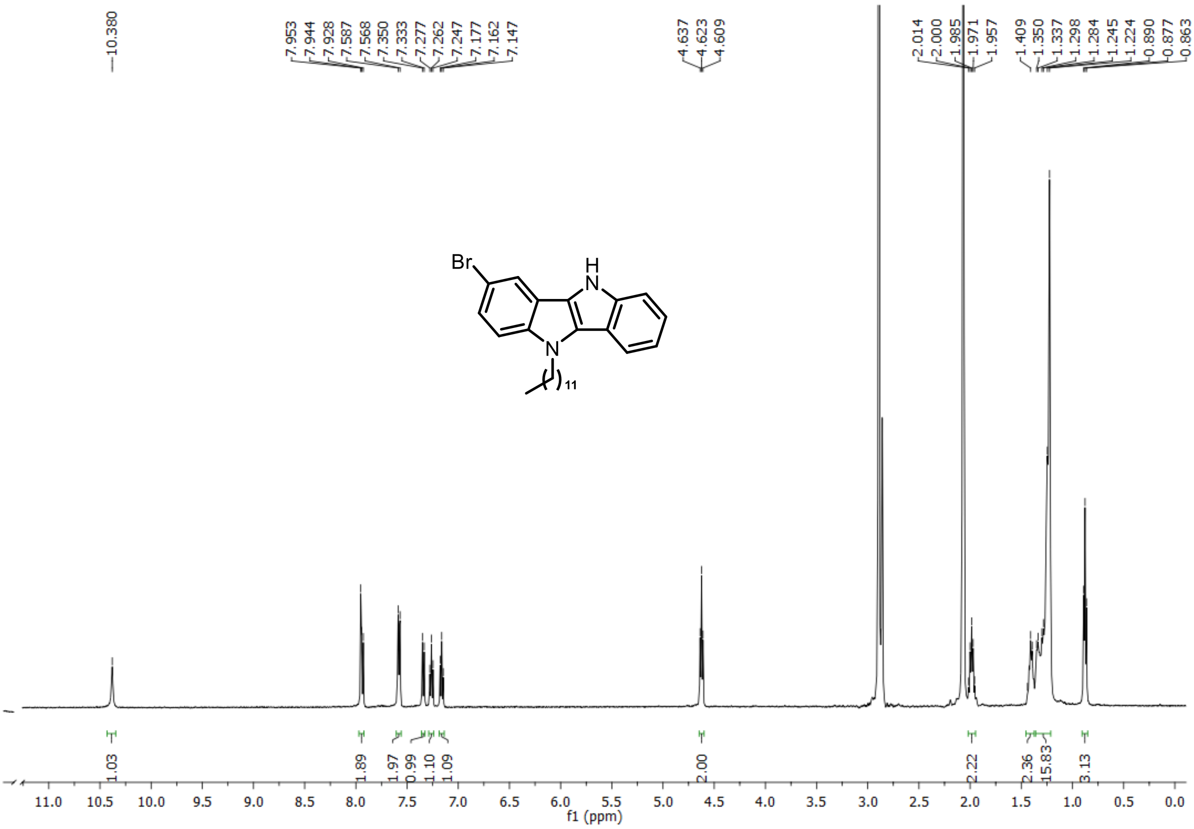


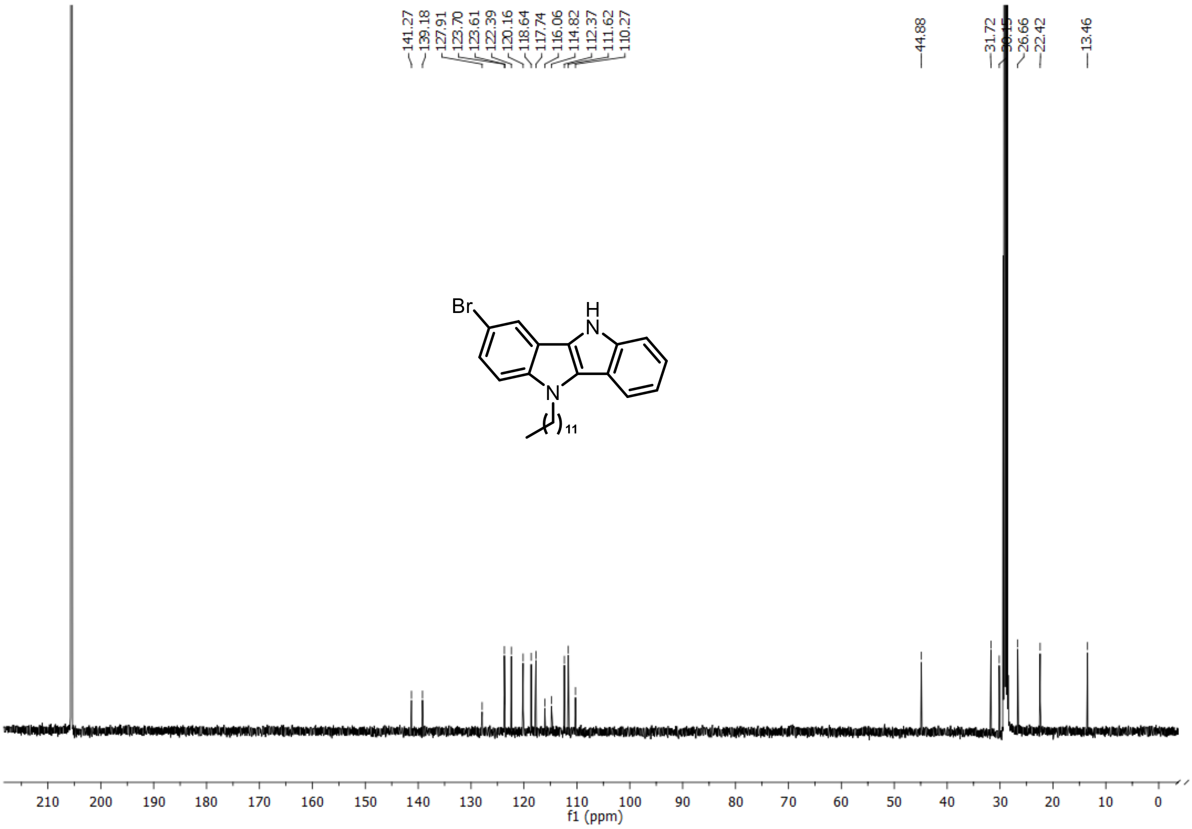
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **4**



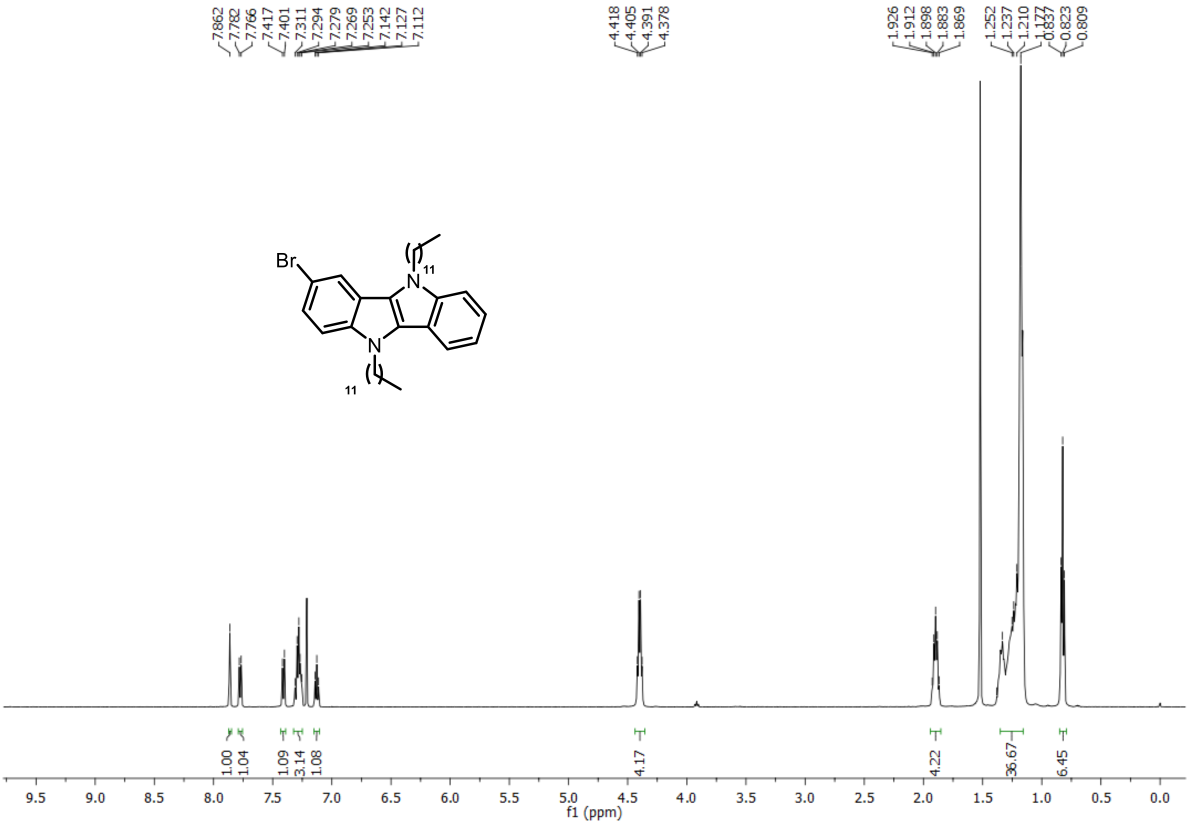


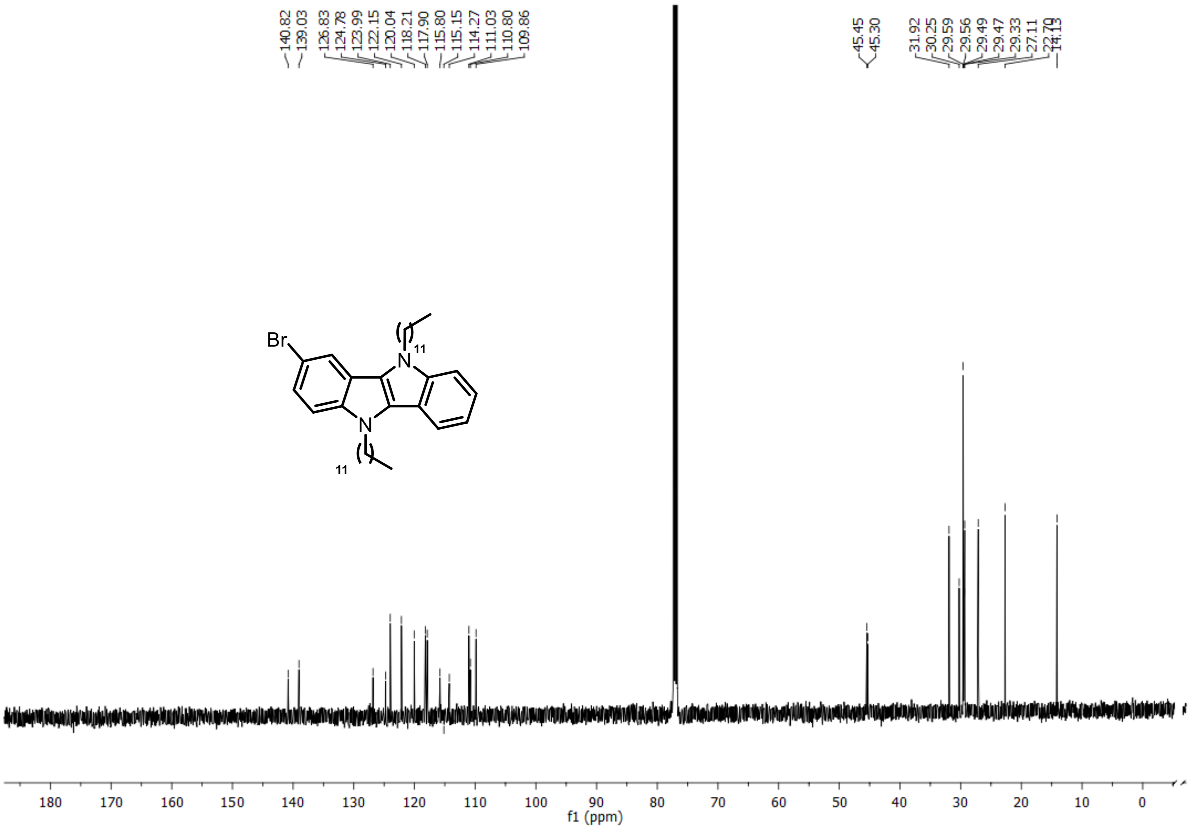
^{1}H NMR (500 MHz, $(CD_3)_2O$) & ^{13}C{^{1}H} (125 MHz, $(CD_3)_2O$) Spectra of **5**



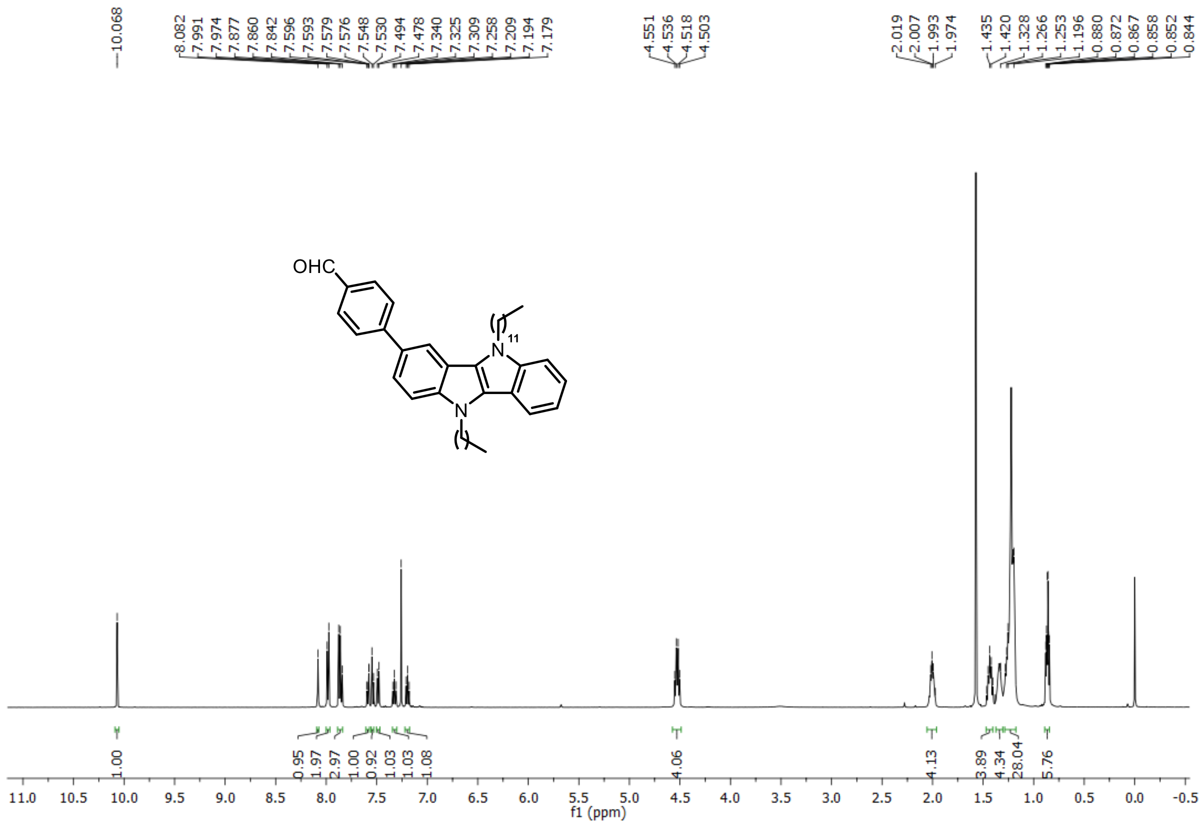


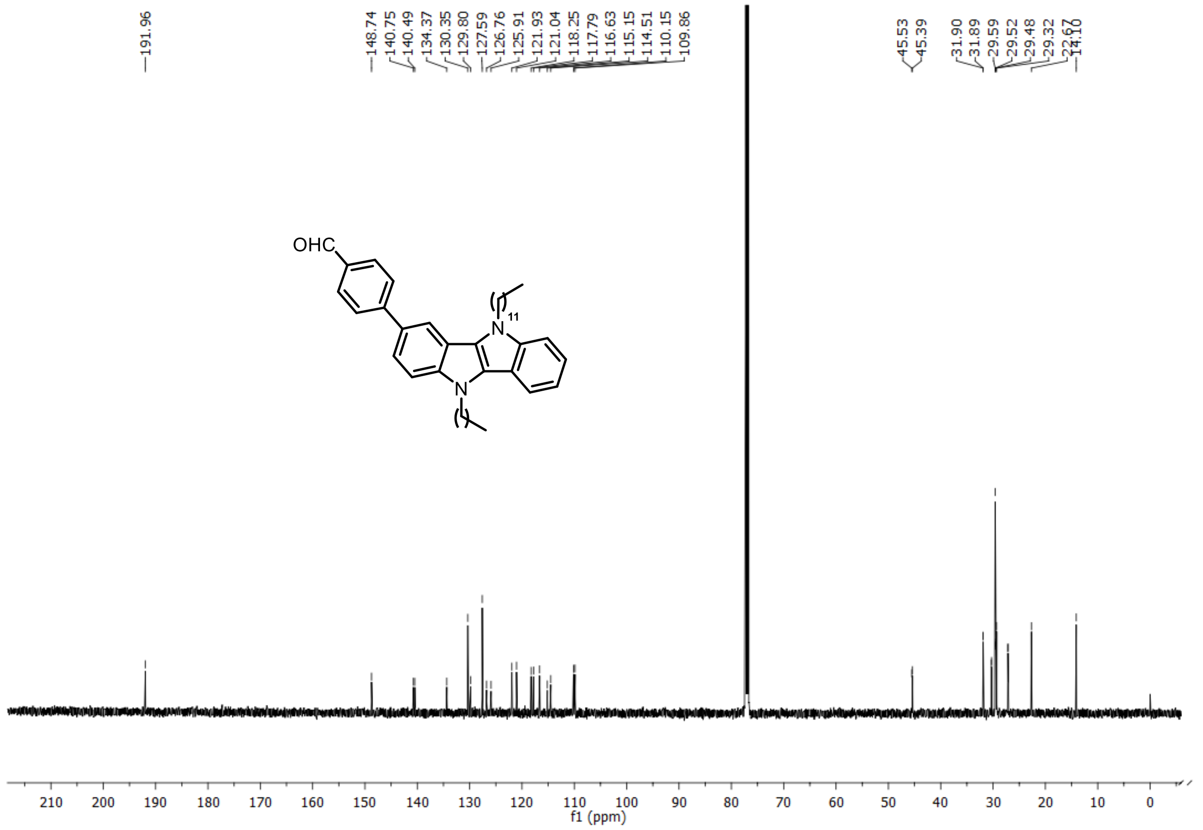
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) Spectra of **6**



