Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Impact of Constitution of the Terthiophene-Vinylene Conjugated Side Chain on the Optical and Photovoltaic Properties of Two-Dimensional Polythiophenes

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7. The photovoltaic devices of P3HT/$PC_{71}BM$

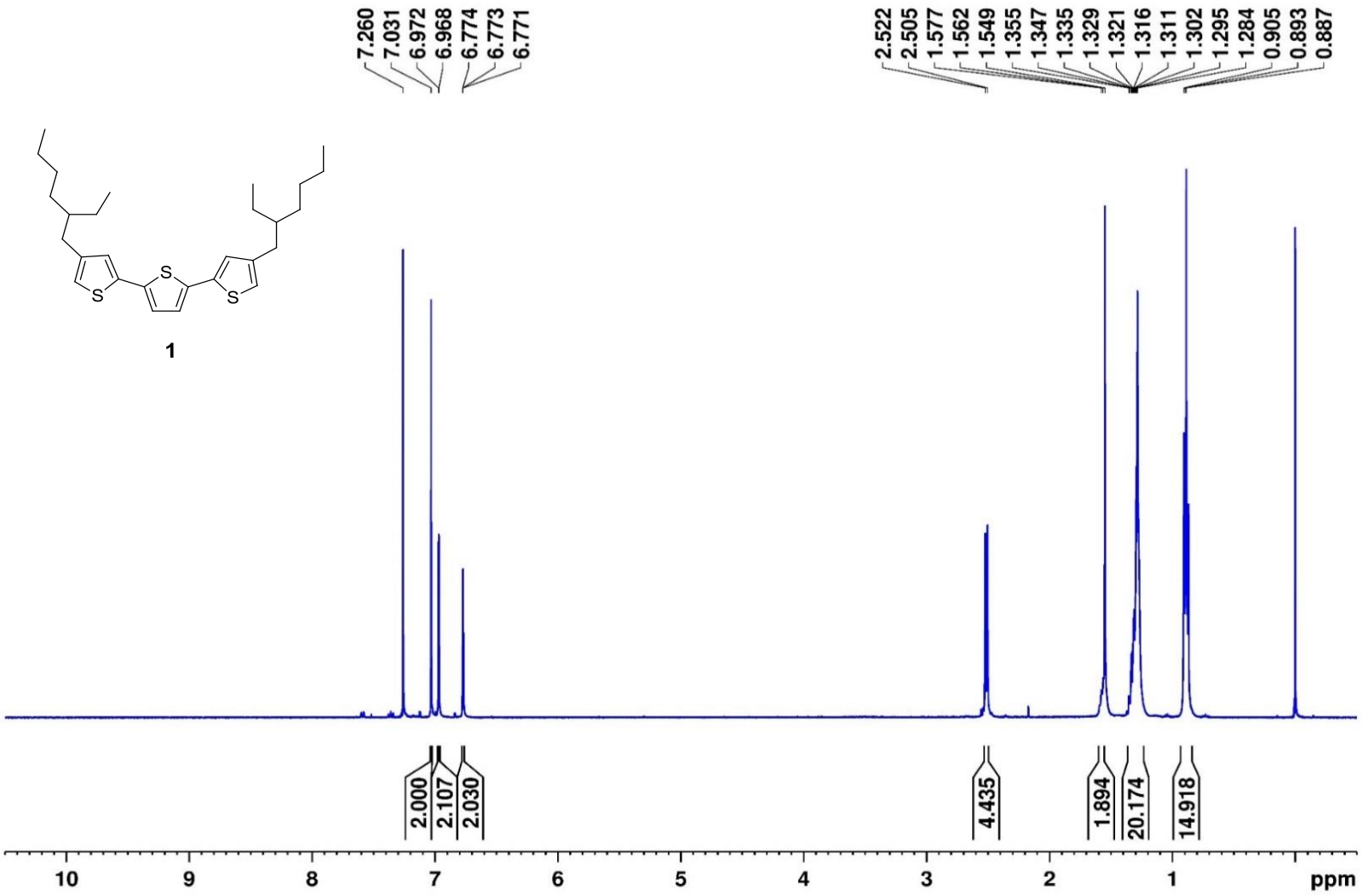


