

Pt-acetylide Organometallic Polymers as Active Materials for Organic Solar Cells

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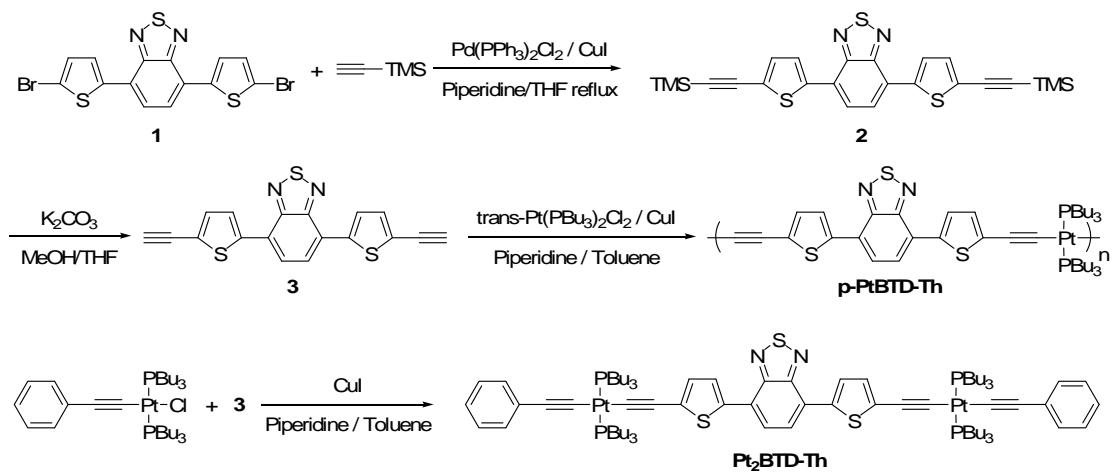
Supporting Information

	Page
Synthetic details for polymer and model compounds	2
NMR spectra of compounds	6
Figure S1. UV-visible absorption spectra of p-PtBTD-EDOT in xylene at T = 10 - 95 °C	22
Figure S2. The mass spectrum (MALDI) of p-PtBTD-EDOT	23
Figure S3. Cyclic voltammograms of Pt-Acetylide EDOT series	24
Figure S4. Light intensity dependence on PV performance of p-PtBTD-EDOT/PCBM photovoltaic devices	25
Measurement of Optical Properties of p-PtBTD-Th	26
Figure S5. Optical constants of p-PtBTD-Th film.	27
Table S1. I-V characteristics of p-PtBTD-EDOT/PCBM photovoltaic devices	29
Table S2. Light intensity dependence of PV performance of p-PtBTD-EDOT/PCBM photovoltaic devices	29

1. Synthetic details for polymers and model compounds.

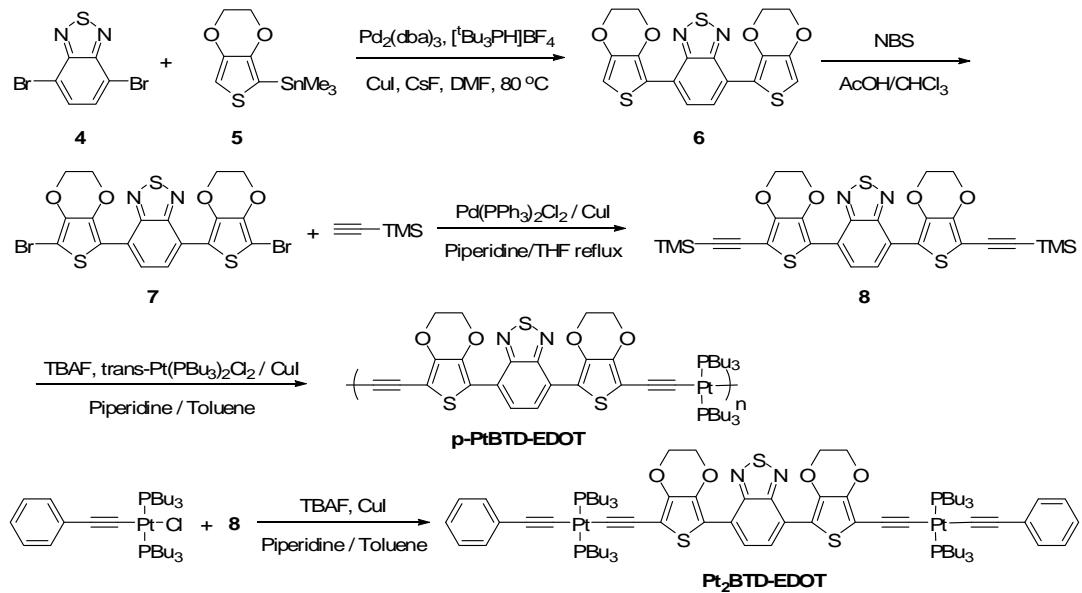
General Synthetic Procedures and Source of Starting Materials. All chemicals used for synthesis were of reagent grade and purchased from Sigma-Aldrich Chemical Co. unless otherwise noted. *trans*-Dichlorobis(triphenylphosphine)palladium (II), tri-*t*-butylphosphonium tetrafluoroborate, tris(dibenzylideneacetone)dipalladium (0) and potassium tetrachloroplatinate (II) were purchased from Strem Chemicals Inc. Poly-(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS, Baytron P VP Al 4083) was purchased from Bayer Corporation (PA, USA). All procedures involving air- and moisture-sensitive reagents were performed using standard Schlenk techniques. Toluene and tetrahydrofuran (THF) were purified with a dry solvent system. Compounds **1**,¹ **4**,² **5**,³ and *trans*-dichlorobis(tributylphosphine)platinum⁴ were prepared according to literature procedures.

The synthetic route to p-PtBTD-Th and Pt₂BTD-Th is illustrated in Scheme 1. Palladium-catalyzed Sonogashira reaction of compound **1** and TMS-acetylene gave compound **2** in 92% yield. Deprotection of compound **2** gave compound **3** in quantitative yield. The polymer and model compounds were synthesized as described in the main text.



Scheme S1. Synthesis of p-PtBTD-Th and Pt₂BTD-Th.

The synthetic route to p-PtBTD-EDOT and Pt₂BTD-EDOT is illustrated in Scheme 2. Stille coupling of compound **4** and **5** gave compound **6** in 74% yield. Compound **6** was brominated with NBS to give compound **7**. Sonogashira coupling of compound **7** and TMSA gave compound **8** in 63% yield. Polymer and model compounds were synthesized as described in the main text.



Scheme S2. Synthesis of p-PtBTD-EDOT and Pt₂BTD-EDOT.

4, 7-bis(5-((Trimethylsilyl)ethynyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2) To a 100 mL Schlenk tube, piperidine-THF (v : v = 1:4, 50 mL) co-solvent was added and degassed for 30 min by argon bubbling. Compound **1** (2.29 g, 5 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.05 mmol) and CuI (38 mg, 0.2 mmol) were added subsequently under argon. Trimethylsilyl acetylene (1.23 g, 12.5 mmol) was injected through a septum and the resulting mixture was refluxed overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography with CH₂Cl₂ / hexane (1:9). The desired product was obtained as red needle-crystals (2.26 g, 92 %). ¹H-NMR (300 MHz, CDCl₃): 7.96 (d, J = 4 Hz, 2H), 7.85 (s, 2H), 7.30 (d, J = 4 Hz, 2H), 0.275 (s, 18H); ¹³C-NMR (75 MHz, CDCl₃): 152.4, 140.4, 133.4, 127.1, 125.6,

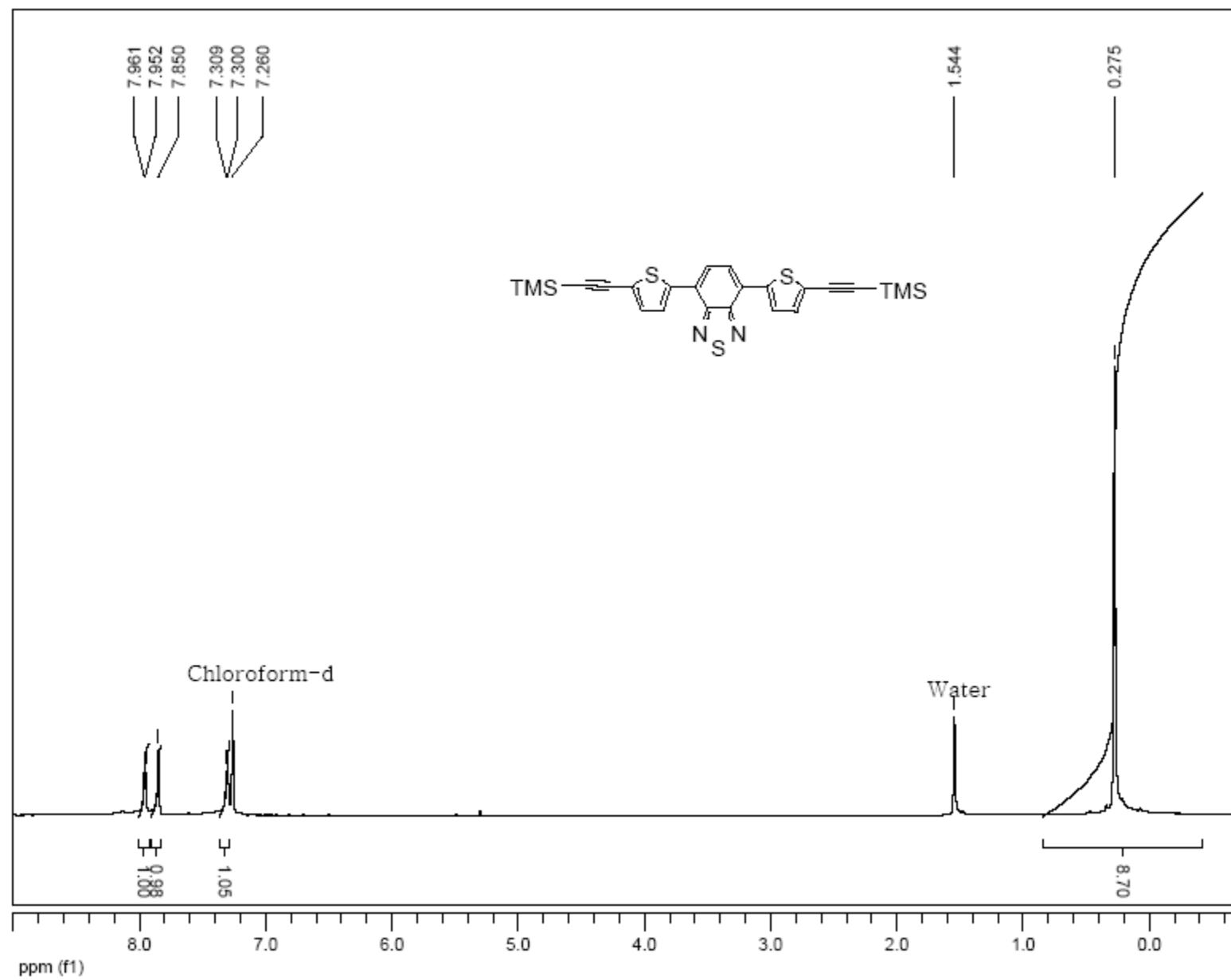
124.7, 101.1, 97.6, 77.2, 0.15; HRMS (ESI) Calculated for $C_{24}H_{25}N_2S_3Si_2$ ($M + H^+$): m/z 493.0712. Found: m/z 493.0724.

