Supporting Information

A bromine and chlorine concurrently functionalized end group for benzo[1,2-*b*:4,5-*b*']diselenophene-based nonfluorinated acceptors: new hybrid strategy to balance the crystallinity and miscibility of blend films enabling highly efficient polymer solar cells

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Experimental Section

Materials and Characterization: All air and water-sensitive reactions were carried out under N_2. Toluene and THF were dried by Na and then freshly distilled before to use. The other precursors were used as the common commercial level. ^1H and ^{13}C NMR spectra were carried out on a Bruker Ascend-400 and 700 NMR spectrometer. All chemical shifts were reported in ppm. Chemical shifts in ^1H NMR were referenced to TMS and in ^{13}C NMR were referenced to $CDCl_3$. MALDI-TOF-MS was recorded on a Bruker BIFLEX III mass spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q600 analyzer under nitrogen gas flow with a heating rate of 10 ºC min^{-1}. Elemental analyses were performed using a German Vario EL III elemental analyzer. UV-vis absorption spectra were taken on a Hitachi UH5300 UV-vis spectrometer. The electrochemical cyclic voltammetry was carried out on CHI electrochemical workstation with glass carbon disk, Ag/Ag^+ electrode, and Pt wire, as working electrode, reference electrode, and counter electrode, respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. During CV measurements, the films were drop-cast on the glass carbon working electrode from chloroform solution. Atomic force microscopy (AFM) measurements were taken on a Bruker Inova atomic microscope in tapping mode. 2D-GIWAXS measurements were performed at beamline 7.3.3 8 at the Advanced Light Source. Samples were prepared on the Si substrates using identical blend solutions as those used in PSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector. R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source

(ALS). Photoluminescence (PL) and the transient Photoluminescence (TPL) measurements were performed on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon). PL spectra of the pristine PM7 and active blend films were recorded by excited with a 600 nm light source, while PL spectra of the pristine acceptors were recorded by excited with a 760 nm light source. TPL decays were recorded with a Deltadiode Laser (635 nm, Horiba Scientific) as the excitation source and a picosecond photon detection module (PPD-850, Horiba Scientific) as the detector.

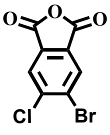
BHJ-OSC Fabrication and Characterization: The device structure was Glass/ITO/ZnO/active layer/MoO_3/Ag. The hole-only devices structure was Glass/ITO/PEDOT:PSS/active layer/MoO_3/Au and the electron-only device structure was Glass/Al/active layer/Al. A glass substrate with a pre-patterned ITO (sheet resistance = 15 Ω sq^{-1}) was ultrasonicated subsequently in detergent, deionized water, acetone, and isopropanol. After the plates were dried by high-pressure air flow, the substrates were cleaned by UV-ozone treatment for 30 min. ZnO precursor (2M diethylzinc solution in toluene, diluted with THF) was spin-coated on the substrates at 5000 rpm for 30 s in dry air, which were then baked on a hot plate at 180 °C for about 30 min. After cooled to room temperature, the substrates were sent to an argon filled glove box. A blend film of PM7: NF-SMAs (**BDSe-4Cl, BDSe-2(BrCl)** or **BDSe-4Br)** (1:1, w/w) was prepared by spin-coating its hot solution (80 ^{o}C) of chlorobenzene/1,8-diiodoctane (99.5:0.5, total concentration: 18 mg mL^{-1}) at 3000 rpm for 30 s. The substrates were then thermal annealed at 100 ^{o}C for 10 min. A thin layer (10 nm) of MoO_3 and Ag cathode (100 nm) were deposited by thermal evaporation in a high vacuum chamber (~10^{-6} mbar). The optimal thickness of the active layer was typical 100 nm, which was measured using a Dektak 6 M surface profilometer. The device area was exactly fixed at 4.0 mm^2. The *J-V* characterization of the devices was carried out on a computer-controlled Keithley 2400 Source Measurement system with a solar simulator (XES-70S1, SAN EI Co., Ltd.) was used as the light source. The light intensity was monitored by using a standard Si solar cell (KONICA MINOLTA, INC.). The EQE values were tested with a Newport Model 77890 (Newport Co., Ltd.) during illumination with monochromatic light from a xenon lamp.

SCLC mobility measurement (SCLC)

SCLC method was used to determine the hole and electron mobilities in a solar cell device by constructing different single-carrier-transporting device. The carrier mobility of the blend films were measured with the hole-only and electron-only device structure of glass/Al/active layer/Al and glass/ITO/PEDOT:PSS/active layer/MoO_3/Au, respectively. The active layers for the two devices are spin-coated under same condition as that of the real solar cell. The mobilities were determined by fitting the dark current to a SCLC model which is described as:

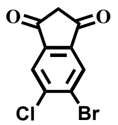
$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3} exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

where J is the current density, L is the film thickness of the active layer, μ is the holeor electron mobility, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the transport medium, V (= V_{appl} - V_{bi}) is the internal voltage in the device, where V_{appl} is the applied voltage and V_{bi} is the built-in voltage reflecting the difference of work functions of the two electrodes.

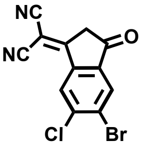


Compound 2: In a 100 mL round-bottom flask, compound **1** (2.03 g, 7.7 mmol) in 35 mL of acetic anhydride was stirred for 24 h at 140 ^{o}C. After the temperature of reaction mixture is

cooled to room temperature. The crude product was poured into hexane (100 mL) and the precipitate was filtered off and washed with hexane. Then the crude product was treated to the next step without further purification.



5-bromo-6-chloro-1H-indene-1,3(2*H*)-dione (Compound **3**): In a 100 mL round-bottom flask, 5-bromo-6-chloroisobenzofuran-1,3-dione (compound **2**) (1.50 g, 5.7 mmol), acetoacetic ester (0.82 g, 6.3 mmol) in 30 mL of anhydrous acetic anhydride. The reaction mixture was refluxed overnight. When reaction mixture is cooled to room temperature, 3 mL of HCl was added into the reaction mixture and acidified by H_2O:HCl (v/v = 1:1) (pH 1-2) in an ice-water bath. Then the reaction mixture was refluxed for 1 h and the precipitate was filtered and washed with water and petroleum ether. The crude product was stirred in 5 mL Et_2O at room temperature for 2 h, the precipitate was filtered to afford the product as light yellow solid (0.39 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.25 (s, 1H, Ph-H), 8.04 (s, 1H, Ph-H), 3.27 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 195.0, 194.7, 142.9, 142.6, 141.8, 131.6, 128.5, 124.6, 44.9.



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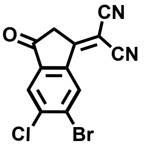
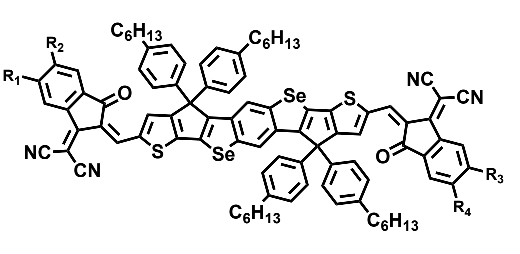


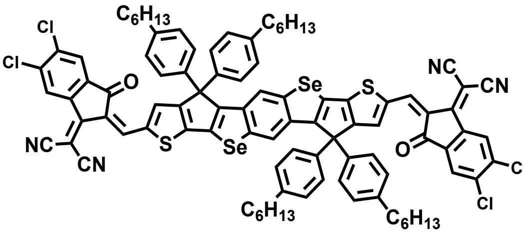
IC-BrCl^1 IC-BrCl^2

IC-BrCl: In a 100 mL round-bottom flask, sodium acetate (0.38 g, 4.6 mmol) was added to a solution of malononitrile (0.30 g, 4.6 mmol) and compound **3** (1.0 g, 3.8 mmol) in 30 mL of anhydrous EtOH. The reaction mixture was stirred at room temperature for 10 h. Then 10 mL of water was added into the reaction mixture and acidified by HCl (pH =1-2) and the precipitate was filtered and washed with water and petroleum ether. The crude product was purified by flash column chromatography (silica gel), eluting with petroleum ether/dichloromethane (2:1) to afford the product with two isomers (IC-BrCl^1 : IC-BrCl^2 = 0.9:1) as gray solid (0.89 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.90 (s, 1H, Ph-H), 8.70 (s, 0.9H, Ph-H), 8.23 (s, 0.9H, Ph-H), 8.02 (s, 1H, Ph-H), 3.75 (s, 3.8H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 192.6, 192.3, 163.8, 163.5, 143.4, 143.3, 141.5, 140.9, 139.9, 139.1, 132.1, 131.9, 130.8, 129.7, 126.9, 125.7, 111.6, 111.62, 111.5, 111.52, 43.2, 43.17, 43.15.