Figure S1. ^{1}H-NMR (400 MHz) spectrum of compound **1**

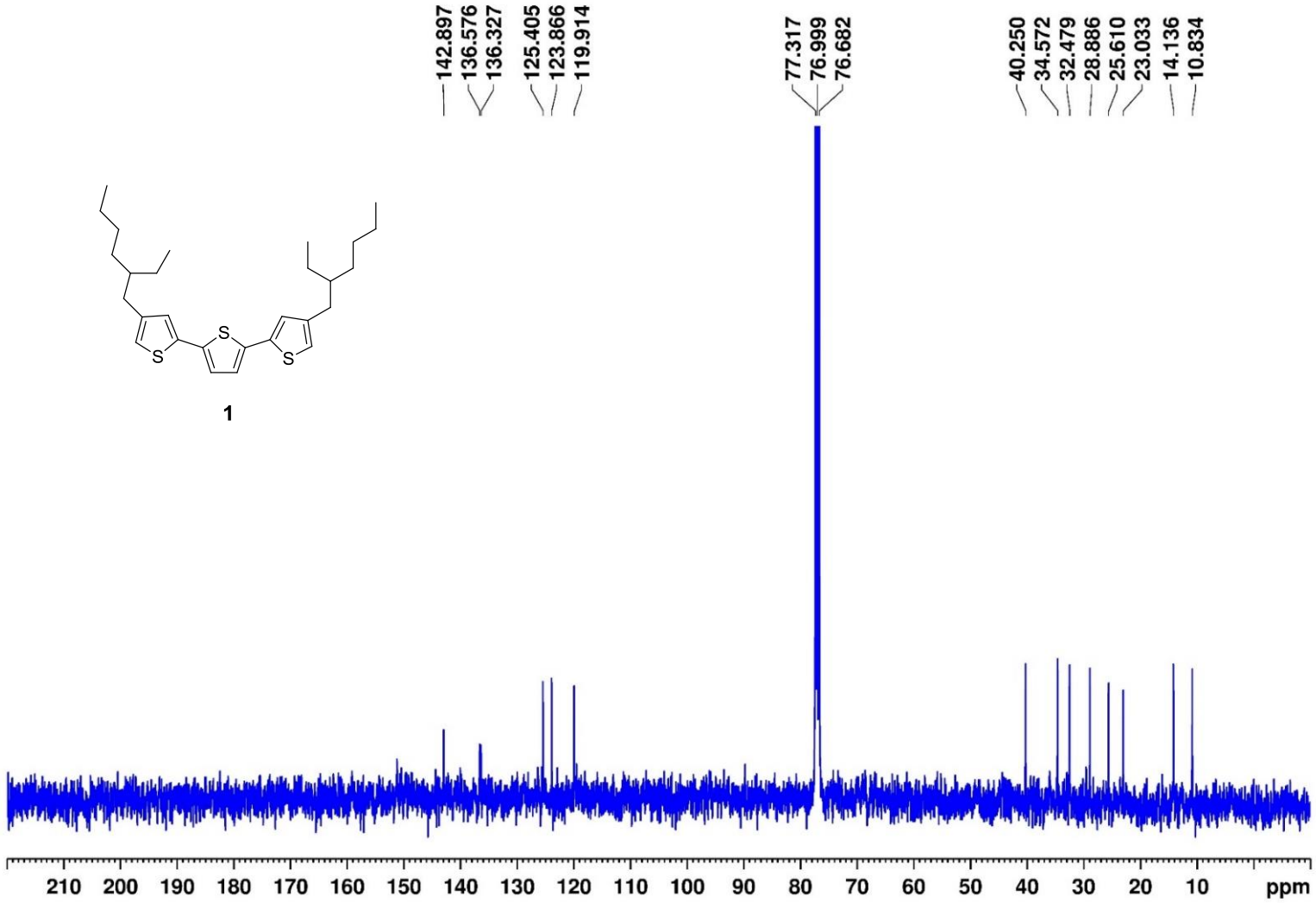


Figure S2. ^{13}C-NMR (100 MHz) spectrum of compound **1**

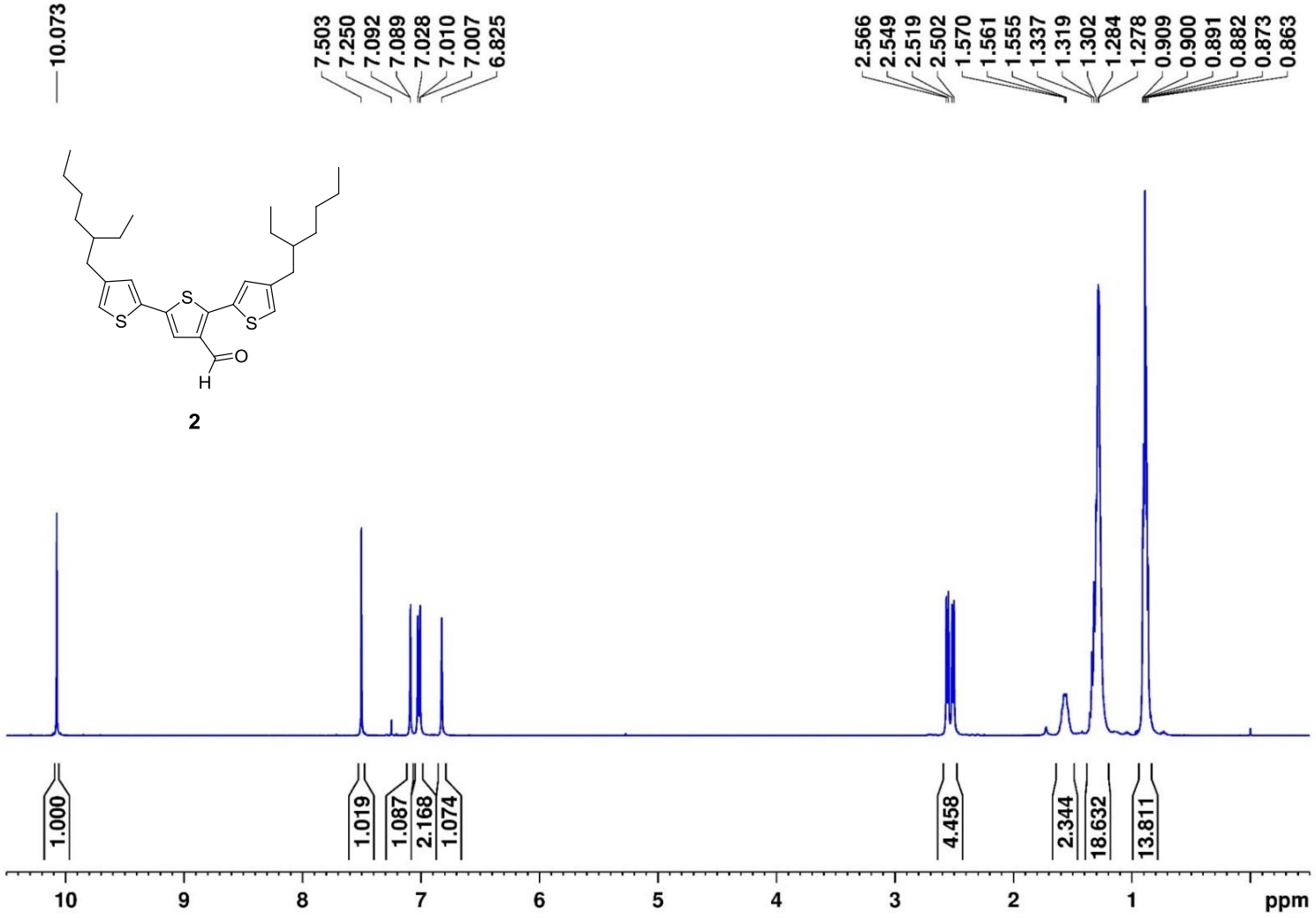


Figure S3. ^{1}H-NMR (400 MHz) spectrum of compound **2**

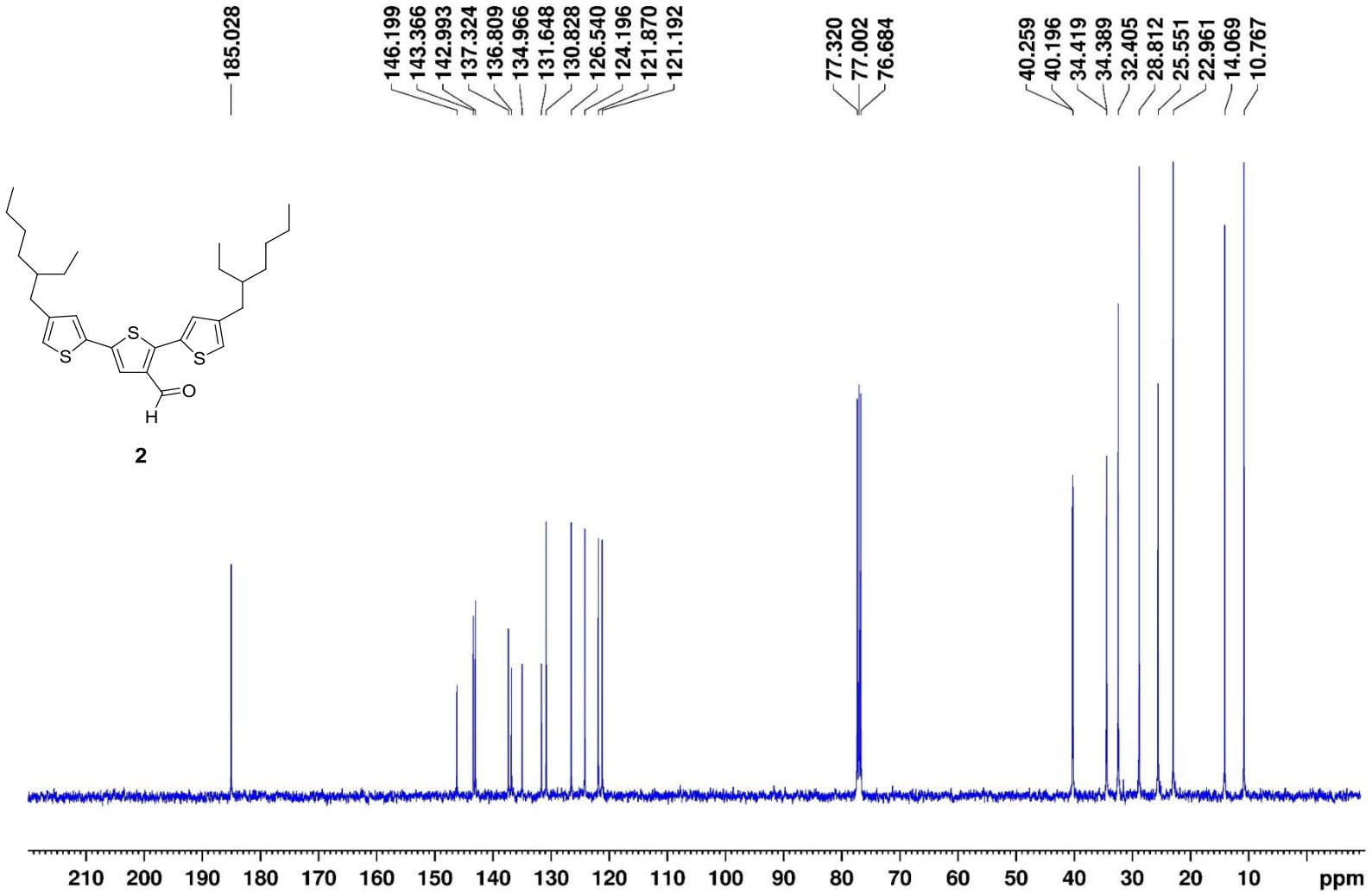


Figure S4. ^{13}C-NMR (100 MHz) spectrum of compound **2**

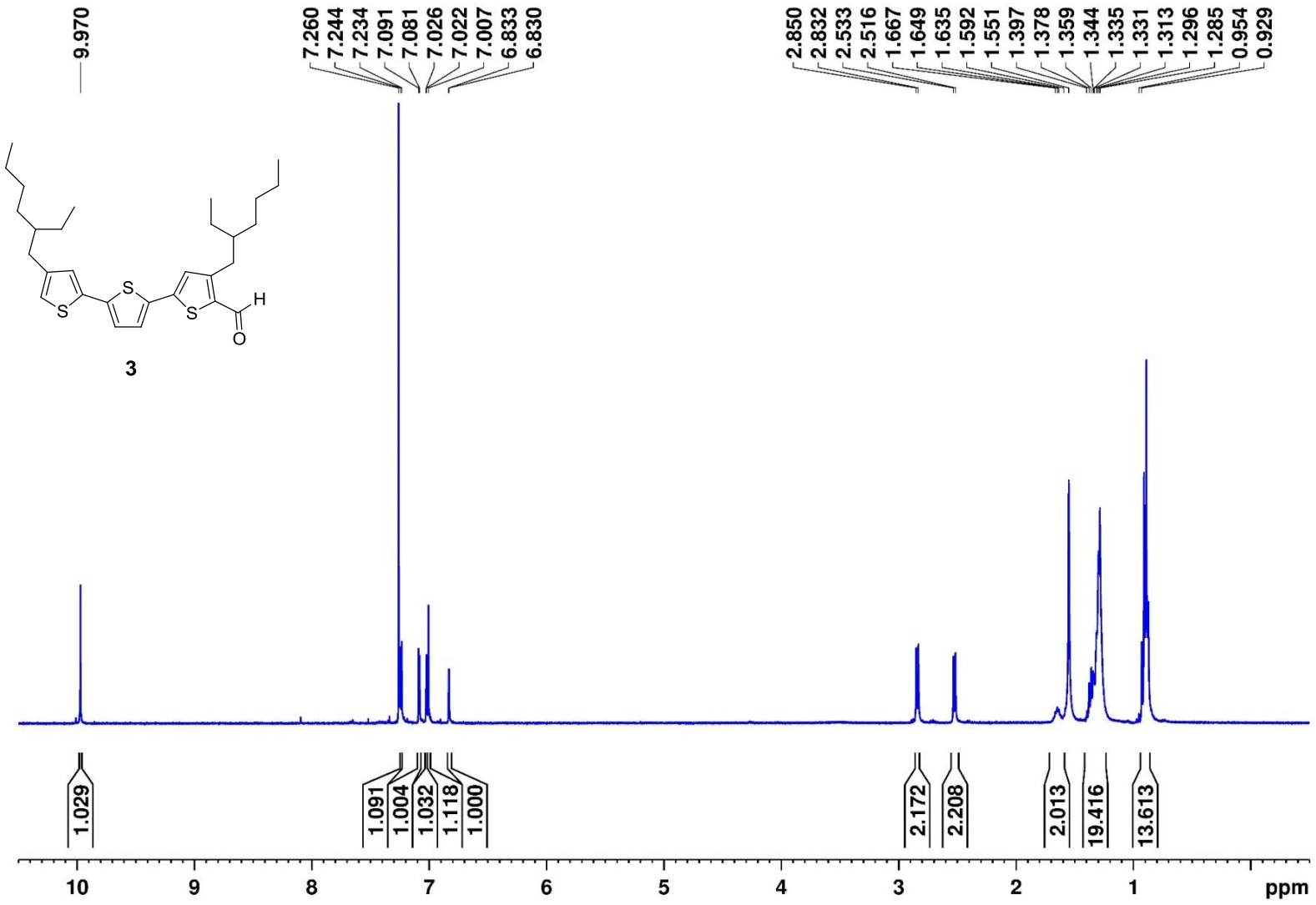


