Electronic Supplementary Information (ESI)

A Facile method to synthesize [A`(D`AD)$_2$]-based push-pull small molecules for organic photovoltaics

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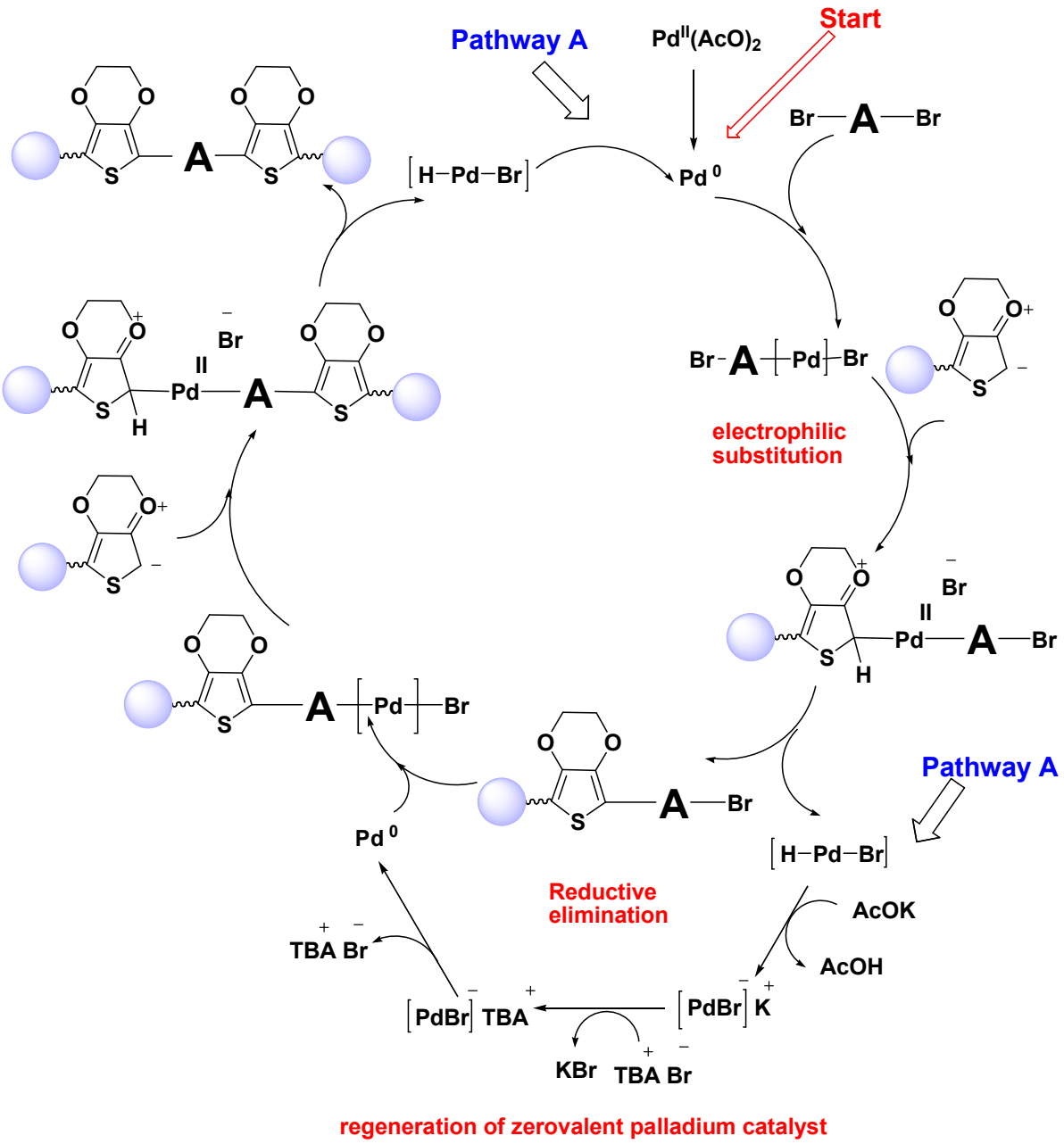
Table S1 Reaction conditions for the direct C-H arylation