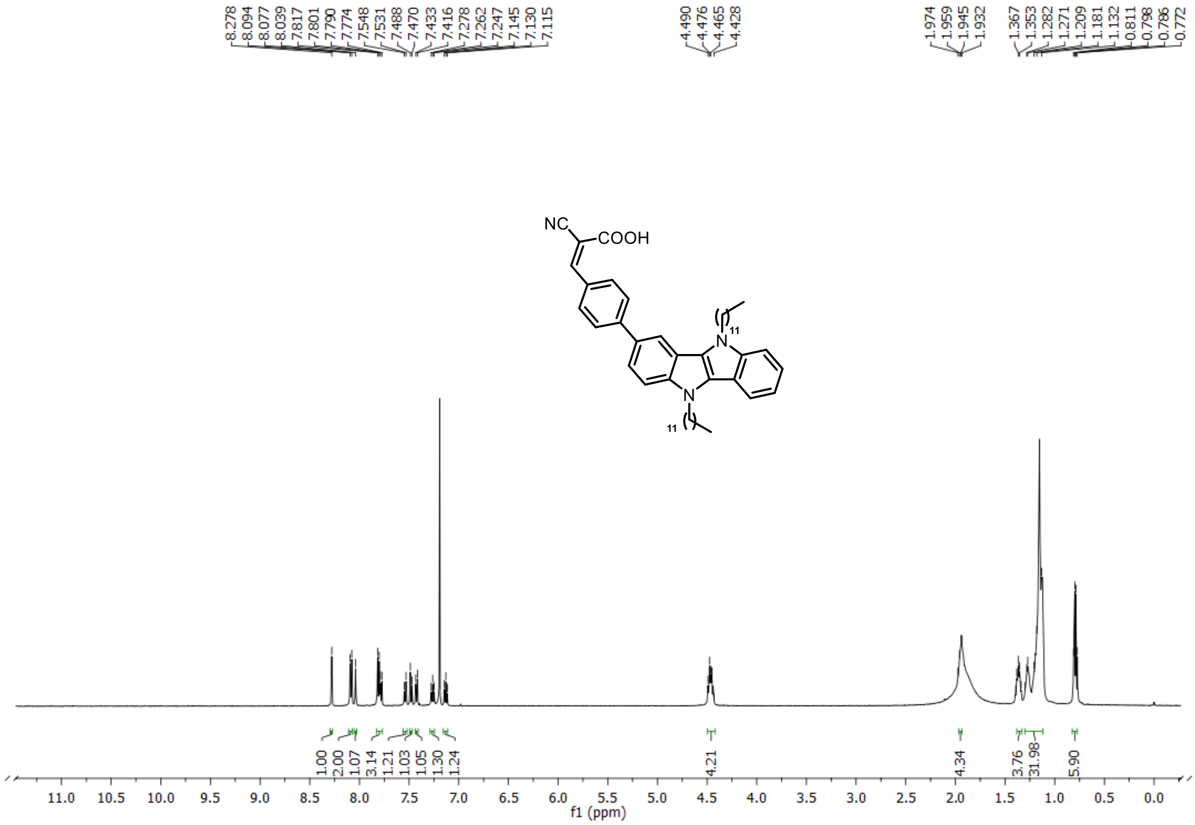


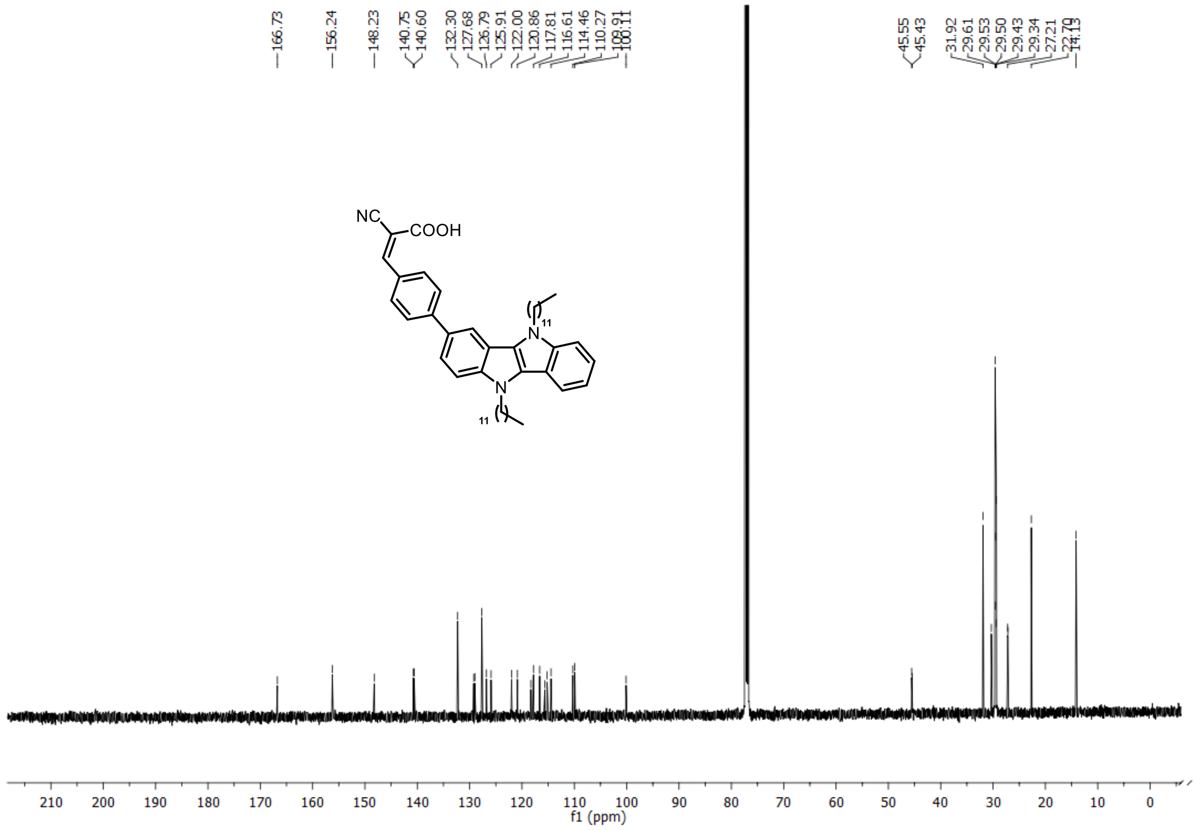
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **7**



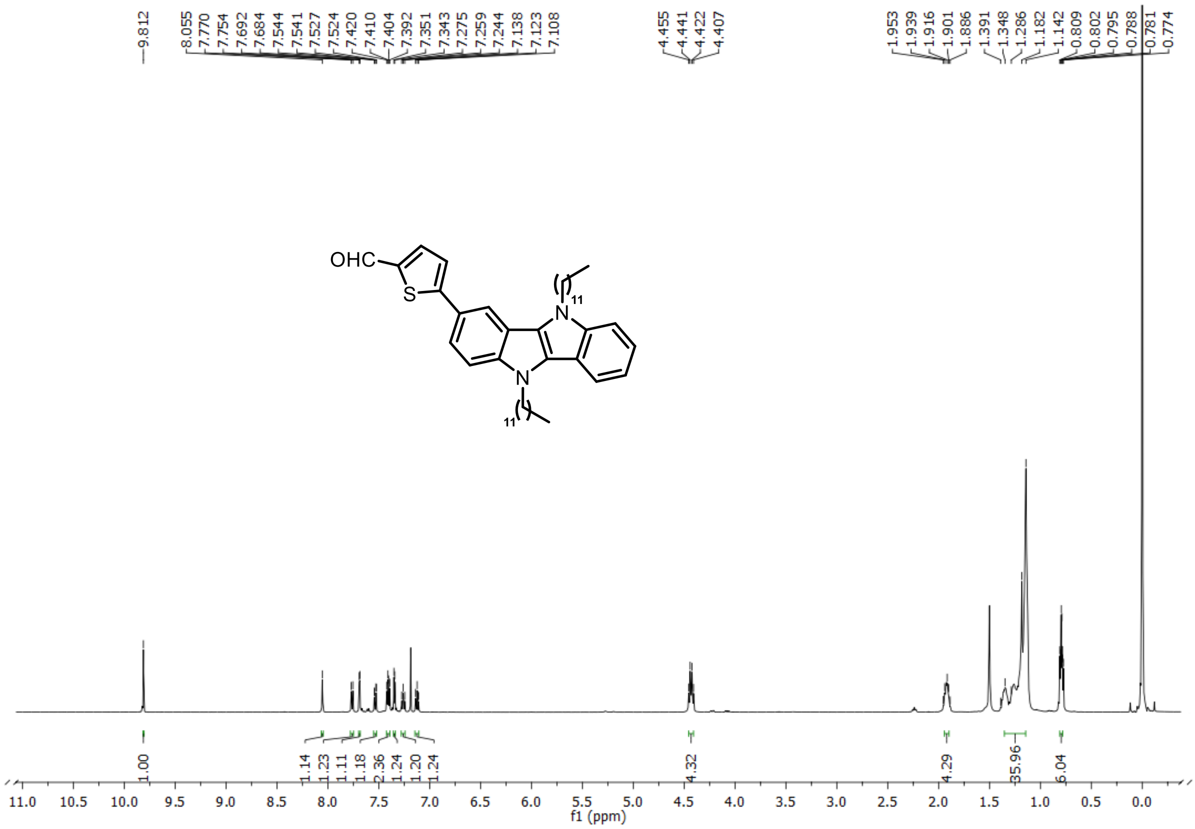


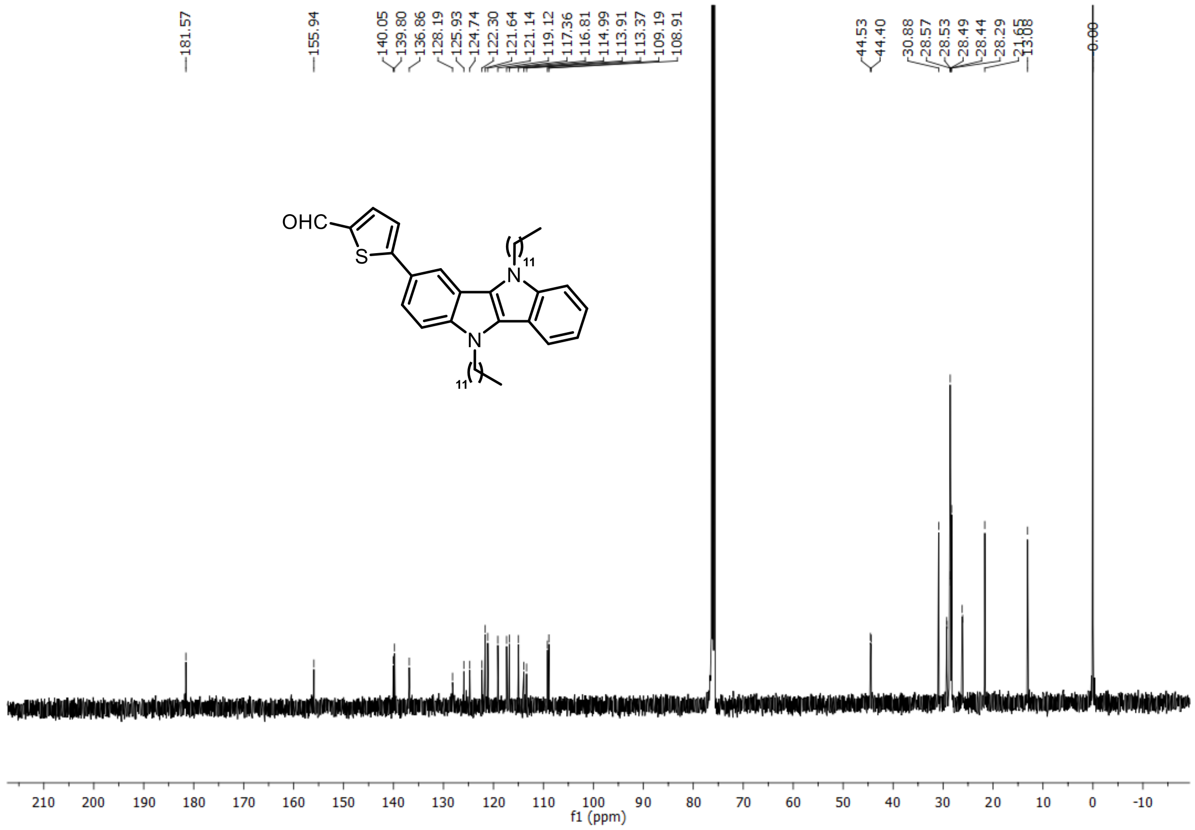
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **IID-4**



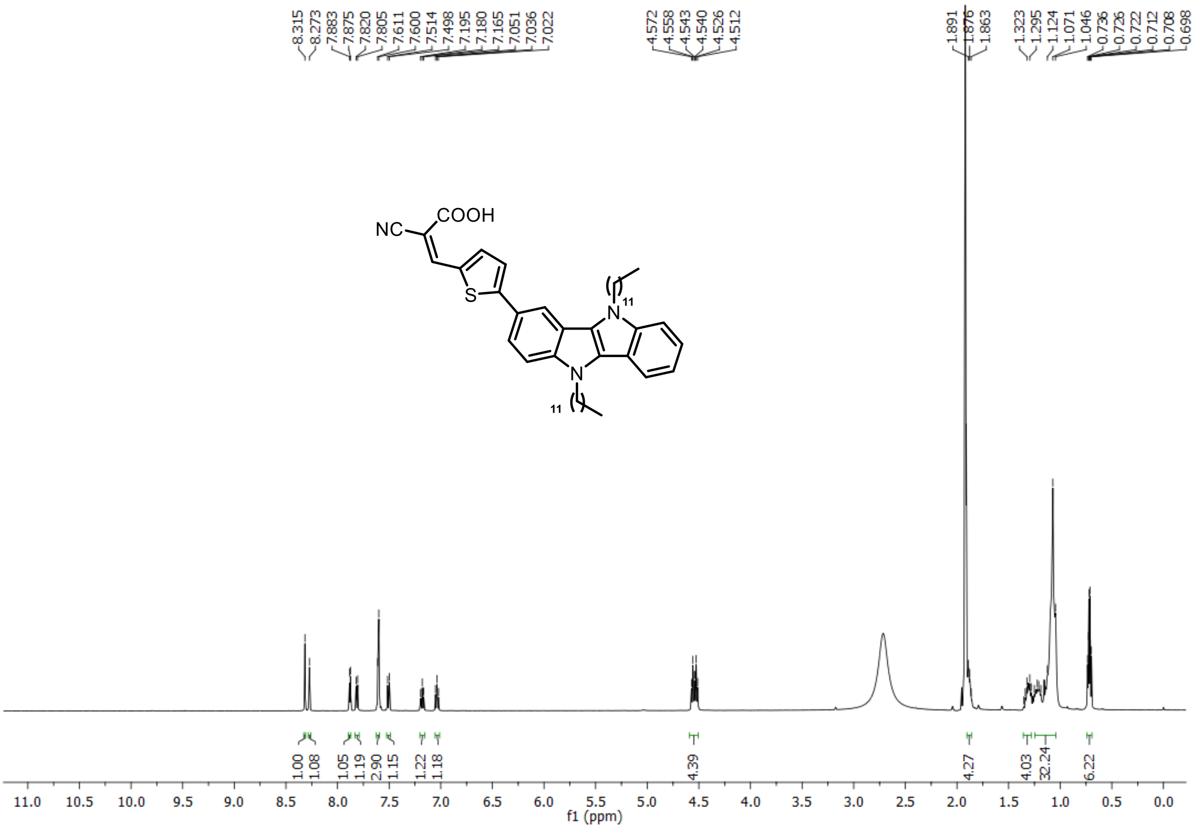


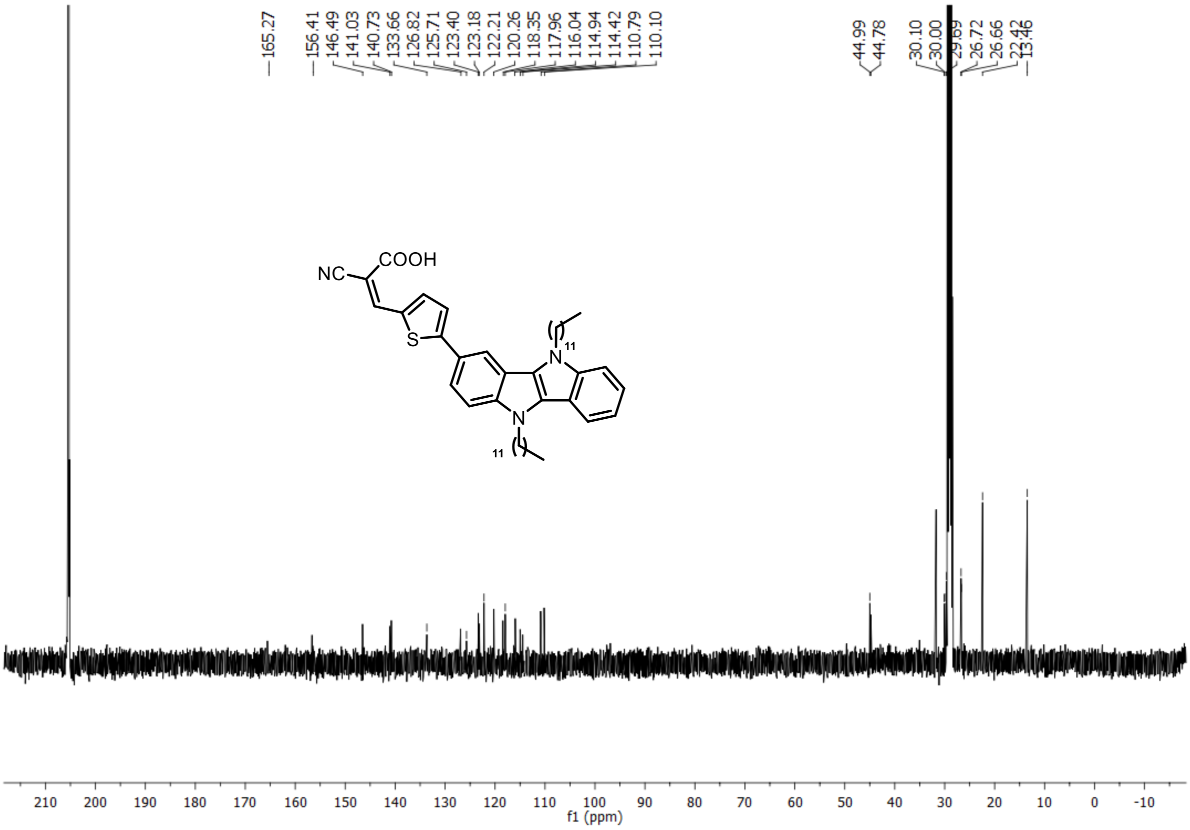
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **8**