Figure S5. ^{1}H-NMR (400 MHz) spectrum of compound **3**

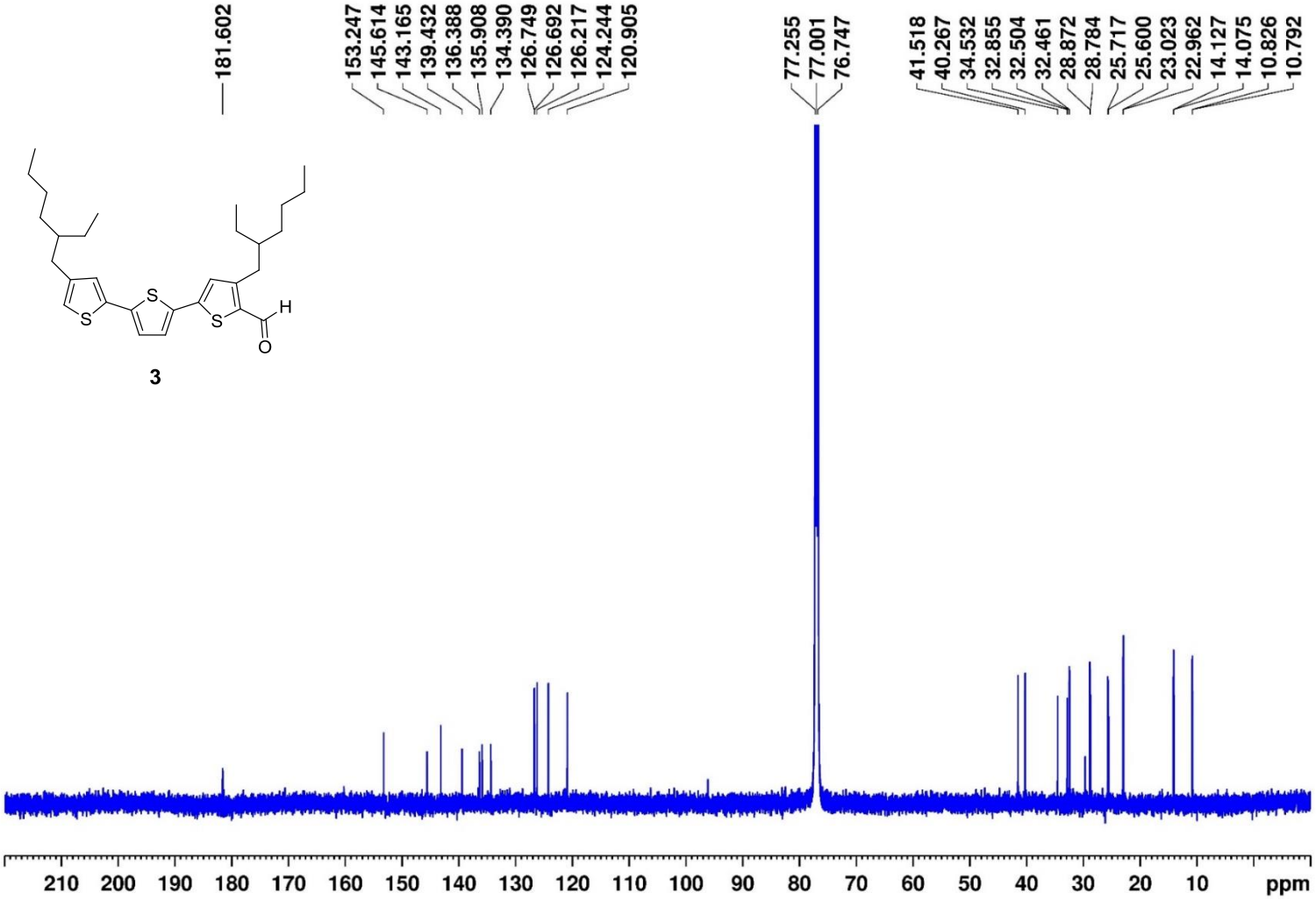


Figure S6. ^{13}C-NMR (100 MHz) spectrum of compound **3**

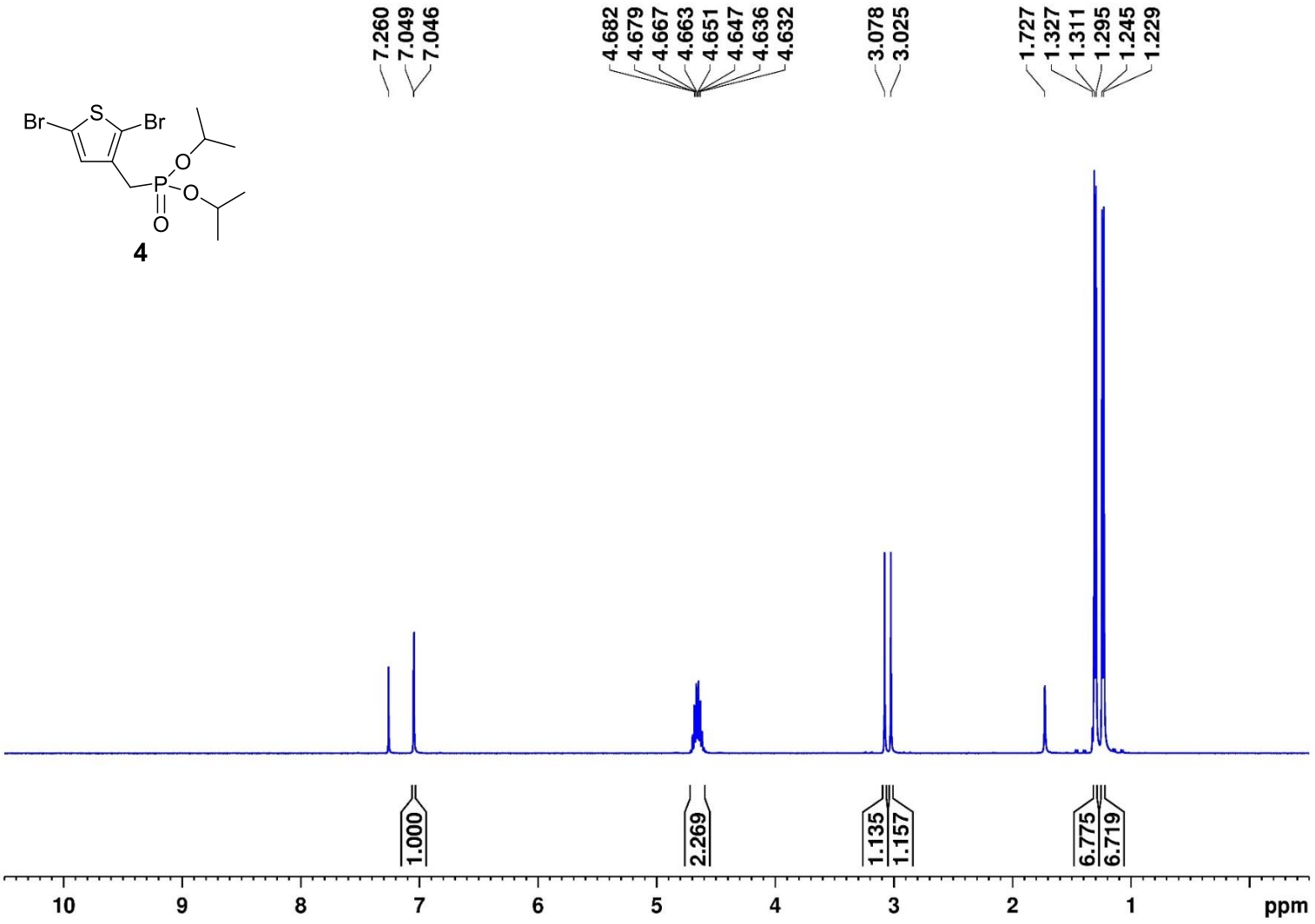


Figure S7. ^{1}H-NMR (400 MHz) spectrum of compound **4**

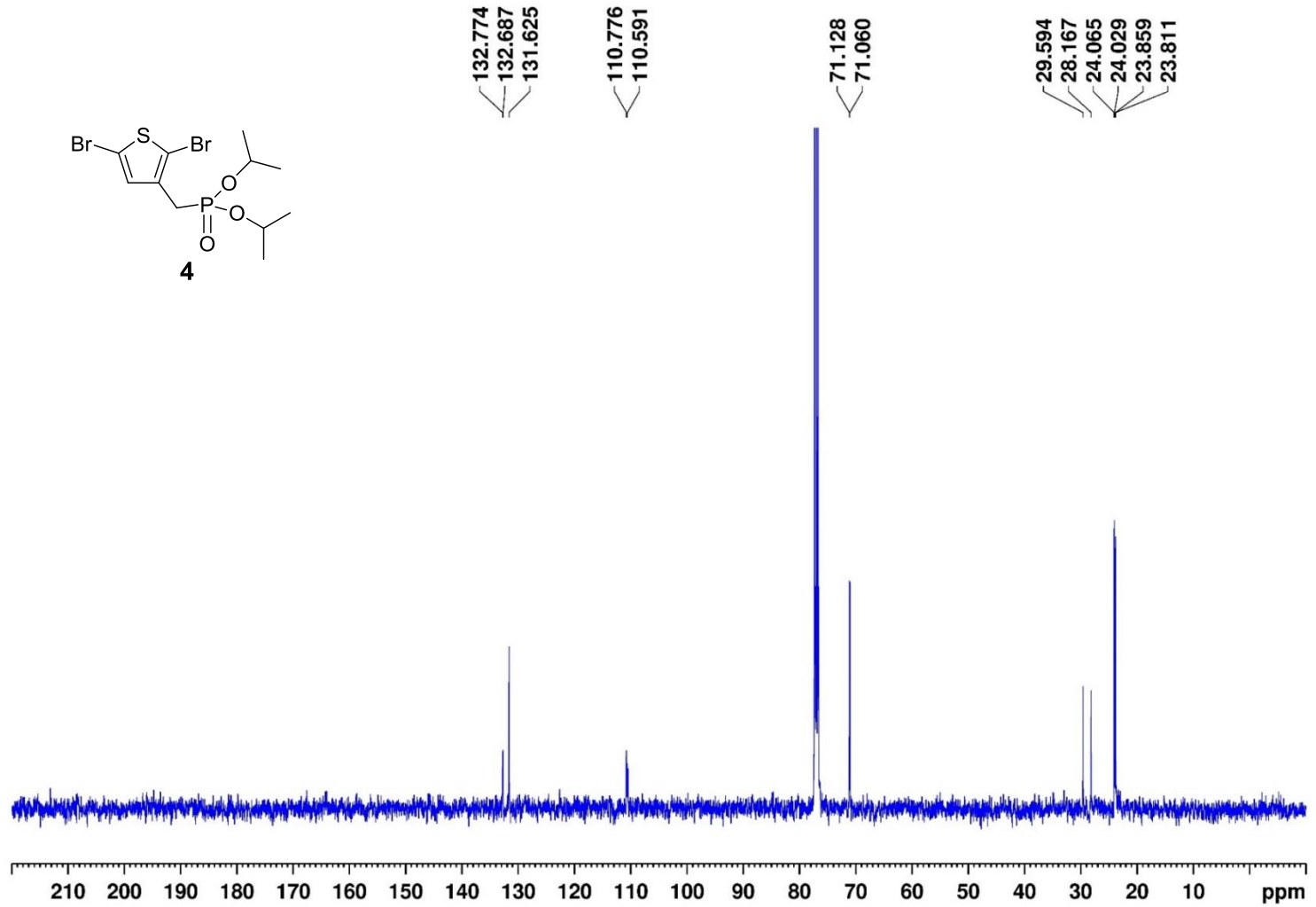


Figure S8. ^{13}C-NMR (100 MHz) spectrum of compound **4**

