

Supporting Information

Isomeric Indacenedibenzothiophenes: Synthesis, Photoelectric Properties and Ambipolar Semiconductivity

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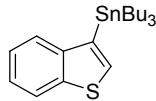
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Part 1. Synthesis

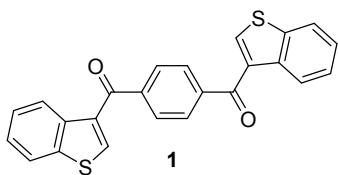
All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Unless stated otherwise, starting materials were obtained from Adamas, Aldrich, and J&K, Alfa, and were used without any further purification. Anhydrous Et₂O, toluene, and THF were distilled over Na/benzophenone prior to use. Hydrogen nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were measured on Bruker Fourier 300, Bruker Avance 400, and Bruker Avance 600 spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent (CDCl₃: δ 7.26). ¹³C NMR spectra were recorded at 100 MHz or 75 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.2). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz (Hz), and integration. EI-MS measurements were performed on UK GCT-Micromass or Shimadzu G-MS-QP2010 spectrometers. MALDI measurements were performed on MALDI-FT 9.4T, Bruker solariX, or MALDI-TOF MS Bruker Autoflex III. Elemental analyses were measured on Flash EA 1112 Series from ThermoQuest. UV-vis and fluorescence spectra were recorded on a Jasco V-570 and Jasco FP-6600 spectrometers respectively. Cyclic voltammetry (CV) was performed on a CHI620D potentiostat. All measurements were carried out in a one-compartment cell under an N₂ atmosphere, equipped with a glassy-carbon electrode, a platinum counter-electrode, and an Ag/Ag⁺ reference electrode with a scan rate of 100 mV/s. The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected against Fc/Fc⁺.

Benzo[b]thiophen-3-yltributylstannane



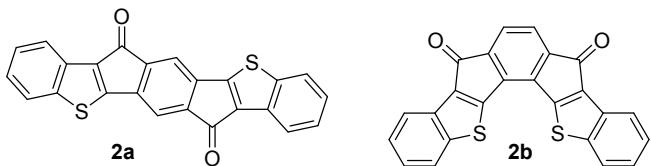
A solution of 3-bromobenzo[b]thiophene (23.44 g, 0.11 mol) in anhydrous Et₂O (150 mL) was added *n*-butyllithium (72.2 mL, 0.116 mmol, 1.60 M in hexane) at -78 °C under nitrogen atmosphere. After stirring for 2 h, tributylchlorostannane (39.9 g, 0.118 mol) was added and stirred at -78 °C for another 1 h. The reaction solution was warmed to room temperature over 0.5 h, quenched with a few drops of saturated NH₄Cl aqueous solution, washed with saturated NaHSO₃ aqueous solution and saturated NaHCO₃ aqueous solution, and extracted three times with CH₂Cl₂. The organic layer was collected, dried over MgSO₄, and concentrated under reduced pressure. 45.63 g of benzo[b]thiophen-3-yltributylstannane was obtained as pale-yellow oil in 98% yield, which was used for the next step without further purification. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, ³J = 8.0 Hz, 1H), 7.78 (d, ³J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.34 (t, ³J = 7.2 Hz, 2H), 1.39–1.58 (m, 6H), 1.28–1.37 (m, 6H), 1.15–1.20 (m, 6H), 0.86–0.94 (m, 12H).

1,4-Phenylenebis(benzo[b]thiophen-3-ylmethanone) (1)



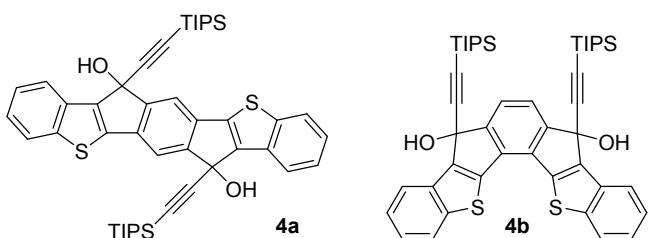
benzo[*b*]thiophen-3-yltributylstannane (42.3 g, 0.10 mol) and Pd(PPh₃)₄ (2.31 g, 2.00 mmol) was added to an oven-dried round-bottomed flask containing terephthaloyl dichloride (9.23 g, 0.045 mol) in dry toluene (180 mL) under nitrogen atmosphere. The mixture was stirred and refluxed at 110 °C for 36 h in the dark. The reaction mixture was cooled to room temperature and was added saturated KF aqueous solution. Then, the mixture was poured into MeOH (200 mL). The precipitate was collected to give 7.25 g of compound **3** in 40% yield as white solid after recrystallization. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (d, ³J = 8.0 Hz, 2H), 8.07 (s, 2H), 7.99 (s, 4H), 7.95 (d, ³J = 8.0 Hz, 2H), 7.56 (t, ³J = 7.6 Hz, 2H), 7.49 (t, ³J = 7.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 190.2, 142.5, 140.2, 139.5, 137.4, 134.6, 129.6, 126.1, 126.0, 125.4, 122.6; HRMS (EI) calcd for C₂₄H₁₄O₂S₂ [M]⁺: 398.0435, found 398.0431.

Compounds **2a** and **2b**



Compound **1** (5.18 g, 13.0 mmol), K₂CO₃ (0.72 g, 5.22 mmol), AgOAc (11.72 g, 70.2 mmol) and Pd(OAc)₂ (0.29 g, 1.29 mmol) was added to an oven-dried round-bottom flask containing pivalic acid (100 mL). The mixture was stirred and heated at 140 °C for 4 d. The reaction mixture was cooled to room temperature and washed with NaOH aqueous solution until pH = 7. Then, the mixture was filtered to give the crude product which was washed with CH₂Cl₂. The **2a** and **2b** mixture was dried and used for the next step without further purification. HRMS (EI) calcd for C₂₄H₁₀O₂S₂ [M]⁺: 394.0122, found 394.0125.

Compounds **4a** and **4b**



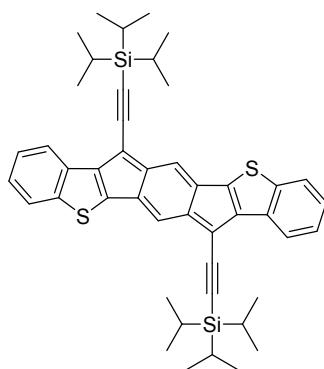
Ethynyltriisopropylsilane (14.59 g, 80 mmol) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere, which was cooled to -78 °C and added *n*-butyllithium (48.75 mL, 78.0 mmol, 1.60 M in hexane). After stirring at -78 °C for 1 h, the reaction solution was added a mixture of compound **2a** and **2b** (3.94 g) in one portion and stirred for another 1 h. Then, the reaction was warmed to room temperature over 0.5 h and heated to 50 °C for 1 d. The reaction was quenched with a few drops of saturated NH₄Cl aqueous solution and filtered through a short silica-gel column. The filtrate was concentrated under reduced pressure. The crude product was purified by

recrystallization to give compound **4a**. The remaining crude product was purified on silica-gel column chromatography to give 2.5 g of compound **4a** (total yield with the last step: 30%) and 0.55 g compound **4b** (total yield with the last step: 7%).