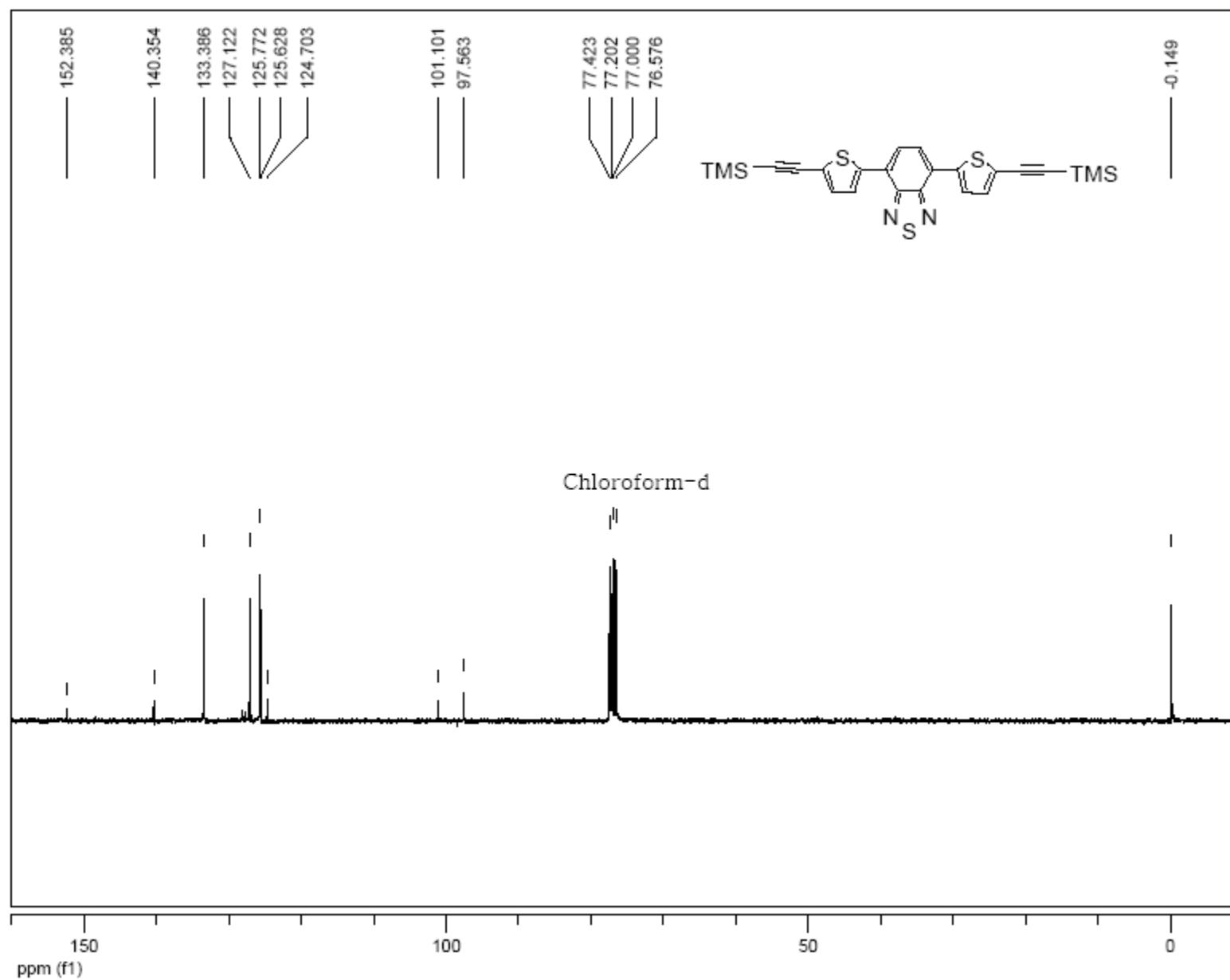
4, 7-bis(5-Ethynylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3) Compound **2** (1.24 g, 2.5 mmol) was dissolved into methanol and THF ($v : v = 1:1$, 50 mL). K_2CO_3 (1.38 g, 10 mmol) was then added. The resulting mixture was stirred at room temperature and monitored by TLC. After compound **2** was consumed, the solvent was removed under reduced pressure. Deionized water (10 mL) was added. The product was extracted with CH_2Cl_2 (10 mL, three times). The combined organic phase was then washed with brine and dried over $MgSO_4$. Removal of the solvent gave the desired product as a red solid (845 mg, 97 %). 1H -NMR (300 MHz, $CDCl_3$): 7.98 (d, $J = 4$ Hz, 2H), 7.87 (s, 2H), 7.36 (d, $J = 4$ Hz, 2H), 3.49 (s, 2H); ^{13}C -NMR (75 MHz, $CDCl_3$): 152.3, 140.6, 133.9, 127.1, 125.7, 125.6, 123.5, 83.1, 77.2; HRMS (ESI) Calculated for $C_{18}H_9N_2S_3$: m/z 348.9922. Found: m/z 349.9944 ($M + H^+$).

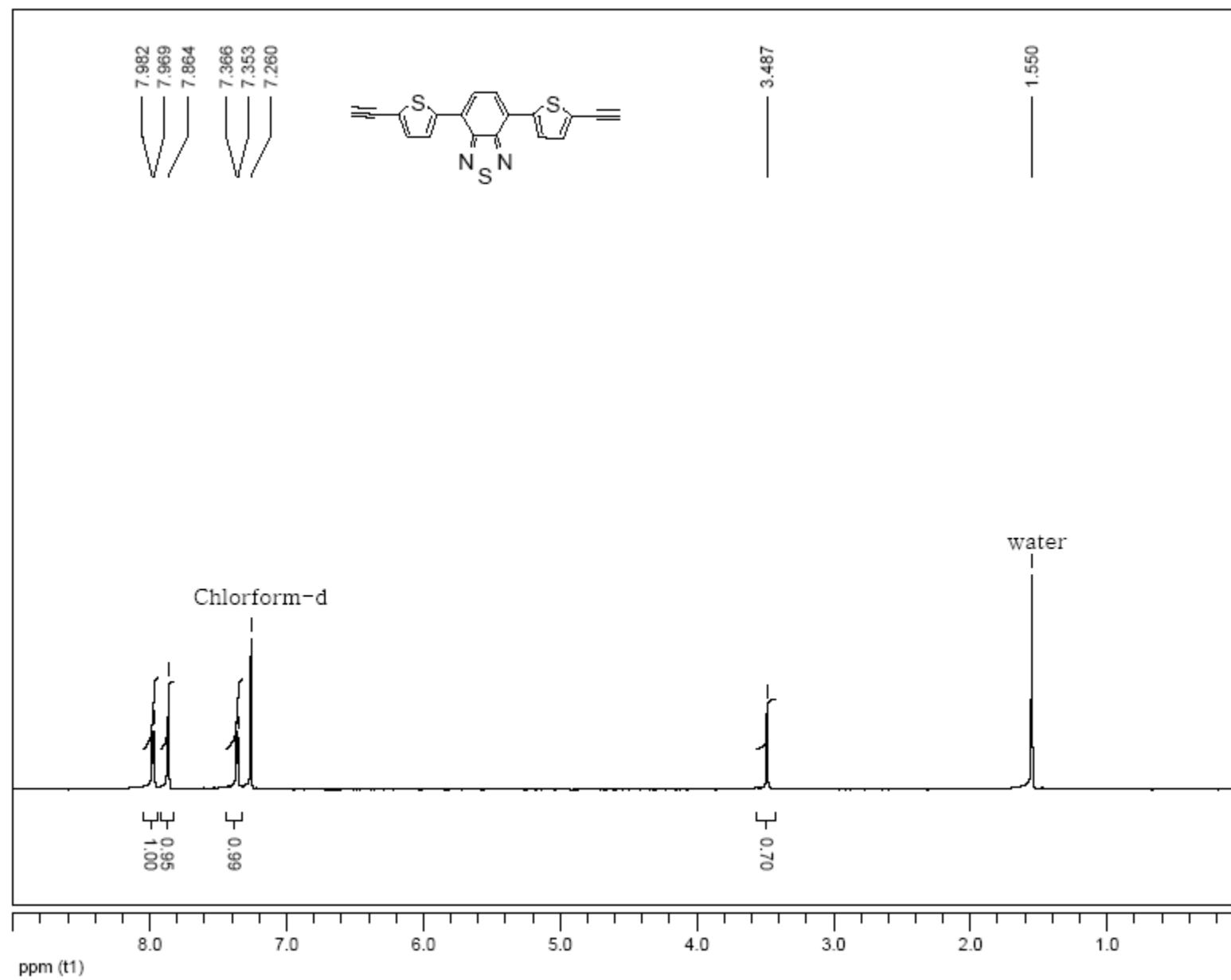
4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole (6) To a solution of compound **4** (1.47 g, 5 mmol) and compound **5** (4.27 g, 14 mmol) in DMF (50 mL), $PdCl_2$ (35 mg, 2 mol %), $[^tBu_3PH]BF_4$ (116 mg, 4 mol %), CuI (10 mol %, 95 mg) and CsF (10 mmol, 1.50 g) were added. The resulting mixture was refluxed overnight under argon. After the mixture was cooled to room temperature, deionized water (400 mL) was added. The product was then extracted with CH_2Cl_2 (200 mL three times). The combined organic phase was subsequently passed through a frit with a pad of ceilite, washed with brine and dried over $MgSO_4$. The solvent was concentrated under reduced pressure to afford a dark red solid. The solid was filtered off and washed with hexane to afford pure compound (1.54 g, 74 %) 1H -NMR (300 MHz, $CDCl_3$): 8.39 (s, 2H), 6.65 (s, 2H), 4.31-4.40 (m, 8H); HRMS (ESI) Calculated for $C_{18}H_{12}N_2O_4S_3Na$ ($M + Na^+$): m/z 438.9953. Found: m/z 438.9937.

