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π-Conjugation Expanded Isoindigo Derivatives and the Donor-Acceptor Conjugated Polymers: Synthesis and Characterization

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1. Materials and Characterization

(*E*)-6-bromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione, (*E*)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione, di-*tert*-butyl-2,5-dibromterephthalate (**2**) and (*E*)-1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (**6**) were synthesized following the reported literatures. ^{1}H NMR and ^{13}C NMR spectra were measured by a Bruker 400-MHz spectrometer in $CDCl_3$, CD_2Cl_2 or 1,1,2,2-$C_2D_2Cl_4$ at room temperature or 120 °C with tetramethylsilane (TMS) as internal standard. Molecular mass was characterized by a Bruker/AutoflexIII Smartbean MALDI mass spectrometer with 2-[(2*E*)-3-(4-tert-buthylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix in reflection mode. High temperature gel permeation chromatography (GPC) analysis of the polymers was carried out on a PL-GPC 220 system with polystyrene as the standard and 1,2,4-trichlorobenzene as the eluent at 150 °C. Elemental analysis was conducted on a VarioEL elemental analysis system. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were performed by a Perkin-Elmer TGA-7 and Perkin-Elmer DSC7 thermal analyzer, respectively, with a heating/cooling rate of 10 °C/min under N_2. UV-vis-NIR Absorption spectra were obtained on a UV-3600 spectrophotometer (Shimadzu). The optical bandgap was calculated according to film absorption onset ($E_g^{opt} = 1240/\lambda_{onset}$ eV). Cyclic voltamograms (CV) of the small compounds were obtained by a CHI660 electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV/s in anhydrous chloroform ($CHCl_3$) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 mol/L) as the supporting electrolyte. A glassy carbon with 10 mm diameter, a Pt wire and a saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. CV of the polymers were measured in anhydrous acetonitrile (CH_3CN) and the films were spin coated on the working electrode. The potential was calibrated by ferrocene/ferrocenium (Fc/Fc^+), and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: $E_{HOMO} = -(4.46+E_{onset}^{ox})$ eV, $E_{LUMO} = -(4.46+E_{onset}^{re})$ eV. DFT calculation was carried out on the Gaussian 09 package program by means of B3LYP/6-31G, all alkyl substituents were replaced with methyl groups in order to simplify the calculations. Out-of-plane XRD was measured by a Bruker D8 Advance using CuK_α radiation ($\lambda = 1.54056$ Å) and operated at 40 kV and 30 mA. In-plane XRD was conducted on a Rigaku Smart Lab with CuKα source ($\lambda = 1.54056$ Å). Atomic force microscopy (AFM) images were recorded in tapping mode on a SPI3800N (Seiko Instruments Inc., Japan).

2. Fabrication and characterization of organic field-effect transistors (OFETs) devices

Top-gate/bottom-contact (TGBC) configuration OFETs were fabricated on silicon wafers covered with SiO_2. The substrates were cleaned by an ultrasonic cleaner with deionized water, acetone and isopropanol, then dried under a nitrogen flow. The substrates were heated at 110 °C for 30 min and treated with UV-zone instrument for 15 min. 25 nm thicker Au were evaporated as S/D electrodes with W/L = 70 (W = 5.6 mm, L = 80 μm). Semiconductor layer was spin-coated using *o*-DCB as solution with a concentration of 4.0 mg mL^{-1} at 1000 rpm yield the thickness of ~ 30 nm, then annealed at 150, 200 and 250 °C for 15 min. Afterward, the solution of PMMA (poly(methyl methacrylate, Mw = 120 kDa) in butyl acetate (80 mg/Ml) was spin-cast on polymer active layer with the thickness ~600 nm at 1200 rpm for 1 min and then annealed for 60 min at 100 °C. Finally, 70 nm thicker Au was deposited on it as gate electrode. All devices were tested with two Keithley 236 source/measure units at room temperature in ambient conditions. Field-effect mobility was calculated in the saturation regime by using the equation: $I_{DS}^{sat} = (\mu C_i W/2L)(V_{GS} - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer, V_{GS} and V_T are the gate voltage and threshold voltage, respectively.

3. Synthetic procedure

(*E*)-1,1'-Bis(2-hexyldecyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione **(1)**

The solution of bis(pinacolato)diboron (1.79 g, 7.0 mmol), (*E*)-6-bromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (2.78 g, 3.5 mmol), KOAc (1.86 g, 1.9 mmol) and $Pd(dppf)Cl_2$ (139 mg, 0.19 mmol) in dioxane (60 mL) was stirred at 80 °C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water (300 mL) and extracted with CH_2Cl_2(100 mL). The organic extracts were washed with brine (300 mL×3) and dried with $MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using PE:CH_2Cl_2 (1:1, v/v) as the eluent to afford **1** as a brownness solid in a yield of 78% (2.30 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.18 (d, *J* = 8.0 Hz, 1H), 9.13 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17 (s, 1H), 7.03(t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 3.70-3.65 (m, 4H), 1.93 (m, 2H), 1.36-1.24 (m, 57H), 0.85 (m, 12H).

Di-*tert*-butyl 2,5-bis((*E*)-1,1'-bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl) terephthalate **(3)**

To a 100 mL Schlenk tube, compound **1** (2.3 g, 2.75 mmol) and **2** (390 mg, 0.92 mmol), K_3PO_4 (1.95 g, 8.0 mmol), P(*o*-tol)$_3$ (1.39 mg, 0.046 mmol), $Pd_2(dba)_3$ (57 mg, 0.062 mmol) and toluene/H_2O (30/6 mL) were added. The mixture was stirred at 95 °C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed with brine (200 mL×3) and dried with

$MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using PE: CH_2Cl_2 (1:3, v/v) as the eluent to afford **3** as a brown solid in a yield of 87% (1.35 g). ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm) = 9.28 (d, *J* = 8.4 Hz, 2H), 9.22 (dd, *J* = 8.0 Hz, 2H), 7.79 (s, 2H), 7.36 (dt, *J* = 7.6 Hz, 2H), 7.04 (m, 4H), 6.79 (dt, *J* = 7.6 Hz, 4H), 3.71-3.68 (m, 8H), 1.94 (m, 4H), 1.36-1.23 (m, 114H), 0.85 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.54, 168.32, 166.58, 145.26, 145.17, 144.73, 140.93, 134.63, 133.60, 132.93, 132.34, 131.46, 129.82, 129.66, 122.69, 122.14, 121.78, 121.04, 108.28, 108.15, 82.21, 44.47, 44.60, 36.29, 36.24, 31.86, 31.83, 31.79, 31.66, 30.07, 30.00, 29.72, 29.67, 29.53, 29.27, 29.24, 27.75, 22.65, 22.62, 22.61, 22.59, 14.06. MALDI-TOF MS: Calcd. for $C_{112}H_{166}N_4O_8$: 1695.2706; Found: 1695.2716.

2,5-Bis((*E*)-1,1'-bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl) terephthalic acid **(4)**

Compound **3** (1.1 g, 0.65 mmol) was stirred in a mixture of trifluoroacetic acid (15 mL) and CH_2Cl_2 (45 mL) over night at room temperature. The mixture was poured into water (200 mL). The organic phase was separated, washed with brine (300 mL×3) and dried with anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give **7** as a brown solid (~100%), which was used directly without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.26 (d, *J* = 8.4 Hz, 2H), 9.18 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.05 (m, 4H), 6.80-6.77 (m, 4H), 3.68-3.67 (m, 8H), 1.92 (m, 4H), 1.36-1.23 (m, 96H), 0.84 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.84, 168.48, 145.16, 145.17, 144.72, 143.26, 133.02, 132.54, 131.58, 131.25, 129.48, 128.52, 127.75, 122.33, 120.94, 108.98, 44.50, 36.12, 31.90, 31.77, 31.53, 29.65, 29.30, 26.35, 26.27, 26.24, 22.65, 22.63,14.07, 14.02. MALDI-TOF MS: Calcd. for $C_{104}H_{150}N_4O_8$: 1583.1454; Found: 1583.1433.

(3*E*, 10*E*)-1,8-Bis(2-hexyldecyl)-3,10-bis(1-(2-hexyldecyl)-2-oxoindolin-3-ylidene) -s-indaceno[2,1-f:6,5-f']diindole-2,5,9,12(1*H*,3*H*,8*H*,10*H*)-tetraone **(DIID-PhCO)**

To the solution of **4** (1.0 g, 0.625 mmol) and oxalyl chloride (0.55 mL, 6.25 mmol) in anhydrous CH_2Cl_2 (50 mL), two drops of DMF were added. The mixture was stirred for 0.5 hours at room temperature, then the solvent and volatile materials were evaporated under reduced pressure. The solid was dissolved in anhydrous CH_2Cl_2 (45 mL) and then added to the suspension solution of anhydrous $AlCl_3$ (660 mg, 5.0 mmol) in CH_2Cl_2 (15 mL) at 0 ^{o}C dropwisely. The mixture was stirred at room temperature until the reaction was completed as monitored by thin-layer chromatography (TLC), then poured into ice HCl aqueous solution (1 mol/L). The organic phase was separated, washed with brine (300 mL × 3) and dried with anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the residue was purified by chromatography on silica gel (PE:CH_2Cl_2 = 1:2) to give **DIID-PhCO** as a dark brown solid (650 mg, Yield: 76%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.29 (s, 2H), 8.93 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 2H), 7.14 (m, 2H), 6.82 (t, *J* = 8.0 Hz, 2H), 6.75 (s, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.70 (m, 8H), 1.99-1.89 (m, 2H), 1.41-1.26 (m, 96H), 0.89-0.83 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 190.49, 168.18, 167.39, 150.74, 147.33, 145.48, 144.54, 140.23, 133.40, 132.14, 130.58, 129.85, 127.23, 126.55, 121.33, 121.06, 114.75, 108.15, 101.12, 44.88, 44.62, 36.49, 36.11, 31.96, 31.91, 31.87, 31.74, 30.30, 30.14, 29.80, 29.68, 29.60, 29.42, 29.33, 26.78, 26.22, 22.75, 22.68, 22.64, 14.13, 14.08, 14.05. Elemental Anal. Calcd.: C, 80.68; H, 9.50; N, 3.62. Found: C, 80.56; H, 9.35; N, 3.38. MALDI-TOF MS: Calcd. for $C_{104}H_{146}N_4O_6$: 1547.1242; Found: 1547.1263.

(E)-1,1'-Bis(2-hexyldecyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione **(5)**

To a 100 mL Schlenk tube, compound **1** (340 mg, 0.4 mmol) and **2** (1.06 g, 2.4 mmol), KCO_3 (207 mg, 1.5 mmol), $Pd(PPh)_4$ (23 mg, 0.02 mmol) and toluene/ethanol/H_2O (15/7/1.5 mL) were added. The mixture was stirred at 95 ^{o}C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed with brine (200 mL×3) and dried with $MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using PE: CH_2Cl_2 (1:1, v/v) as the eluent to afford **5** as a brown solid in a yield of 81% (350 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.24 (d, *J* = 8.4 Hz, 2H), 9.20 (d, *J* = 8.0 Hz, 2H), 8.04 (s, 2H), 7.62 (s, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.68 (s, 2H),3.68-3.66 (m, 8H), 1.90 (m, 4H), 1.33-1.22 (m, 96H), 0.84 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.58, 168.54, 168.33, 166.60, 166.57, 145.24, 145.21, 145.16, 144.84, 144.74, 140.97, 134.63, 133.63, 133.02, 132.94, 132.39, 131.50, 129.81, 129.67, 122.70, 122.17, 121.76, 121.07, 121.04, 108.28, 108.18, 82.25, 36.28, 31.85, 31.81, 31.64, 31.51, 31.45, 30.09, 30.02, 29.74, 29.69, 29.55, 29.29, 29.27, 27.78, 27.75, 26.53, 26.47, 26.38, 26.32, 22.65, 22.62, 14.11. HRMS (ESI): Calcd. for

$C_{64}H_{93}BrN_2O_6$: 1064.6217; Found: 1064.6230.