Ent.[a]	Cat. (mole%)	L. (mole%)	Base (mole%)	Time hr	Y.[c] %
1. **(8)**	$Pd(OAc_2)_2$ (0.2)	------	------	12	0[b]
2. **(8)**	$Pd(OAc_2)_2$ (0.2)	TBAB (2)	------	12	0[b]
3. **(8)**	$Pd(OAc_2)_2$ (0.2)	TBAB (2)	KOAc (6)	12	40
4. **(8)**	$Pd(OAc_2)_2$ (0.2)	TBAB (2)	KOAc (6)	24	60
5. **(8)**	$Pd(OAc_2)$(O-Tol) (0.2)	TBAB (2)	KOAc (6)	24	15
6. **(8)**	$Pd(OAc_2)$(O-Tol) (0.2)	L2 (2)	------	12	0[b]
7. **(10)**	$Pd(OAc_2)_2$ (0.2)	TBAB (2)	KOAc (6)	24	57
8.**(12)**	$Pd(OAc_2)_2$ (0.2)	TBAB (2)	KOAc (6)	24	37

[a]All materials were synthesized by direct C-H arylation following the procedure described in the experimental section. [b]No reaction occurred and all reactants were recovered. [c]Isolated yield after purification.
TBAB = teterabutylammonium bromide
L2 = tris(2-methoxyphenyl)phosphine

Table S2 Thermal properties of all small molecules

Materials	T_m (°C)	T_c (°C)	T_d (°C)
HTPD(EDBTT)$_2$	85	.....	388
DHID(EDBTT)$_2$	174	132	434
DTDPP(EDBTT)$_2$	157	124	350



Scheme S1 The proposed reaction mechanism pathway.

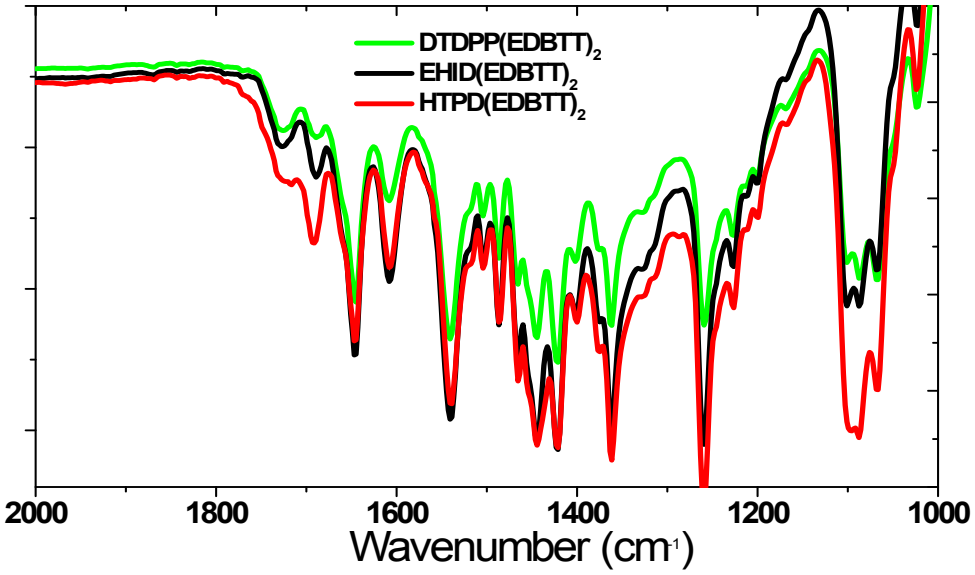


Figure S1. FT-IR spectra of DTDPP(EDBTT)$_2$, EHID(EDBTT)$_2$ and HTPD(EDBTT)$_2$.

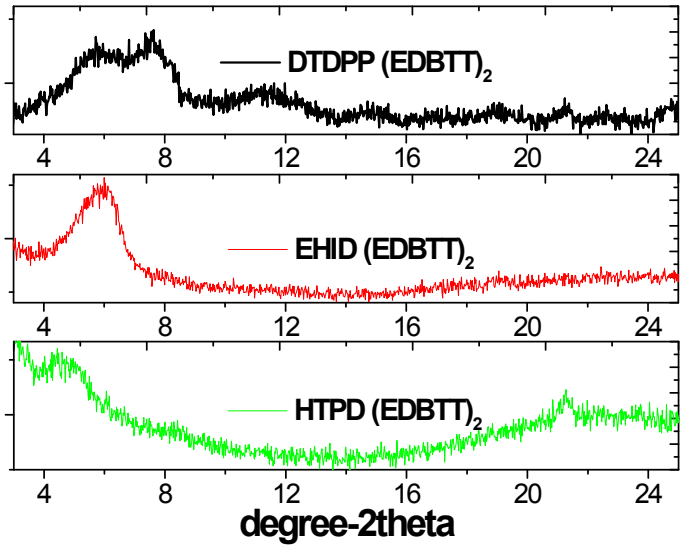


Figure S2. XRD profiles of materials DTDPP(EDBTT)$_2$, EHID(EDBTT)$_2$ and HTPD(EDBTT)$_2$ on ITO drop casted films.