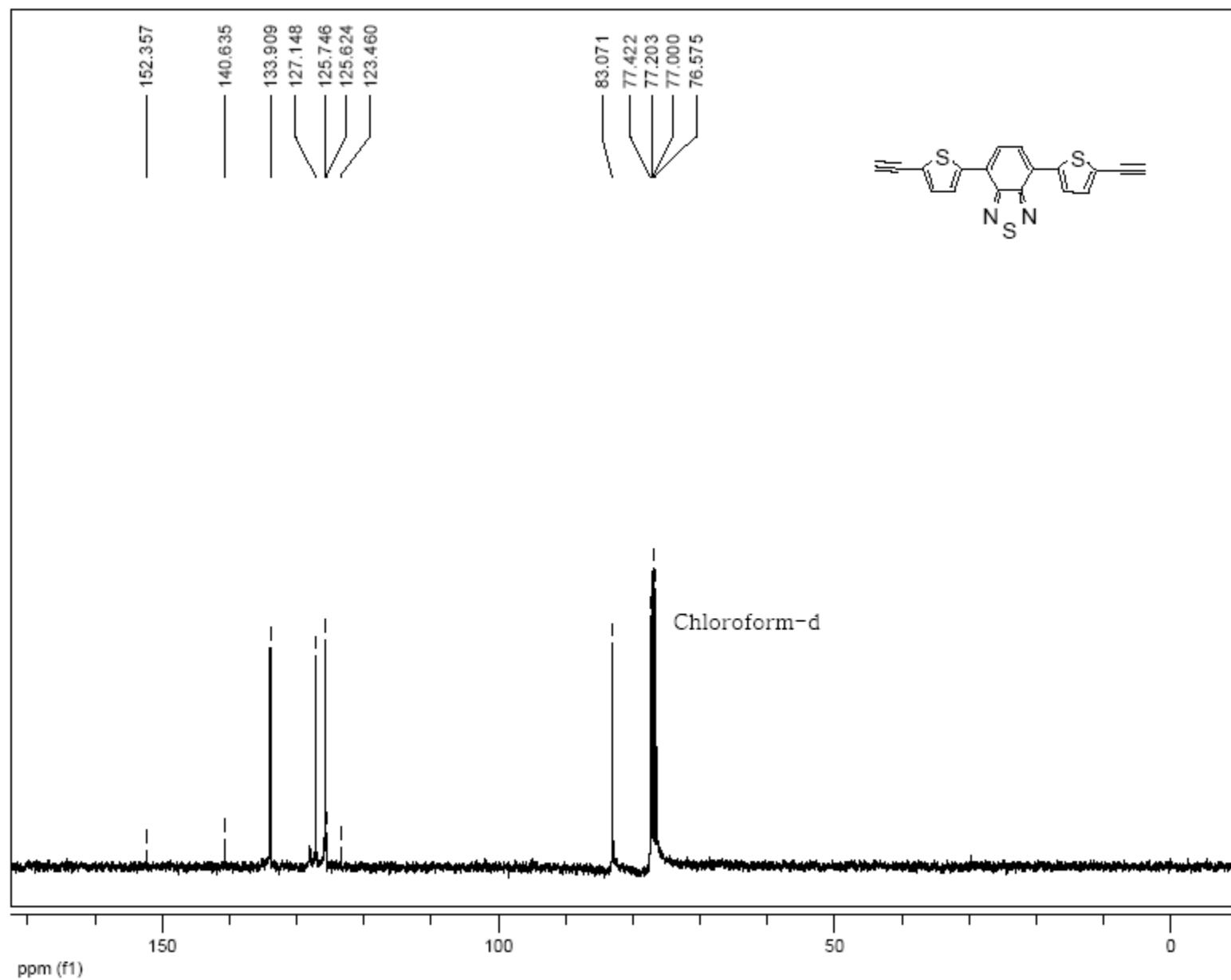
4,7-bis(7-Bromo-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole (7) To a 100 mL flask charged with compound **6** (1.67 g, 4.0 mmol) in CHCl₃ (350 mL), N-iodosuccinimide (NBS, 1.80 g, 10 mmol) was added. A catalytic amount of acetic acid (0.2 ml) was added. The resulting mixture was stirred at room temperature for 2 days. The precipitate formed was filtered off, washed with water, methanol and chloroform. Dark purple solid was obtained (2.10 g, 91 %). ¹H-NMR (300 MHz, C₂D₂Cl₄, 80 °C): 4.38-4.46 (m, 8H); HRMS (CI) Calculated for C₁₈H₁₀Br₂N₂O₄S₃ (M⁺): *m/z* 571.8164. Found: *m/z* 571.8218.

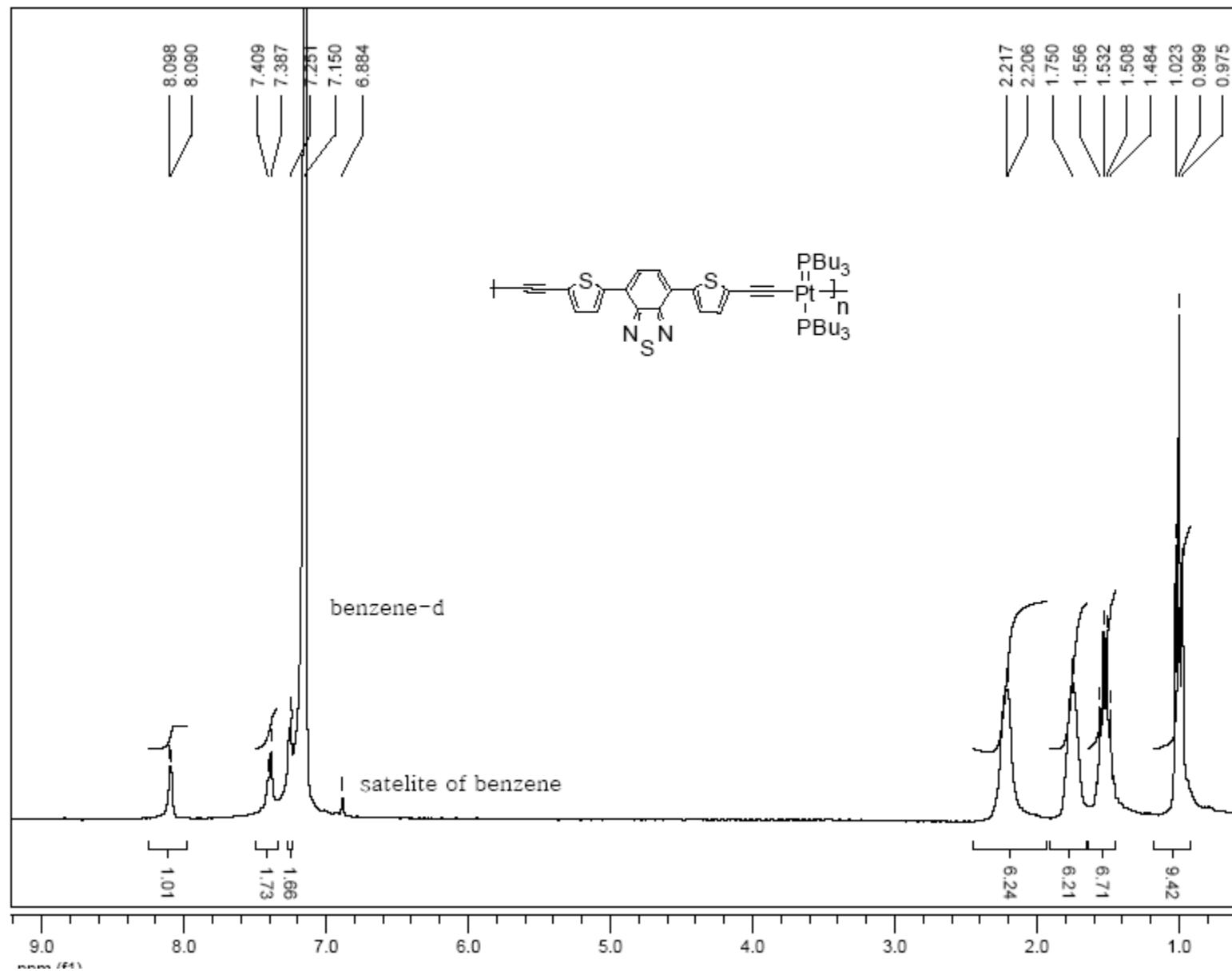
4,7-bis(7-((trimethylsilyl)ethynyl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole (8) To a 100 mL Schlenk tube, piperidine-THF (v : v = 1:5, 60 mL) was added and degassed for 30 min. Compound **7** (1148 mg, 2 mmol), Pd(PPh₃)₂Cl₂ (112 mg, 0.16 mmol, 4 mol %) and CuI (76 mg, 0.4 mmol, 10 mol %) were added subsequently under argon. Trimethylsilyl acetylene (588 mg, 6 mmol) was injected through a septum. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography with CH₂Cl₂ and hexane (1:9, silica gel). After removing solvent, the desired product was obtained as a purple solid (766 mg, 63%). ¹H-NMR (300 MHz, C₆D₆): 8.50 (s, 2H), 3.40-3.36 (m, 8H), 0.23 (s, 18H); ¹³C-NMR (75 MHz, C₆D₆): 152.4, 145.2, 139.9, 126.8, 124.1, 115.6, 103.9, 101.9, 96.7, 64.4, 64.0, 0.03. HRMS (ESI) Calculated for C₂₈H₂₉N₂O₄S₃Si₂Na (M + Na⁺): *m/z* 632.0720. Found: *m/z* 632.0742.