4a: ^1H NMR (300 MHz, CDCl_3): δ 8.06 (d, $^3J = 7.8$ Hz, 2H), 7.89 (d, $^3J = 7.8$ Hz, 2H), 7.68 (s, 2H), 7.47 (t, $^3J = 7.2$ Hz, 2H), 7.37 (t, $^3J = 7.2$ Hz, 2H), 2.63 (s, 2H), 1.04 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.8, 144.1, 143.8, 135.8, 133.0, 125.2, 124.5, 123.9, 121.8, 115.6, 104.7, 85.8, 72.0, 18.6, 11.1; HRMS (MALDI) calcd for $\text{C}_{46}\text{H}_{54}\text{O}_2\text{S}_2\text{Si}_2$ [$\text{M}+\text{H}]^+$: 759.317652, found 759.318017.

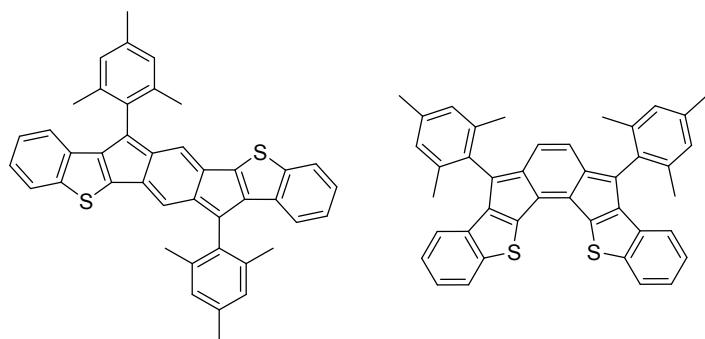
4b: ^1H NMR (300 MHz, CDCl_3): δ 8.12 (d, $^3J = 7.6$ Hz, 2H), 7.96 (d, $^3J = 7.6$ Hz, 2H), 7.62 (s, 2H), 7.48 (t, $^3J = 7.2$ Hz, 2H), 7.40 (t, $^3J = 7.2$ Hz, 2H), 2.62 (s, 2H), 1.04 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.9, 145.0, 144.8, 141.8, 132.8, 128.5, 125.4, 125.0, 124.0, 122.6, 122.2, 85.8, 72.2, 18.8, 11.4; HRMS (MALDI) calcd for $\text{C}_{46}\text{H}_{54}\text{O}_2\text{S}_2\text{Si}_2$ [$\text{M}+\text{H}]^+$: 759.317652, found 759.318271.

IDBT-*I*-TIPSA



Under nitrogen atmosphere, a solution of compound **4a** (0.50 g, 0.66 mmol) in anhydrous toluene (35 ml) was added SnCl_2 (0.50 g, 2.64 mmol) and stirred at 40 °C. The reaction progress was monitored by TLC until we found the main green spot. Then, the reaction mixture was quenched with a few drops of saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2 . The organic layer was separated, dried over MgSO_4 , and concentrated under reduced pressure. The crude product was purified on an Al_2O_3 (neutral) column chromatography and further recrystallized to give **IDBT-*I*-TIPSA** (0.103 g, 20%) as blue needle crystals. ^1H NMR (300 MHz, CDCl_3): δ 7.81 (d, $^3J = 7.5$ Hz, 2H), 7.49 (d, $^3J = 7.5$ Hz, 2H), 7.18 (t, $^3J = 7.2$ Hz, 2H), 7.10 (t, $^3J = 7.2$ Hz, 2H), 6.38 (s, 2H), 1.19 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3): 150.2, 143.6, 143.0, 142.3, 132.6, 131.1, 126.5, 125.7, 124.7, 124.3, 123.7, 121.4, 112.7, 102.8, 18.8, 11.4; Anal. Calcd for $\text{C}_{46}\text{H}_{52}\text{S}_2\text{Si}_2$ (%): C, 76.18; H, 7.23; Found: C, 76.07; H, 7.03.

IDBT-*I*-Mes and IDBT-*a*-Mes



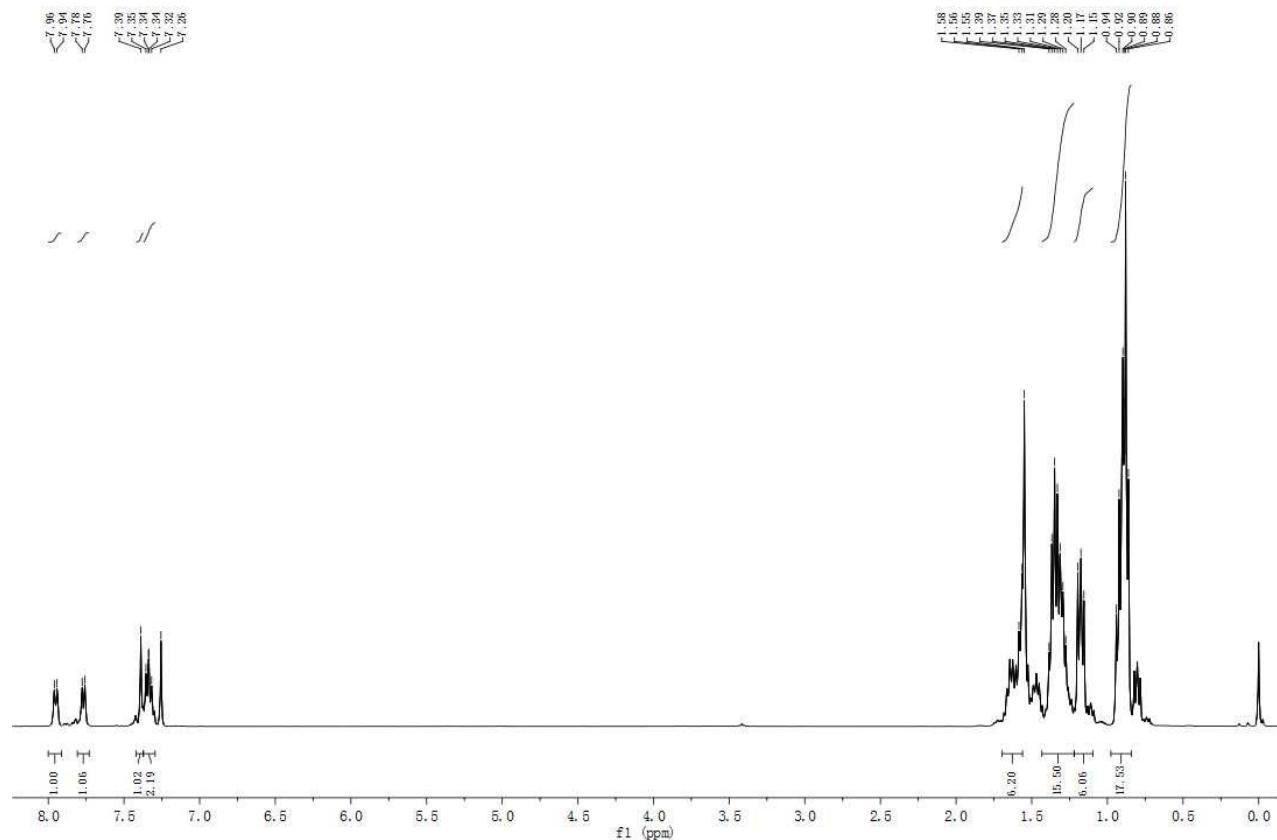
A solution of 2-bromo-1,3,5-trimethylbenzene (10.00 g, 0.050 mol) in anhydrous THF (70 mL) was added *n*-butyllithium (20 mL, 0.050 mol, 2.50 M in hexane) at -78 °C under nitrogen atmosphere, stirred for 1 h. Then, the reaction solution was added a mixture of compound **2a** and **2b** (1.97 g, 5.0 mmol) in one portion and stirred for another 1 h. The reaction was warmed to room temperature over 12 h, quenched with a few drops of saturated NH₄Cl aqueous solution, and filtered through a short silica-gel column. The filtrate was concentrated under reduced pressure. The crude product containing **compound 3a** and **3b** was dissolved in anhydrous toluene (10ml), added SnCl₂ (0.19 g, 1.0 mmol), and stirred overnight under nitrogen atmosphere. Then, the reaction mixture was quenched with a few drops of saturated NH₄Cl aqueous solution and extracted with CH₂Cl₂. The organic layer was separated, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified on a silica-gel column chromatography to give **IDBT-*I*-Mes** (0.019 g, total yield of the last three steps: 0.6%) as a blue solid and **IDBT-*a*-Mes** (0.010 g, total yield of the last three steps: 0.3%) as a yellow solid.