Table S3 Angels and *d*-spacing in XRD data of all materiales under study

Material	2θ (°)	*d*-spacing (A°)
DTDPP(EDBTT)$_2$	**5.79**	**15.4**
	21.46	**4.1**
EHID(EDBTT)$_2$	**6.64**	**14.0**
HTPD(EDBTT)$_2$	**5.45**	**17.1**
	21.30	**4.3**

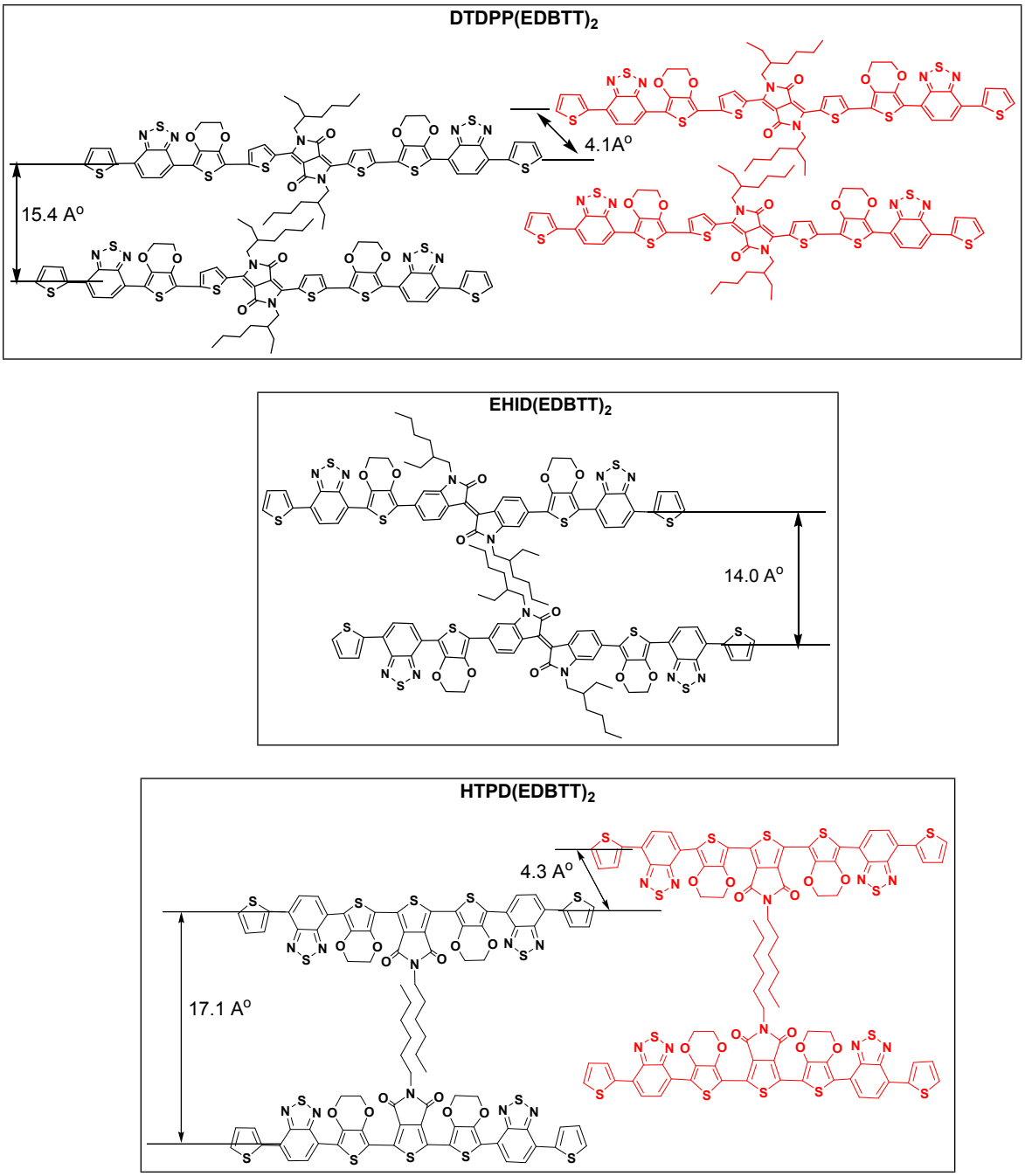


Figure S3. Proposed packed structures in solid stat for DTDPP(EDBTT)$_2$, EHID(EDBTT)$_2$ and HTPD(EDBTT)$_2$.