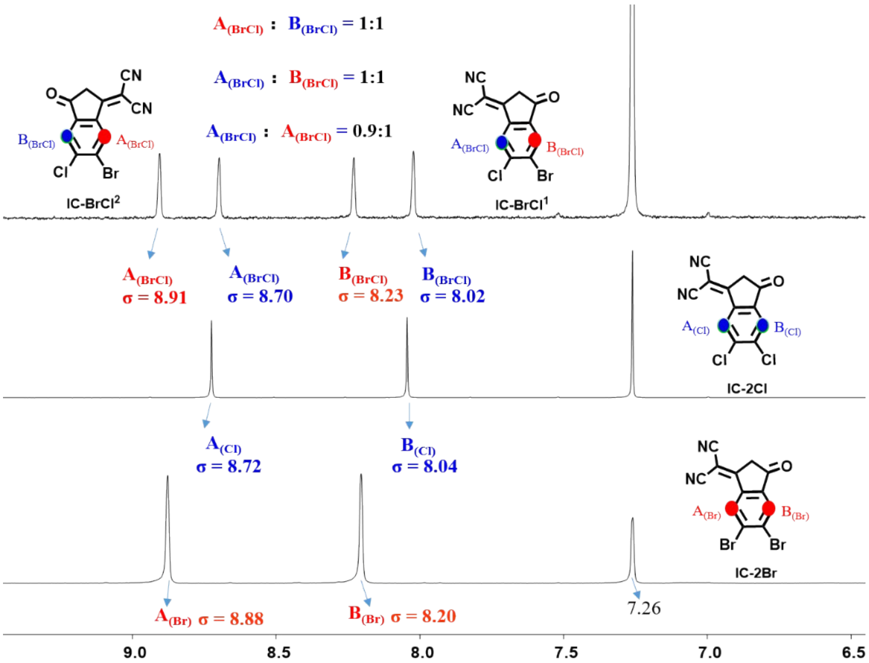


$R_1 = R_3$ = Br and $R_2 = R_4$ = Cl
or
$R_1 = R_3$ = Cl and $R_2 = R_4$ = Br
or
$R_1 = R_4$= Br and $R_2 = R_3$ = Cl

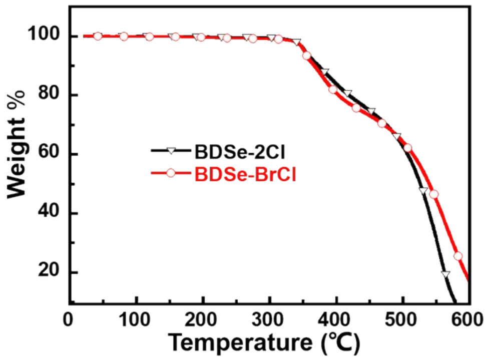
BDSe-2(BrCl): In a 100 mL two-neck round-bottom flask, **BDSeT-CHO** (0.16 g, 0.13 mmol), **IC-BrCl** (0.14 g, 0.60 mmol) was added. The reaction mixture was evacuated and backfilled with N_2 three times, and then freshly degassed chloroform (40 mL) and pyridine (0.5 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 12 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (3:2) to give the product as purple solid (0.23 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.93 (s, 1H, =CH), 8.86 (s, 2H, =CH and Ph-H), 8.73 (s, 1H, Ph-H), 8.09 (s, 1H, Th-H), 8.03 (s, 2H, Th-H and Ph-H), 7.90 (s, 1H, Ph-H), 7.68 (s, 2H, Ph-H), 7.14-7.16 (d, J = 8.0 Hz, 8H, Ph-H), 7.09-7.11 (d, J = 8.0 Hz, 8H, Ph-H), 2.56 (t, J = 8.0 Hz, 8H, CH_2), 1.54-1.58 (m, 8H, CH_2), 1.26-1.29 (m, 12H, CH_2), 0.84-0.88 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 175 MHz, ppm): δ 186.3, 186.0, 162.9, 159.9, 159.7, 158.1, 157.9, 144.7, 142.7, 141.5, 141.2, 140.8, 140.7, 139.3, 138.9, 138.6, 138.54, 138.51, 136.6, 135.7, 133.4, 130.2, 130.0, 129.6, 128.9, 128.4, 128.1, 126.6, 124.7, 123.2, 120.5, 120.4, 114.4, 114.3, 69.1, 69.0, 63.7, 35.5, 31.7, 31.2, 29.1, 22.6, 14.1. MALDI-TOF MS (*m/z*): calcd. for $C_{94}H_{78}Br_2Cl_2N_4O_2S_2Se_2$: 1748.1. Found: 1748.0. Elemental Analysis: calcd for $C_{94}H_{78}Br_2Cl_2N_4O_2S_2Se_2$: C, 64.57; H, 4.50; N, 3.20. Found: C, 64.26; H, 4.50; N, 3.05.



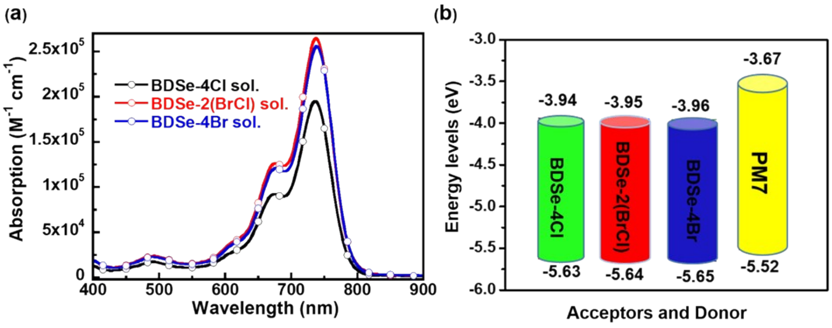
BDSe-4Cl: In a 100 mL two-neck round-bottom flask, **BDSeT-CHO** (0.15 g, 0.12 mmol), **IC-2Cl** (0.19 g, 0.72 mmol) was added. The reaction mixture was evacuated and backfilled with N_2 three times, and then freshly degassed chloroform (50 mL) and pyridine (0.6 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 12 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (3:2) to give the product as purple solid (0.19 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.86 (s, 1H, =CH), 8.75 (s, 1H, Ph-H), 8.03 (s, 1H, Th-H), 7.92 (s, 1H, Ph-H), 7.68 (s, 1H, Ph-H), 7.16-7.18 (d, J = 8.0 Hz, 4H, Ph-H), 7.09-7.11 (d, J = 8.0 Hz, 4H, Ph-H), 2.56 (t, J = 8.0 Hz, 4H, CH_2), 1.54-1.58 (m, 4H, CH_2), 1.26-1.29 (m, 12H, CH_2), 0.84-0.88 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 175 MHz, ppm): δ 186.2, 162.9, 159.9, 159.7, 158.0, 144.7, 142.7, 140.7, 139.6, 138.8, 138.6, 138.5, 136.6, 135.9, 133.4, 128.9, 128.1, 126.9, 125.0, 123.2, 120.5, 114.4, 114.3, 69.1, 63.7, 35.5, 31.7, 31.2, 29.1, 22.6, 14.1. MALDI-TOF MS (*m/z*): calcd. for $C_{94}H_{78}Cl_4N_4O_2S_2Se_2$: 1658.2. Found: 1658.1.