IDBT-*I*-Mes: ¹HNMR (400 MHz, CDCl₃): δ 7.48 (d, ³J = 8.0Hz, 2H), 6.94–7.03 (m, 8H), 6.60 (d, ³J = 8.0Hz, 2H), 6.07 (s, 2H), 2.38 (s, 6H), 2.31 (s, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 148.0, 143.9, 143.1, 137.8, 136.8, 136.6, 133.0, 131.7, 129.9, 128.2, 125.8, 125.5, 124.0, 123.6, 120.6, 29.7, 20.6; HRMS (MALDI) calcd for C₄₂H₃₂S₂ [M]⁺: 600.193994, found 600.193828.

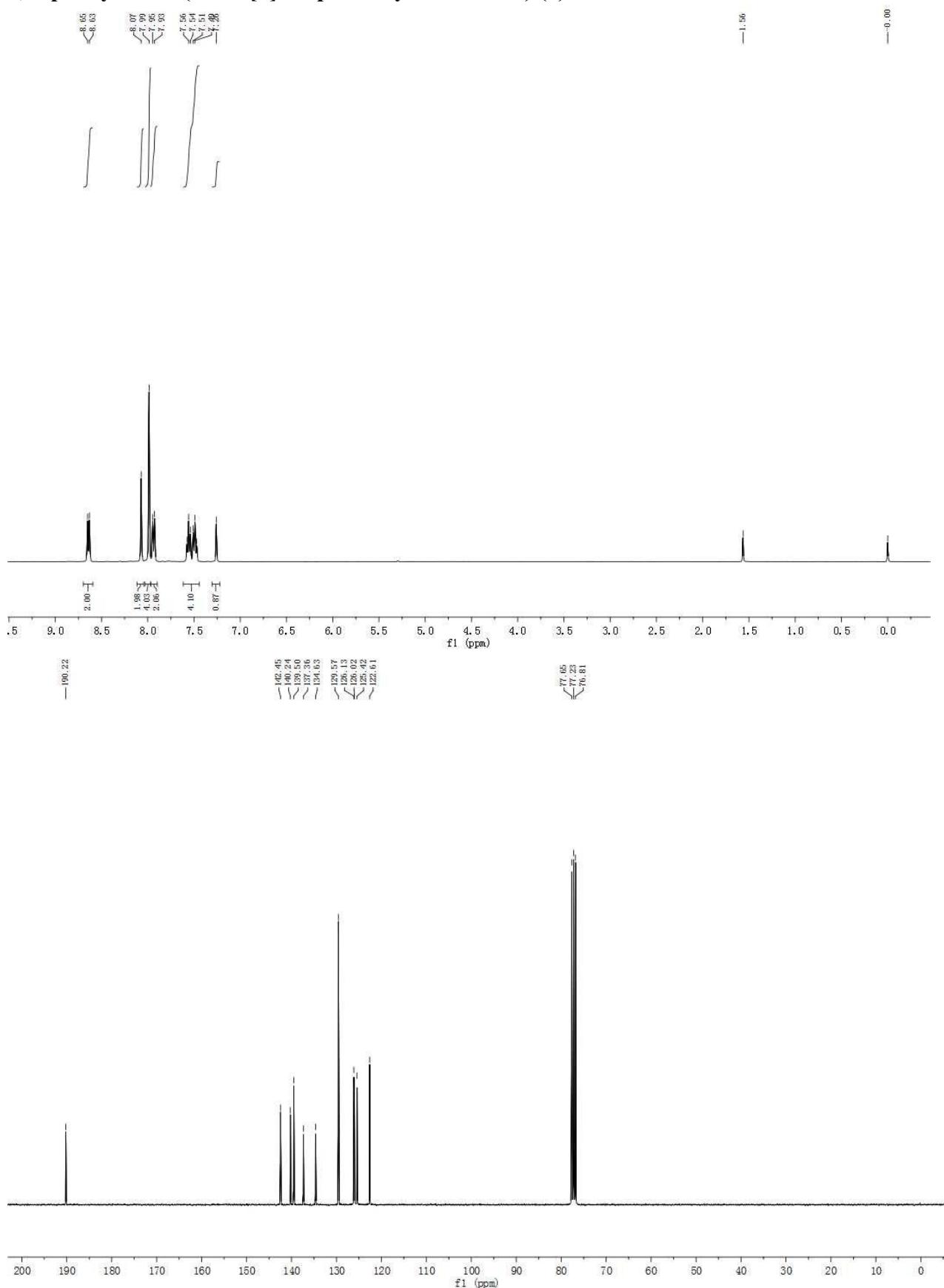
IDBT-*a*-Mes: ¹HNMR (400 MHz, CDCl₃): δ 7.72 (d, ³J = 8.0 Hz, 2H), 7.15 (t, ³J = 8.0 Hz, 2H), 7.06 (t, ³J = 8.0 Hz, 2H), 6.95 (s, 2H), 6.76 (d, ³J = 8.0 Hz, 2H), 5.50 (s, 2H), 2.35 (s, 6H), 2.31 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 146.9, 137.6, 136.7, 135.6, 133.1, 128.2, 125.5, 124.6, 124.0, 121.6, 118.6, 29.7, 20.6; HRMS (MALDI) calcd for C₄₂H₃₂S₂ [M]⁺: 600.193994, found 600.193744; Anal. Calcd for C₄₂H₃₂S₂ (%): C, 83.96; H, 5.37; Found: C, 83.85; H, 5.71.