(*E*)-Tetra-tert-butyl-5,5'-((*E*)-1,1'-bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6,6'-diyl) bis(2-((E)-1,1'-bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)terephthalate) **(7)**

To a 100 mL Schlenk tube, compound **5** (430 mg, 0.4 mmol) and **6** (167 mg, 0.17 mmol), K_3PO_4 (650 mg, 2.66 mmol), P(*o*-tol)$_3$ (0.5 mg, 0.016 mmol), $Pd_2(dba)_3$ (19 mg, 0.02 mmol) and toluene/H_2O (10/2 mL) were added. The mixture was stirred at 95 ^{o}C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed with brine (200 mL×3) and dried with $MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using PE: CH_2Cl_2 (1:3, v/v) as the eluent to afford **7** as a brown solid in a yield of 57% (263 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.30 (m, 4H), 9.22 (d, *J* = 8.0 Hz, 2H), 7.81 (s, 4H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.08-7.03 (m, 6H), 6.80 (d, *J* = 4.4 Hz, 6H), 3.70 (m, 12H), 1.94 (m, 6H), 1.35-1.24 (m, 180H), 0.86 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 191.89, 168.27, 151.24, 149.18, 142.69, 135.74, 133.90, 131.74, 129.99, 127.80, 126.26, 123.73, 121.22, 120.43, 100.73, 44.92, 36.51, 31.88, 31.60, 30.03, 29.70, 29.63, 29.34, 26.57, 26.52, 11.67, 14.10. MALDI-TOF MS: Calcd. for $C_{176}H_{258}N_6O_{14}$: 2679.9661; Found: 2679.9671.

(*E*)-5,5'-((*E*)-1,1'-Bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6,6'-diyl)bis(2-((E)-1,1'-bis(2-hexyldecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)terephthalate) **(8)**

The procedure for the synthesis of **8** was followed to synthesis of **4**. The compound **8** was obtained as a brown solid (yield: ~100%). We did not get the ^{1}HNMR spectrum because of the low solubility of compound **8**. MALDI-TOF MS: Calcd. for $C_{160}H_{226}N_6O_{14}$: 2455.7157; Found: 2455.7145.

(3*E*,10*E*,10'*E*)-1,1',8,8'-Tetrakis(2-hexyldecyl)-10,10'-bis(1-(2-hexyldecyl)-2-oxoindolin-3-ylidene)-1*H*,1'*H*-[3,3'-bis-indaceno[2,1-f:6,5-f']diindolylidene]-2,2',5,5',9,9',12,12'(8*H*,8'*H*,10*H*,10'*H*)-octaone **(TIID-PhCO)**

To the solution of **8** (0.53 g, 0.216 mmol) and oxalyl chloride (0.18 mL, 2.16 mmol) in anhydrous CH_2Cl_2 (50 mL), two drops of DMF were added. The mixture was stirred for 0.5 hours at room temperature. The solvent and volatile materials were evaporated under reduced pressure. The solid was dissolved in anhydrous CH_2Cl_2 (45 mL) and then the solution was added to the suspension solution of anhydrous $AlCl_3$ (342 mg, 2.6 mmol) in CH_2Cl_2 (15 mL) at 0 ^{o}C dropwisely. The mixture was stirred at room temperature until the reaction was completed as monitored by thin-layer chromatography (TLC), then poured into ice HCl aqueous solution (1 mol/L). The organic phase was separated, washed with brine (300 mL × 3) and dried with anhydrous $MgSO_4$. After the solvent was evaporated under reduced pressure, the residue was purified by chromatography on silica gel with $CHCl_3$ as the eluent to give **TIID-PhCO** as a black solid (0.42 g, Yield: 81%). Some broad peaks were observed in the NMR spectra of **TIID-PhCO** even measured at 120 ^{o}C, therefor it is difficult to assign the NMR spectrum. ^{13}C NMR was not measured due to the limited solubility. Elemental Anal. Calcd.: C, 80.56; H, 9.21; N, 3.52. Found: C, 80.40; H, 9.27; N, 3.29. MALDI-TOF MS: Calcd. for $C_{160}H_{218}N_6O_{10}$: 2383.6734; Found: 2383.6737.

Di-*tert*-butyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)terephthalate **(10)**

The solution of bis(pinacolato)diboron (1.79 g, 7.0 mmol), compound **2** (1.3 g, 3.0 mmol), KOAc (1.76 g, 18.0 mmol) and Pd(dppf)Cl_2 (66 mg, 0.09 mmol) in dioxane (30 mL) was stirred at 80 °C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water (300 mL) and extracted with CH_2Cl_2 (100 mL). The organic extracts were washed with brine (300 mL×3) and dried with $MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using CH_2Cl_2 as the eluent to afford **10** as a white solid in a yield of 78% (1.23 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.86 (s, 2H), 1.58 (s, 18H), 1.42 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.09, 138.16, 131.27, 83.97, 81.93, 28.17, 24.86, 131.74, 129.99, 127.80, 126.26, 123.73, 121.22, 120.43, 100.73, 44.92, 36.51, 31.88, 31.60, 30.03, 29.70, 29.63, 29.34, 26.57, 26.52, 11.67, 14.10. Elemental Anal. Calcd.: C, 63.42; H, 8.36. Found: C, 63.49; H, 8.44. MALDI-TOF MS: Calcd. for $C_{176}H_{258}N_6O_{14}$: 530.32; Found: 530.3.

Di-*tert*-butyl 2,5-bis((*E*)-6'-bromo-1,1'-bis(2-decyltetradecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)terephthalate **(11)**

To a 100 mL Schlenk tube, compound **9** (3.6 g, 2.64 mmol) and **10** (178 mg, 0.33 mmol), K_3PO_4 (430 g, 2.64 mmol), P(*o*-tol)$_3$ (5.2mg, 0.017 mmol), $Pd_2(dba)_3$ (21 mg, 0.023 mmol) and toluene/H_2O (10/2 mL) were added. The mixture was stirred at 95 °C for 12 hours under argon. After cooling to room temperature, the mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (50 mL). The organic extracts were washed with brine (200 mL×3) and dried with $MgSO_4$ before filtration and concentration under vacuum. The product was purified by chromatography on silica gel using PE: CH_2Cl_2 (1:2, v/v) as the eluent to afford **11** as a brown solid in a yield of 34% (0.36 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.27 (d, *J* = 8.0 Hz, 2H), 9.14 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 6.80 (s, 2H), 3.66 (t, *J* = 8.8 Hz, 8H), 1.94 (m, 4H), 1.23-1.34 (m, 202H), 0.88 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 173.07, 168.48, 145.15, 144.89, 143.32, 132.82, 131.68, 131.32, 129.49, 122.32, 109.04, 44.49, 36.10, 31.91, 31.78, 31.51, 29.94, 29.67, 29.50, 29.31, 26.31, 22.65, 14.04. Elemental Anal. Calcd.: C, 75.09; H, 9.98; N, 2.43. Found: C, 75.17; H, 9.69; N, 2.34. MALDI-TOF MS: Calcd. for $C_{144}H_{288}Br_2N_4O_8$: 2299.59; Found: 2299.6.

2,5-Bis((*E*)-6'-bromo-1,1'-bis(2-decyltetradecyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl) terephthalic acid **(12)**

The procedure for the synthesis of **11** was followed to synthesis of **4**. The compound **11** was obtained as a brown solid (yield: ~100%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 9.25 (d, *J* = 8.4 Hz, 2H), 9.09 (d, *J* = 8.4 Hz, 2H), 7.99 (s, 2H), 7.16 (dd, *J* = 8.8 Hz, 2H), 7.05 (dd, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 1.6 Hz, 2H), 6.79 (s, 2H), 3.63 (t, *J* = 7.6 Hz, 8H), 1.90 (m, 4H), 1.23-1.34 (m, 184H), 0.85 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.37, 168.14, 146.25, 145.27, 143.46, 141.86, 133.19, 132.79, 132.58, 132.10, 131.05, 129.95, 126.58, 125.08, 122.52, 121.46, 120.49, 111.52, 108.43, 44.72, 36.36, 36.13, 31.94, 31.52, 30.07, 30.01, 29.66, 29.38, 26.41, 22.70, 14.14. MALDI-TOF MS: Calcd. for $C_{136}H_{212}Br_2N_4O_8$: 2187.48; Found: 2187.5.

(3*E*,10*E*)-3,10-Bis(6-bromo-1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)-1,8-bis(2-decyltetradecyl)-s-indaceno[2,1-f:6,5-f']diindole-2,5,9,12(1*H*,3*H*,8*H*,10*H*)-tetraone **(DIID-PhCO-2Br)**

The procedure for the synthesis of **DIID-PhCO-2Br** was followed to synthesis of **DIID-PhCO**. **DIID-PhCO-2Br** was obtained as a dark brown solid (512 mg, yield: 92%).^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ (ppm) = 9.61 (s, 2H), 9.10 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.77 (dd, *J* = 8.4 Hz, 8H), 2.08 (d, *J* = 8.8 Hz, 4H), 1.36-1.53 (m, 184H), 0.97 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 187.32, 148.07, 145.69, 144.73, 144.04, 137.98, 137.32, 137.13, 132.47, 132.25, 125.17, 124.78, 122.32, 114.68, 108.24, 44.84, 32.08, 31.92, 29.87, 30.07, 29.54, 25.71, 22.65, 14.09. Elemental Anal. Calcd.: C, 75.80; H, 9.73; N, 2.60. Found: C, 75.85; H, 9.64; N, 2.43. MALDI-TOF MS: Calcd. for $C_{136}H_{208}Br_2N_4O_8$: 2152.45 Found: 2152.5.

PDIO-BT

In a Schlenk tube was added **DIID-PhCO-2Br** (235 mg, 0.109 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (55 mg, 0.109 mmol), $Pd_2(dba)_3$ (2.0 mg, 2.2×10^{-3} mmol), $P(o\text{-tol})_3$ (5.3 mg, 1.7×10^{-2} mmol) and anhydrous toluene (10 mL). The mixture was heated to 110 °C and stirred for 48 h in the absence of light. 2-Bromothiophene (0.5 mL) was added and the mixture was stirred for another 12 h. After cooling to room temperature, the mixture was droped into 200 mL methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with ethanol, acetone and hexane sequentially. The remaining solid was dissolved in *o*-DCB. The resulting solution was filtered by 0.45 μm filter and added dropwise into methanol for precipitation. **PDIO-BT** as a black solid was obtained after filtration and drying in vacuum (224 mg, 95%). GPC: M_n = 35.0 kDa, $Đ$ = 2.54. Elemental Anal. Calcd.: C, 80.02; H, 9.98; N, 2.59. Found: C, 80.27; H, 9.66; N, 2.38.

PDIO-TVT

PDOTVT (233 mg, 97%) was obtained as a black solid from **DIID-PhCO-2Br** (237mg, 0.11mmol) and (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (57 mg, 0.11 mmol) following the procedure for the synthesis of **PDIO-BT**. M_n = 26 kDa, $Đ$ = 1.99. Elemental Anal. Calcd.: C, 80.17; H, 9.95; N, 2.56. Found: C, 80.51; H, 9.71; N, 2.46.

4. Supplementary data

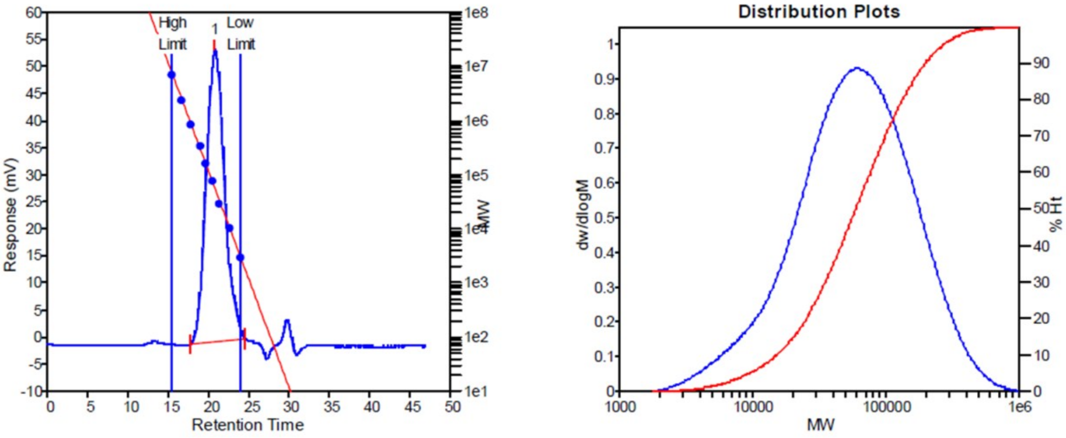


Figure S1. Gel permeation chromatography (GPC) trace of **PDIO-BT**. The molecular weight was evaluated with 1,2,4-tricholorobenzene as eluent at 150 ºC.

