# Electronic Supplementary Information

## Narrow-optical-gap π-conjugated small molecules based on terminal isoindigo and thienoisoindigo acceptor units for photovoltaic application

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## Experimental Section

*Materials*:

Reagents were purchased from Wako Pure Chemical Industries, Tokyo Kasei Chemical Industries, Merck, and Aldrich, and used without further purification. bis(trimethylstannyl)benzodithiophene derivative was synthesized accordance with literature procedures.[1]

*Apparatus*:

UV-visible spectra were recorded on Shimadzu UV-3100PC. All spectra were obtained in spectrograde solvents using quartz cells with a 1 cm path length. $^1$H and $^{13}$C NMR spectra were recorded with a JEOL JNM-ECS400 (400 MHz) spectrometer and a Bruker BioSpin AVANCE III 700 (700 MHz) spectrometer in chloroform-*d* [chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane as an internal standard]. Cyclic voltammetry was carried out on a BAS CV-50W voltammetric analyzer using Pt working and counter electrodes in a dichloromethane solution containing 0.1 mol/L $Bu_4NPF_6$. Synthesized compounds were purified with recycling gel-permeation liquid chromatography (GPC) with use of Japan Analytical Industry LC-908 equipped with JAI-GEL 1H/2H columns (eluent: $CHCl_3$). The HPLC measurements were carried out by gel permeation chromatography in chloroform at 40 °C. Hitachi UV/Vis detector (L-2400), Hitachi pump (L-2130), TOSOH GPC system (GPC-8200 model II ver. 6.0), and Shodex column (GPC K-803L and GPC K-G Guard Column) were used. The flow rate was 1.0 mL/min. Column chromatography was performed on silica gel, KANTO Chemical silica-gel 60N (40–50 μm). Thin-layer chromatography plates (TLC, TLC silica gel 60 $F_{254}$, Merck) were visualized with UV light. Thermogravimetric analyses were conducted using Shimadzu TGA-50 with an aluminum pan. Hole mobility of blend film was measured by the space-charge limited current (SCLC) method according to literature procedure, using a device configuration of ITO/ PEDOT:PSS /**1** or **2**:$PC_{71}BM$/Al.[2] Elemental analyses were performed on Perkin Elmer LS-50B by the Elemental Analysis Section of Comprehensive Analysis Center (CAC), ISIR, Osaka

University. The thicknesses of deposited organic films were measured using a KLA-Tencor alpha-step IQ surface measurement profiler. UV photoelectron spectroscopic analysis was conducted using a $PC_{61}BM$ film on ITO-glass substrates. The HOMO energy level of the $PC_{61}BM$ film was estimated for –6.06 eV.

## Device fabrication and measurements

Glass slides patterned with ITO (Sanyo Vacuum Industries Co., Ltd.) were treated in an $O_2$ plasma oven for 5 min. Thereafter, the ITO-coated grass slides were spin-coated (500 rpm for 5 s and then 3000 rpm for 60 s) with a filtered (0.45 μm pore size PTFE membrane filter) aqueous suspension of poly(ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT-PSS) (Clevios P VP Al 4083), and then baked at 135 °C for 10 min in air. Compound **1** or **2** and PCBM (1:2, wt/wt) were dissolved in chlorobenzene with 1,8-diiodeoctane (3%, v/v) at room temperature and then spun-cast on the top of the PEDOT-PSS layer at 1000 rpm for 60 s. The thicknesses of the resulting oligomer/PCBM films were found to be ca. 100 nm. The device fabrication was completed by the vacuum deposition of calcium (30 nm) and Al cathode (ca. 70 nm). The active area of each solar cell device was 3 x 3 mm. The solar cells were subsequently tested under simulated air mass (AM) 1.5 G solar irradiation (100 mW/cm$^2$, SAN-EI ELECTRIC CO., LTD. XES-301S). Current–voltage (*J*–*V*) characteristics were recorded using a PC-controlled Keithley 2400 source meter.

## Synthesis

### Small molecule **1**

To a solution of compound **A** (153 mg, 0.26 mmol) and bis(trimethylstannyl)benzodithiophene (90 mg, 0.12 mmol) in anhydrous toluene (1 mL), $Pd(PPh_3)_4$ (12 mg, 0.012 mmol) was added. The resulting mixture was refluxed for 24 h. After the Pd catalyst was removed by filtration, the solvent was removed under reduced pressure. The residue was purified by preparative GPC to give conjugated small molecule **1** (112 mg, 74 %). Greenish-black solid; TLC $R_f$ = 0.72 (EtOAc:hexane = 1:4); $^1$H NMR (700 MHz, $CDCl_3$): 0.85–0.89 (m, 12H), 0.99 (t, $J$ = 7.0 Hz, 6H), 1.07 (t, $J$ = 7.7 Hz, 6H), 1.23–1.48 (m, 48H) 1.60-1.81 (m, 14H), 1.90–1.95 (m, 2H), 3.80–3.87 (m, 8H), 4.22 (d, $J$ = 5.6 Hz, 4H), 6.88 (d, $J$ = 7.7 Hz, 2H), 6.97 (s, 2H), 7.11 (d, $J$ = 7.7 Hz, 2H), 7.35 (t, $J$ = 7.0 Hz, 2H), 7.74 (s, 2H), 9.22 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR (175 MHz, $CDCl_3$, δ): 11.31, 14.10, 14.27, 22.62, 23.23, 23.72, 26.96, 27.08, 27.73, 28.51, 29.14, 29.20, 29.26, 29.34, 30.25, 31.78, 40.17, 40.63, 41.81, 108.00, 108.30, 115.11, 117.72, 121.31, 122.36, 128.78, 129.12, 129.44, 130.94, 132.71, 136.85, 143.68, 144.50, 146.94, 152.65, 169.02, 170.09; UV–vis ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 655 nm (4.8 x $10^4$ $M^{-1}$ $cm^{-1}$); Anal. calcd for $C_{86}H_{114}N_4O_6S_4$: C 72.33, H 8.05, N 3.92%; Found: C 72.27, H 8.03, N 4.00%.

