

Electronic supplementary information (ESI)

for

**Vinylene-bridged difluorobenzo[*c*][1,2,5]thiadiazole (FBTzE):
a new electron-deficient building block for high-performance
semiconducting polymers in organic electronics**

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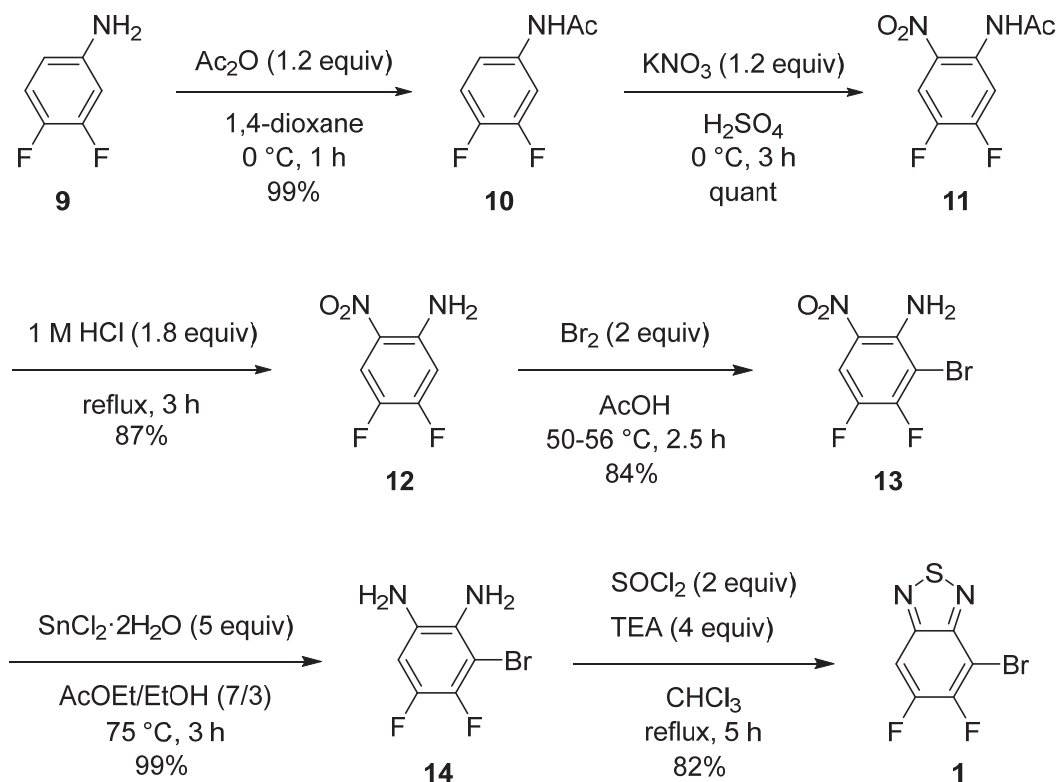
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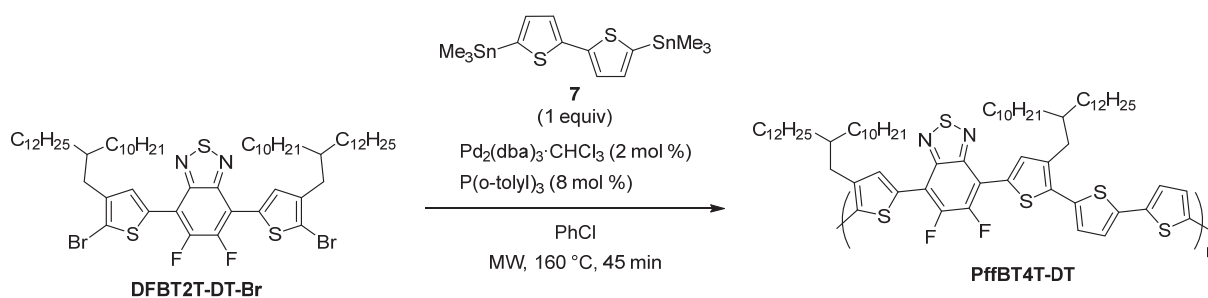
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1. Experimental Procedures and Spectroscopic Data for Compounds.

Scheme S1. Synthetic procedure of 4-bromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**1**)



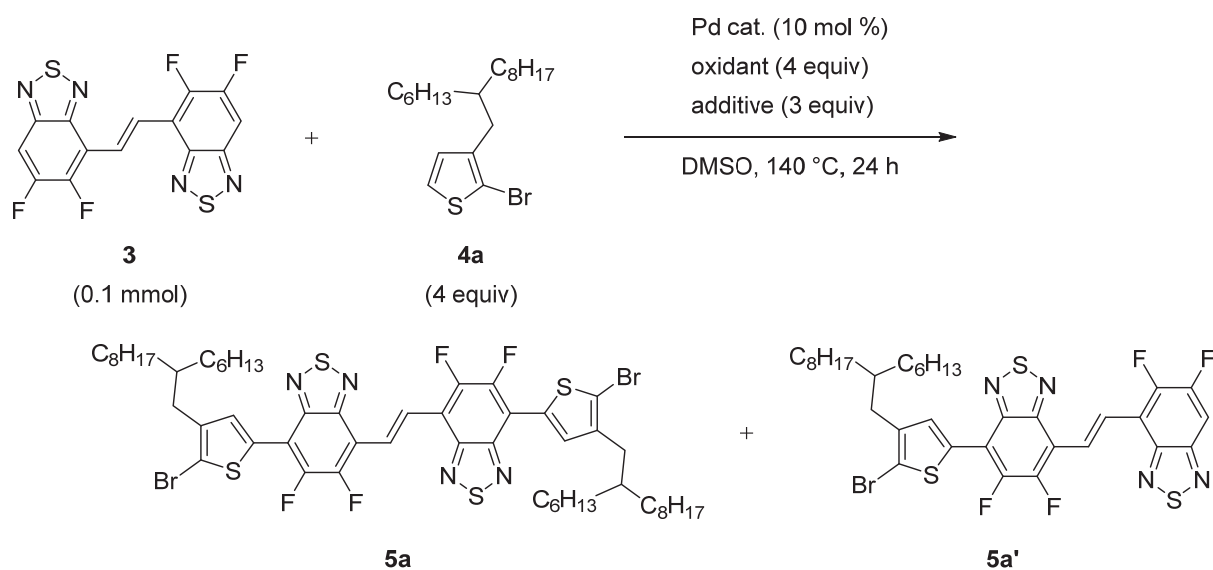
Scheme S2. Synthesis of standard PffBT4T-DT



Synthesis of Standard Polymers PffBT4T-DT. Monomers DFBT2T-DT-Br (116.7 mg, 0.1 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**7**, 49.2 mg, 0.1 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (Pd₂(dba)₃·CHCl₃, 2.1 mg, 2 μmol), tri(*o*-tolyl)phosphine (P(*o*-tolyl)₃, 2.4 mg, 8 μmol) and chlorobenzene (3.0 mL) were added to a reaction vessel, which was sealed and refilled with argon. The

reaction mixture was heated at 160 °C for 45 min in a microwave reactor. After being cooled to room temperature, the reaction mixture was poured into 100 mL of methanol containing 5 mL of concentrated hydrochloric acid and stirred for 3 h. The precipitate was then subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular-weight fractions. The residue was extracted with chloroform, and concentrated solution was poured into 50 mL of methanol. The formed precipitates were collected by filtration and dried in vacuo to afford **PfBT4T-DT** (103.3 mg, 88%) as a metallic purple solid. GPC (*o*-DCB, 140 °C): $M_n = 23.9$ kDa, $M_w = 39.9$ kDa, PDI = 1.67.

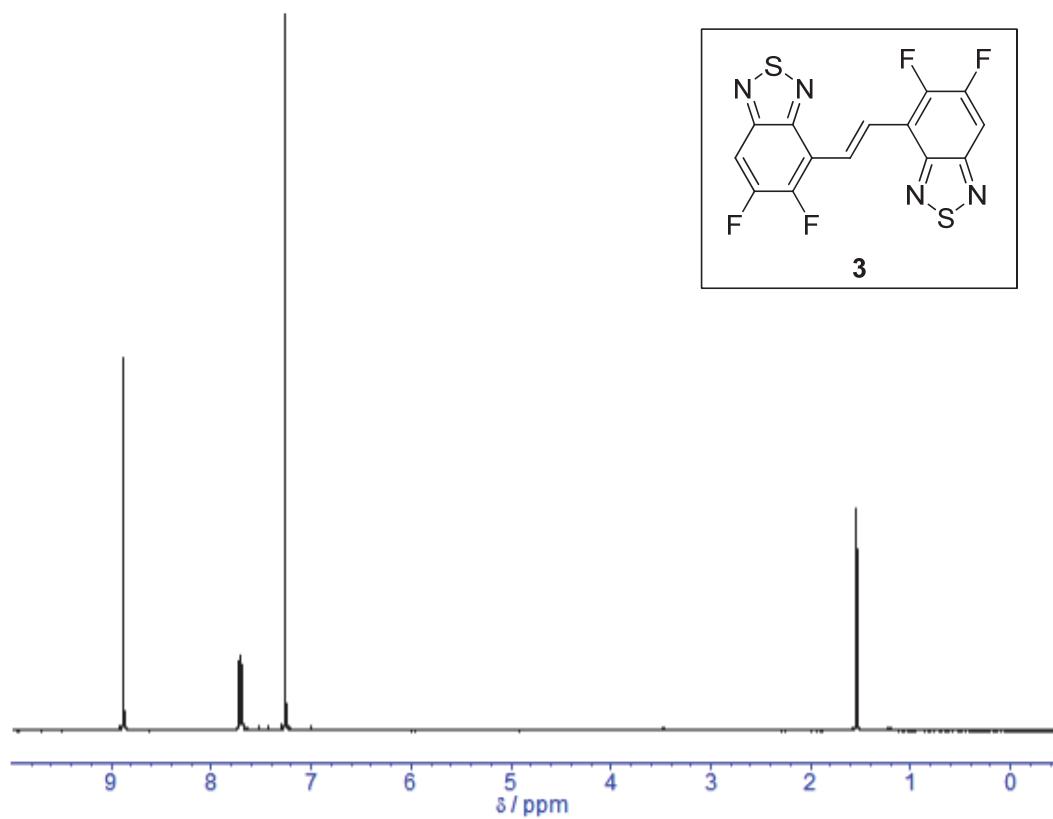
Table S1. Optimization of the Catalysts, Oxidants, and Additives in Dehydrogenative Coupling¹⁻³