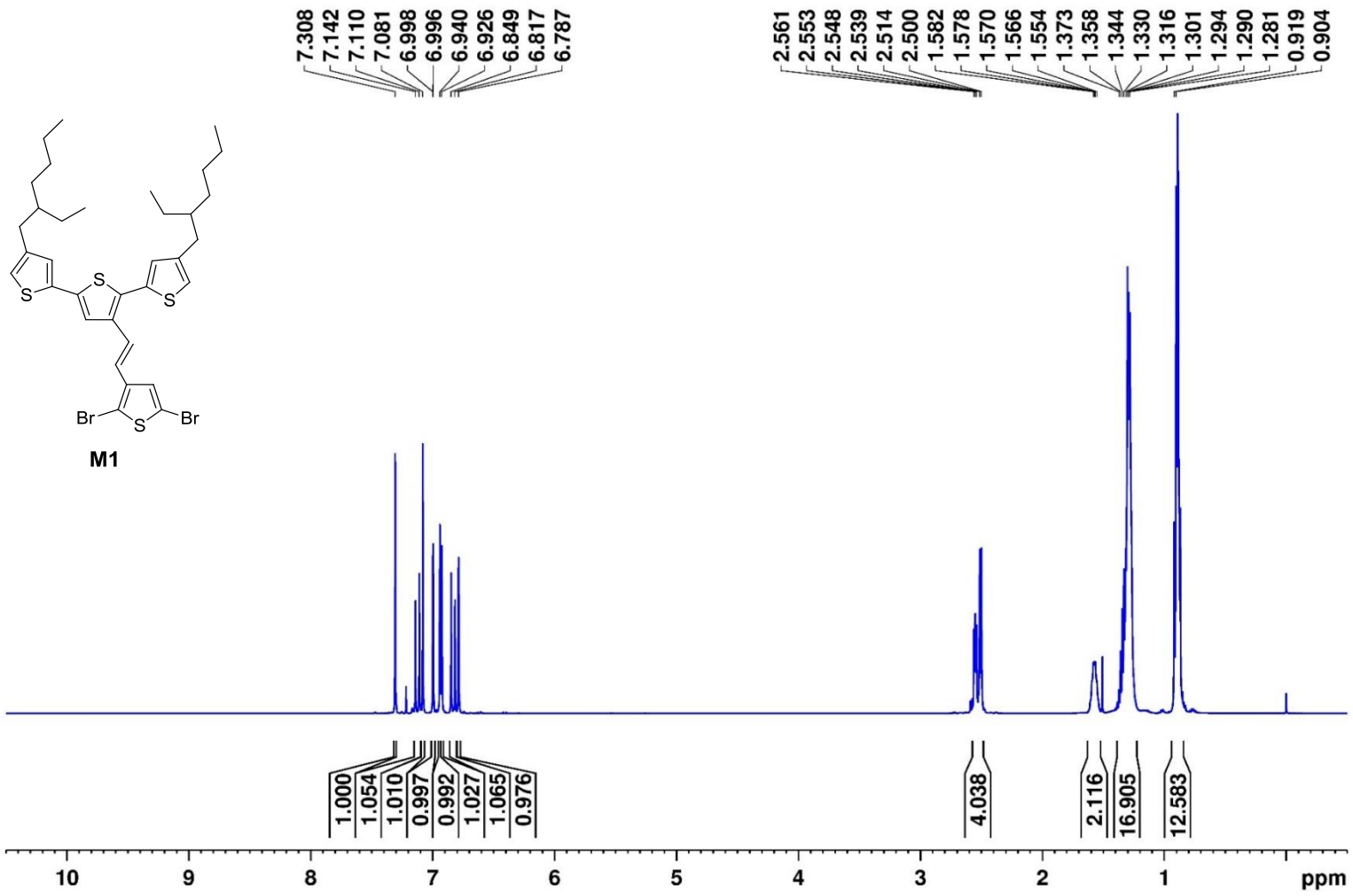


Figure S9. ^{1}H-NMR (400 MHz) spectrum of compound **M1**

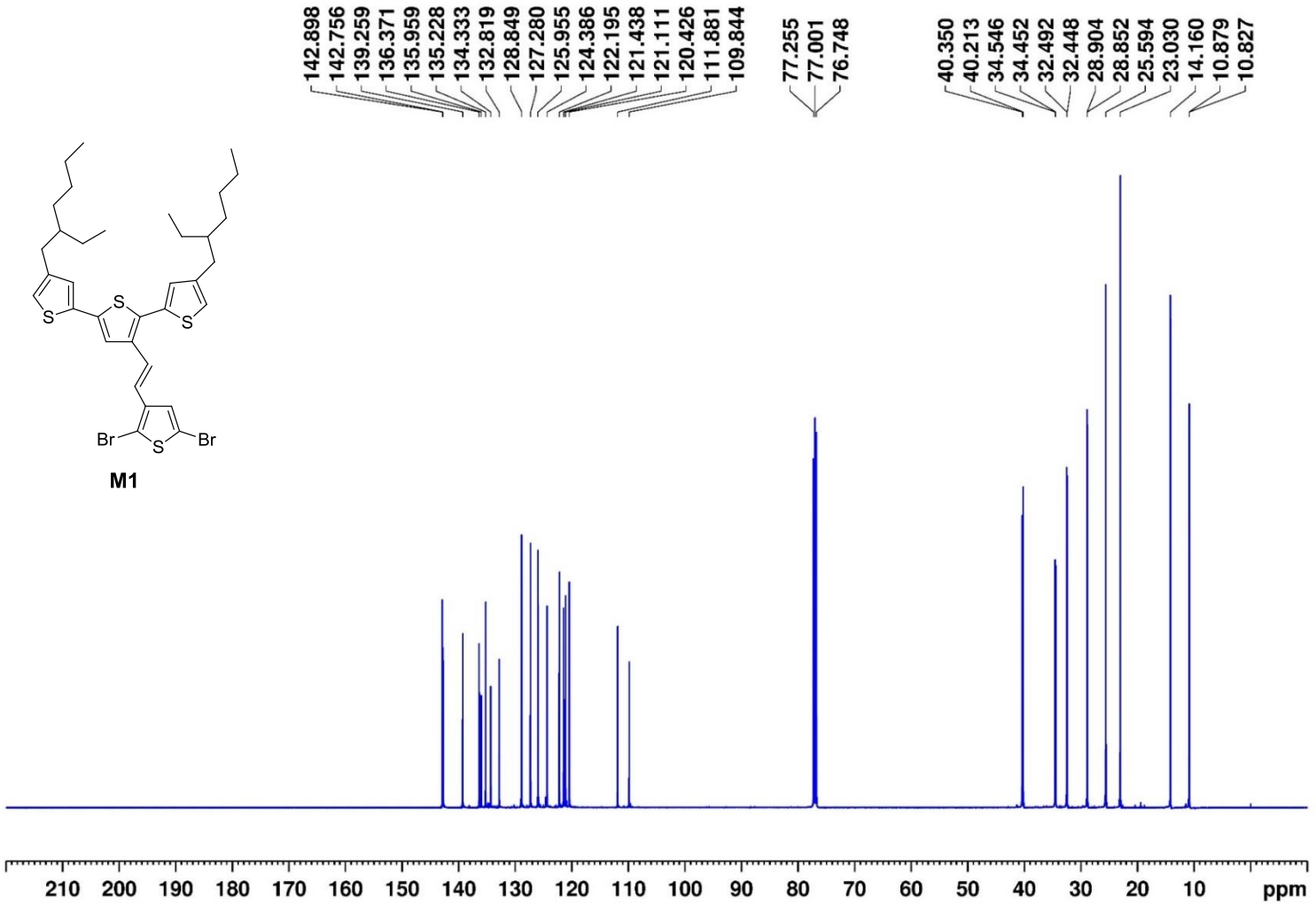


Figure S10. ^{13}C-NMR (100 MHz) spectrum of compound M**1**

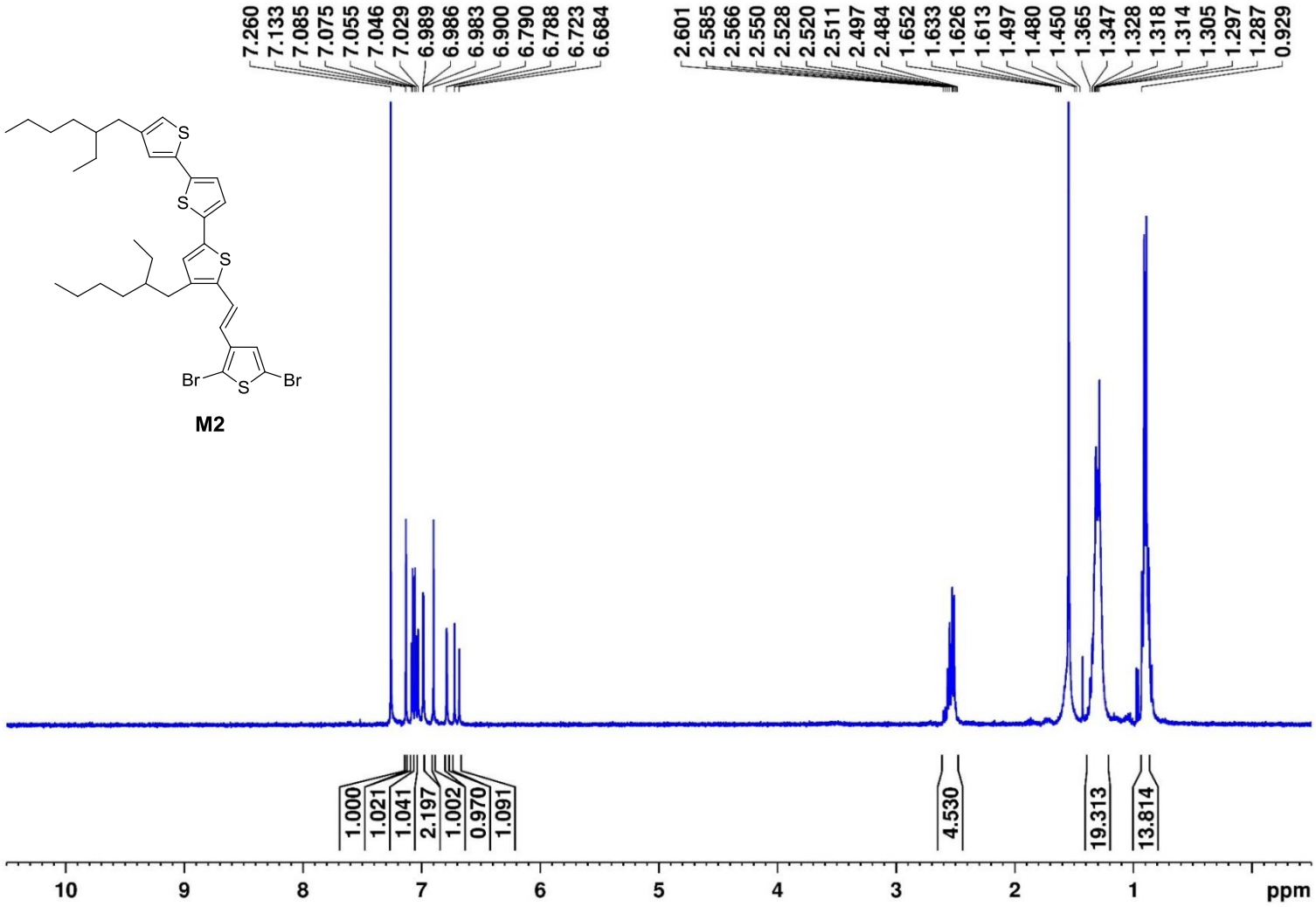


Figure S11. ^{1}H-NMR (400 MHz) spectrum of compound M**2**

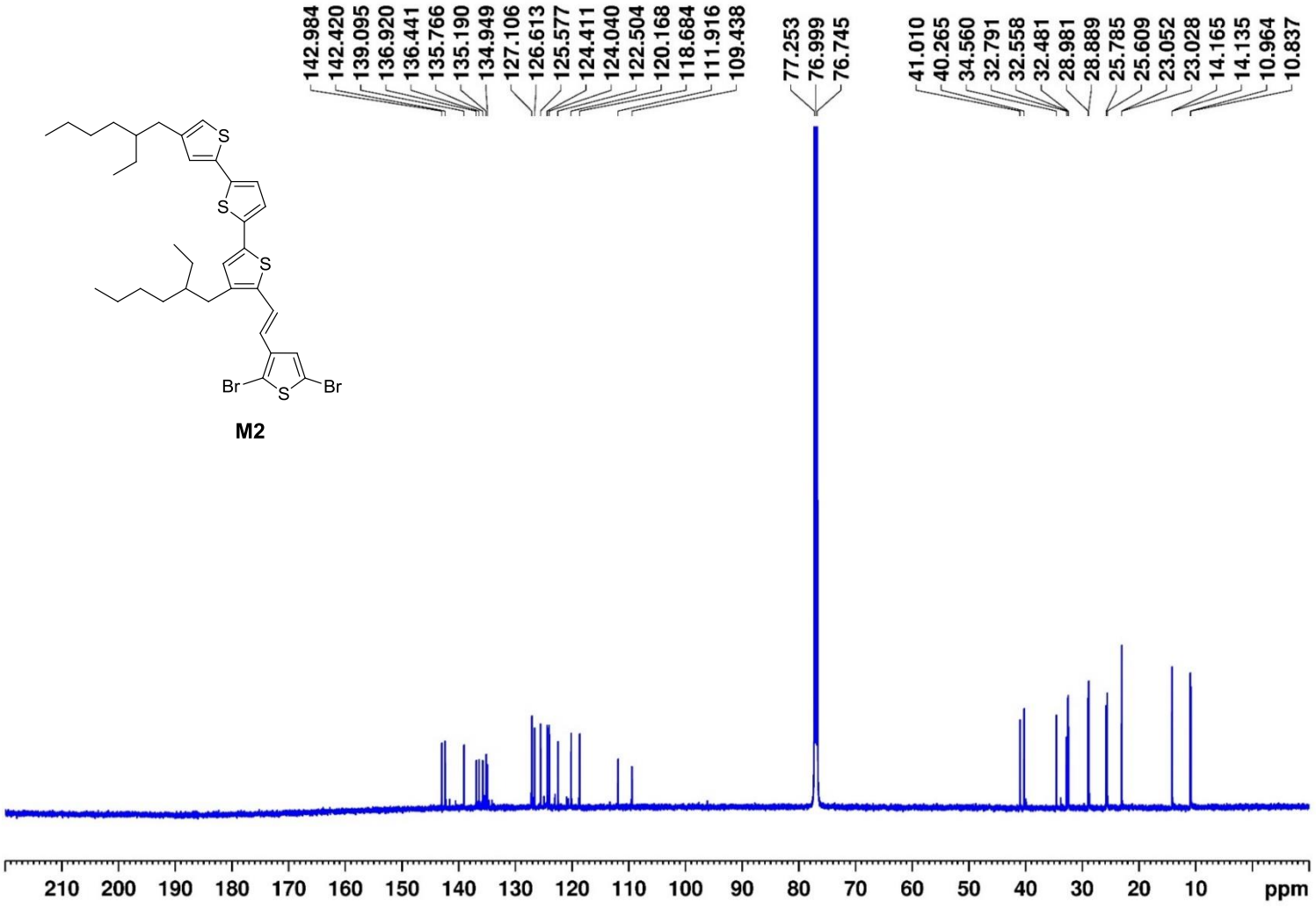


