

Supporting Information

for

Cyclopentadithiophene-Benzothiadiazole Copolymers with Permutations of
Repeating Unit Length and Ratios; Synthesis, Optical and Electrochemical
Properties and Photovoltaic Characteristics

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1. ^1H and ^{13}C and HSQC NMR and FABMS spectra

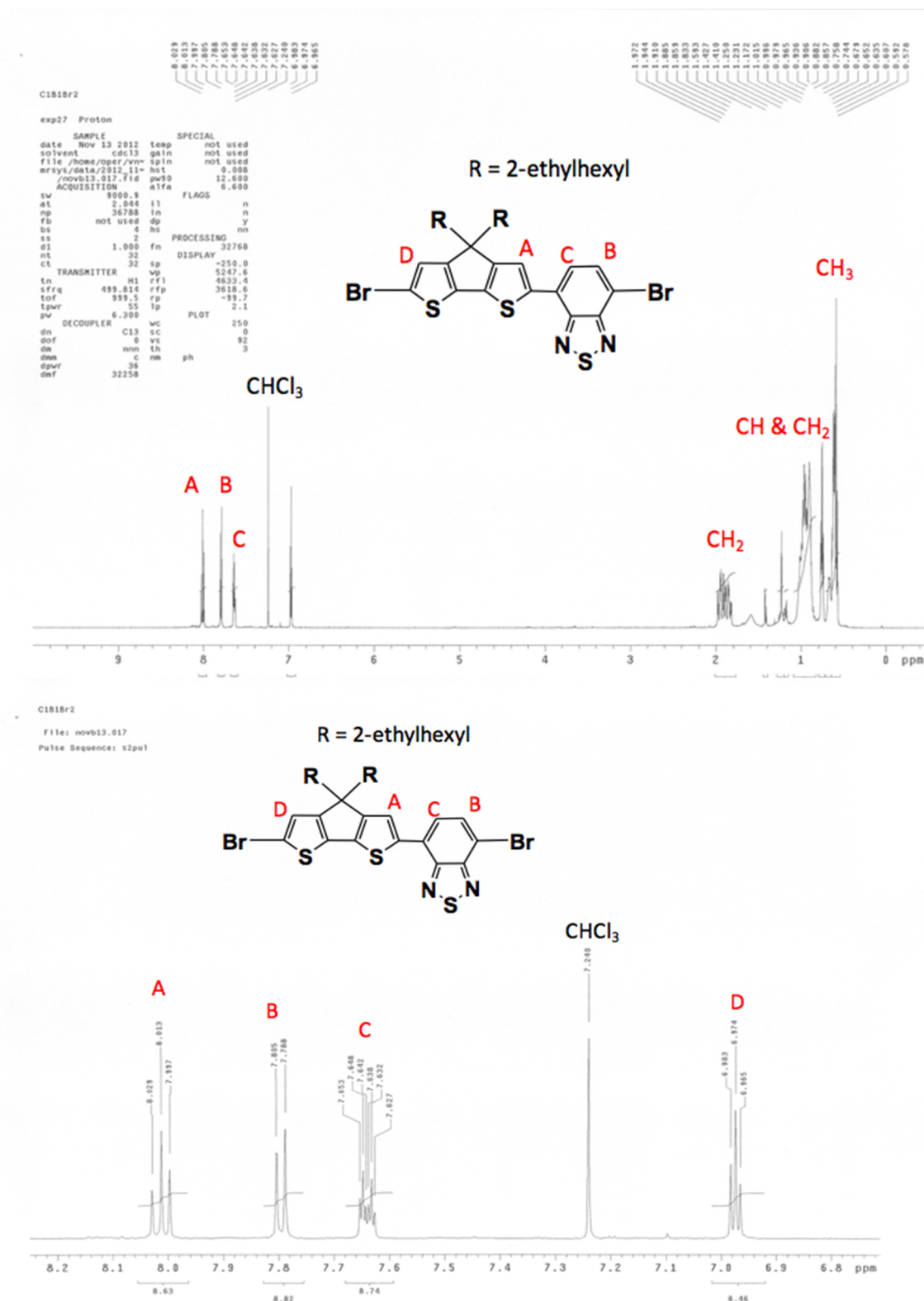


Figure S1. ^1H NMR spectra (500 MHz, CDCl_3) of **3**.

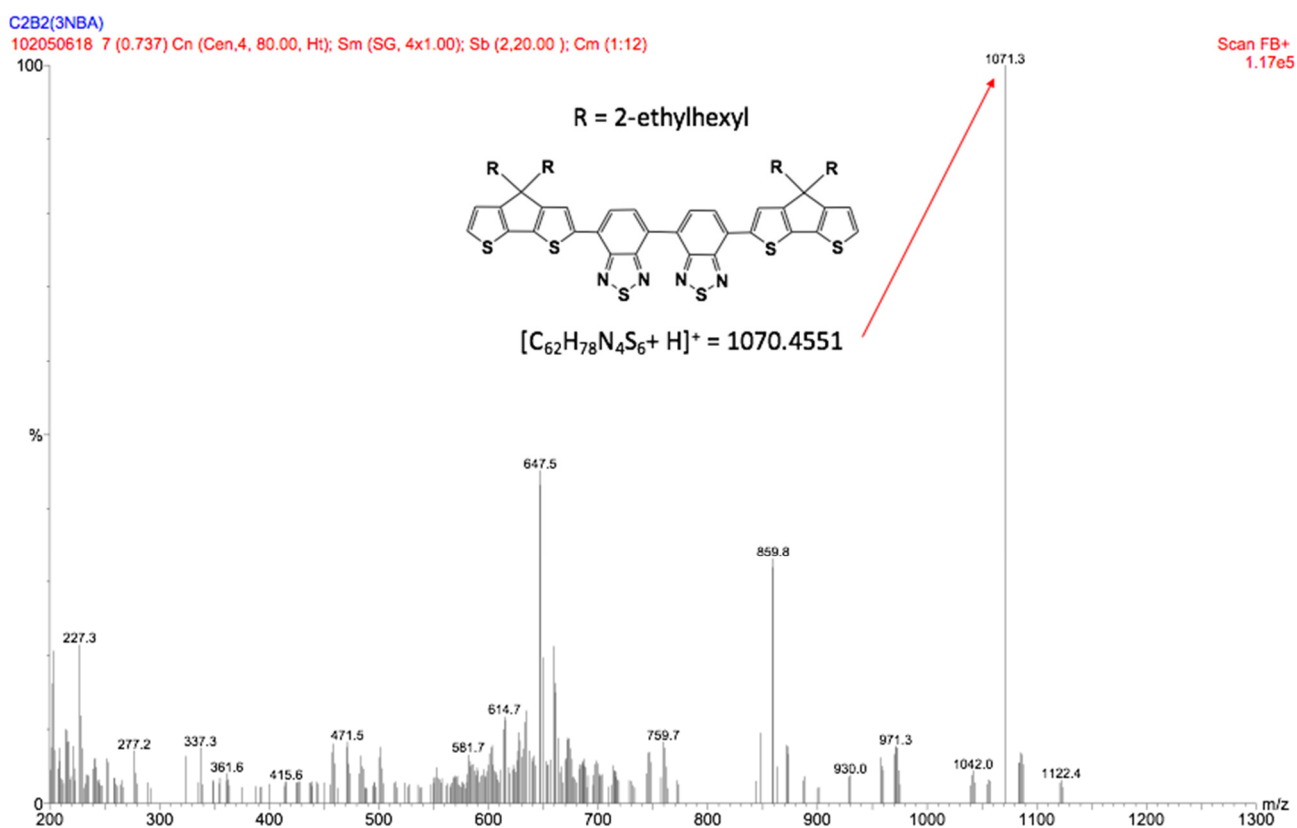


Figure S2. FAB mass spectrum of **3** with 3-nitrobenzyl alcohol (3NBA) matrix.