NMR Spectra

Figure S4.[1]H NMR Spectrum of 4-bromo-7-(thiophen-2-yl)-2,1,3-benzothiadiazole (3)

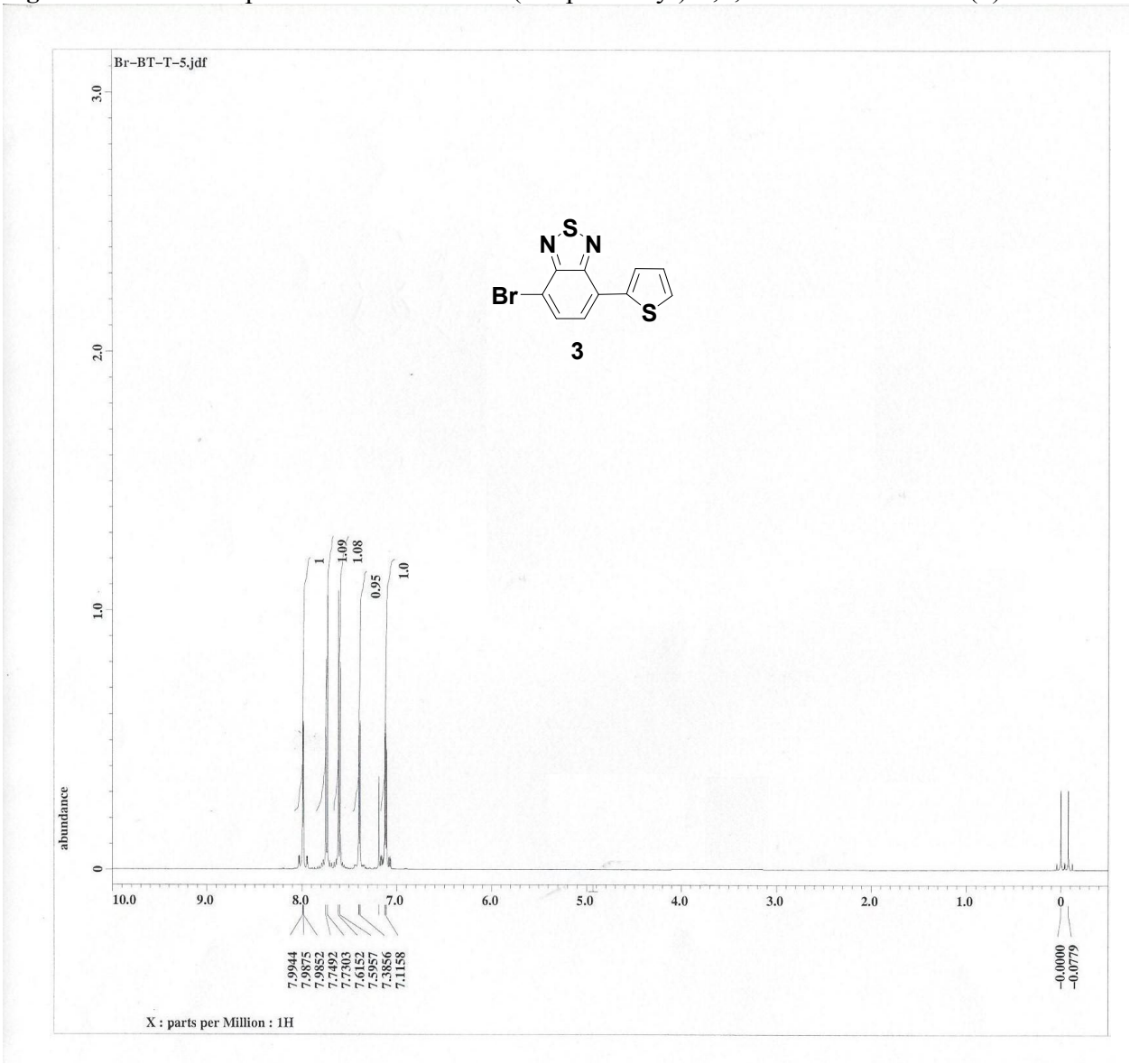


Figure S5. ^{13}C NMR Spectrum of 4-bromo-7-(thiophen-2-yl)-2,1,3-benzothiadiazole (3)