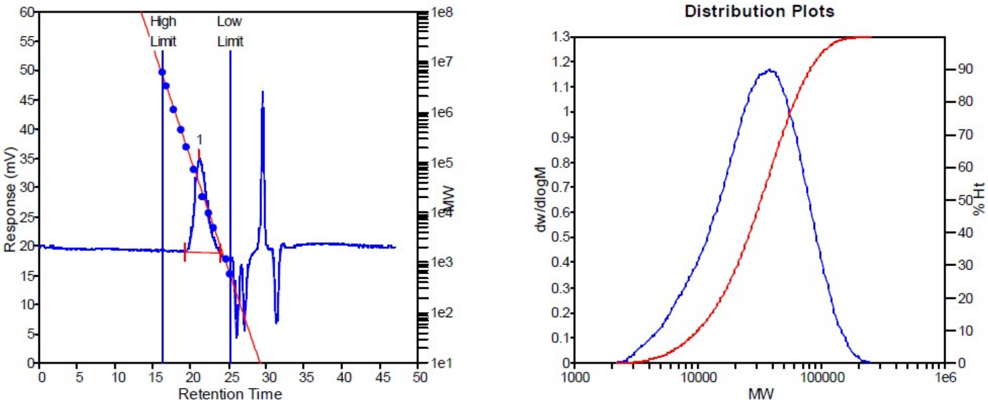


Figure S2. Gel permeation chromatography (GPC) trace of **PDIO-TVT**. The molecular weight was evaluated with 1,2,4-tricholorobenzene as eluent at 150 ºC.

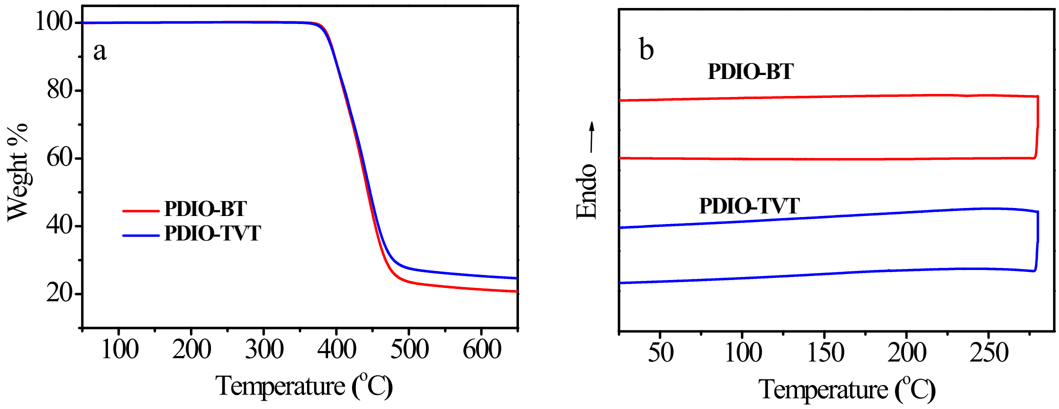


Figure S3. TGA (a) and DSC (b) curves of the polymers.

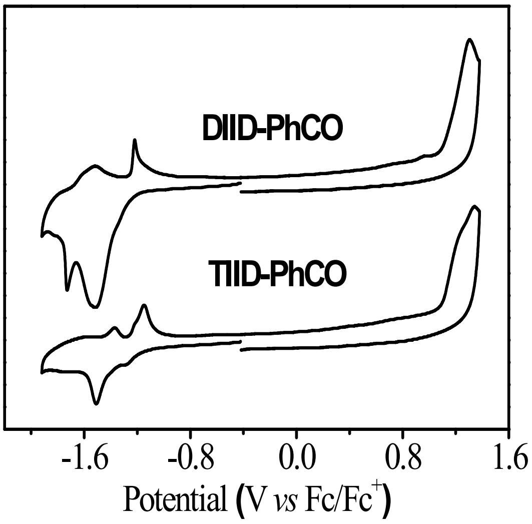


Figure S4. Solution CV curves of the **DIID-PhCO** and **TIID-PhCO**.

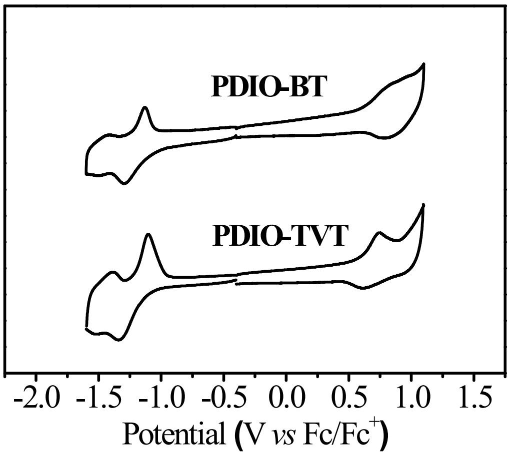


Figure S5. Film CV curves of the polymers.

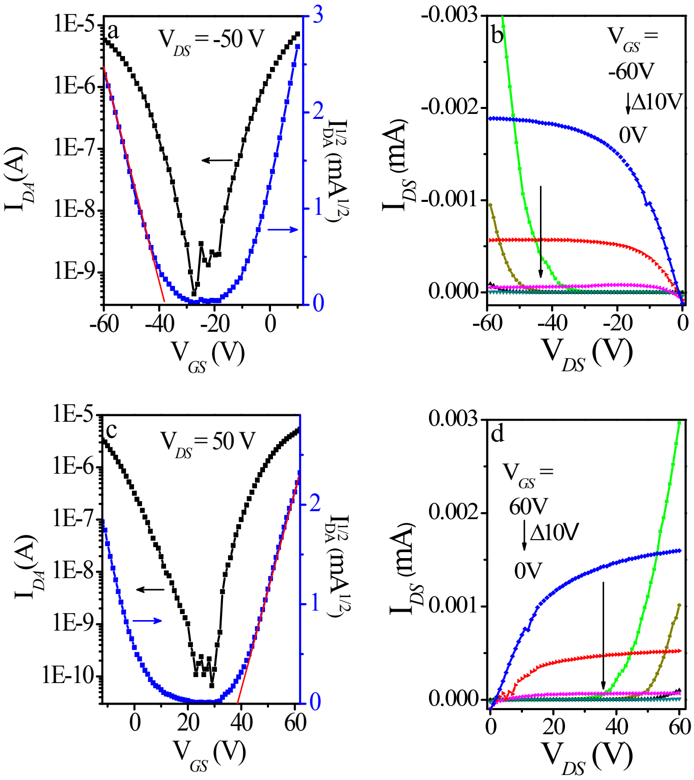


Figure S6. Typical p-channel (a, b) and n-channel (c, d,) transfer (a, c) and output (b, d) characteristics of **PDIO-BT** based TGBC OTFT device, the devices were annealed at 200 °C for 15 min.

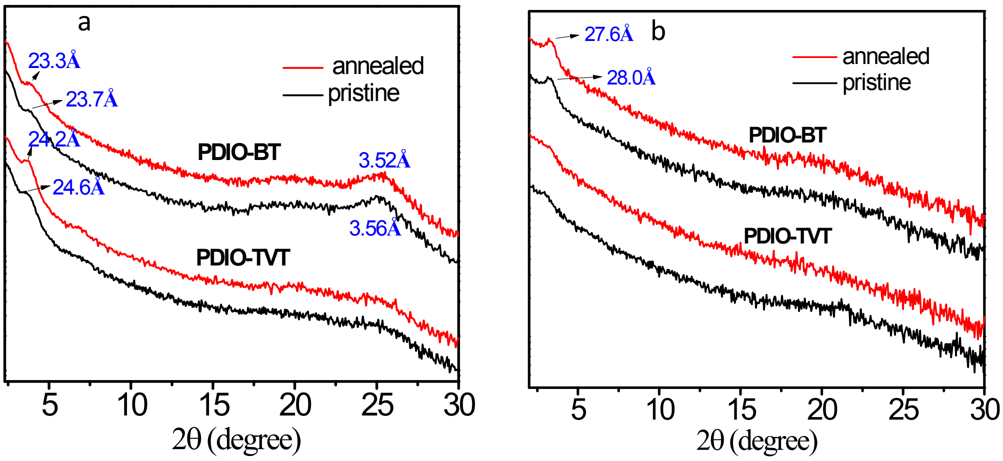


Figure S7. Out-of-plane (a) and in-plane (b) thin film X-ray diffraction patterns of the polymers.

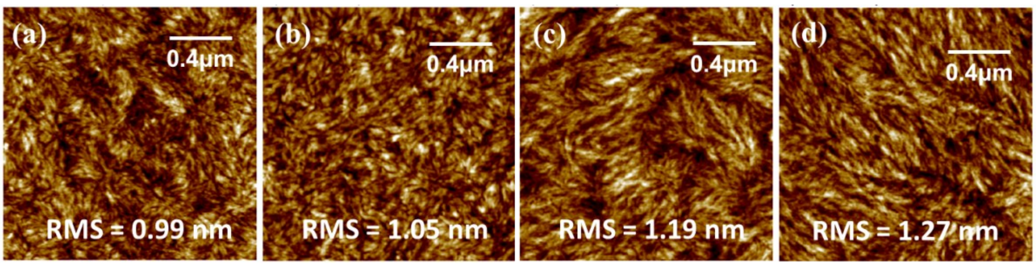


Figure S8. AFM height images of as-cast (a, b) and thermally annealed (c, d) films of **PDIO-BT** (a, c) and **PDIO-TVT** (b, d). Thermal annealing of the films was conducted at 200 °C for 15 min.

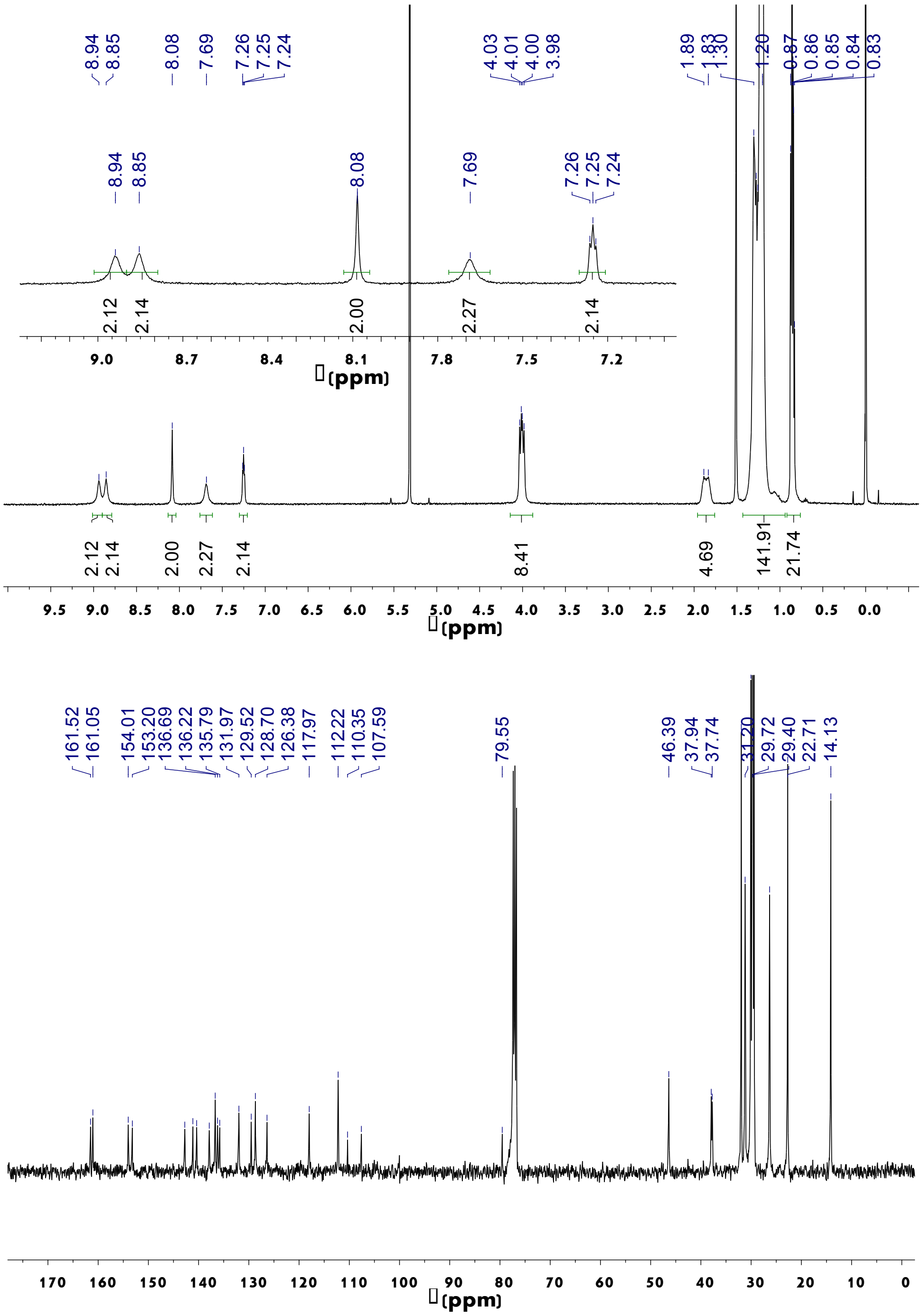


Figure S9. 400 MHz ^{1}H NMR(top) and 100 MHz ^{13}C NMR (bottom) spectrum of **3** measured in CD_2Cl_2.