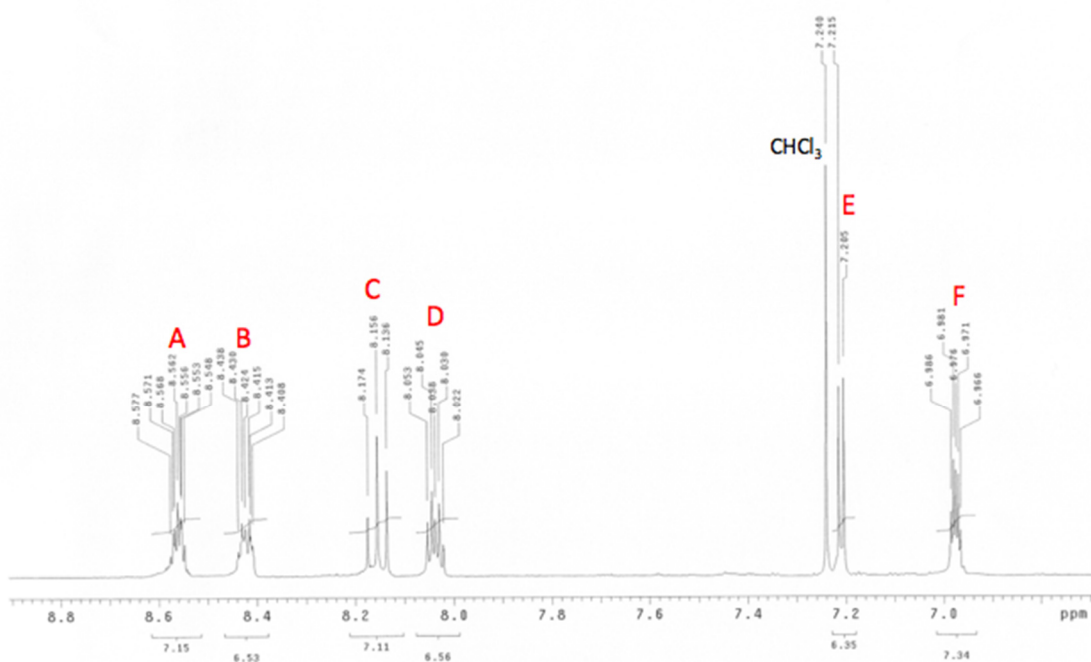
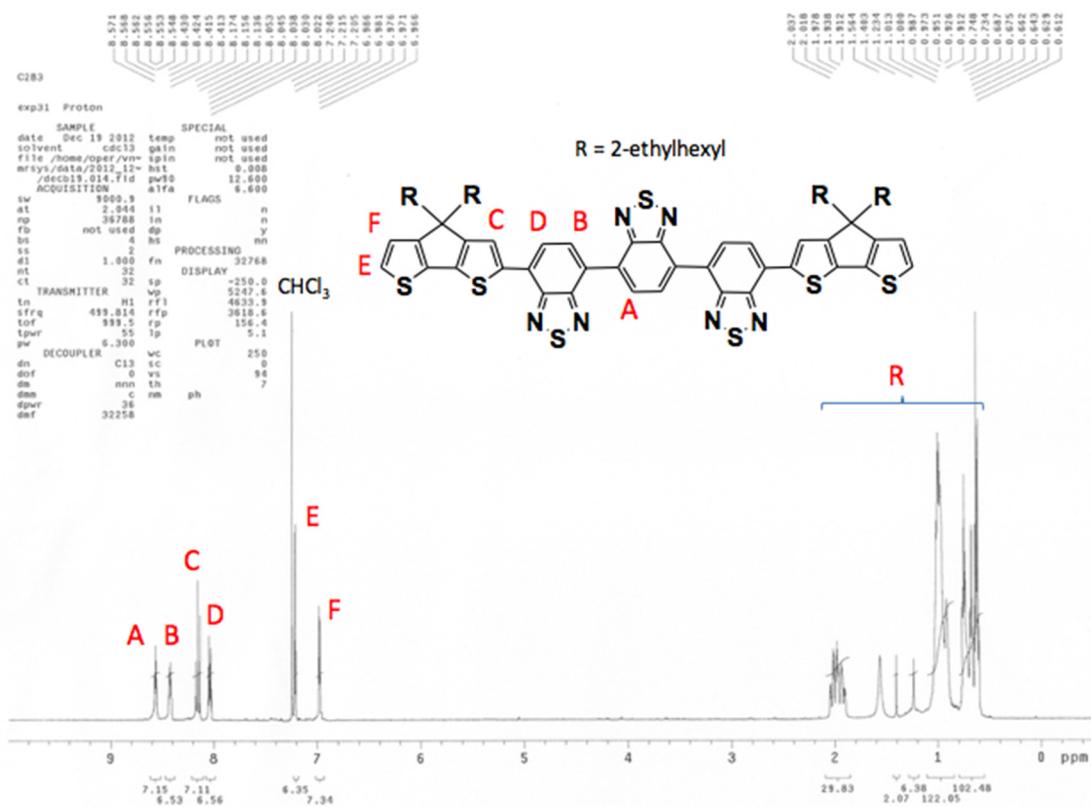


Figure S3. ¹H NMR spectra (500 MHz, CDCl₃) of 4.