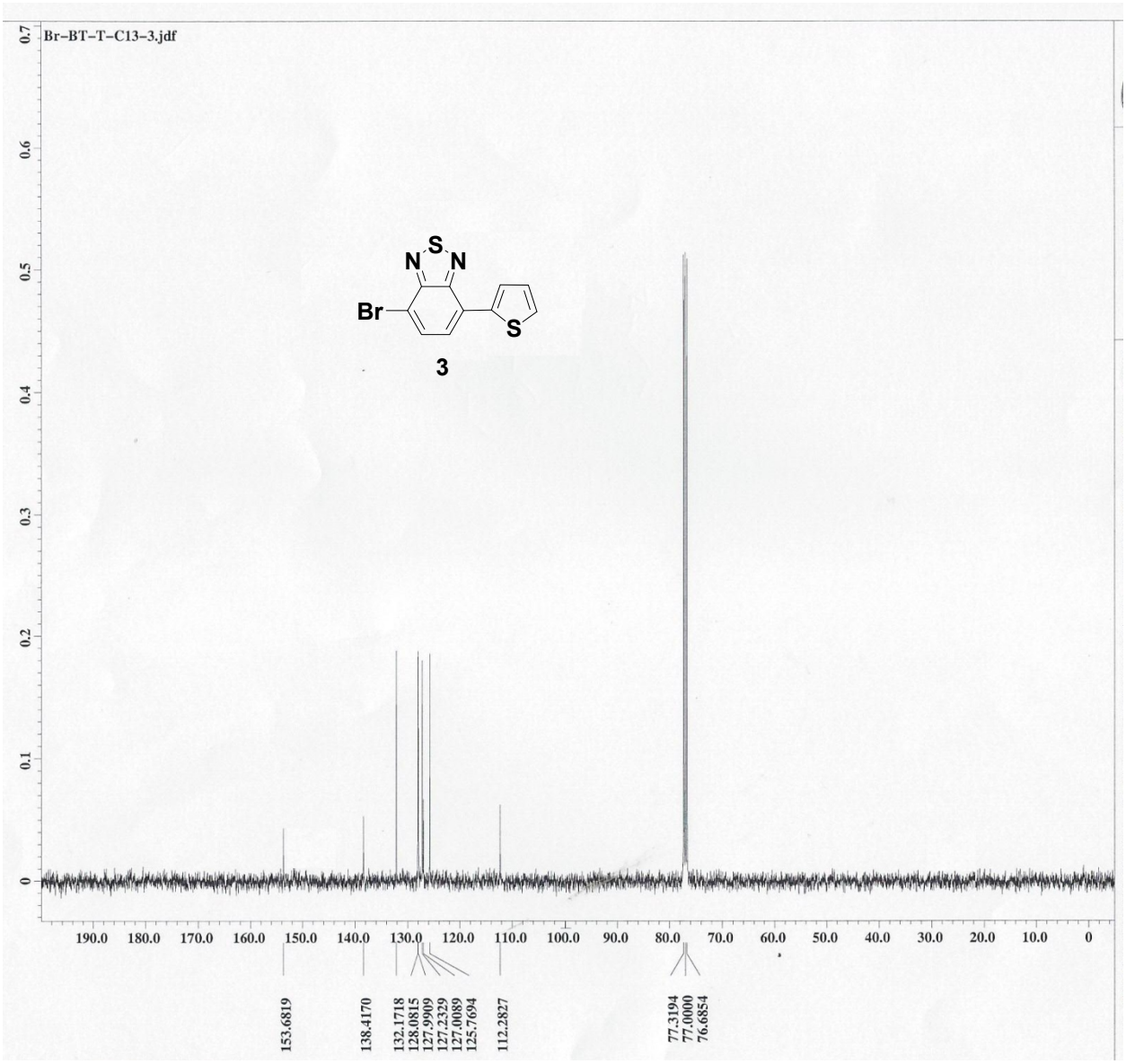


Figure S6.[1]H NMR Spectrum of 4-(3,4-ethylenedioxythiophene-7`-yl)-7-(thiophen-2-yl)-2,1,3-benzothiadiazole (5)(EDBTT)