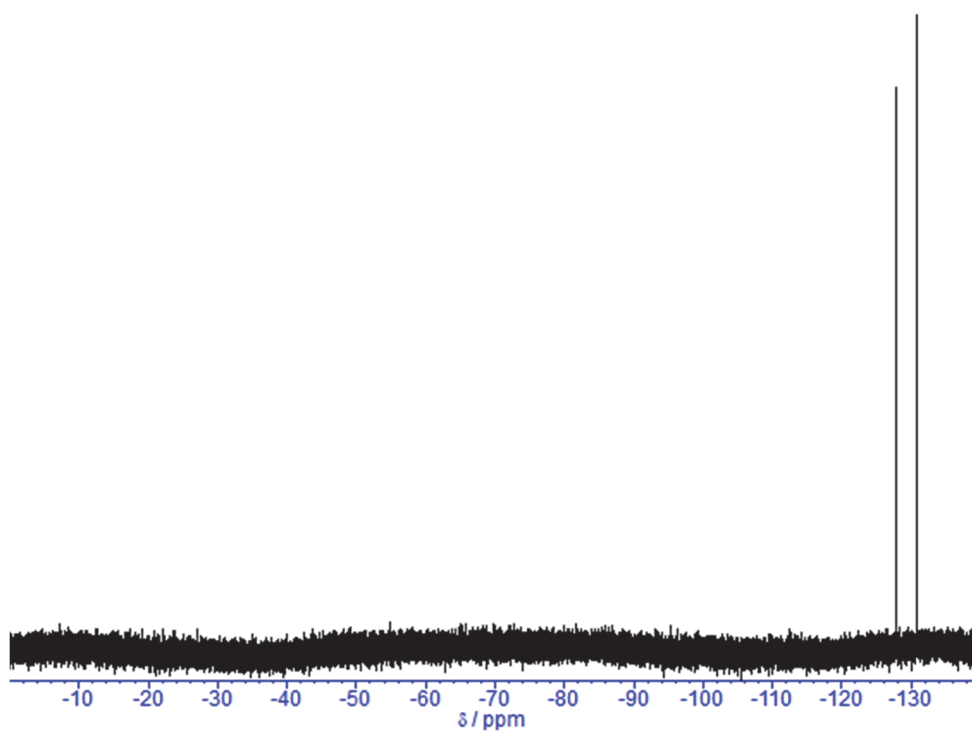
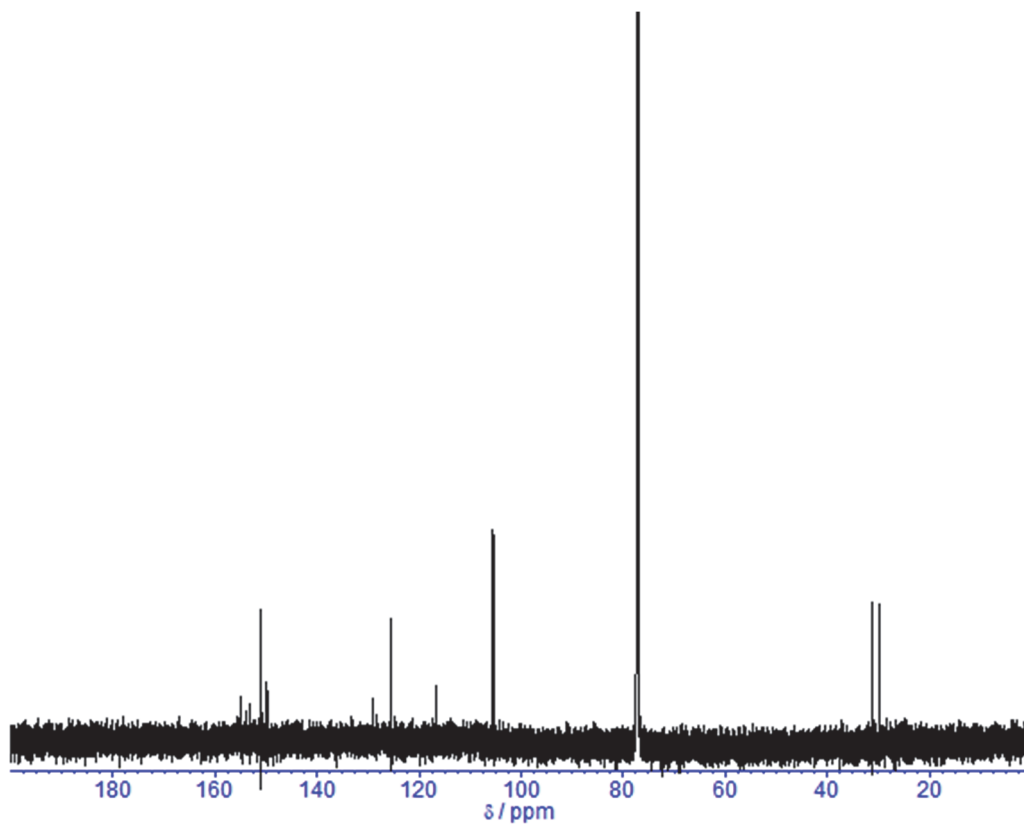


entry	Pd cat.	oxidant	additive	NMR yield (%)		
				5a	5a'	3
1 ^a	Pd(OAc) ₂	Ag ₂ O	none	11	63	37
2	Pd(OAc) ₂	Ag ₂ CO ₃	none	13	45	6
3	Pd(OAc) ₂	Ag ₂ CO ₃	AcOH	13	39	9
4	Pd(OAc) ₂	Ag ₂ CO ₃	PivOH	29	37	trace
5	Pd(OAc) ₂	Ag ₂ CO ₃	1-AdCOOH	13	9	2
6 ^b	Pd(OAc) ₂	Ag ₂ CO ₃	PivOH	22 (26 ^c)	32 (23 ^c)	3
7	Pd(OAc) ₂	Ag ₂ O	PivOH	26	39	1
8	Pd(tfa) ₂	Ag ₂ CO ₃	PivOH	33	33	trace
9	PdCl ₂ (NCPPh) ₂	Ag ₂ CO ₃	PivOH	33	27	trace
10	PdCl ₂ (PPh ₃) ₂	Ag ₂ CO ₃	PivOH	27	32	1
11^d	Pd(tfa) ₂	Ag ₂ CO ₃	PivOH	54 (51^c)	12	trace
12	Pd(OAc) ₂	AgOAc	2-methylpyridine	9	33	25

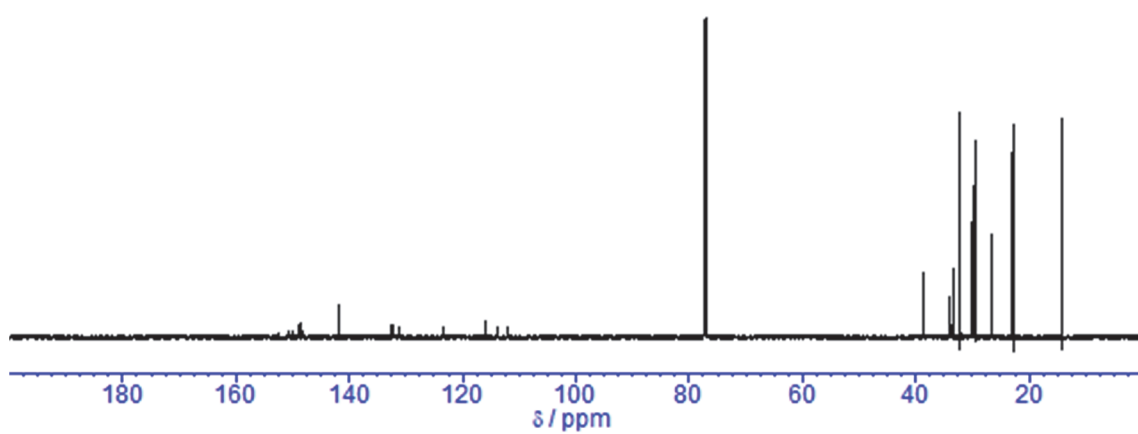
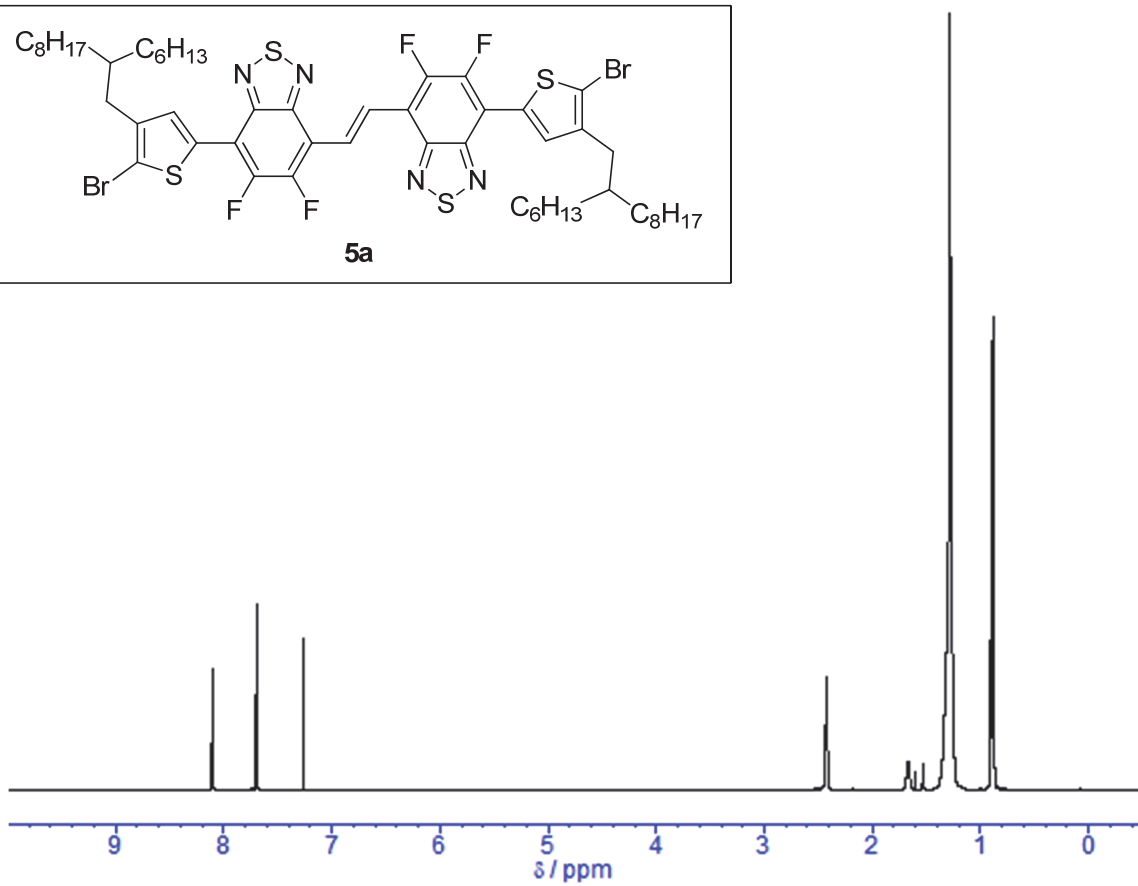
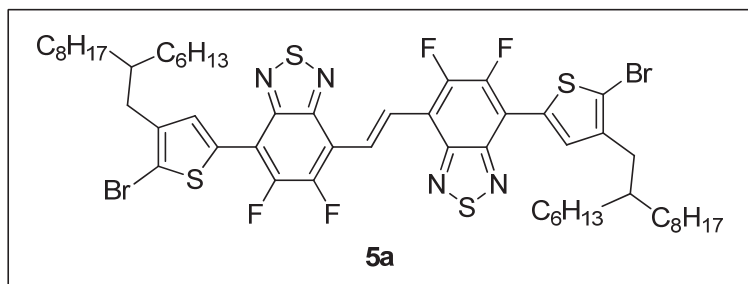
^aPd(OAc)₂ (5 mol %), 80 °C. ^bAdditional Pd(OAc)₂ (10 mol %) and **4a** (2 equiv) were added after 12 h. ^cAn isolated yields. ^dPd(tfa)₂ (20 mol %), Ag₂CO₃ (8 equiv), PivOH (6 equiv).