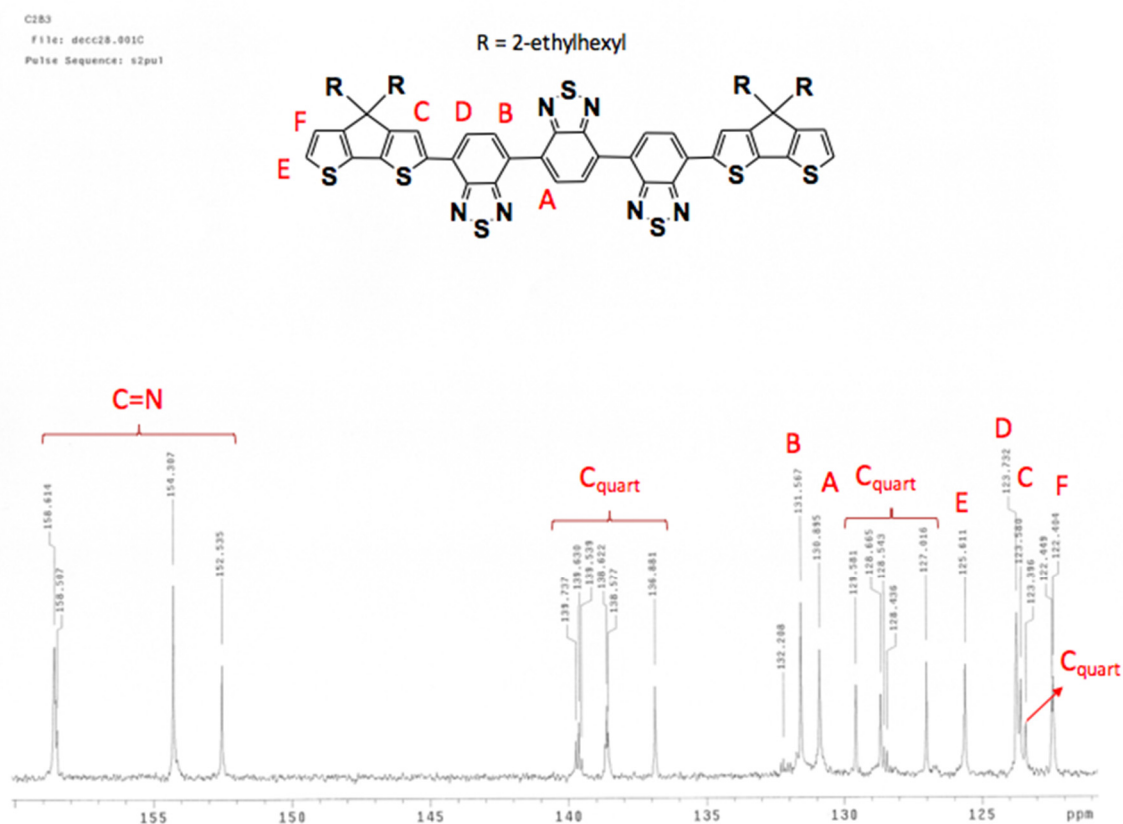
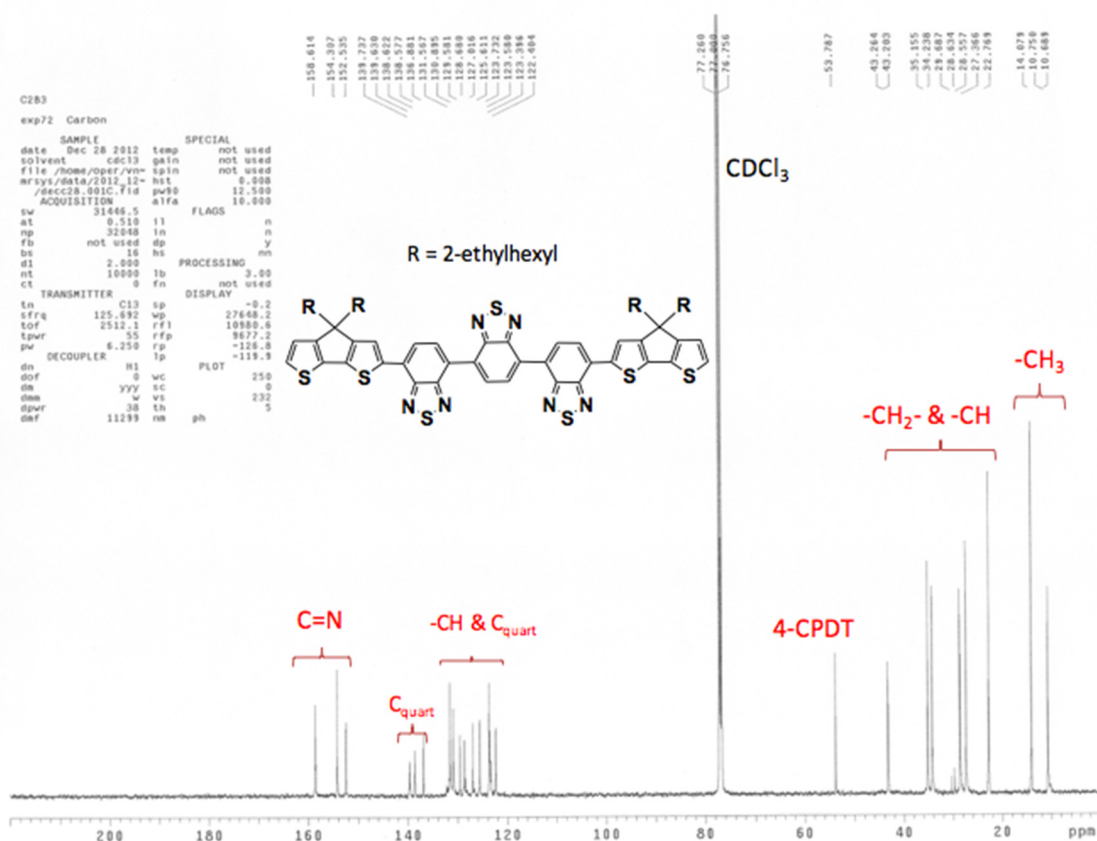


Figure S4. ¹³C NMR (125 MHz, CDCl₃) spectra of 4.