Small molecule **2**

To a solution of compound **D** (79 mg, 0.15 mmol) and bis(trimethylstannyl)benzodithiophene (50 mg, 0.06 mmol) in anhydrous toluene (1 mL), $Pd(PPh_3)_4$ (6.6 mg, 0.006 mmol) was added. The reaction mixture was stirred at reflux temperature for 24 h. After the Pd catalyst was removed by filtration, the solvent was removed under reduced pressure. The residue was purified by preparative GPC to give conjugated small molecule **2** (61 mg, 72 %). Red solid; TLC $R_f$ = 0.79 ($CHCl_3$); $^1H$ NMR (700 MHz, $CDCl_3$): 0.88–0.92 (m, 12H), 0.99 (t, *J* = 7.0 Hz, 6H), 1.10 (t, *J* = 7.7 Hz, 6H), 1.30–1.52 (m, 32H), 1.63-1.82 (m, 14H), 1.87–1.92 (m, 2H), 3.78 (t, *J* = 7.0 Hz, 4H), 3.87 (t, *J* = 7.0 Hz, 4H), 3.78 (t, *J* = 7.0 Hz, 4H),4.24 (m, 4H), 6.76 (d, *J* = 7.7 Hz, 2H), 7.22 (s, 2H), 7.04 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 2H), 9.16 (d, *J* = 7.0 Hz, 2H), 9.21 (d, *J* = 8.4 Hz, 2H); $^{13}C$ NMR (175 MHz, $CDCl_3$, δ): 11.37, 14.06, 14.27, 22.57, 22.59, 23.18, 23.84, 26.75, 26.79, 27.47, 27.54, 29.21, 30.48, 31.54, 40.08, 40.15, 40.61, 105.11, 107.87, 117.17, 119.91, 121.68, 121.71, 122.10, 129.59, 129.92, 130.31, 132.30, 132.53, 133.04, 133.15, 137.52, 143.19, 144.54, 144.69, 145.22, 167.82, 168.06; UV–vis ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 564 nm (4.0 x $10^4$ $M^{-1}$ $cm^{-1}$); Anal. calcd for $C_{82}H_{102}N_4O_6S_2$: C 75.54, H 7.89, N 4.30%; Found: C 75.14, H 7.75, N 4.19%.

Compound **A**

To a solution of the thiophene-alternative isoindigo derivative (100 mg, 0.20 mmol) in THF (25 mL), NBS (42 mg, 0.24 mmol) was added, and the mixture was stirred at room temperature for 1 h. The reaction was quenched with water. The mixture was diluted with EtOAc and washed with distilled water and brine. After drying under reduced pressure, the residual solid containing compound **A** was purified by column chromatography ($CH_2Cl_2$:Hex = 2:1) to give pure compound **A** (97 mg, 84 %). Purple solid; TLC $R_f$ = 0.83 ($CH_2Cl_2$:Hex = 2:1); $^1$H NMR (400 MHz, $CDCl_3$): 0.87 (t, *J* = 7.2 Hz, 6H), 1.19-1.42 (m, 22H), 1.64-1.79 (m, 4H), 3.73 (t, *J* = 7.2 Hz, 2H), 3.80 (t, *J* = 7.2 Hz, 2H), 6.82 (s, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 9.19 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR (175 MHz, $CDCl_3$, δ): 14.09, 22.61, 26.88, 27.01, 27.64, 28.40, 29.15, 29.18, 29.21, 29.25, 29.28, 31.75, 31.77, 40.14, 41.80, 108.09, 114.31, 114.94, 121.10, 122.43, 122.68, 125.53, 128.82, 128.89, 131.17, 143.76, 150.99, 168.94, 169.57; UV–vis ($CHCl_3$): $\lambda_{max}$ = 551 nm; Anal. calcd for $C_{30}H_{39}N_2O_2SBr$: C 63.04, H 6.88, N 4.90%; Found: C 62.78, H 6.76, N 4.77%.

Compound **D**

To a suspension of *N*-hexyl-oxindole (120 mg, 0.55 mmol) and 6-bromo-*N*-hexyl-isatin (171 mg, 0.55 mmol) in AcOH (2 mL), conc. HC1 solution (0.01 ml) was added, and the mixture was heated under reflux for 24 h. The mixture was allowed to cool and diluted with EtOAc. The diluted mixture was washed with distilled water, $NaHCO_3$ aq., and brine. After drying under reduced pressure, the residual solid containing compound **D** was recrystallized from EtOH to afford pure compound **D** (175 mg, 62%). Red crystal; TLC $R_f$ = 0.60 ($CH_2Cl_2$:Hex = 1:1.5); $^1$H NMR (700 MHz, $CDCl_3$): 0.87–0.90 (m, 6H), 1.30–1.39 (m, 8H), 1.39–1.45 (m, 4H), 1.69–1.75 (m, 4H), 3.76–3.80 (m, 4H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 1.4 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.37 (dt, *J* = 15.4, 7.7 Hz, 1H), 9.09 (d, *J* = 8.4 Hz, 2H), 9.16 (dt, *J* = 7.7, 1.4 Hz, 2H) ; $^{13}$C NMR (175 MHz, $CDCl_3$, δ): 14.04, 22.54, 26.67, 26.71, 27.37, 27.41, 31.47, 31.50, 40.11, 40.23, 108.03, 111.18, 120.49, 121.57, 122.29, 124.99, 126.33, 129.99, 131.05, 132.20, 132.67, 134.07, 144.81, 145.66, 167.72, 167.83; UV–vis ($CHCl_3$): $\lambda_{max}$ = 497 nm; Anal. calcd for $C_{28}H_{33}N_2O_2Br$: C 66.01, H 6.53, N 5.50%; Found: C 66.15, H 6.61, N 5.48%.

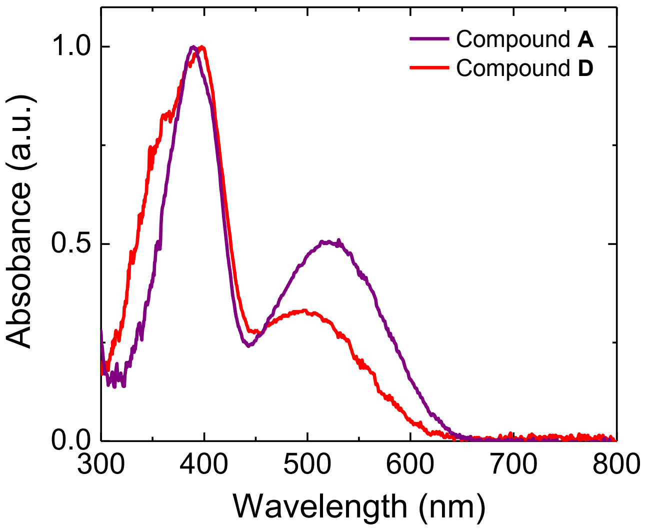


Figure S1. UV-Vis absorption spectra of the terminal units, **A** and **D**, for conjugated small molecules **1** and **2**

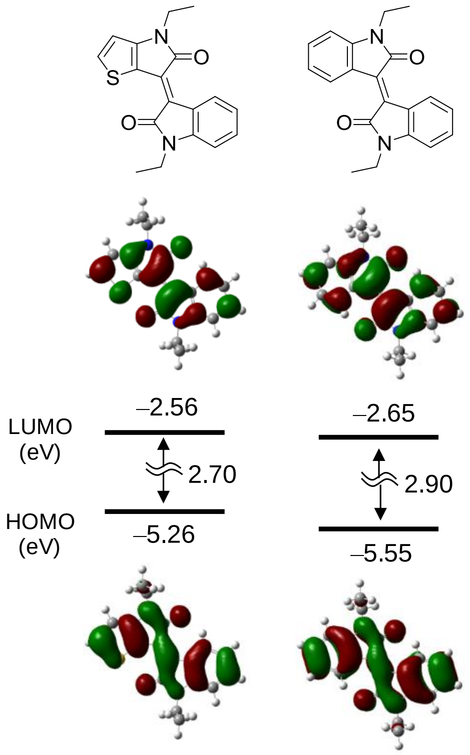


Figure S2. Calculated electron density distribution and energy diagrams of the terminal units of the conjugated small molecules, obtained from Gaussian 09 calculation program (B3LYP/6-31G level)