Part 2. NMR Charts

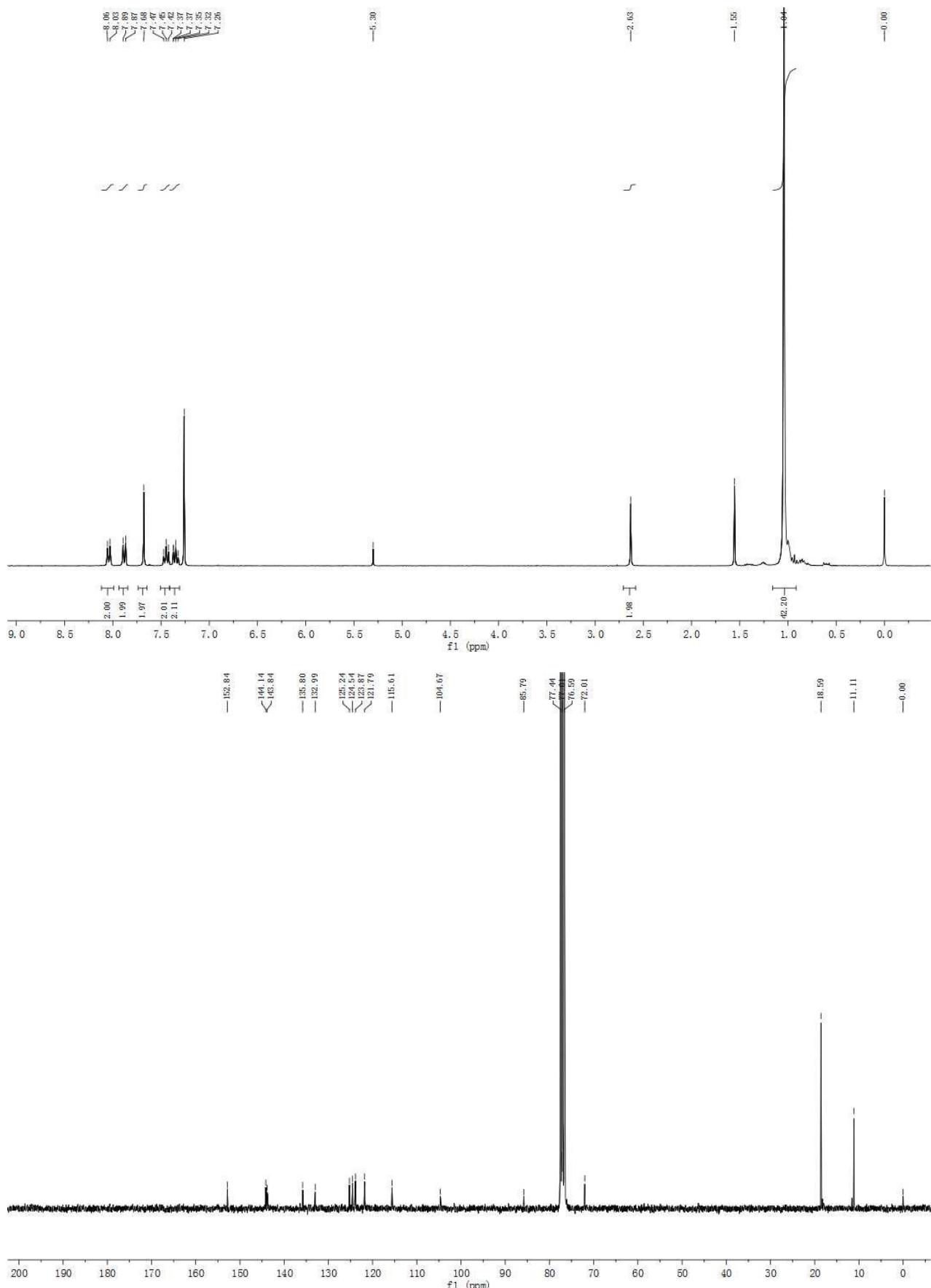
Benzo[*b*]thiophen-3-yltributylstannane



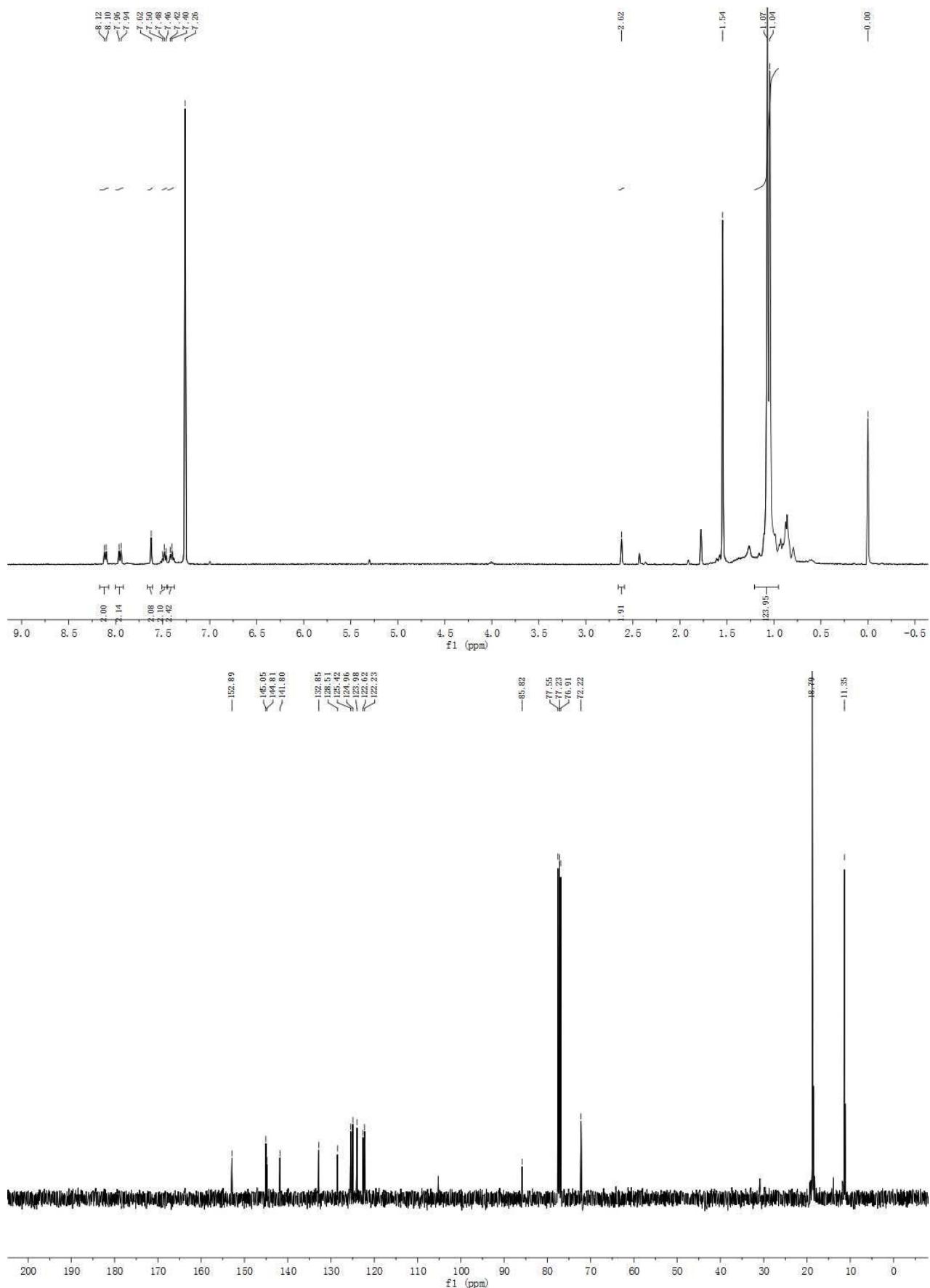
1, 4-phenylenebis(benzo[*b*]thiophen-3-ylmethanone) (1)