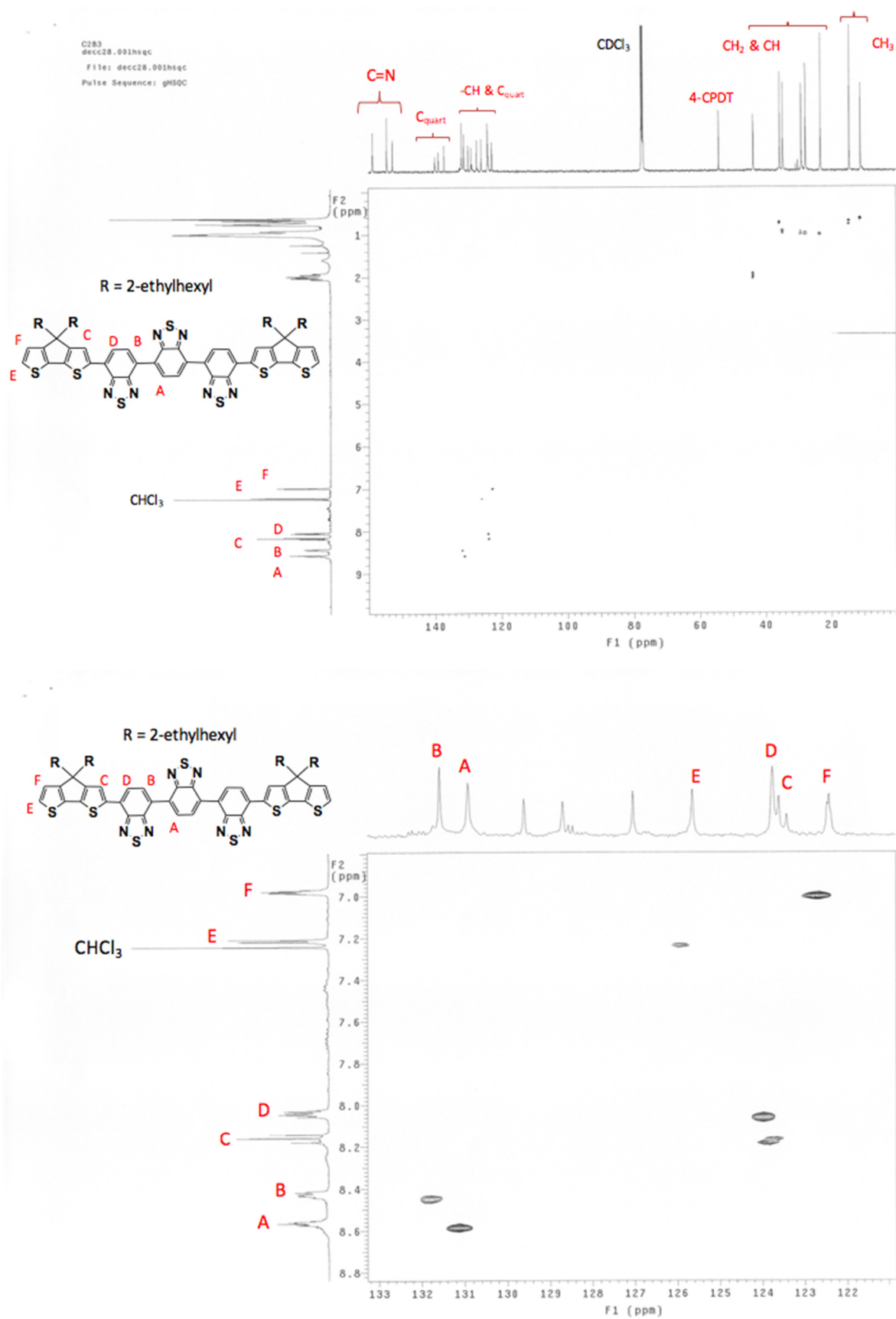


Figure S5. ^{13}C - ^1H COSY NMR spectra of **4** in CDCl_3 .

C2B3(3NBA)

102030508 14 (1.448) Cn (Cen,4, 80.00, Ht); Sm (SG, 4x1.00); Sb (2,50.00); Cm (1:14)

Scan FB+
9.77e4

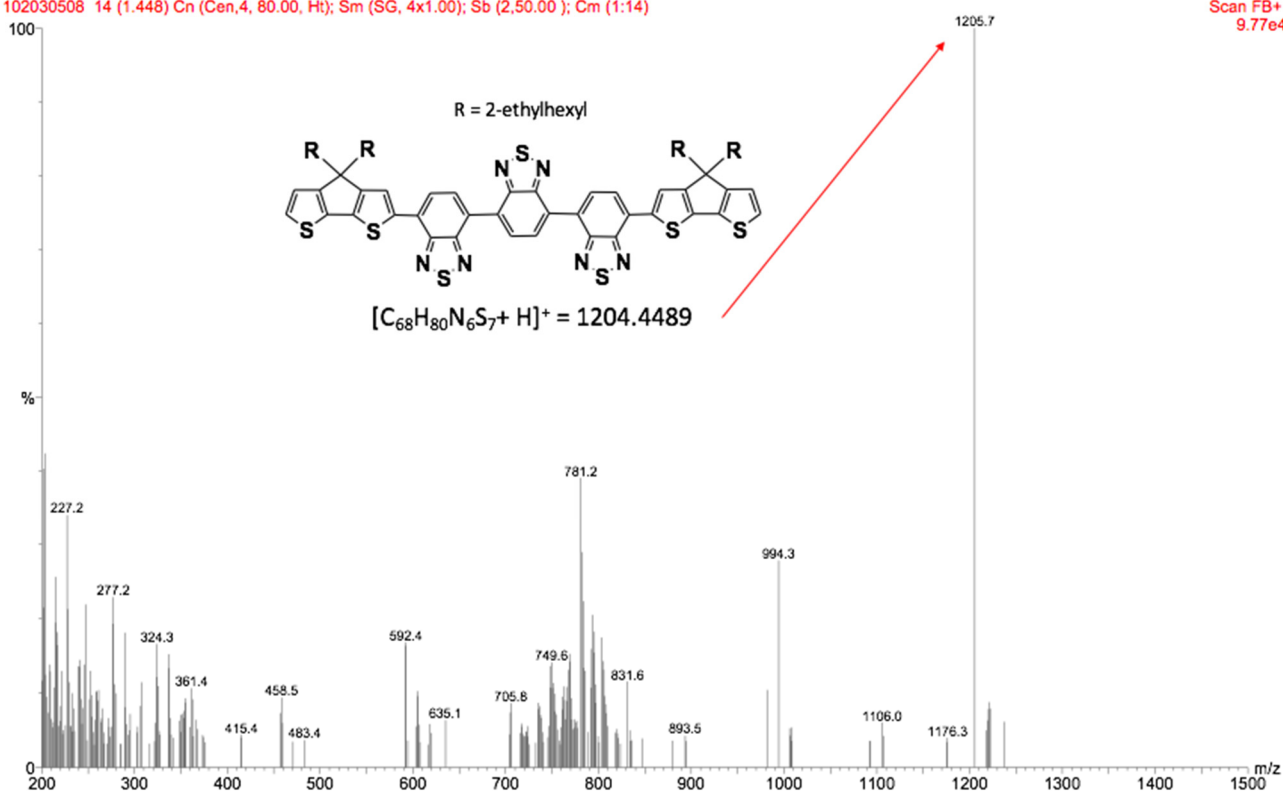


Figure S6. FAB mass spectrum of **4** with 3NBA matrix.