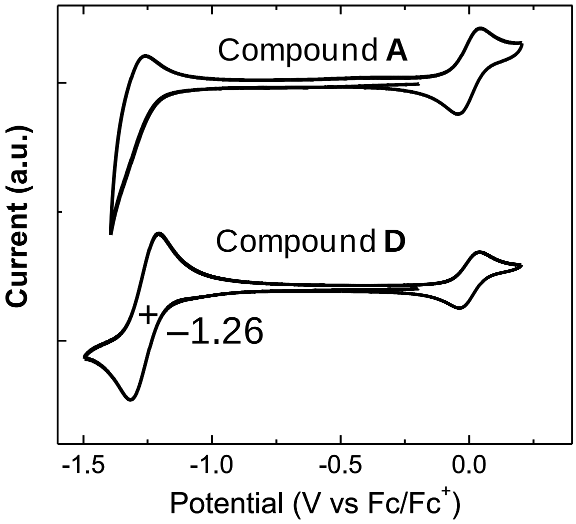


Figure S3. Cyclic voltammograms of the terminal units **A** and **D** with ferrocene as an internal standard

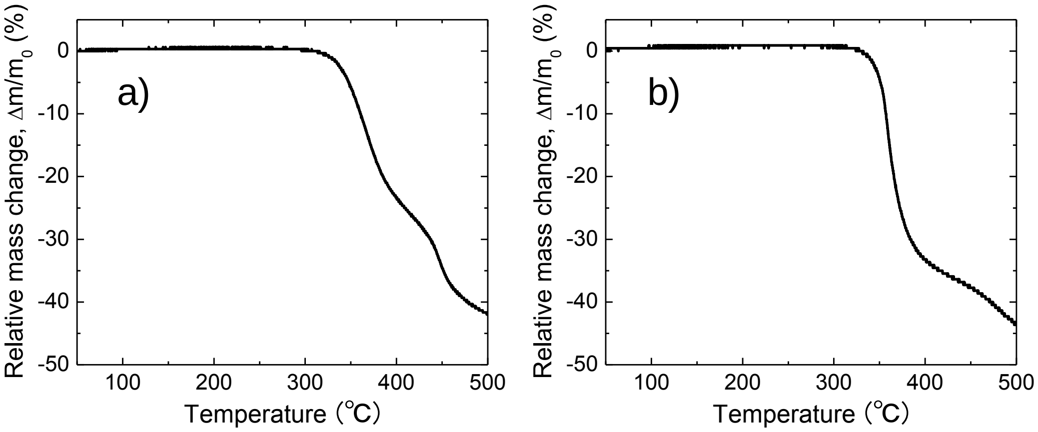


Figure S4. Thermogravimetric analyses of compounds **1** (a) and **2** (b)

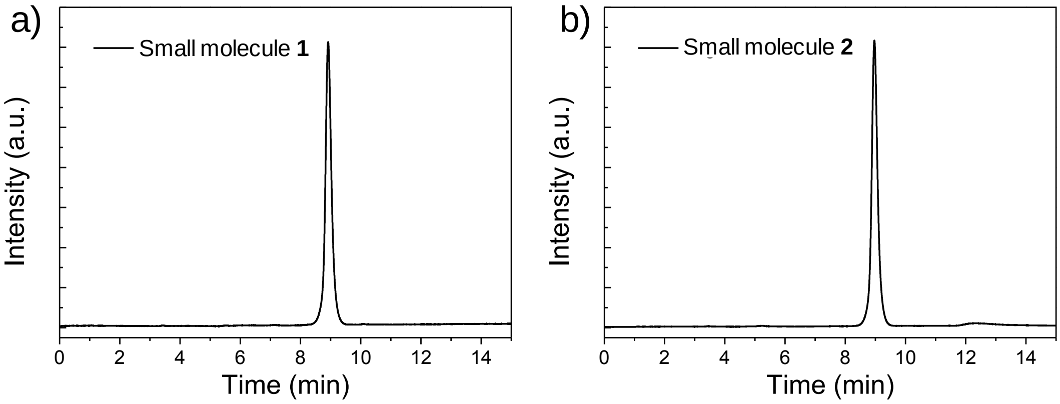


Figure S5. HPLC charts of compounds **1** (a) and **2** (b). (UV light at 254 nm was used for detecting compounds)

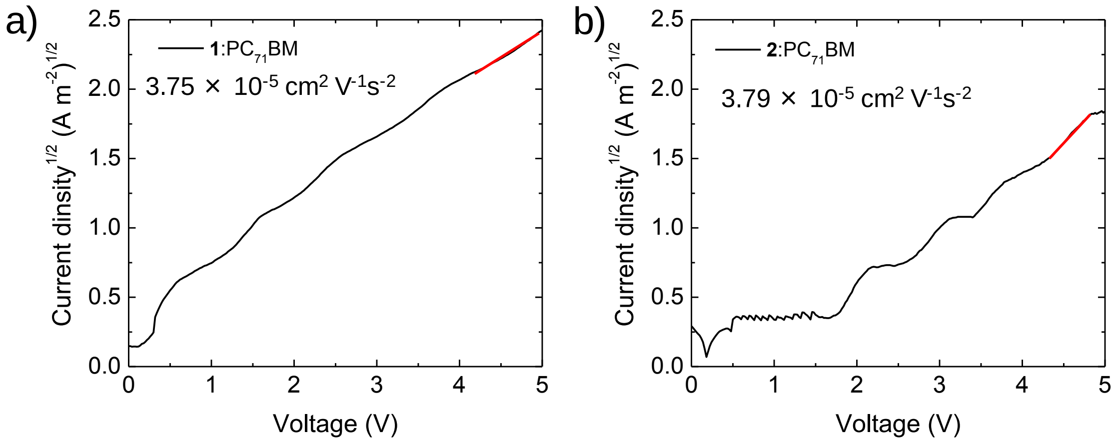


Figure S6. Current dinsity$^{1/2}$ vs *V* plots of the blend film, obtained from SCLC method; (a) **1**:PC$_{71}$BM (1:2, wt/wt) and (b) **2**:PC$_{71}$BM (1:2, wt/wt). The insetted red lines are simulated using the mobility estimated from the plots.