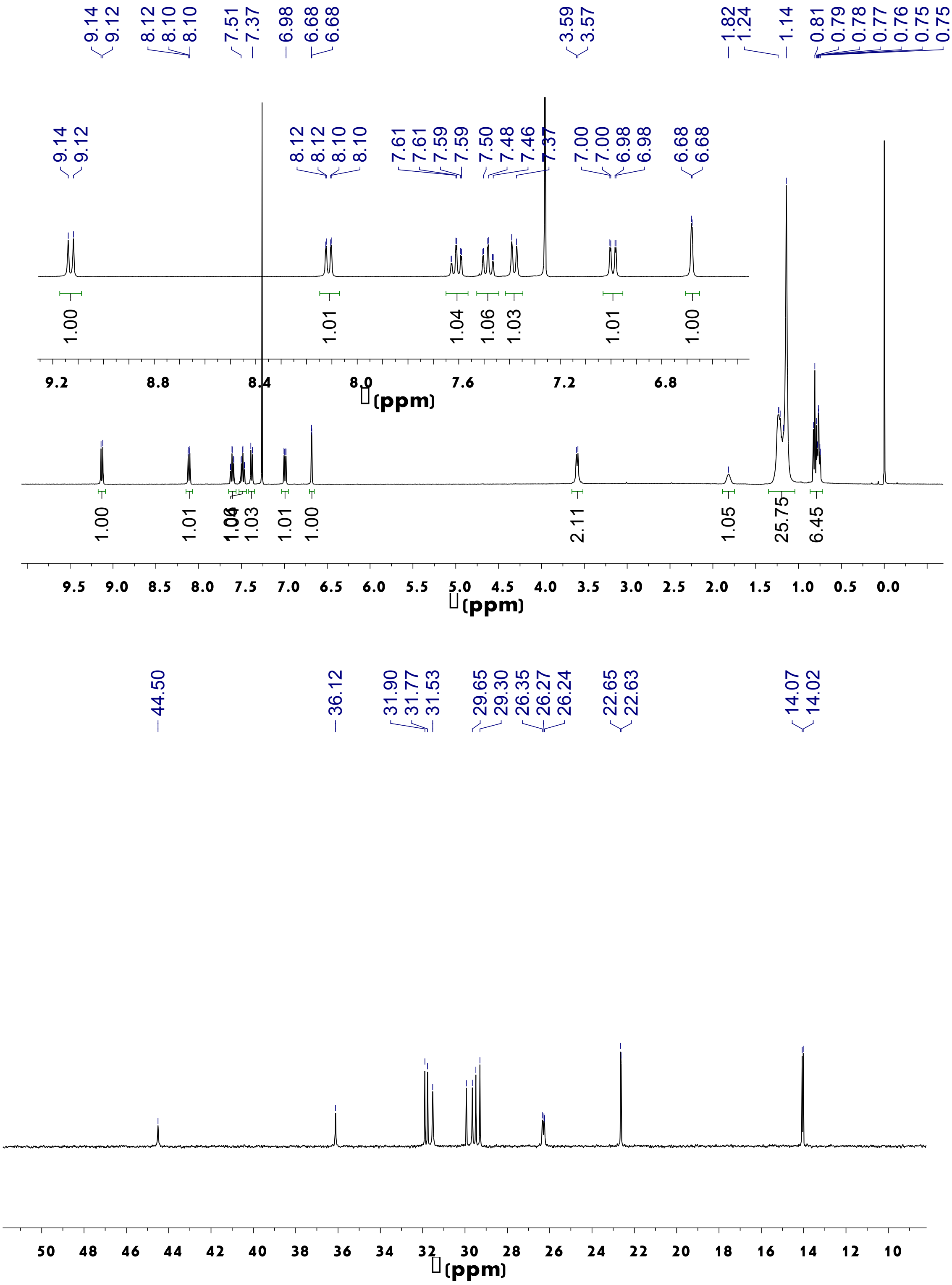


Figure S10. 400 MHz ^{1}H NMR(top) and 100 MHz ^{13}C NMR (bottom) spectrum of **4** measured in $CDCl_3$.

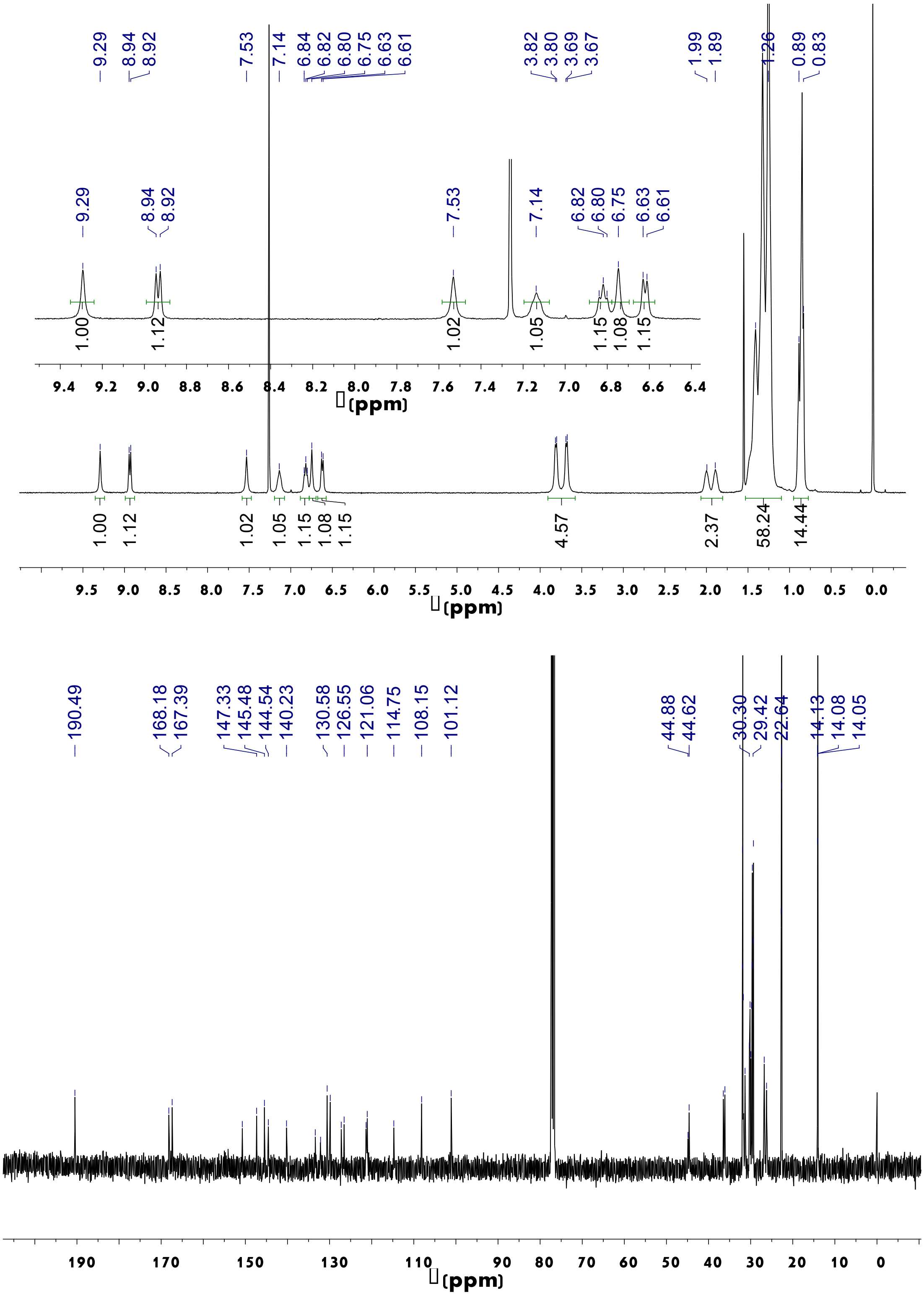


Figure S11. 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of compound **DIID-PhCO** measured in $CDCl_3$.

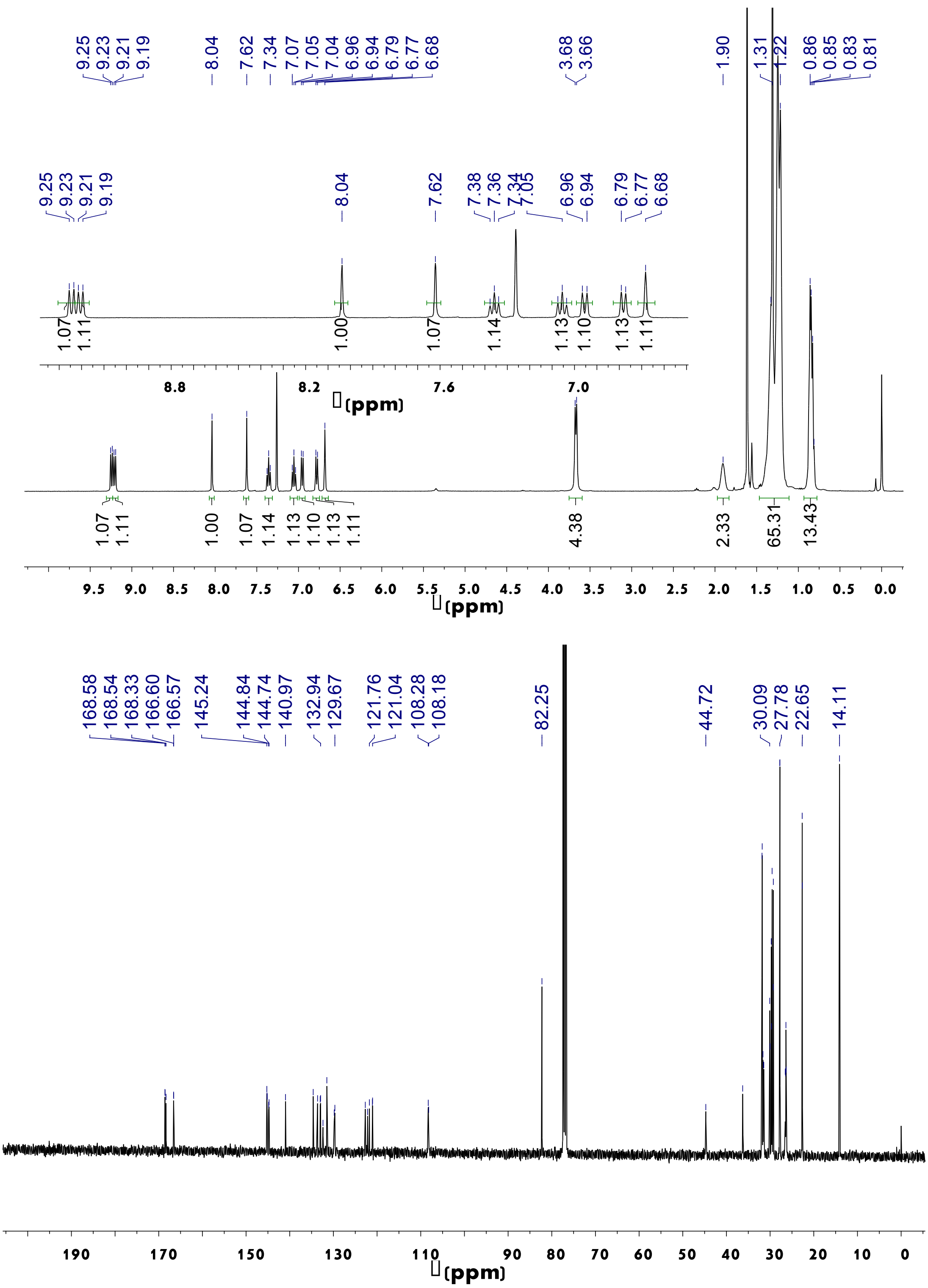


Figure S12. 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of compound **5** measured in $CDCl_3$.