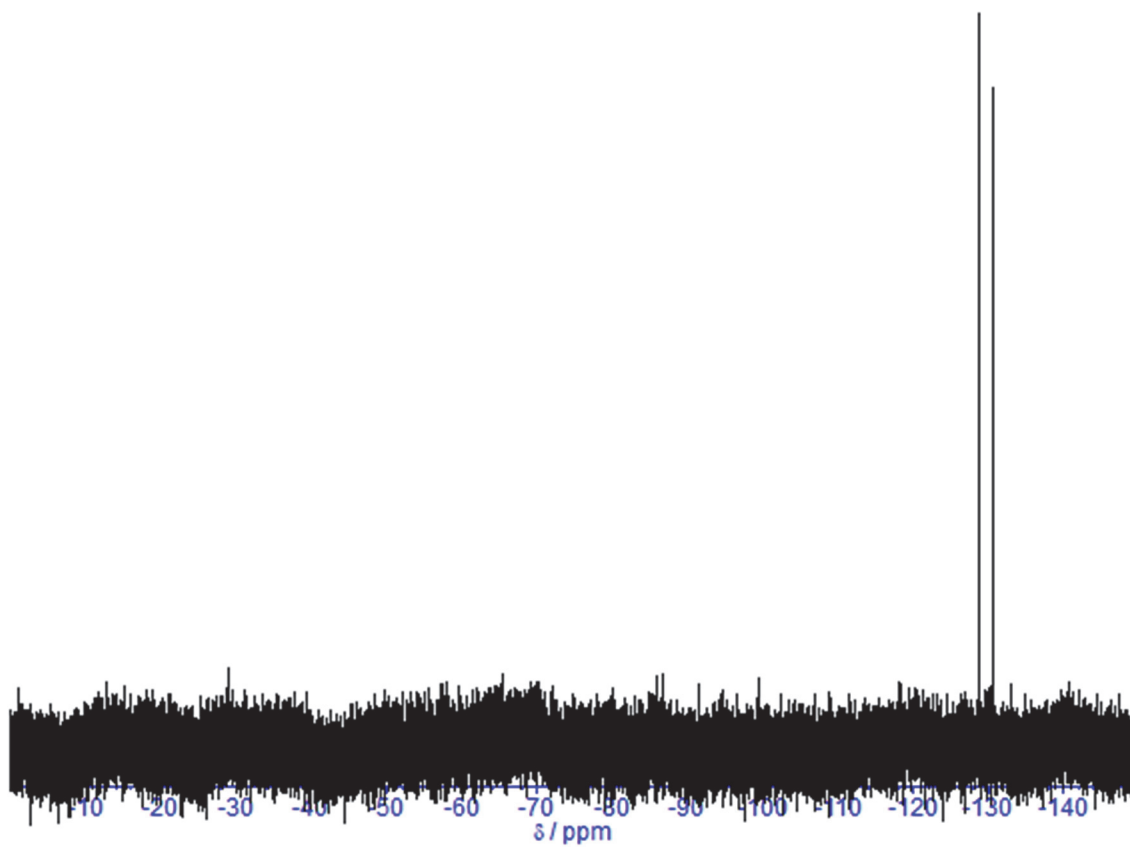
2. Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR Charts for the New Compounds



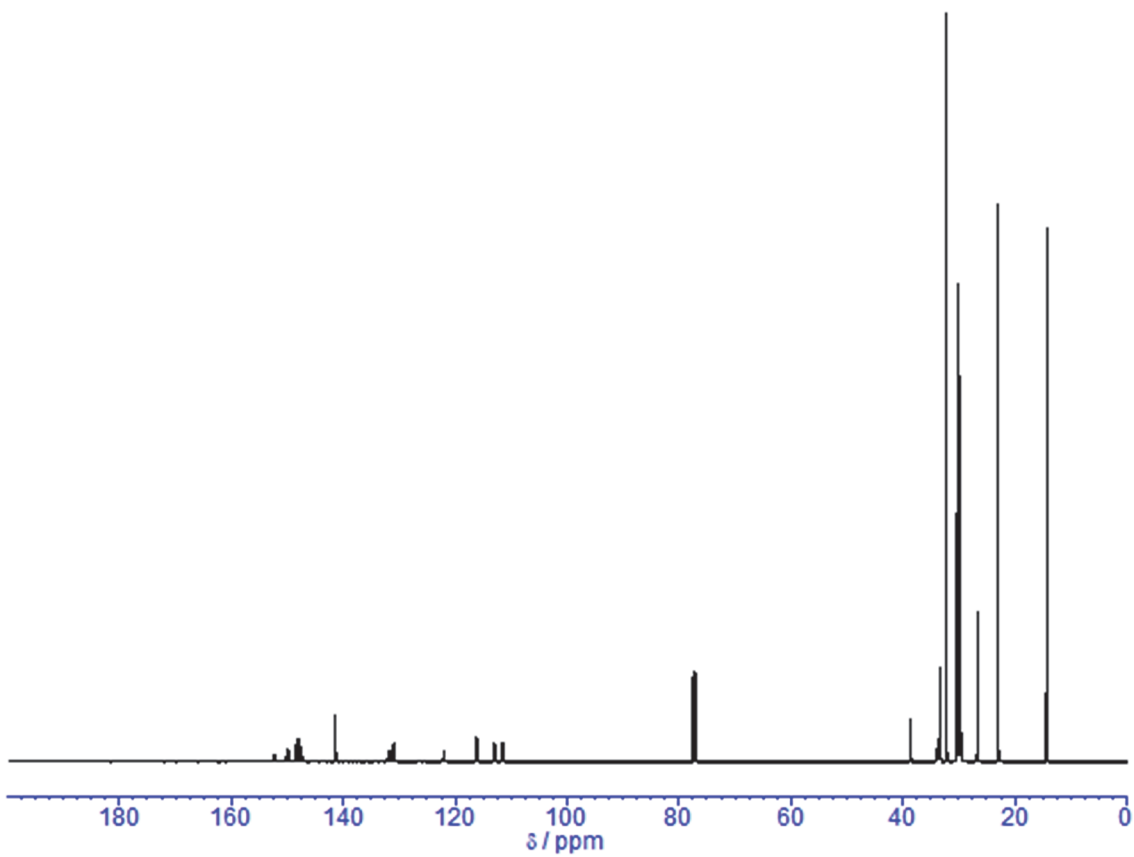
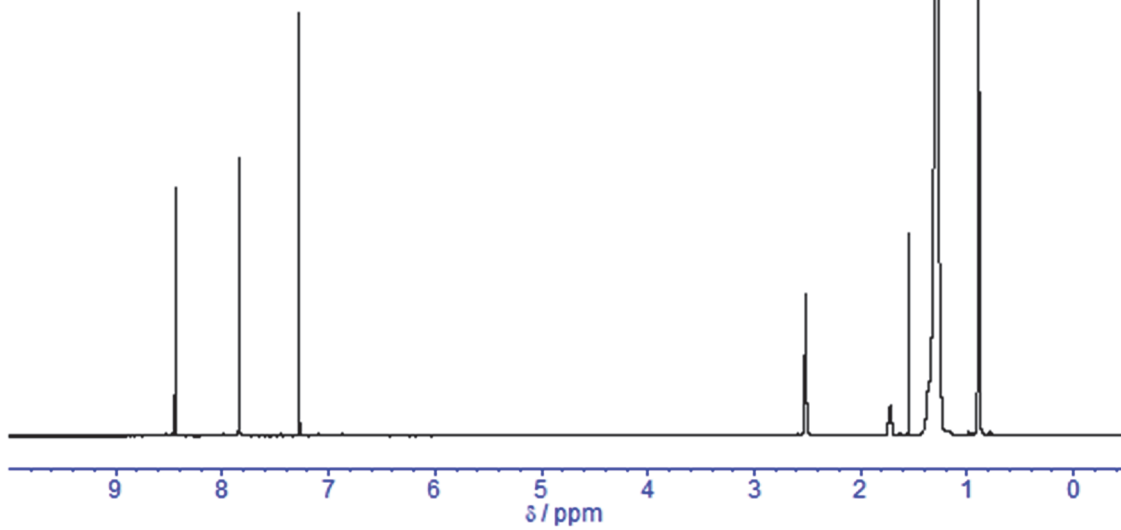
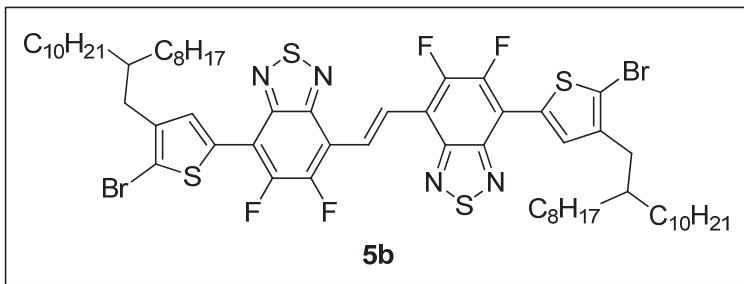


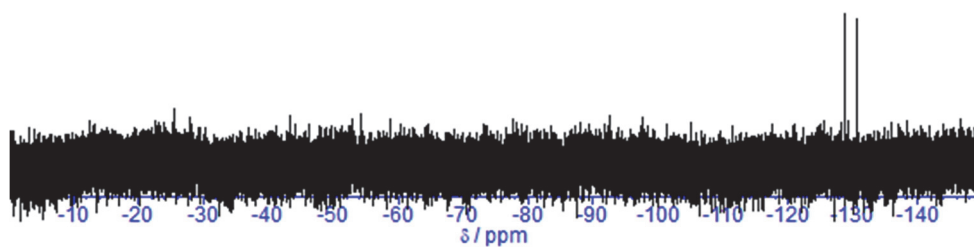
The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **3** (in CDCl_3).