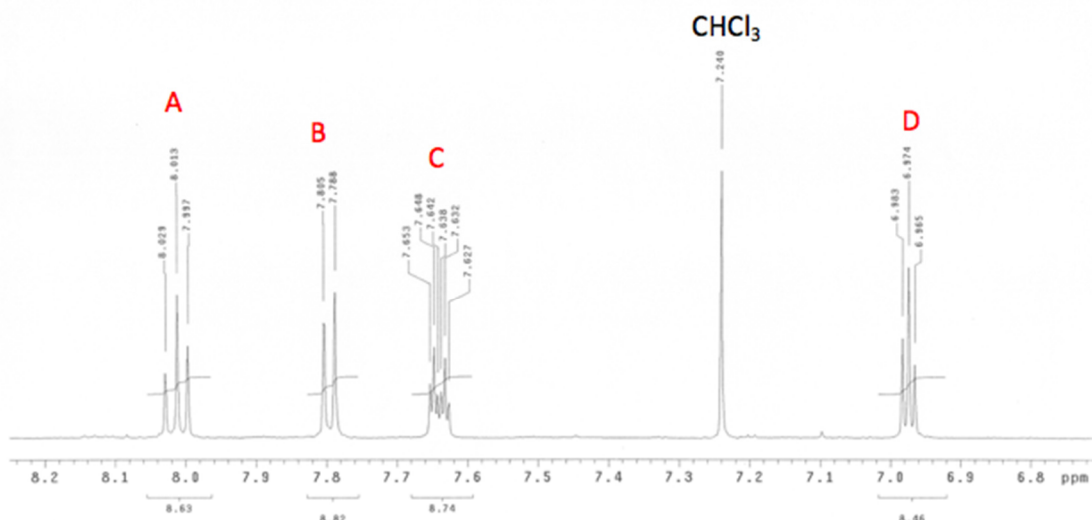
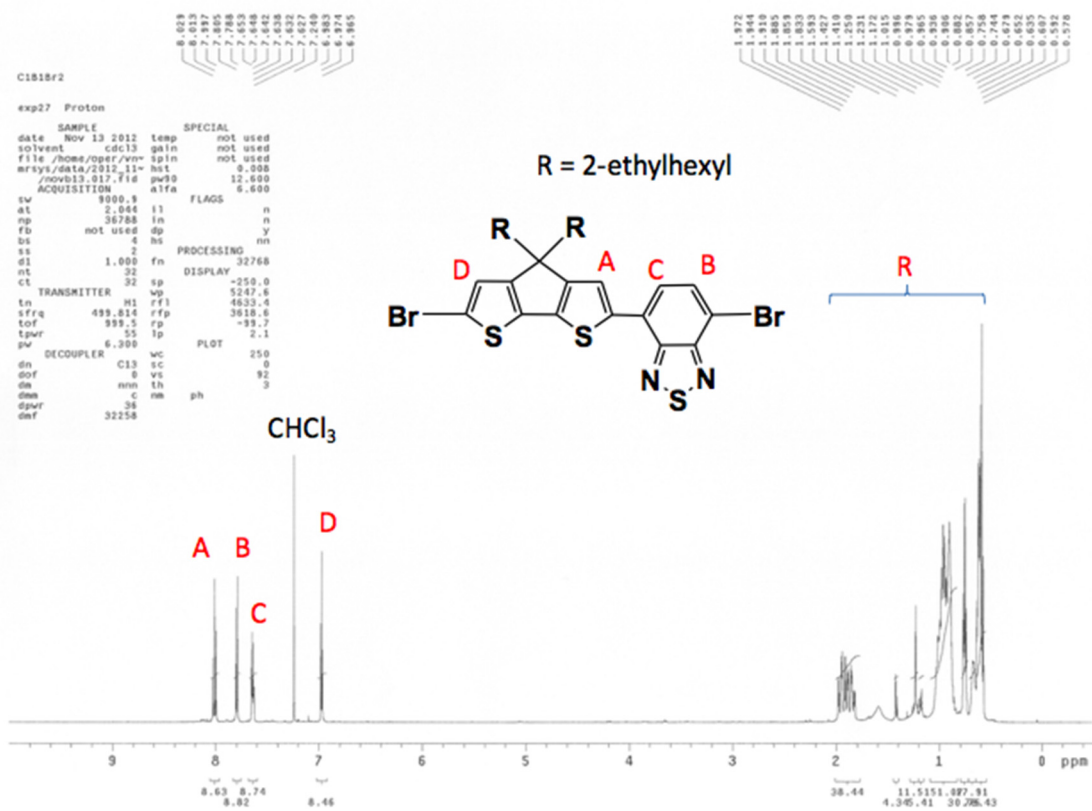


Figure S7. ¹H NMR spectra (500 MHz, CDCl₃) of **5**.

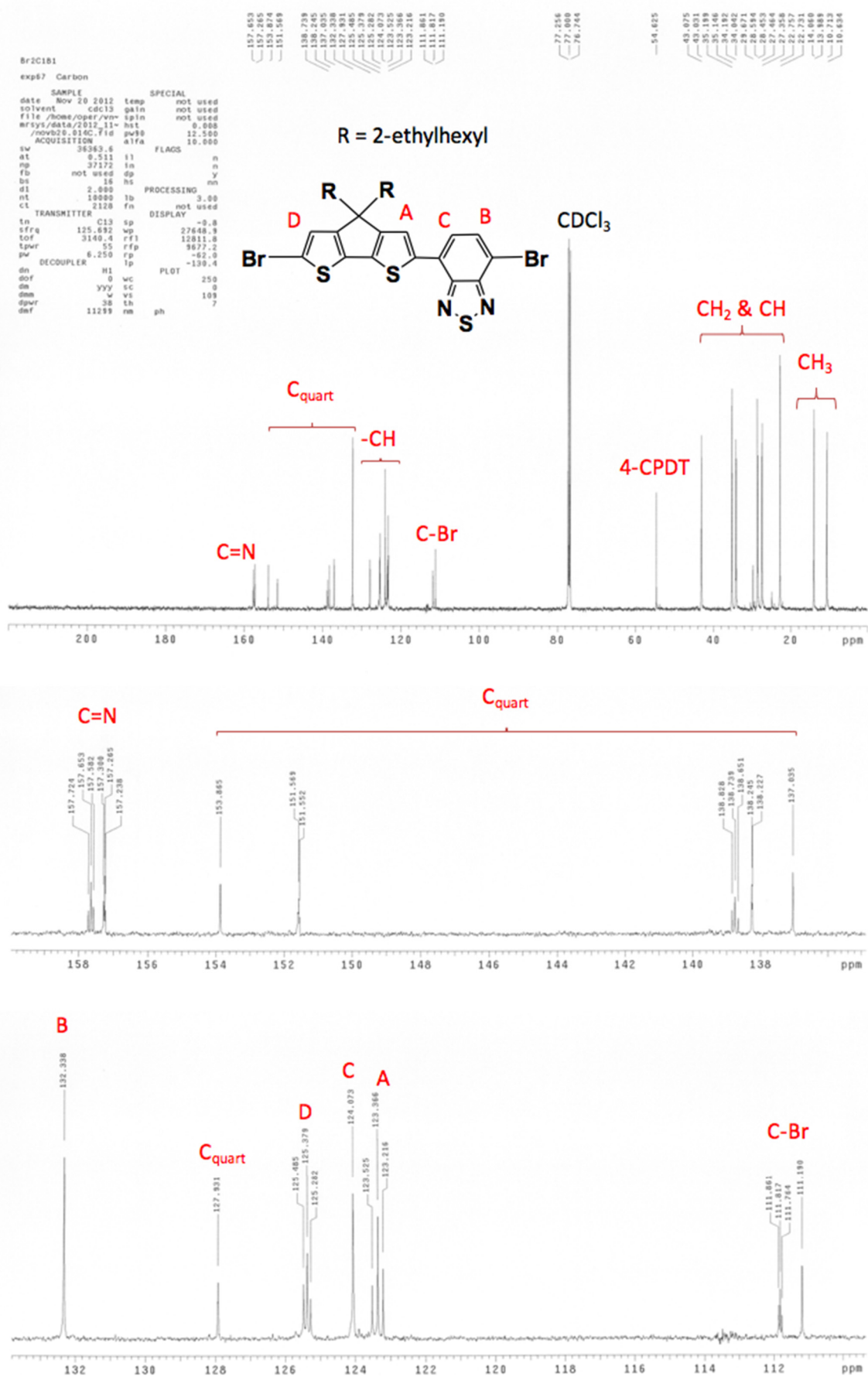


Figure S8. ¹³C NMR spectra (125 MHz, CDCl₃) of 5.

