Supporting Information (SI)

Synergistic Side-Chain and End-Group Engineering of C-Shaped A–D–A Acceptors for Enhanced Performance of Organic Photovoltaics

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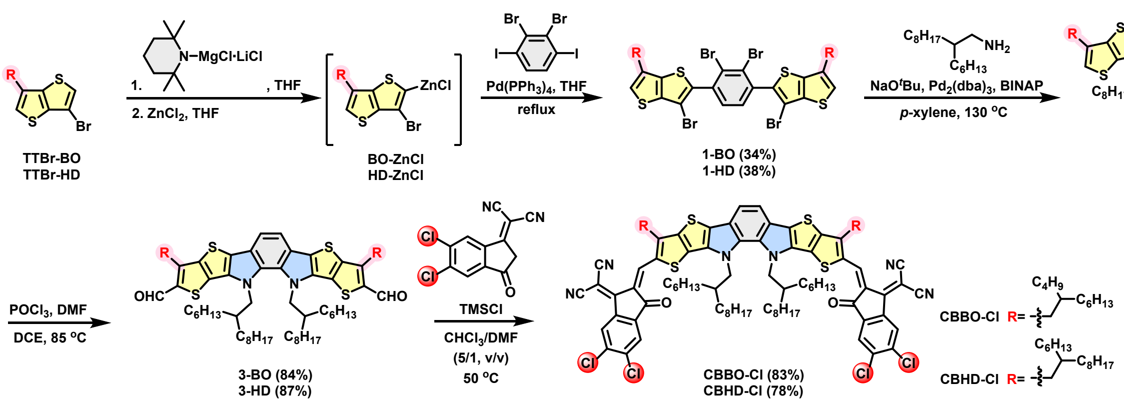
1. Instruments and characterization

^{1}H and ^{13}C NMR spectra were measured using Varian-400 MHz and JEOL-400 MHz instrument spectrometer. Deuterated chloroform ($CDCl_3$) with TMS as internal and benzene (C_6D_6) were used as references unless otherwise stated. Chemical shifts (δ) are reported in parts per million. The mass spectra of the samples were recorded on JEOL T200-GC high resolution spectrometer using electron impact (EI) or field desorption (FD) method. UV-vis absorption spectra were measured on HP8453 UV-vis spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted on a TA Q200 Instrument and a TA TGA55 Instrument under nitrogen atmosphere at heating/cooling rate of 10 °C min^{-1}. Surface topography was investigated using Veeco diInnova AFM and standard tips (Tapping mode; Length: 240 μm; Resonance Frequency: 70 kHz; Spring Constant: 2 N m^{-1}).

2. Synthetic procedures



Synthesis of compound 1-BO:

Compound **TTBr-BO** was synthesized following the procedures described in the literature.[1] To a solution of compound **TTBr-BO** (600 mg, 1.55 mmol) in THF (3 mL) was added TMPMgCl·LiCl (1 M in THF, 1.7 mL, 1.70 mmol) dropwise at 0 °C. After stirring 2 h at 0 °C, the mixture was added the solution of $ZnCl_2$ (245 mg, 1.80 mmol) in THF (1.2 mL) and kept stirring 2 h at 0 °C to prepare the zinc reagent. The solution of 2,3-dibromo-1,4-diiodobenzene (292.6 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (69.4 mg, 0.06 mmol) in THF (2.5 mL) was added the zinc reagent slowly at 0 °C. The mixture was stirred 16 h under refluxing. After cooling to room temperature, the reaction solution was quenched by $NH_4Cl_{(aq)}$ and extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to give **1-BO** (205.37 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 2H), 7.06 (s, 2H), 2.67 (d, J = 7.2 Hz, 4H), 1.83 (m, 2H), 1.35-1.20 (m, 32H), 0.91-0.84 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.91, 138.38, 137.58, 137.32, 135.13, 131.12, 129.26, 123.15, 104.27, 37.53, 34.74, 33.67, 33.74, 33.67, 33.38, 31.96, 29.72, 28.93, 26.66, 23.10, 22.77, 14.25, 14.23. HRMS (FD, $C_{42}H_{54}$ Br_4S_4): calcd, 1001.9847; found, 1001.9848.

Synthesis of compound 2-BO:

To a solution of compound **1-BO** (408.1 mg, 0.40 mmol), ^{t}BuONa (346.2 mg, 3.60 mmol), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, 199.25 mg, 0.32 mmol), and $Pd_2(dba)_3$ (73.2 mg, 0.08 mmol) in degassed *p*-xylene (4.8 mL) was added 2-hexyldecan-1-amine (579.5 mg, 2.40 mmol) at room temperature. After stirring 21 h at 110 °C, the reaction solution was extracted with EA/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to get **2-BO** (113.0 mg, 24% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.53 (s, 2H), 6.69 (s, 2H), 4.76 (d, J = 7.6 Hz, 4H), 2.67 (d, J = 6.8 Hz, 4H), 2.28 – 2.20 (m, 2H), 2.14 – 2.02 (m, 2H), 1.49 – 1.35 (m, 16H), 1.34 – 1.20 (m, 24H), 1.21 – 1.09 (m, 20H), 1.01 – 0.91 (m, 32H), 0.83 – 0.71 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ141.72, 139.01, 136.13, 132.02, 124.77, 122.82, 122.81, 120.16, 113.62, 54.95, 38.93, 37.79, 34.83, 32.37, 32.13, 30.96, 30.93, 30.27, 30.19, 30.17, 29.91, 29.86, 29.74, 29.33, 27.12, 25.99, 25.88, 23.50, 23.18, 23.17, 23.03, 14.50, 14.45, 14.40. HRMS (FD, $C_{74}H_{120}N_2S_4$): calcd, 1164.8340; found, 1164.8346.

Synthesis of compound 3-BO:

$POCl_3$ (89.8 μL, 0.96 mmol) was added in DMF (1.0 mL) and stirred for 30 mins at 0°C. To a solution of compound **2-BO** (113 mg, 0.096 mmol) in DCE (6 mL) was added the mixture dropwise and stirred for 16 h at 85°C. After cooling to room temperature, the mixture was poured into water and stirred for 1 h for hydrolysis. The resulting solution was then extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane and DCM as the eluent (hexane/DCM, v/v, 3/2) to get **3-BO** (98 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 2H), 7.57 (s, 2H), 4.55 (d, J = 7.6 Hz, 4H), 3.07 (d, J = 7.2 Hz, 4H), 2.10 –1.90 (m, 4H), 1.45 – 1.21 (m, 36H), 1.20 – 0.95 (m, 24H), 0.94 – 0.79 (m, 32H), 0.79 – 0.64 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.99, 146.35, 142.19, 137.94, 137.54, 132.26, 130.21, 127.13, 122.45, 114.20, 54.85, 39.31, 38.73, 33.96, 33.64, 33.19, 30.50, 29.84, 29.78, 29.71, 29.45, 29.39, 29.31, 28.94, 26.72, 25.58, 25.47, 23.10, 22.78, 22.76, 22.62, 14.26, 14.23, 14.13. HRMS (FD, $C_{76}H_{120}N_2O_2S_4$): calcd, 1220.8238; found, 1220.8200.

Synthesis of compound CBBO-Cl:

To a solution of compound **3-BO** (70 mg, 0.057 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1*H*-inded-1-ylidene)malononitrile (60.5 mg, 0.23 mmol) in $CHCl_3$/DMF (5.80 mL, v/v, 5/1) was added trimethylsilyl chloride (TMSCl, 1.46 mL, 11.5 mmol) at room temperature. After stirring 16 h at 40 ^{o}C, the solution was extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed by MeOH and then purified by column chromatography on silica gel using hexane and DCM as the eluent (hexane/ dichloromethane, v/v, 3/2). The resulting solid was purified by recrystallization with DCM/MeOH to get **CBBO-Cl** (75 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (s, 2H), 8.79 (s, 2H), 7.95 (s, 2H), 7.60 (s, 2H), 4.69 (d, J = 7.5 Hz, 4H), 3.15 (d, J = 7.1 Hz, 4H), 2.04 (m, 4H), 1.51 – 1.31 (m, 28H), 1.31 – 1.01 (m, 34H), 1.01 – 0.91 (m, 14H), 0.91 – 0.75 (m, 22H), 0.75 – 0.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.97, 159.10, 153.72, 144.27, 139.31, 138.98, 138.70, 138.54, 136.86, 136.25, 136.09, 134.38, 133.41, 131.47, 126.79, 124.84, 123.19, 119.53, 115.31, 115.25, 114.69, 68.18, 55.13, 40.11, 38.88, 34.61, 33.56, 33.29, 31.88, 31.84, 31.56, 30.57, 29.75, 29.57, 29.40, 29.33, 29.23, 28.83, 26.58, 25.63, 25.60, 25.49, 25.45, 22.95, 22.64, 22.50, 14.12, 14.08, 14.07, 14.06. HRMS (FD, $C_{100}H_{124}N_6O_2$ S_4Cl_4): calcd, 1708.7428; found, 1708.7428.

Synthesis of compound 1-HD:

Compound **TTBr-HD** was synthesized following the procedures described in the literature.[1] To a solution of compound **TTBr-HD** (691 mg, 1.56 mmol) in THF (3 mL) was added TMPMgCl·LiCl (1 M in THF, 1.7 mL, 1.70 mmol) dropwise at 0 °C. After stirring 2 h at 0 °C, the mixture was added the solution of $ZnCl_2$ (245 mg, 1.80 mmol) in THF (1.2 mL) and kept stirring 2 h at 0 °C to prepare the zinc reagent. The solution of 2,3-dibromo-1,4-diiodobenzene (292.6 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (69.4 mg, 0.06 mmol) in THF (2.5 mL) was added the zinc reagent slowly at 0 °C. The mixture was stirred 16 h under refluxing. After cooling to room temperature, the reaction solution was quenched by $NH_4Cl_{(aq)}$ and extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to give **1-HD** (253.9 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (s, 2H), 7.05 (s, 2H), 2.66 (d, J = 6.8 Hz, 4H), 1.82 (m, 2H), 1.35-1.20 (m, 48H), 0.89-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.96, 138.45, 137.64, 137.38, 135.20, 131.16, 129.31, 123.19, 104.32, 37.63, 34.82, 33.77, 33.74, 32.06, 32.02, 30.09, 29.77, 29.75, 29.48, 26.75, 26.73, 22.84, 22.83, 14.28. HRMS (FD, $C_{50}H_{70}$ Br_4S_4): calcd, 1114.1099; found 1114,1090.