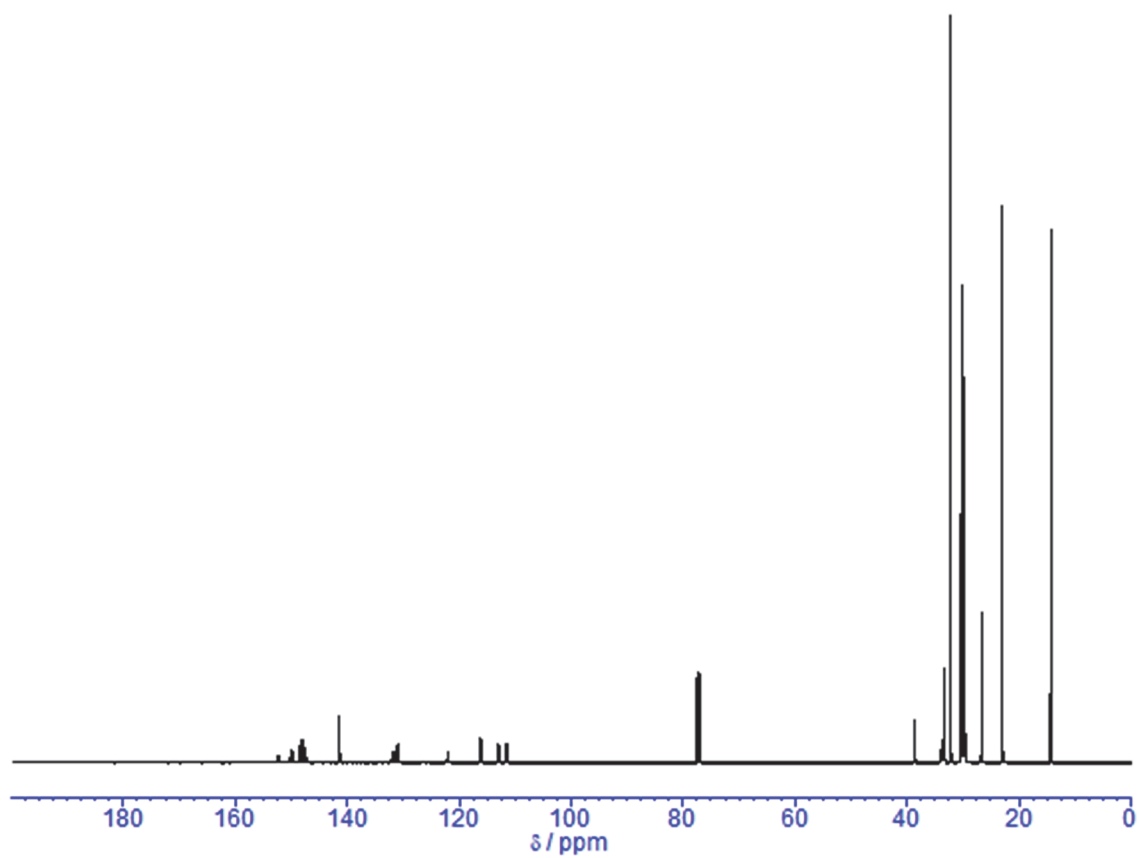
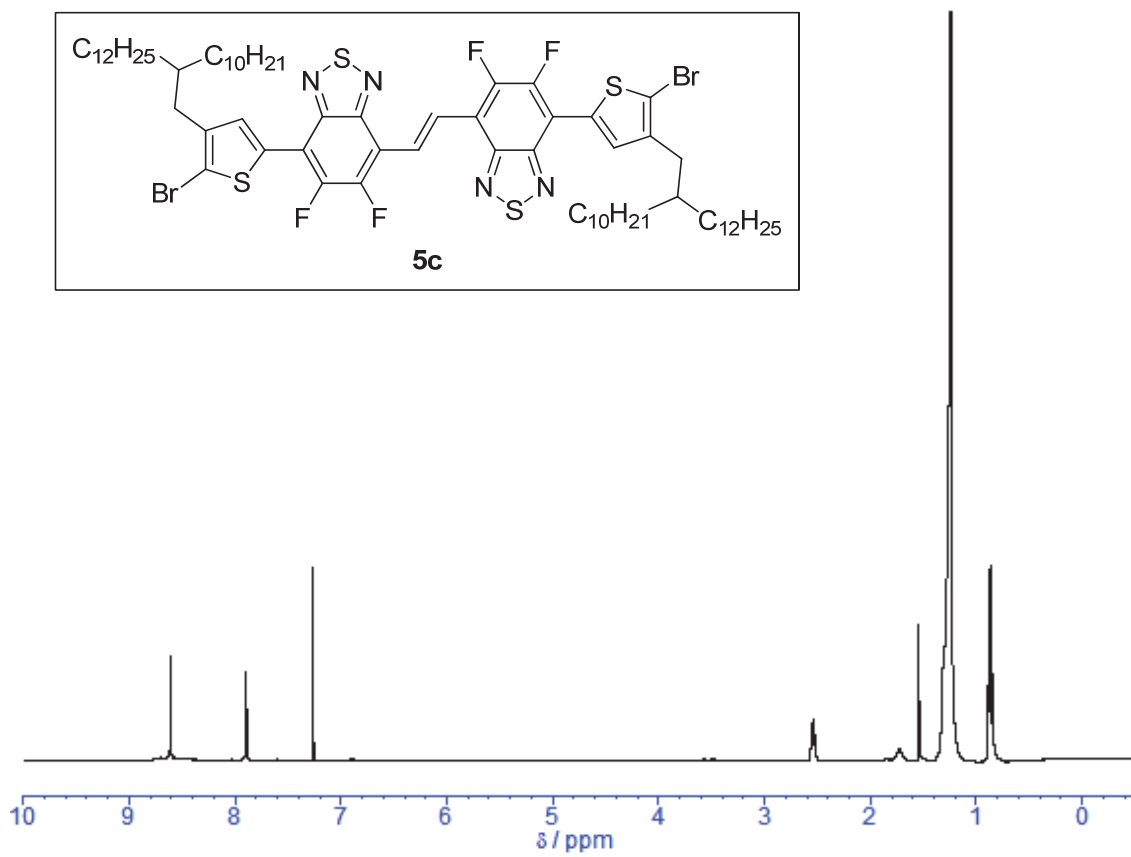
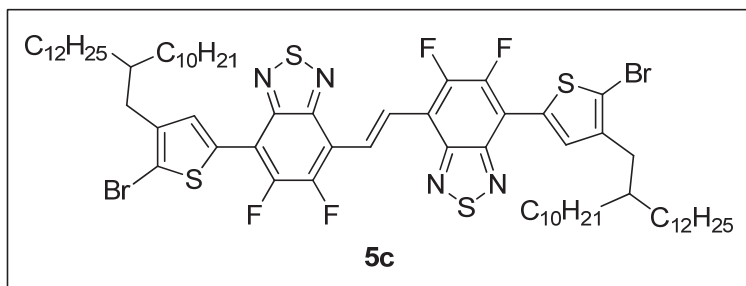


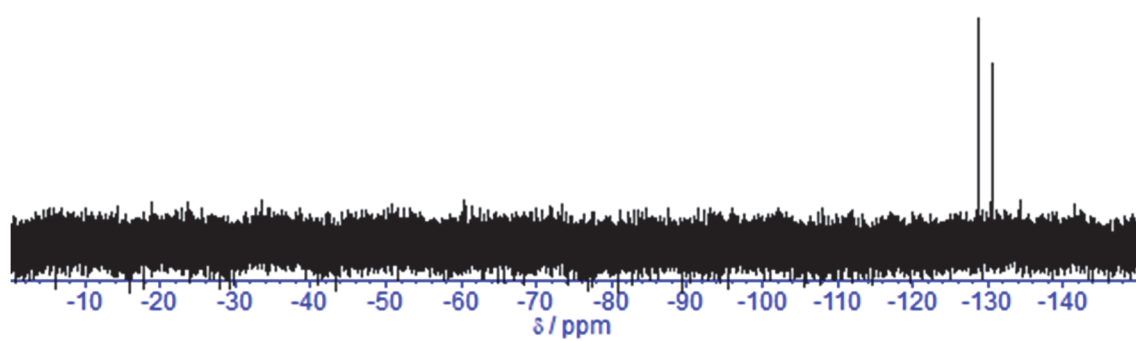
The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **5a** (in CDCl_3).



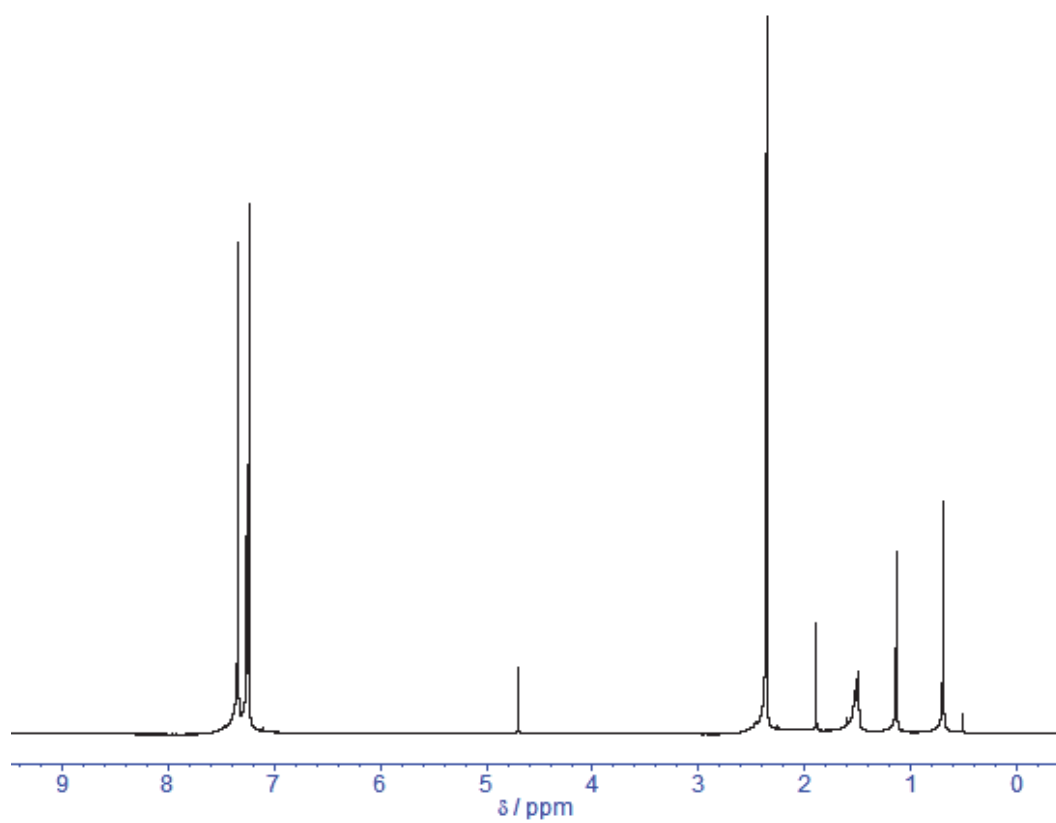
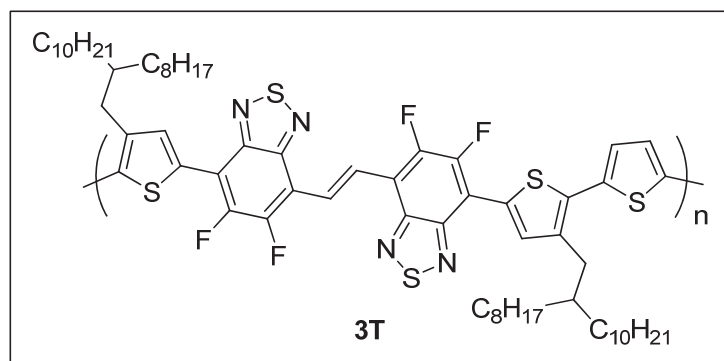


The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **5b** (in CDCl_3).