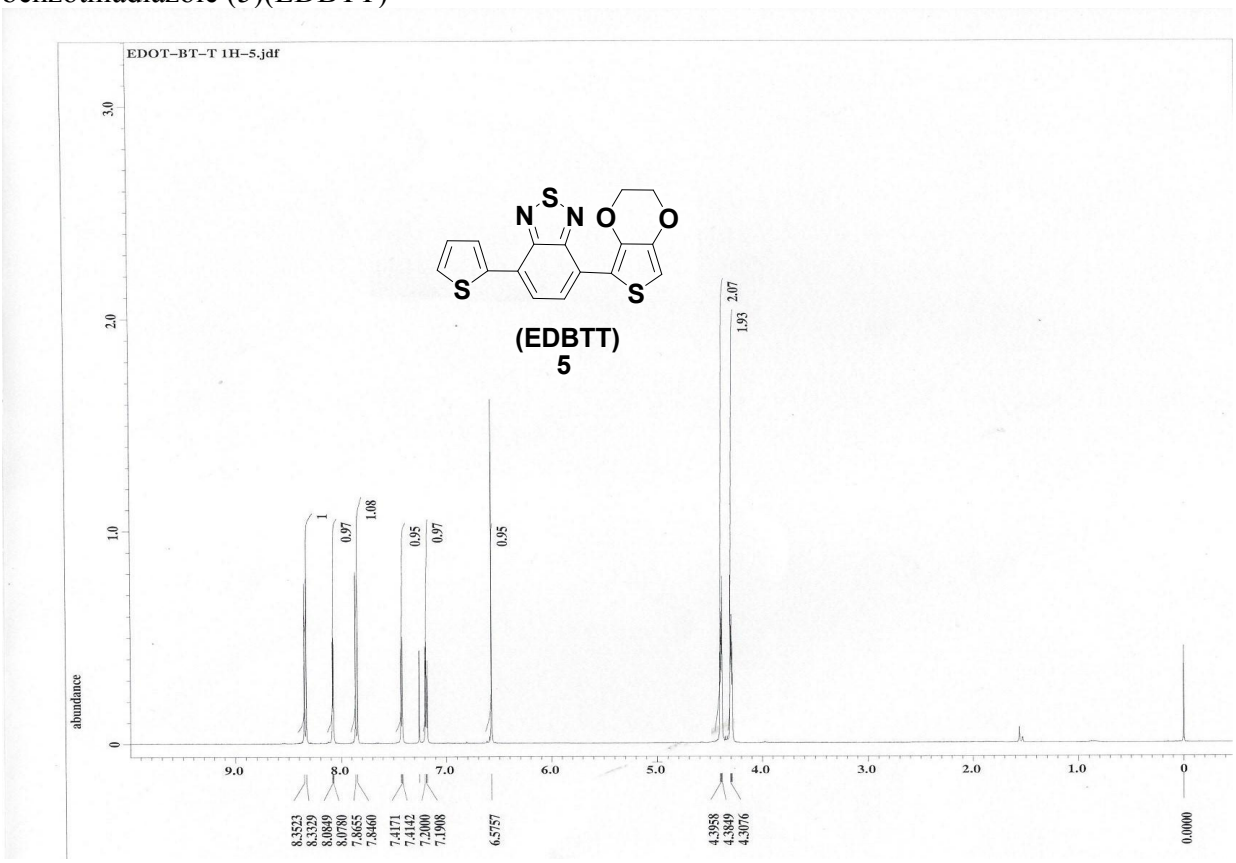


Figure S7.[13]C NMR Spectrum of 4-(3,4-ethylenedioxythiophene-7`-yl)-7-(thiophen-2-yl)-2,1,3-benzothiadiazole (5)(EDBTT)