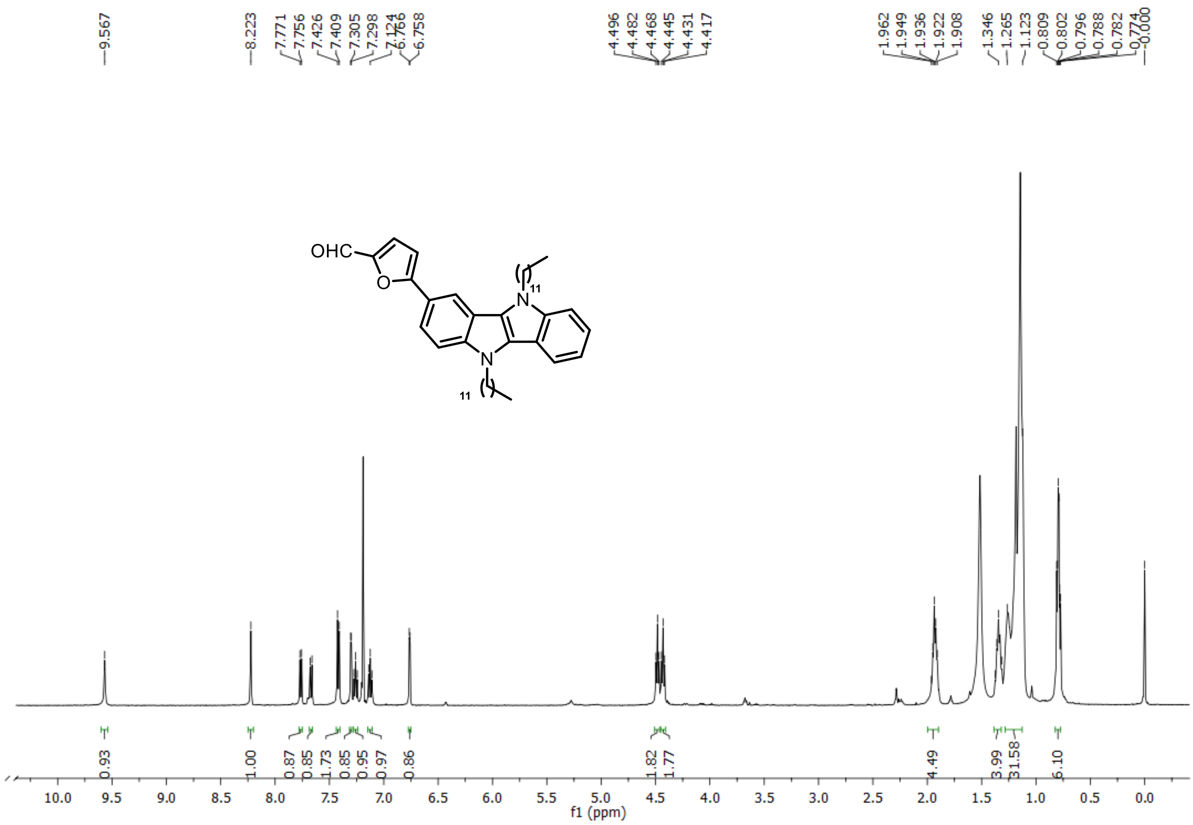


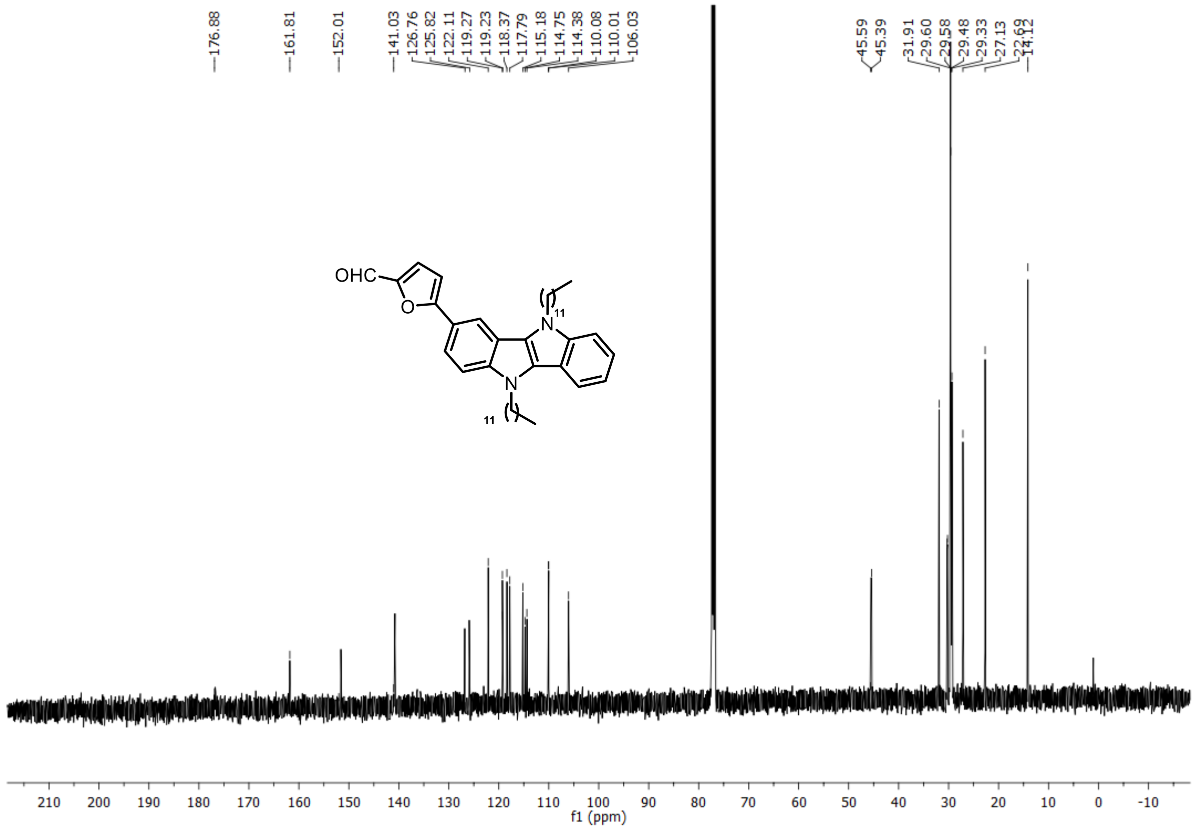
^{1}H NMR (500 MHz, $(CD_3)_2O$) & $^{13}C\{^{1}H\}$ (125 MHz, $(CD_3)_2O$) Spectra of **IID-5**



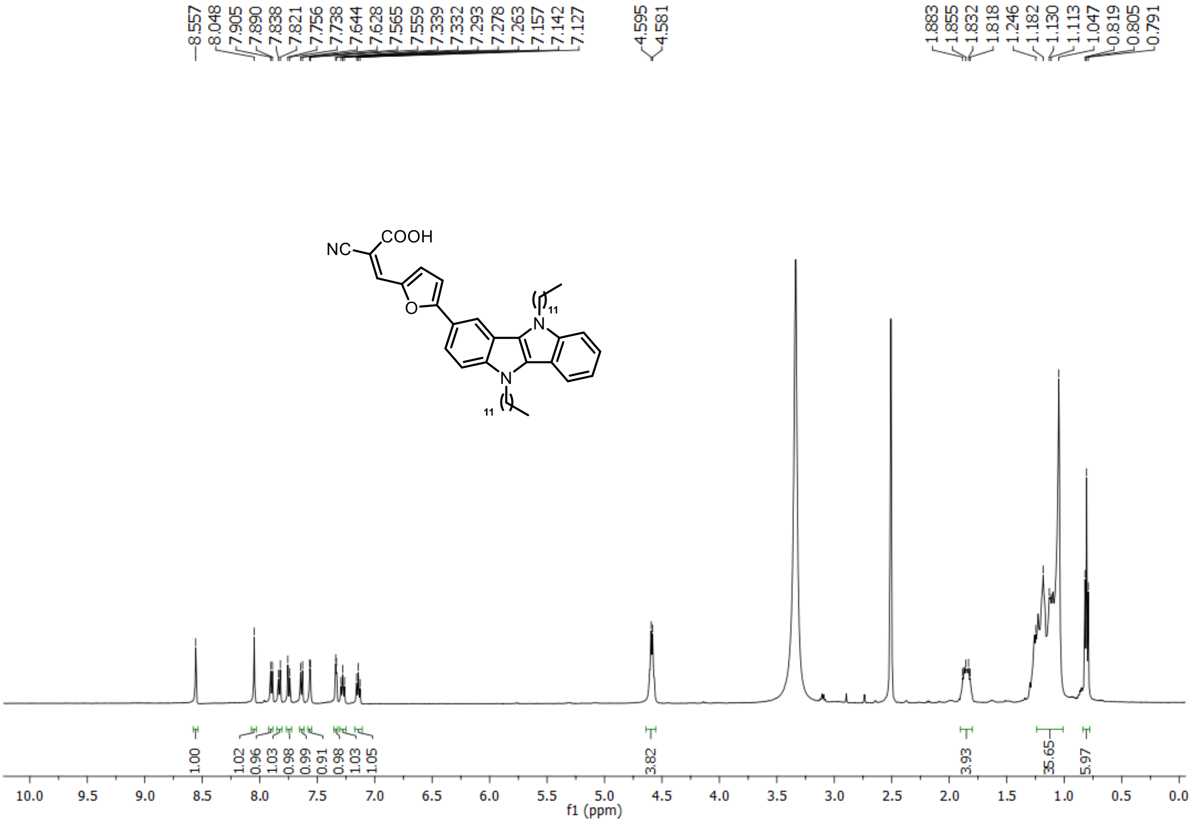


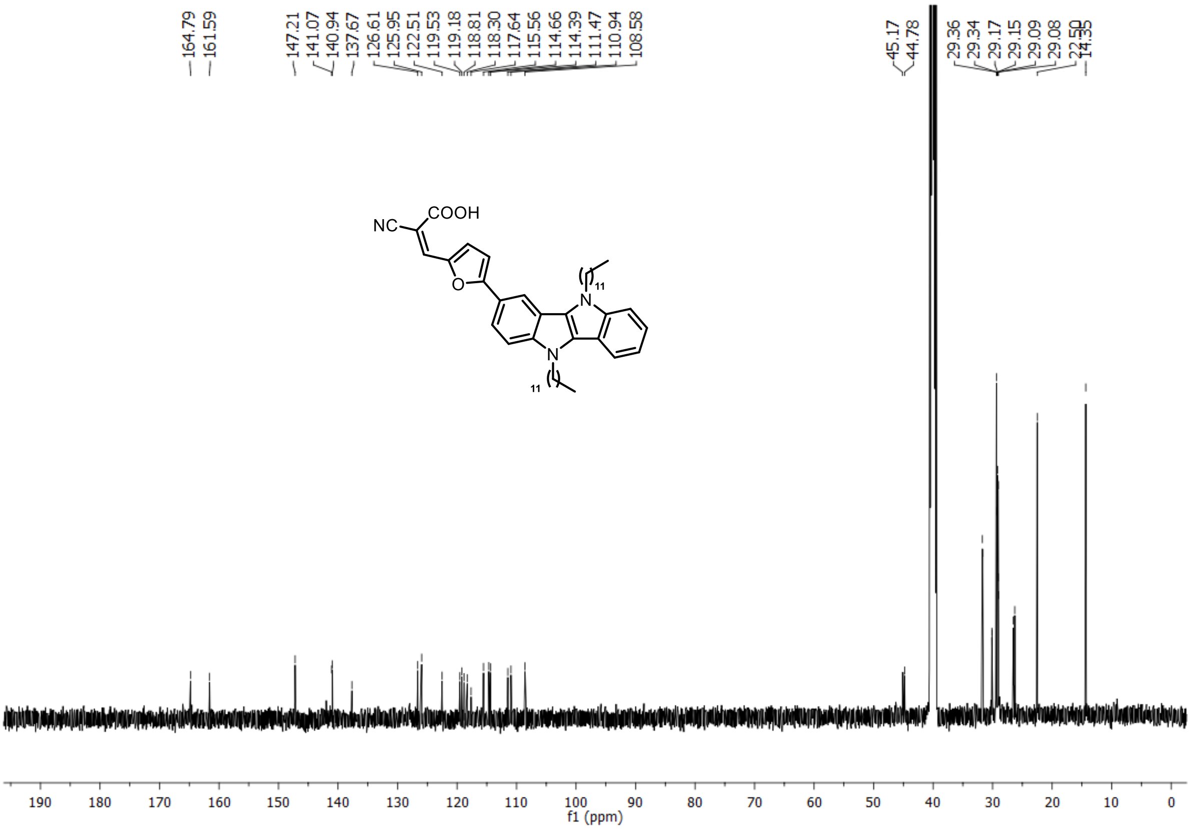
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **9**



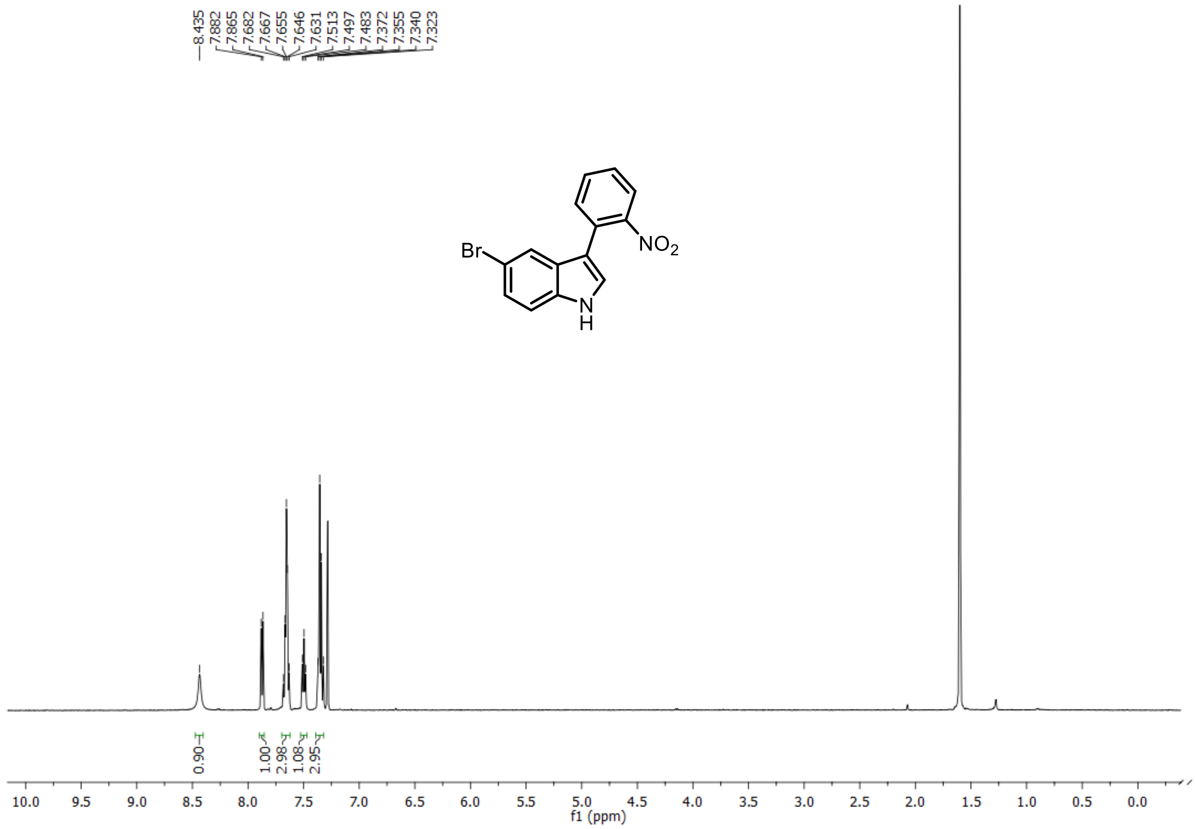


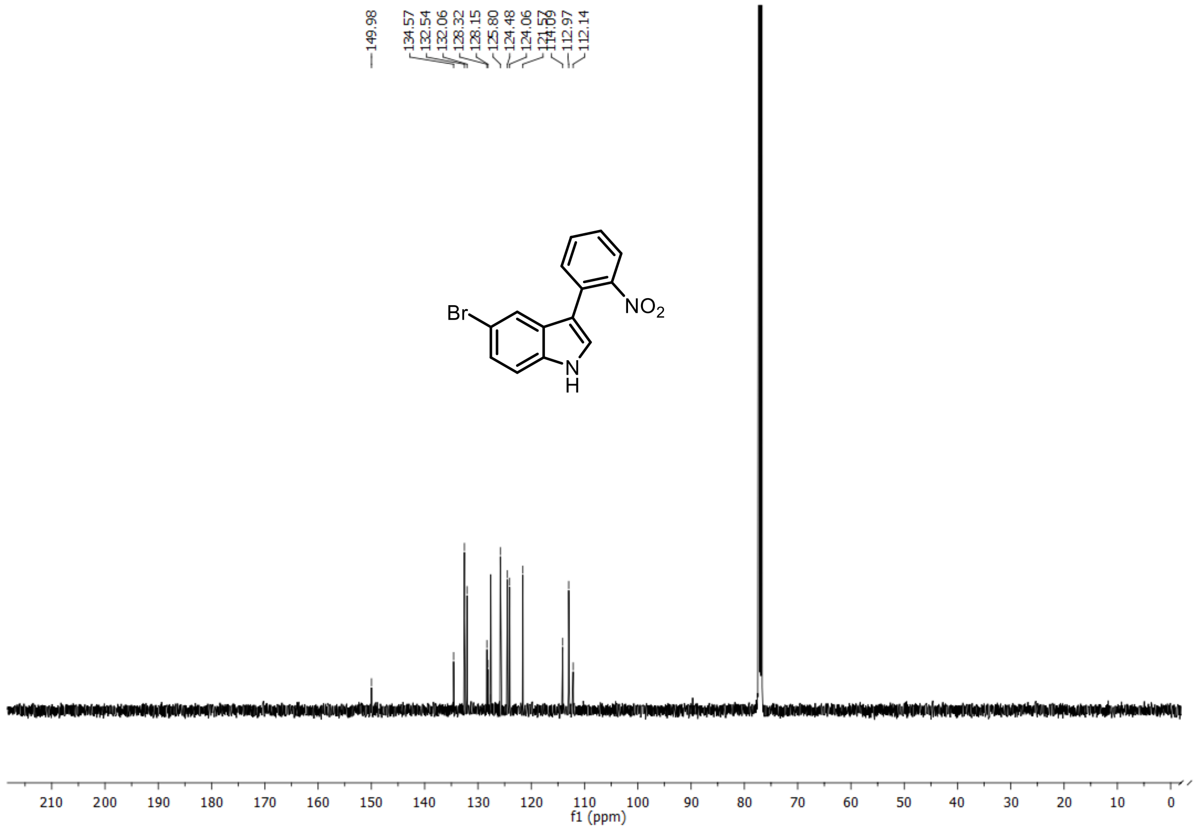
^{1}H NMR (500 MHz, $(CD_3)_2SO$) & $^{13}C\{^{1}H\}$ (125 MHz, (CD$_3$)2SO) Spectra of **IID-6**