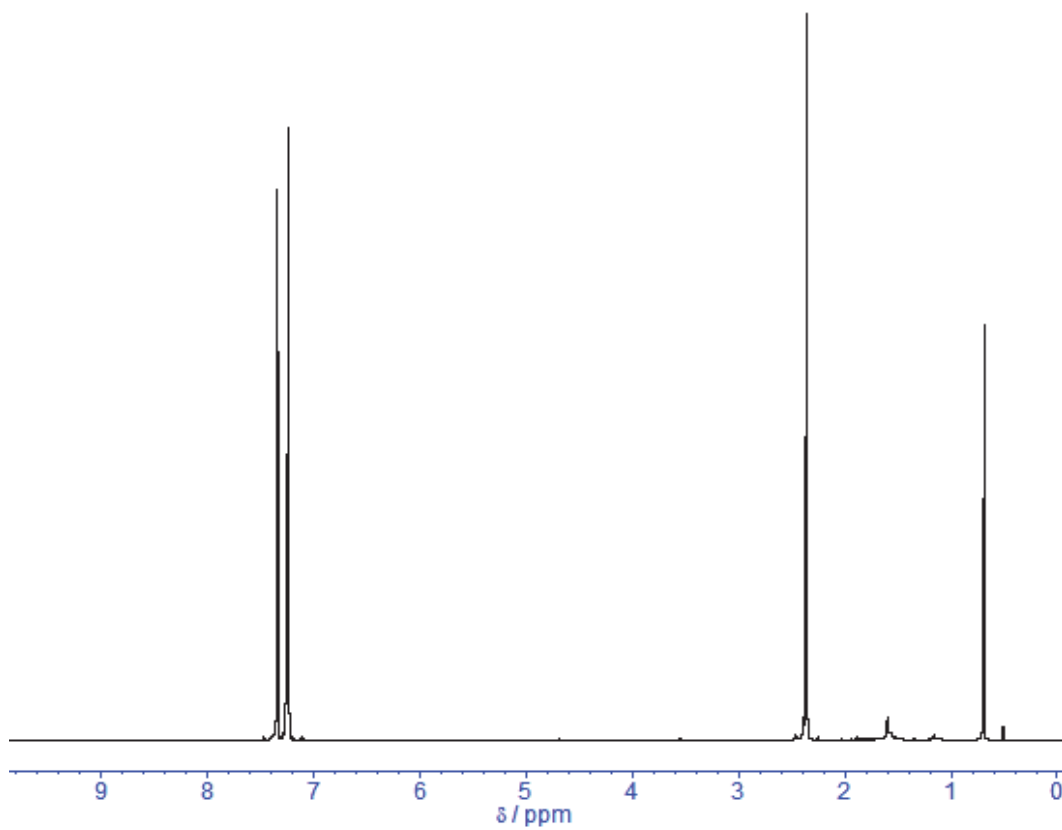
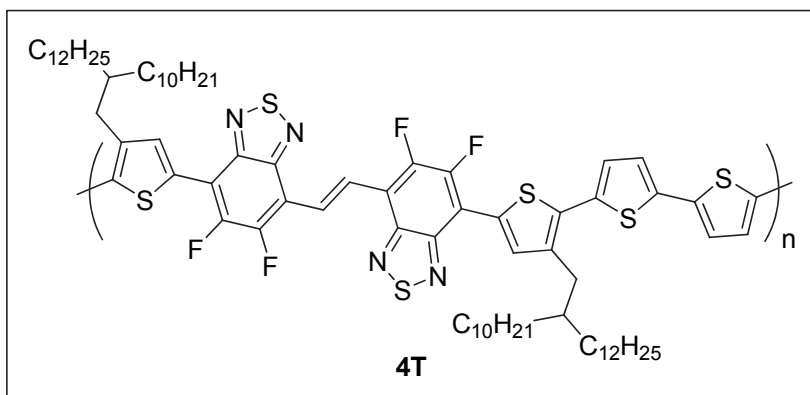




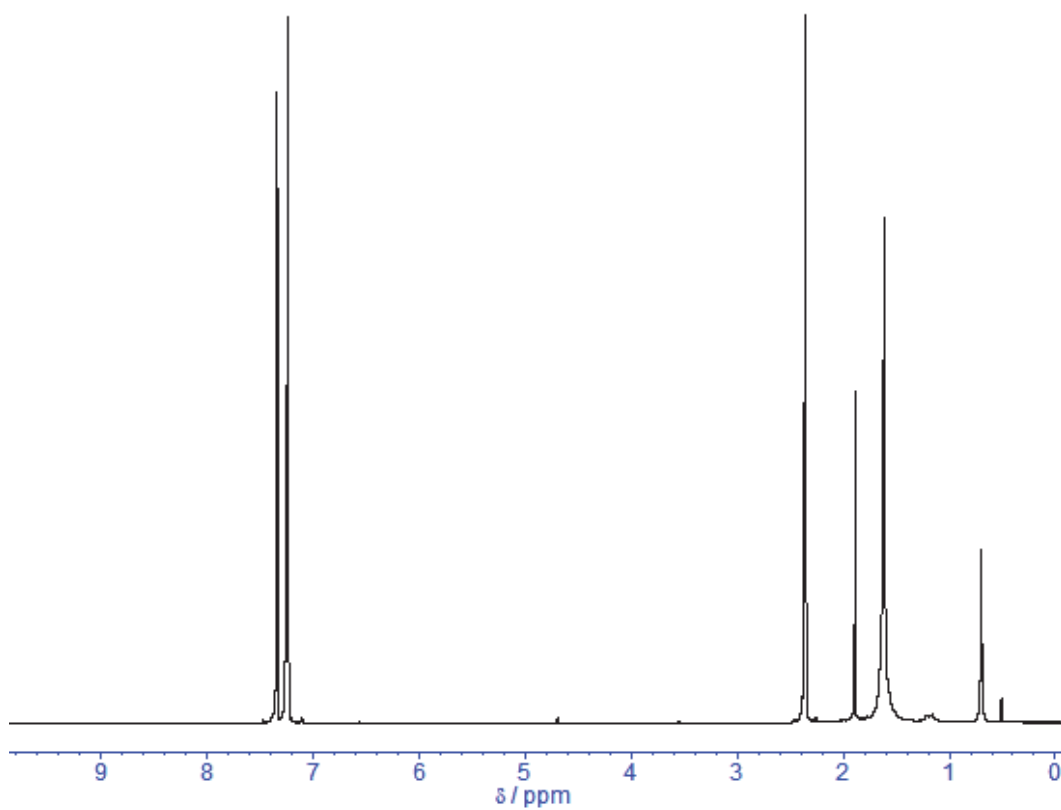
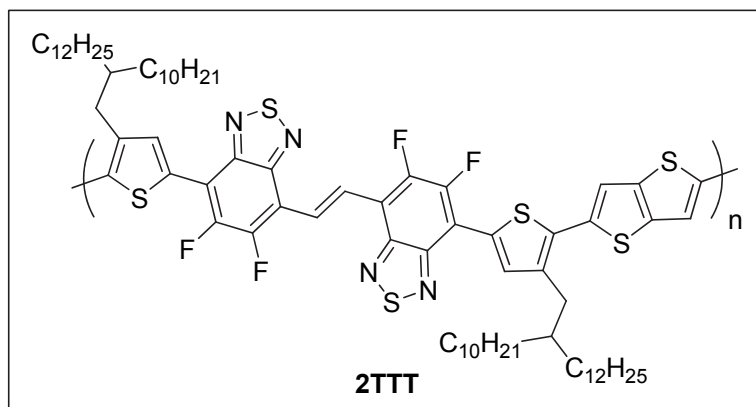
The ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of **5c** (in CDCl_3).



The ^1H NMR spectra of **3T** (in toluene- d_8 , 80 °C).



The ^1H NMR spectra of **4T** (in toluene- d_6 , 80 °C).



The ^1H NMR spectra of **2TTT** (in toluene- d_8 , 80 °C).

3. DFT Calculations of Model Compound of FBTzE Derivatives

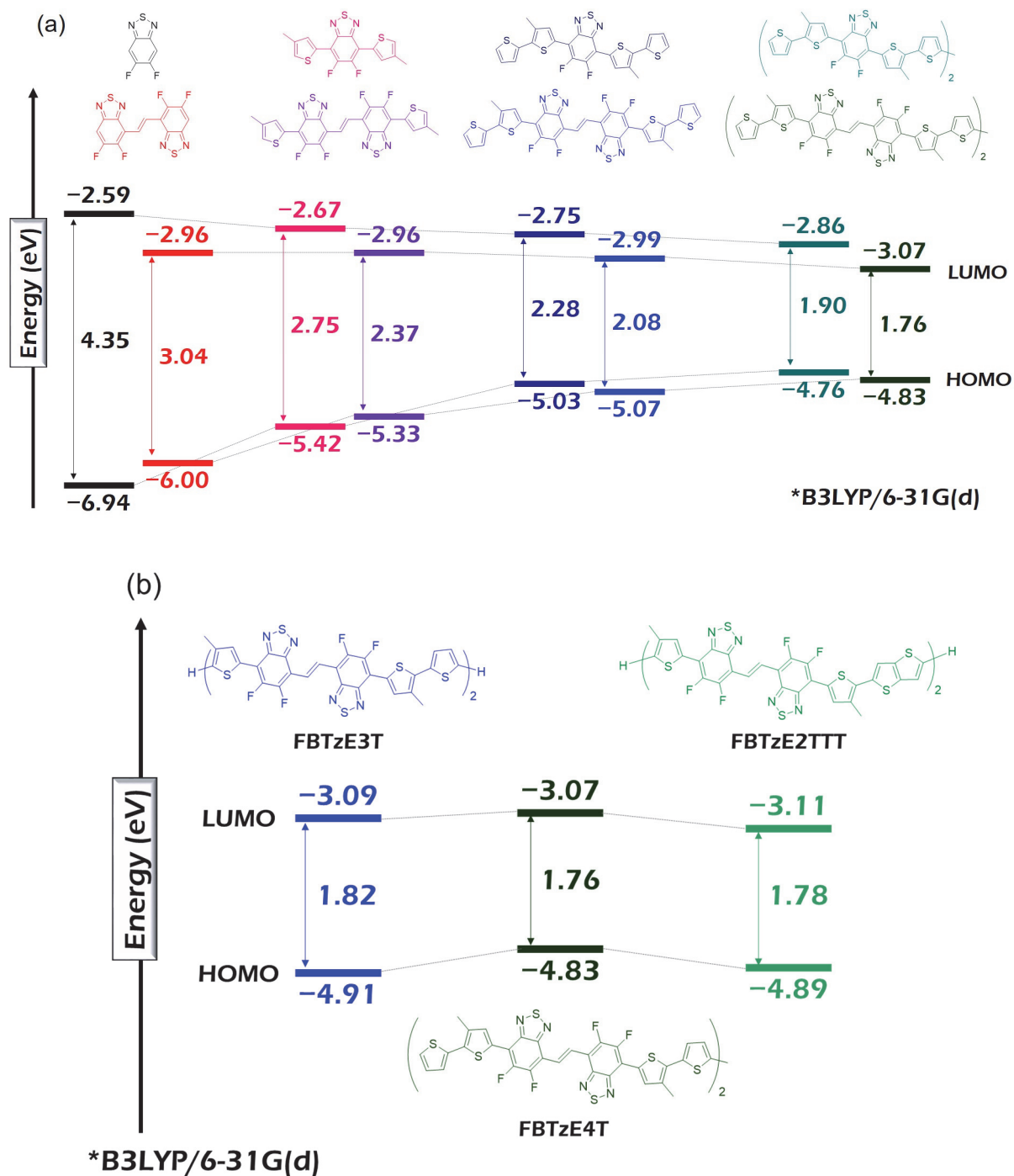


Figure S1. Energy diagrams calculated by using DFT at B3LYP/6-31G(d); (a) **DFBT** and **FBTzE** derivatives, and (b) dimer structure of model compound for **PFBTzE3T-OD (3T)**, **PFBTzE4T-DT (4T)**, and **PFBTzE2TTT-DT (2TTT)**.