Synthesis of compound 2-HD:

To a solution of compound **1-HD** (280 mg, 0.25 mmol), ^{t}BuONa (216 mg, 2.25 mmol), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, 124.5 mg, 0.20 mmol), and $Pd_2(dba)_3$ (45.8 mg, 0.05 mmol) in degassed *p*-xylene (3.0 mL) was added 2-hexyldecan-1-amine (363 mg, 1.50 mmol) at room temperature. After stirring 21 h at 110 °C, the reaction solution was extracted with EA/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane as the eluent to get **2-HD** (82.9 mg, 26% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.55 (s, 2H), 6.71 (s, 2H), 4.78 (d, J = 7.6 Hz, 4H), 2.70 (d, J = 6.8 Hz, 4H), 2.28 – 2.19 (m, 2H), 2.14 – 2.04 (m, 2H), 1.50 – 1.38 (m, 16H), 1.37 – 1.26 (m, 40H), 1.21 – 1.07 (m, 16H), 1.01 – 0.91 (m, 36H), 0.89 – 0.81 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ141.73, 139.01, 136.16, 132.04, 124.79, 122.84, 122.80, 120.20, 113.64, 67.83, 54.90, 38.93, 37.84, 34.87, 34.18, 32.38, 32.36, 32.12, 30.92, 30.89, 30.50, 30.19, 30.15, 29.90, 29.86, 29.73, 27.16, 27.12, 25.96, 25.83, 23.16, 23.02, 14.49, 14.43, 14.40. HRMS (FD, $C_{82}H_{136}N_2S_4$): calcd, 1276.95920; found, 1276.9604.

Synthesis of compound 3-HD:

$POCl_3$ (98 μL, 1.04 mmol) was added in DMF (1.0 mL) and stirred for 30 mins at 0°C. To a solution of compound **2-HD** (134 mg, 0.104 mmol) in DCE (6.5 mL) was added the mixture dropwise and stirred for 16 h at 85°C. After cooling to room temperature, the mixture was poured into water and stirred for 1 h for hydrolysis. The resulting solution was then extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane and DCM as the eluent (hexane/DCM, v/v, 3/2) to get **3-HD** (120.6 mg, 87 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 2H), 7.56 (s, 2H), 4.55 (d, J = 6.4 Hz, 4H), 3.06 (d, J = 6.4 Hz, 4H), 2.00 (m, 4H), 1.45 – 1.34 (m, 16H), 1.32 – 1.15 (m, 40H), 1.14 – 0.95 (m, 16H), 0.94 – 0.80 (m, 36H), 0.79 – 0.65 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.03, 146.40, 142.18, 137.72, 132.25, 130.22, 127.14, 122.43, 114.19, 77.32, 76.84, 54.80, 39.33, 38.71, 33.93, 33.18, 31.98, 31.63, 30.45, 30.04, 29.72, 29.42, 29.33, 26.72, 25.55, 25.43, 22.77, 22.62, 14.25, 14.14. HRMS (FD, $C_{84}H_{136}N_2S_4$): calcd, 1332.9490; found, 1332.9500.

Synthesis of compound CBHD-Cl:

To a solution of compound **3-HD** (95 mg, 0.07 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1*H*-inded-1-ylidene)malononitrile (75.0 mg, 0.28 mmol) in $CHCl_3$/DMF (7.20 mL, v/v, 5/1) was added trimethylsilyl chloride (TMSCl, 1.80 mL, 14.20 mmol) at room temperature. After stirring 16 h at 40 °C, the solution was extracted with DCM/H_2O. The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed by MeOH and then purified by column chromatography on silica gel using hexane and DCM as the eluent (hexane/ dichloromethane, v/v, 3/2). The resulting solid was purified by recrystallization with DCM/MeOH to get **CBHD-Cl** (97 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ9.15 (s, 2H), 8.79 (s, 2H), 7.95 (s, 2H), 7.60 (s, 2H), 4.69 (d, J = 7.35 Hz, 4H), 3.14 (d, J = 7.15 Hz, 4H), 2.04 (m, 4H), 1.50 – 1.30 (m, 14H), 1.29 – 1.14 (m, 34H), 1.13 – 0.93 (m, 36H), 0.93 – 0.75 (m, 30H), 0.75 – 0.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.95, 159.10, 153.73, 144.26, 139.31, 138.98, 138.70, 138.54, 136.86, 136.27,136.09, 134.37, 133.41, 131.46, 126.79, 124.84, 123.19, 119.53, 115.31, 115.24, 114.69, 68.19, 55.13, 40.13, 38.88, 34.59, 33.58, 31.87, 31.84, 31.56, 30.57, 29.91, 29.75, 29.58, 29.57, 29.40, 29.33, 29.30, 29.23, 26.59, 25.62, 25.60, 25.48, 25.44, 22.64, 22.50, 14.12, 14.08, 14.06. HRMS (FD, $C_{108}H_{140}N_6O_2S_4Cl_4$): calcd, 1820.8680; found, 1820.8652.

3. UV-vis spectrophotometer

UV-vis absorption spectra were measured on HP8453 UV-vis spectrophotometer. The neat films were prepared by spin-coating chloroform solution of the materials (10 mg mL^{-1}) at 3000 rpm for 30 s on the quartz substrate.

4. Cyclic voltammetry (CV) characteristics

CV was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and an Ag/Ag^+ electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was the electrolyte. CV curves were calibrated using ferrocene as the standard, whose HOMO energy level is set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation $E_{HOMO} = -| E\text{onset ox} - E\text{onset ferrocene} + 4.8|$ eV. The LUMO energy levels were obtained from the equation $E_{LUMO} = -| E\text{onset red} - E\text{onset ferrocene} + 4.8|$ eV.

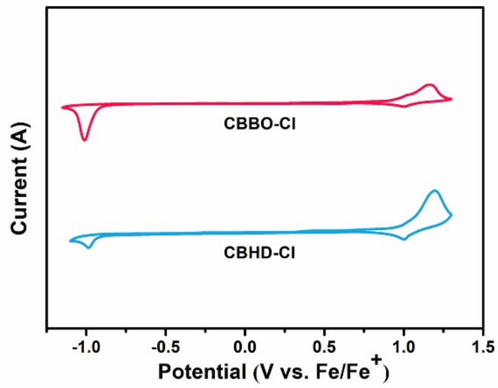


Fig. S1 Cyclic voltammogram of CBBO-Cl and CBHD-Cl in thin films at a scan rate of 100 mV s^{-1}.

5. Single crystal growth and the crystallographic data

Two solutions were prepared by dissolving 2 mg of CBBO-Cl and 2 mg of CBHD-Cl separately in 1.6 mL of chloroform. Each solution was then transferred into a 4 mL vial, which was capped with a piece of aluminum foil punctured with an 18G needle in the middle to allow slow vapor diffusion. These vials were placed into larger 20 mL vials containing 2.5 mL of acetonitrile, and the outer vials were sealed tightly. After standing for approximately 7 days, small crystal clusters of CBBO-Cl and CBHD-Cl formed in their respective vials.

Two dark blue single crystals were mounted on a CryoLoop with Parabar 10312 oil for the single-crystal X-ray diffraction experiments at −73 °C. The crystal size is 0.392 × 0.167 × 0.130 mm^3 for CBBO-Cl and 0.439 × 0.140 × 0.137 mm^3 for CBHD-Cl. The single-crystal X-ray diffraction data of CBBO-Cl and CBHD-Cl were individually collected in-house on a Bruker D8 Venture diffractometer equipped with a Mo-target (Kα = 0.71073 Å) microfocus X-ray generators and a PHOTON-II CMOS detector. The temperature was adjusted with a nitrogen flow (Oxford Cryosystems, 800+ series). After collection, the cell refinement and the data integration were carried out by Bruker SAINT software package using a narrow-frame algorithm and were corrected for absorption effects using the Multi-

Scan method (SADABS). Moreover, the molecular structure was solved by SHELXT (Sheldrick 2015) and refined by SHELXL-2019/1 (Sheldrick, 2019). The final anisotropic full-matrix least-squares method was used to refine on F2 with variables parameters to determine crystal structure. All calculations were performed using the APEX4 software package. The crystallographic parameters of CBBO-Cl and CBHD-Cl are listed in **Table S1.**

Table S1 The crystallographic data of CBBO-Cl and CBHD-Cl.

Material	CBBO-Cl	CBHD-Cl
Identification code	ic22397	ic22400_sq
Empirical formula	C100 H124 Cl4 N6 O2 S4	C108 H140 Cl4 N6 O2 S4
CCDC number	2496869	2496870
Formula weight	1712.08	1824.29
Temperature/K	200(2)	200(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
a/Å	24.7904(7)	25.5771(5)
b/Å	23.8797(7)	25.1142(6)
c/Å	34.3524(9)	33.9785(8)
α/°	90	90
β/°	108.5501(10)	110.0289(8)
γ/°	90	90
Volume/Å^3	19279.6(9)	20506.0(8)
Z	8	8
Density/Mg/m^3	1.180	1.182
Absorption coefficient/mm^{-1}	0.259	0.248
F(000)	7312	7824

Crystal size/mm^3	0.392 × 0.167 × 0.130	0.439 × 0.140 × 0.137
θ range for data collection/°	1.932 to 25.250	1.935 to 25.250
Index ranges	−24<=h<=29, −28<=k<=28, −40<=l<=41	−30<=h<=30, −30<=k<=27, −37<=l<=40
Reflections collected	55711	60355
Independent reflections	17455 [R(int) = 0.0639]	18583 [R(int) = 0.0539]
Completeness to θ = 22.464°	99.8 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9585 and 0.8385	0.9583 and 0.8215
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	17455 / 377 / 925	18583 / 337 / 901
Goodness-of-fit on F^2	1.512	1.819
Final R indices [I>2sigma(I)]	R1 = 0.1486, wR2 = 0.4003	R1 = 0.1921, wR2 = 0.4773
R indices (all data)	R1 = 0.2236, wR2 = 0.4644	R1 = 0.2598, wR2 = 0.5313
Extinction coefficient	n/a	n/a
Largest diff. peak and hole/e.Å^{-3}	1.037 and −1.044	1.428 and −1.346

6. Photovoltaic device fabrication and characterization

The fabrication of the inverted devices follows the procedures: The ITO-coated glass substrates were cleaned by ultrasonic cleaner in detergent, DI-water, acetone and isopropyl alcohol for 10 min, respectively, and subsequently treated with UV-ozone for 45 min. The ZnO layer was prepared by the ZnO precursor (zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Aldrich, 99.9%, 1 g)) and ethanolamine ($NH_2CH_2CH_2OH$, Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.8%, 10 mL) and spin-coated onto the pre-treated ITO-coated glass, followed by 180 °C baking in the air at relative humidity below 50% for 20 min. The PM6:CBBO-Cl and PM6:CBHD-Cl blends in 1:1.2 wt% with 7.5 mg mL^{-1} PM6 concentration were all dissolved in chloroform and stirred for 1.5 h at 45 °C.

Active layers were formed by spin-coating on top of the ZnO/ITO substrate. Moreover, the substrates were thermally annealed at 150 °C for 10 minutes in a glove box, the 2PACz solution (0.6 mg/mL in EtOH) was subsequently dropped on the substrate. Finally, the MoO_3 layer (7 nm) and silver anode (150 nm) were deposited by thermal evaporation at a pressure below 10^{-6} torr. The devices without encapsulation were characterized under ambient conditions. Current-voltage characteristics were measured by a Keithley 2400 SMU under the irradiation of AM 1.5G San-Yi solar simulator with JIS AAA spectrum. The characteristics of the solar cells were optimized by testing approximately 10 cells. EQE spectra were measured using a lock-in amplifier with a current preamplifier under short-circuit conditions with illumination by monochromatic light from a 250 W quartz-halogen lamp (Osram) passing through a monochromator (Spectral Products CM110).