Figure S12. ^{13}C-NMR (125 MHz) spectrum of compound **M2**

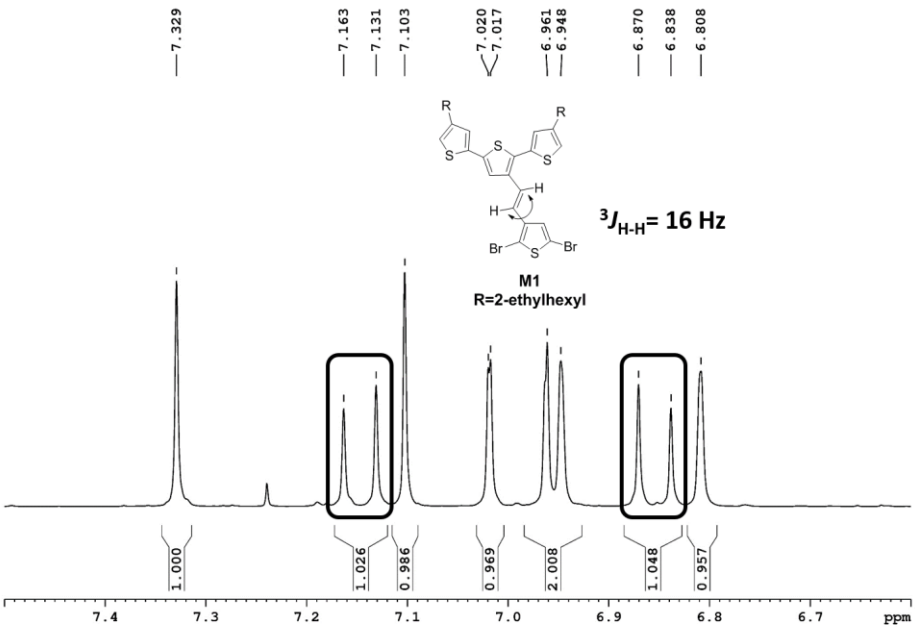


Figure S13. ^{1}H-NMR (500 MHz) spectrum of compound **M1** (7.5 – 6.6 ppm); A coupling constant of ca. 16.0 Hz was observed.

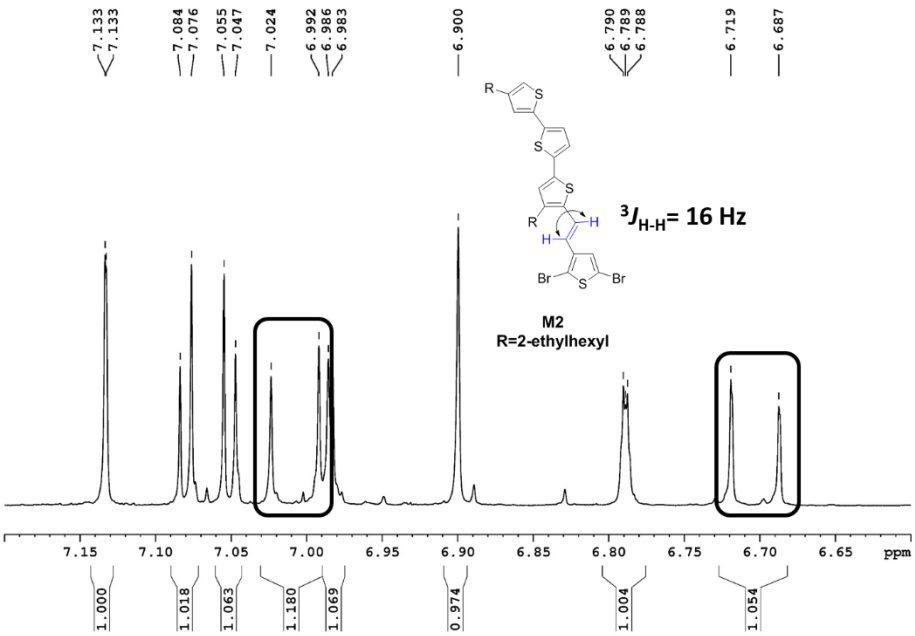


Figure S14. 1H-NMR (500 MHz) spectrum of compound M2 (7.2 – 6.6 ppm); A coupling constant of ca. 16.0 Hz was observed.