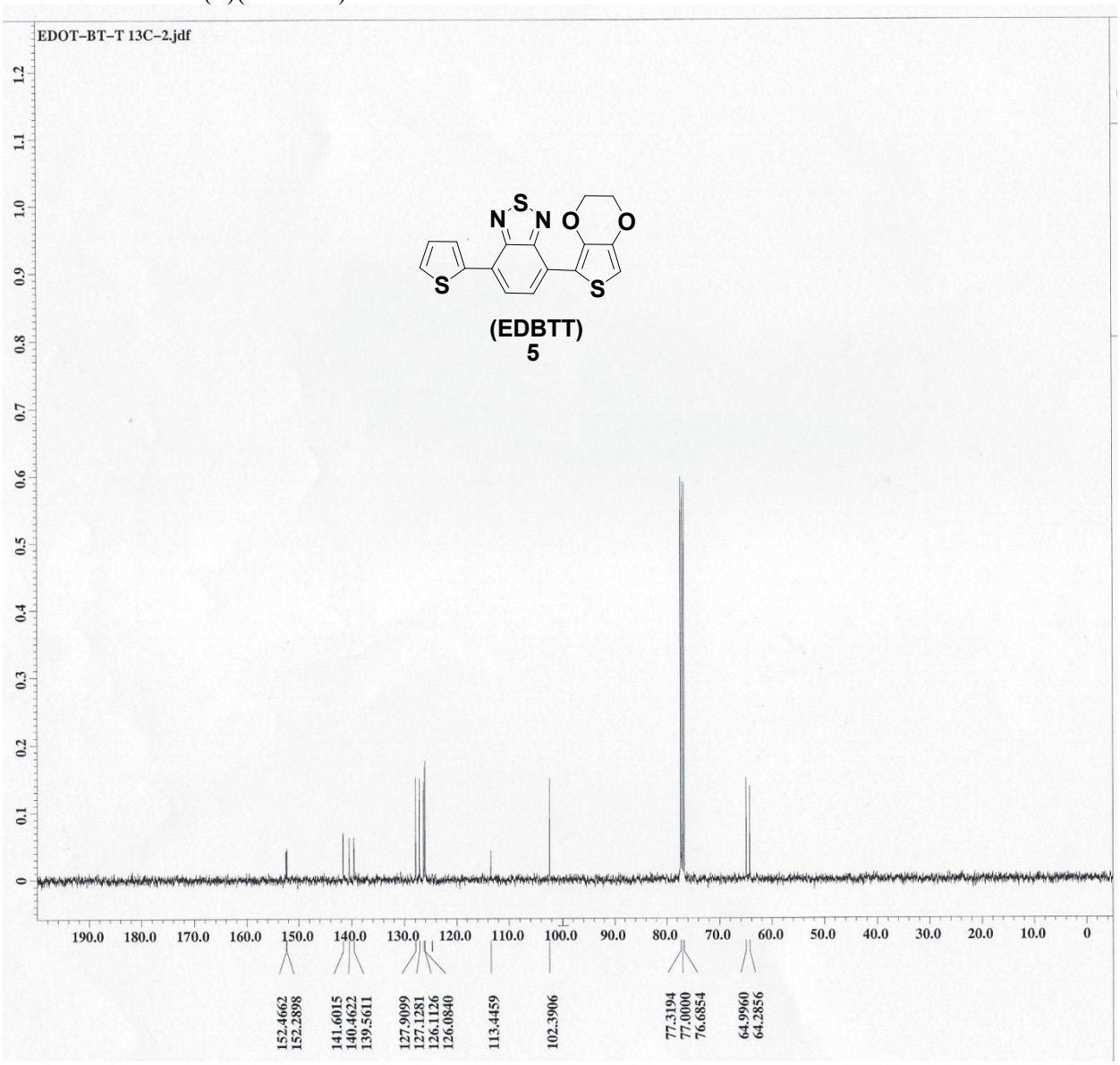


Figure S8. ^{1}H NMR Spectrum of DTDPP(EDBTT)$_2$ (8)