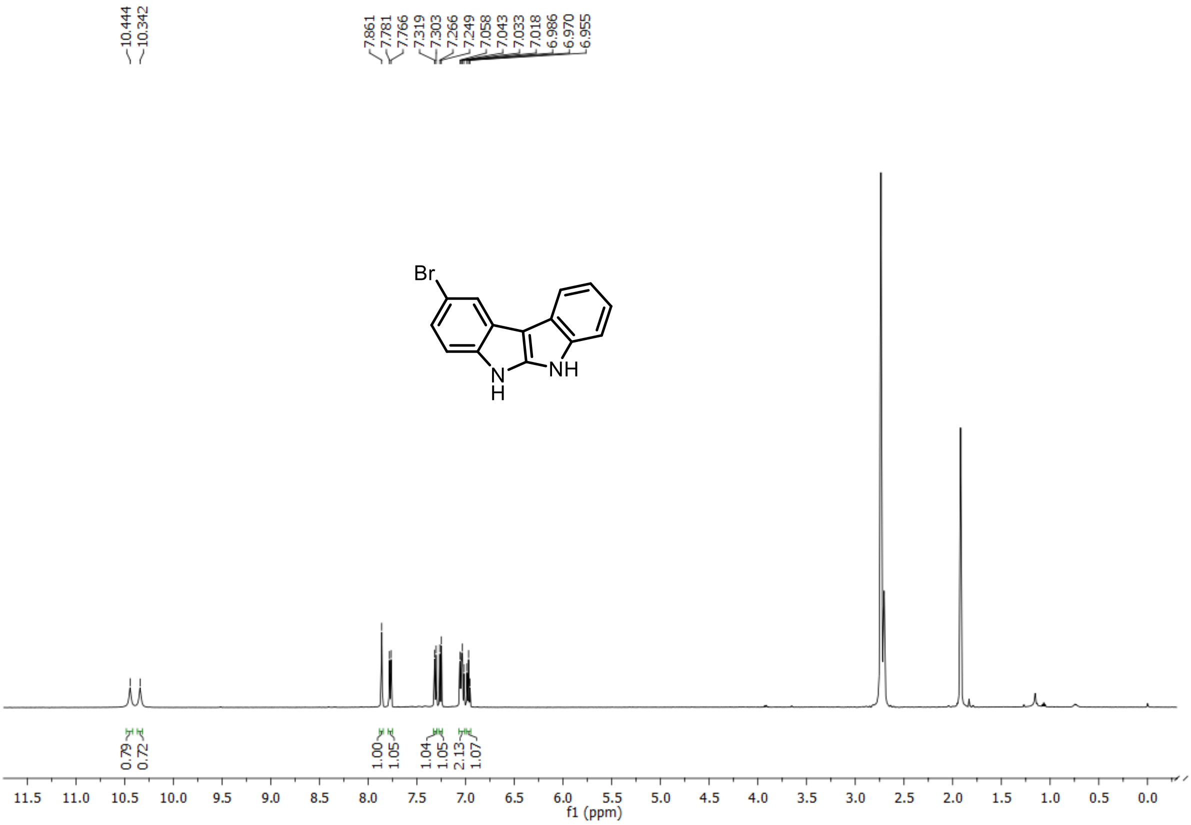


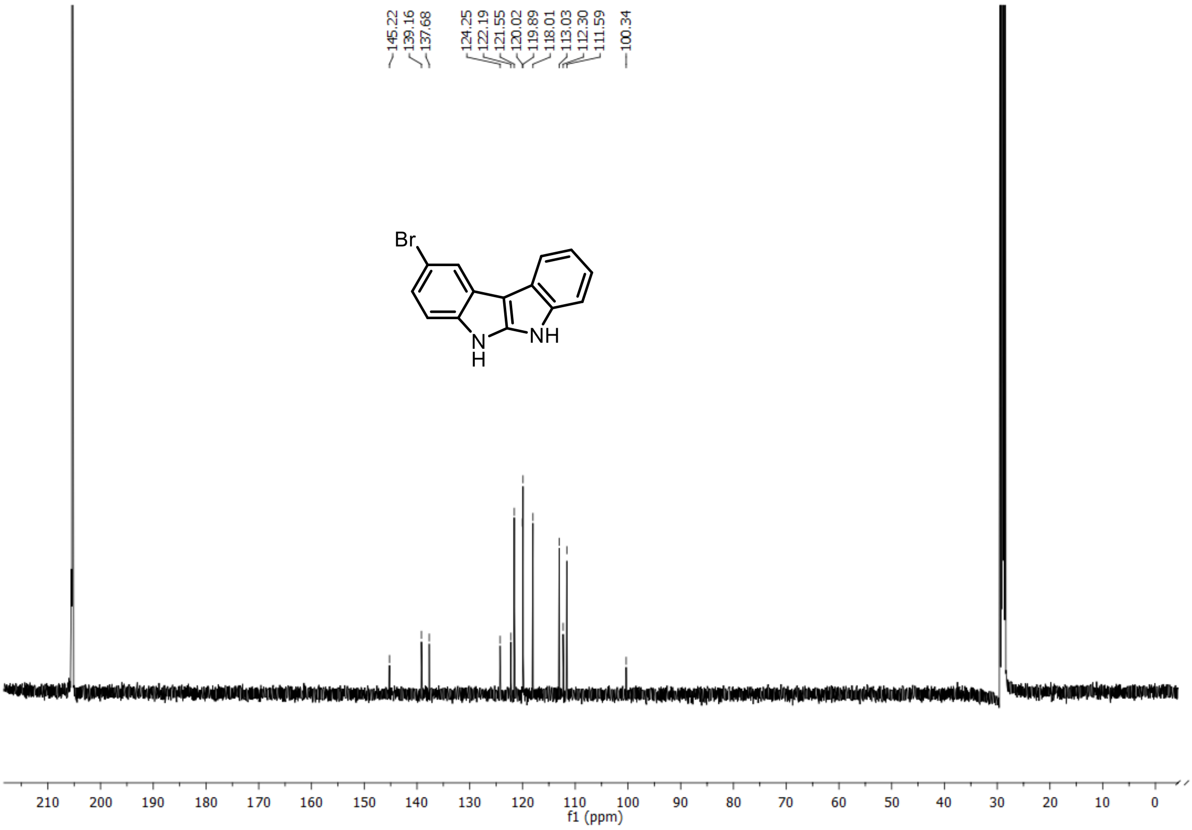
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) Spectra of **12**



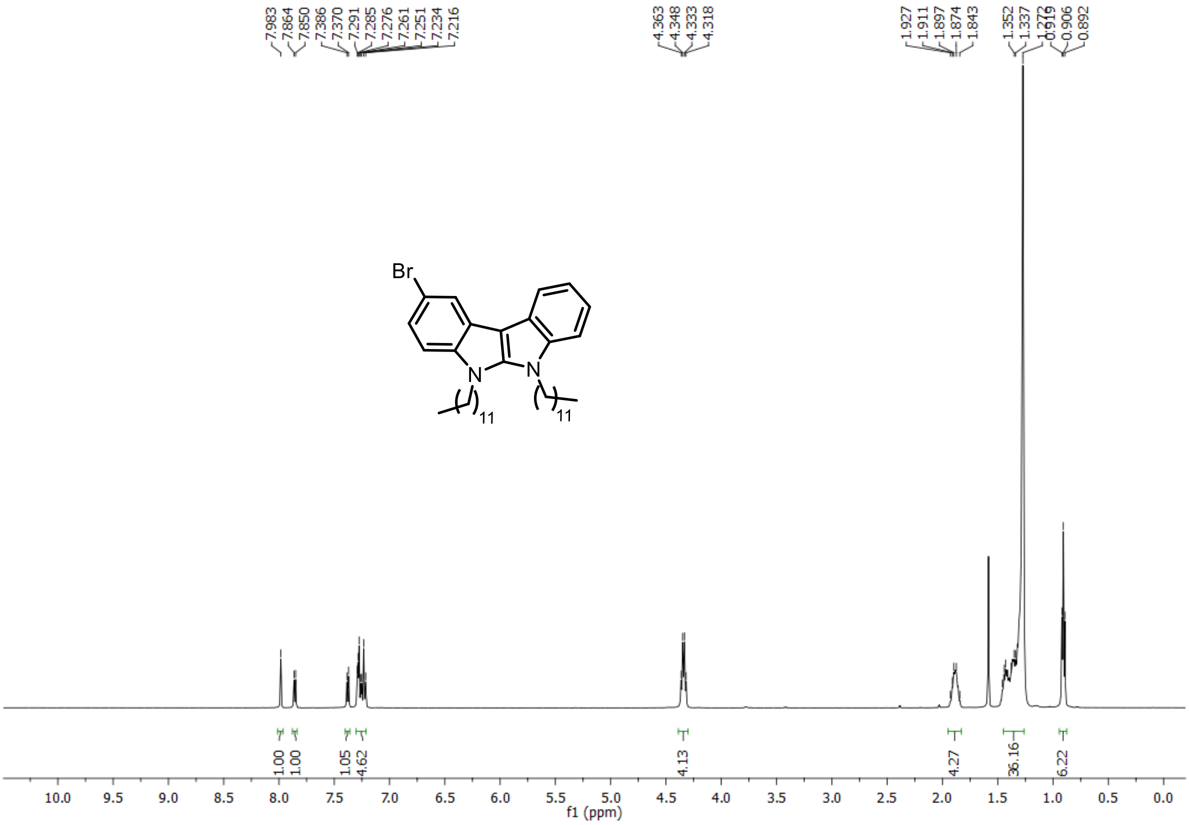


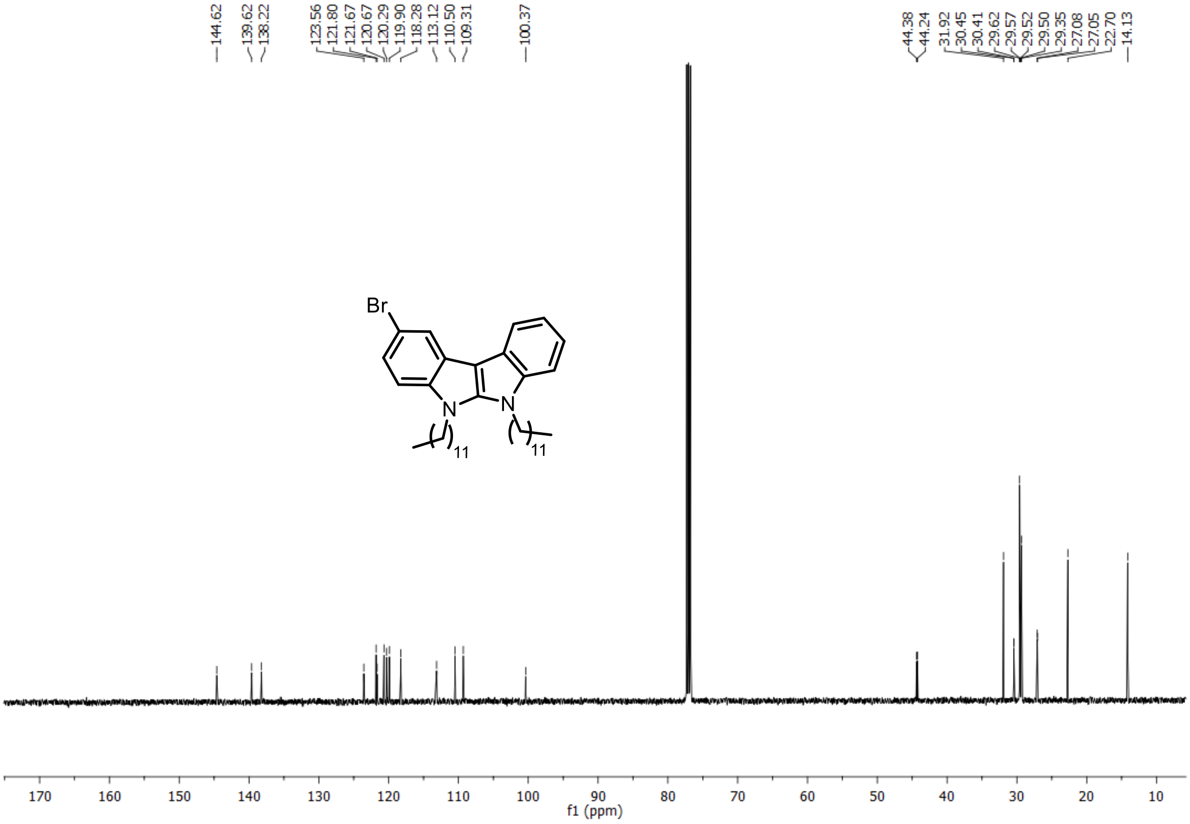
^{1}H NMR (500 MHz, $(CD_3)_2CO$) & ^{13}C{^{1}H} (125 MHz, $(CD_3)_2O$) Spectra of **13**



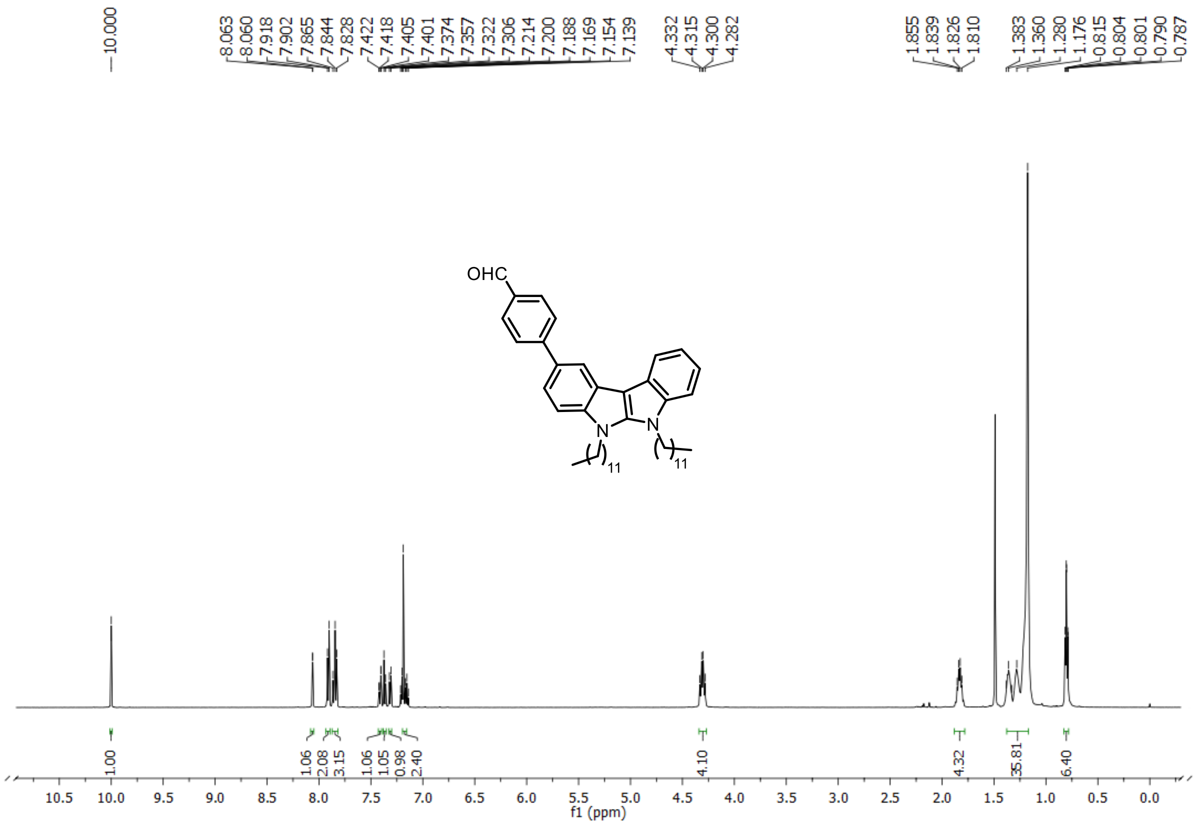


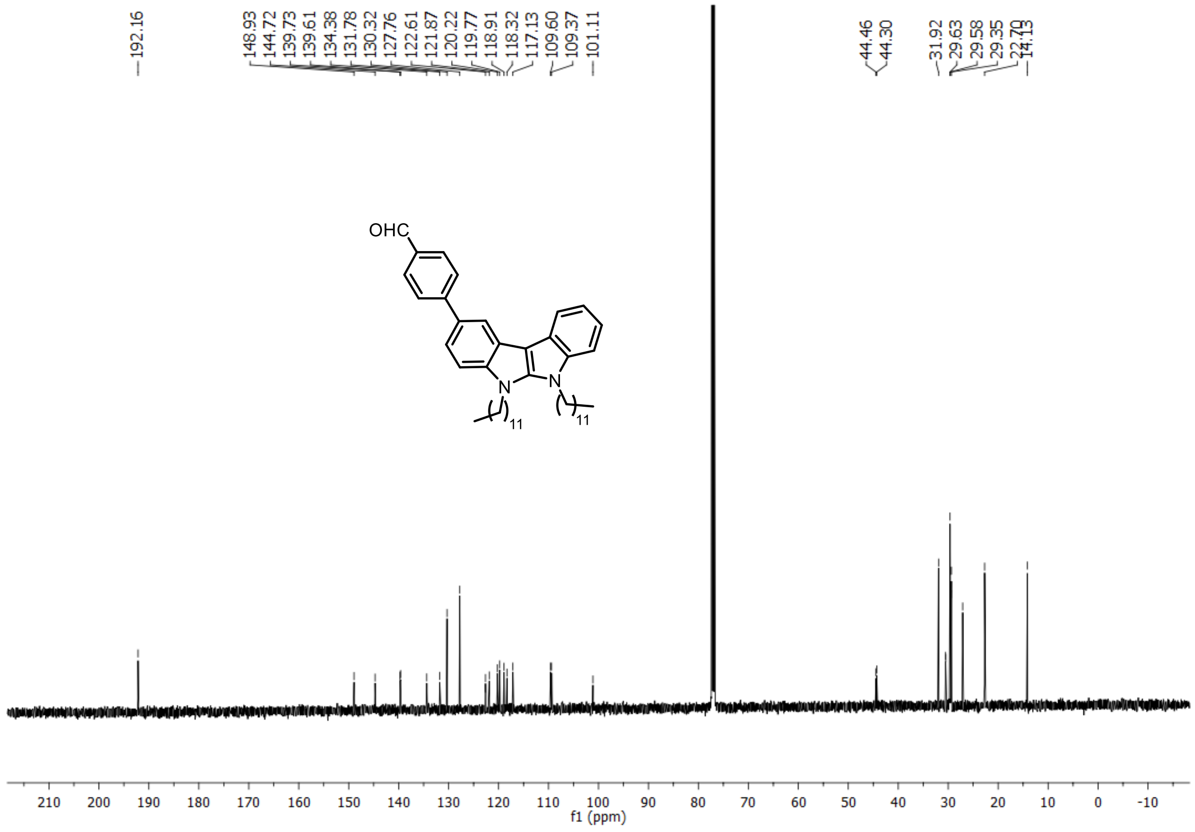
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) Spectra of **14**