7. Space-charge limited current (SCLC) characteristics

The hole-only and electron-only devices were fabricated by employing the following device structure: ITO/PEDOT:PSS/active layer/Au for holes and ITO/ZnO/active layer/Al for electrons. The mobilities were obtained by taking current-voltage curves and fitting the results to the equation $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, ε_0 the vacuum permittivity, ε_r the relative dielectric constant, μ the mobility, V the voltage, and L the film thickness.

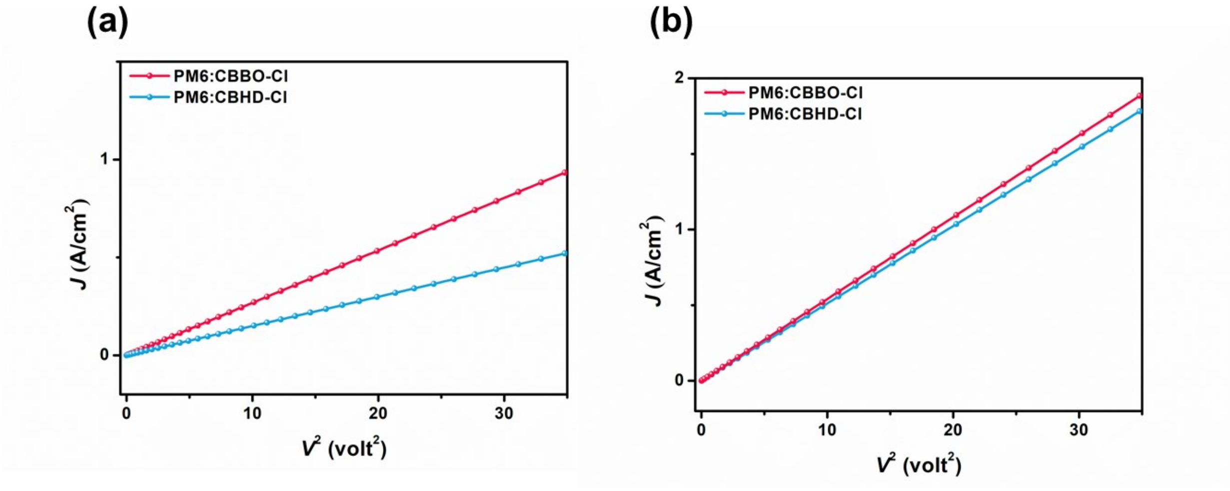


Fig. S2 *J*-*V* curves of the (a) hole-only and (b) electron-only of PM6:CBBO-Cl and PM6:CBHD-Cl binary devices.

8. Exciton dissociation and collection

The exciton dissociation probability (P_{diss}) and charge collection efficiency (P_{coll}) were systemically studied by measuring photocurrent density ($J_{ph} = J_L - J_D$) versus effective voltage ($V_{eff} = V_0 - V_{app}$), where J_L and J_D is the current in the light and in the dark, V_0 is the effective voltage when the $J_{ph} = 0$ V, and V_{app} is the applied bias voltage. The P_{diss} and P_{coll} can be estimated by the formula J_{sc}/J_{sat} and J_{mpp}/J_{sat}, where J_{sat} is the saturation photocurrent, J_{sc} and J_{mpp} represent photocurrent density under short circuit condition and maximum power point, respectively.

9. Charge recombination analysis

To investigate the charge recombination properties, the relationship between J_{sc} and light intensity (P_{light}) was measured. The parameter α in the formula $J_{sc} \propto P_{light}^{\alpha}$ represents bimolecular recombination. The linear relationship between V_{oc} and P_{light} was also evaluated by $V_{oc} \propto$ n(kT/q)ln(P_{light}) where n, q, T, and k, represent the ideality factor, elementary charge, temperature (in

Kelvin), and Boltzmann constant, respectively. A value of n = 2 indicates that trap-assisted recombination dominates in the devices, while n~1 suggests less trap-assisted recombination.

10. GIWAXS film measurements

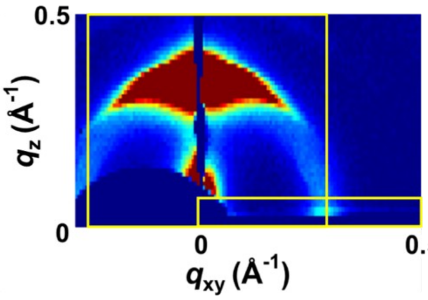


Fig. S3 2D GIWAXS in the scattering vector space presentation. The GIWAXS profiles were extracted along the areas highlighted by the two rectangle long the in-plane q_{xy} and out-of-plane q_z directions as indicated.

Grazing incidence wide-angle X-ray scattering (GIWAXS) of the neat NFA and blend films with PM6 was conducted in Taiwan Photon Source (TPS) 25A coherent X-ray scattering beamline at National Synchrotron Radiation Research Center (NSRRC). The corresponding 1D scattering profiles extracted from the selected zones along the in-plane (q_{xy}) and out-of-plane (q_z) directions of the 2D GIWAXS patterns collected with an Eiger X 1M detector for the sample thin films are illustrated in **Fig. S3**. The X-ray beam was of 5 μm size and with an incident angle set to 0.03^o; the sample-to-detector distance was 70.0 mm. 2D GIWAXS patterns were further converted to the scattering vector space, with q_{xy} and q_z representing the scattering vector components respectively along the in-plane and out-of-plane directions; after the conversion, there is a missing wedge of no diffraction information available in the vertical direction of each 2D GIWAXS pattern, due to the scattering geometry with a fixed-angle incidence.[2, 3]

11. References

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12. ^{1}H and ^{13}C

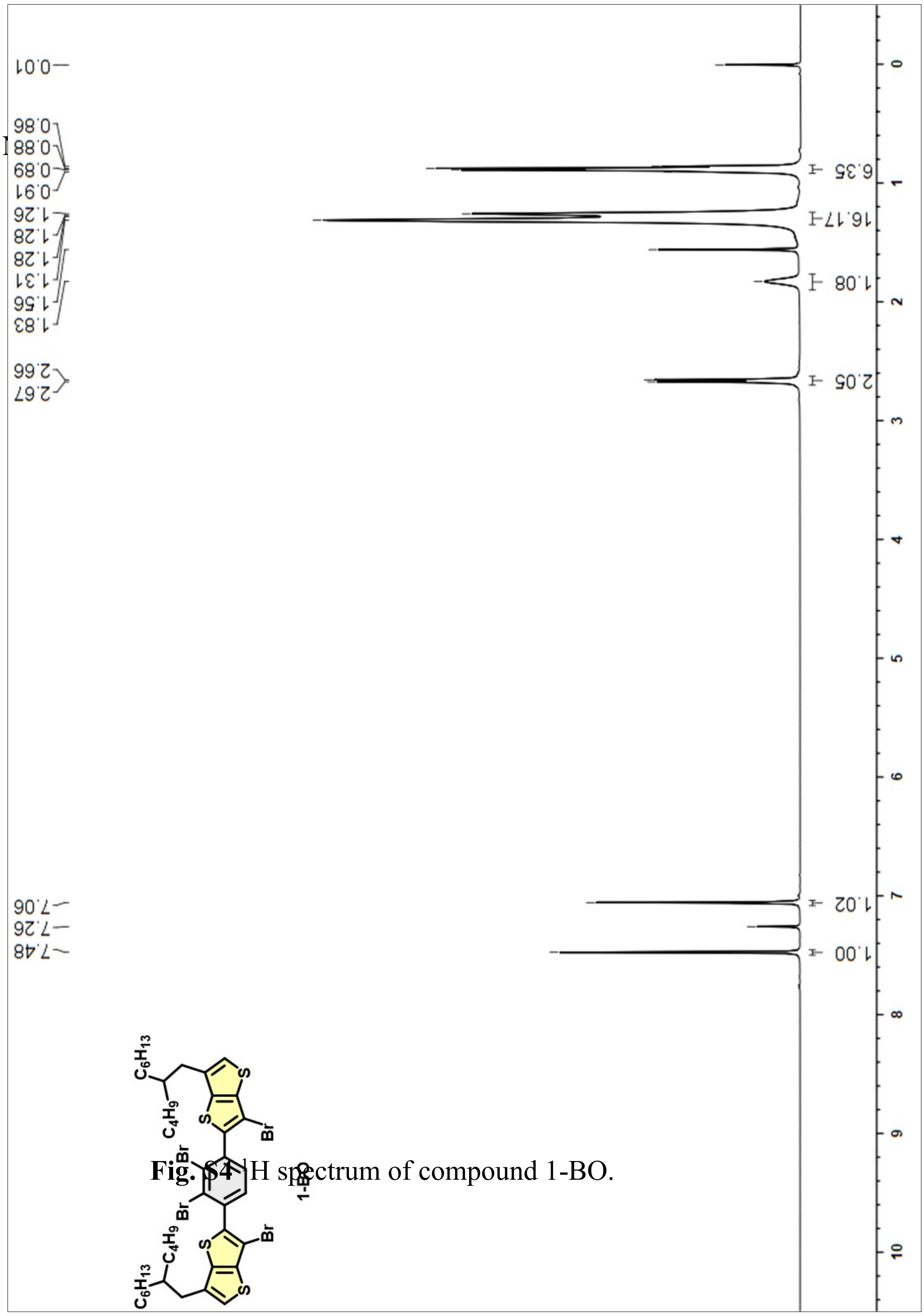

Fig. S4 ^{1}H spectrum of compound 1-BO.