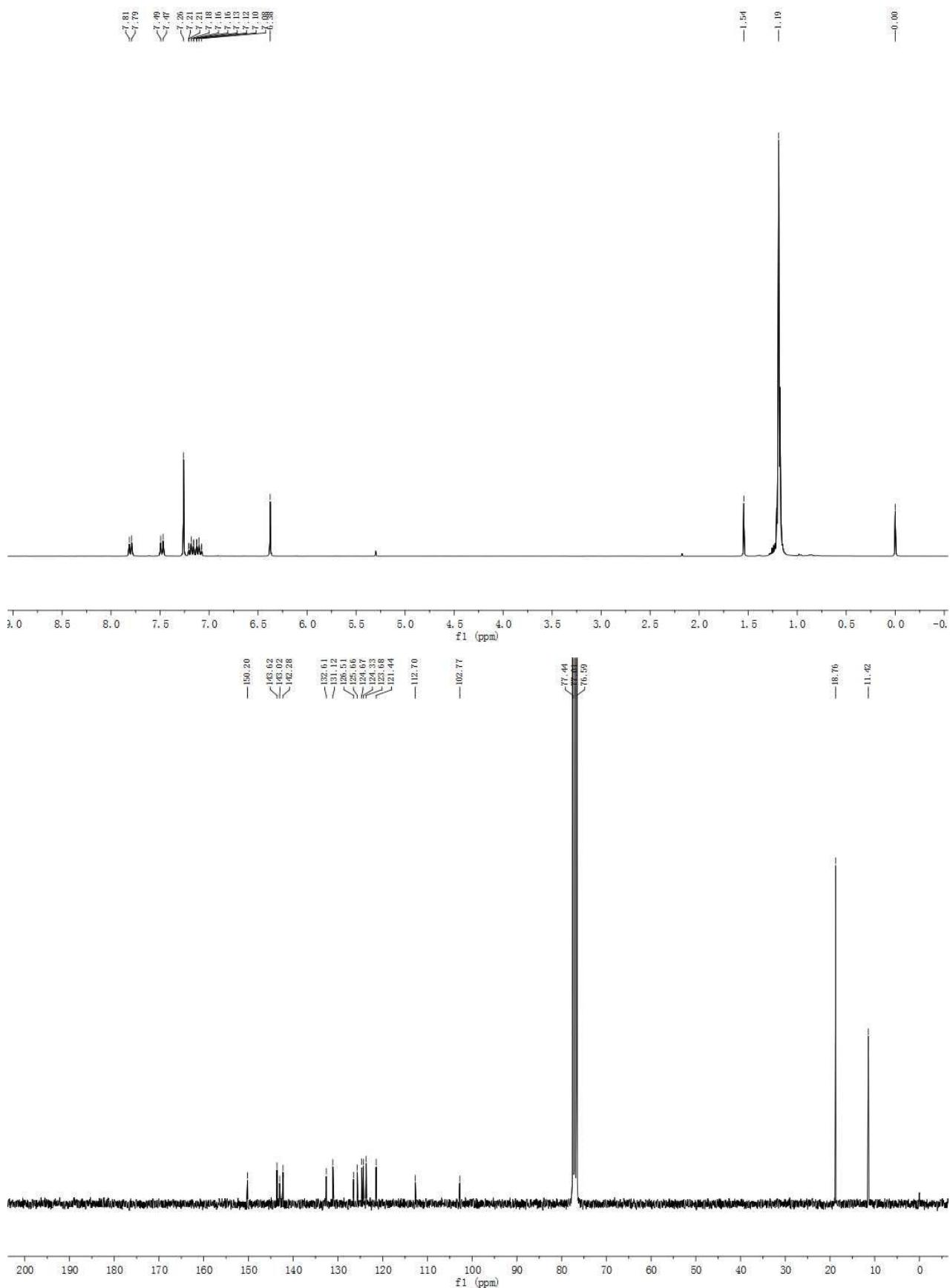
Compound 4a



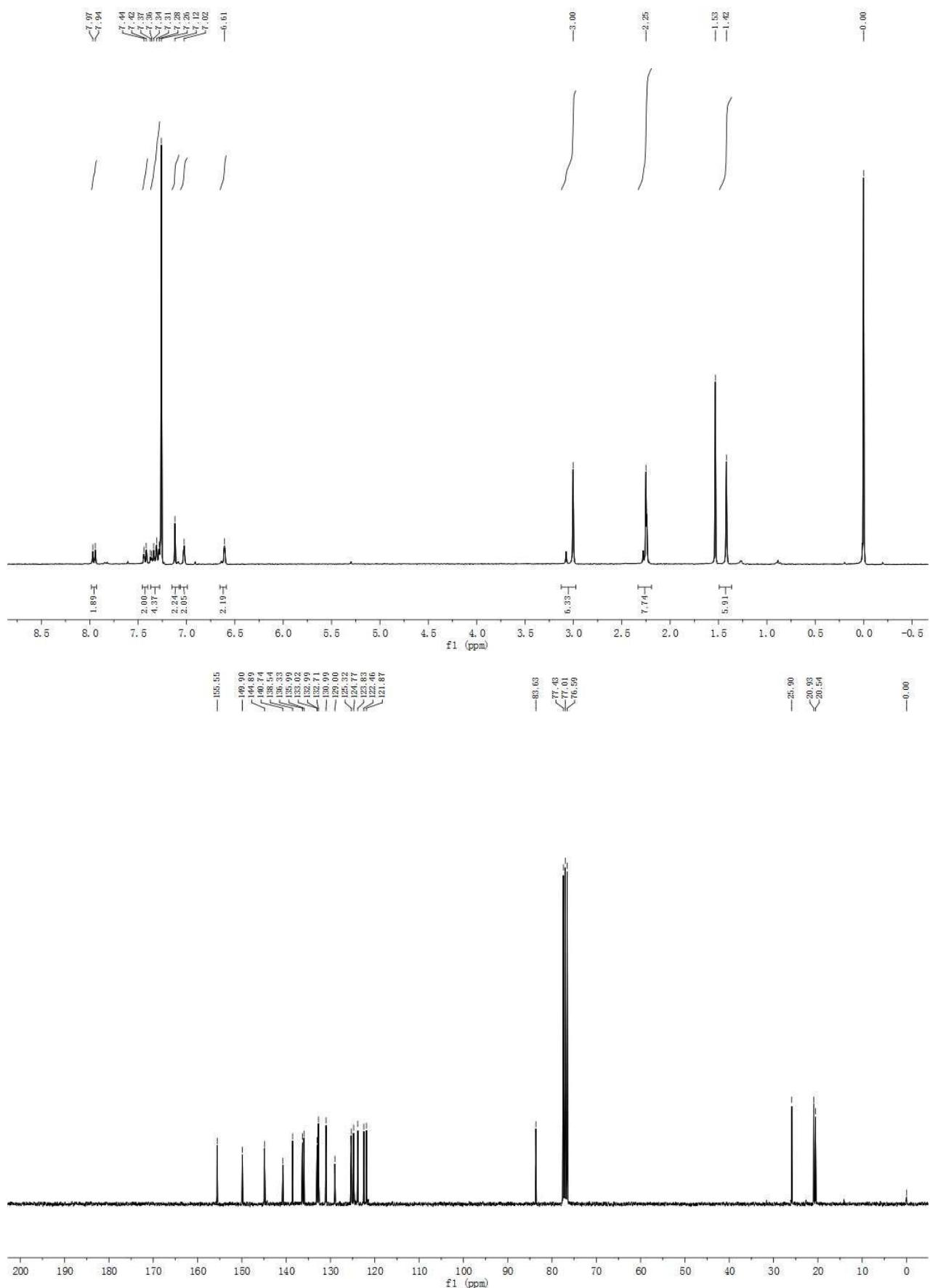
Compound 4b



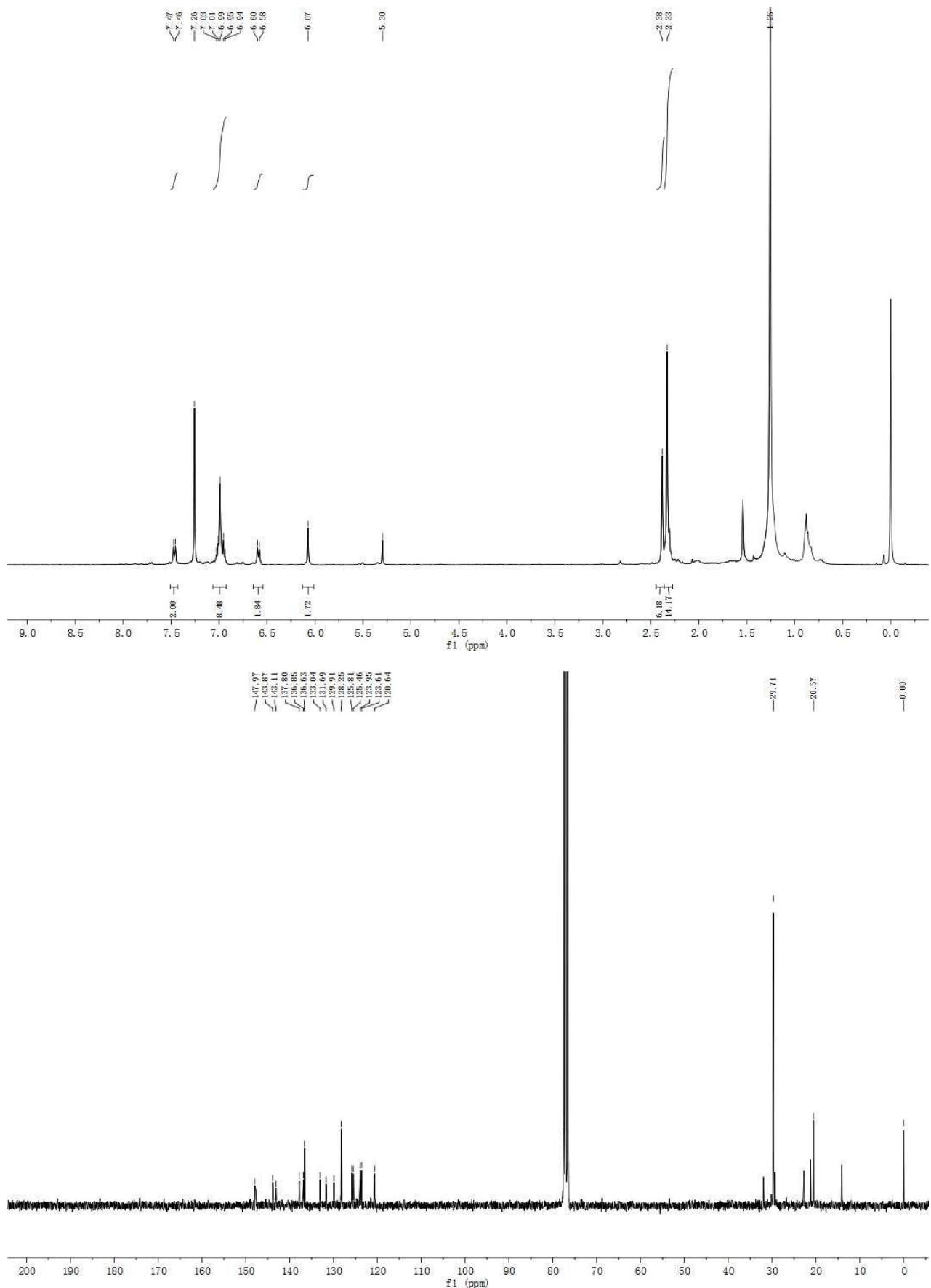
IDBT-*t*-TIPSA



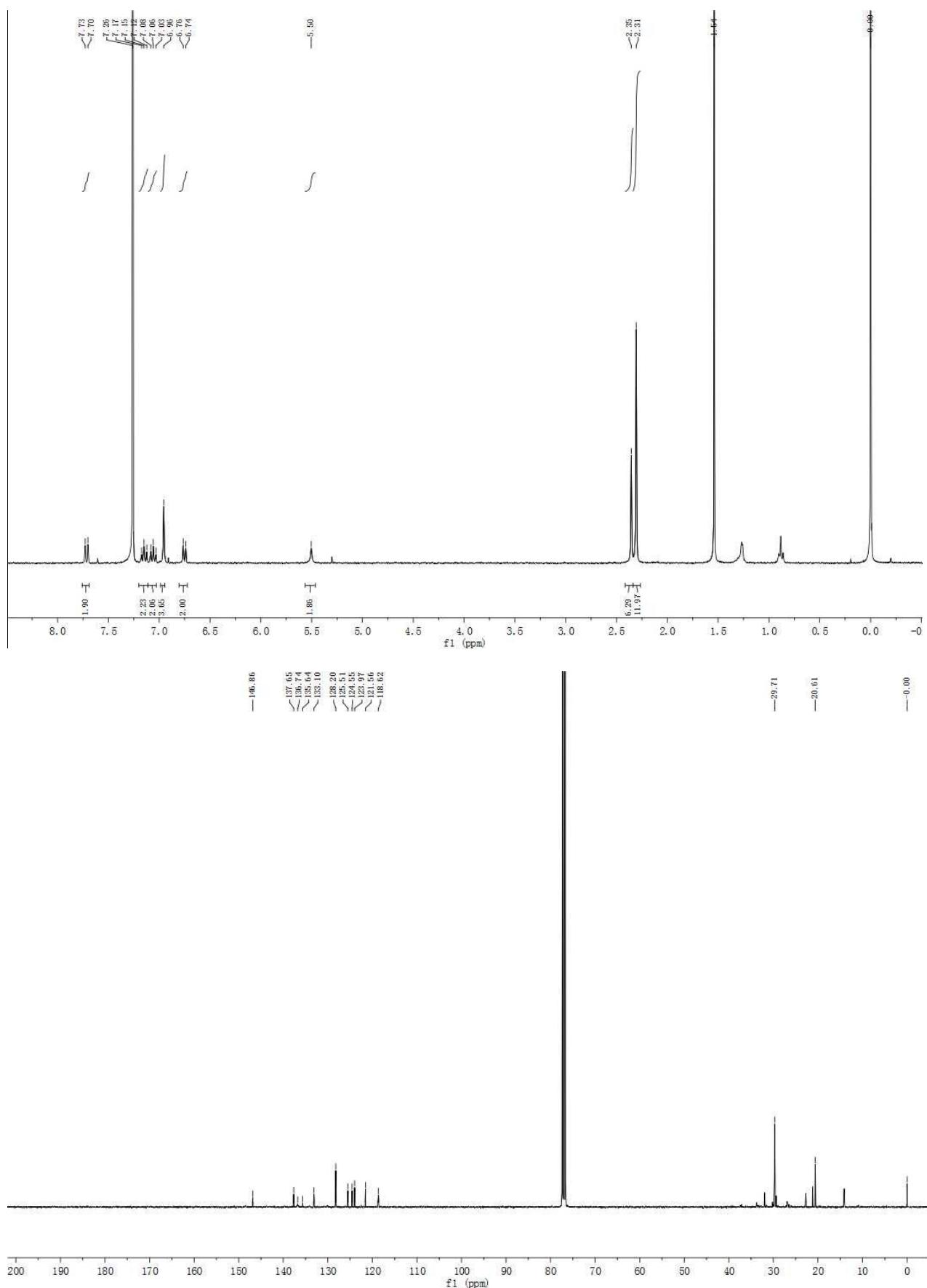
Compound 3b



IDBT-*l*-Mes

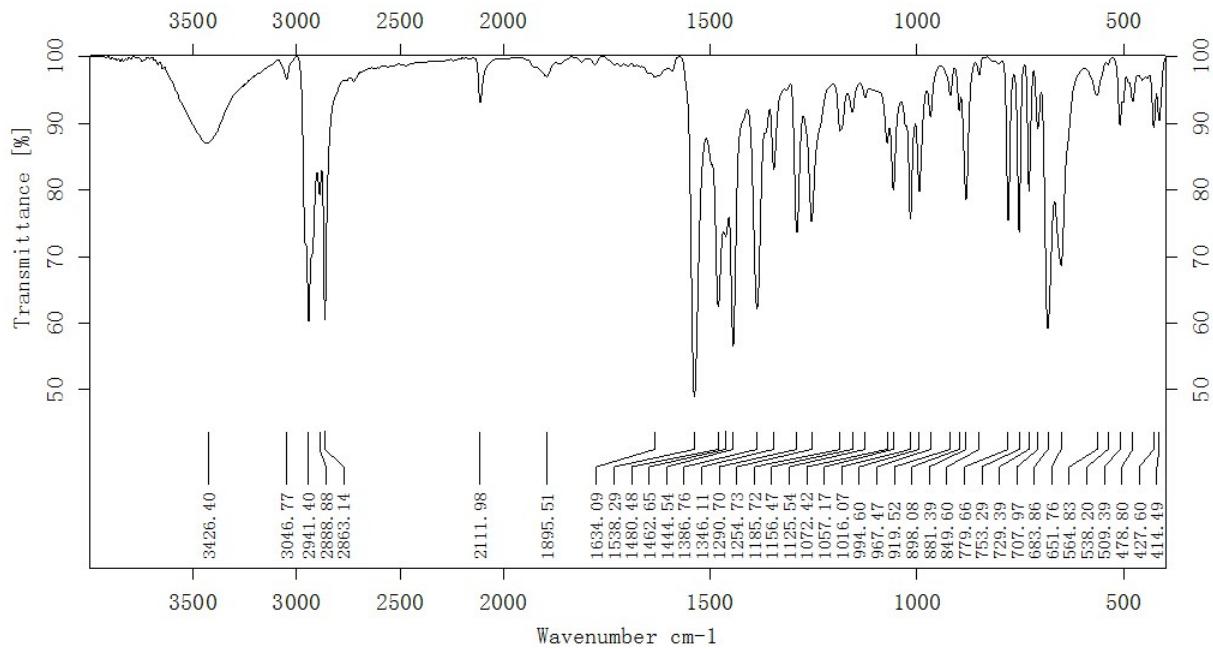


IDBT-*a*-Mes

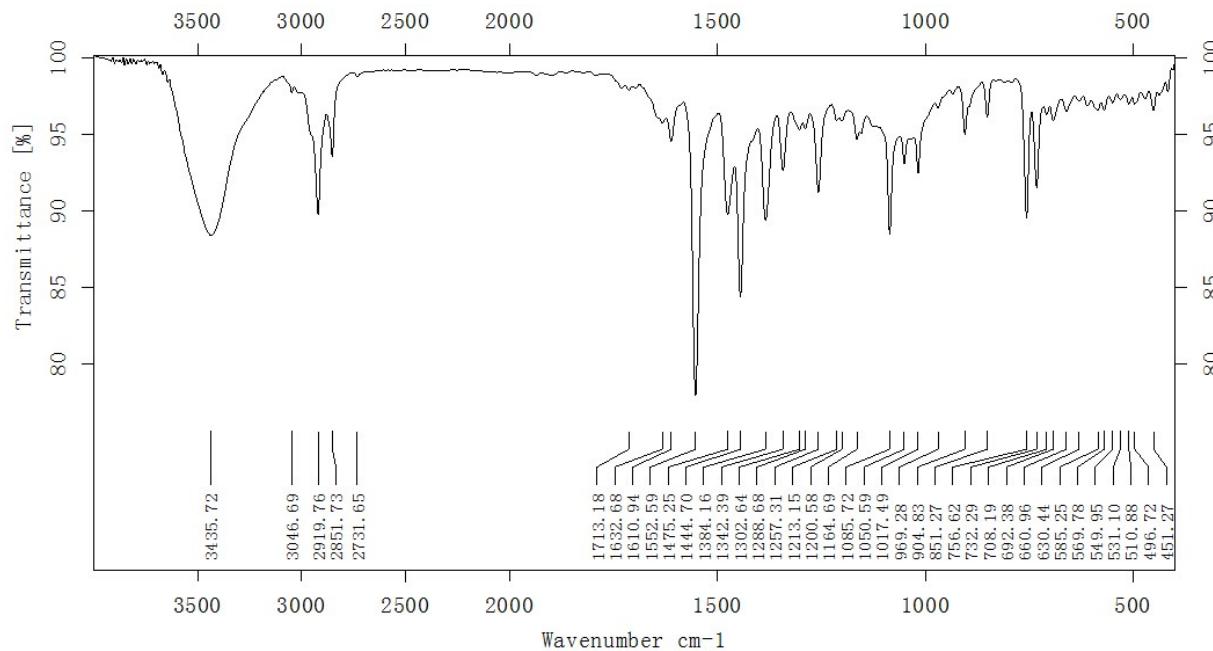


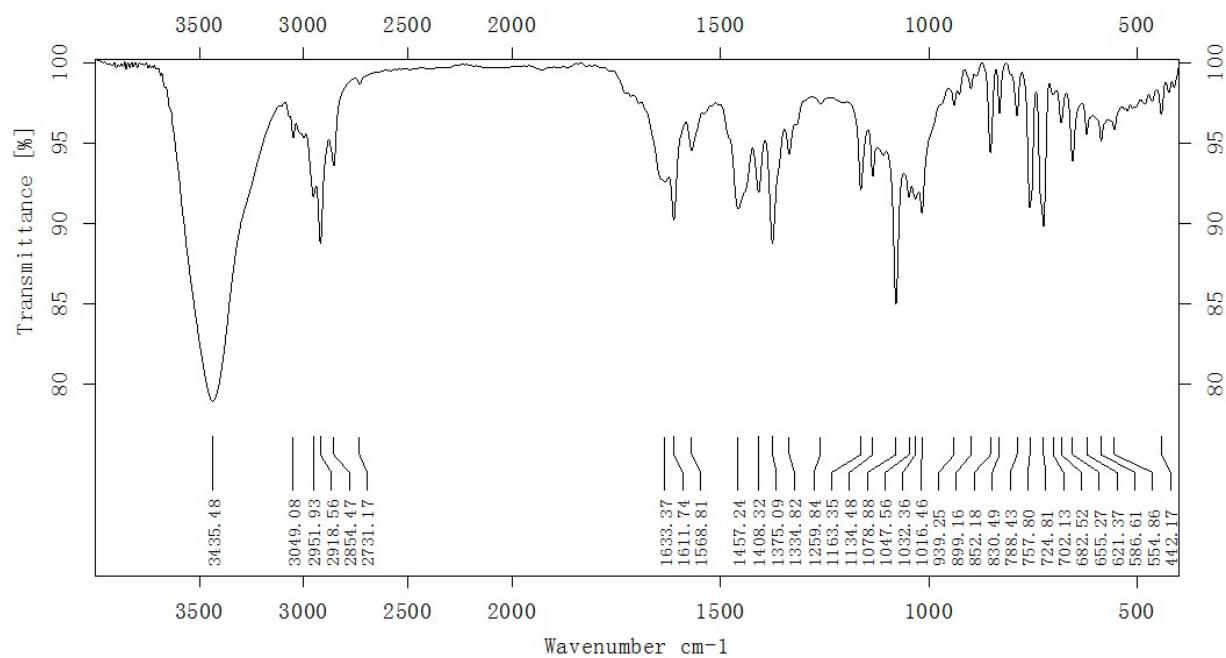
IR Charts

IDBT-*I*-TIPSA:



IDBT-*I*-Mes:



IDBT-*a*-Mes:

Part 3. Crystal structure data of **IDBT-*I*-TIPSA**

Compound	IDBT-<i>I</i>-TIPSA
Empirical formula	<chem>C46H52S2Si2</chem>
Formula weight	725.17
Temperature	173.1500 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P -1
Unit cell dimensions	$a = 8.07(5)$ Å $\alpha = 106.171$ (10) deg. $b = 11.393(7)$ Å $\beta = 106.915(8)$ deg. $c = 12.568(7)$ Å $\gamma = 99.301(3)$ deg.
Volume	1025(6) Å ³
Z, Calculated density	1, 1.175 Mg/m ³
Absorption coefficient	0.219 mm ⁻¹
F(000)	388