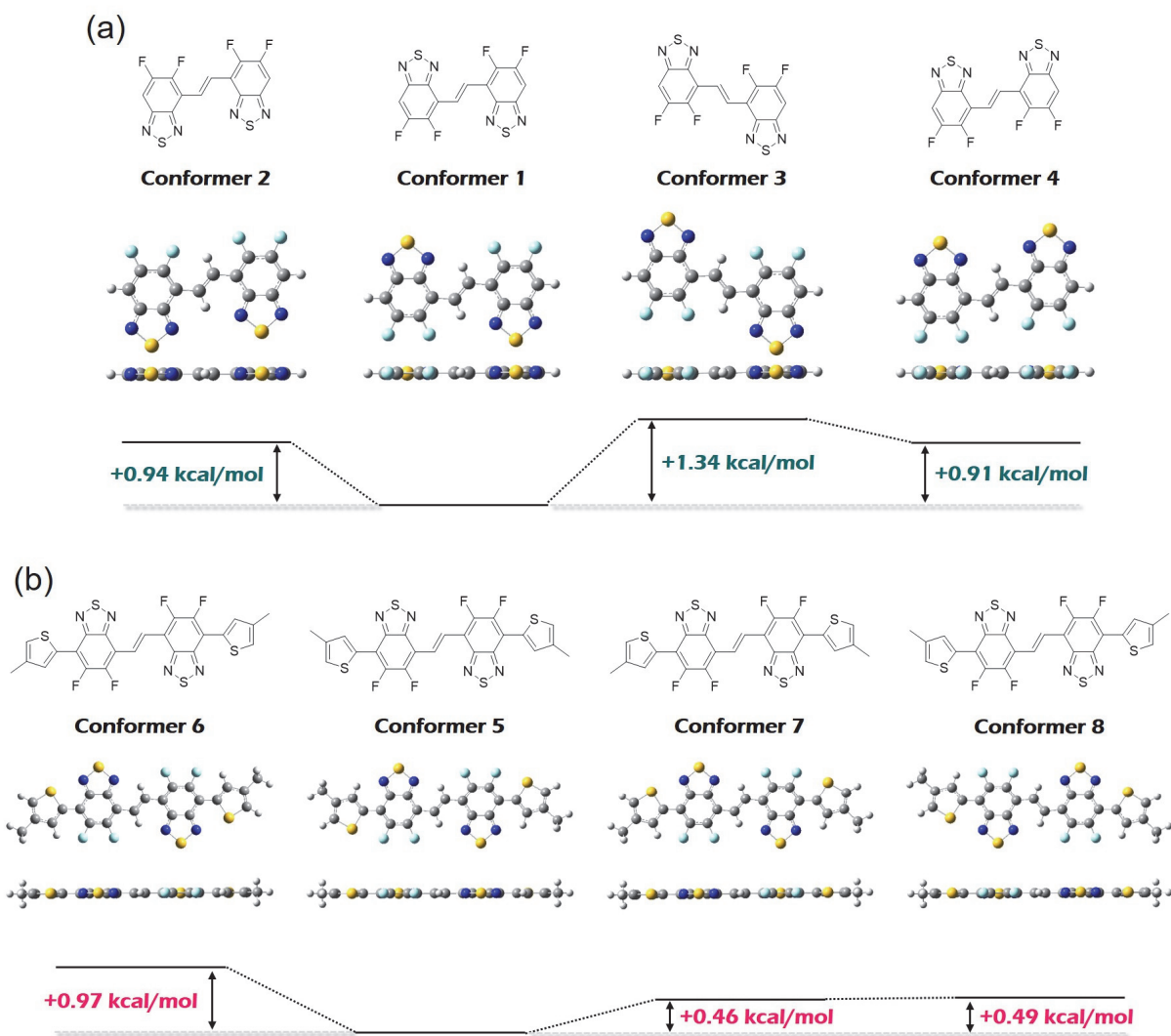


Figure S2. Four possible conformations of (a) **FBTzE** core and (b) bis(4-methylthienyl)**FBTzE** (**FBTzE2T**). Geometry optimization was performed by using DFT at B3LYP/6-31G(d).

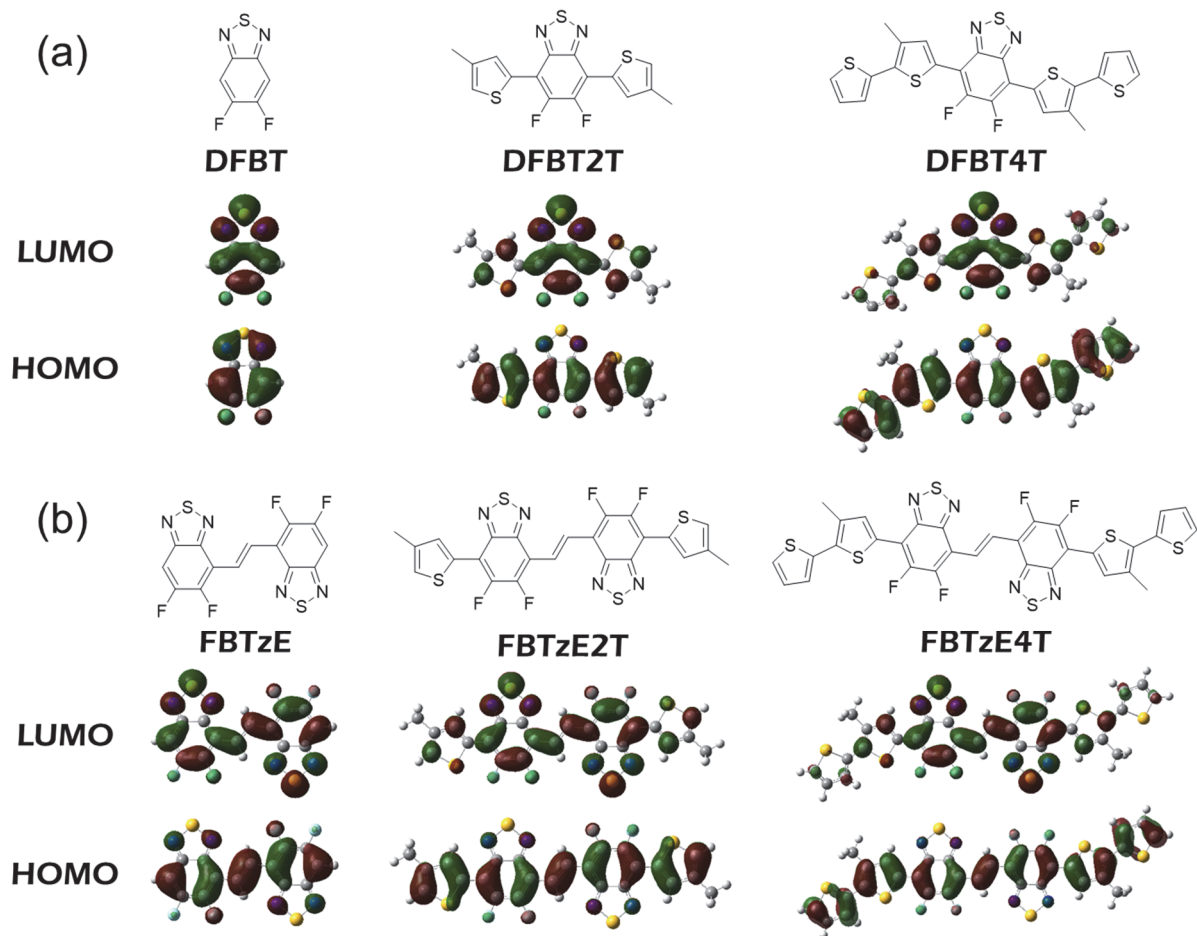
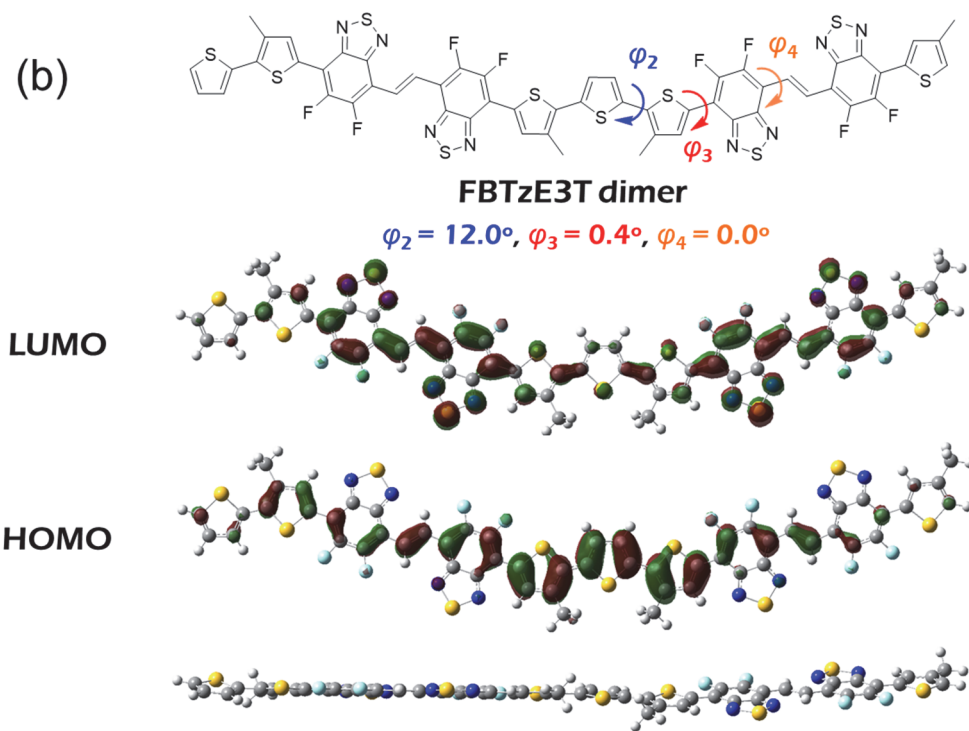
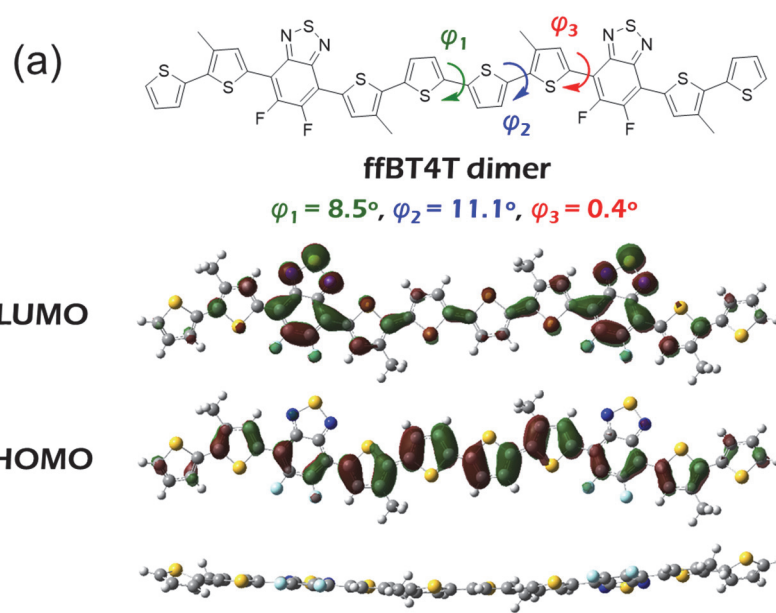


Figure S3. Geometry of HOMO and LUMO orbitals for (a) parent **DFBT**, and bis(alkylthienyl) **DFBT** derivatives (**DFBT2T** and **DFBT4T**), and (b) parent **FBTzE**, and bis(alkylthienyl) **FBTzE** derivatives (**FBTzE2T** and **FBTzE4T**) calculated by using DFT at B3LYP/6-31G(d).