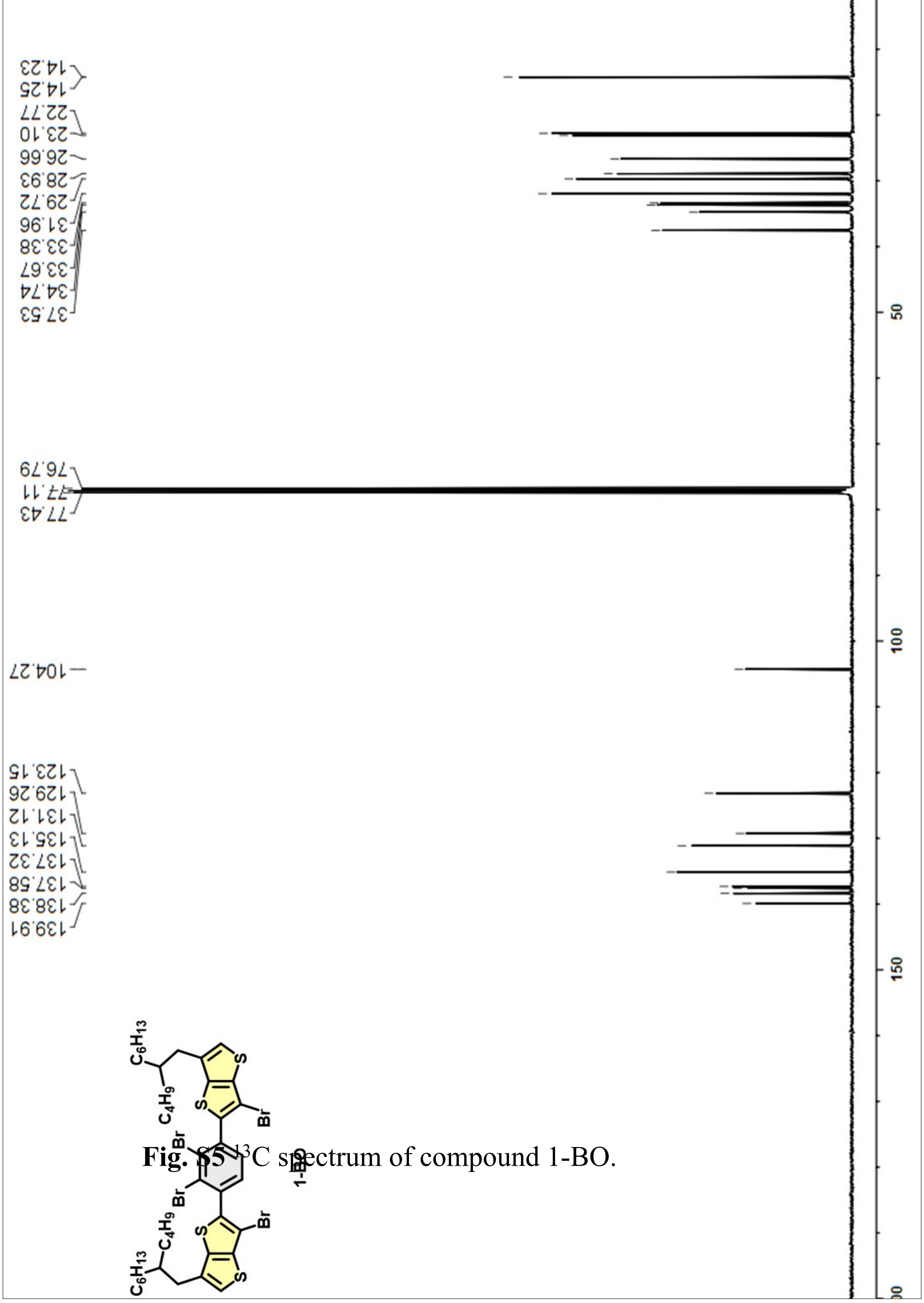

Fig. S5 ^{13}C spectrum of compound 1-BO.

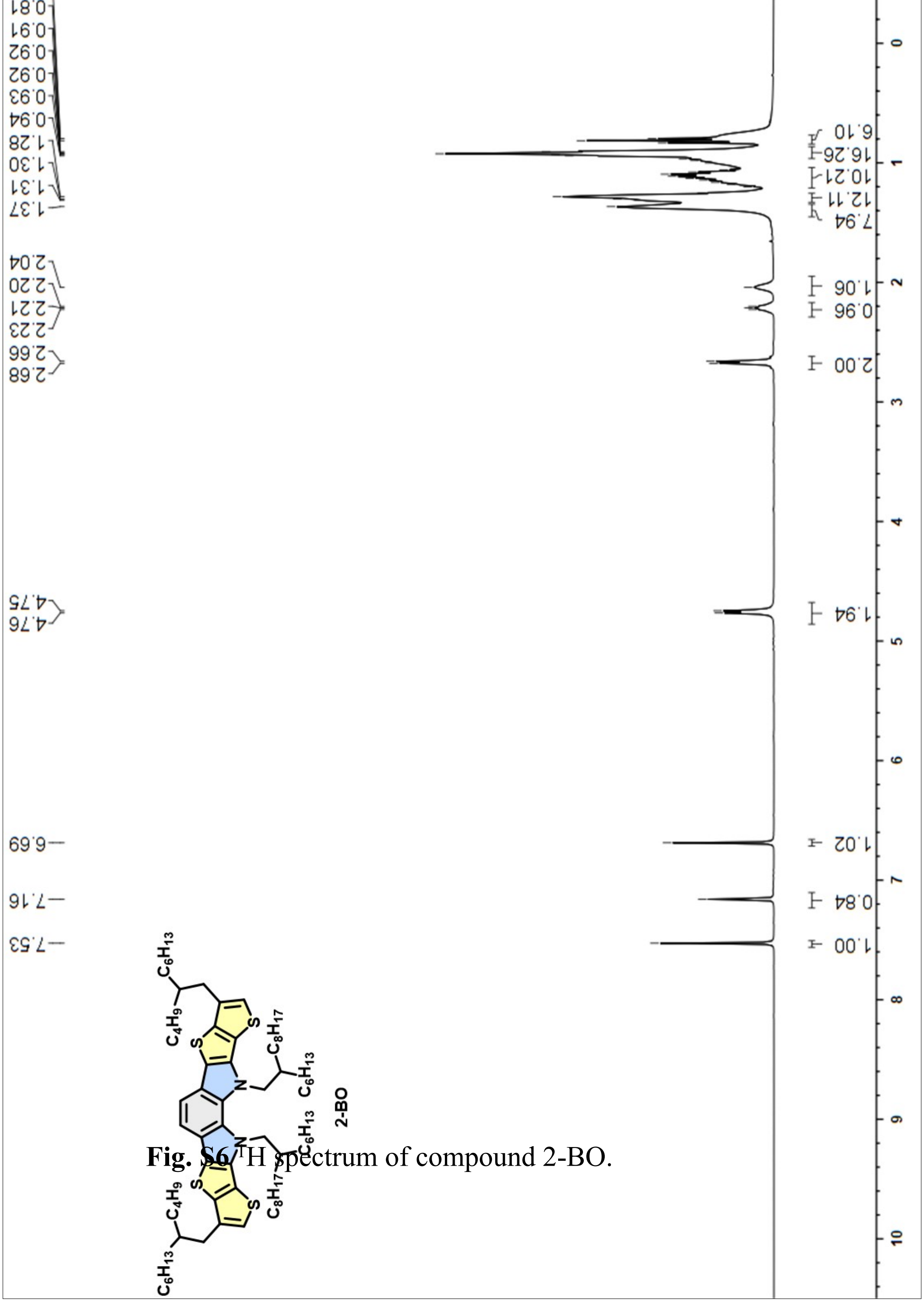

Fig. S6 ^{1}H spectrum of compound 2-BO.

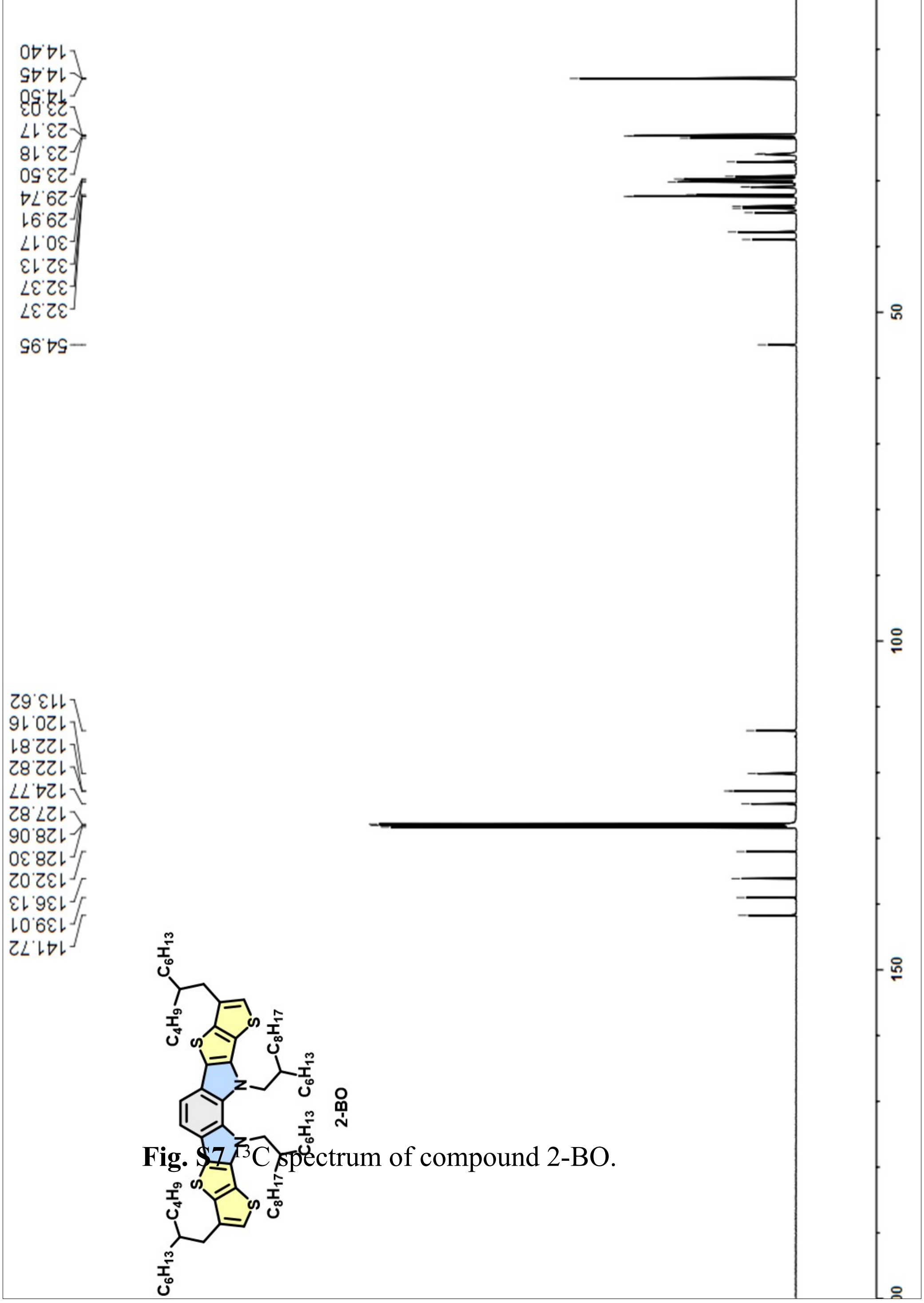

Fig. S7 ^{13}C spectrum of compound 2-BO.