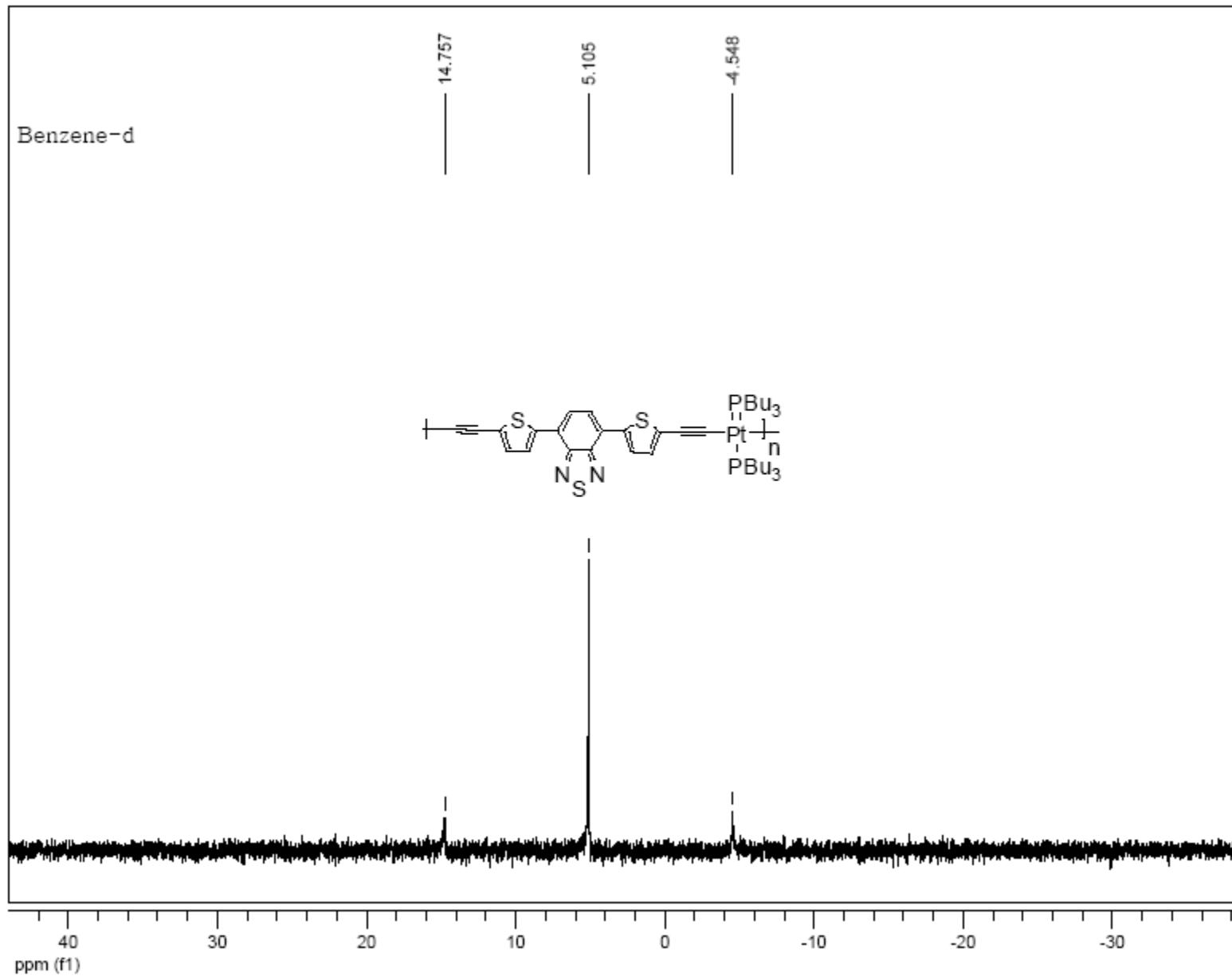


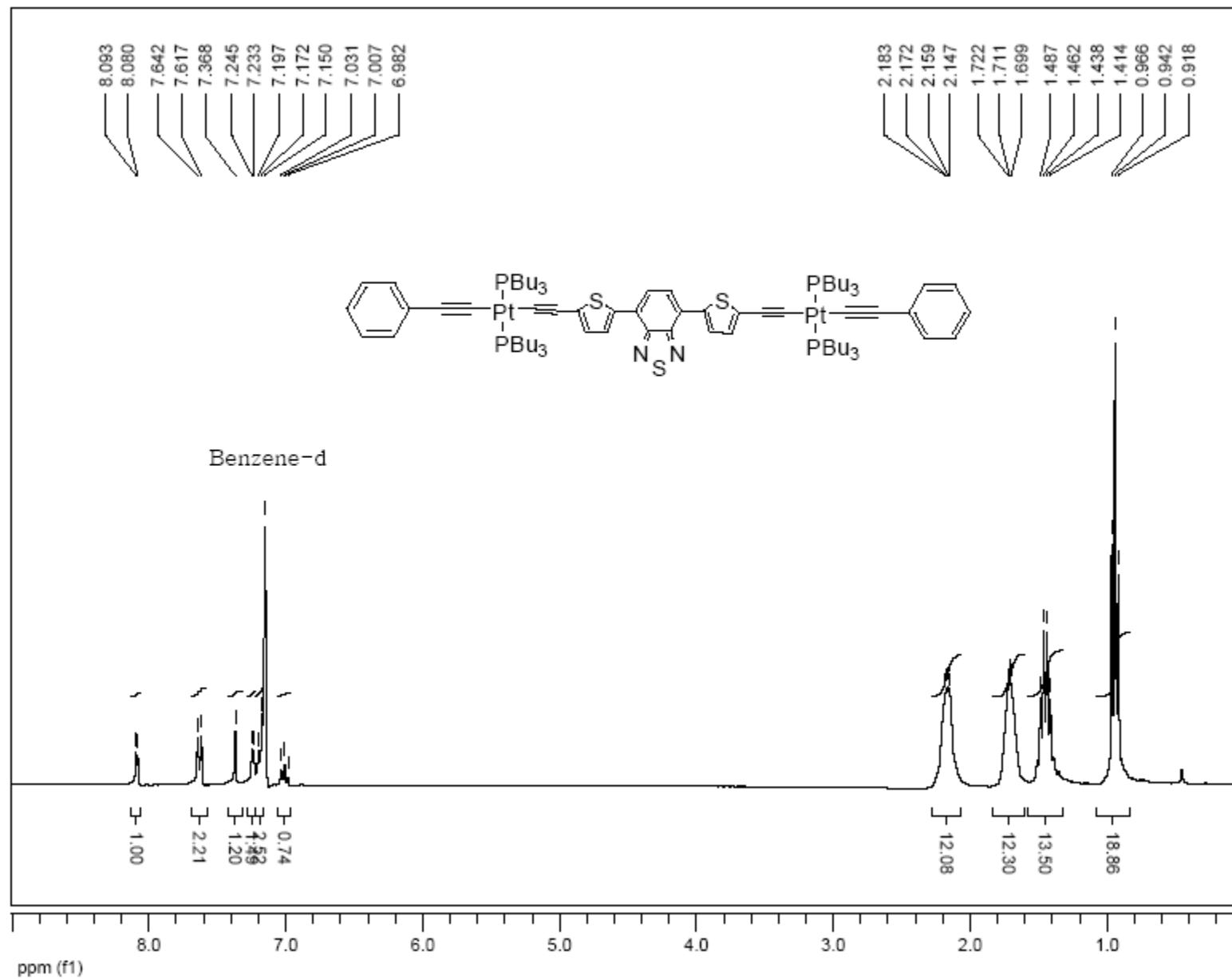






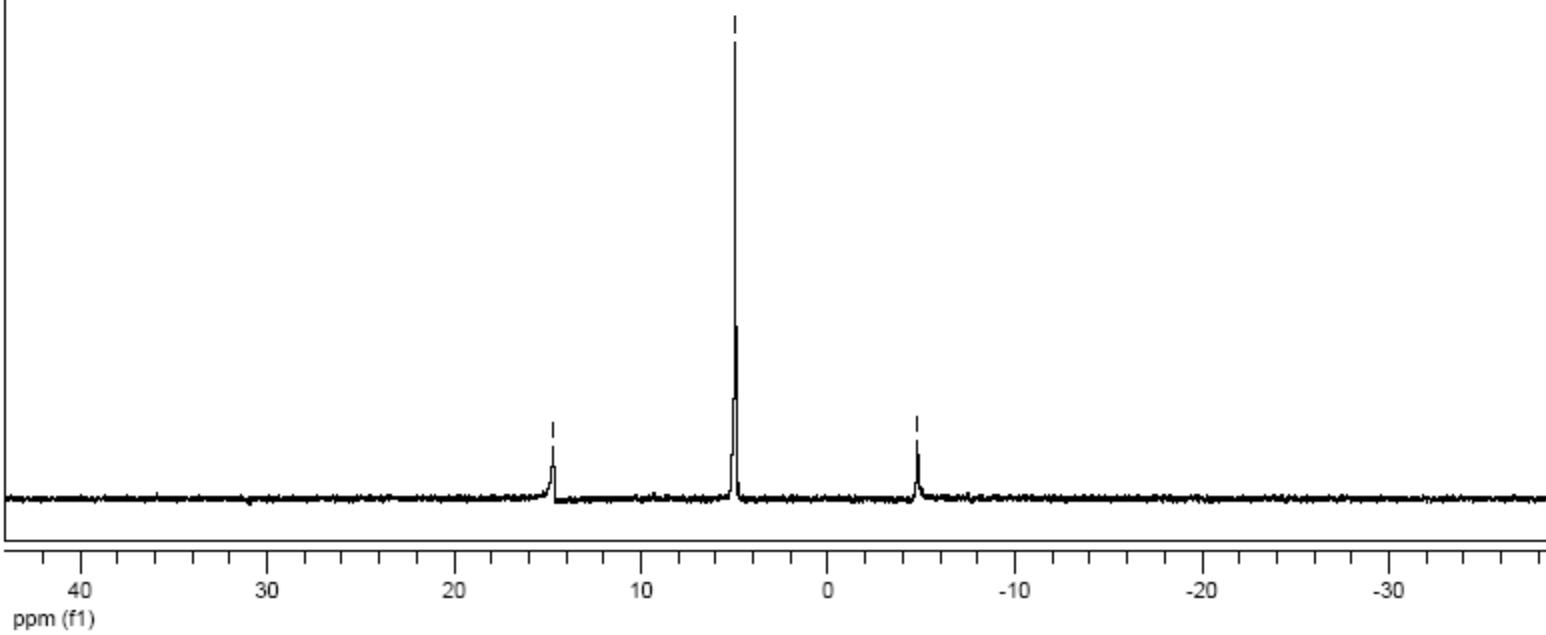
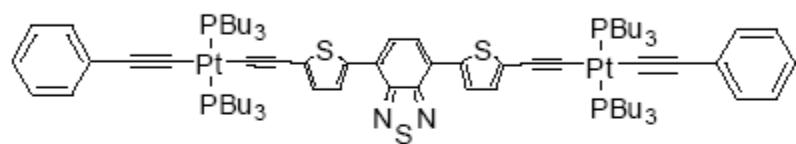