Crystal size	0.29 × 0.1 × 0.09 mm
Theta range for data collection	2.690 to 27.466 deg.
Limiting indices	-10≤=h≤=10, - -14≤=k≤=13, -16≤=l≤=15
Reflections collected/unique	9184 / 4649 [R(int) = 0.0796]
Absorption correction	Semi-empirical from equivalents

Part 4. DFT calculation on IDs

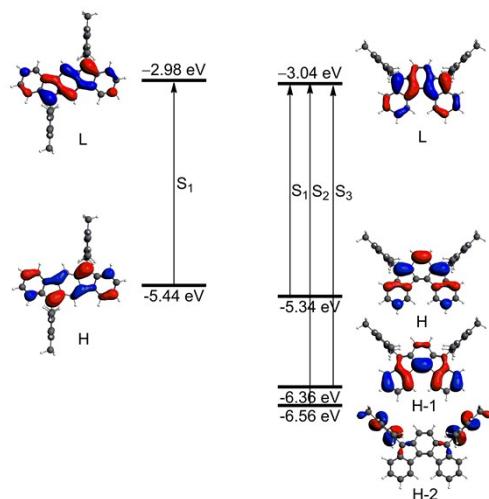


Fig. S1 DFT-calculated orbital energy diagram and pictorial representation of frontier orbitals for IDs.

Part 5. Device fabrication and characterization

Device fabrication. The substrates used here were successively cleaned with pure water, piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=2:1$), pure water, isopropyl alcohol, and finally were blown dry with high-purity nitrogen gas. Treatment of the Si/SiO_2 (thickness of SiO_2 : 300nm) wafers with octadecyltrichlorosilane (OTS) was carried out with the vapor-deposition method. The wafers were vacuum-dried at 90 °C for 1 h. When the