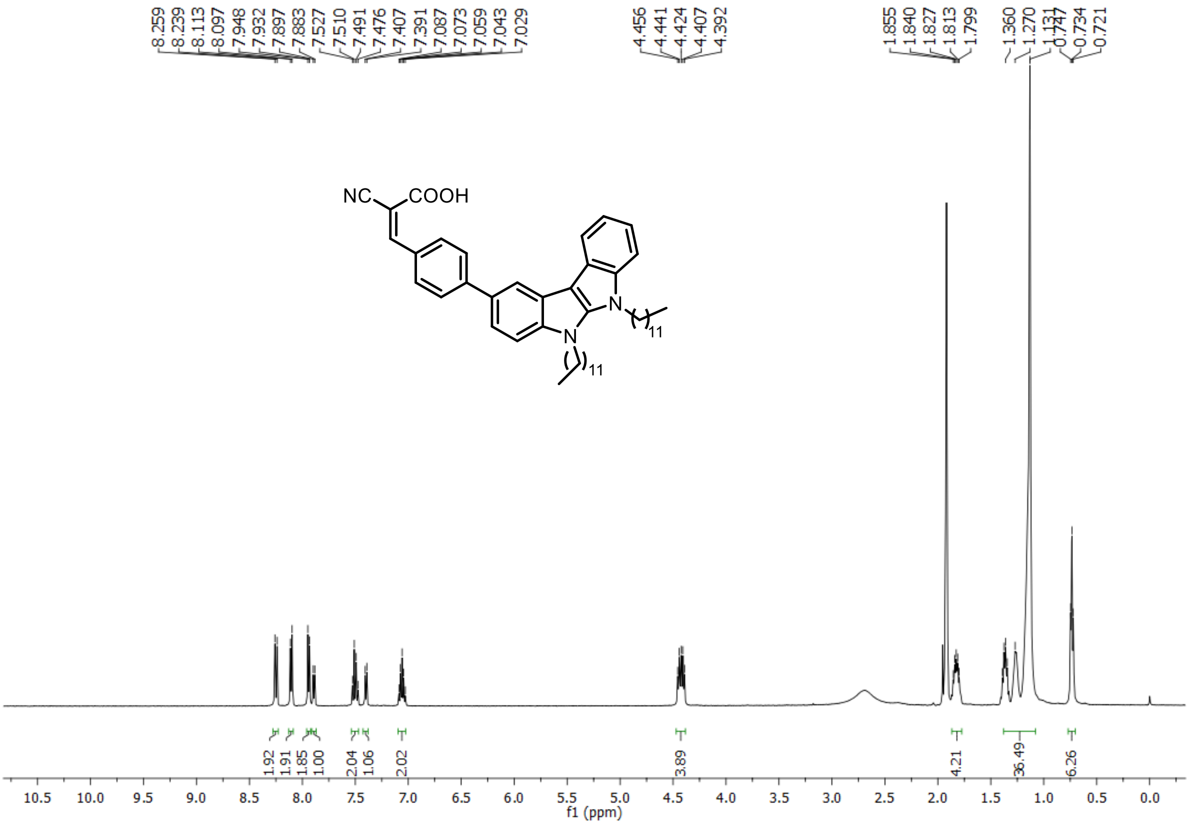


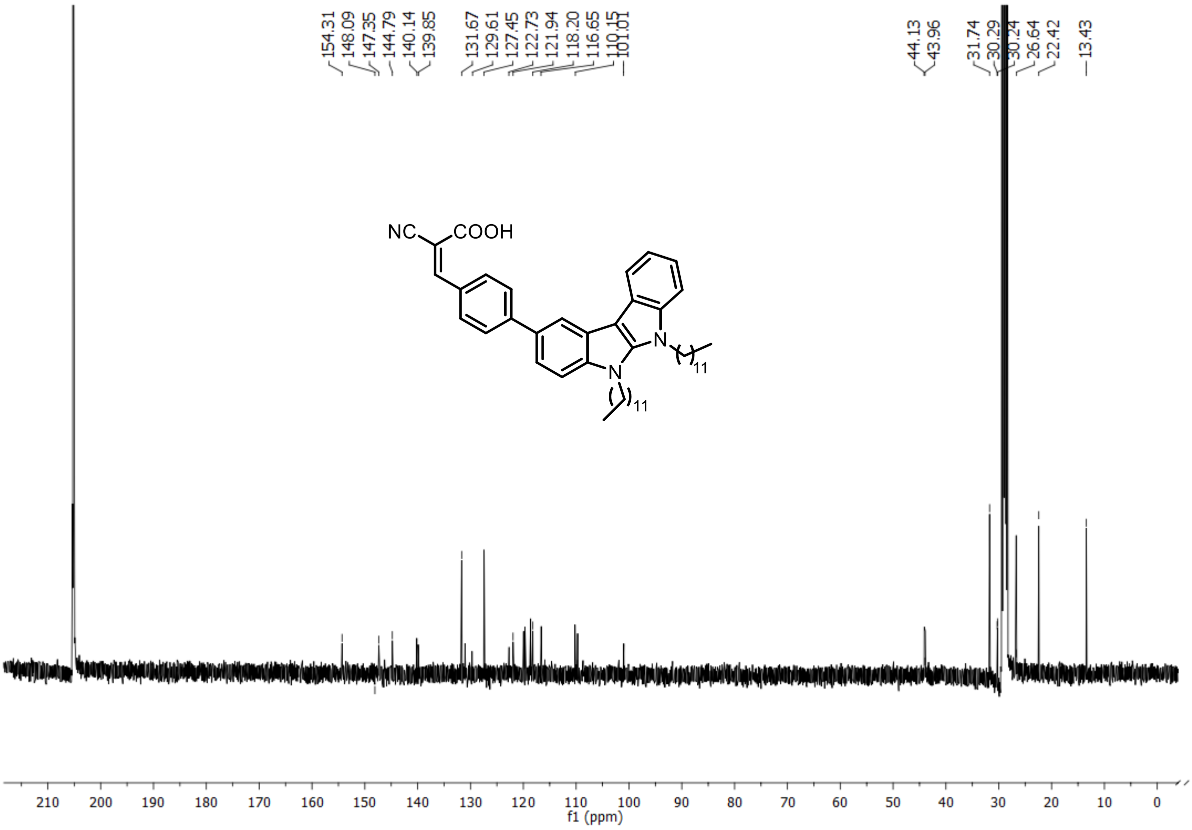
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) Spectra of **15**



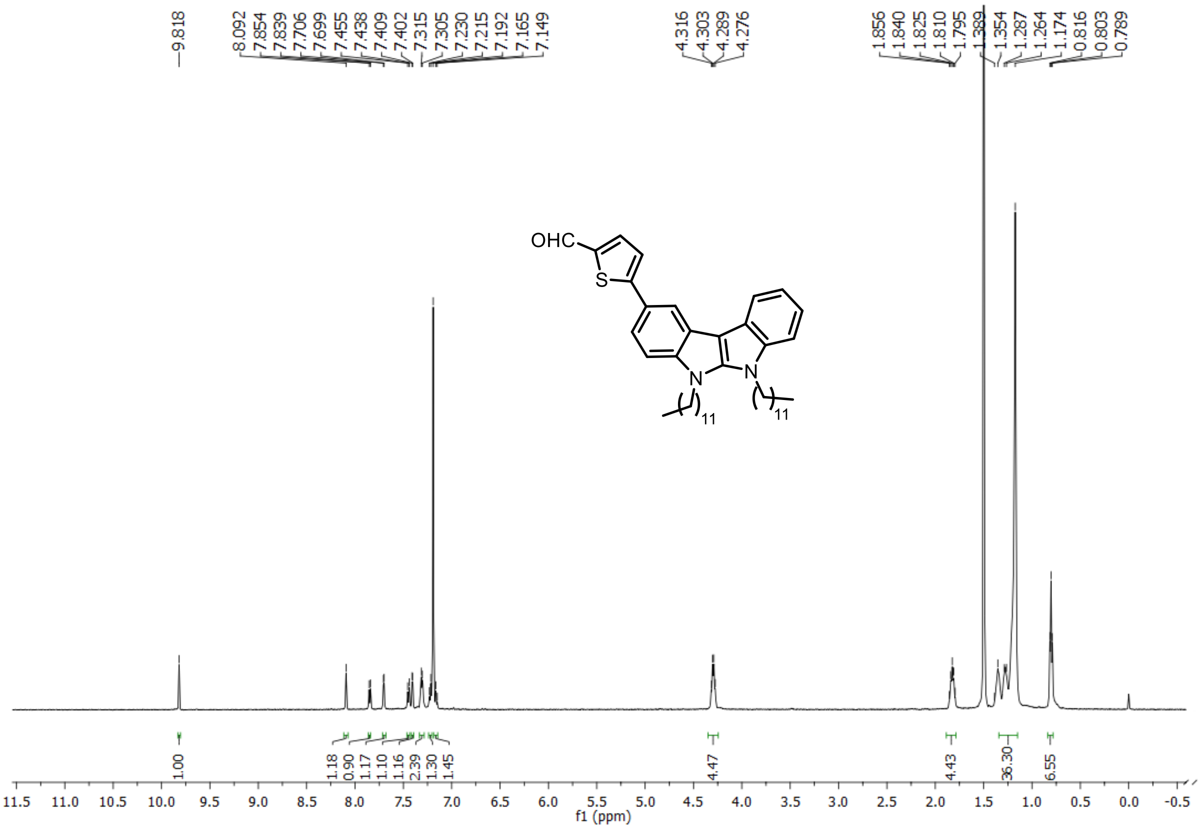


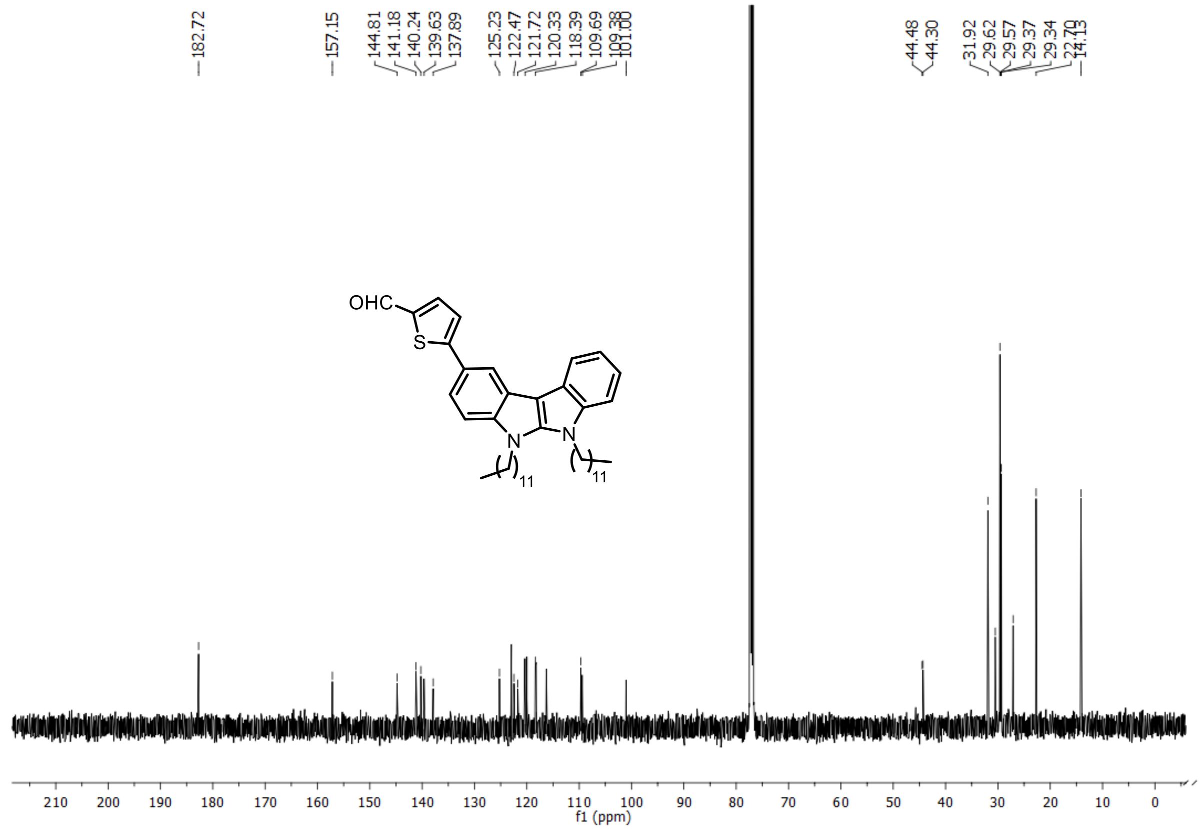
^{1}H NMR (500 MHz, (CD$_3$)$_2$CO) & ^{13}C{^{1}H} (125 MHz, (CD$_3$)$_2$O) Spectra of **IID-7**



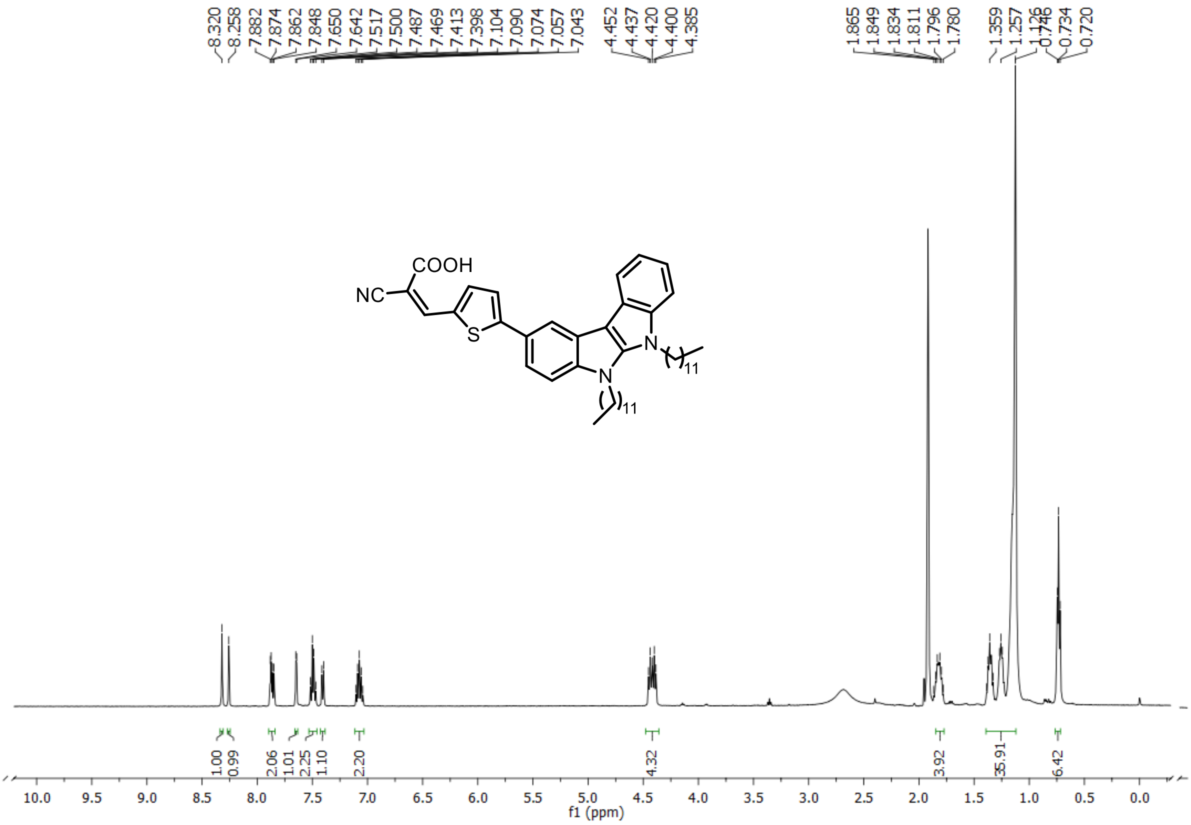


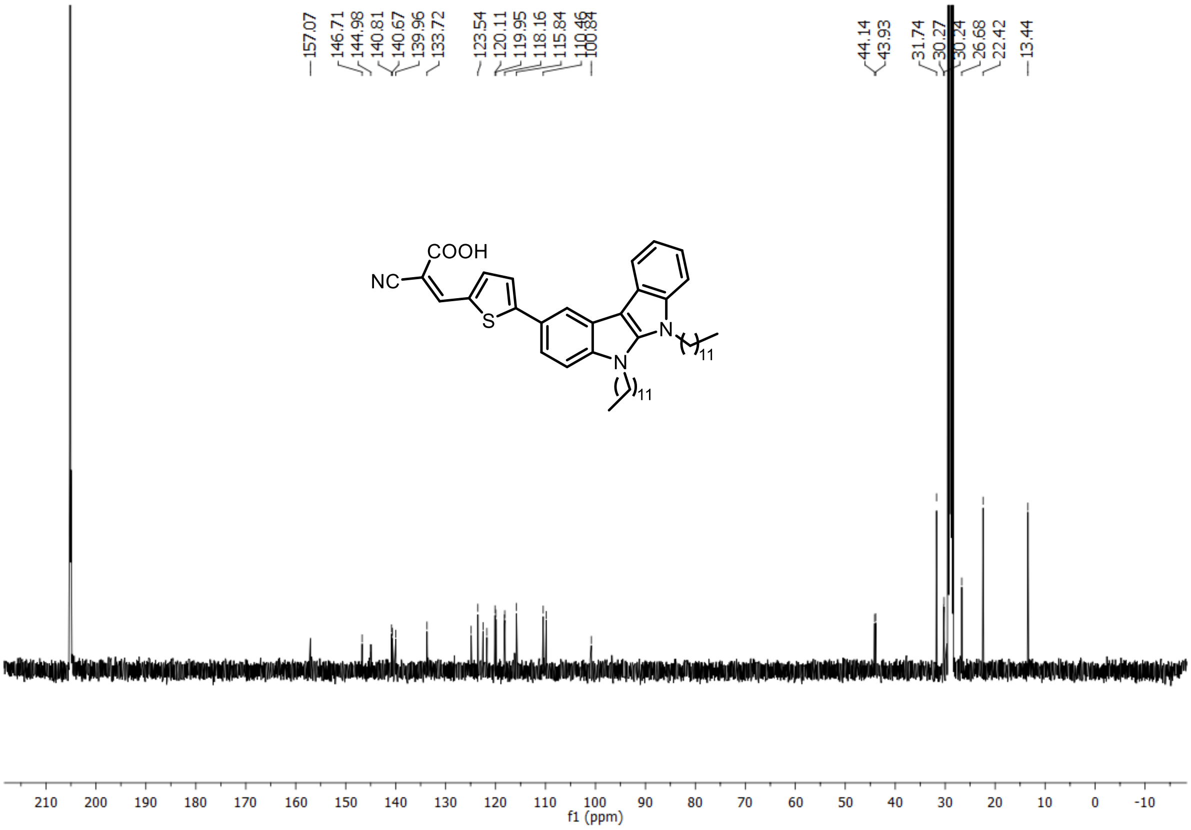
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) Spectra of **16**