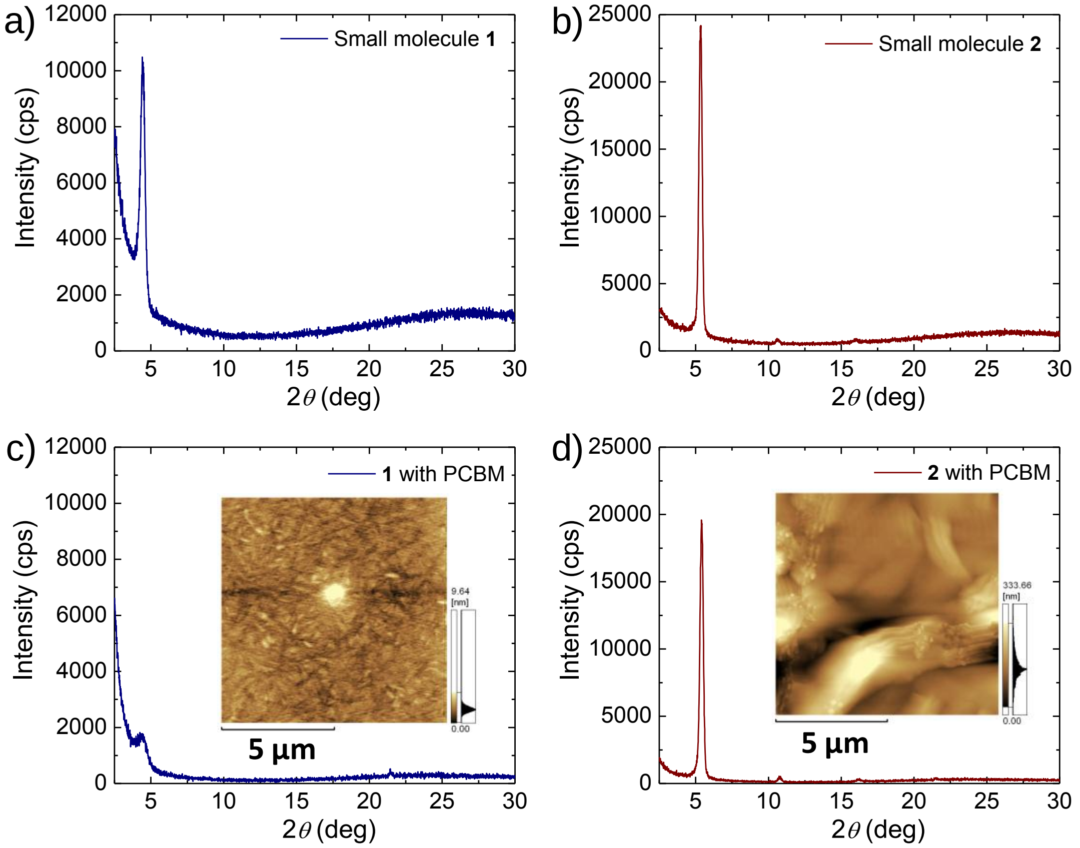
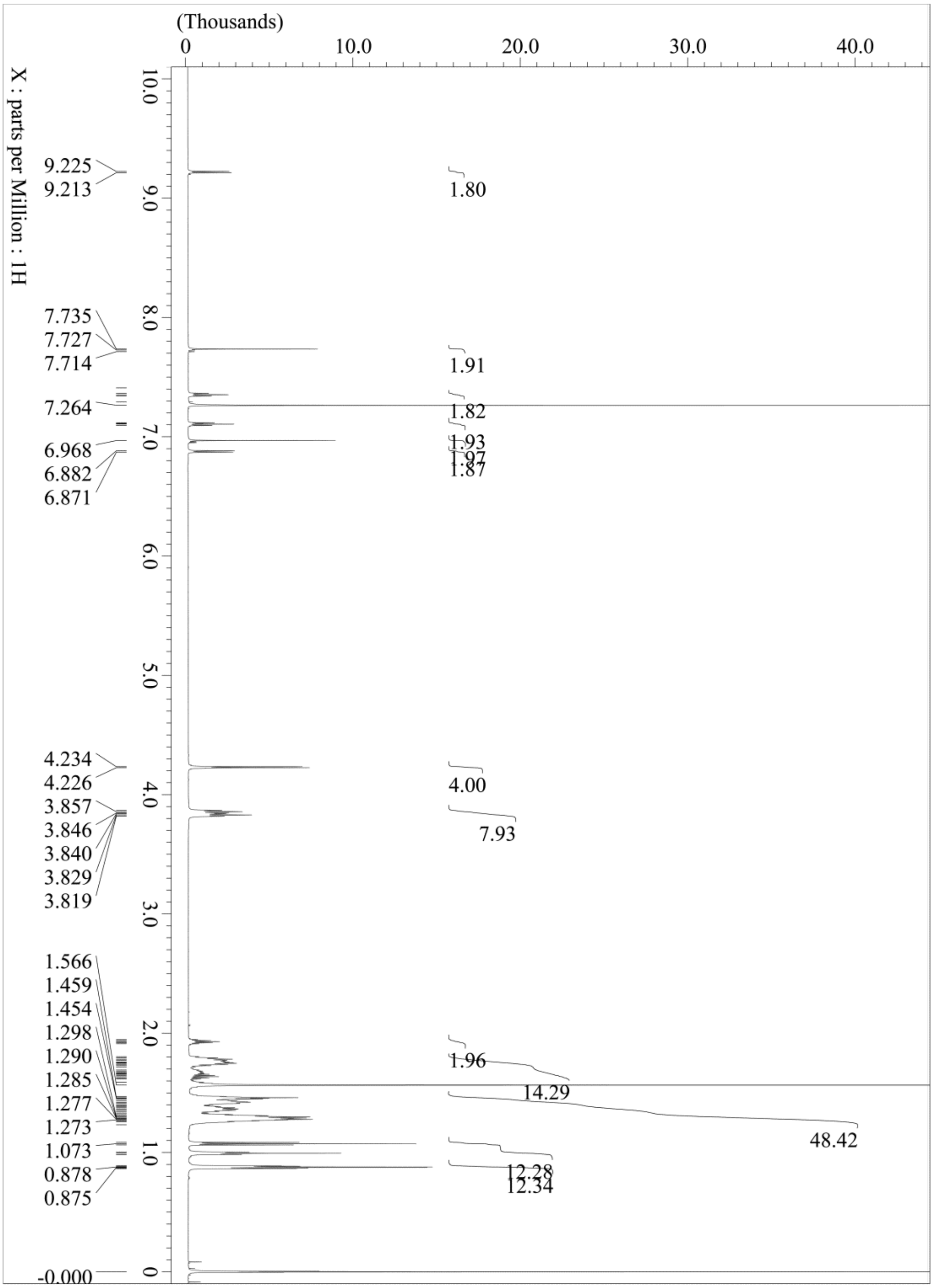
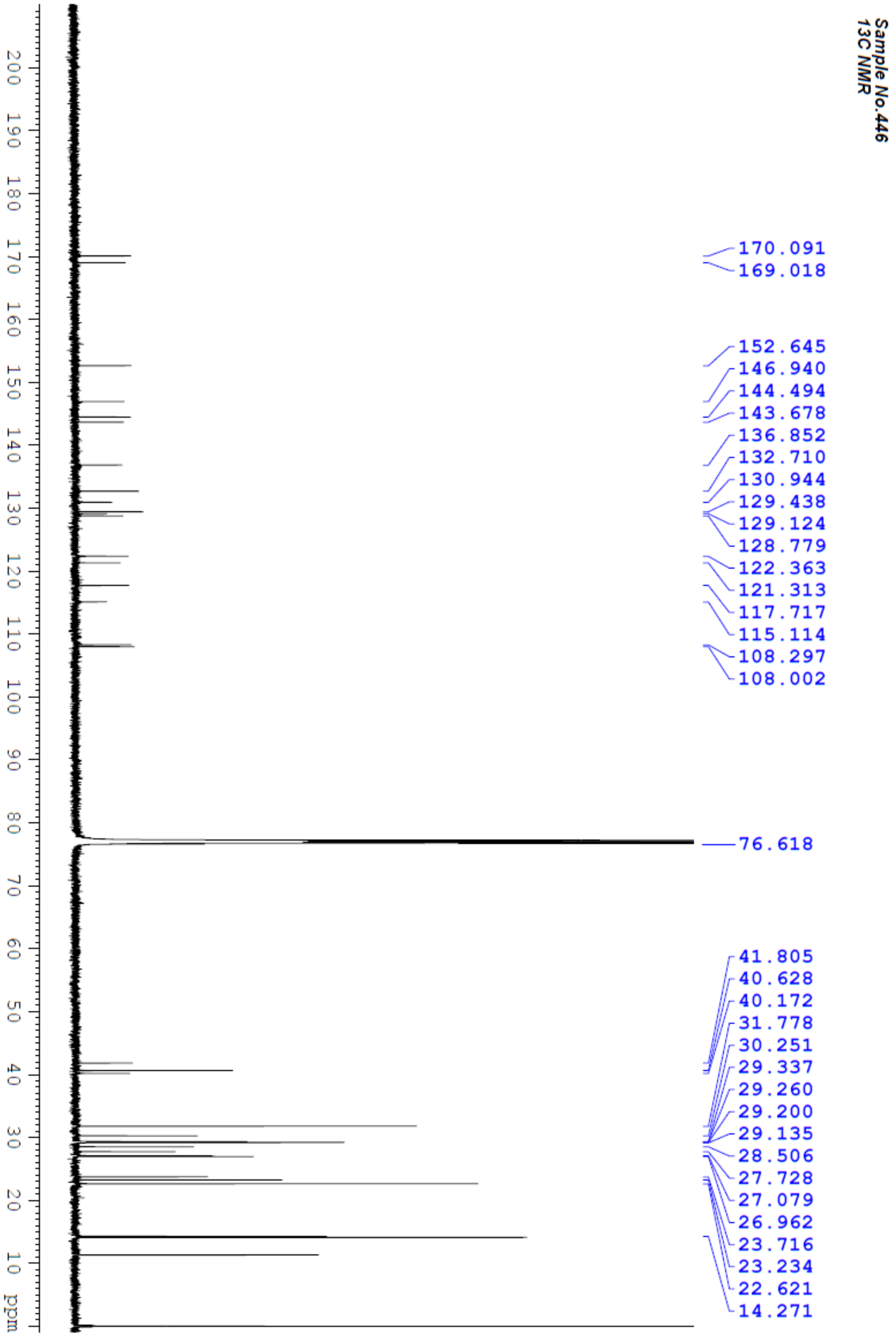