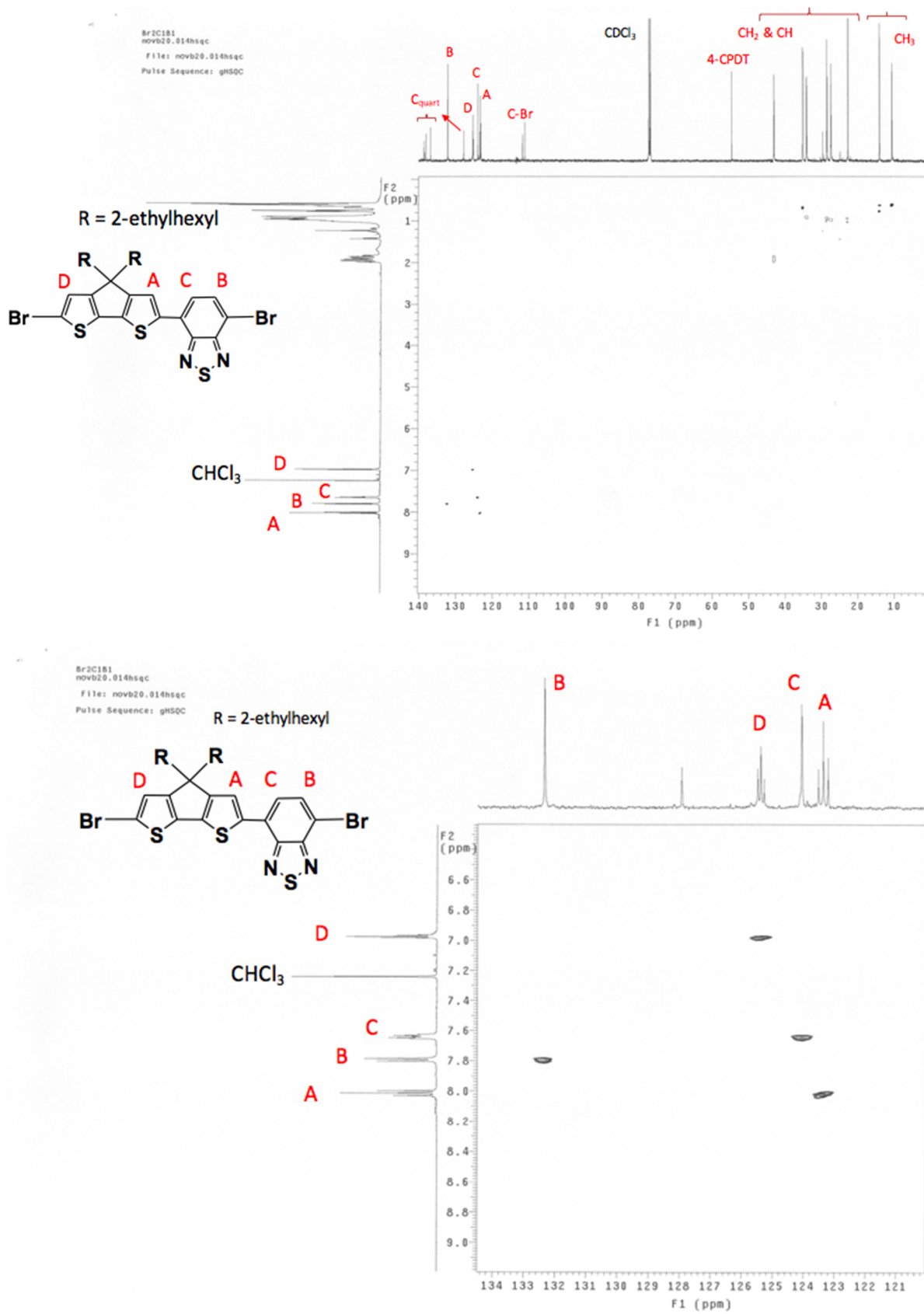


Figure S9. ^{13}C - ^1H COSY NMR spectra of **5** in CDCl_3 .

C1B1Br2(3NBA)

102030510 1 (0.127) Cn (Cen,4, 80.00, Ht); Sm (SG, 4x1.00); Sb (2,50.00); Cm (1:14)

Scan FB+
5.42e5

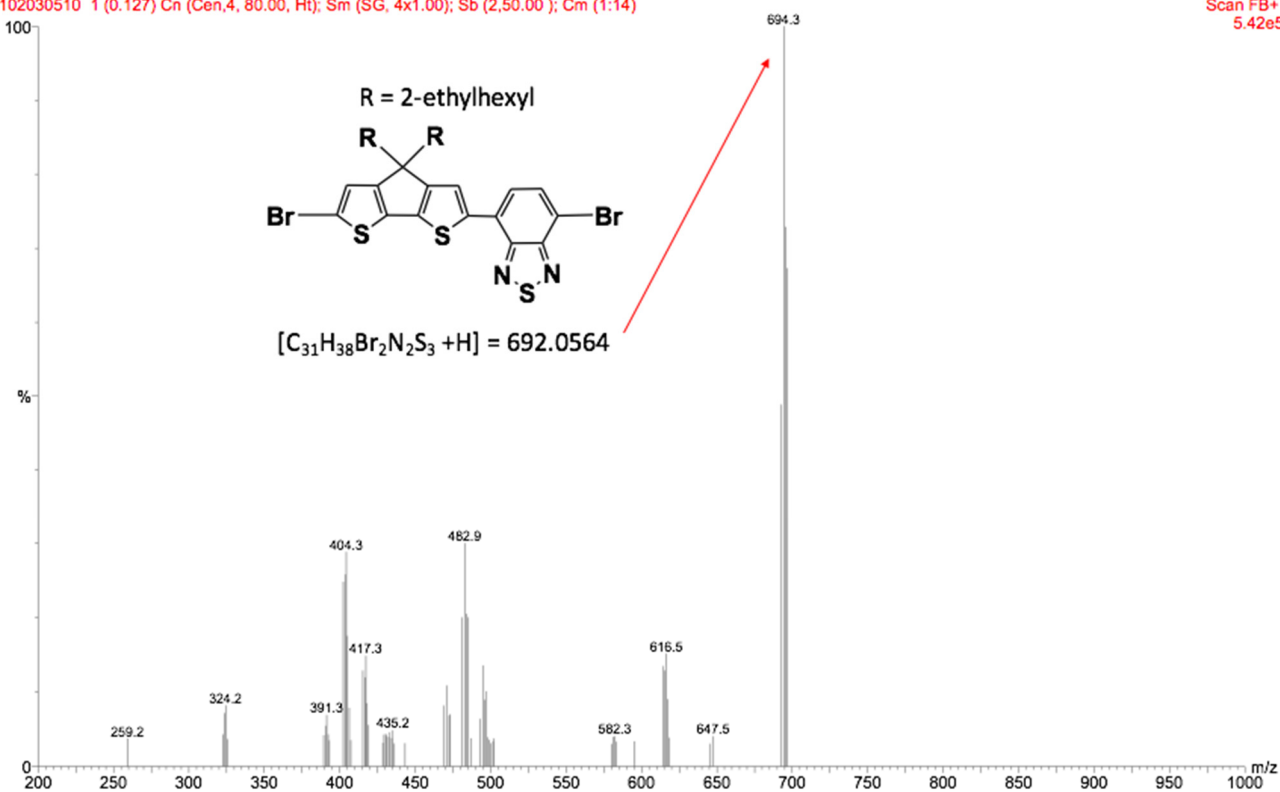


Figure S10. FAB mass spectrum of **5** with 3NBA matrix.