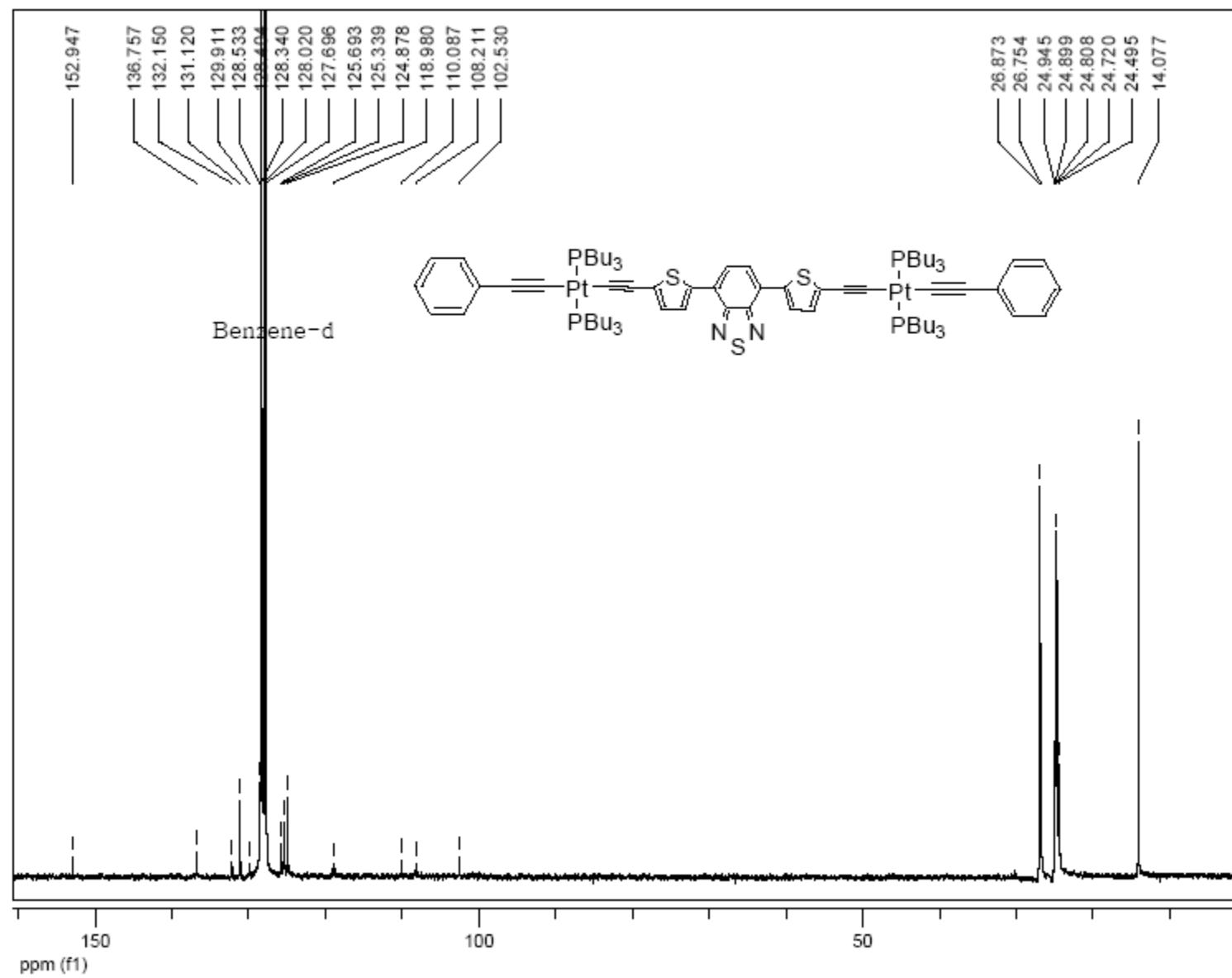


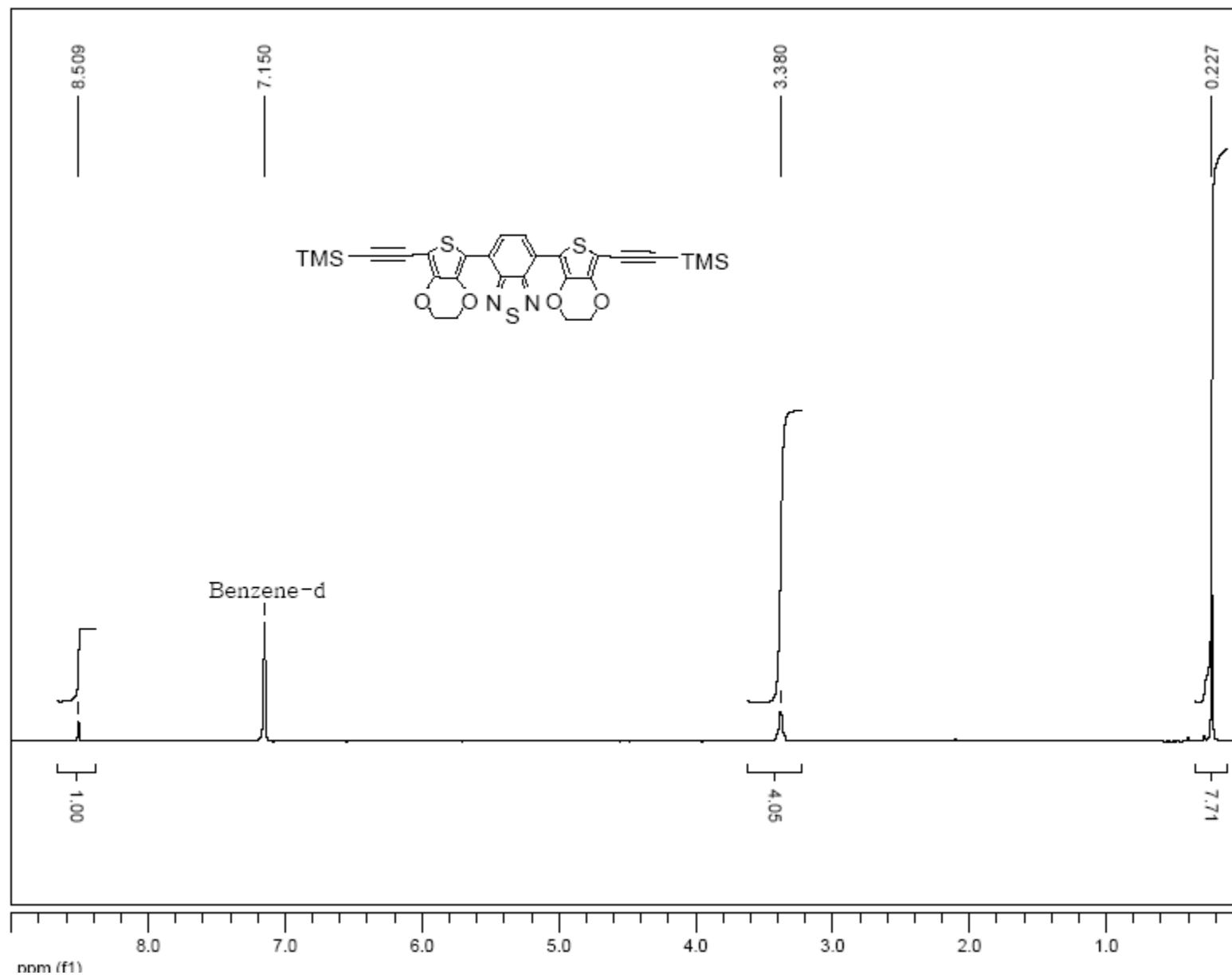


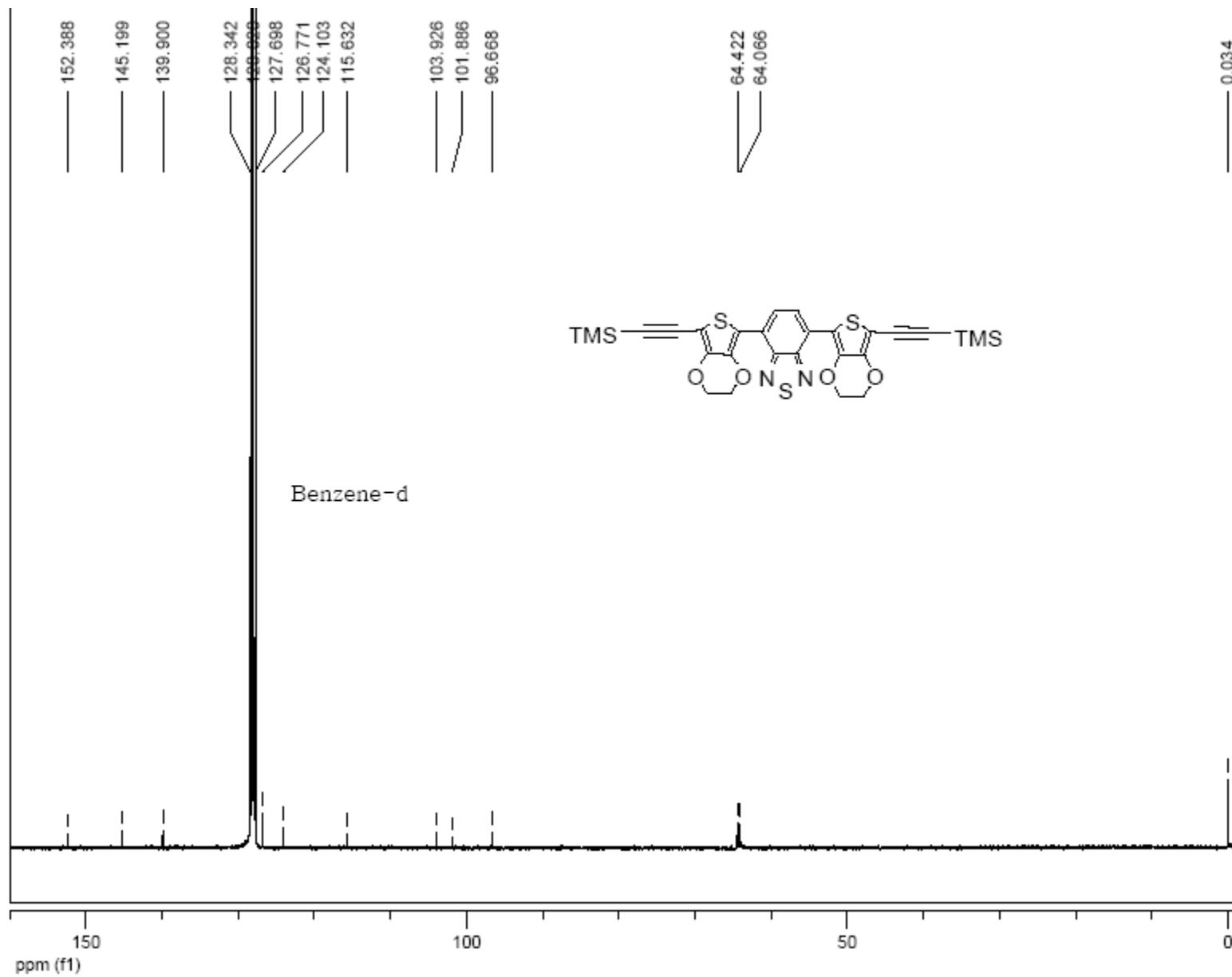
Benzene-d

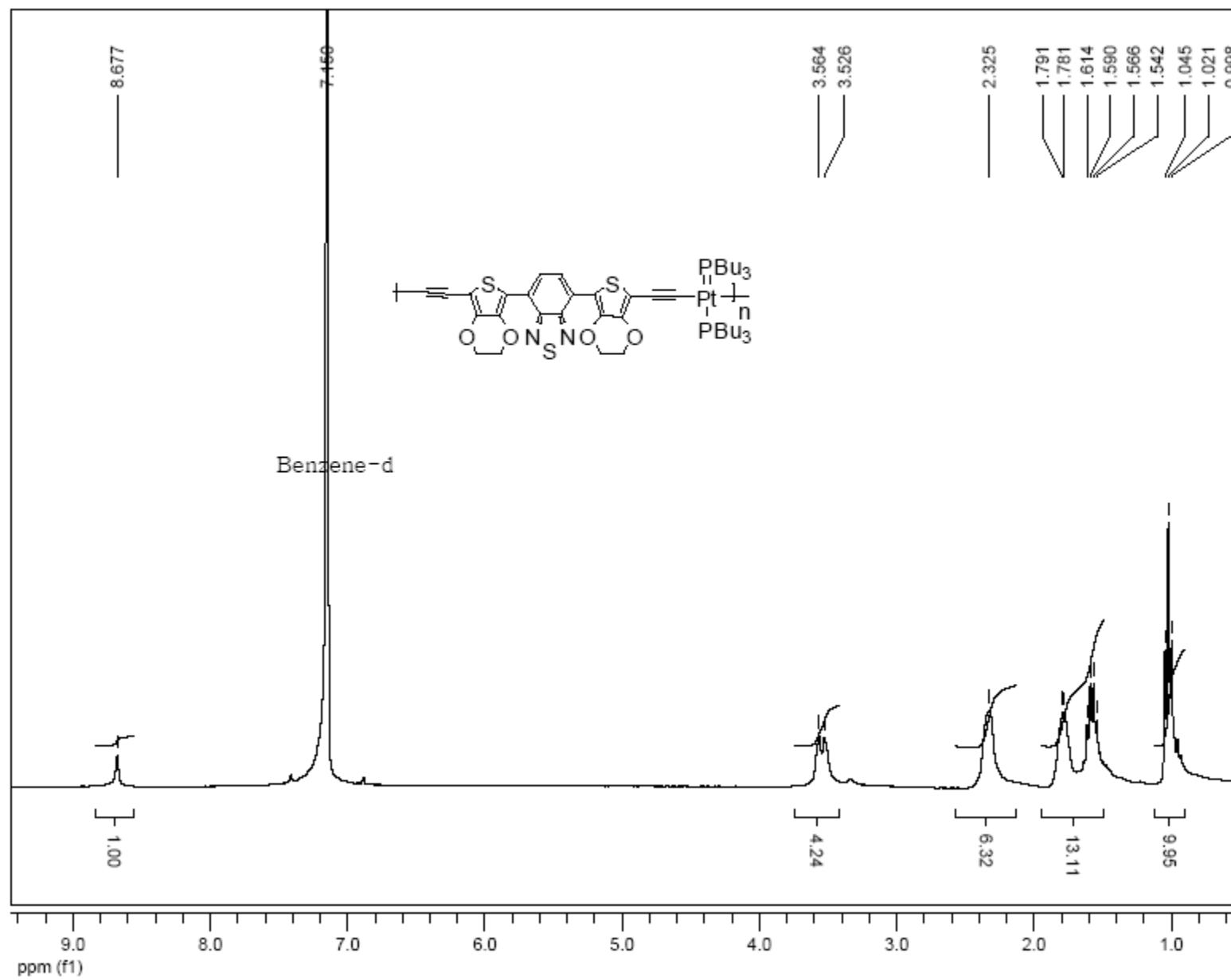
14.675
4.932
-4.801

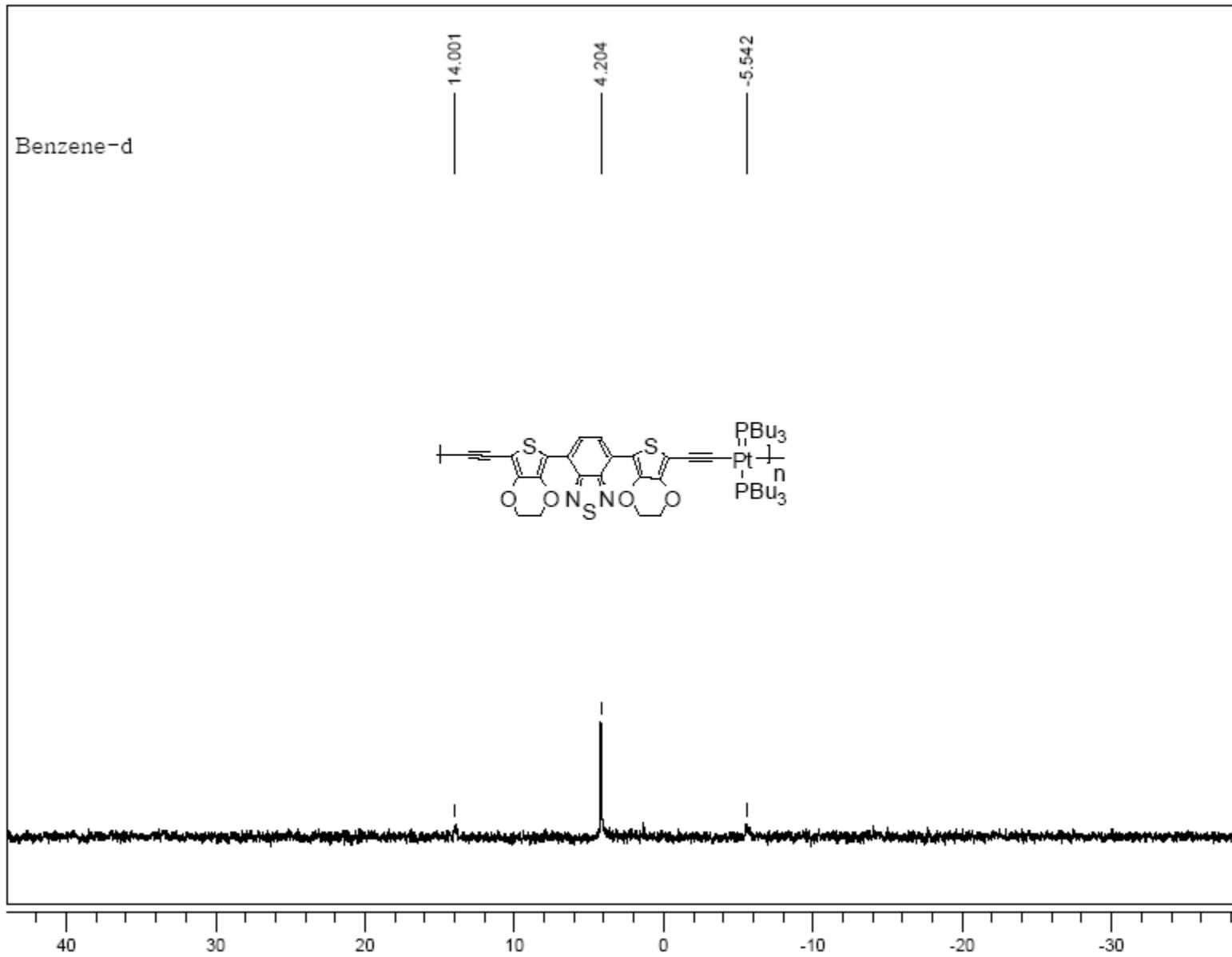


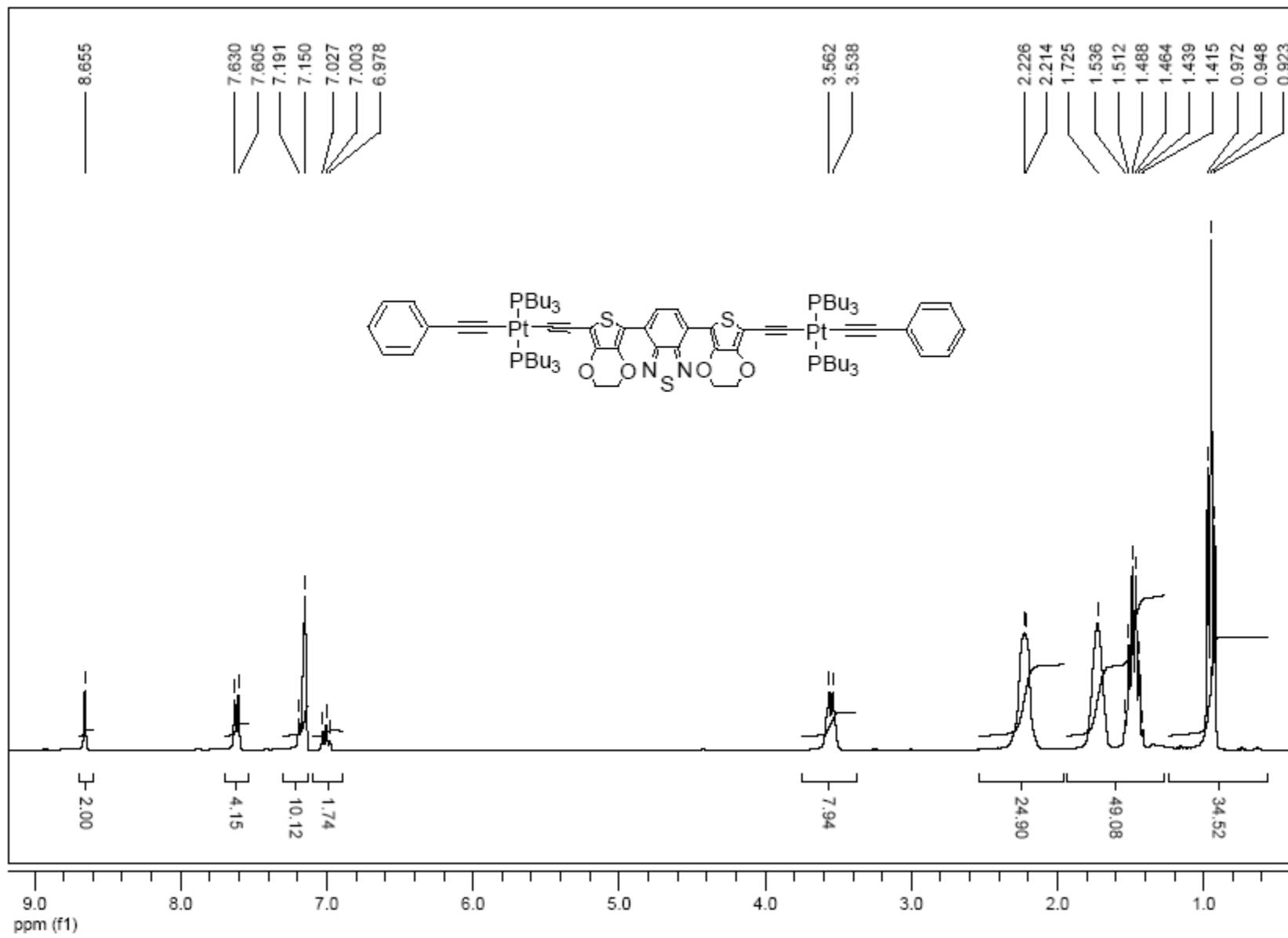


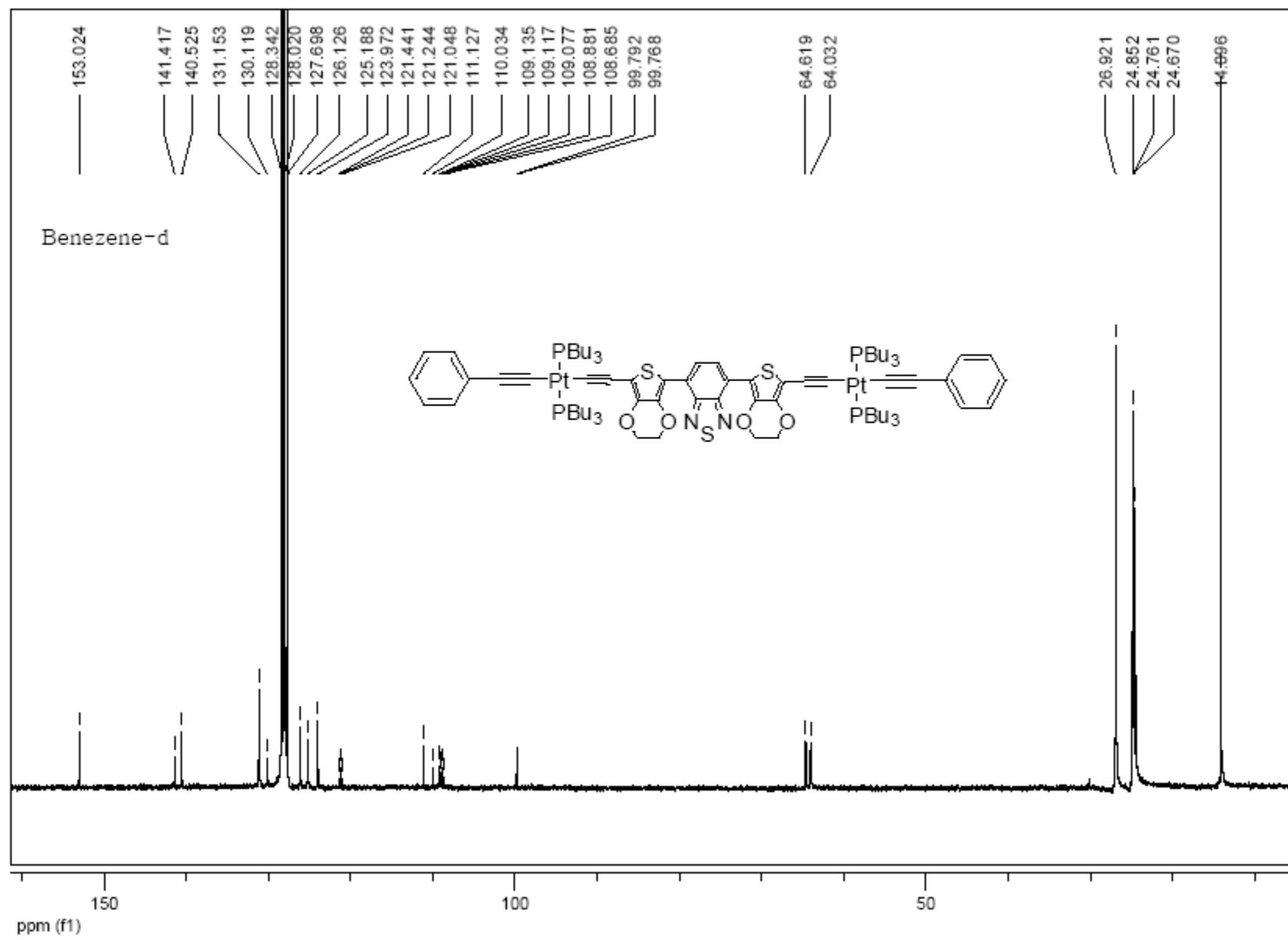