Figure S7. XRD diffractgrams of films composed of pristine **1** (a), pristine **2** (b), **1**–$PC_{71}BM$ blend (c), and **2**–$PC_{71}BM$ blend (d). AFM images of the corresponding films were inserted to (c) and (d).

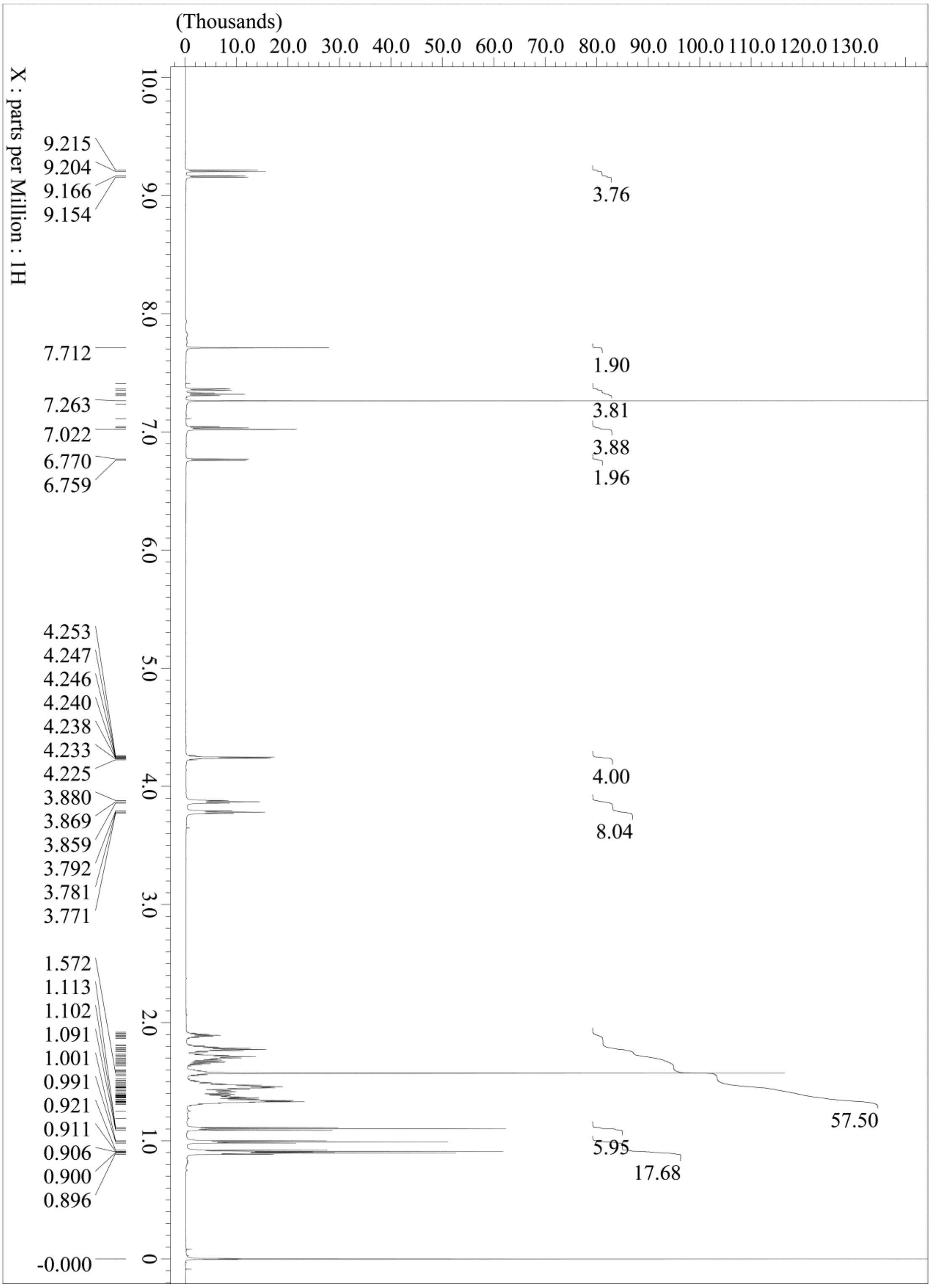
$^1$H NMR spectrum (700 MHz ) of **1**



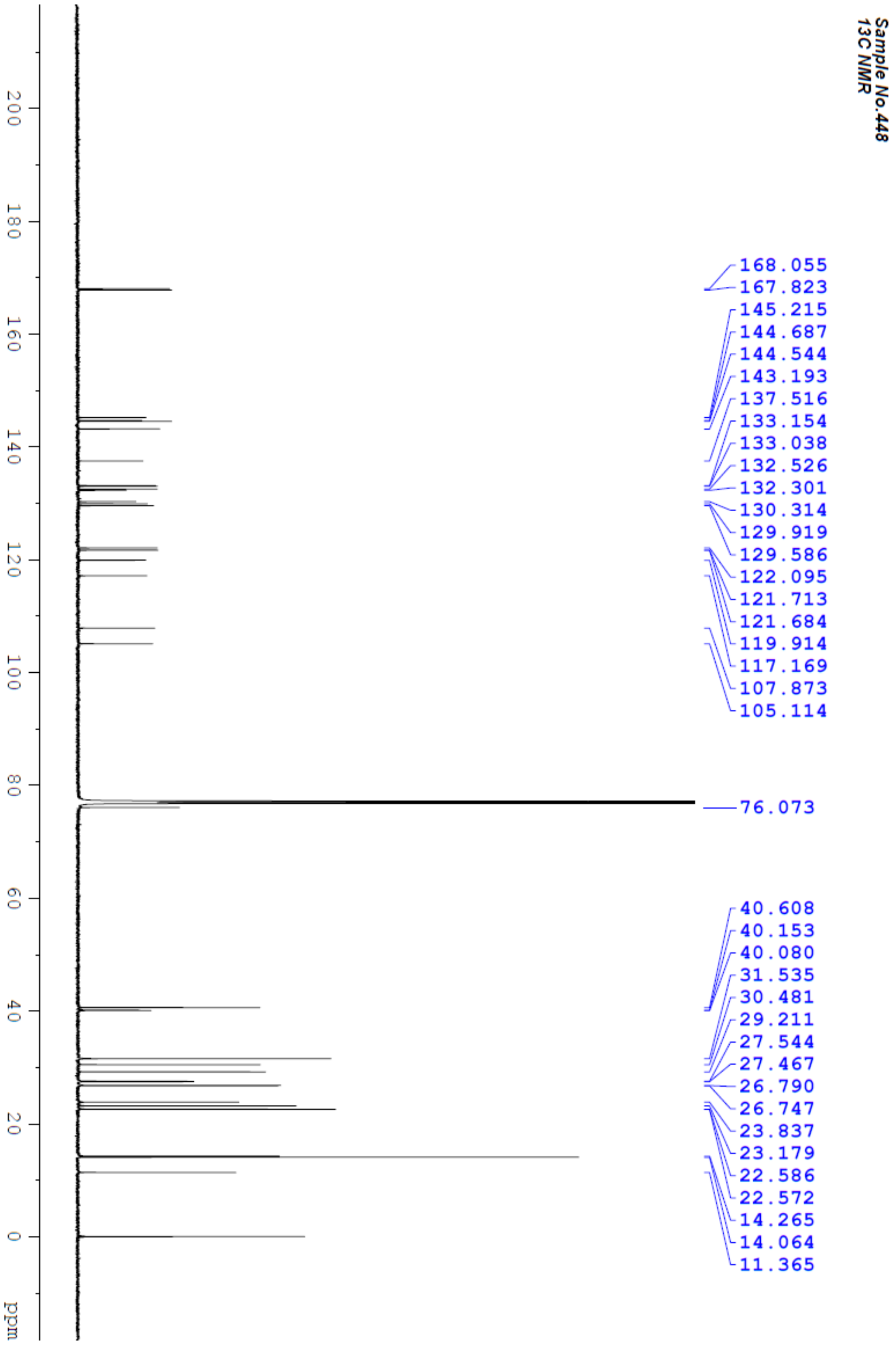
$^{13}$C NMR spectrum (175 MHz ) of **1**



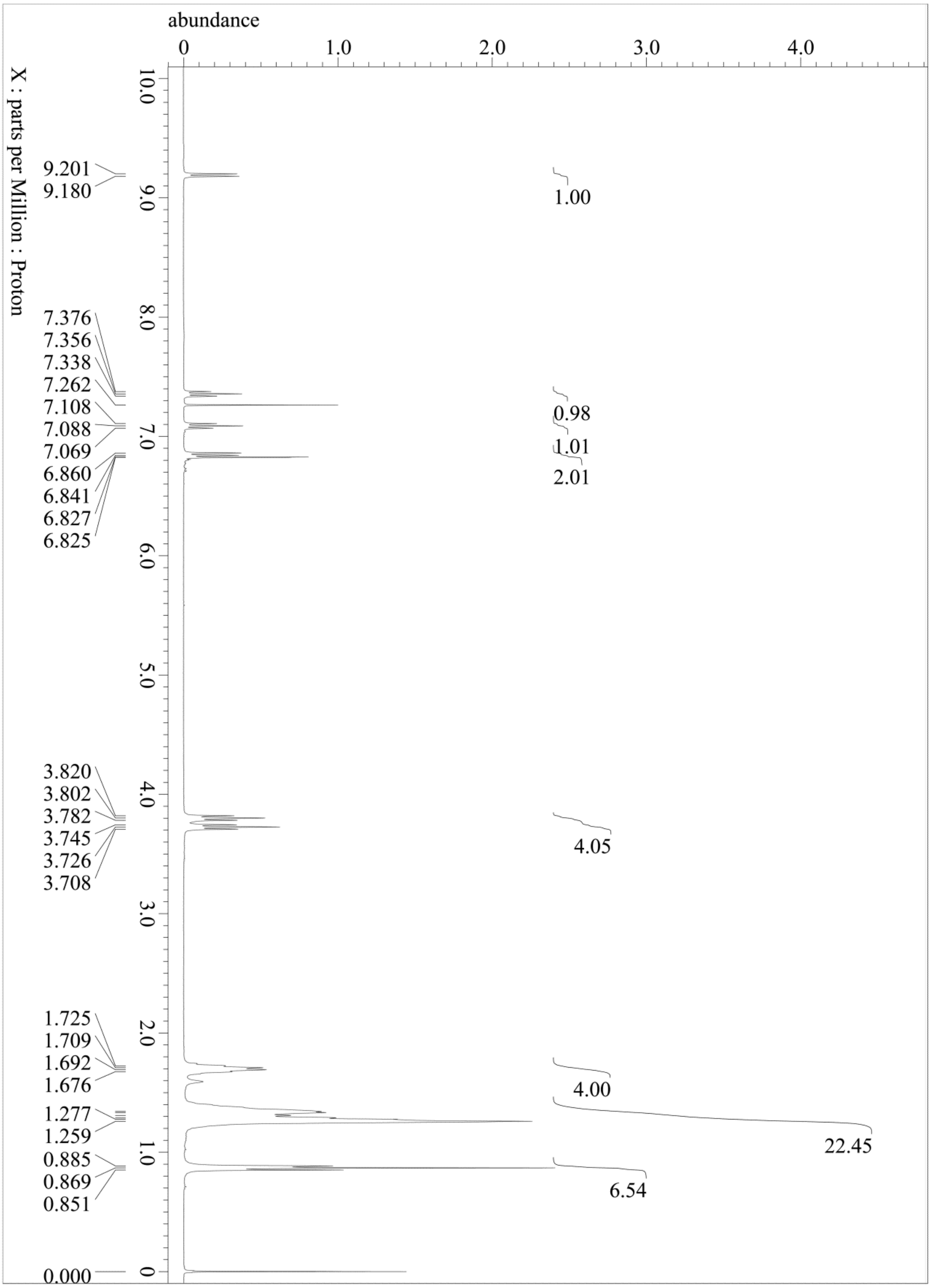
$^{1}$H NMR spectrum (700 MHz ) of **2**