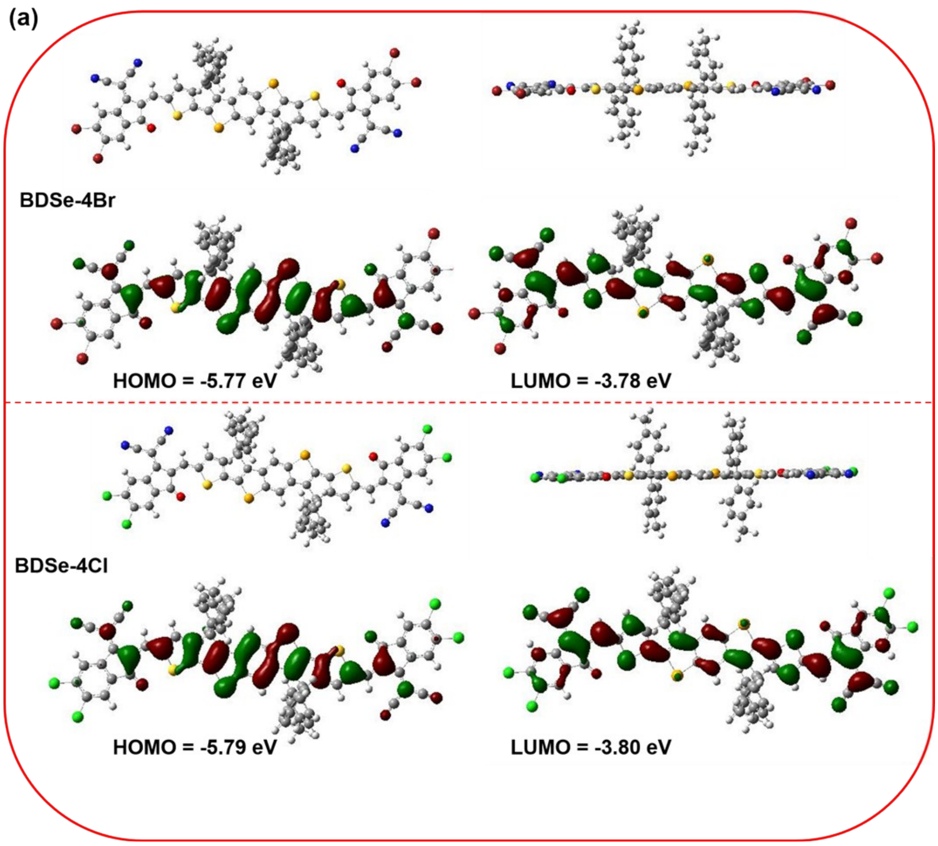
Figur S1. The comparison chart of ^{1}H NMR for IC-BrCl, IC-2Cl and IC-2Br.



Figur S2. Thermal gravity analyse (TGA) of **BDSe-4Cl** and **BDSe-2(BrCl)** with a heating rate of 10 °C/min under N_2 atmosphere.



Figur S3. (a) Absorption spectra of **BDSe-4Cl**, **BDSe-2(BrCl)** and **BDSe-4Br** in solution (in chloroform solution, 2×10^{-6} M). (b) The energy levels alignment of **BDSe-4Cl**, **BDSe-2(BrCl),** **BDSe-4Br** and **PM7**.


(a)
BDSe-4Br
HOMO = -5.77 eV
LUMO = -3.78 eV
BDSe-4Cl
HOMO = -5.79 eV
LUMO = -3.80 eV

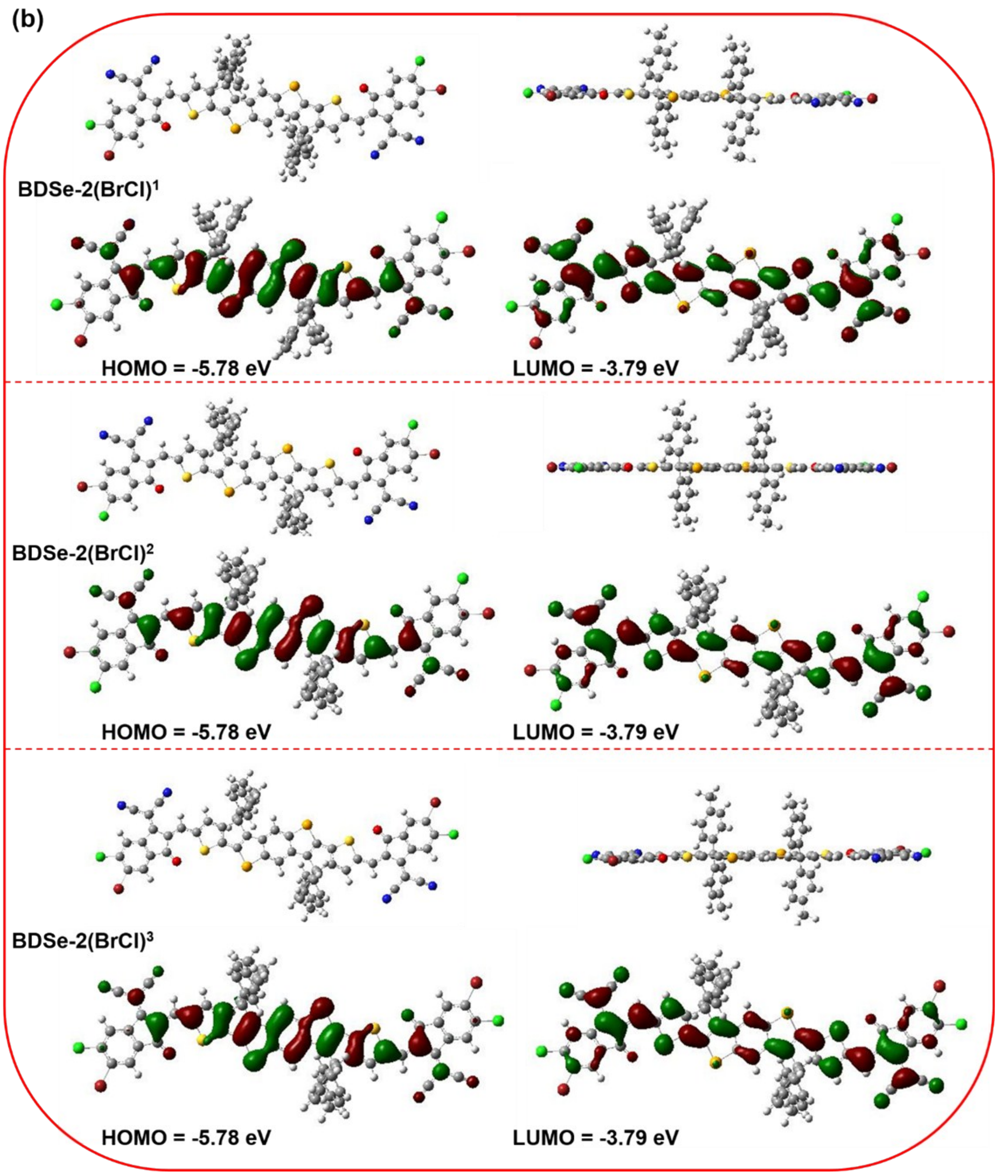


Figure S4. (a) Molecular geometry and energy levels for the **BDSe-4Cl** and **BDSe-4Br**. (b) Molecular geometry and energy levels for the **BDSe-2(BrCl)** with three isomers.