Benzene-d

14.228

4.479

-5.275

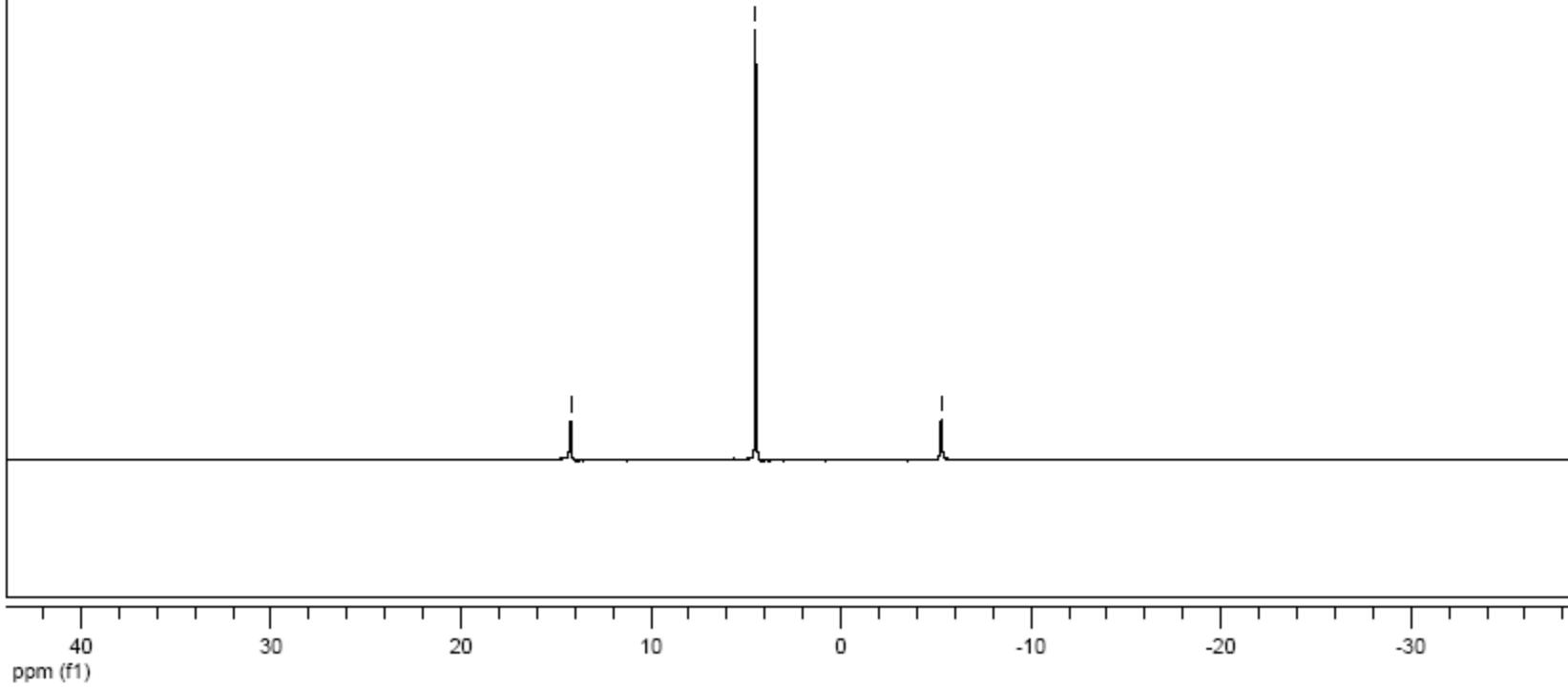
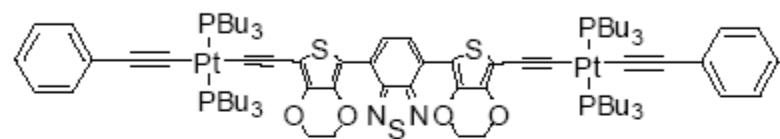


Figure S1. UV-visible absorption spectra of p-PtBTD-EDOT in xylene at $T = 10 - 95 \text{ }^{\circ}\text{C}$.

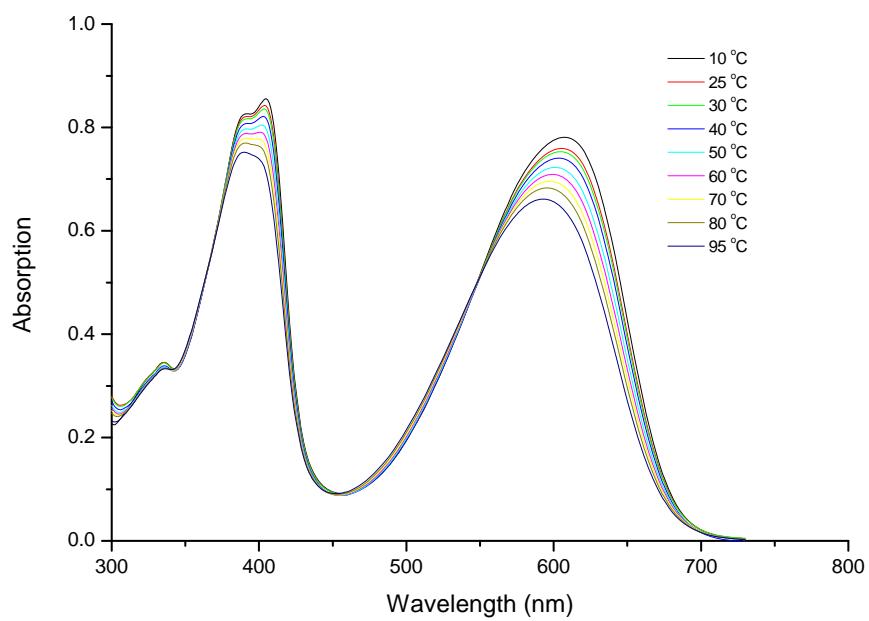