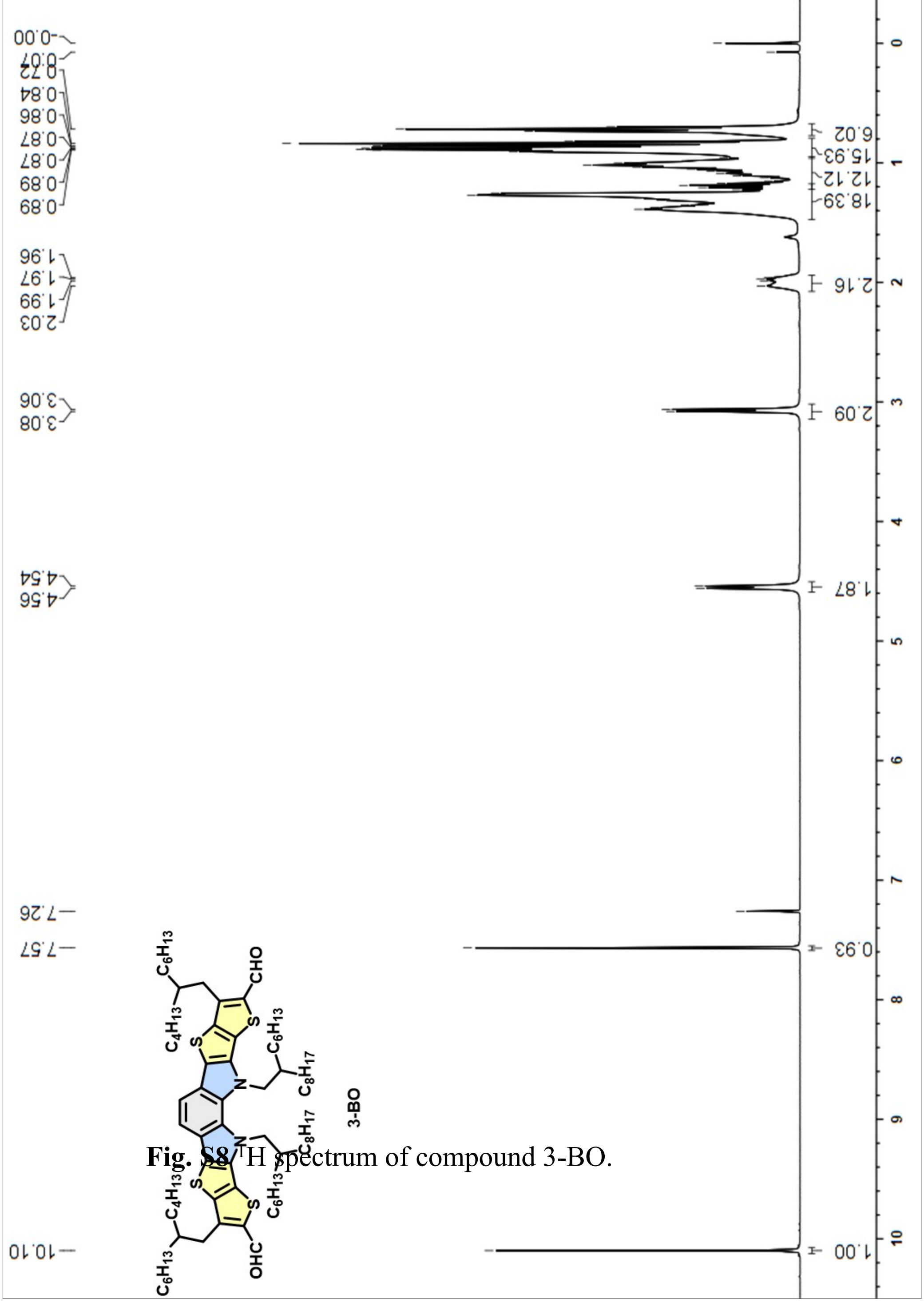

Fig. S8 ^{1}H spectrum of compound 3-BO.

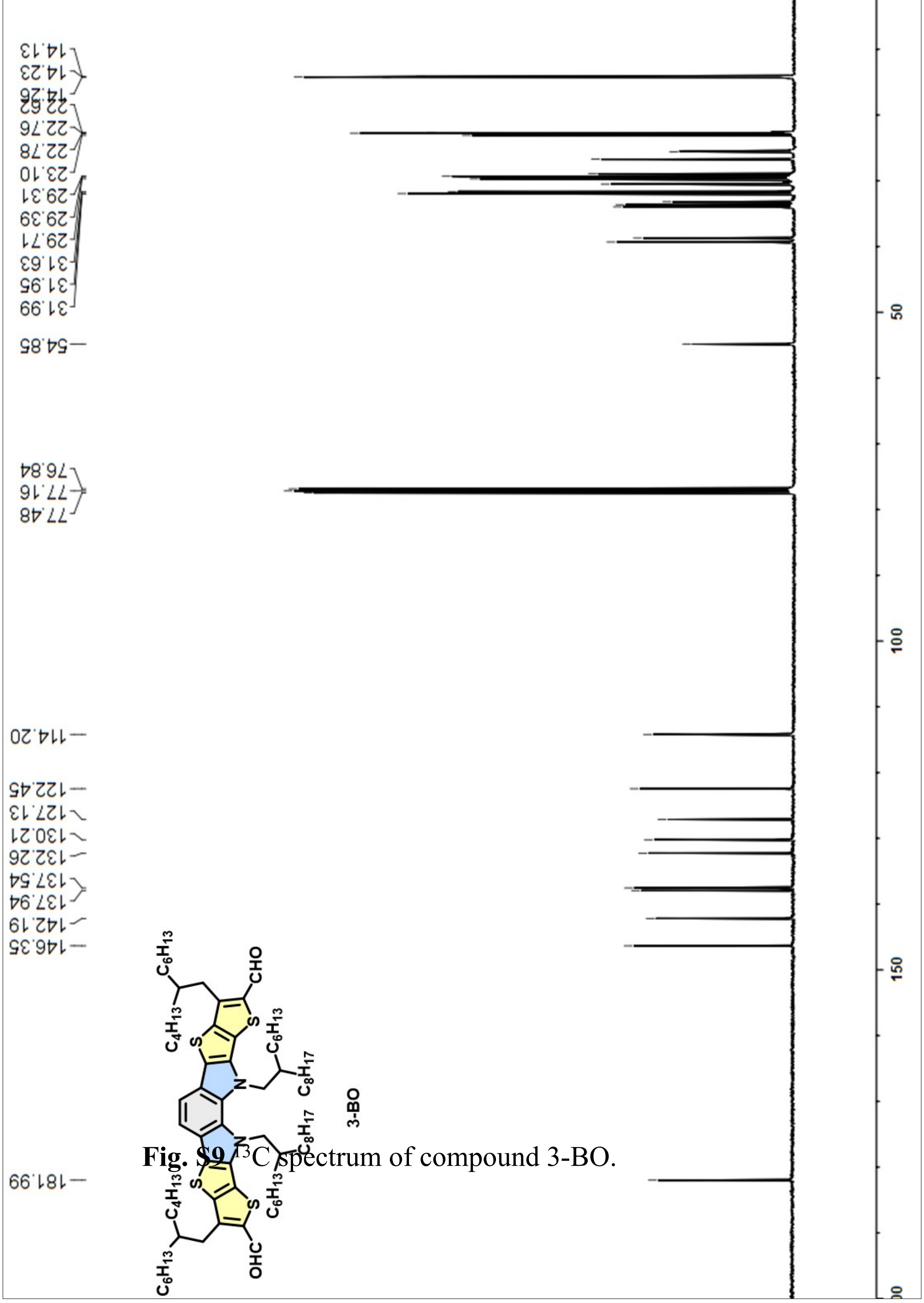

Fig. S9 ^{13}C spectrum of compound 3-BO.

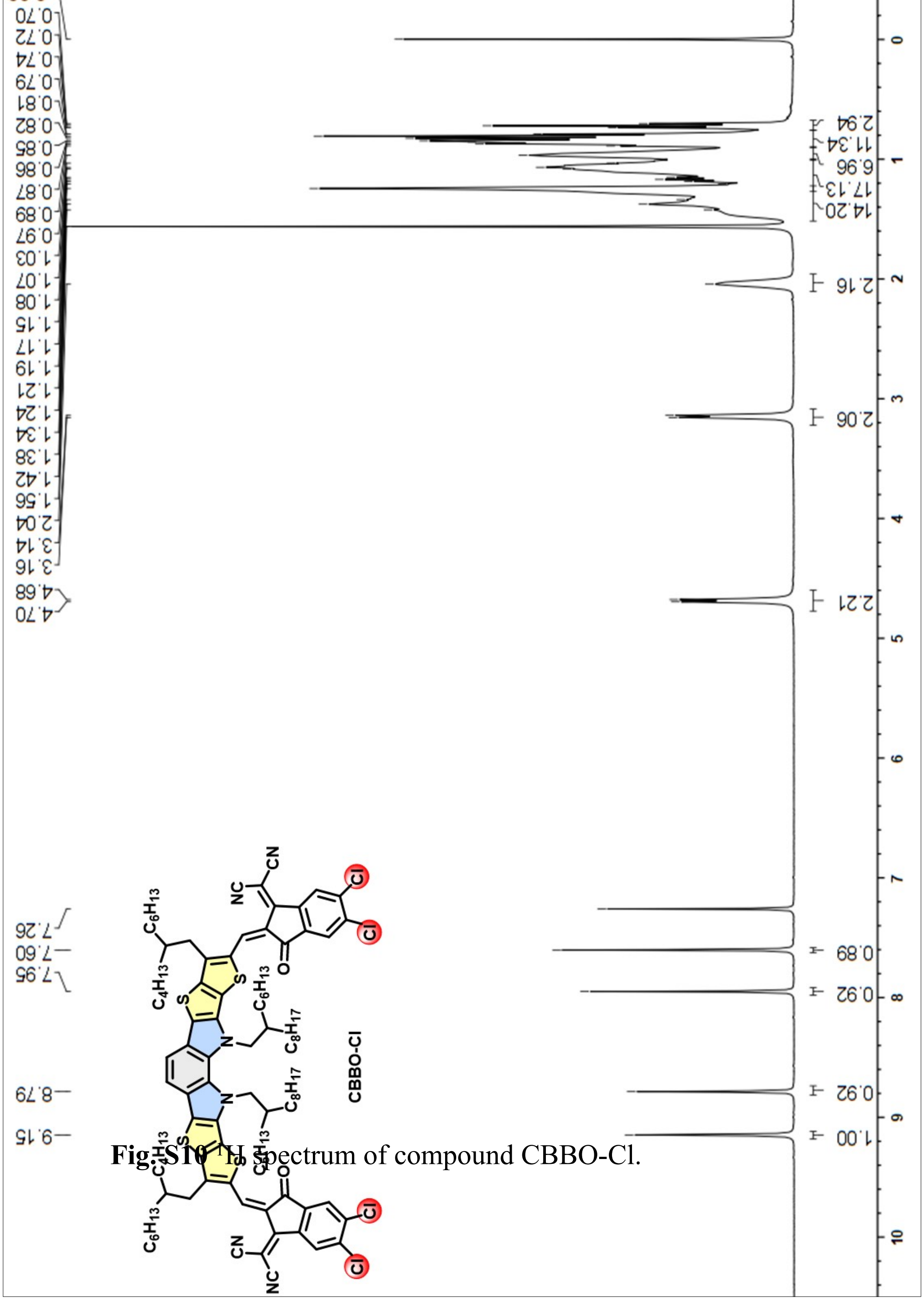

Fig. S10 ^{1}H spectrum of compound CBBO-Cl.