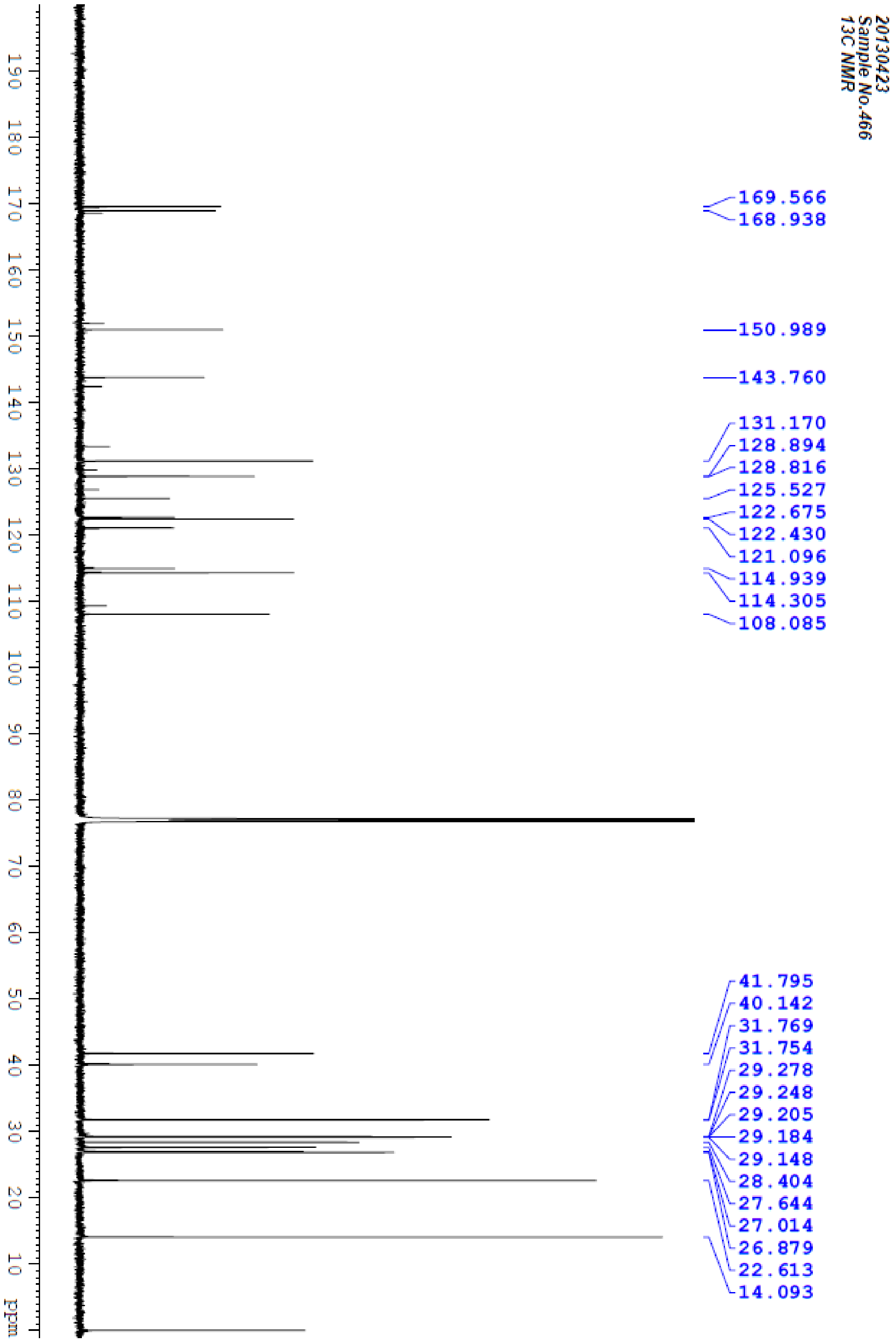
$^{13}$C NMR spectrum (175 MHz ) of **2**