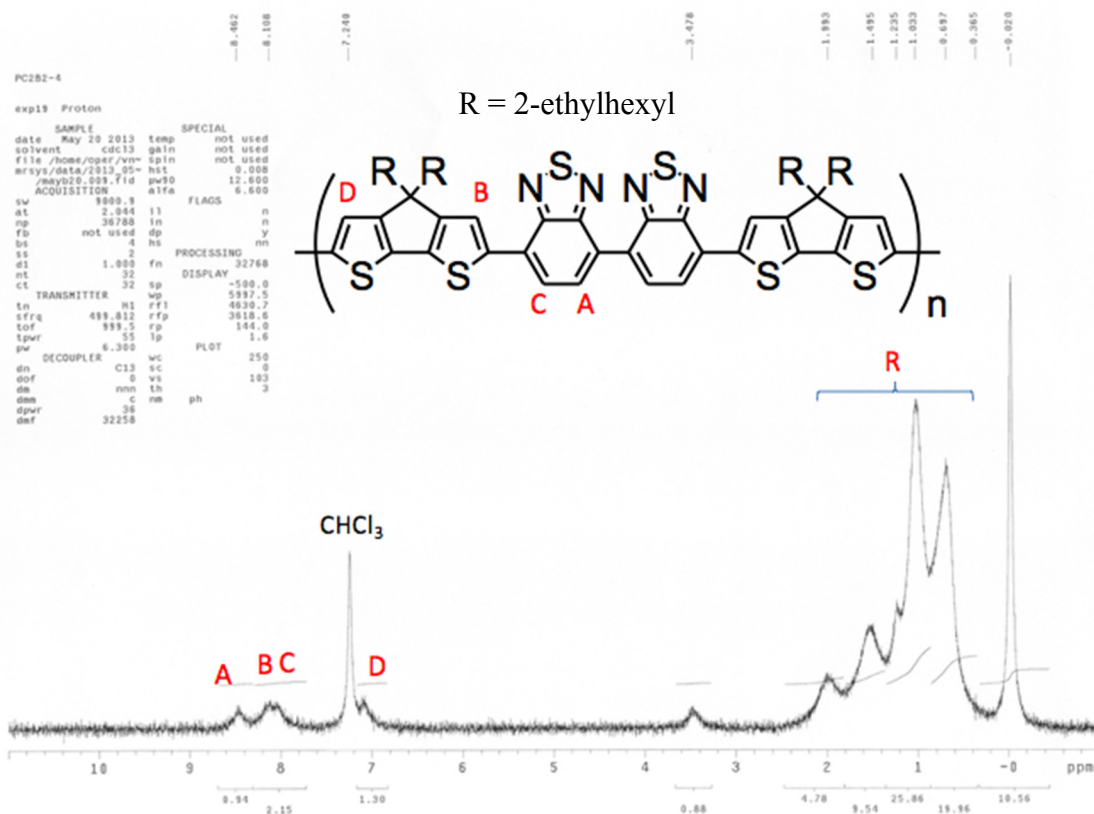


Figure S11. ^1H NMR spectrum (500 MHz, CDCl_3) of **P2**.

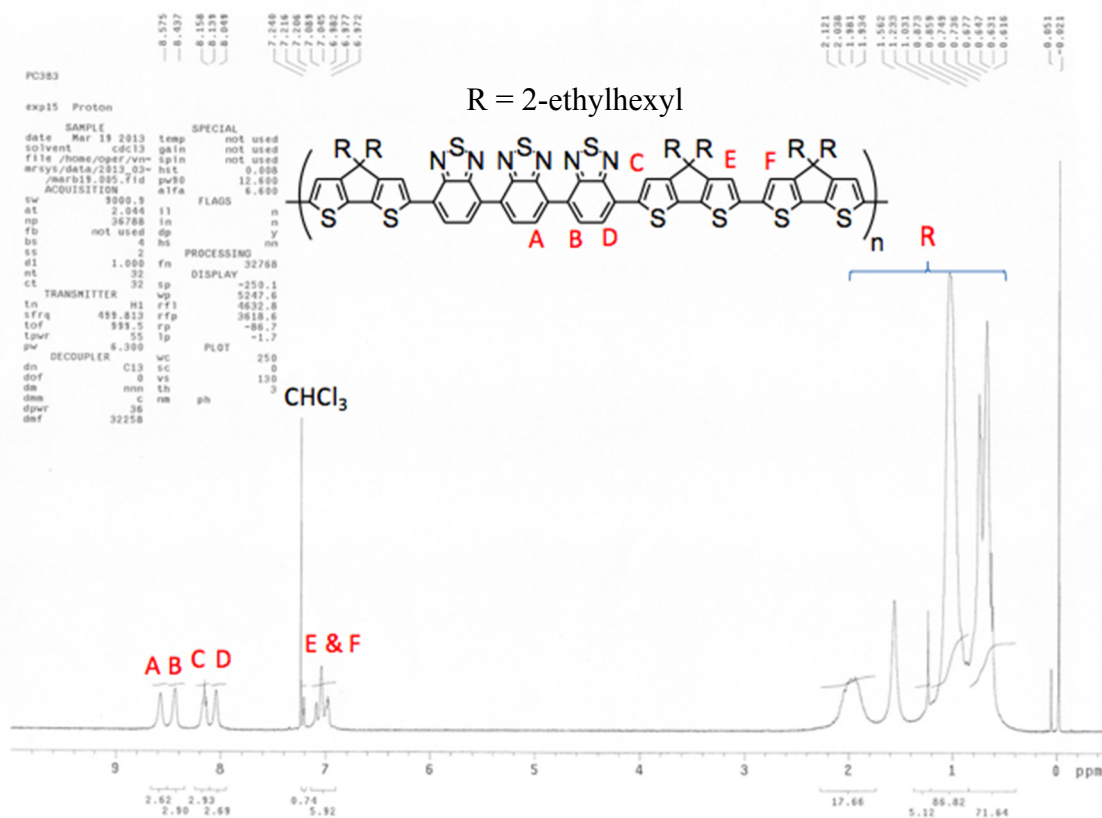


Figure S12. ^1H NMR spectrum (500 MHz, CDCl_3) of **P3**.