Figure S2. Mass spectrum (MALDI) of p-PtBTD-EDOT

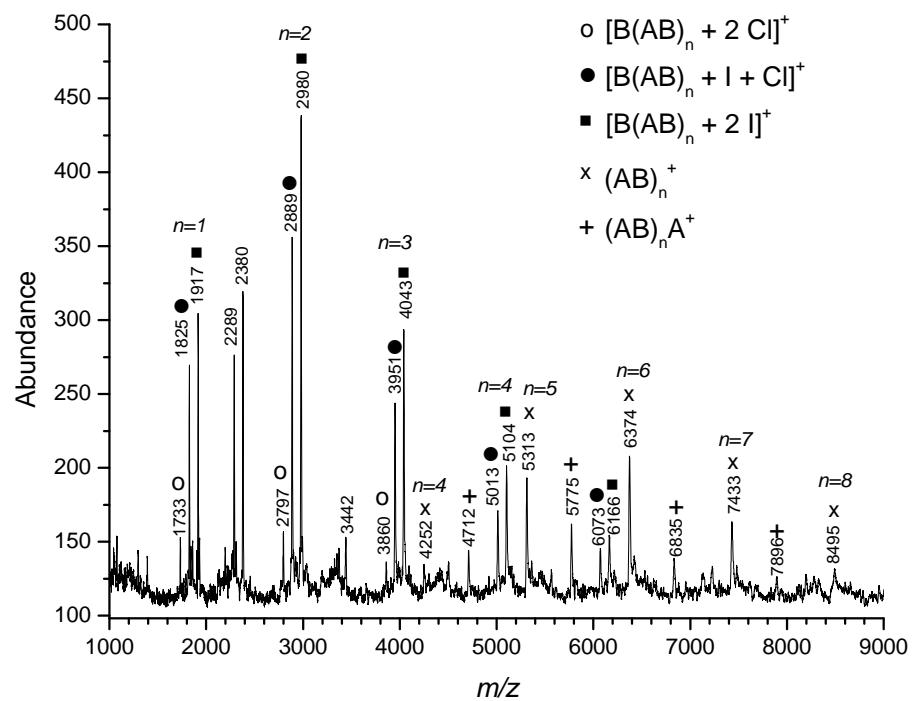


Figure S3. Cyclic voltammograms of a) Pt₂BTD-EDOT and b) p-PtBTD-EDOT. Sweep rate 100 mV/s, in dichloromethane with 0.10 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potential reported vs. Fc/Fc⁺ redox couple (-4.8 eV vs. vacuum).