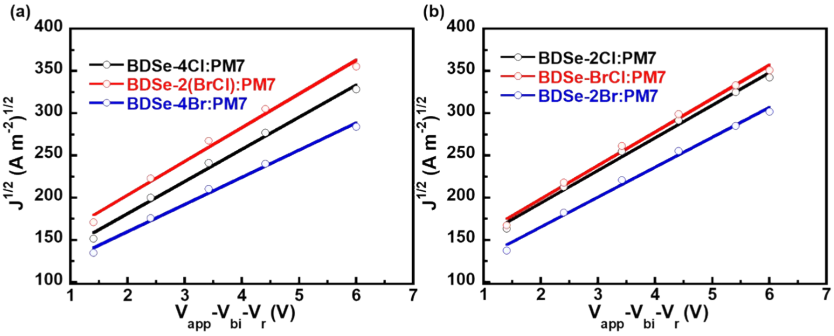


Figure S5. (a) The dark *J-V* plots of hole-only devices based on **BDSe-4Cl**:**PM7**, **BDSe-2(BrCl)**:**PM7** and **BDSe-4Br**:**PM7** blend films, respectively. (b) The dark *J-V* plots of electron-only devices based on **BDSe-4Cl**:**PM7**, **BDSe-2(BrCl)**:**PM7** and **BDSe-4Br**:**PM7** blend films, respectively.

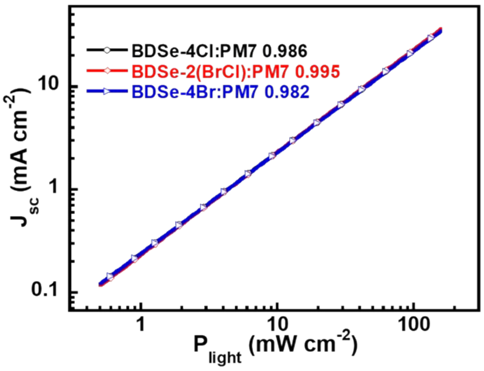
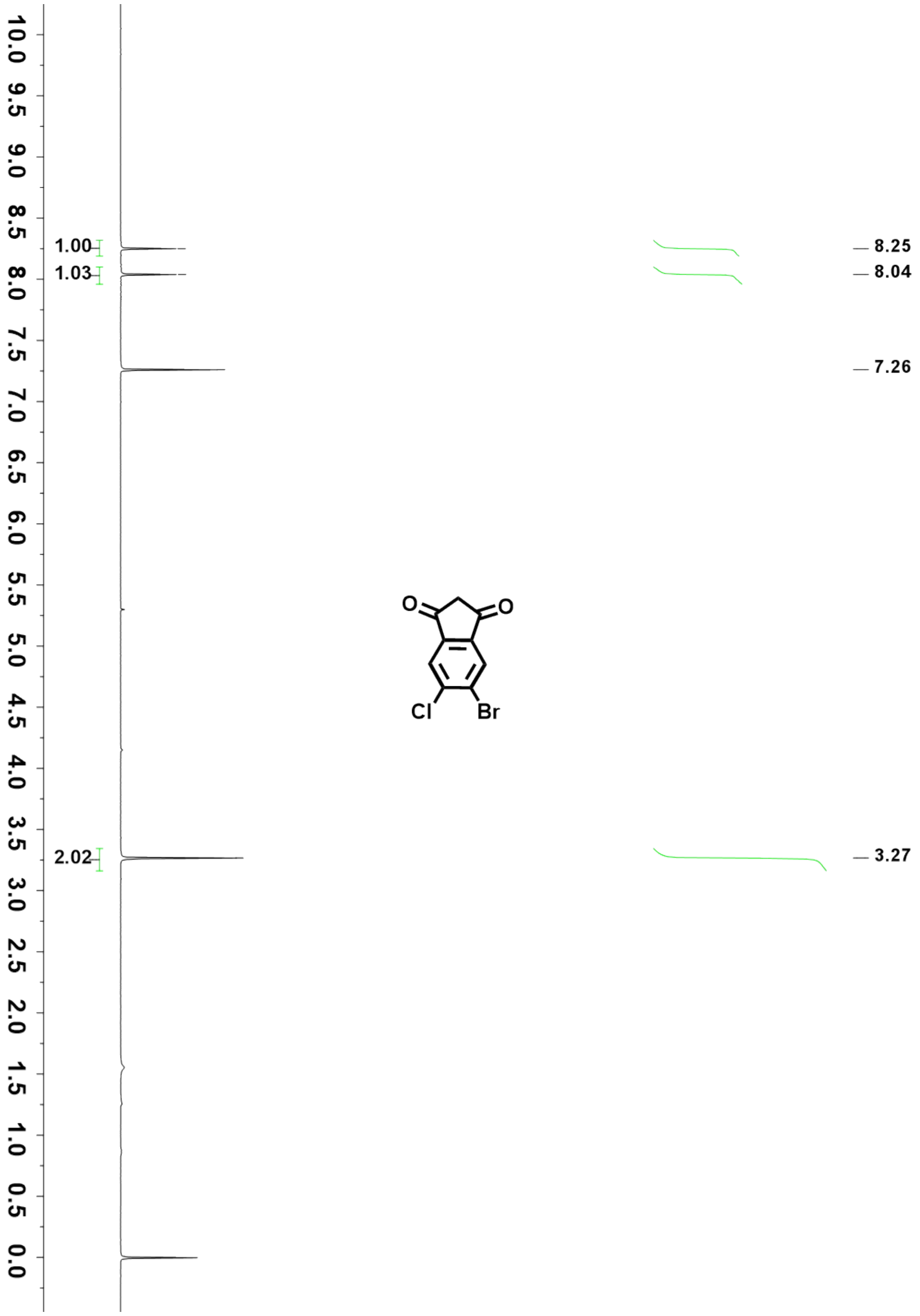
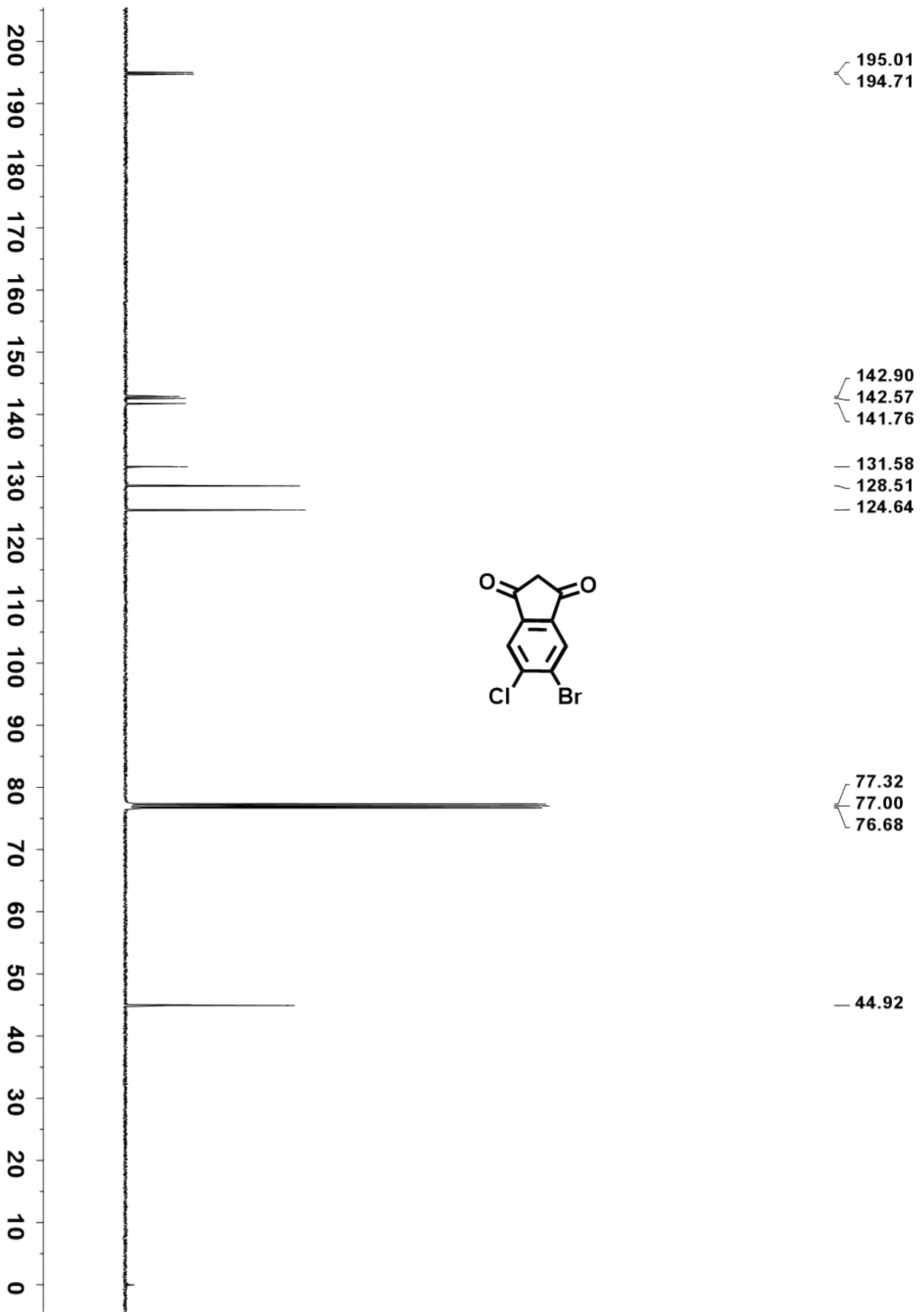