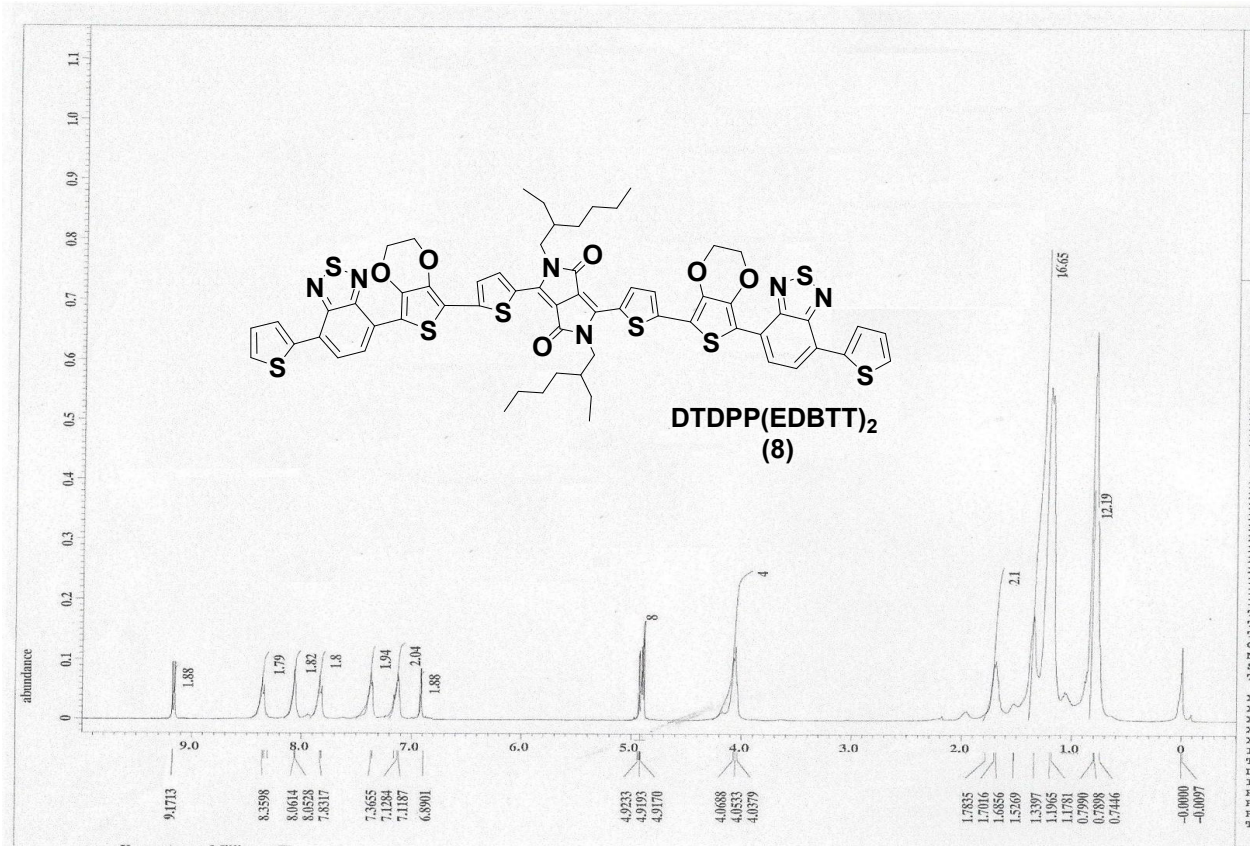


Figure S9. ^{1}H NMR Spectrum of EHID(EDBTT)$_2$ (10)

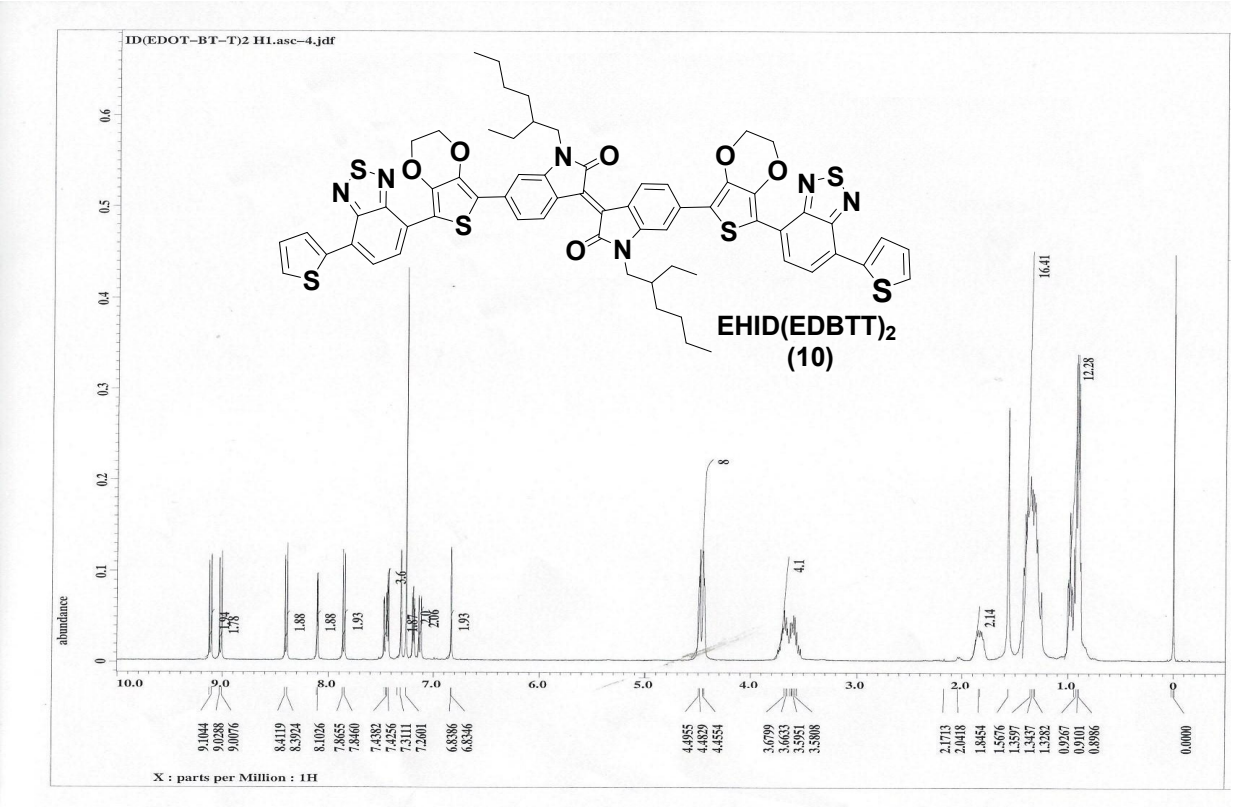


Figure S10. ^{1}H NMR Spectrum of HTPD(EDBTT)$_2$ (12)