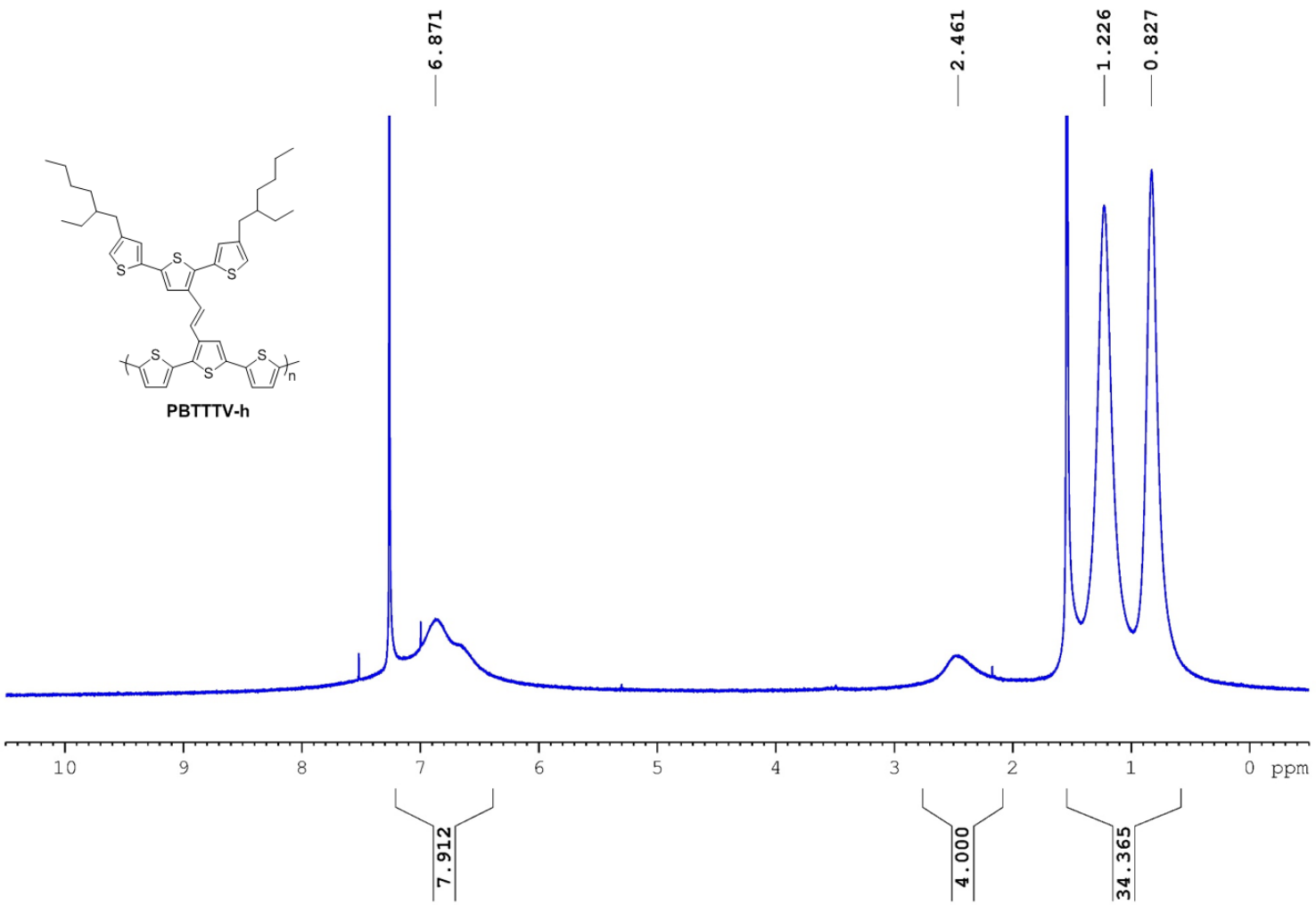


Figure S15. ^{1}H-NMR (400 MHz) spectrum of compound **PBTTTV-h**

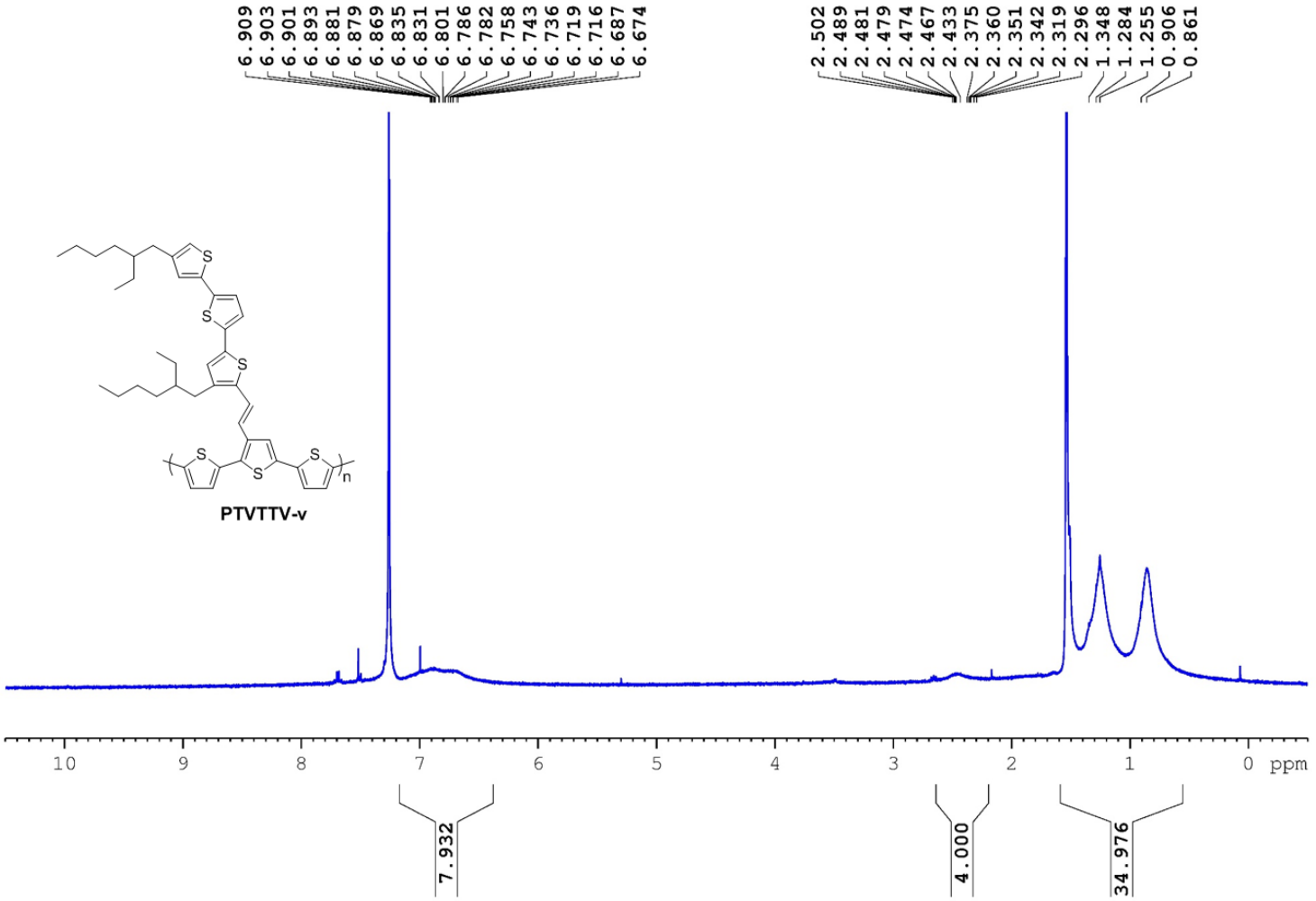


Figure S16. ^{1}H-NMR (400 MHz) spectrum of compound **PBTTTV-v**

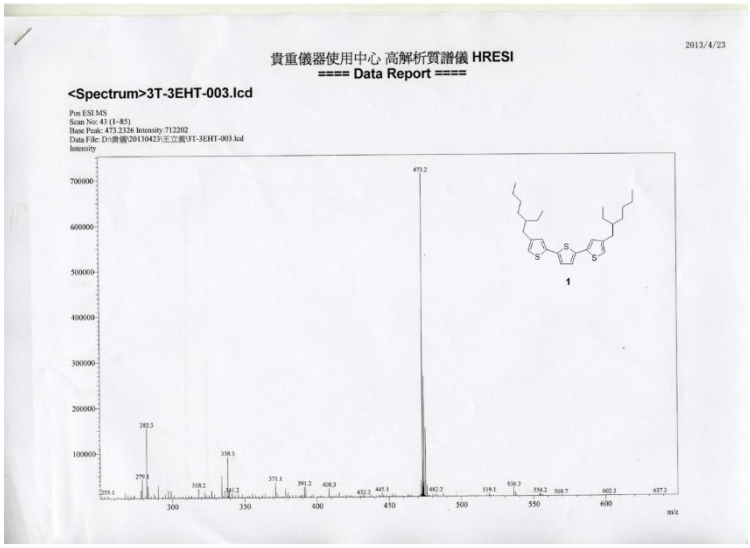


Figure S17. Mass spectrum of **1**

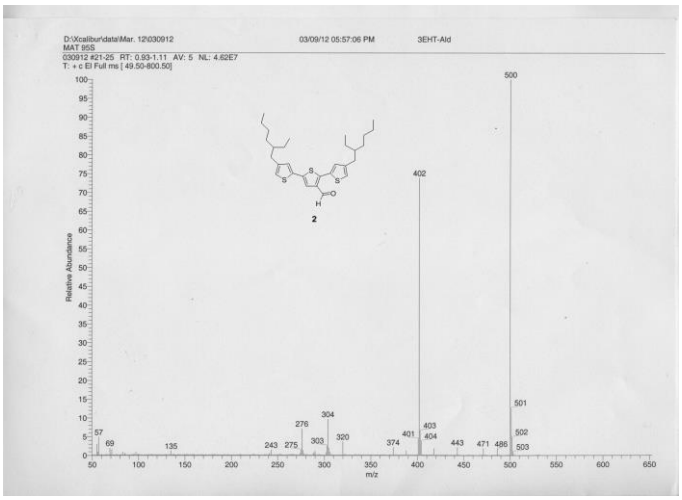


Figure S18. Mass spectrum of **2**

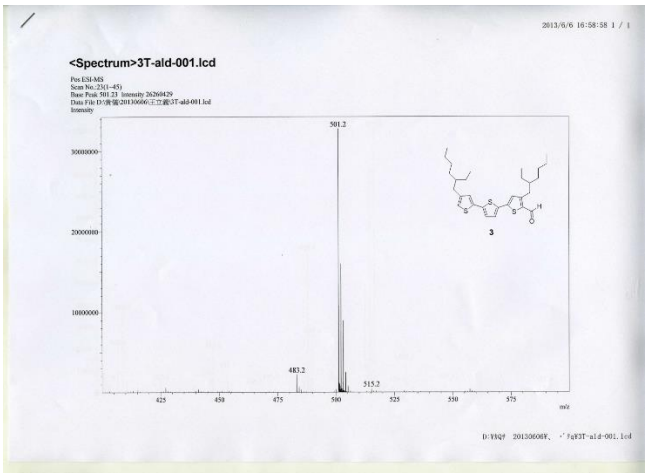
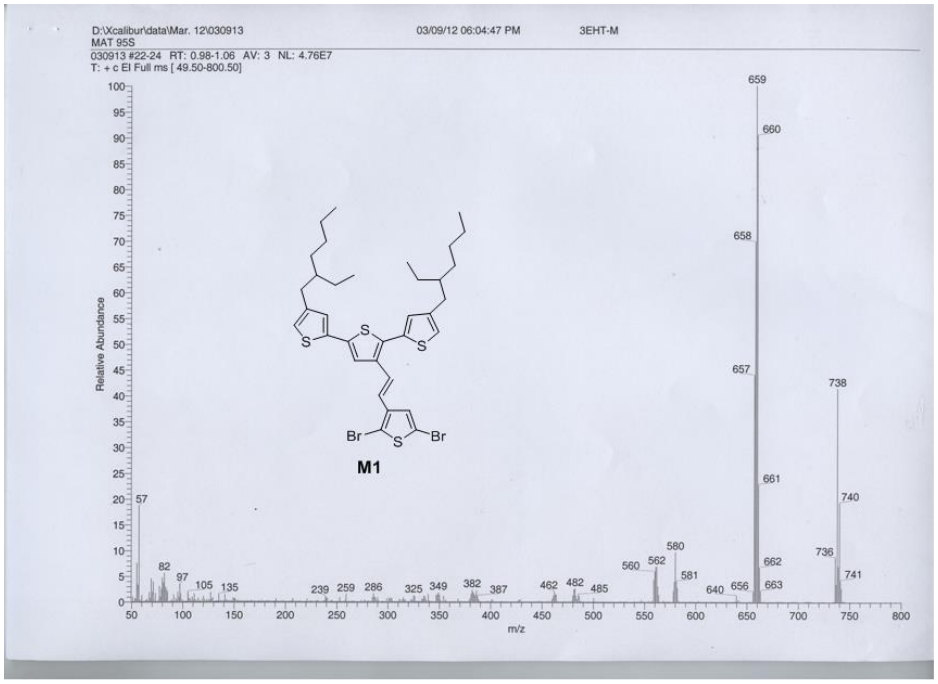
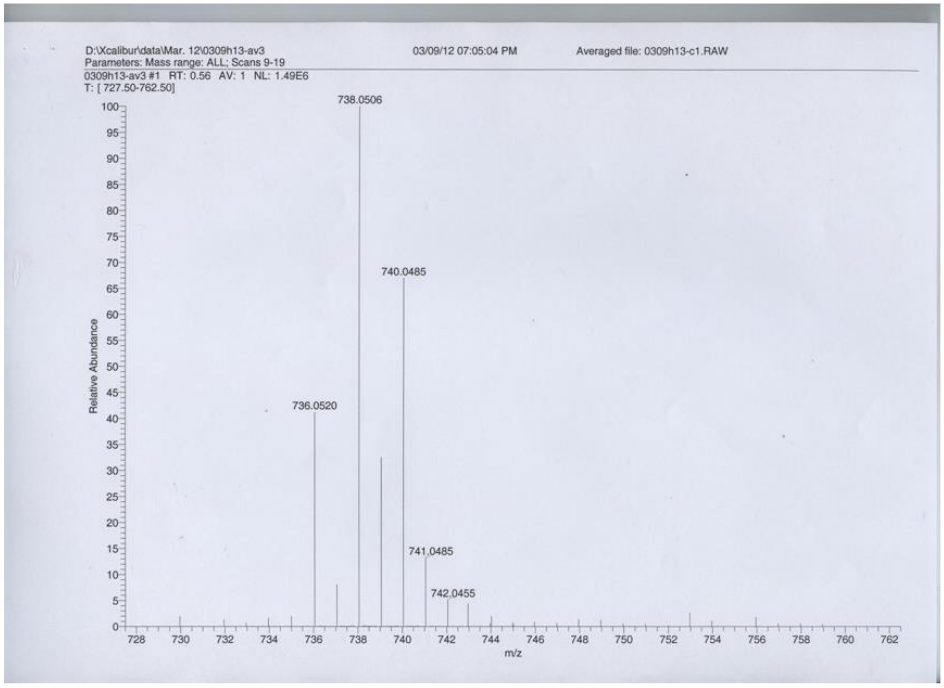


Figure S19. Mass spectrum of **3**



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Isotope:        Min. .. Max.
1 H             0....500
12 C            0....100
79 Br           0....2
81 Br           0....2
32 S            0....4
Tolerance Window:                +- 6.00 mmu
Db/Ring Equiv: -1.. 100          N-Rule:   Do not use
Fits:           3                Charge:   1