Figure S6. Light-intensity (P) dependence of J_{sc} curves of **BDSe-4Cl**/**BDSe-2(BrCl)**/**BDSe-4Br**:**PM7-**based PSCs with/without thermal annealing under AM 1.5 G irradiation (100 mW cm^{-2}).

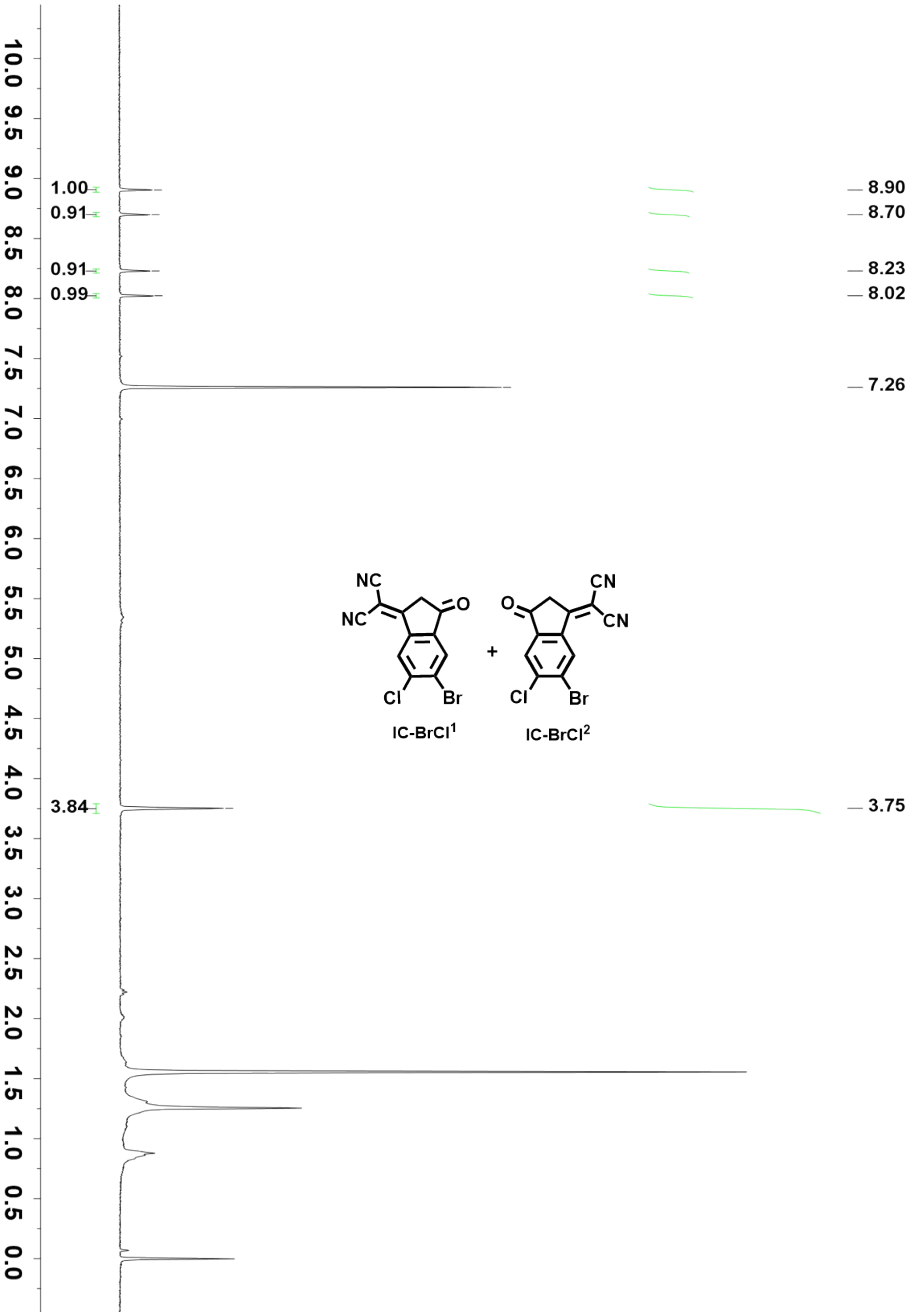
^{1}H NMR , ^{13}C NMR, and MALDI-TOF-MS spectrum of new compounds