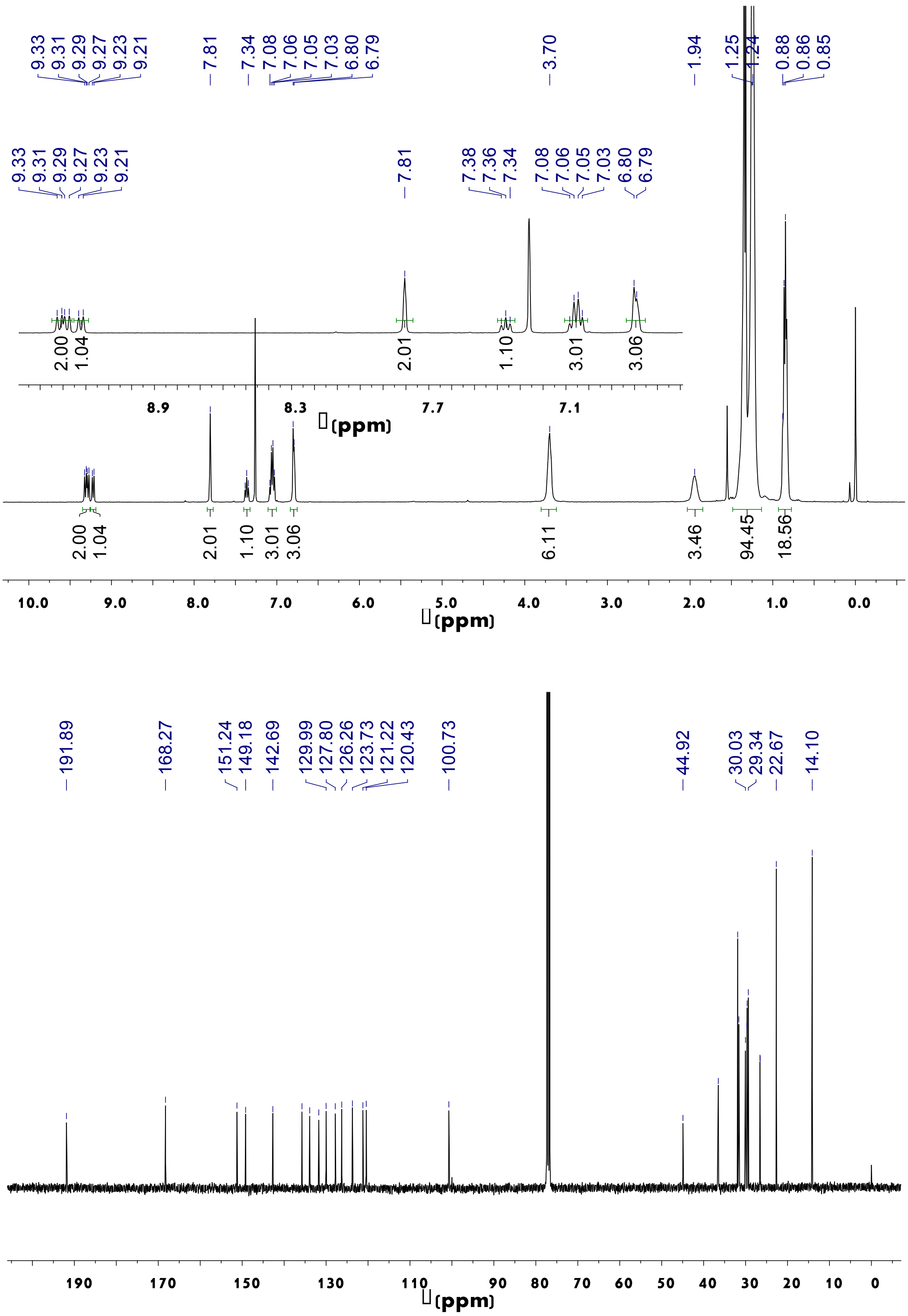


Figure S13. 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of **7** measured in $CDCl_3$.

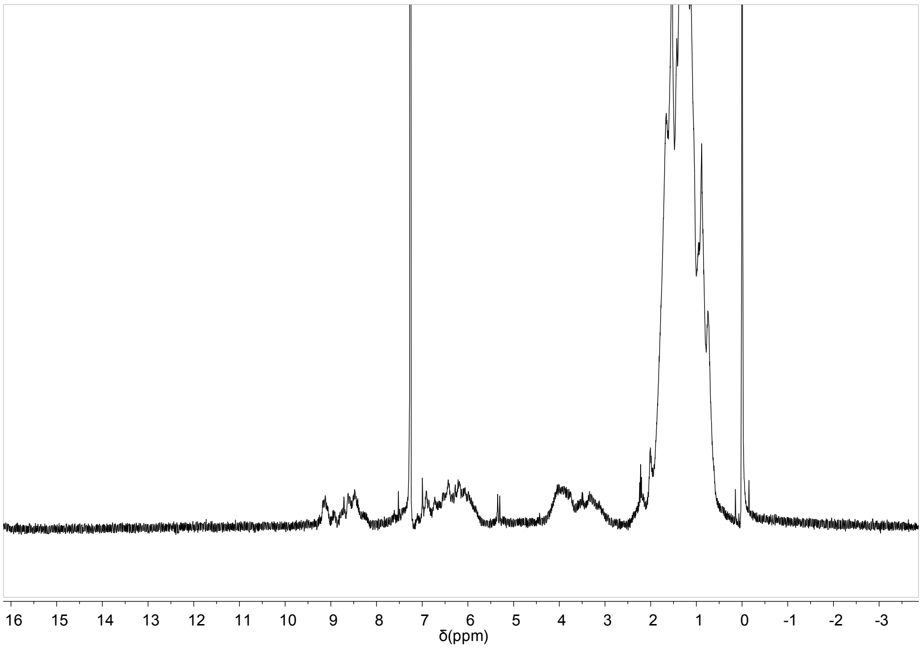


Figure S14. 400 MHz ^{1}H NMR spectra of **TIID-PhCO** measured in $CDCl_3$.

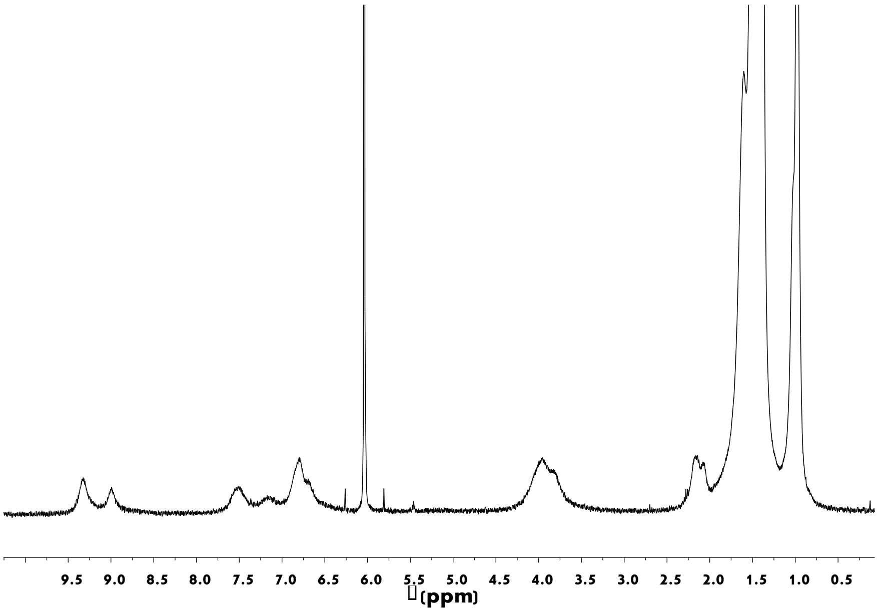
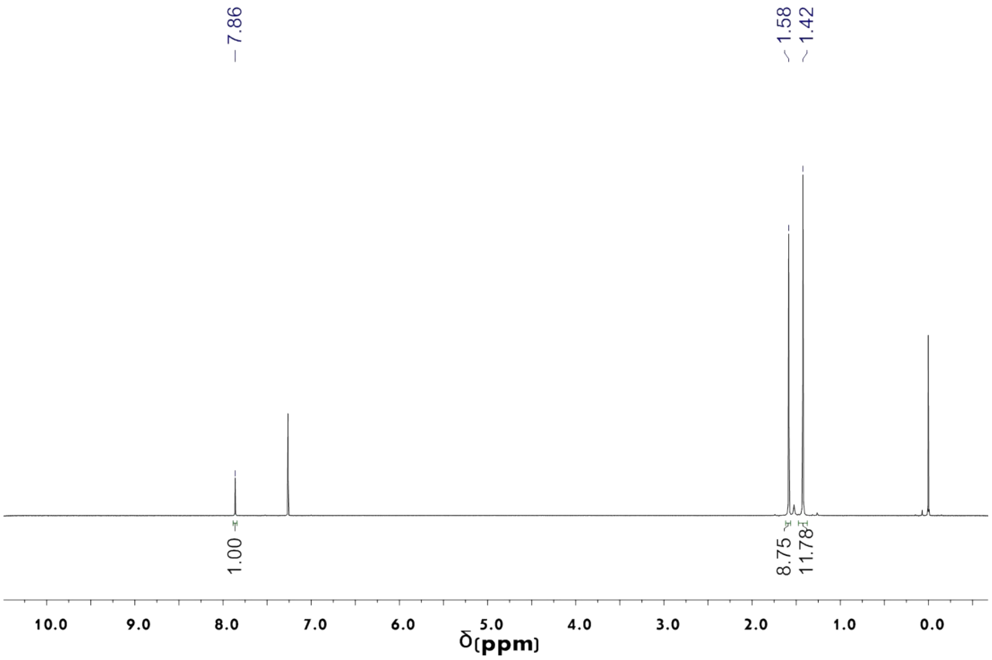


Figure S15. 400 MHz ^{1}H NMR spectra of **TIID-PhCO** measured in 1,1,2,2-$C_2D_2Cl_4$ at 120 ^{o}C.



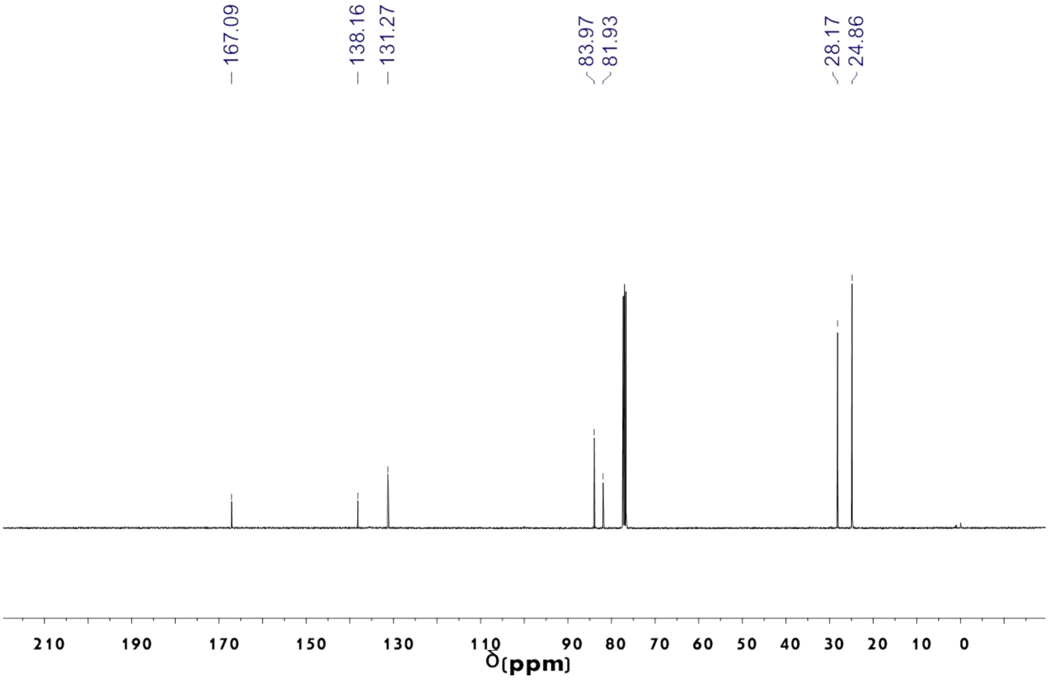


Figure S16. 400 MHz ^{1}H NMR(top) and 100 MHz ^{13}C NMR (bottom) spectrum of **10** measured in $CDCl_3$.