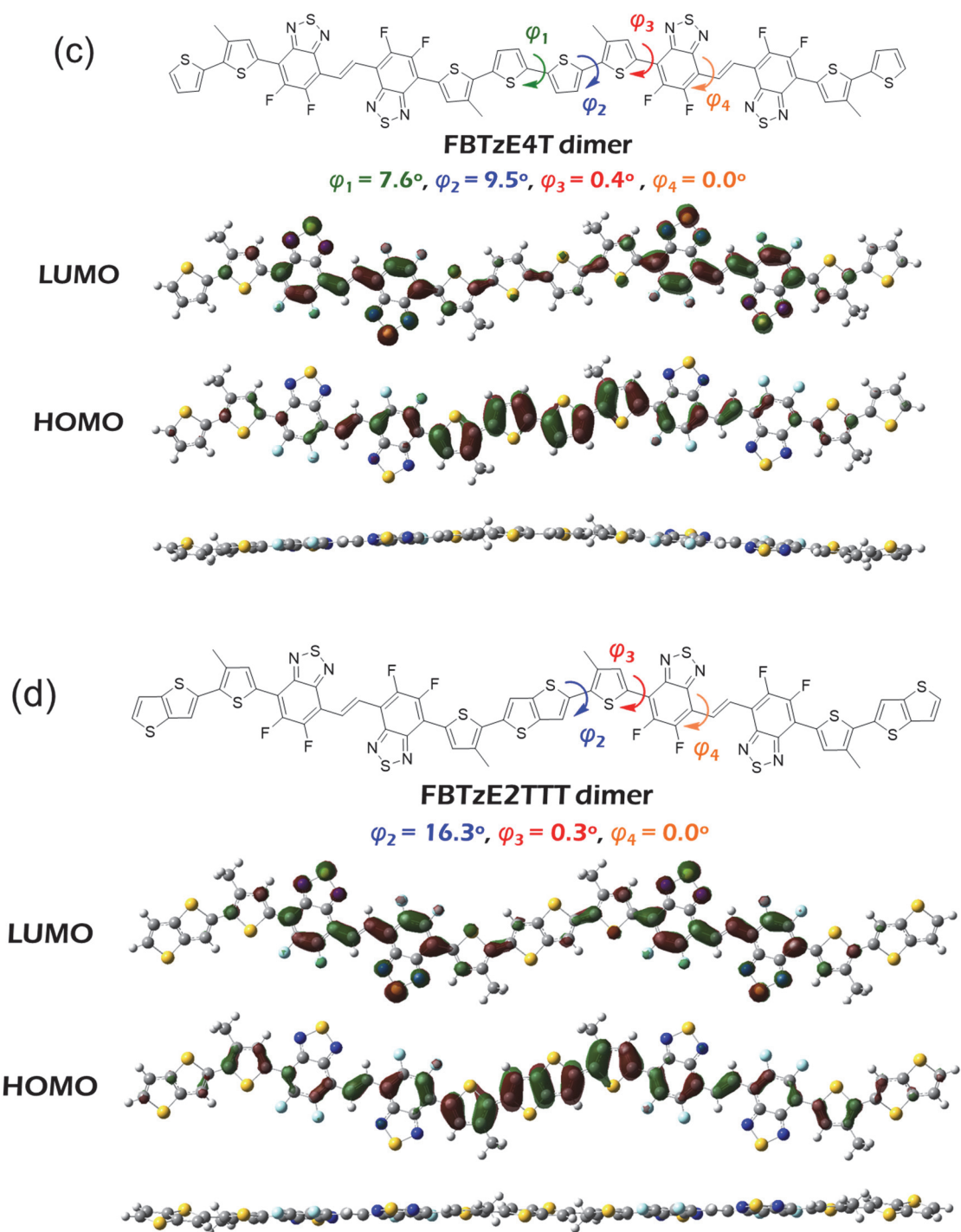


Figure S4. The optimized dimer structure of model compound for (a) **PffBT4T-DT**, (b) **PFBTzE3T-OD (3T)**, (c) **PFBTzE4T-DT (4T)**, and (d) **PFBTzE2TTT-DT (2TTT)** calculated by using DFT at B3LYP/6-31G(d). Branched alkyl chains were replaced with methyl groups, respectively, to simplify the calculation.

4. GPC Charts of FBTzE-Based Copolymers

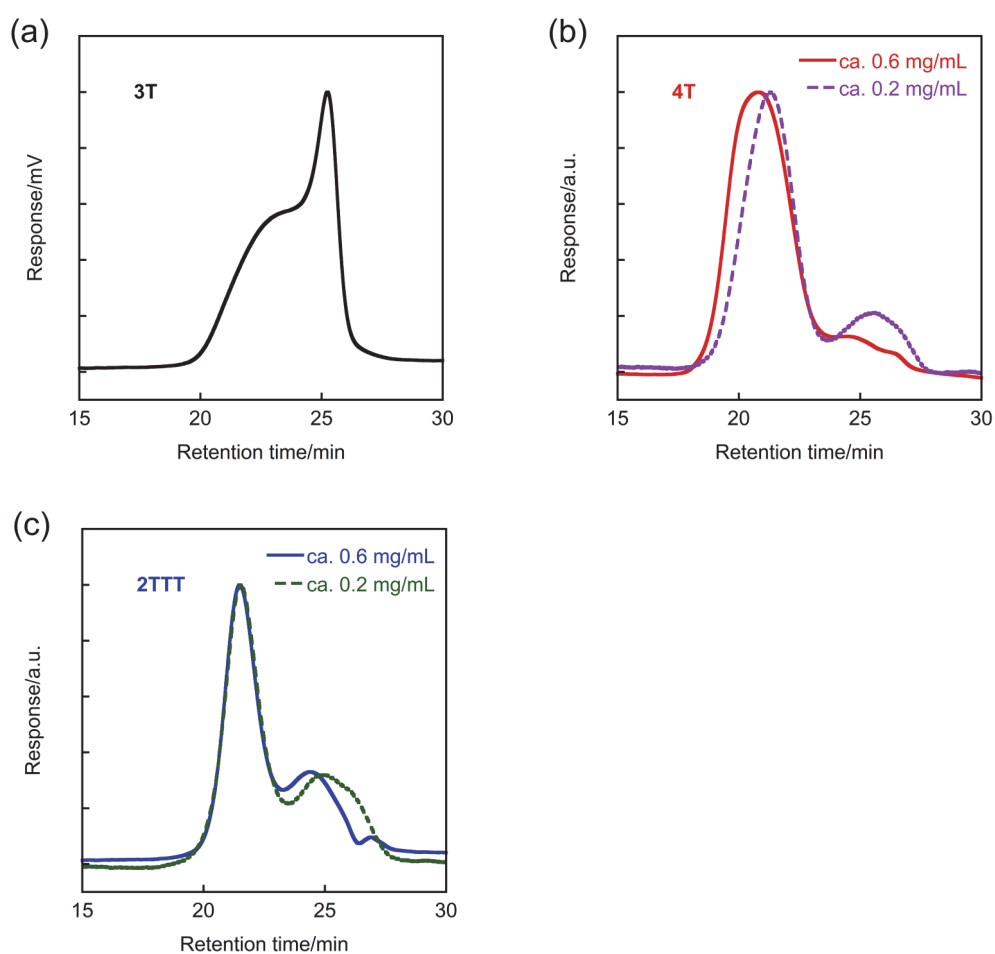


Figure S5. GPC charts of PFBTzEAr polymers; (a) 3T, (b) 4T, and (c) 2TTT.

Table S2. Molecular weights of PFBTzEAr

PFBTzEAr	Conc./mg mL ⁻¹ ^a	M _n /kDa ^b	PDI ^b	DP _n ^c
3T	0.6	46.9	1.98	40
4T	0.6	133.8	2.39	97
	0.2	71.4	3.32	52
2TTT	0.6	76.4	2.18	56
	0.2	53.6	2.98	40

^aConcentrations of polymer solution for the measurement of GPC. ^bDetermined by GPC measurements using polystyrene standards and *o*-dichlorobenzene (*o*-DCB) as the eluent at 140 °C. ^cDegree of polymerization (DP_n) based on the repeating unit.

5. Physicochemical Properties of Difluorobenzothiadiazole (DFBT) Derivatives and Copolymer

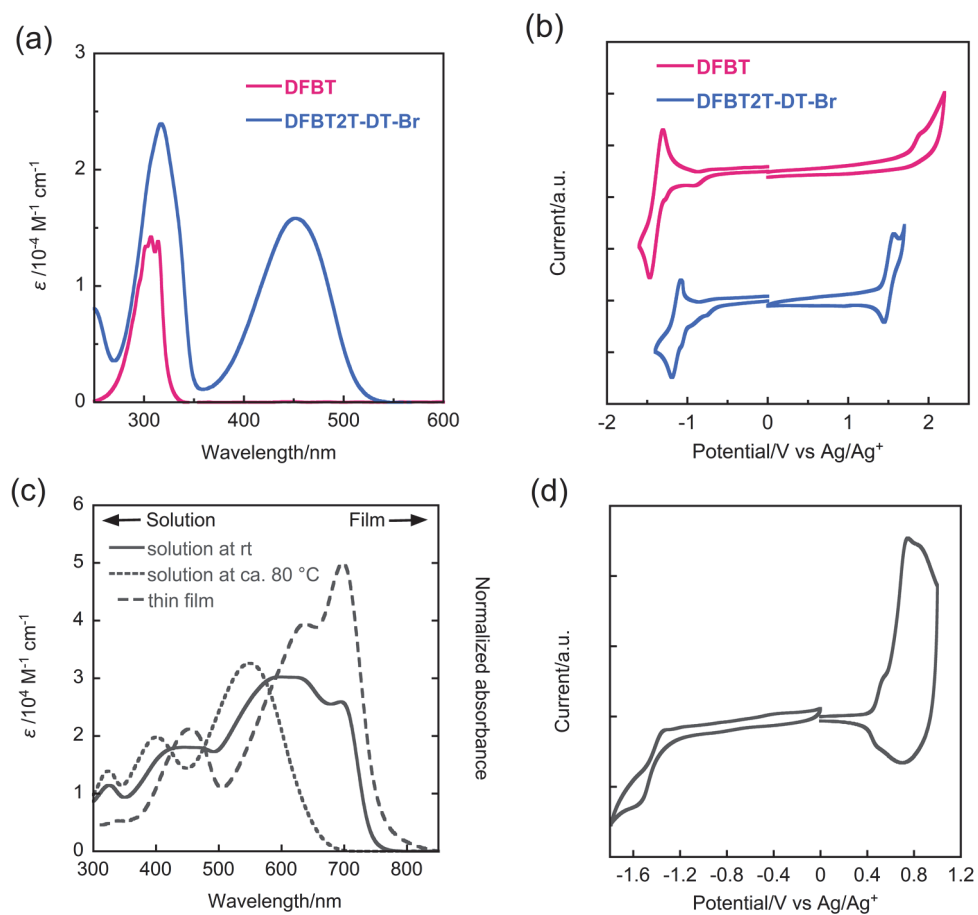


Figure S6. UV-vis absorption spectra of (a) **DFBT** derivatives in CH_2Cl_2 and (c) **PffBT4T-DT** in chlorobenzene and thin film, and cyclic voltammograms of (b) **DFBT** derivatives in CH_2Cl_2 and (d) **PffBT4T-DT** in thin films.