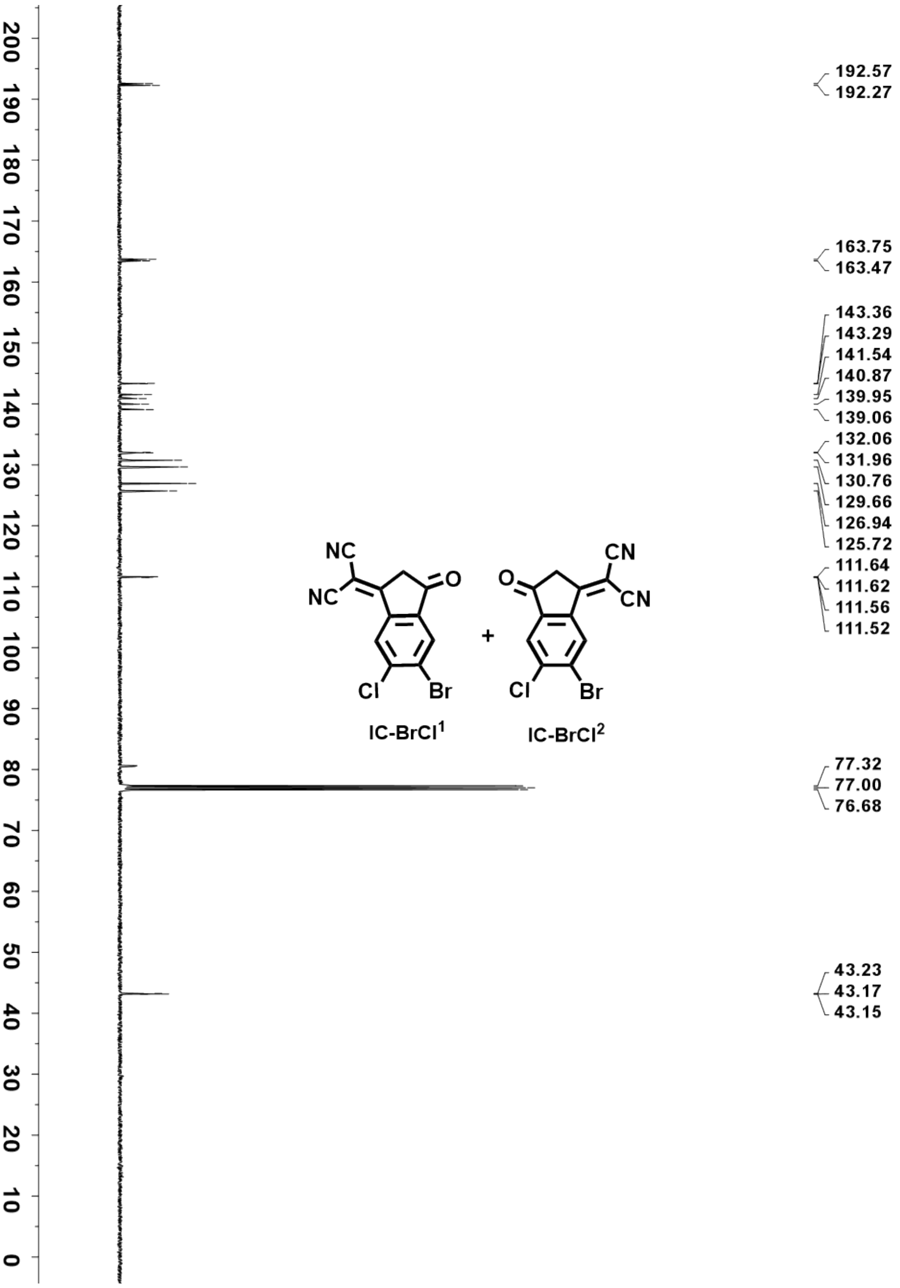
^{1}H NMR spectrum for **compound 2**



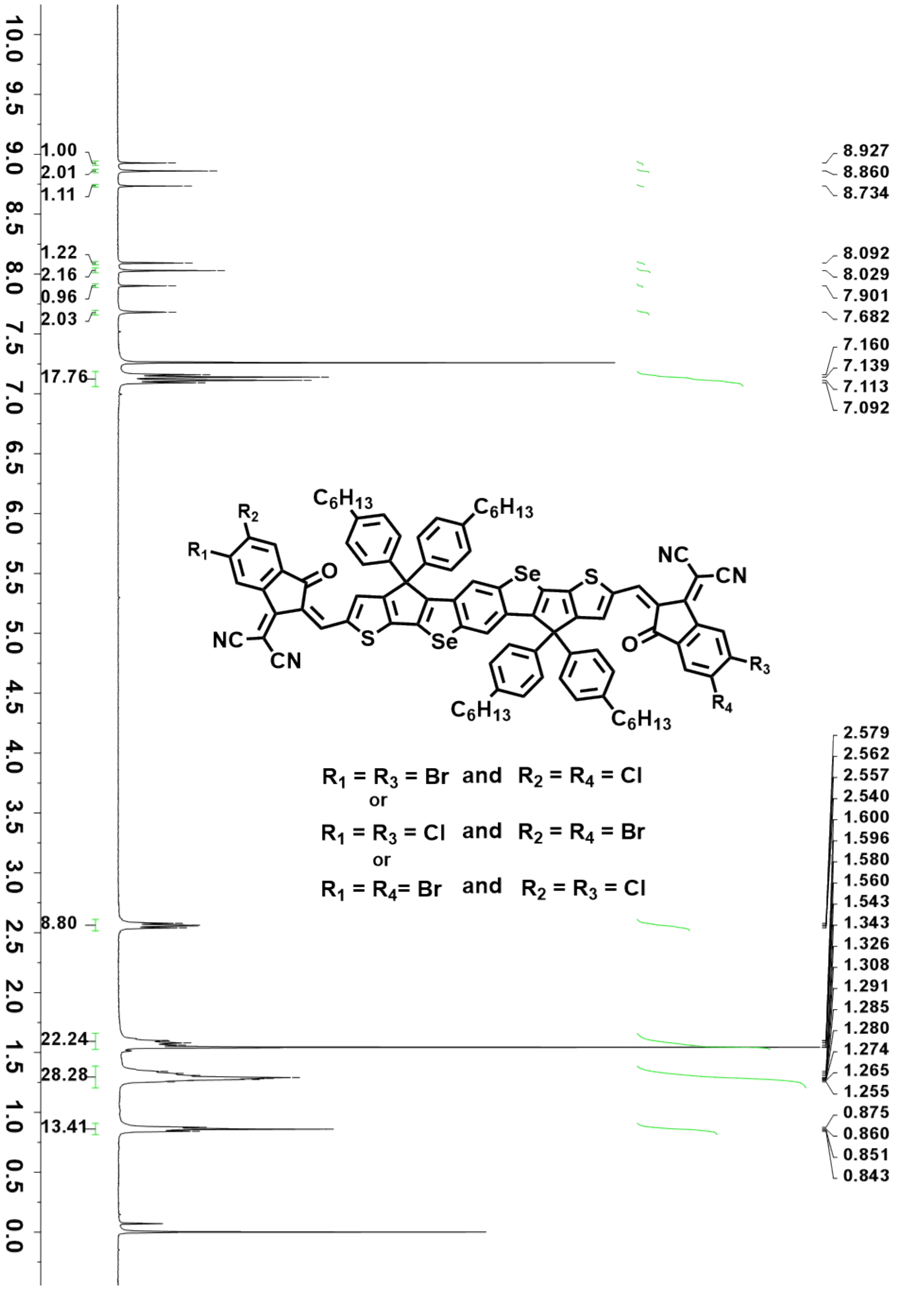
^{13}C NMR spectrum for **compound 2**



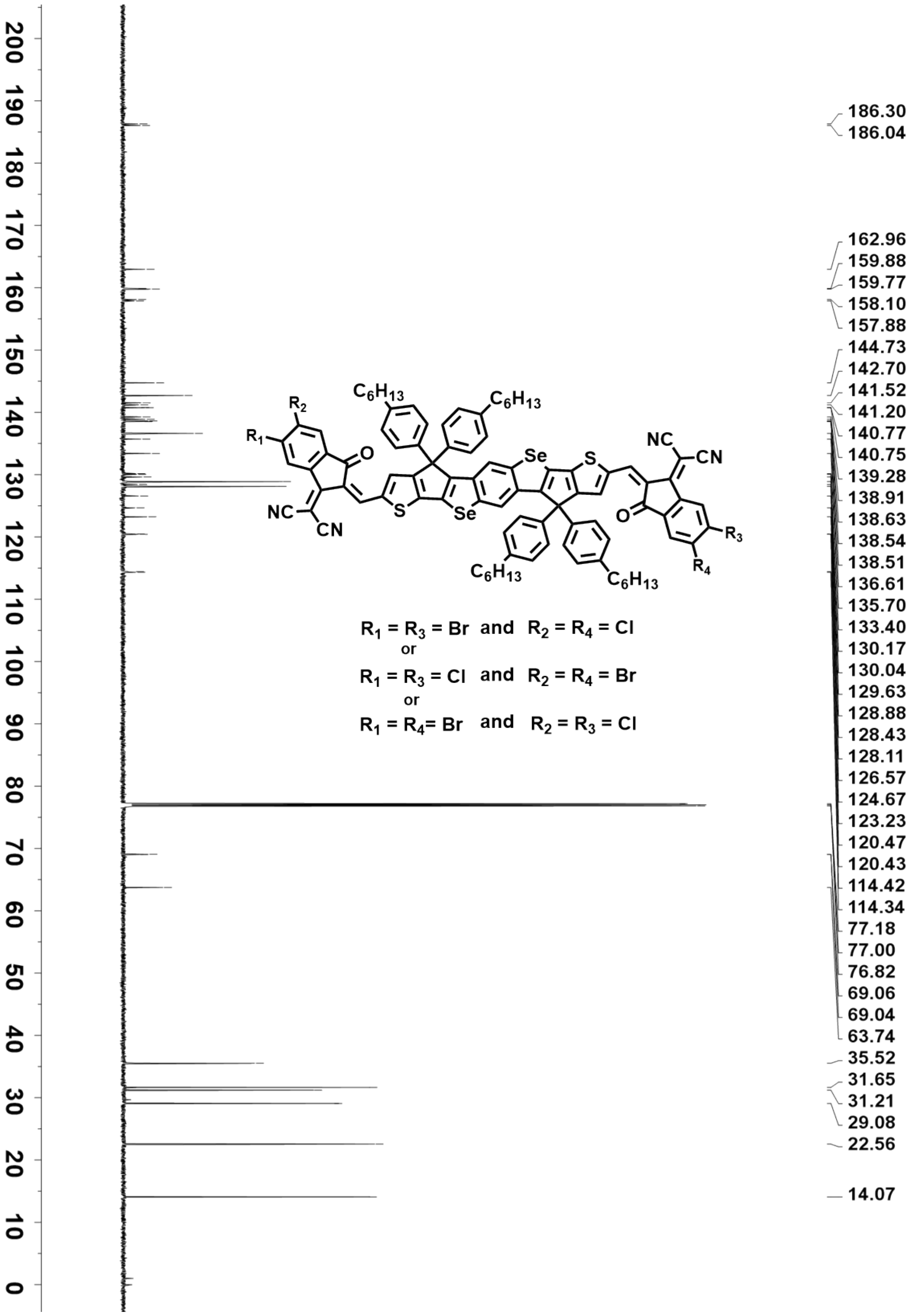
^{1}H NMR spectrum for **IC-BrCl**