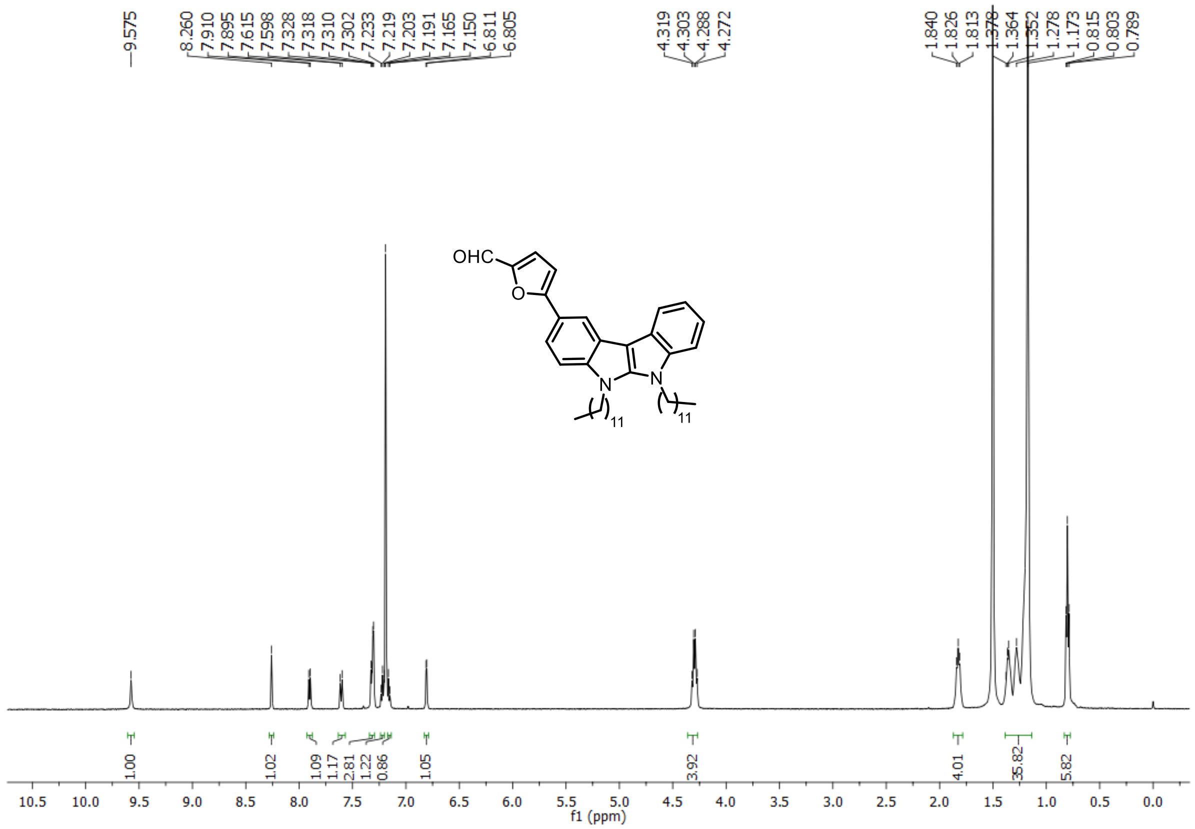


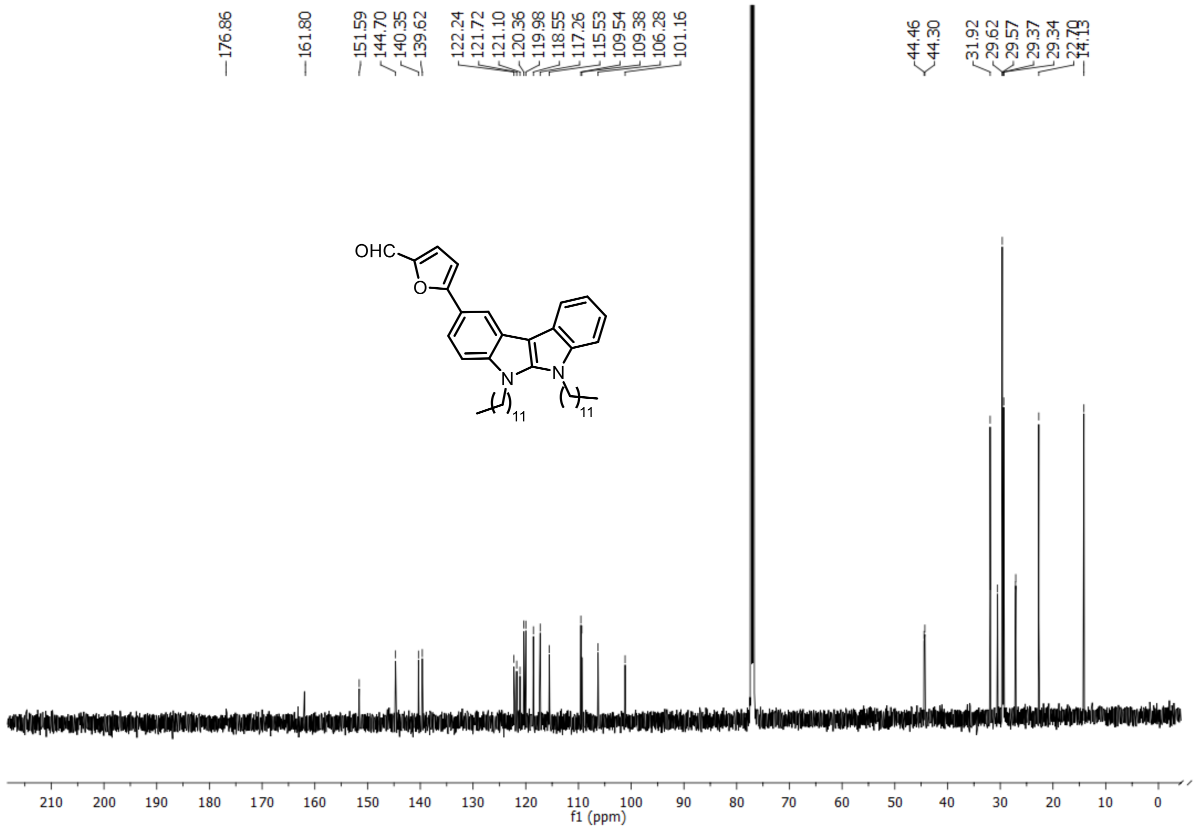
^{1}H NMR (500 MHz, (CD$_3$)$_2$CO) & ^{13}C{^{1}H} (125 MHz, (CD$_3$)$_2$O) Spectra of **IID-8**



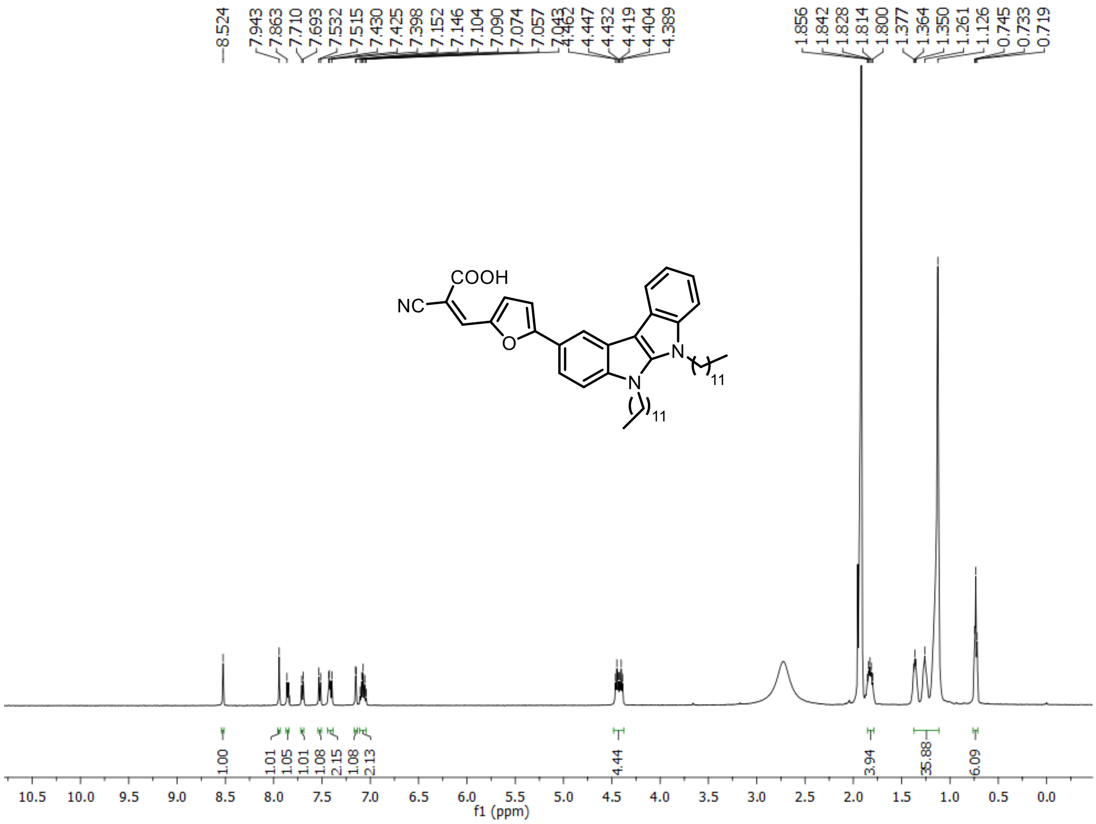


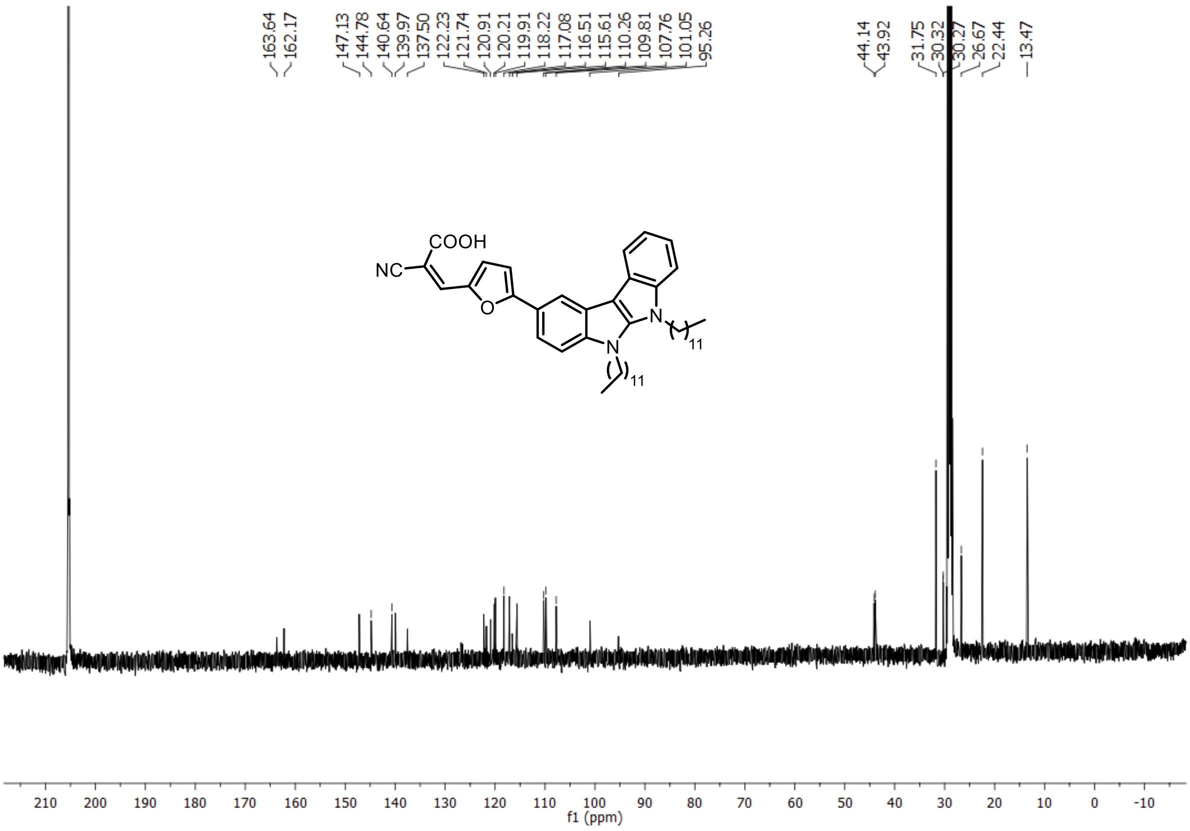
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **17**



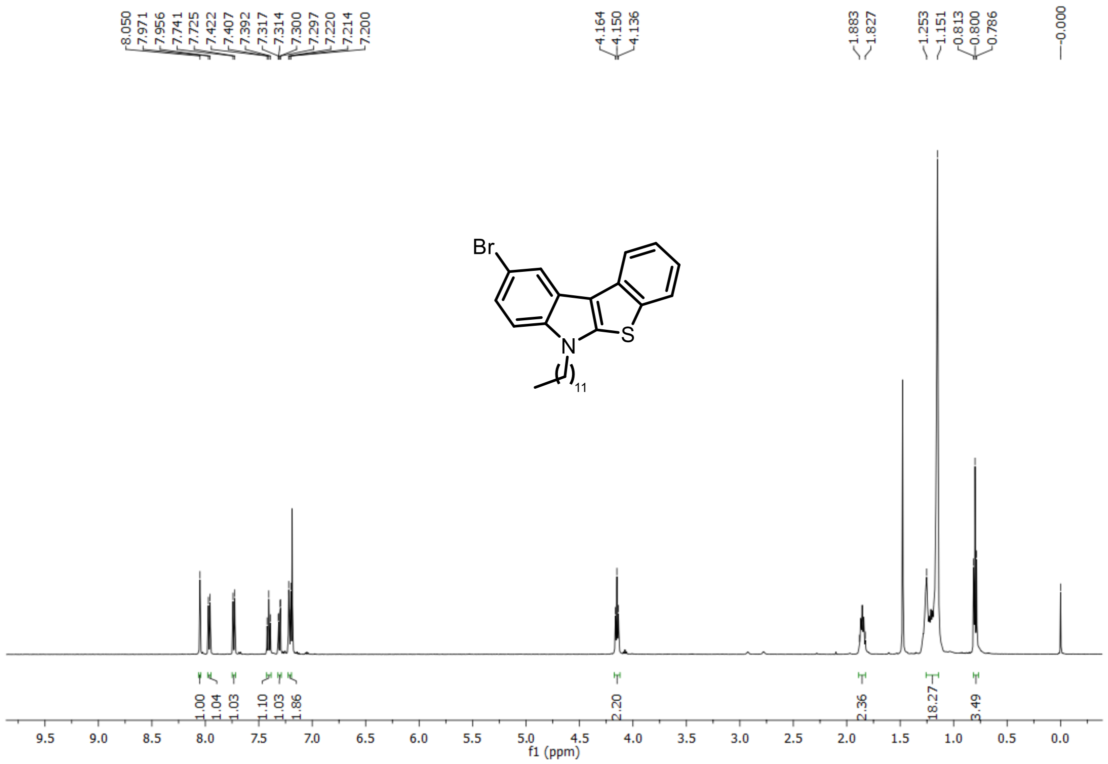


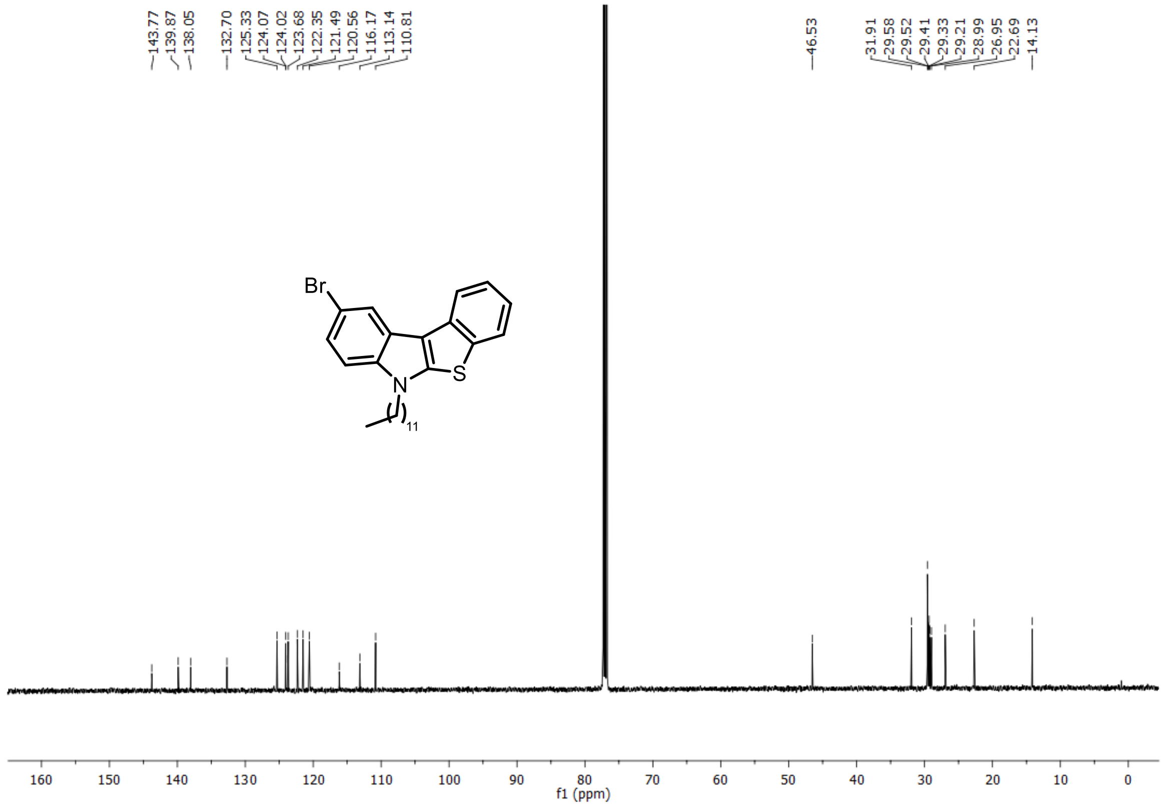
^{1}H NMR (500 MHz, (CD$_3$)$_2$CO) & ^{13}C{^{1}H} (125 MHz, (CD$_3$)$_2$O) Spectra of **IID-9**