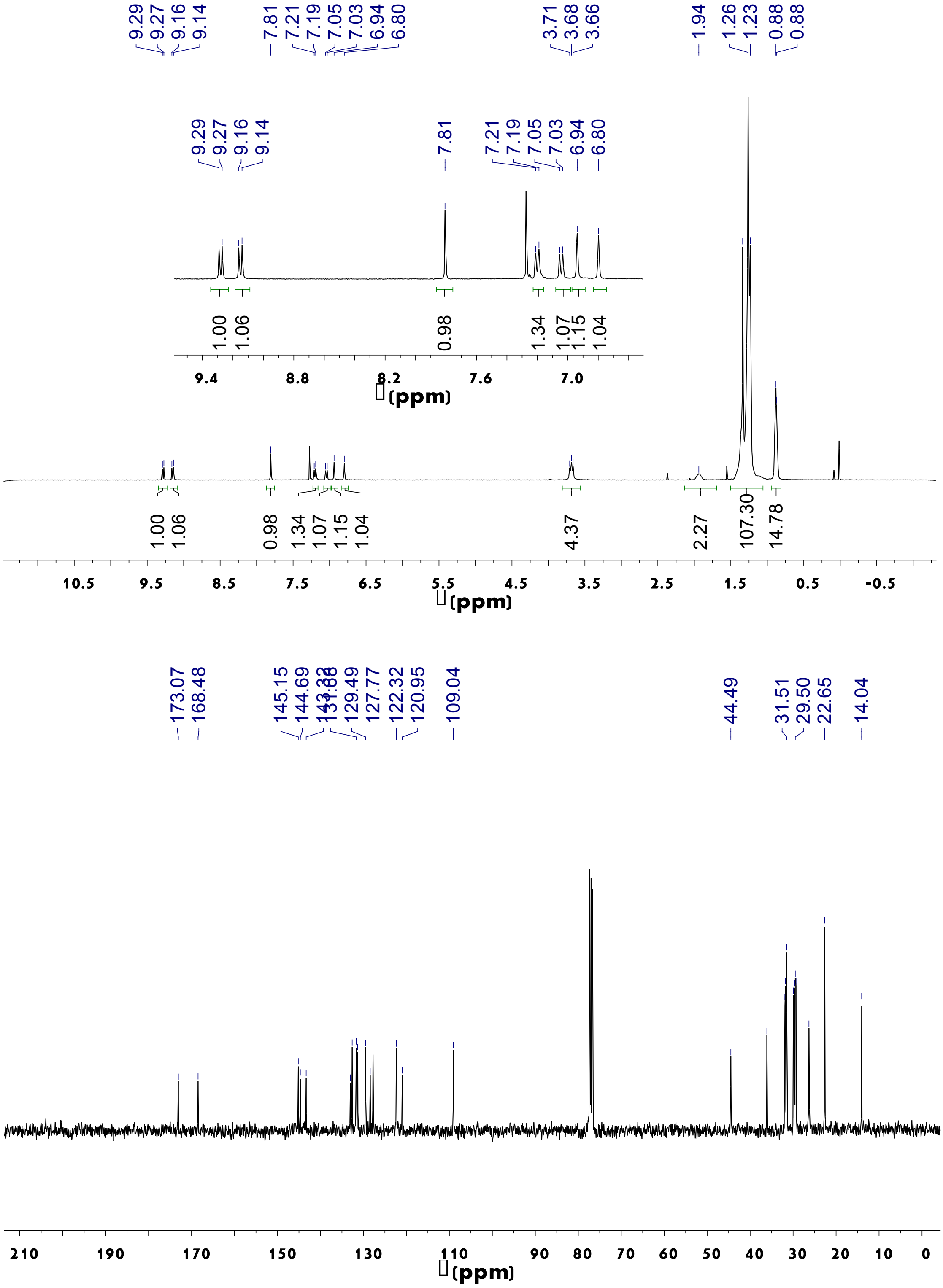


Figure S17. 400 MHz ^{1}H NMR(top) and 100 MHz ^{13}C NMR (bottom) spectrum of **11** measured in CDCl$_3$.

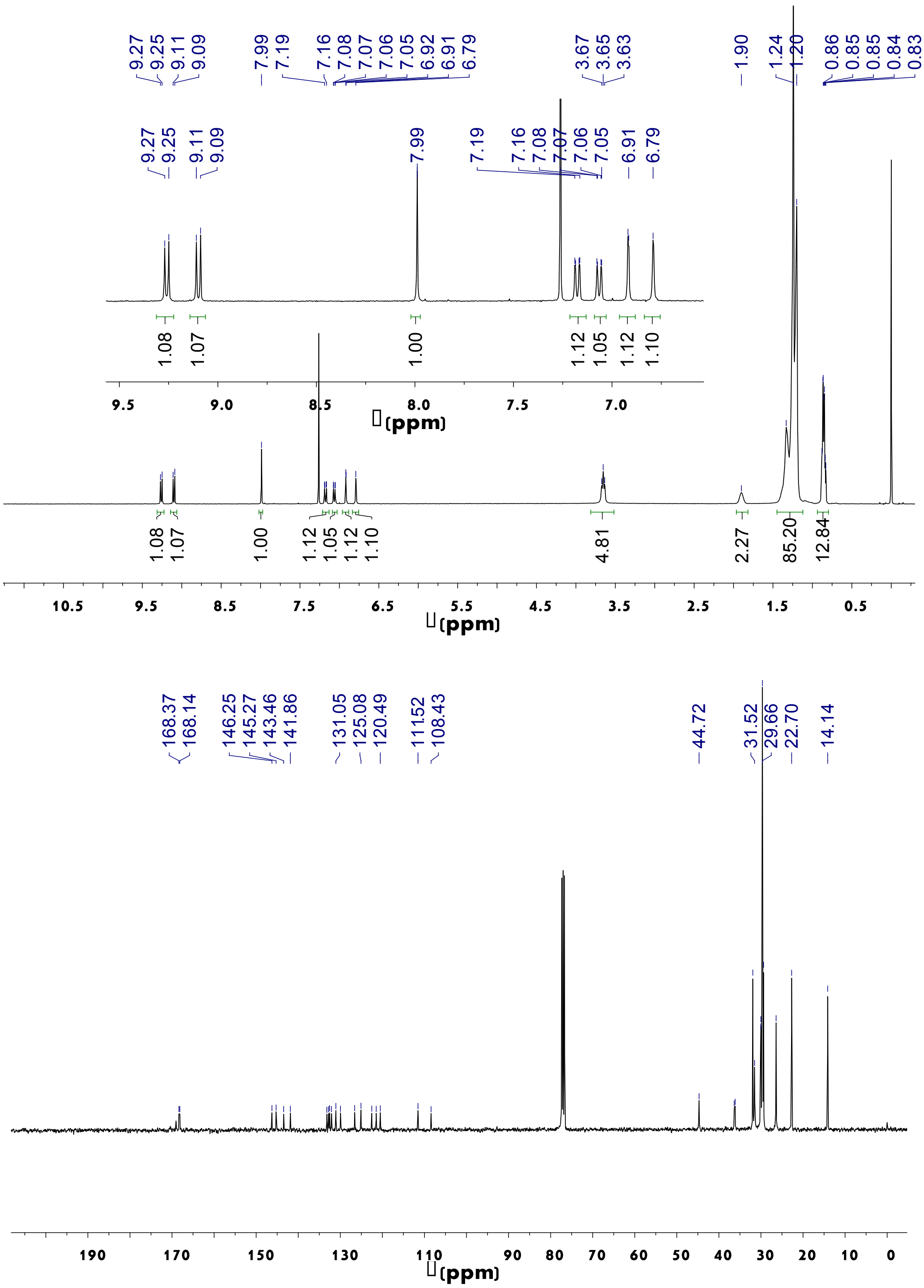


Figure S18. 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom) spectra of compound **12** measured in $CDCl_3$.

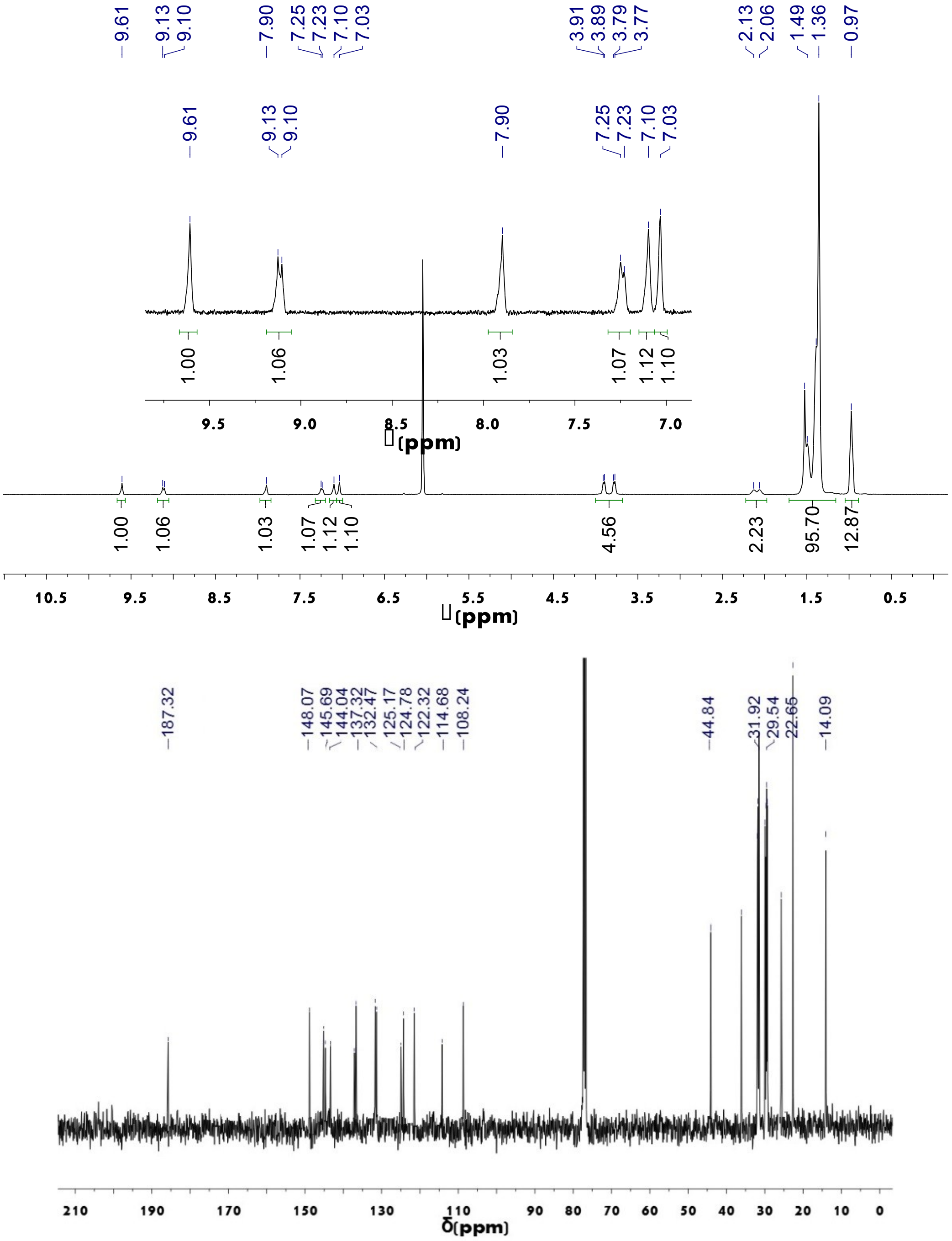


Figure S19. 400 MHz ^{1}H NMR (top) and 100 MHz ^{13}C NMR (bottom)spectrum of compound **DIID-PhCO-2Br** measured in 1,1,2,2-$C_2D_2Cl_4$.

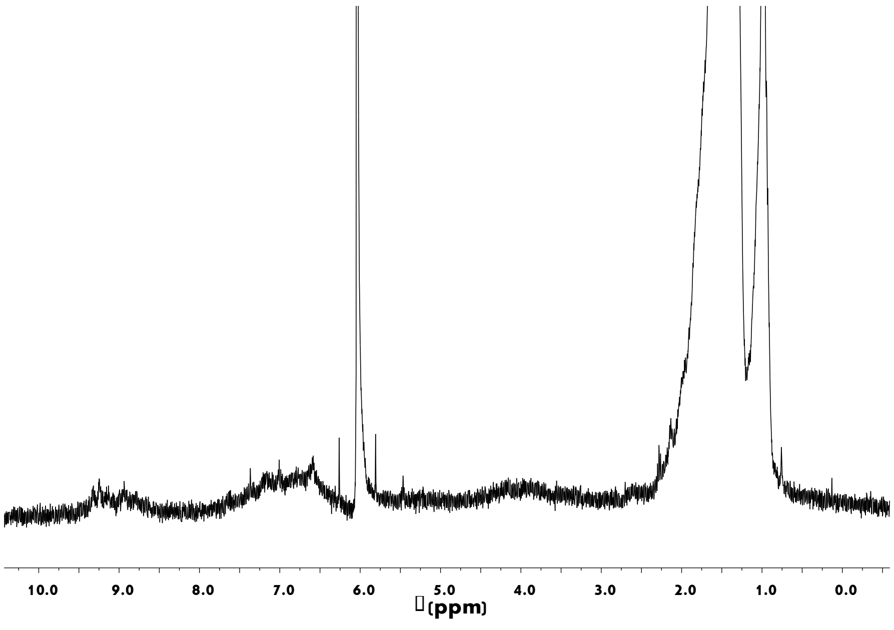


Figure S20. 400 MHz ^{1}H NMR spectrum of **PDIO-BT** measured in 1,1,2,2-$C_2D_2Cl_4$ at 120 °C.