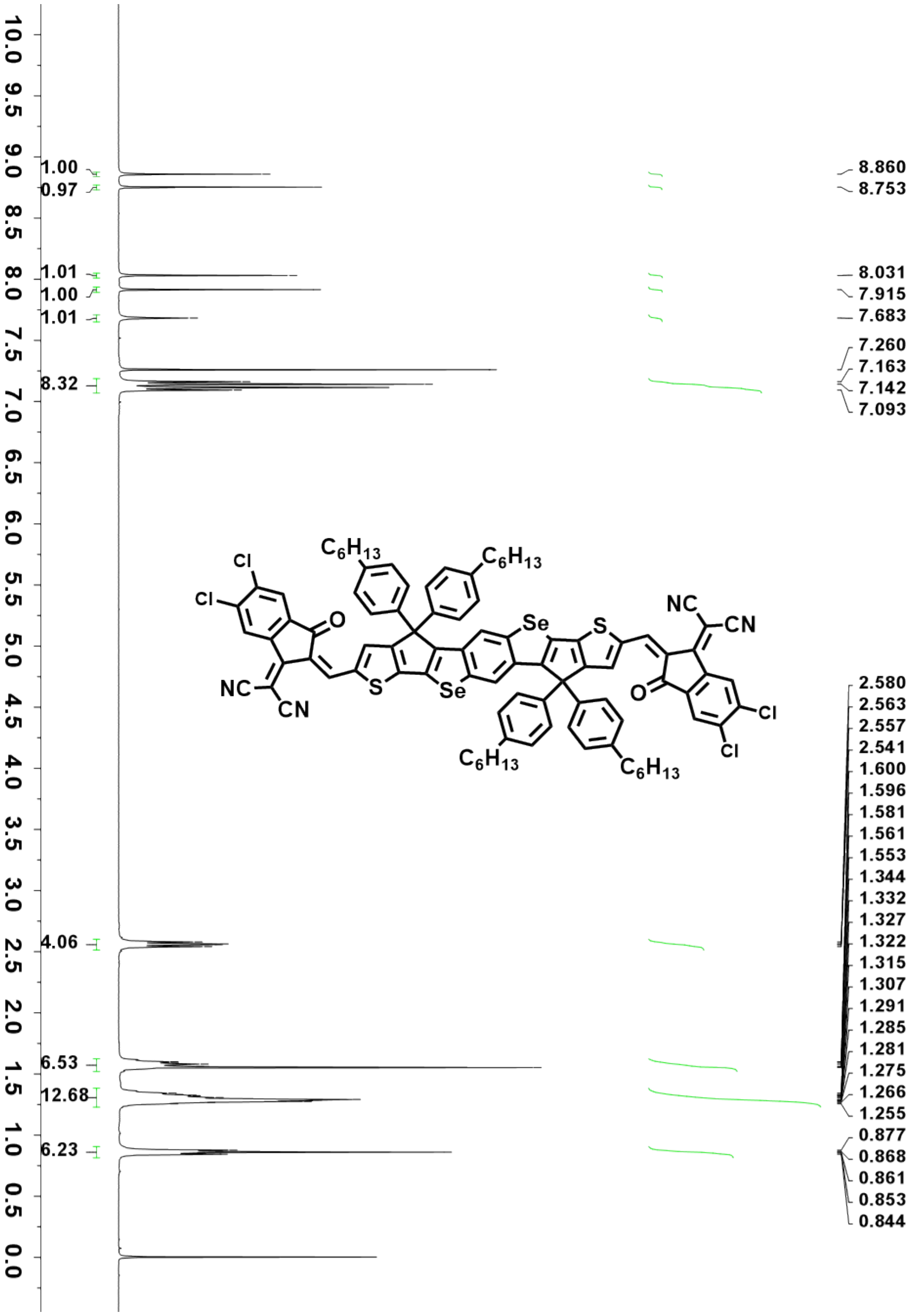
^{13}C NMR spectrum for **IC-BrCl**



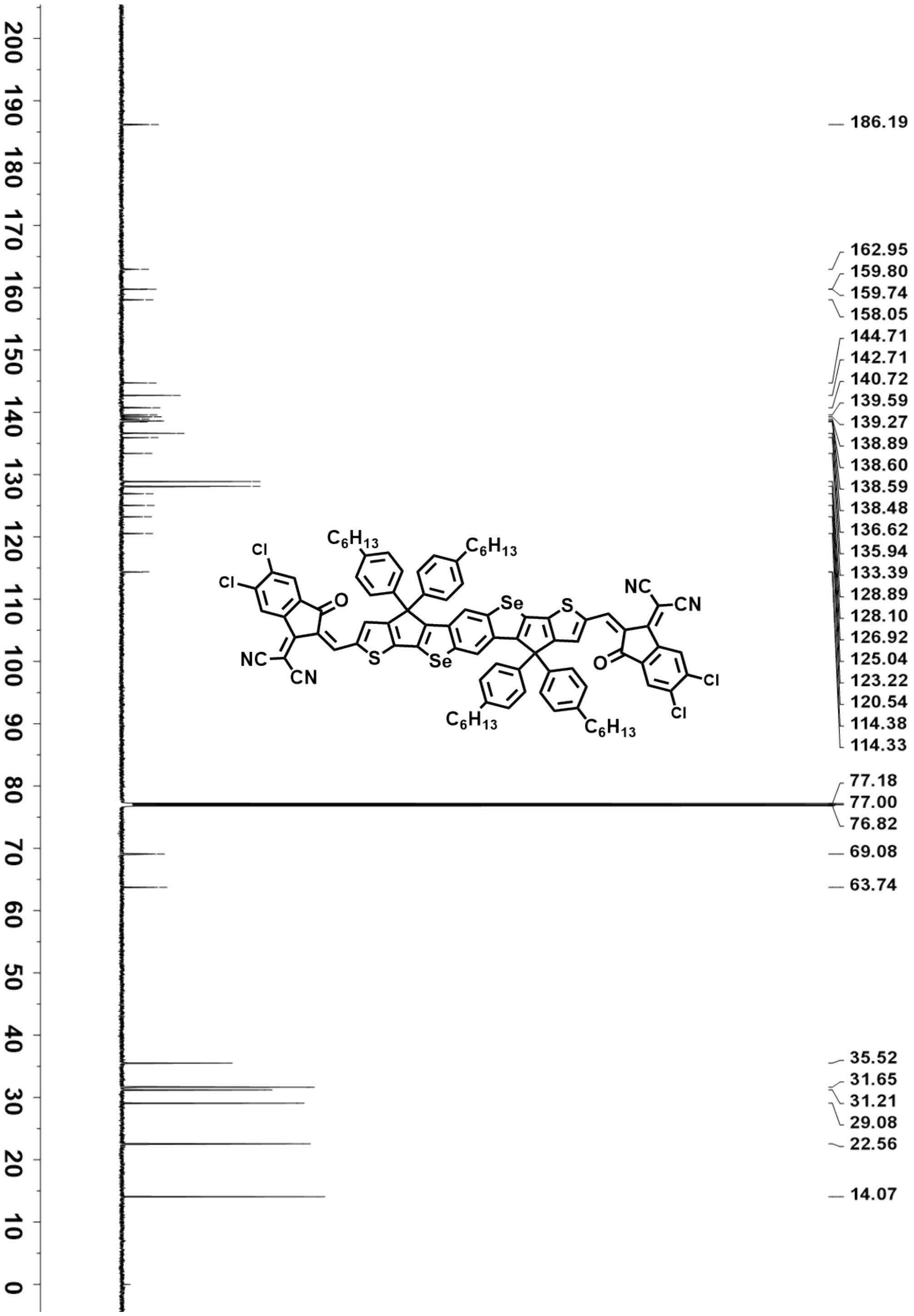
^{1}H NMR spectrum for **BDSe-2(BrCl)**



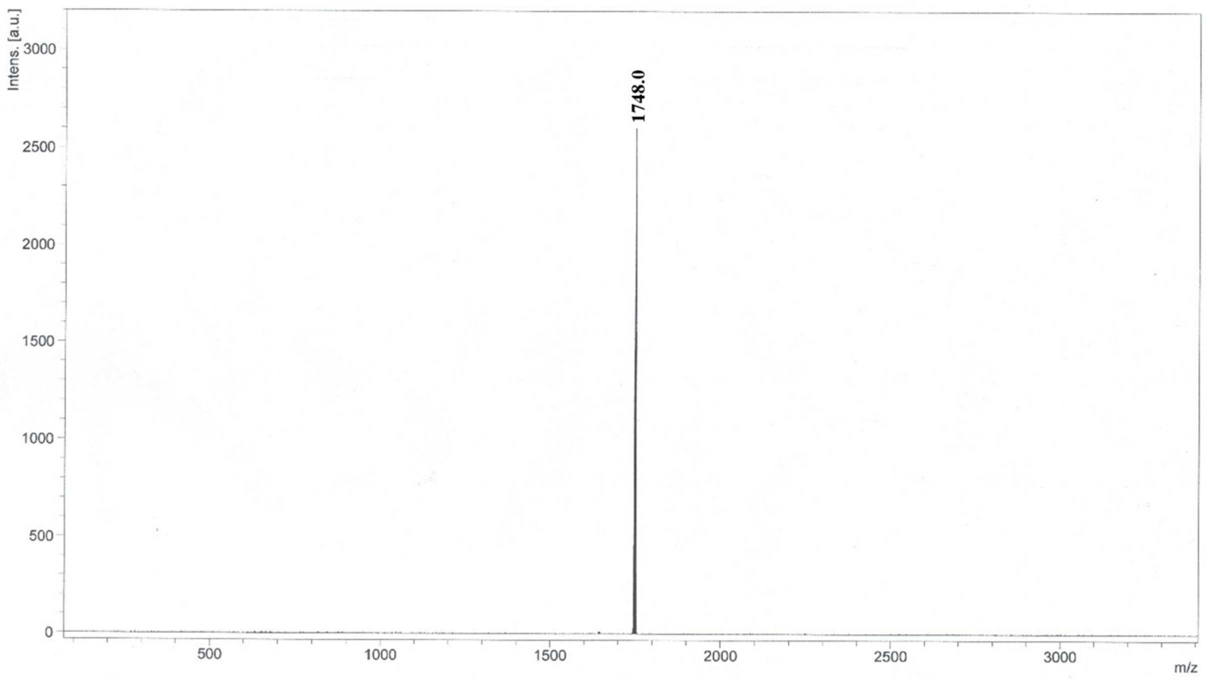