6. Temperature Dependence of UV-vis Absorption Spectra of PFBTzEAr in PhCl Solution

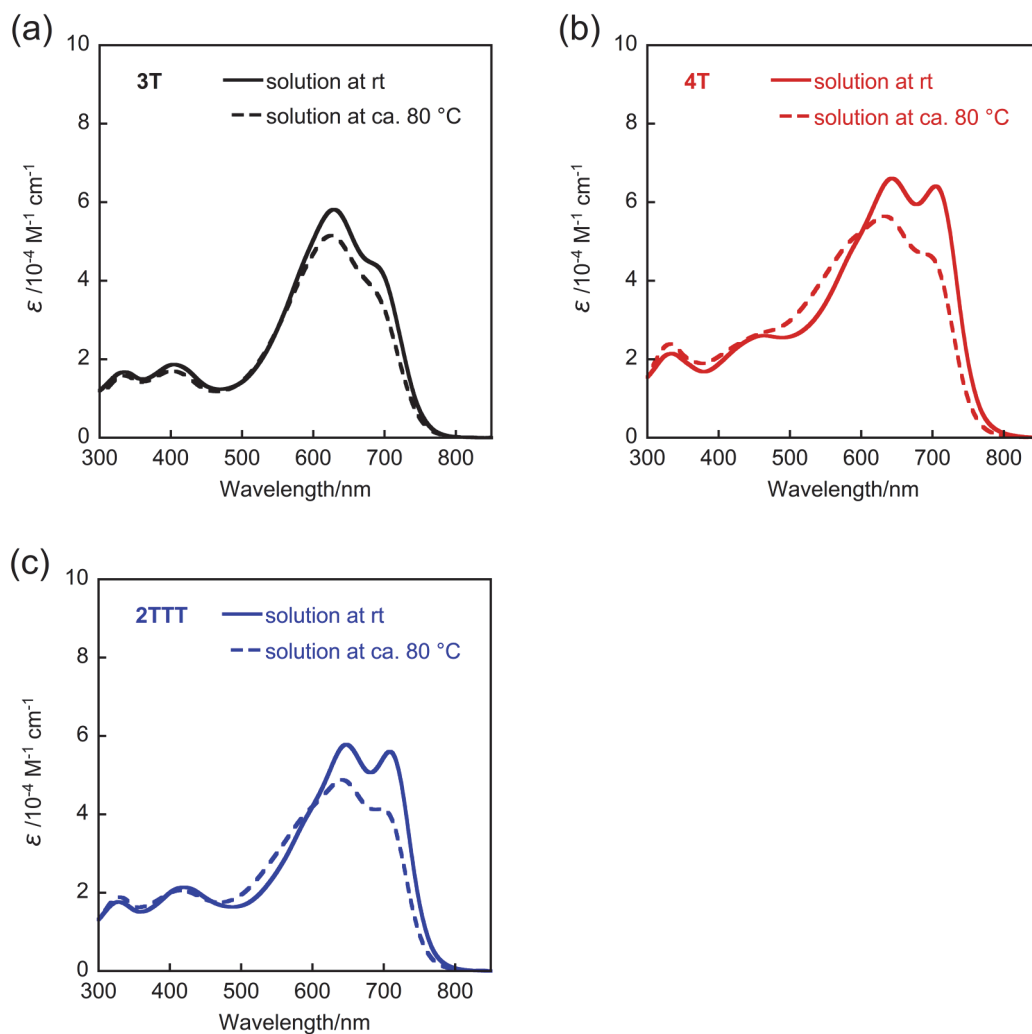


Figure S7. UV-vis absorption spectra of PFBTzEAr polymers in chlorobenzene solution; (a) 3T, (b) 4T, and (c) 2TTT.

Table S3. Optical Properties of PFBTzEAr in Chlorobenzene Solution

PFBTzEAr	$\lambda_{\max,rt}$ ($\lambda_{\max,heat}$)/nm ^a	ϵ_{rt} (ϵ_{heat})/10 ⁻⁴ M ⁻¹ cm ^{-1b}	λ_{edge} /nm ^c	E_g^{opt} /eV ^d
3T	629, 693 (625, 687 [sh])	5.82, 4.36 (5.15, 3.78)	781	1.59
4T	643, 704 (633, 701 [sh])	6.61, 6.41 (5.64, 4.58)	800	1.55
2TTT	648, 708 (642, 696)	5.78, 5.60 (4.88, 4.13)	790	1.57

^aAbsorption maxima in chlorobenzene solution at rt (out of parentheses) and at ca. 80 °C (in parentheses). ^bMolar absorption coefficient in chlorobenzene solution at rt (out of parentheses) and at ca. 80 °C (in parentheses). ^cAbsorption edge (λ_{edge}) in chlorobenzene solution at rt. ^dOptical energy gap in chlorobenzene solution at rt estimated from λ_{edge} .

7. Photovoltaic Properties of PFBTzEAr-Based OPVs

Table S4. Solar Cell Performances of Polymer/PC₆₁BM-based Devices

PFBTzEAr	p/n ratio ^a	solvent ^b	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	PCE _{max} (PCE _{avg})/%
3T	1:1	CB	2.92	0.87	0.35	0.87 (0.83)
	1:2	CB	2.09	0.95	0.39	0.76 (0.68)
	1:1	CB+1 vol% DIO	4.08	0.86	0.42	1.48 (1.42)
	1:1	CB+1 vol% DPE	4.86	0.87	0.41	1.73 (1.50)
	1:1	CB+2.5 vol% DPE	7.00	0.88	0.43	2.66 (2.60)
	1:1	DCB	4.11	0.87	0.41	1.46 (1.32)
4T	1:1	CB	<i>no photovoltaic response</i>			
	1:1	CB+ 1 vol% DIO	<i>no photovoltaic response</i>			
2TTT	1:1	CB	8.36	0.79	0.47	3.09 (2.97)
	1:1	DCB	9.38	0.80	0.49	3.70 (3.37)
	1:2	DCB	9.79	0.80	0.50	3.92 (3.67)
	1:2	CB+2 vol% DIO	11.02	0.78	0.42	3.65 (3.46)
	1:2	CB+2 vol% CN	9.59	0.82	0.61	4.80 (4.58)
	1:2	CB+1 vol% DPE	10.31	0.81	0.59	4.89 (4.39)
	1:2	CB+2 vol% DPE	9.62	0.81	0.65	5.12 (4.83)
	1:2	CB+4 vol% DPE	11.47	0.80	0.57	5.23 (5.09)

^aWeight ratios of polymers and PC₆₁BM. ^bCB = chlorobenzene. DCB = *o*-dichlorobenzene. DIO = 1,8-diiodooctane. DPE = diphenyl ether. CN = 1-chloronaphthalene.

Table S5. Substrate Temperature Dependence of Solar Cell Performances in Polymer/PC₆₁BM-based Devices

PFBTzEAr	Substrate temp./°C ^a	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\text{PCE}_{\text{max}} (\text{PCE}_{\text{avg}})/\%$
3T^b	rt	7.00	0.88	0.43	2.66 (2.60)
	70	3.40	0.86	0.42	1.22 (1.15)
	140	1.85	0.84	0.30	0.47 (0.41)
2TTT^c	rt	11.35	0.79	0.55	4.92 (4.62)
	140	11.47	0.80	0.57	5.23 (5.09)

^aThe substrates were preheated on hot plate before the spin-coating. ^bFor **3T**, the polymer/PC₆₁BM blend ratio is 1:1 (w/w), solvent = chlorobenzene (CB) + 2.5 vol% diphenyl ether (DPE). ^cFor **2TTT**, the polymer/PC₆₁BM blend ratio is 1:2 (w/w), solvent = CB + 4 vol% DPE.

8. SCLC Hole Mobility of PFBTzEAr-Based Hole-Only Devices

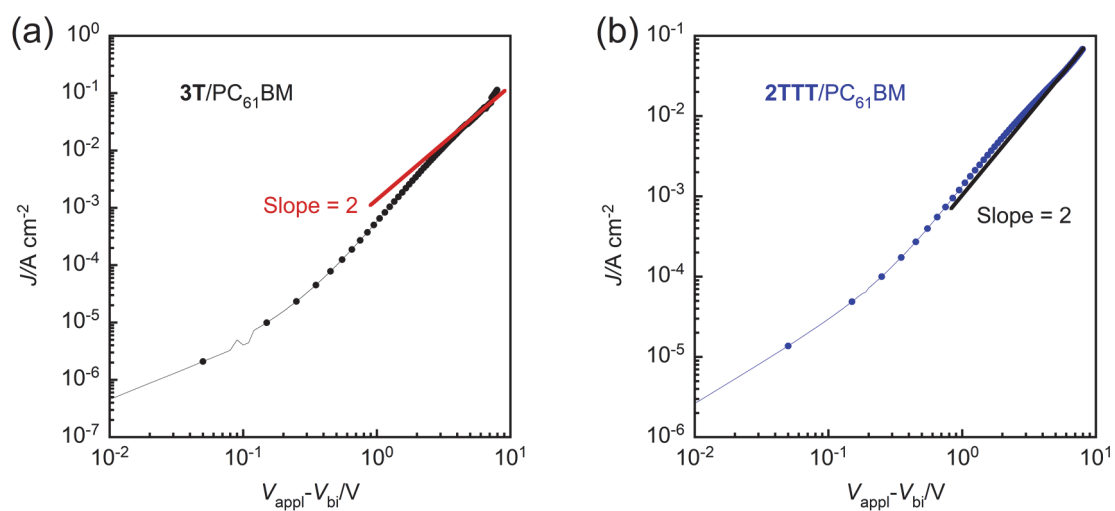


Figure S8. J - V characteristics of PFBTzEAr-based hole-only devices with configuration of ITO/(PEDOT:PSS)/(polymer:PC₆₁BM)/MoO₃/Al; (a) 3T and (b) 2TTT. The thickness of active layer is 240 nm for 3T, and 220 nm for 2TTT.

9. The Calculated Interlayer Distances of PFBTzEAr and Blended Films with PC₆₁BM

Table S5. The calculated interlayer distances of pure polymer and blended films with PC₆₁BM.

compound	$q/\text{\AA}^{-1}$	$d_{\text{im}}/\text{\AA}$	$q/\text{\AA}^{-1}$	$d_{\pi}/\text{\AA}$
3T	0.300	20.9	1.777	3.54
3T/PC₆₁BM	0.298	21.1	1.760	3.57
2TTT	0.298	21.1	1.805	3.48
2TTT/PC₆₁BM	0.292	21.5	1.800	3.49

10. References

1. C.-Y. He, C.-Z. Wu, Y.-L. Zhu and X. Zhang, *Chem. Sci.*, 2014, **5**, 1317–1321.
2. C.-Y. He, S. Fan and X. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 12850–12852.
3. X. Zhang, S. Fan, C.-Y. He, X. Wan, Q.-Q. Min, J. Yang and Z.-X. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 4506–4507.