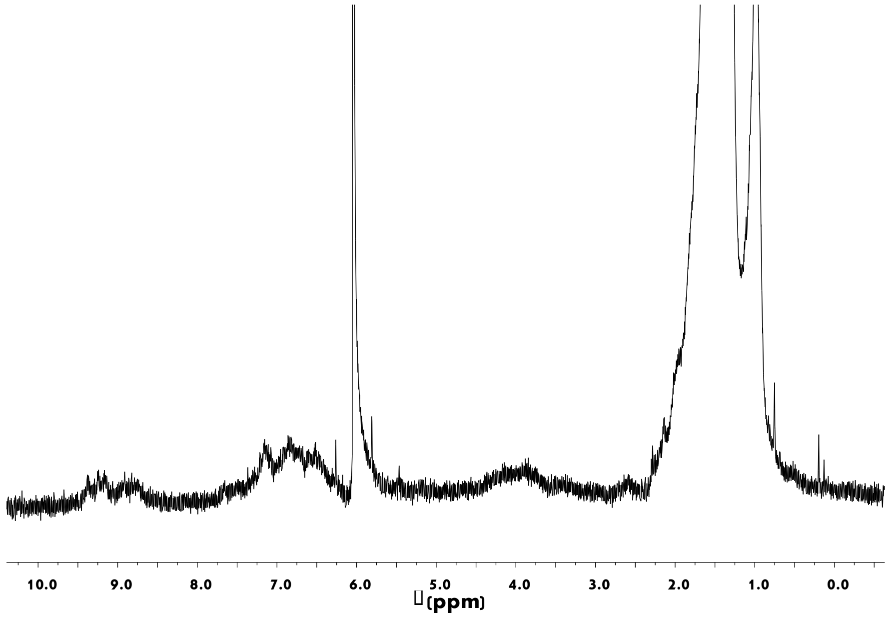


Figure S21. 400 MHz ^{1}H NMR spectrum of **PDIO-TVT** measured in 1,1,2,2-$C_2D_2Cl_4$ at 120 °C.

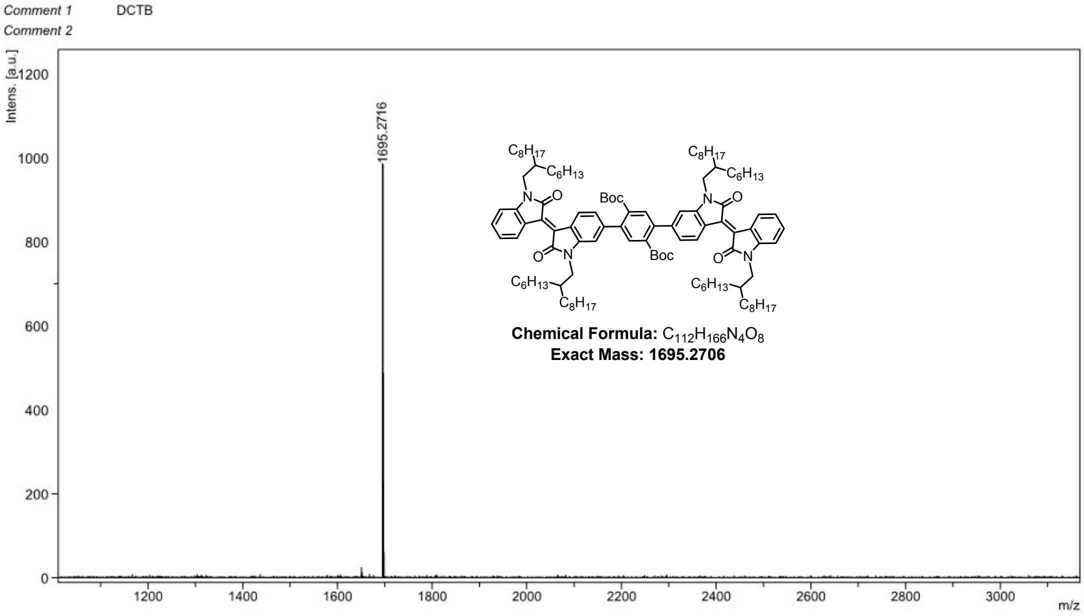


Figure S22. MALDI-TOF mass spectrum of compound **3**.

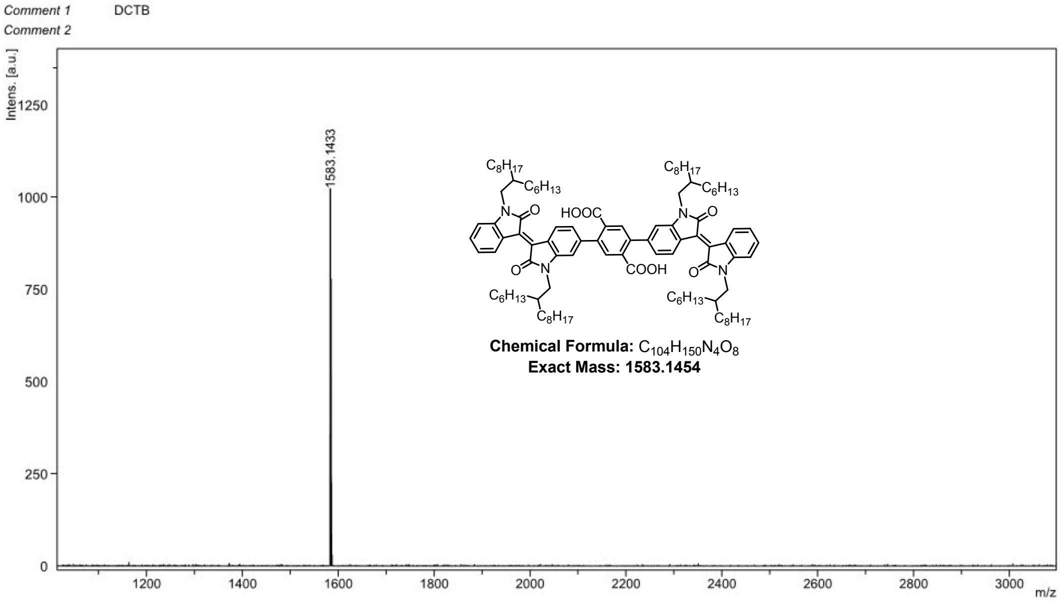


Figure S23. MALDI-TOF mass spectrum of compound **4**.

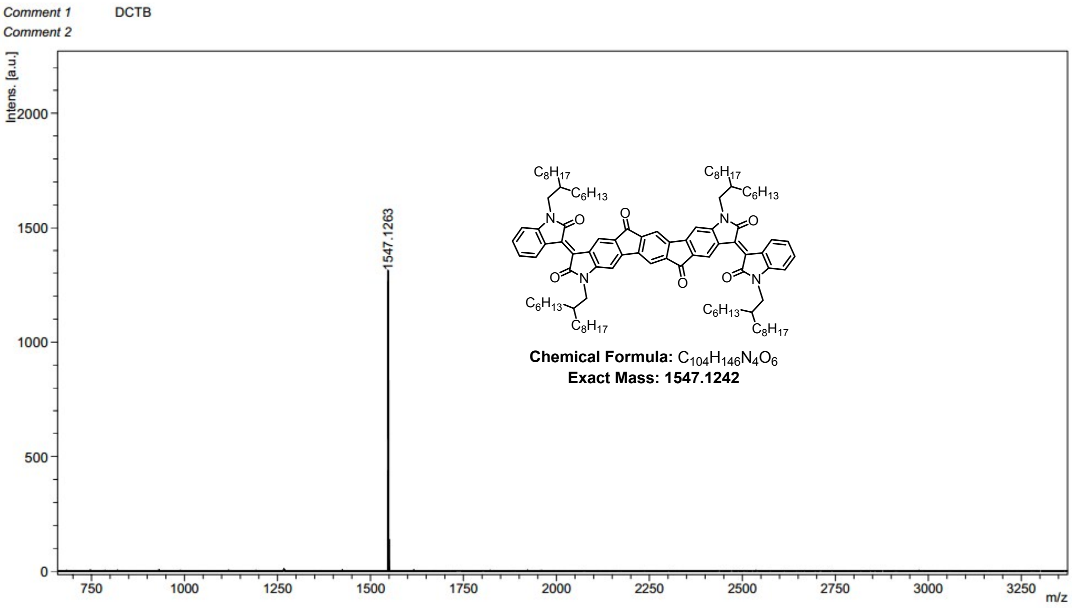


Figure S24. MALDI-TOF mass spectrum of compound **DIID-PhCO**.

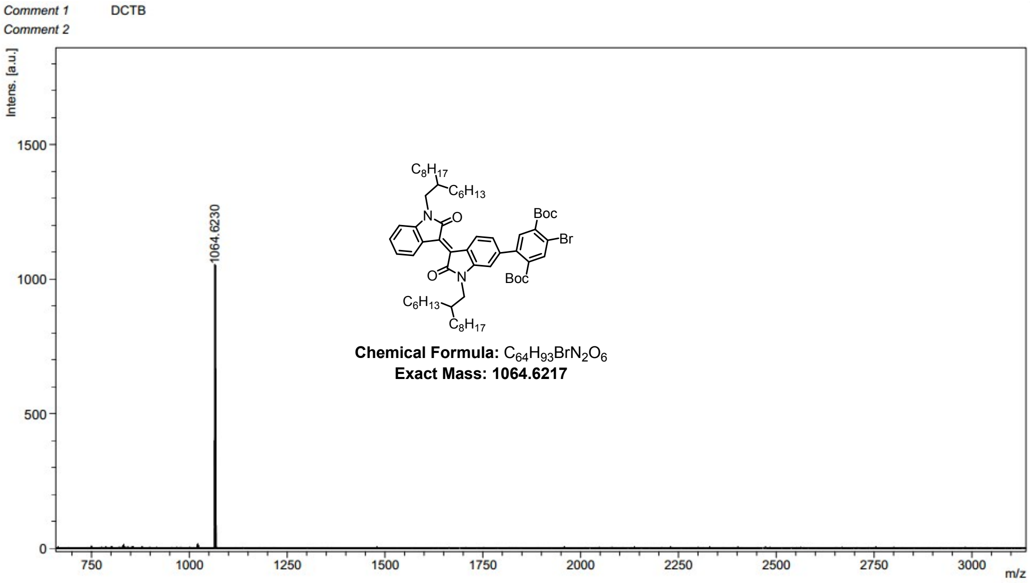


Figure S25. MALDI-TOF mass spectrum of compound **5**.

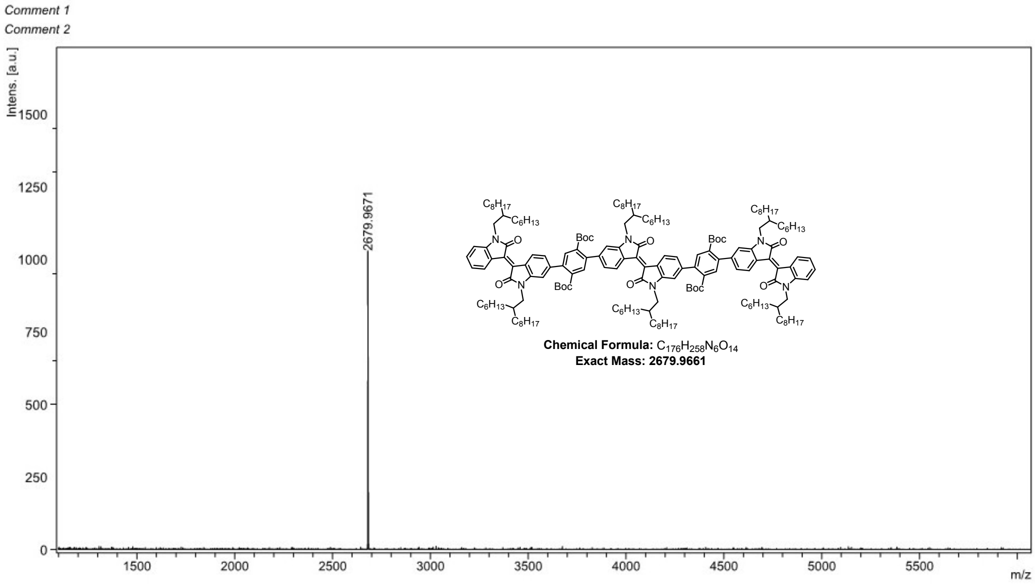


Figure S26. MALDI-TOF mass spectrum of compound **7**.