^{13}C NMR spectrum for **BDSe-2(BrCl)**



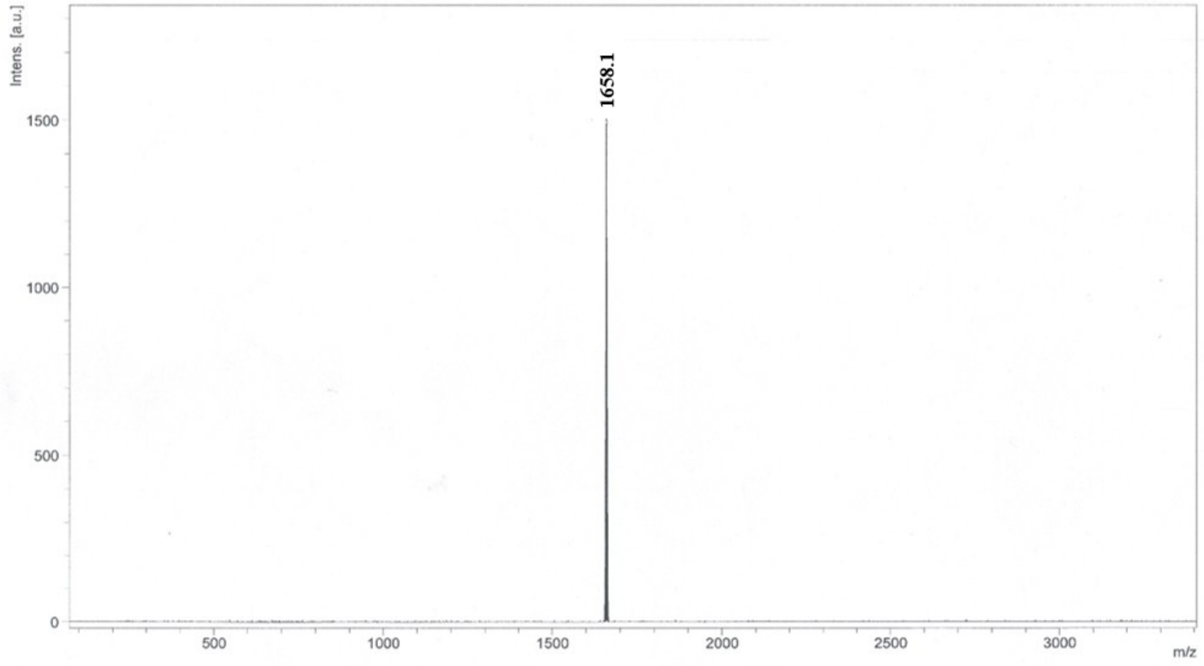
^{1}H NMR spectrum for **BDSe-4Cl**



^{13}C NMR spectrum for **BDSe-4Cl**



MALDI-TOF mass spectrum of **BDSe-2(BrCl)**



MALDI-TOF mass spectrum of **BDSe-4Cl**