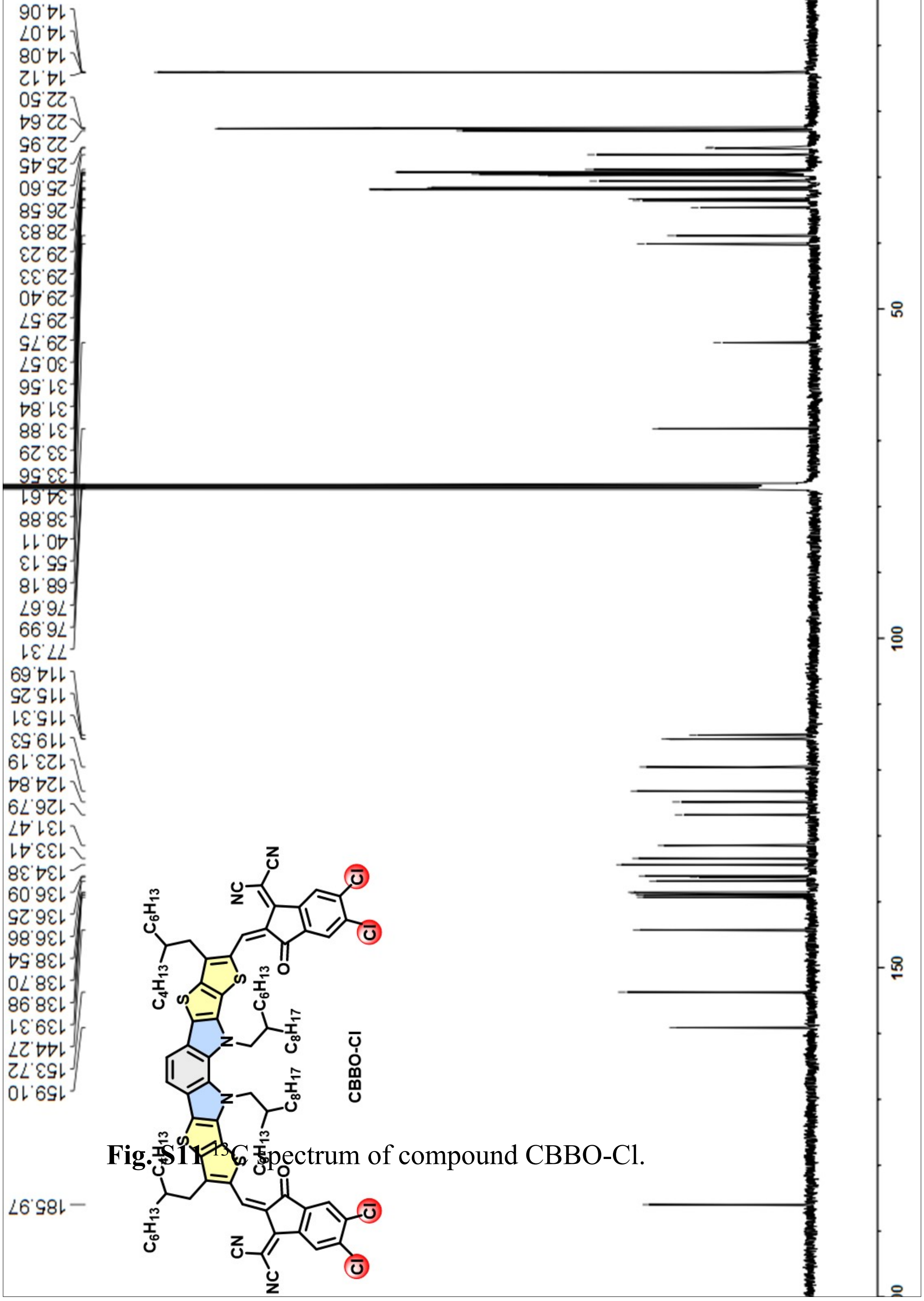

Fig. S11 ^{13}C spectrum of compound CBBO-Cl.

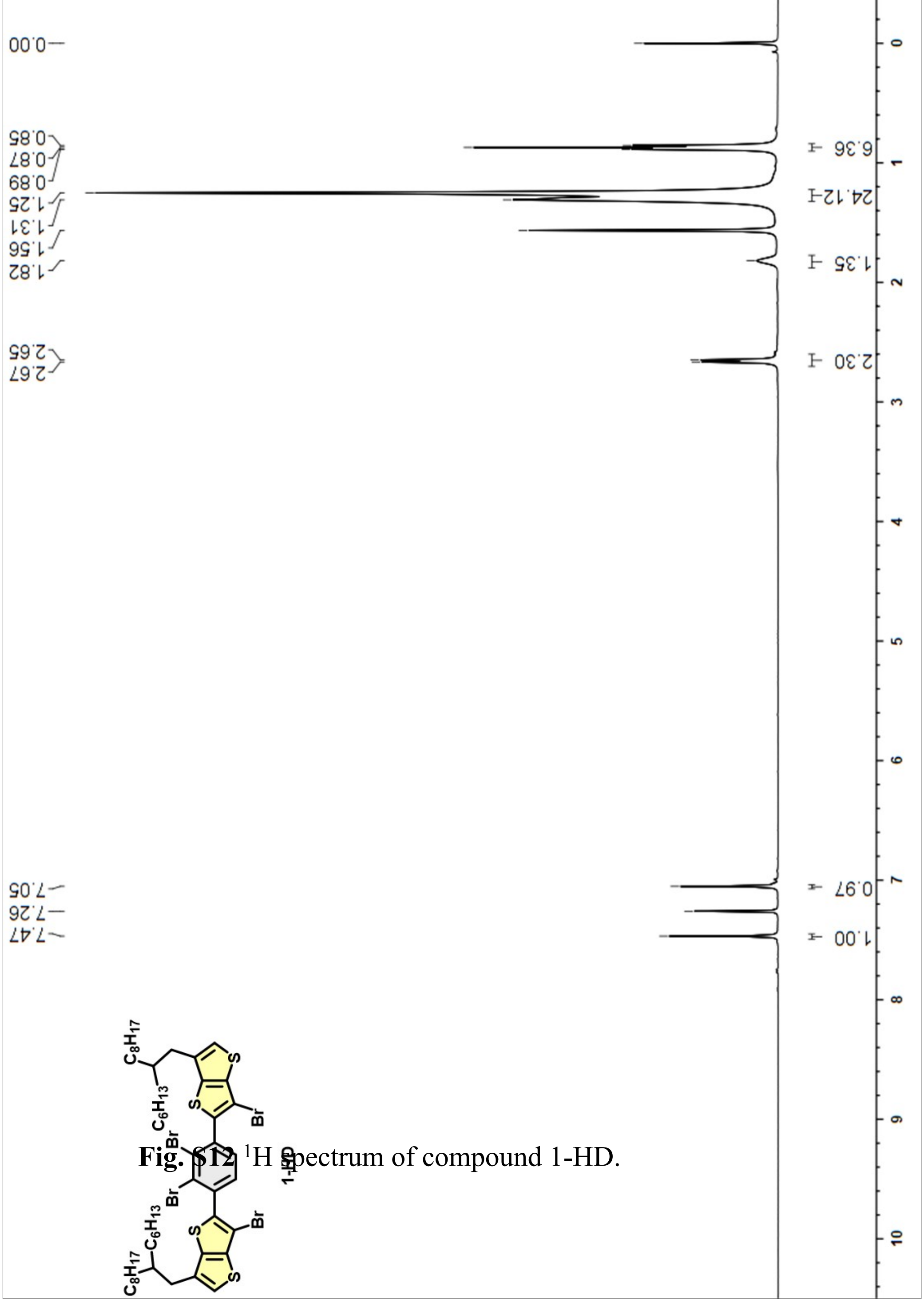

Fig. S12 ^{1}H spectrum of compound 1-HD.

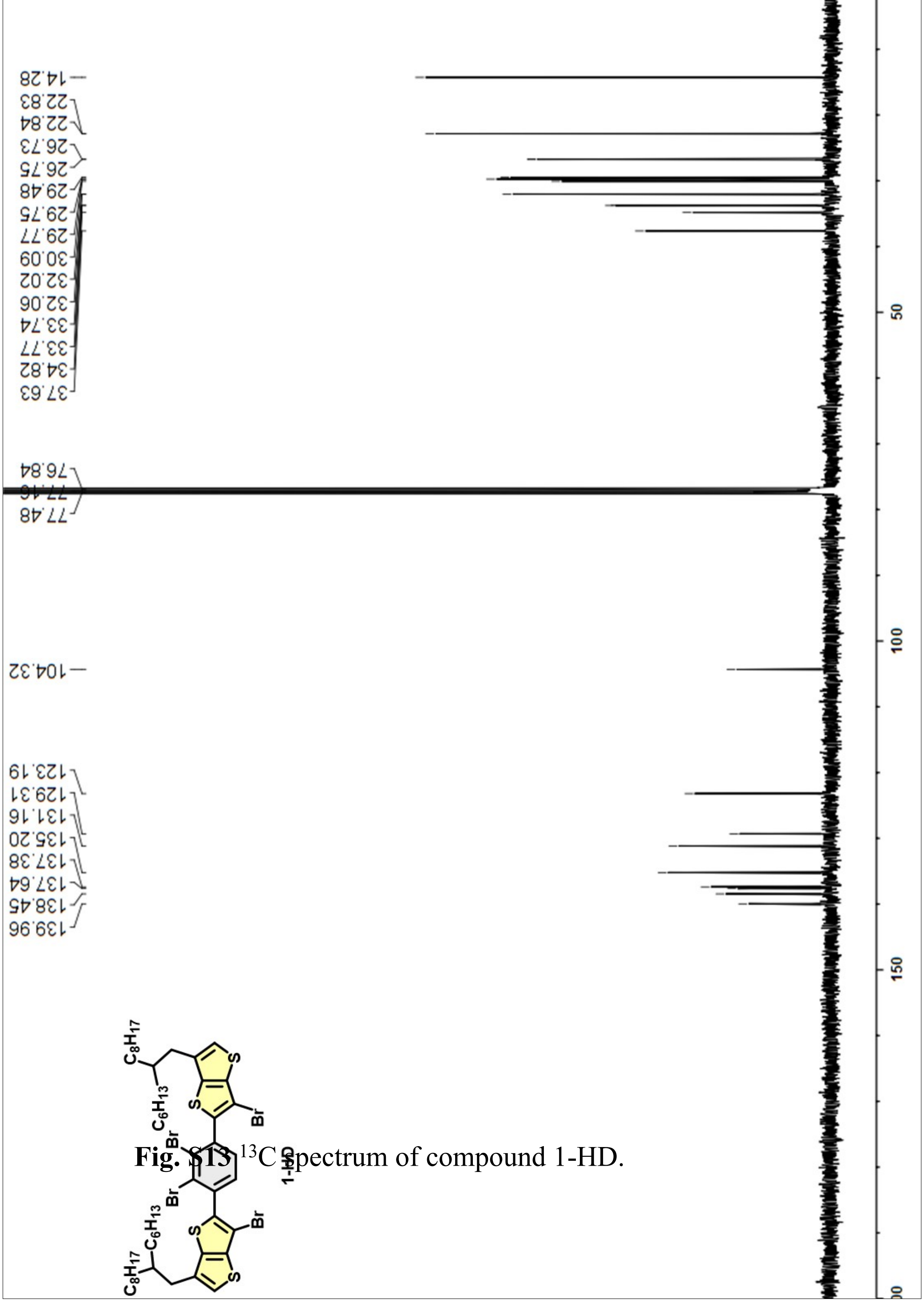

Fig. S13 [13]C spectrum of compound 1-HD.