temperature decreased to 40 °C, a trace of OTS was placed at the center of the culture dish loaded with clean wafers. Subsequently, this system was heated to 120 °C and maintained at 120 °C for 2 h. When the temperature decreased to 40 °C again, it was ultrasonic cleaned by n-hexane, chloroform and isopropanol successively and finally blown dry with high-purity nitrogen gas.

Micro/nanometer-sized single-crystals of the compound IDBT-*I*-TIPSA used in this study were grown in typical growth conditions by physical vapor transport (PVT) in a horizontal-tube furnace and the carrier gas was ultrahigh-purity argon at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. A quartz boat with sample powder was placed in the high-temperature zone and micrometer-sized single crystals were slowly grown on the OTS-modified Si/SiO_2 substrate at a relatively lower temperature. Then we selected some with high quality and suitable size for OFET measurements.

The traditional top-contact bottom-gate devices based on the nano/micro-single crystal were fabricated by pasting the Au electrodes directly onto crystals to avoid the thermal radiation. When we fabricate the devices by thermal gold (Au) deposition, a negative effect from thermal radiation is obvious, so we selected this method finally. It is more convenient and faster than the other method with the least influence from processing conditions.

Device characterization

The representative channel width/length ratios 0.02 with hole mobilities of up to $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 0.027 with electron mobilities of up to $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were measured and recorded. We measured more than 20 devices and all electrical characteristics of the devices were measured at room temperature using a semiconductor parameter analyzer (Keithley 4200 SCS).