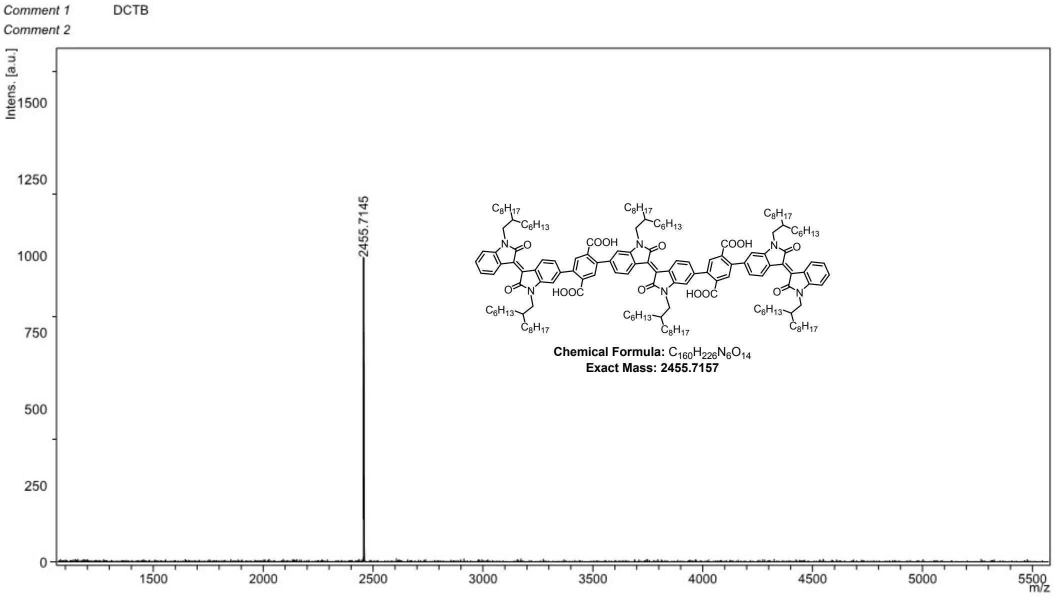


Figure S27. MALDI-TOF mass spectrum of compound **8**.

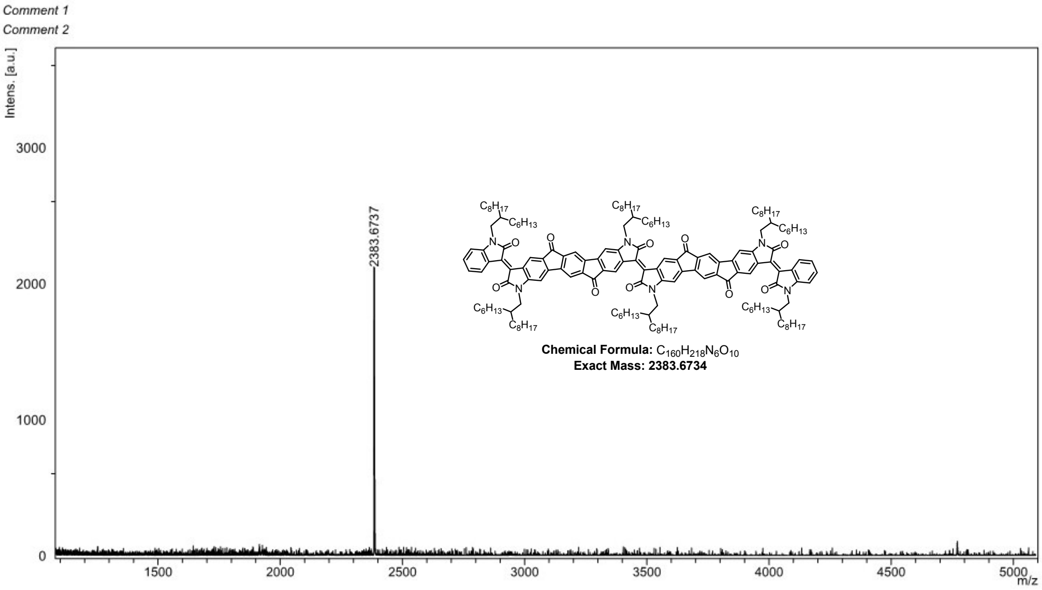


Figure S28. MALDI-TOF mass spectrum of compound **TIID-PhCO**.

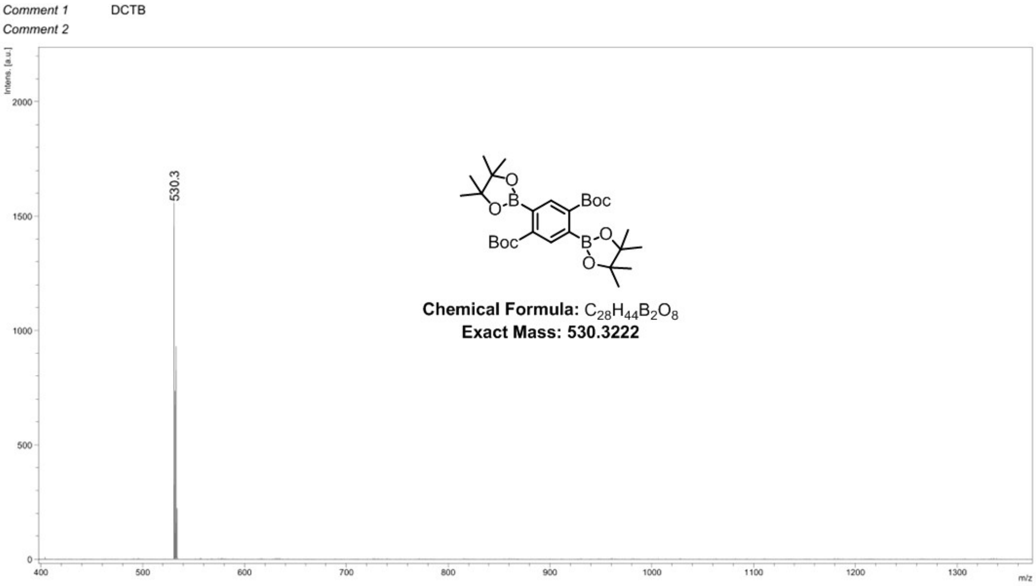


Figure S29. MALDI-TOF mass spectrum of compound **10**.

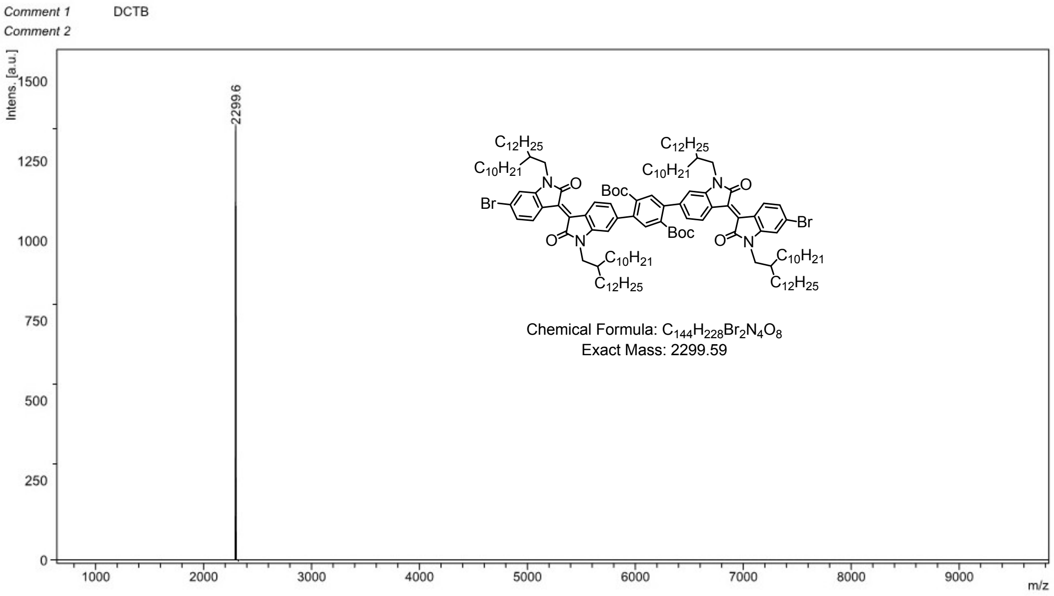


Figure S30. MALDI-TOF mass spectrum of compound **11**.

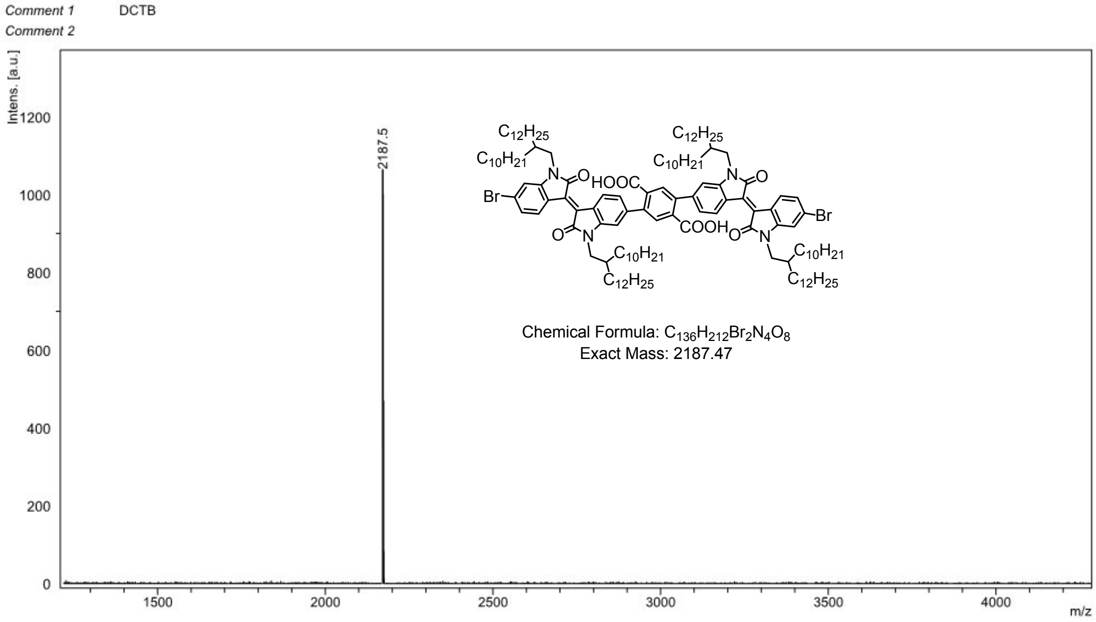


Figure S31. MALDI-TOF mass spectrum of compound **12**.

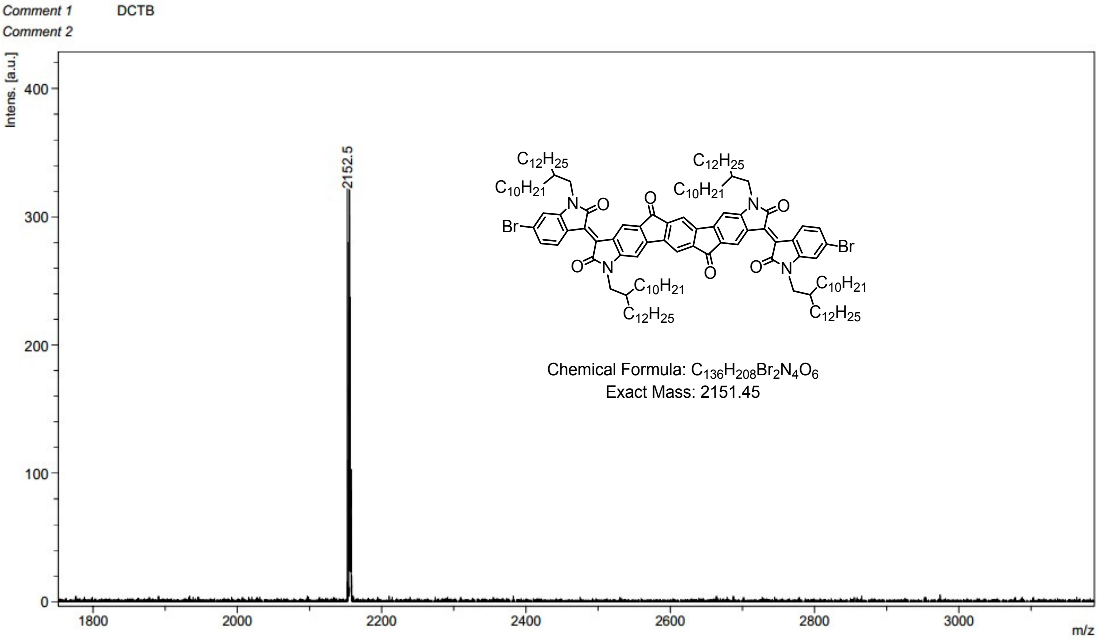


Figure S32. MALDI-TOF mass spectrum of compound **DIID-PhCO-2Br**.