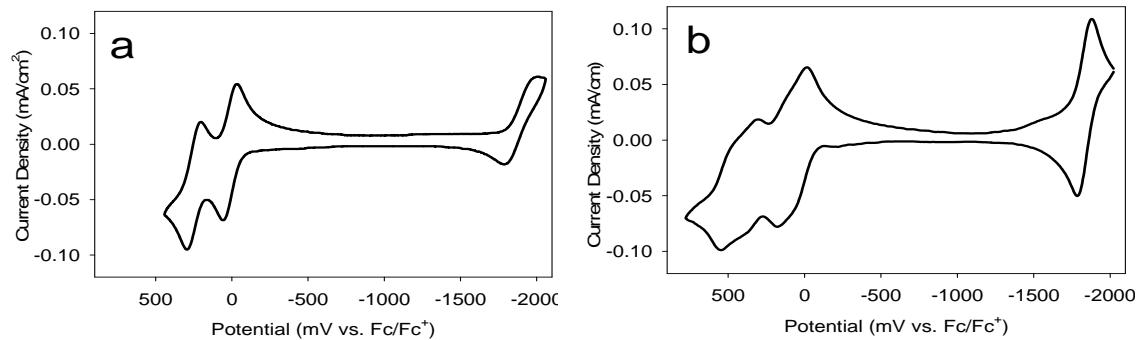
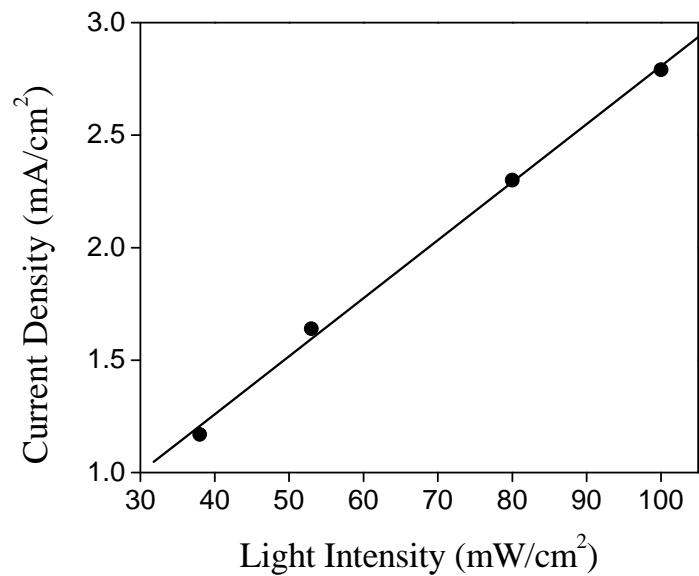


Figure S4. Light intensity dependence of PV performance of p-PtBTD-EDOT.



Measurement of Optical Properties of p-PtBTD-Th.

Pure polymer films of films of *p*-PtBTD-Th were prepared on glass substrates by spin coating from solutions of the polymer in *o*-dichlorobenzene. Prior to spin coating, substrates were cleaned with the same procedure described in the main text. Aliquots of 300 μ L of solution were filtered using 0.20 μ m PTFE filters and spin coated at room temperature at 500 rpm for 60 s. To obtain films of different thicknesses the solution concentrations were varied from 5.0 mg/mL to 25 mg/mL. After depositing, the films were dried under vacuum for 4 hours to remove residual solvent. The thicknesses of the *p*-PtBTD-Th films on glass substrates were obtained by making step height measurements over a clean scratch using a Veeco Innova Scanning Probe Microscope (SPM) in tapping mode.

The transmittance and reflectance of the films in the ultraviolet to near-infrared regions were measured to calculate the absorption coefficient of p-PtBTD-Th. The studies were made on a home-built spectrometer using a Perkin Elmer 16U grating monochromator. We measured the uncoated substrate and four films of different thicknesses (118, 193, 255 and 300 nm) at ambient conditions using an aluminum mirror as reference for the reflectance. Both the reflectance and thin film interference were non-negligible and had to be included in the calculation of the absorption coefficient. A thin film analysis using a Drude-Lorentz model was used to calculate the optical constants (n and k) and to estimate the interference effects.⁵ The absorption coefficient calculated for the different thicknesses using the transmittance and reflectance along with the thin-film analysis yielded consistent data across the four films. The wavelength dependence of the estimated optical constants and the absorption coefficient are plotted below in Figure S5.

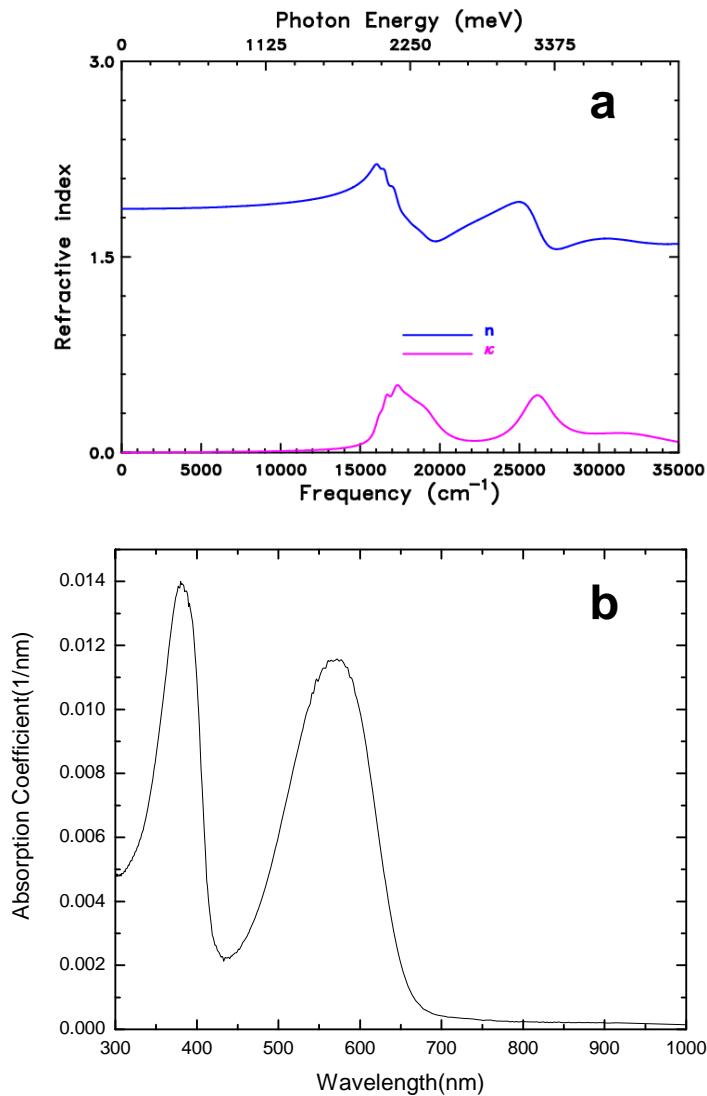


Figure S5. (a) Estimated real (n) and imaginary (κ) components of the refractive index for a p-PtBTD-Th film. (b) Absorption coefficient of p-PtBTD-Th.

Films of active layer material blends and PEDOT-PSS (Bayer Baytron P VP Al 4083) were prepared on tin oxide (ITO) covered glass substrates which had been cleaned using the same procedure as described in the main text. The PEDOT-PSS layer was deposited first from aqueous solution (as received) by spin coating at 4000 rpm onto ITO glass substrates and dried under vacuum for 10 min at 150°C. A solution containing a blend of both PCBM and *p*-PtBTD-Th (4:1 w/w) was prepared by dissolving both materials in *o*-dichlorobenzene. Films from this

solution were deposited on top of the PEDOT-PSS layer (30nm). Blend films of different thicknesses were obtained by varying the spin rate from 500 to 2000 rpm. The samples were subsequently dried under vacuum for 4 hours at ambient temperature.

Blend thicknesses were characterized by step height analysis using a Digital Instruments multimode atomic force microscope (AFM) in tapping mode. The thickness of each blend film was obtained by subtracting the thickness of the PEDOT-PSS (30 nm) layer. UV-visible absorption spectra of the blend films were obtained on a Perkin-Elmer Lambda 25 dual beam absorption spectrometer. An ITO slide with spin-coated PEDOT-PSS layer was used as the background for absorption measurements. Absorption was measured at three different locations in order to insure uniformity of the film. As expected the absorption coefficient of the blend was estimated (neglecting reflection and interference) to be roughly 20% of that of the pure polymer films.

Table S1 I-V characteristics of p-PtBTD-EDOT/PCBM photovoltaic devices^a

Solvents ^b	Entry	Thickness / nm ^c	Relative thickness ^d	V _{oc} / V	I _{sc} / mA·cm ⁻²	FF	η / %
ODCB	K122	29	0.43	0.24	2.31	0.29	0.17
	K127	34	0.50	0.38	3.95	0.34	0.52
	K202	55	0.81	0.41	3.57	0.30	0.44
	K203	59	0.87	0.39	3.33	0.31	0.44
	K126	68	1	0.42	3.84	0.30	0.49
Toluene	K232	34	0.43	0.20	2.42	0.27	0.13
	K231	46	0.58	0.29	2.35	0.26	0.18
	K186	57	0.72	0.50	4.56	0.35	0.78
	K234	79	1	0.47	4.51	0.30	0.63

a) Average values of 3 pixels. b) Used in spin-coating polymer/PCBM blends. c) Photoactive layer. d) Film thickness ratio relative to thickest film in each set. Processing conditions: K122, 300 rpm / 1 min; K126/K127: (300 rpm / 1 min)/(600 rpm / 2 min); K202/K203: without/with 0.45 µm PTFE filter filtering. K186 500 rpm / 2 min; K231/K232: (600 rpm / 2 min)/(1000 rpm / 2 min).

Table S2 Light intensity dependence of PV performance of p-PtBTD-EDOT/PCBM photovoltaic devices^a

Solvents	Entry	Thickness / nm	P _{inc} ^b / mW·cm ⁻²	V _{oc} / V	I _{sc} / mA·cm ⁻²	FF	η / %
ODCB	K202-2i	55 nm	38	0.40	1.17	0.33	0.42
			53	0.41	1.64	0.32	0.42
			80	0.41	2.30	0.32	0.38
			92	0.41	2.58	0.31	0.36
			100	0.41	2.79	0.31	0.35

a) The composition ratio of p-PtBTD-EDOT/PCBM blend is 1/4 wt/wt; b) the power of incident light

References for Supporting Information

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