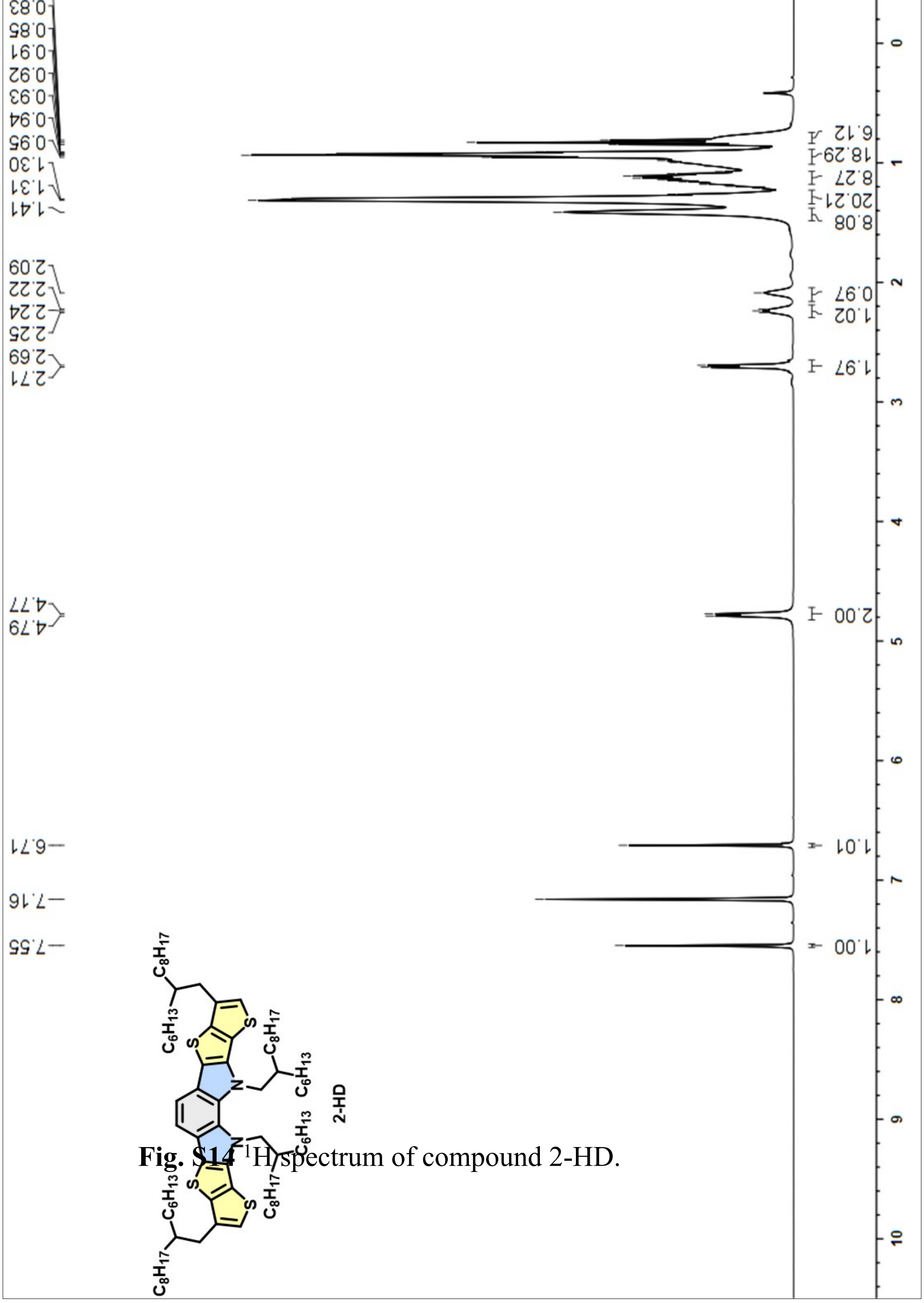

Fig. S14 ^{1}H spectrum of compound 2-HD.

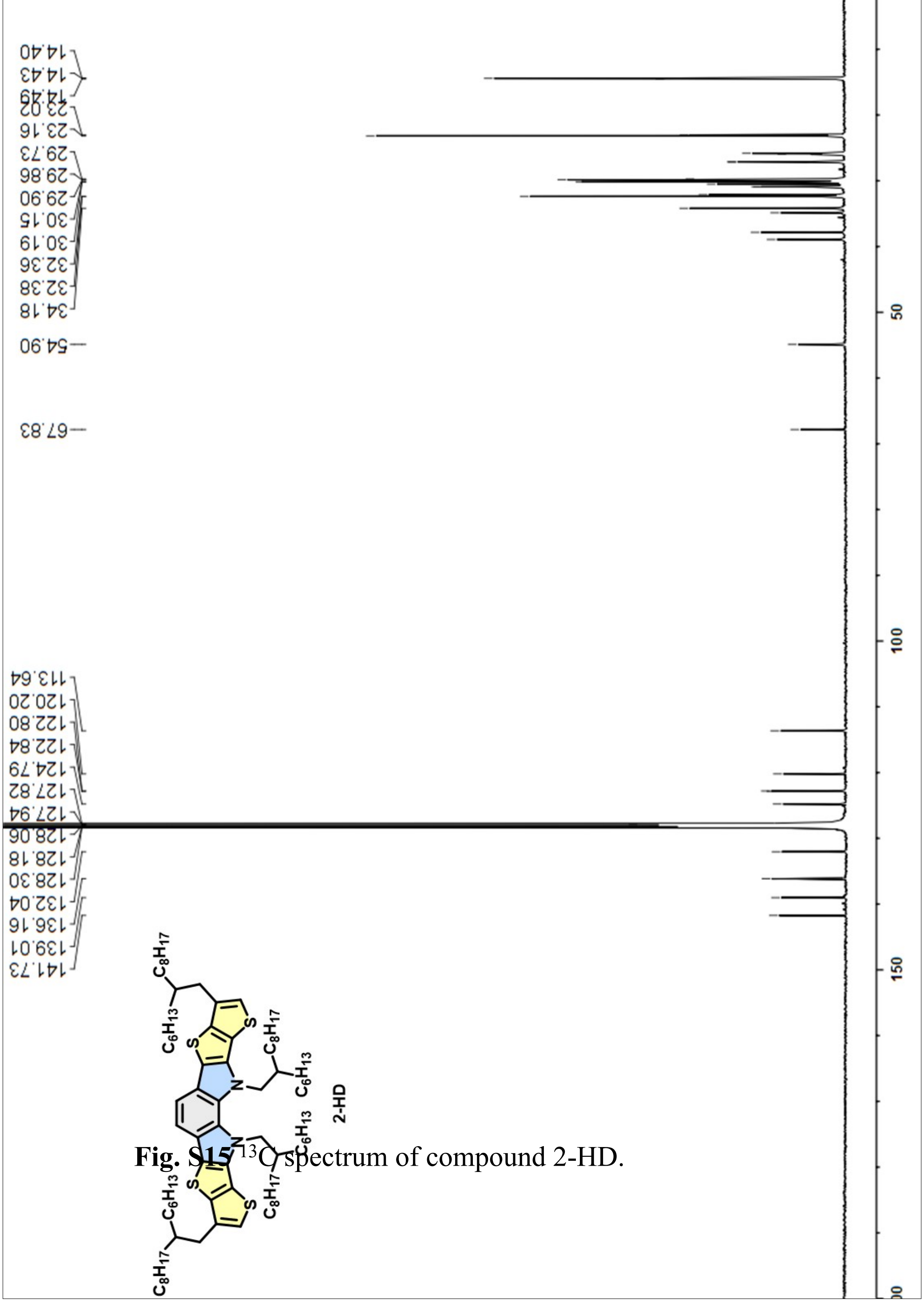

Fig. S15 ^{13}C spectrum of compound 2-HD.

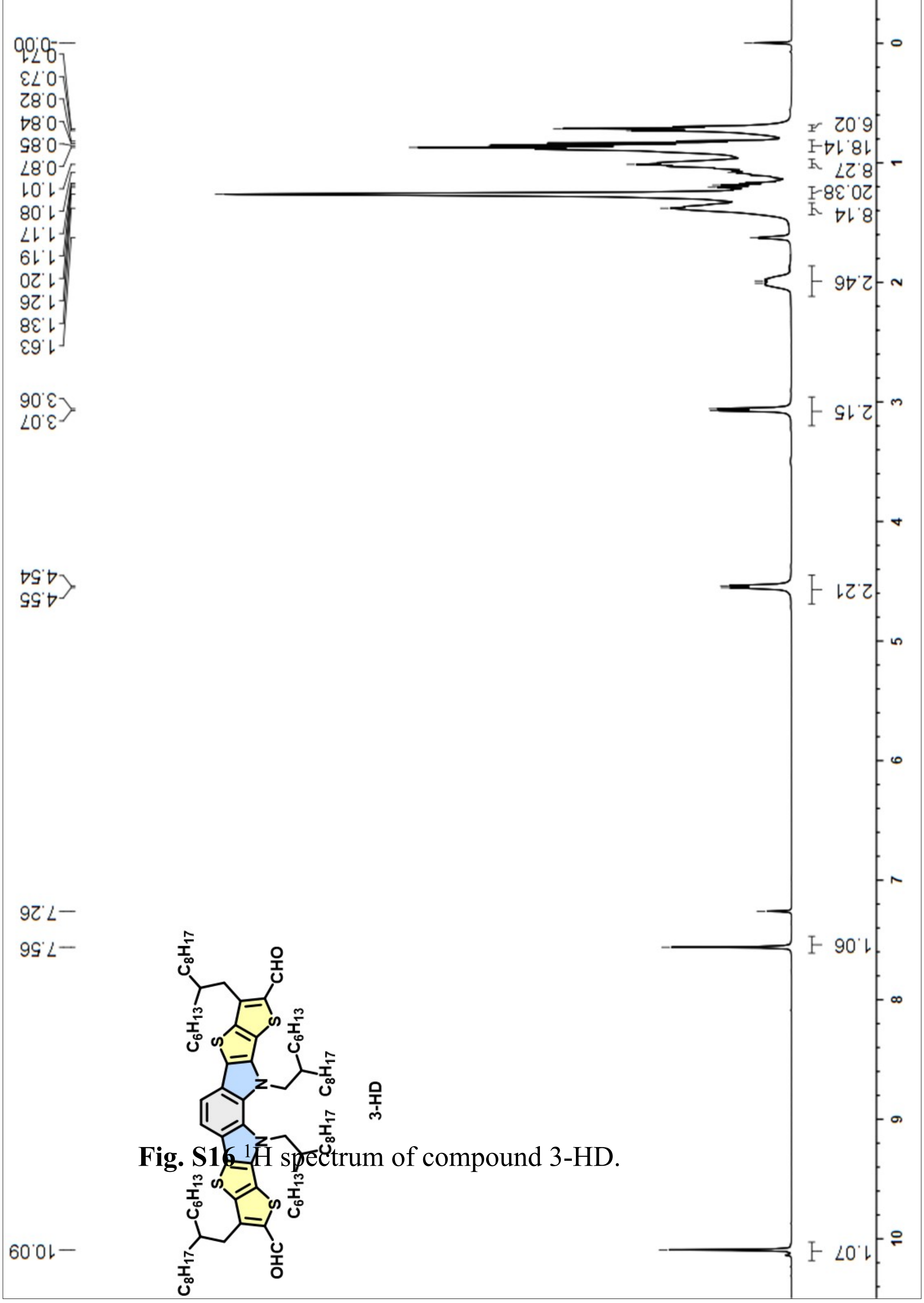

Fig. S16 ^{1}H spectrum of compound 3-HD.