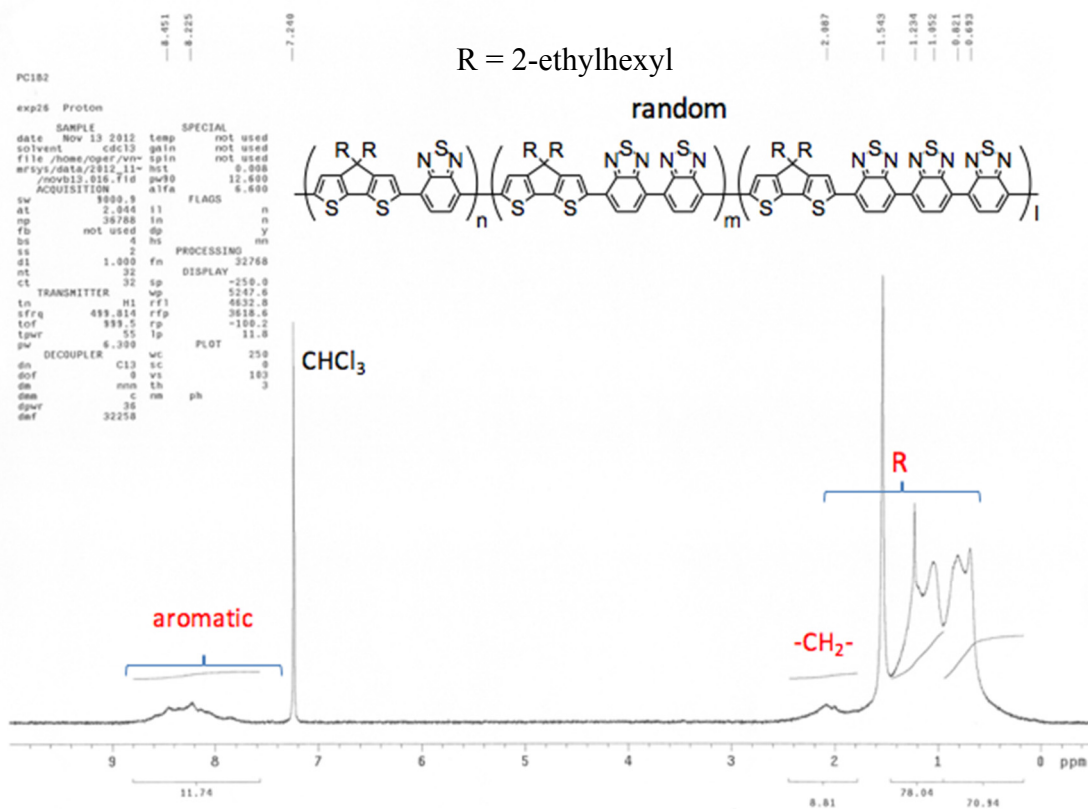


Figure S13. ¹H NMR spectrum (500 MHz, CDCl₃) of **P5**.

2. Optimization of synthesis for **P1**, **P2** and **P3**.

Table S1. Results of Suzuki coupling for **P1**

Entry	Pd amount	Temp. (°C)	Solvent	Yield (%)	M_n	M_w/M_n
1	6 ppm	110	xylenes/H ₂ O	98	27 000	2.67
2	6 ppm	100	xylenes/H ₂ O	99	22 300	2.21
3	6 ppm	100	toluene/H ₂ O	99	13 100	2.00
4	6 ppm	90	xylenes/H ₂ O	98	10 200	1.96
5	10 mol%	80	xylenes/H ₂ O	99	16 000	2.28

Reacted for 2 hours, K₂CO₃ (4.0 eq.), a drop of aliquat336, [monomer] = 0.09 M, yield before Soxhlet extraction.

Table S2. Results of oxidative polymerization for **P2**

Entry	Temp. (°C)	Time (h)	Yield (%)	M_n	M_w/M_n
1	80	24	insoluble	-	-
2	60/70	24/24	30	32 400	6.56
3	70	24	38	21 000	5.92
4	60	48	57	23 000	4.93

FeCl₃ (2.2 eq.), chlorobenzene (0.043 M), yield after Soxhlet extraction.

Table S3. Results of direct arylation for **P3**

Entry	Temp. (°C)	Time (h)	Yield (%)	M_n	M_w/M_n
1	80	3	36	6 500	2.07
2	80	12	50	9 000	1.74
3	80	20	12	17 800	3.53
4	85	24	14	24 000	1.67

Pd(OAc)₂ (10 mol%), NMP (0.08 M), PivOH (30 mol%), K₂CO₃ (2.5 equiv.), yield after Soxhlet extraction.

3. AFM images and roughness factors

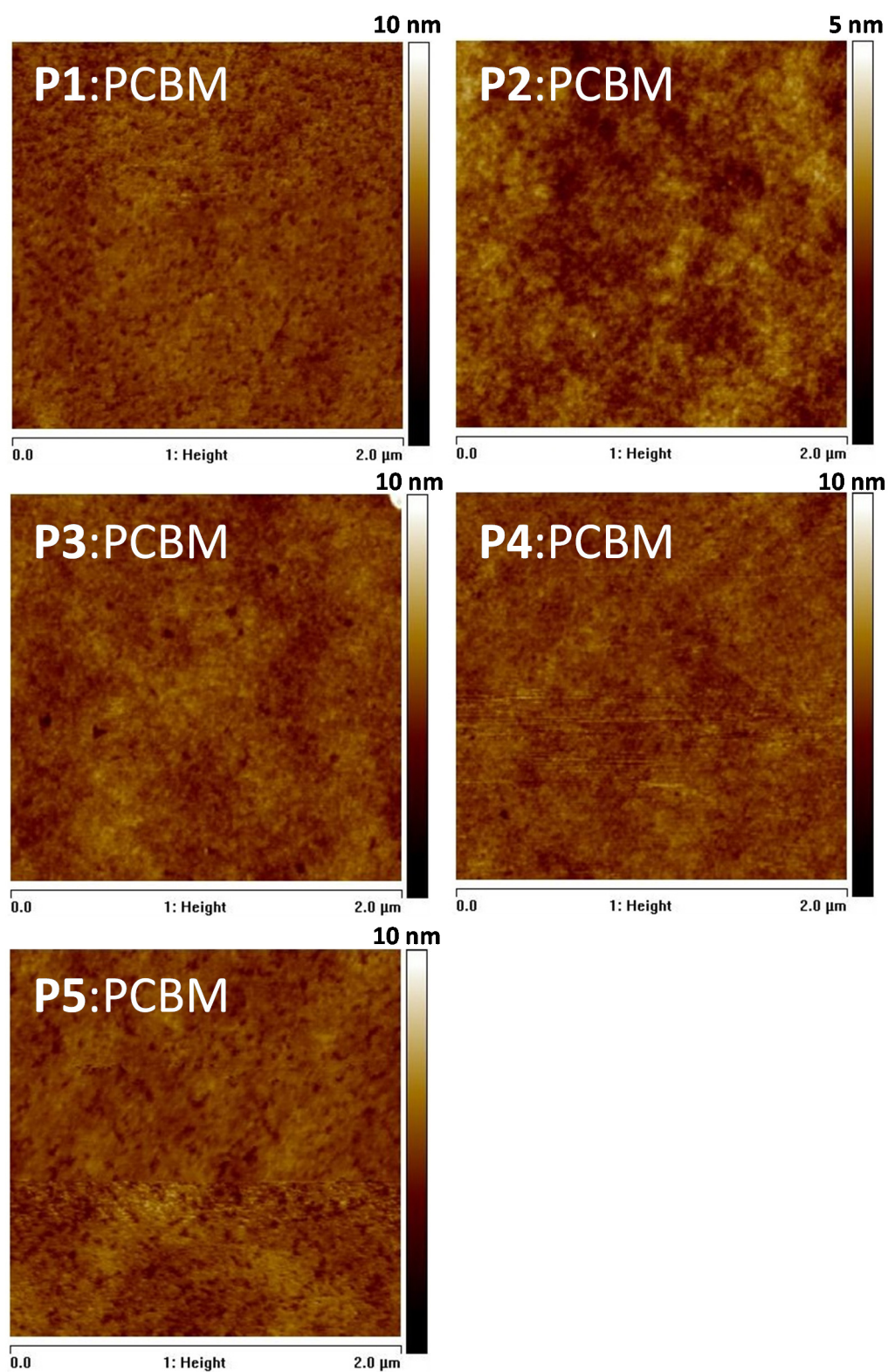


Figure S14. AFM images of polymer:PCBM films.

Table S4. Roughness for AFM images of polymer:PCBM films

Sample	R_a (nm)	R_q (nm)
P1 :PCBM	0.351	0.446
P2 :PCBM	0.292	0.365
P3 :PCBM	0.382	0.498
P4 :PCBM	0.334	0.426
P5 :PCBM	0.391	0.504