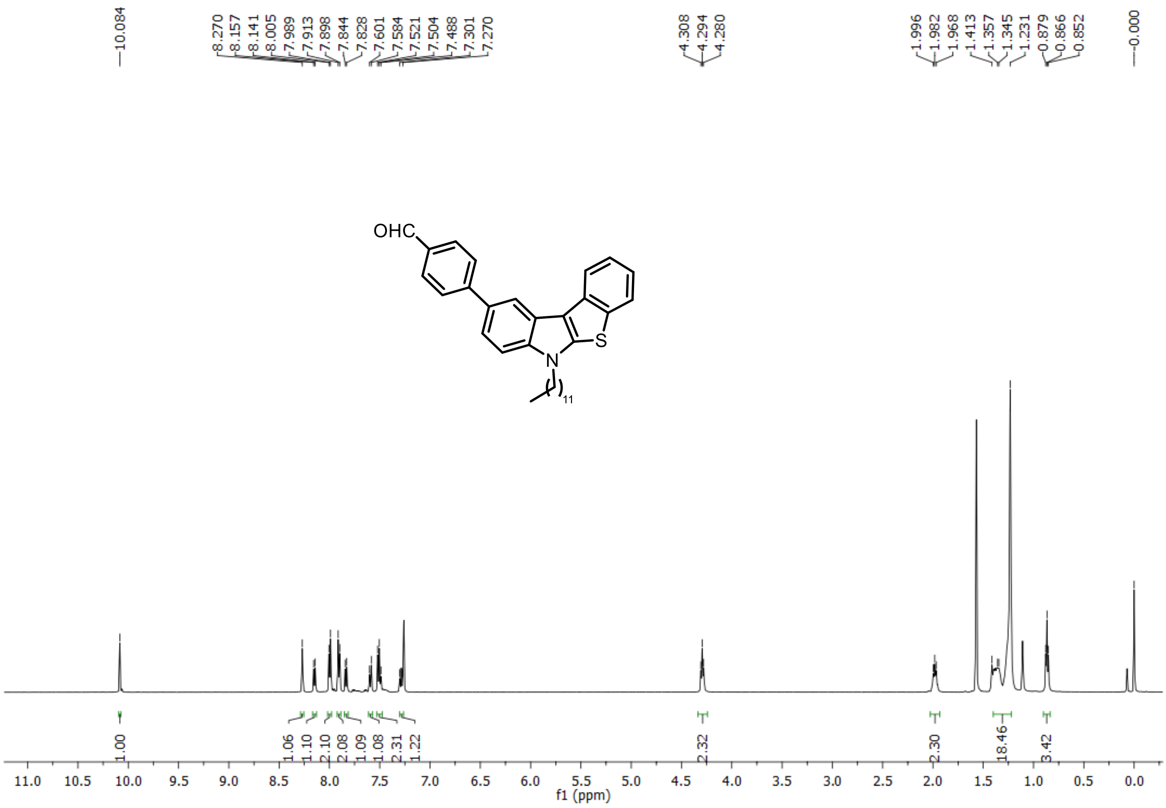


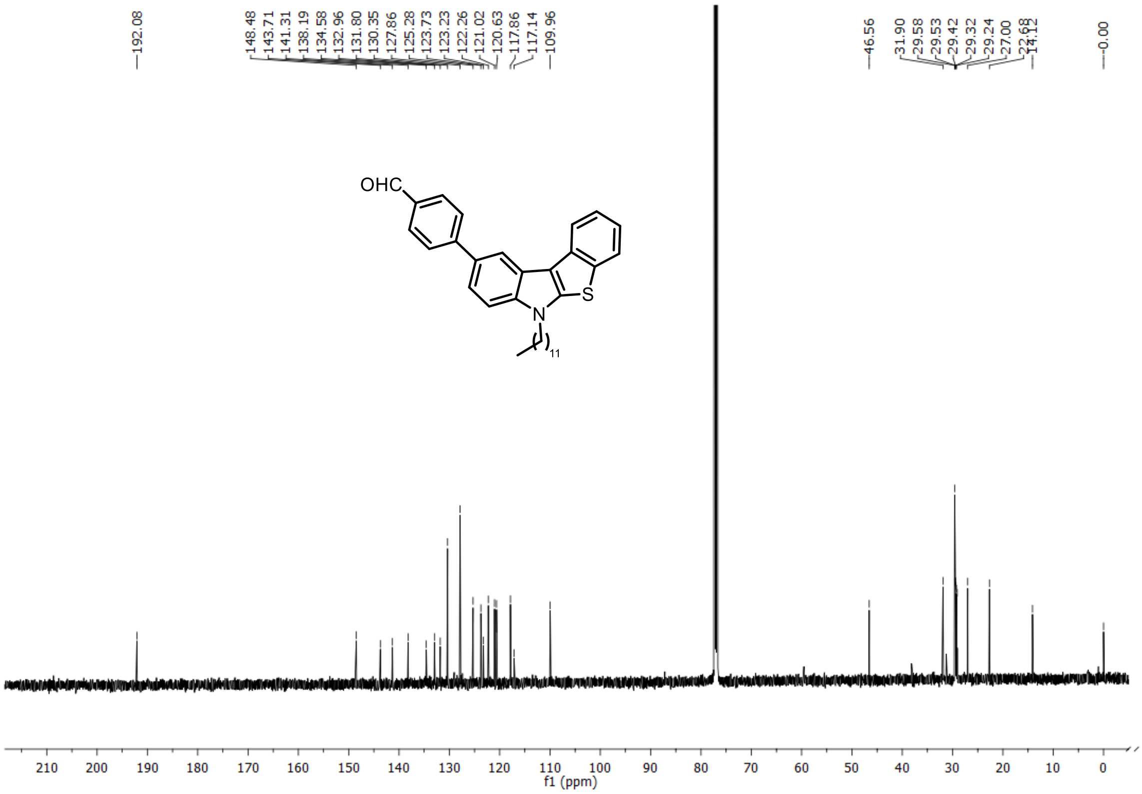
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **19**



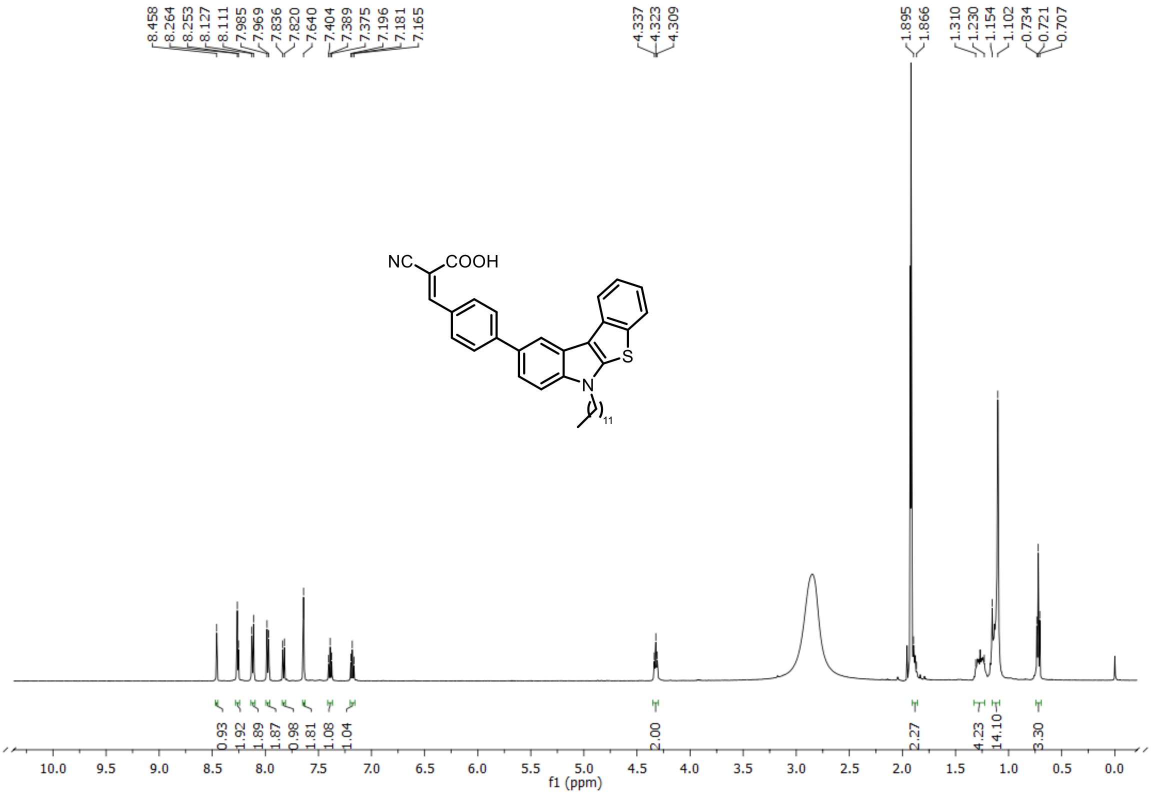


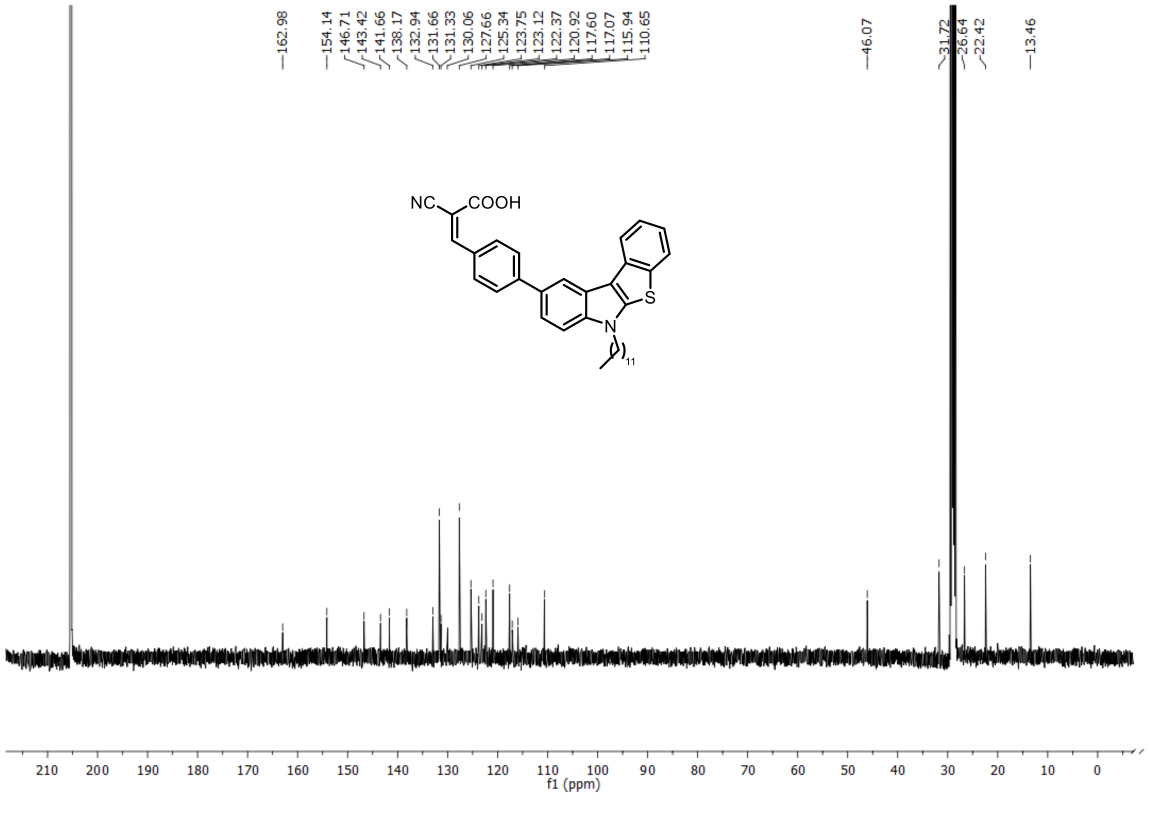
^{1}H NMR (500 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) Spectra of **20**



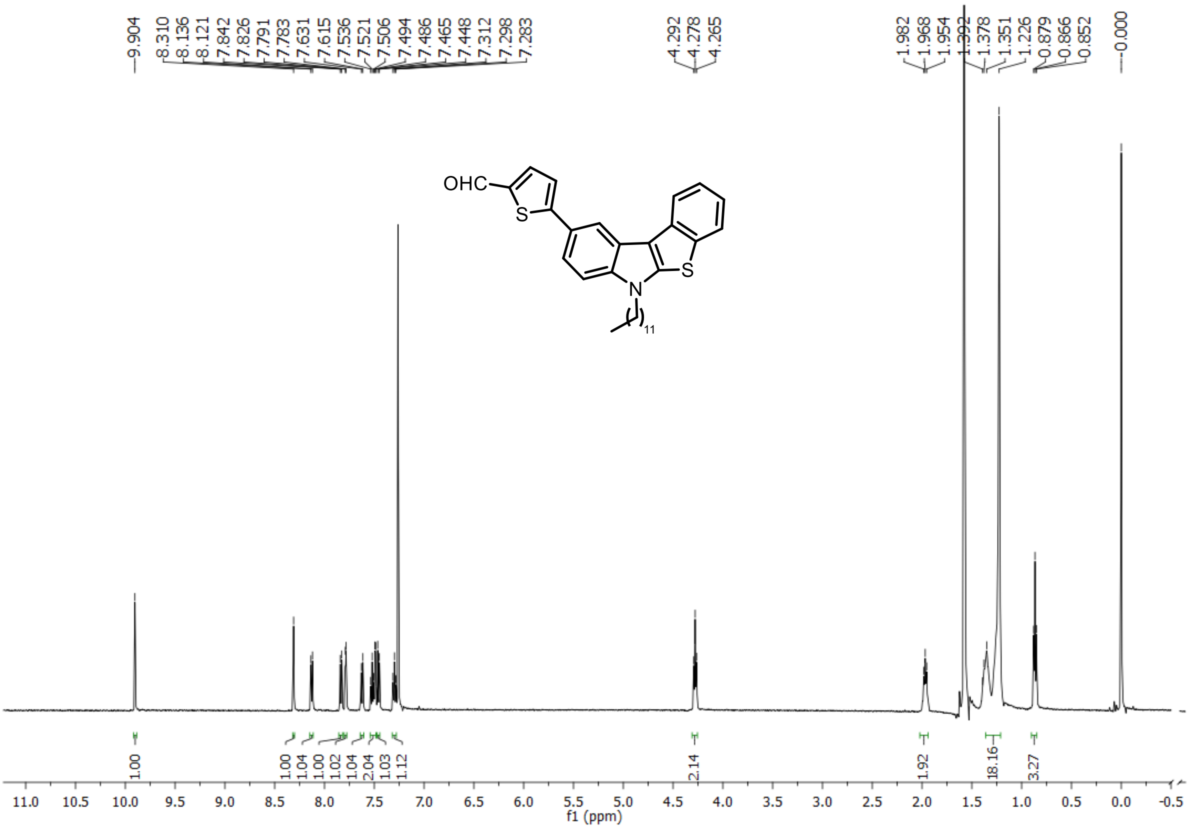


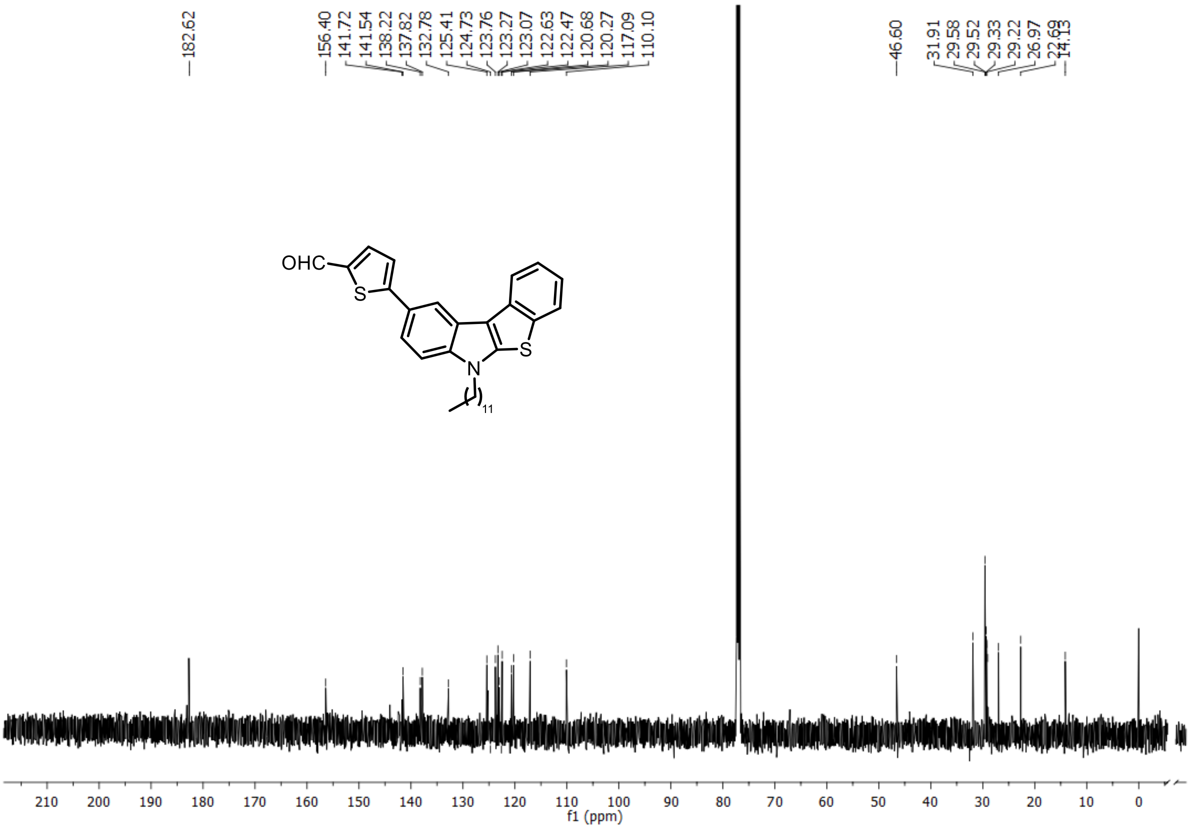
^{1}H NMR (500 MHz, (CD$_3$)$_2$CO) & ^{13}C{^{1}H} (125 MHz, (CD$_3$)$_2$O) Spectra of **BID-4**