File : D:\Xcalibur\data\Mar. 12\0309h13-av3.RAW
Full ms [727.500 - 762.500 ] - Range: 727.500 - 762.500
Scan No. 1 of 1
```

Mass	Relative Intensity	Time	Theoretical Mass	Delta [ppm]	Delta [mmu]	RDB	Composition
736.0520	41.2	-132	736.0531	-1.4	-1.0	13.0	$C_{34}H_{42}Br_2S_4$
			736.0497	3.2	2.3	18.0	$C_{37}H_{38}Br_2S_3$
			736.0555	-4.8	-3.5	18.0	$C_{38}H_{39}Br_1{}^{81}Br_2$
738.0506	100.0	-126	738.0510	-0.6	-0.4	13.0	$C_{34}H_{42}Br_1{}^{81}Br_1S_4$
			738.0498	1.1	0.8	54.0	$C_{58}H_{10}S_1$
			738.0531	-3.4	-2.5	49.0	$C_{55}H_{14}S_2$
740.0485	67.0	-72	740.0490	-0.7	-0.5	13.0	$C_{34}H_{42}{}^{81}Br_2S_4$
			740.0477	1.1	0.8	1.0	$C_{28}H_{52}Br_2{}^{81}Br_2S_1$
			740.0456	3.9	2.9	18.0	$C_{37}H_{38}{}^{81}Br_2S_3$

Figure S20. Mass spectrum of **M1**

Mass Spectrum SmartFormula Report

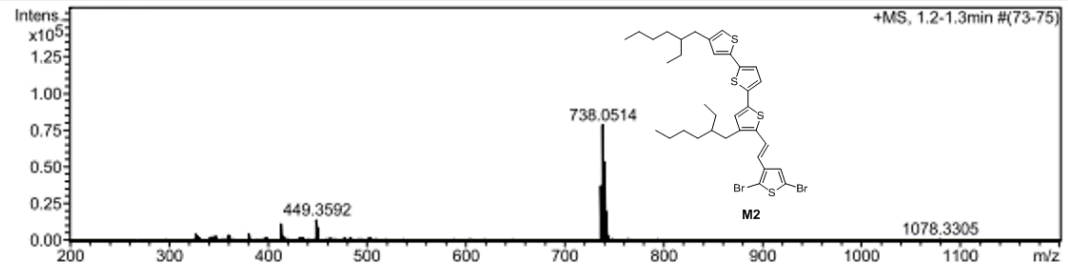
Analysis Info

Analysis Name	D:\Data\Fish\MS20130529_3T-MONO_pos_wide000001.d	Acquisition Date	5/29/2013 11:42:23 AM
Method	tune_wide_20130103.m	Operator	BDAL@DE
Sample Name	TuningMix 1:100	Instrument / Ser#	micrOTOF-Q 10183
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

+MS, 1.2-1.3min #(73-75)



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
736.0515	1	C 34 H 42 Br 2 S 4	100.00	736.0531	1.6	2.1	9.1	13.0	odd	ok

+MS, 1.2-1.3min #(73-75)

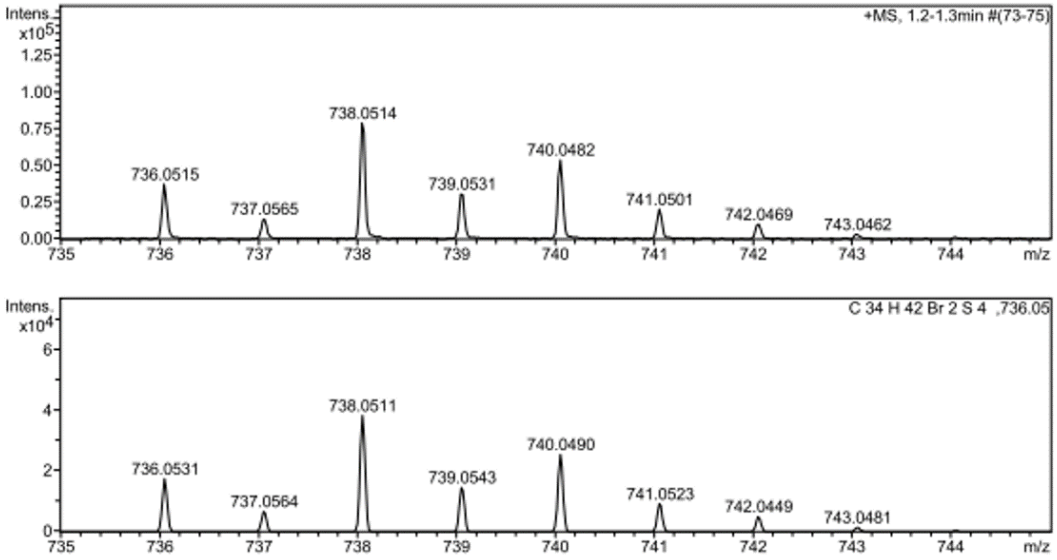


Figure S21. Mass spectrum of **M2**

Table S1. Photovoltaic parameters of PSCs based on **PBTTTV-h** as donor and $PC_{71}BM$ as acceptor (blend weight ratio = 10:8) with different annealing temperature under the illumination of AM1.5G, 100 mW/cm^2

Donor/Acceptor	Annealing temperature	V_{oc} (mV)	J_{sc} ($mAcm^{-2}$)	FF (%)	PCE (%)	Rsh ($k\Omega*cm^2$)	Rs ($\Omega*cm^2$)
PBTTTV-h/$PC_{71}BM$	80 ℃	863±5	7.85±0.03	47.26±0.4	3.20±0.02	0.44	23.25
	100 ℃	**800±0**	**9.11±0.02**	**64.75±0.5**	**4.72+0.04**	**0.94**	**7.89**
	120 ℃	783±5	8.05±0.06	66.14±0.6	4.17±0.07	0.86	8.53

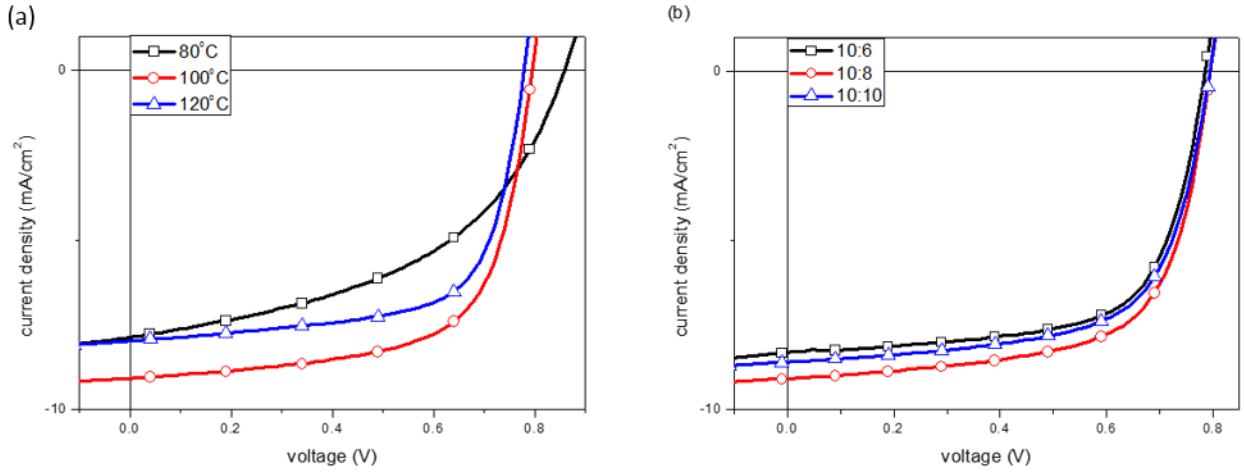


Figure S22. I-V curve of PSCs based on **PBTTTV-h** as donor and $PC_{71}BM$ as acceptor (blend weight ratio = 10:8) with different (a) annealing temperature; (b) weight ratio at annealing temperature 100 ℃ under the illumination of AM1.5G, 100 mW/cm^2

Table S2. Photovoltaic parameters of PSCs based on **PBTTTV-h** as donor and $PC_{71}BM$ as acceptor with different weight ratio at annealing temperature 100 ℃ under the illumination of AM1.5G, 100 mW/cm^2

Donor/Acceptor	Weight ratio	Processing solvent	V_{oc} (mV)	J_{sc} ($mAcm^{-2}$)	FF (%)	PCE (%)	Rsh ($k\Omega*cm^2$)	Rs ($\Omega*cm^2$)
PBTTTV-h/$PC_{71}BM$	10:6	CB	790±0	8.36±0.09	65.70±0.03	4.34±0.05	0.63	9.44
	10:8	**CB**	**800±0**	**9.11±0.02**	**64.75±0.50**	**4.72+0.04**	**1.08**	**7.89**
	10:10	CB	800±0	8.40±0.12	64.67±0.26	4.37±0.11	1.17	9.53

Table S3. Photovoltaic parameters of PSCs based on **PBTTTV-v** as donor and $PC_{71}BM$ as acceptor (blend weight ratio = 10:8) with different annealing temperature under the illumination of AM1.5G, 100 mW/cm^2

Donor/Acceptor	Annealing temperature	V_{oc} (mV)	J_{sc} ($mAcm^{-2}$)	FF (%)	PCE (%)	Rsh ($k\Omega*cm^2$)	Rs ($\Omega*cm^2$)
PBTTTV-v/$PC_{71}BM$	80 ℃	748±5	8.36±0.08	49.69±0.81	3.11±0.07	0.44	15.72
	100 ℃	**720±0**	**8.71±0.04**	**62.19±0.48**	**3.90±0.02**	**0.79**	**8.99**
	120 ℃	715±5	7.63±0.10	63.02±0.41	3.39±0.06	0.69	9.20

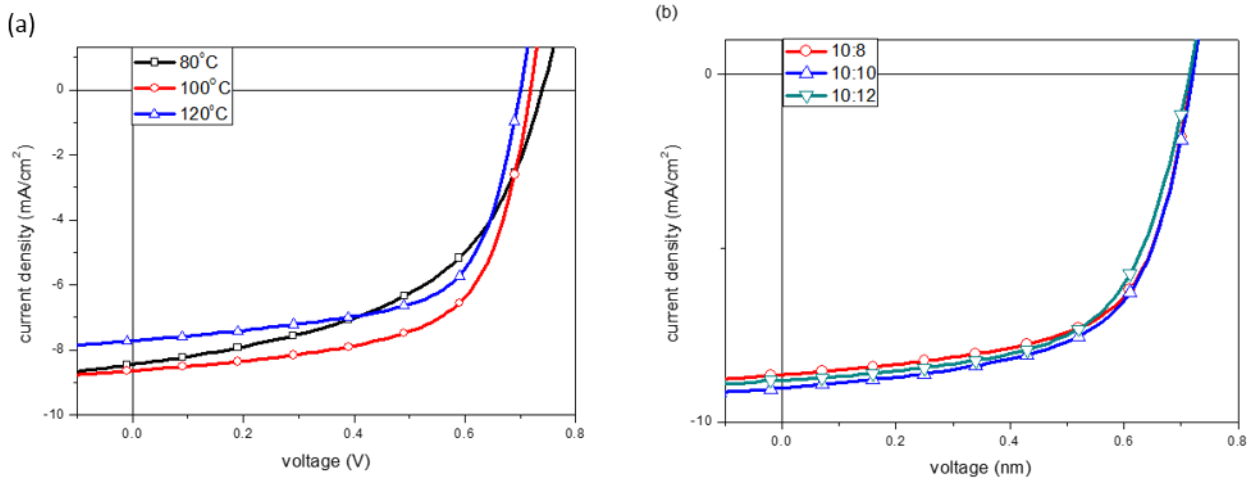