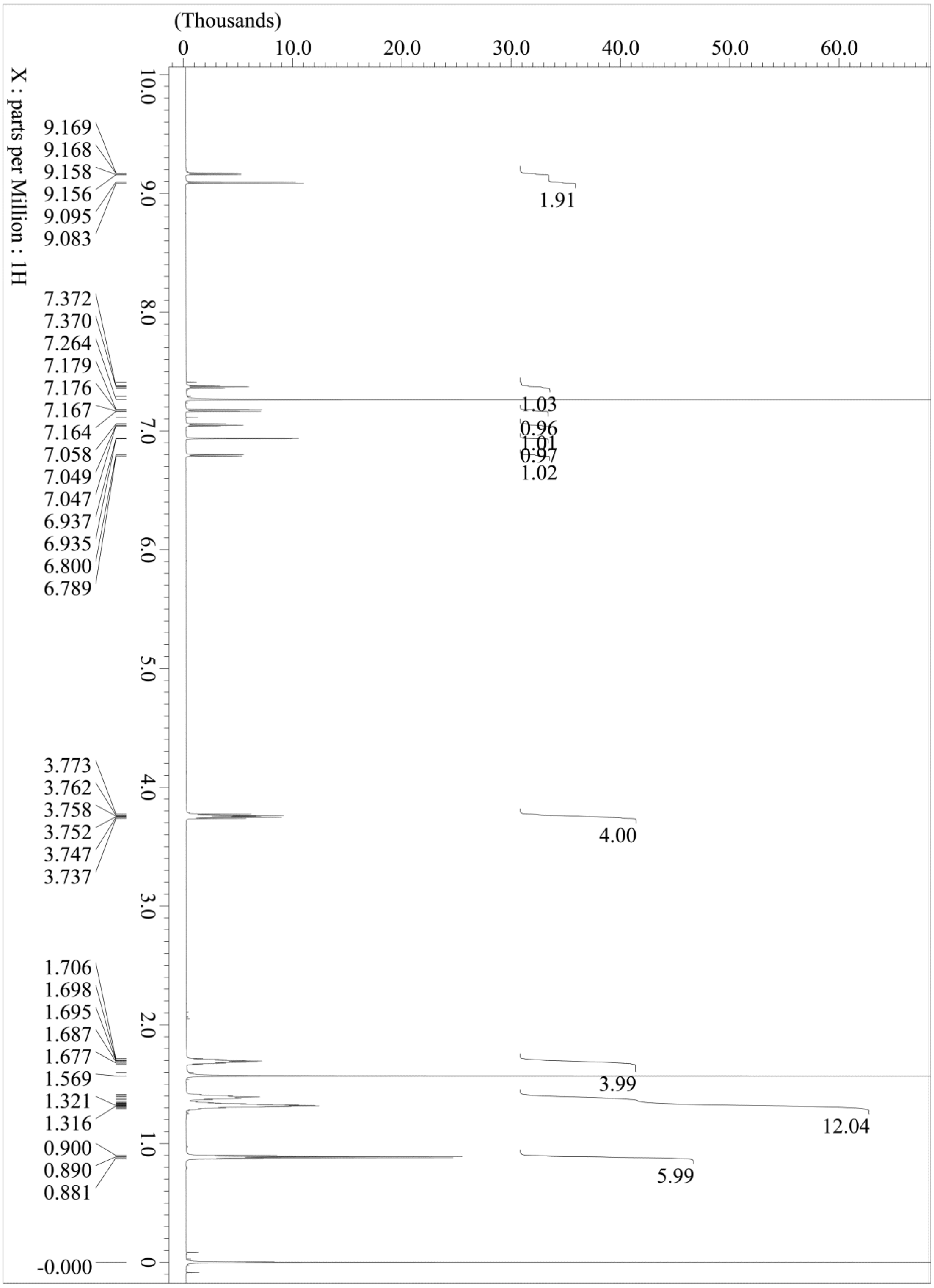
$^1$H NMR spectrum (400 MHz ) of compound **A**



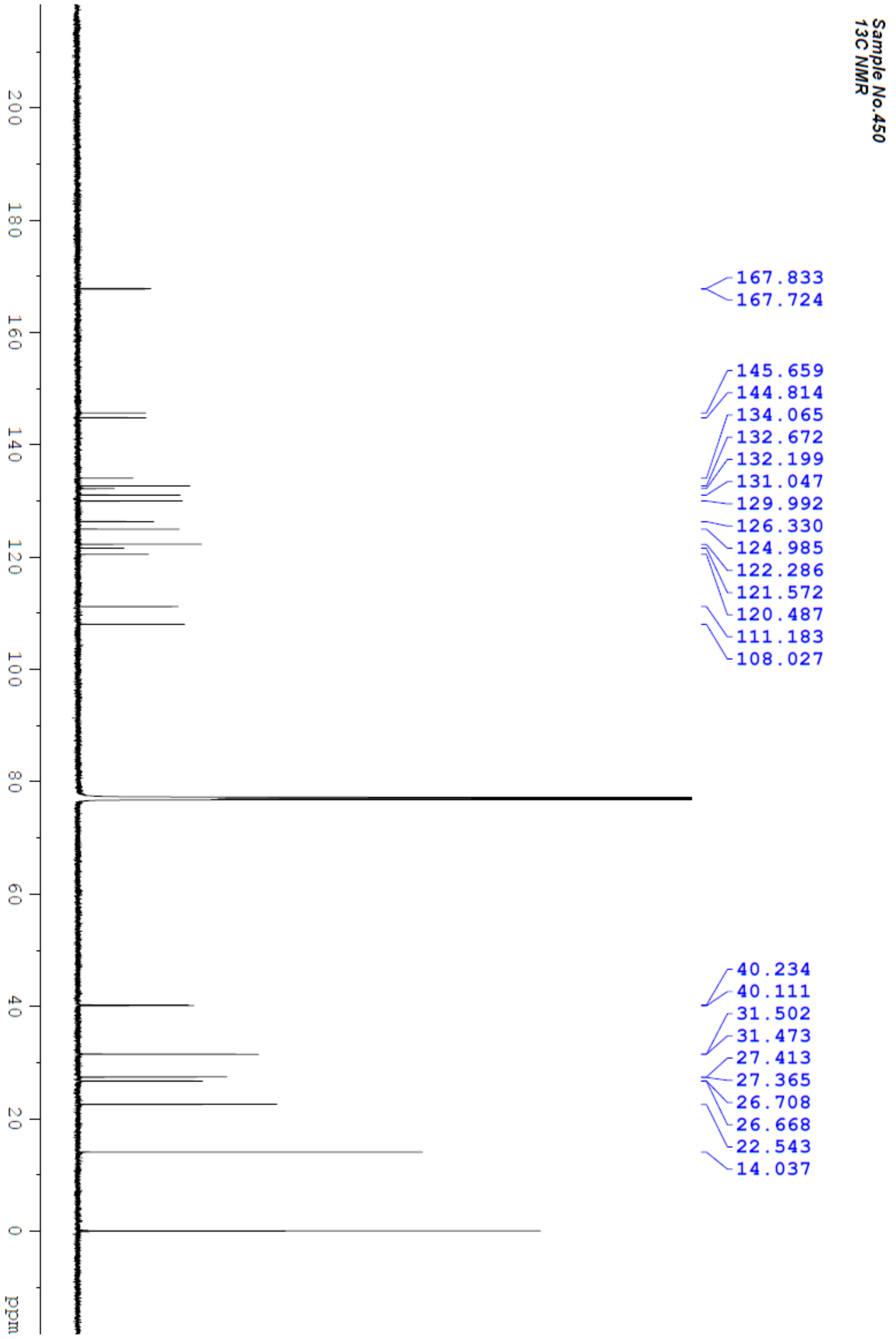
$^{13}$C NMR spectrum (175 MHz ) of compound **A**



$^1$H NMR spectrum (700 MHz ) of compound **D**



$^{13}$C NMR spectrum (175 MHz ) of compound **D**



## References

1. (a) G. Zhang, Y. Fu, Q. Zhang, Z. Xie, *Chem. Commun.*, 2010, **46**, 4997; (b) G. Zhang, Y. Fu, Z. Xie, Q. Zhang, *Macromolecules* 2011, **44**, 1414.

2. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.*, 2010, **22**, E135.