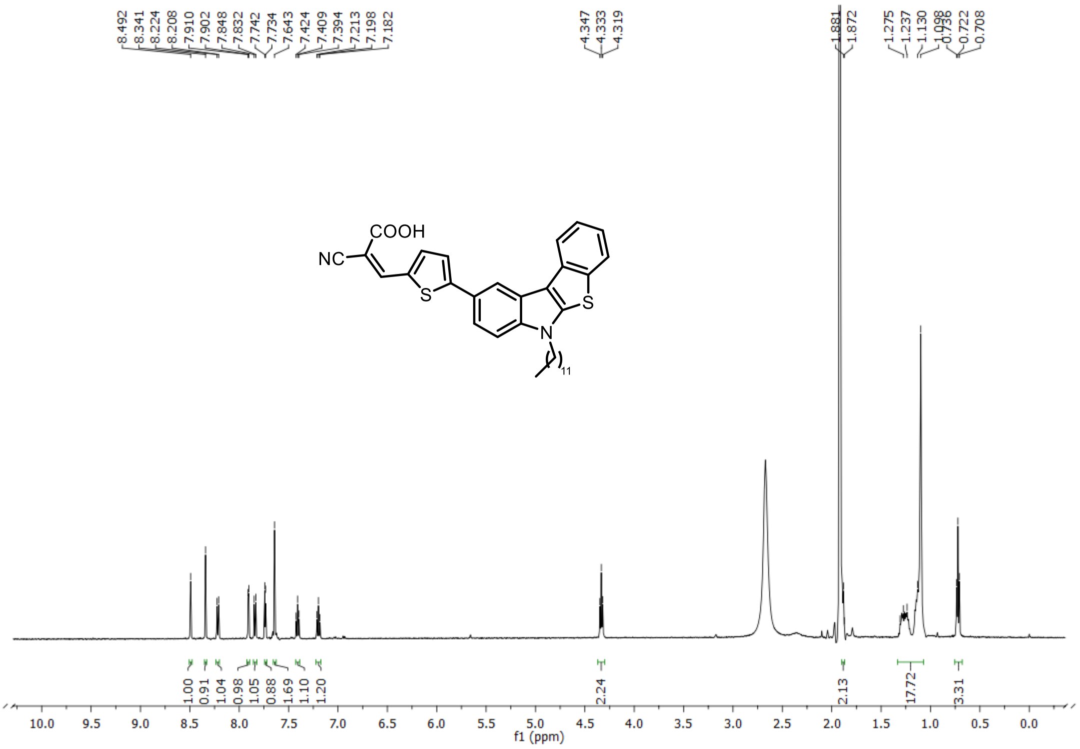


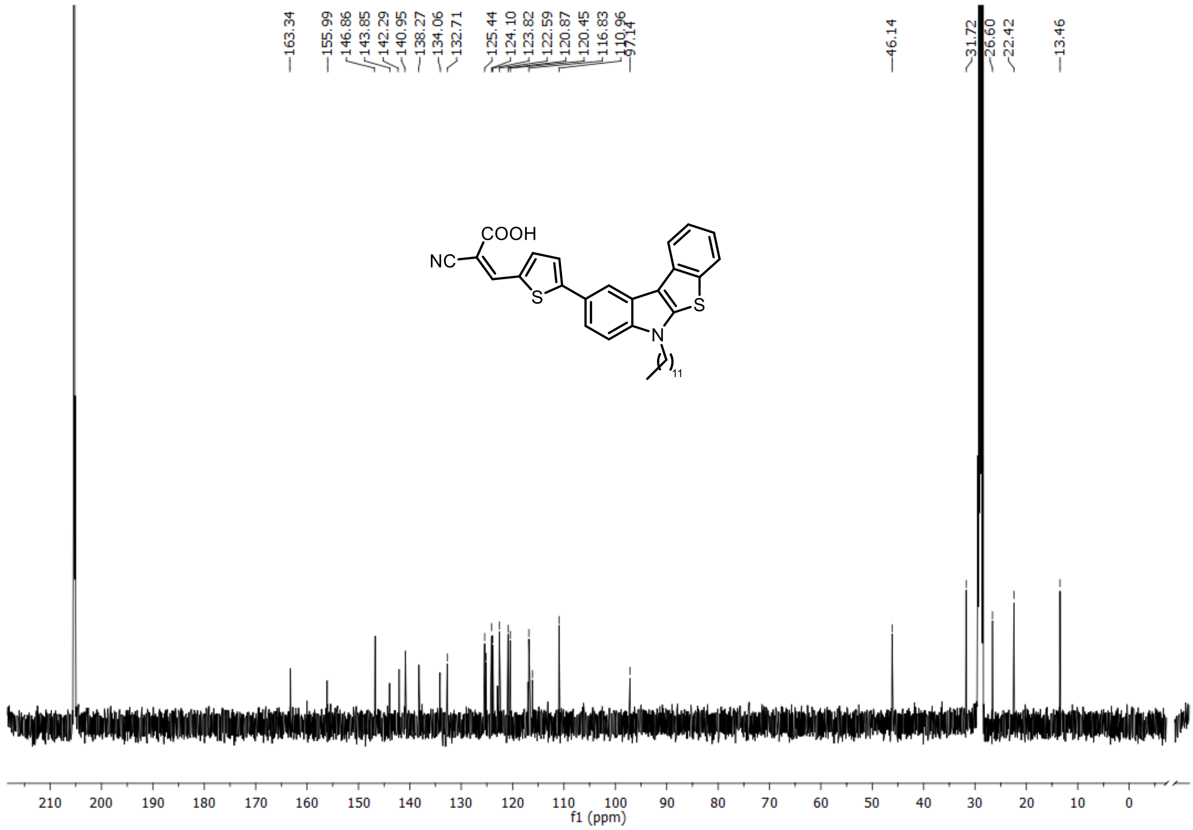
^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **21**



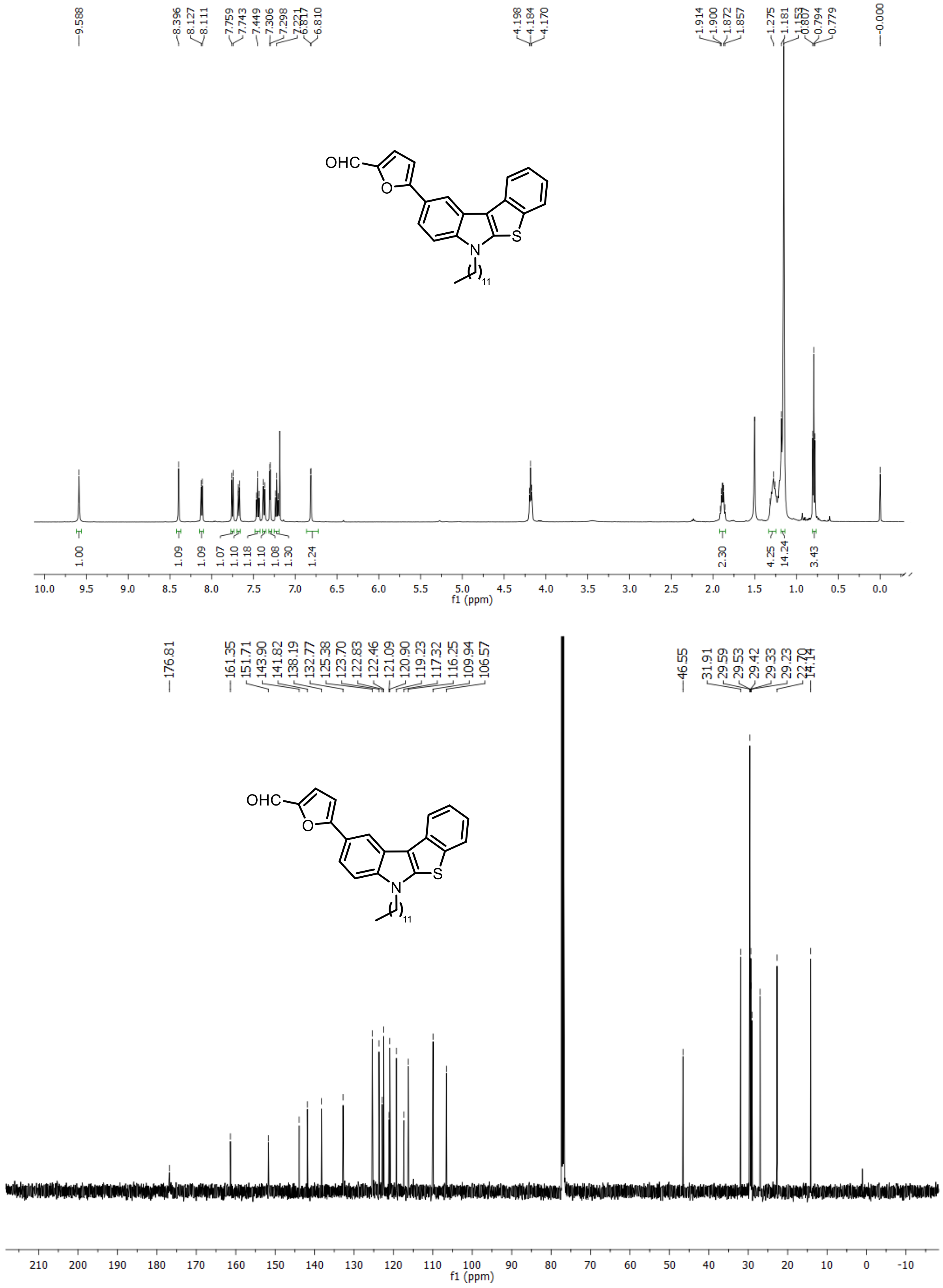


^{1}H NMR (500 MHz, $(CD_3)_2CO$) & $^{13}C\{^{1}H\}$ (125 MHz, $(CD_3)_2O$) Spectra of **BID-5**

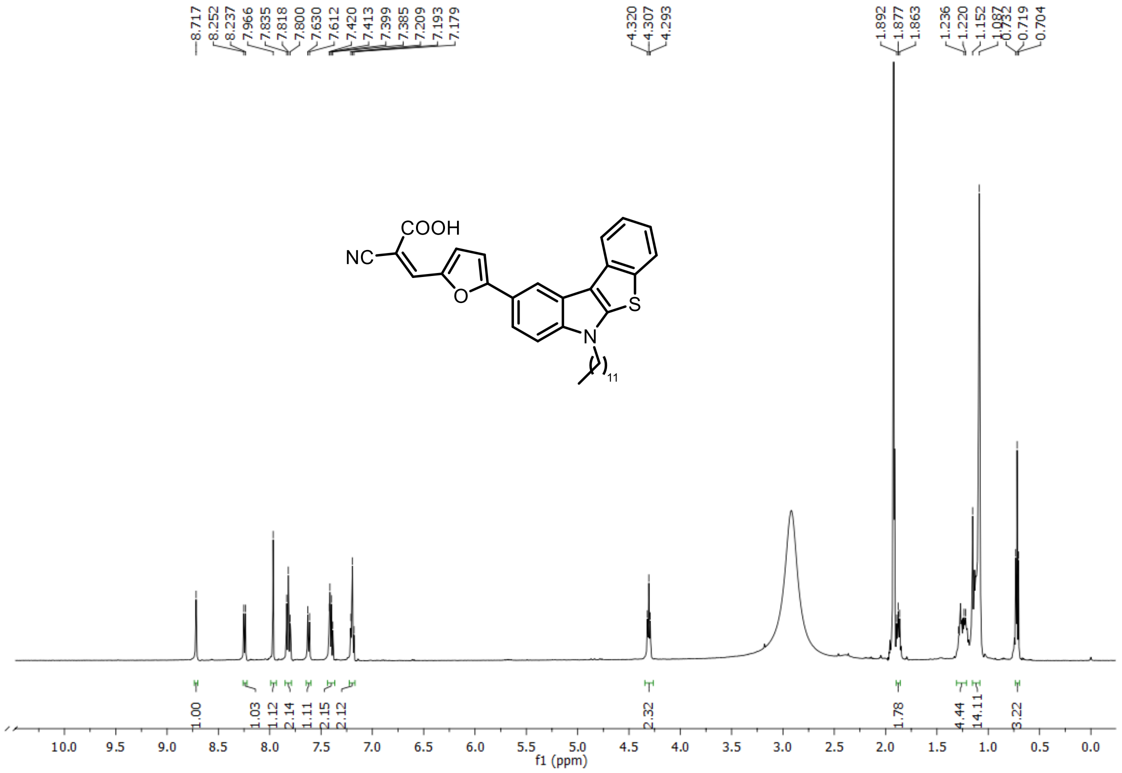


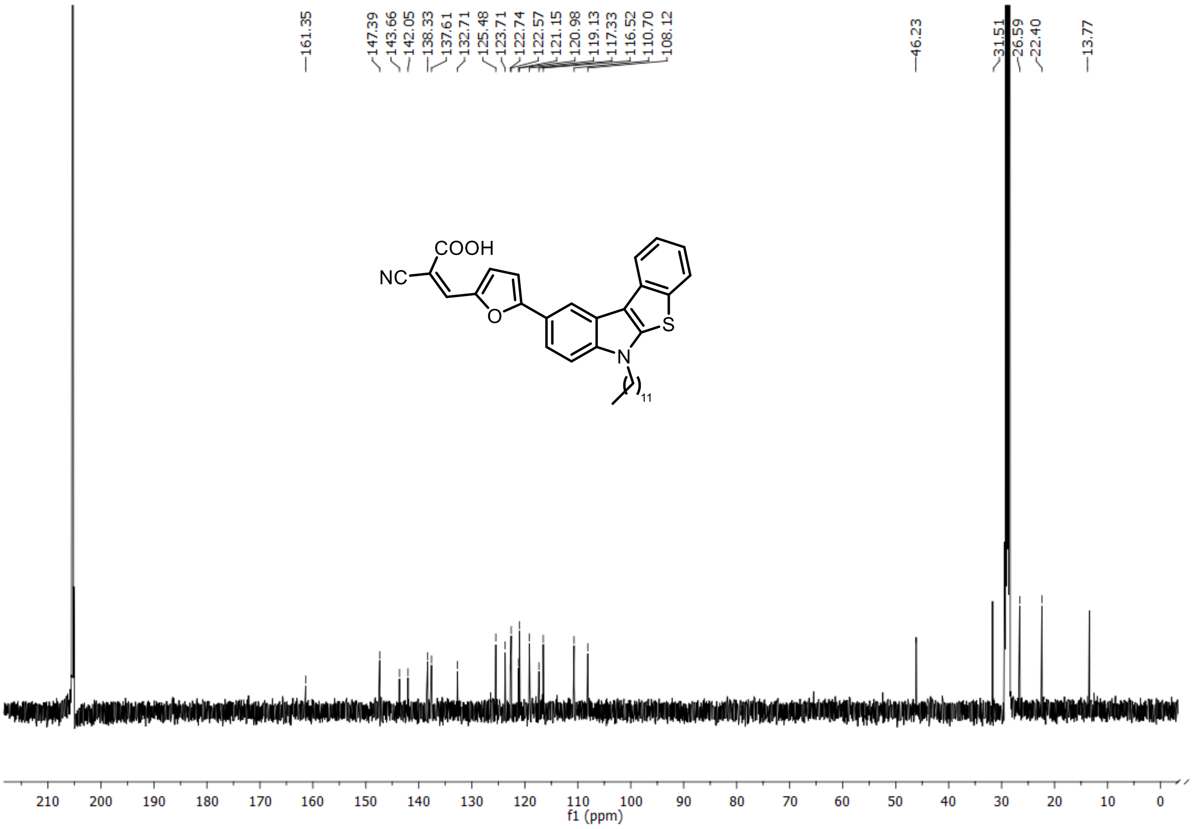


^{1}H NMR (500 MHz, CDCl$_3$) & ^{13}C{^{1}H} (125 MHz, CDCl$_3$) Spectra of **22**



^{1}H NMR (500 MHz, $(CD_3)_2CO$) & $^{13}C\{^1H\}$ (125 MHz, $(CD_3)_2O$) Spectra of **BID-6**





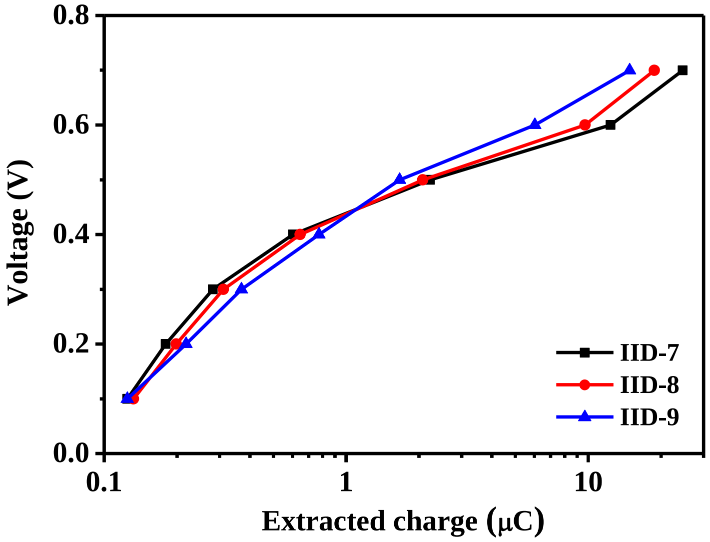


Figure S1. Charge extraction plot for devices fabricated with **IID-7**, **IID-8**, and **IID-9** as sensitizers.

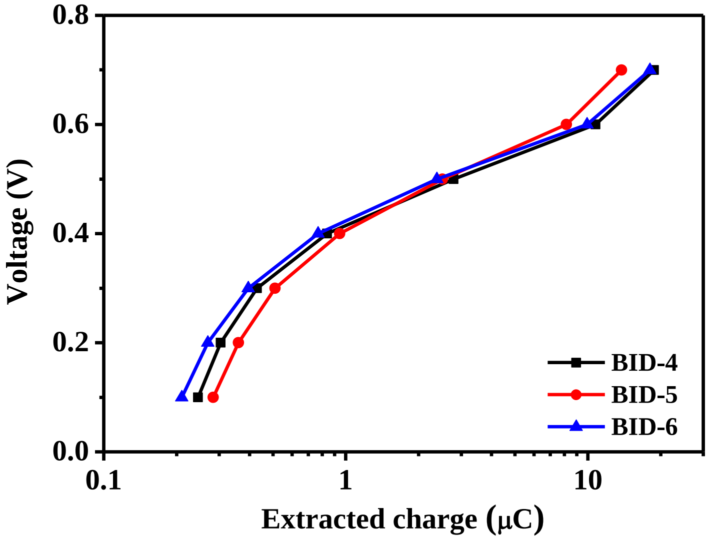


Figure S2. Charge extraction plot for devices fabricated with **BID-4**, **BID-5**, and **BID-6** as sensitizers.

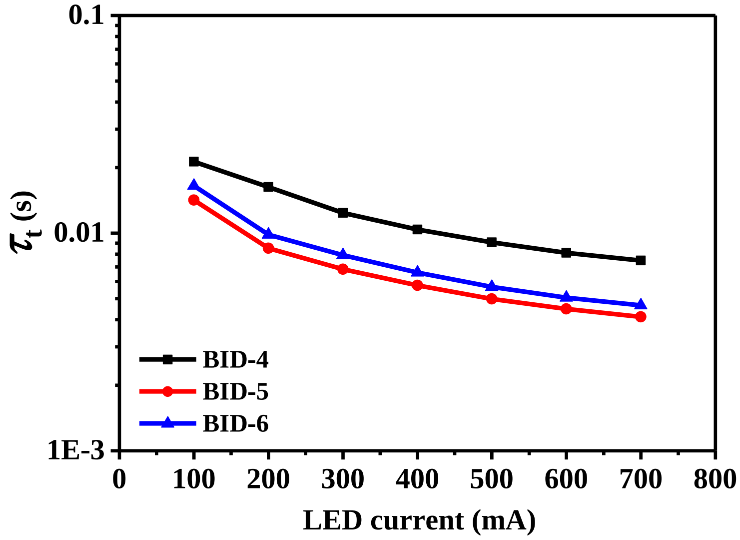


Figure S3. Transport time (τ_t) measured using transient photocurrent decay for DSSCs with **BID-4**, **BID-5**, and **BID-6** sensitizers.