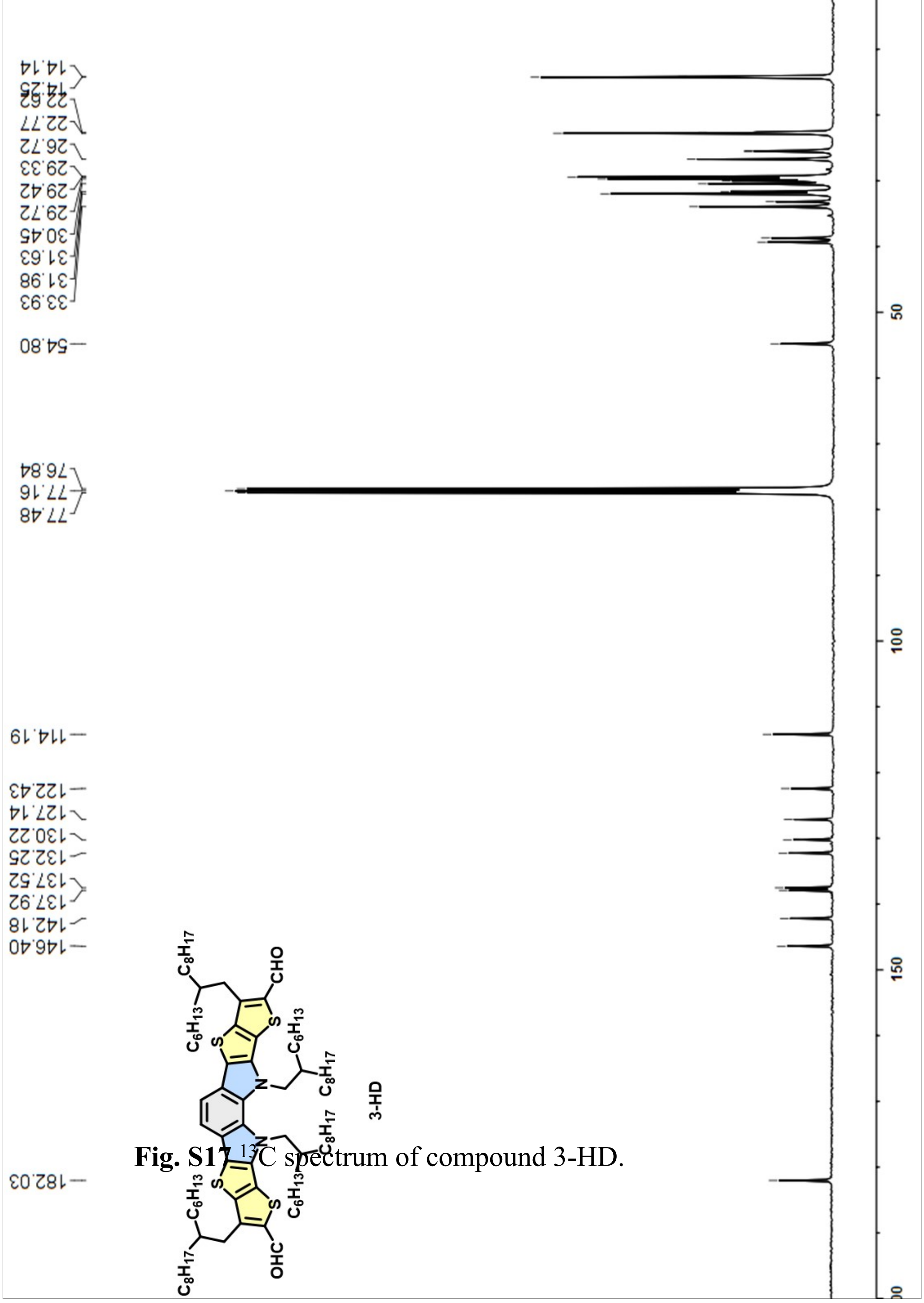

Fig. S17 ^{13}C spectrum of compound 3-HD.

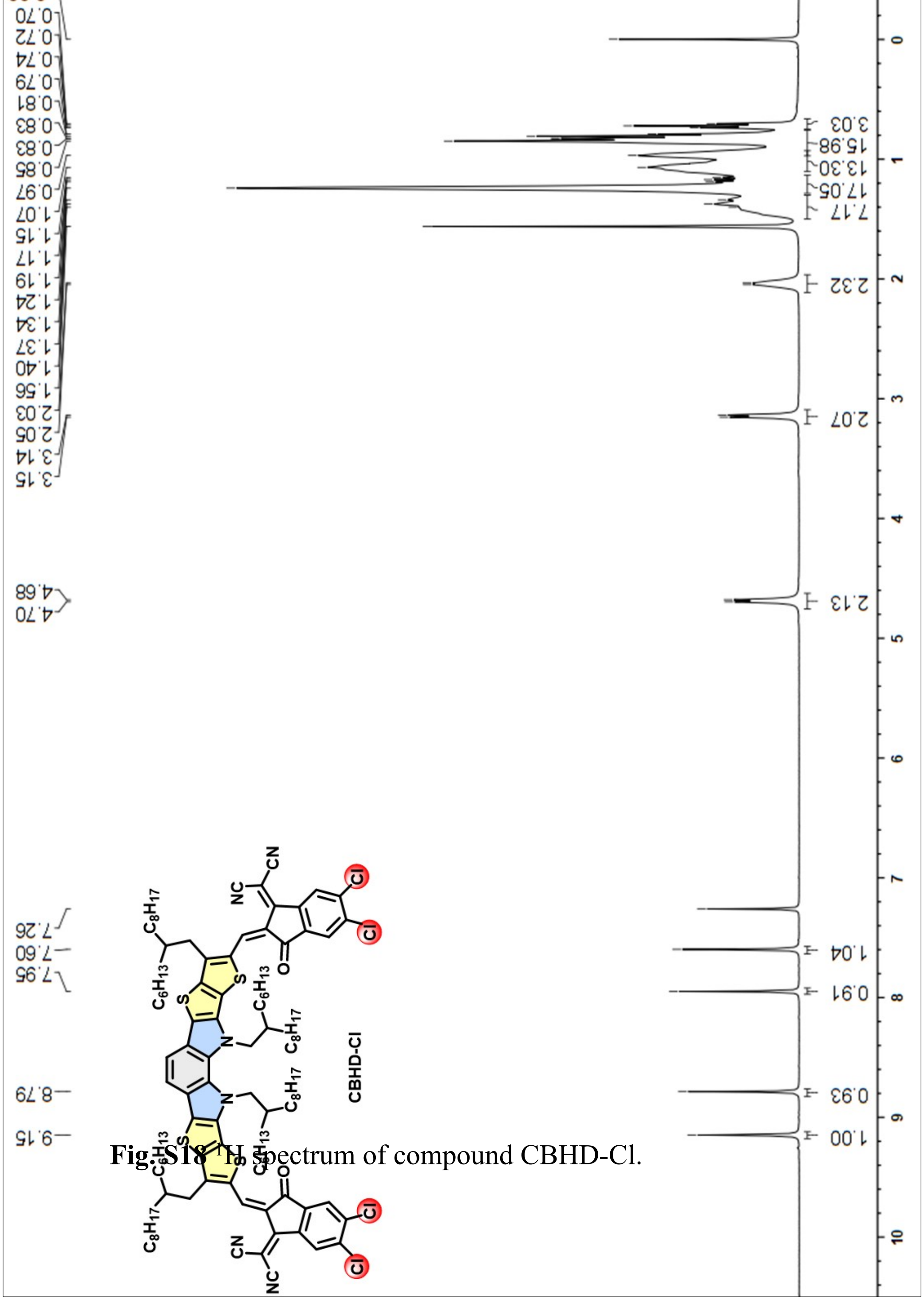

Fig. S18 ^{1}H spectrum of compound CBHD-Cl.

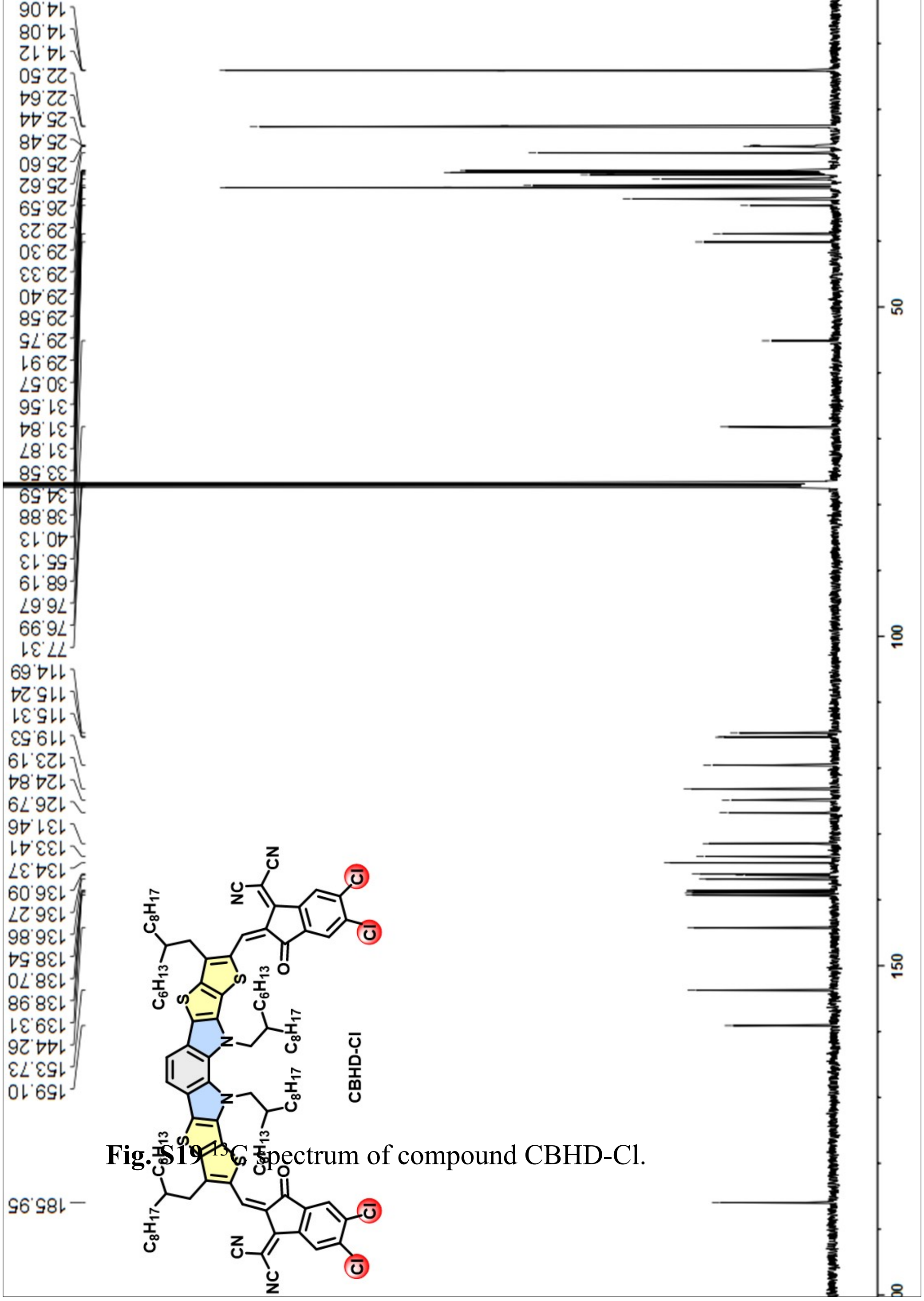

Fig. S19 ^{13}C spectrum of compound CBHD-Cl.