Figure S23. I-V curve of PSCs based on **PBTTTV-v** as donor and $PC_{71}BM$ as acceptor (blend weight ratio = 10:8) with different (a) annealing temperature; (b) weight ratio at annealing temperature 100 ℃ under the illumination of AM1.5G, 100 mW/cm^2

Table S4. Photovoltaic parameters of PSCs based on **PBTTTV-v** as donor and $PC_{71}BM$ as acceptor with different weight ratio at annealing temperature 100 ℃ under the illumination of AM1.5G, 100 mW/cm^2

Donor/Acceptor	Weight ratio	Processing solvent	V_{oc} (mV)	J_{sc} ($mAcm^{-2}$)	FF (%)	PCE (%)	Rsh ($k\Omega*cm^2$)	Rs ($\Omega*cm^2$)
PBTTTV-v/$PC_{71}BM$	10:8	CB	720±0	8.71±0.04	62.19±0.48	3.90±0.02	0.79	8.99
	10:10	**CB**	**730±0**	**9.02±0.07**	**60.13±0.88**	**3.96±0.81**	**0.71**	**9.18**
	10:12	CB	725±5	8.80±0.02	60.72±044	3.87±0.03	0.91	11.83

◎ Mobility (μ_h) are determined by space-charge-limited-current (SCLC) technique using the following equation:

$$J = \frac{9}{8}\epsilon_r\epsilon_0\mu_h\frac{V^2}{L^3}exp\left(0.89\sqrt{\frac{V}{E_0L}}\right)\cdots\cdots eq.(1)$$

$$\Rightarrow J\cdot\left(\frac{9}{8}\epsilon_r\epsilon_0\mu_h\right)^{-1}\cdot\frac{L^3}{V^2} = exp\left(0.89\sqrt{\frac{V}{E_0L}}\right)$$

$$\Rightarrow \ln\left(J\cdot\frac{L^3}{V^2}\right) + \ln\left(\frac{9}{8}\epsilon_r\epsilon_0\mu_h\right)^{-1} = 0.89\sqrt{\frac{V}{E_0L}}$$

$$\Rightarrow \boxed{\ln\left(J\cdot\frac{L^3}{V^2}\right) = \frac{0.89}{\sqrt{E_0}}\cdot\sqrt{\frac{V}{L}} + \ln\left(\frac{9}{8}\epsilon_r\epsilon_0\mu_h\right)\cdots\cdots eq.(2)}$$

$$\text{Plot } \ln\left(J\cdot\frac{L^3}{V^2}\right) \text{ versus } \sqrt{\frac{V}{L}}$$

$$\text{Slope: } \frac{0.89}{\sqrt{E_0}} \text{ ; } \boxed{\text{y-intercept: } \ln\left(\frac{9}{8}\epsilon_r\epsilon_0\mu_h\right)\cdots\cdots eq.(3)}$$

The zero-field hole mobility (μ_h) can then be calculated from the y-intercept using the equation eq. (3).

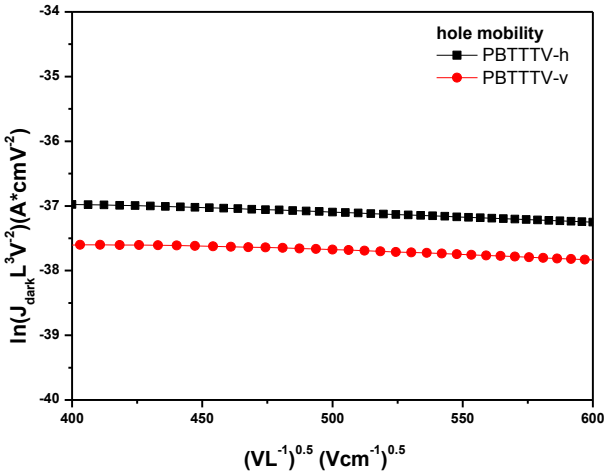


Figure S24. $\ln(J_{dark}L^3V^{-2})$ versus $(VL^{-1})^{0.5}$ plots of the pristine polymers for the measurement of hole mobility by the SCLC method.

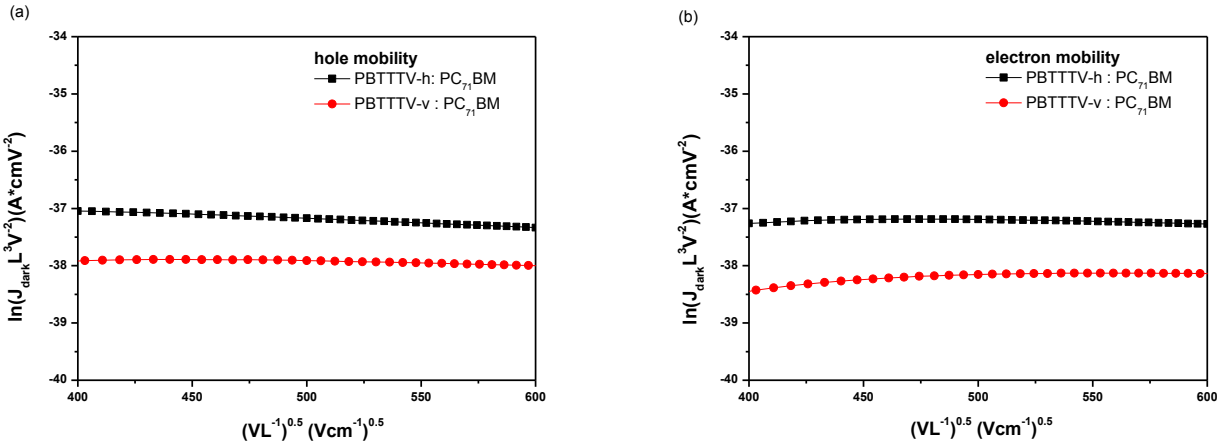


Figure S25. $\ln(J_{dark}L^3V^{-2})$ versus $(VL^{-1})^{0.5}$ plots of the polymers blend $PC_{71}BM$ for the measurement of (a) hole and (b) electron mobility by the SCLC method.

Table S5. Mobility of **PBTTTV-h and PBTTTV-v** with/without $PC_{71}BM$.

	Pure polymer hole mobility ($cm^2/(V*sec)$)	**Blend with $PC_{71}BM$ hole mobility** ($cm^2/(V*sec)$)	**Blend with $PC_{71}BM$ electron mobility** ($cm^2/(V*sec)$)	h^+/e^-
P3HT	$3.8*10^{-4}$	-	-	-
PBTTTV-h	$4.8*10^{-4}$	$3.3*10^{-4}$	$2.5*10^{-4}$	1.32
PBTTTV-v	$3.0*10^{-4}$	$2.8*10^{-4}$	$2.1*10^{-4}$	1.33

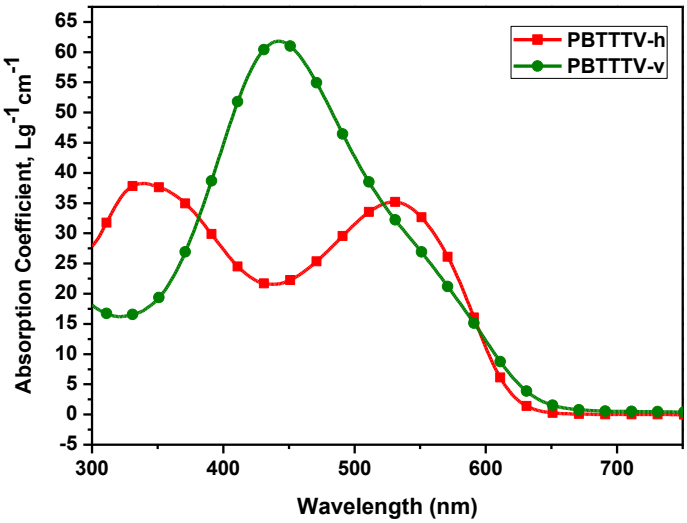


Figure S26. UV−vis absorption spectra of **PBTTTV-h** and **PBTTTV-v** in dilute CB solutions

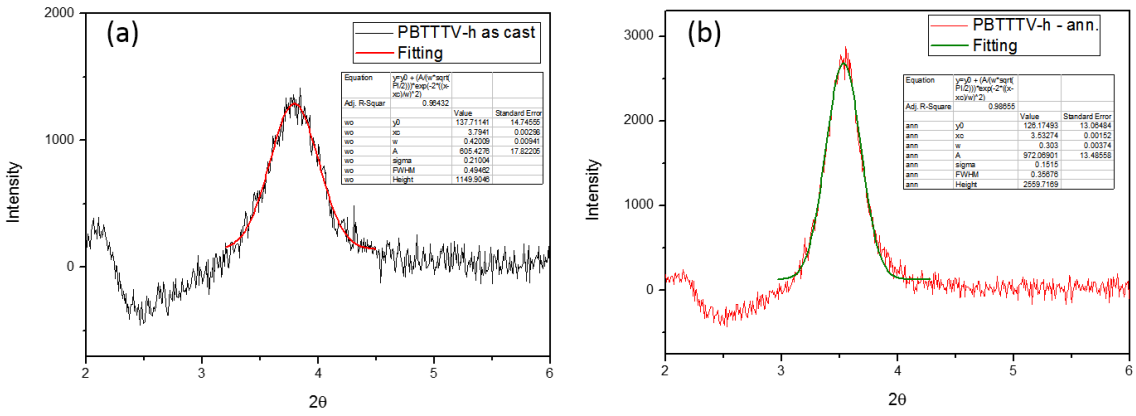


Figure S27. X-ray diffraction patterns and fitting curve of the **PBTTTV-h** films by (a) as cast; (b) as cast with annealing at 120 ℃ for 15 min.

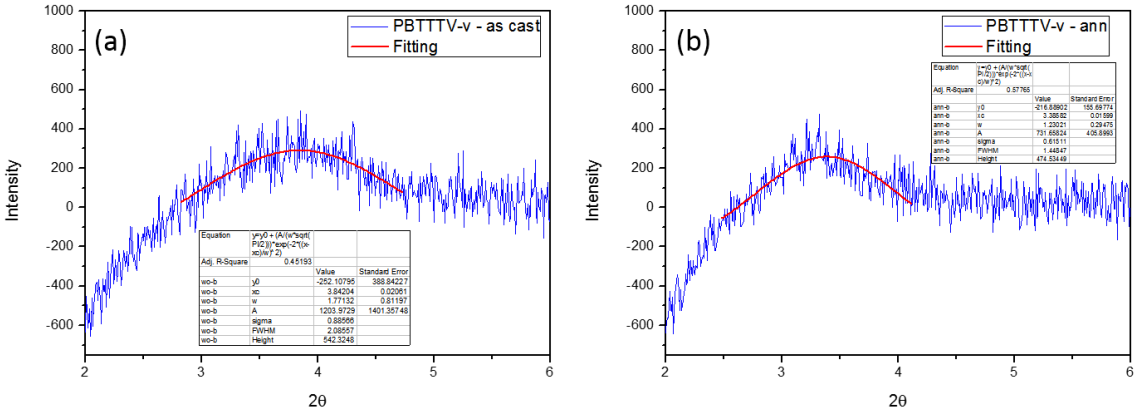


Figure S28. X-ray diffraction patterns and fitting curve of the **PBTTTV-v** films by (a) as cast; (b) as cast with annealing at 120 ℃ for 15 min.

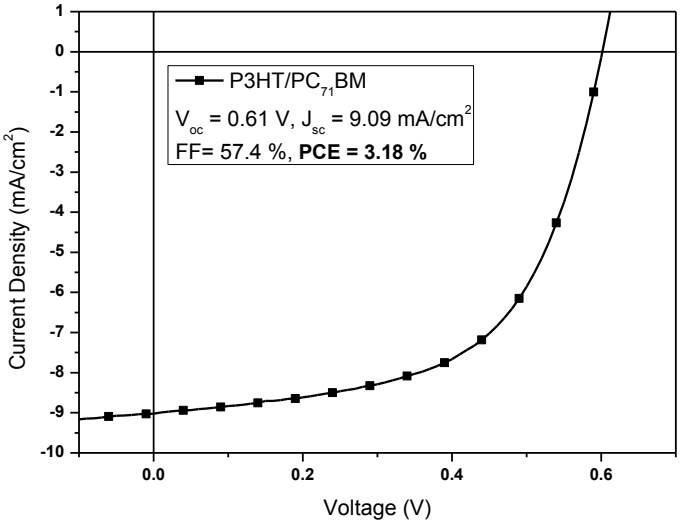


Figure S29. J-V curve of the PSCs using **P3HT** as donor and $PC_{71}BM$ as acceptor (blend weight ratio = 5:4) with an annealing temperature of 150 ℃ measured under AM1.5G illumination with an intensity of 100 mW/cm^2.