Supporting Information

New fused conjugated molecules with fused thiophene and pyran units for organic electronic materials

Daoliang Chen, [a,b] Danlei Zhu, [a,b] Gaobo Lin, [a,b] Mingxu Du, [a] Dandan Shi, [a,b] Qian Peng, [a] Lang Jiang, [a] Zitong Liu, [a] Guanxin Zhang, [a] Deqing Zhang* [a,b]

Table of Contents

1. Experimental section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Fourier 300, AVANCE III 400 MHz and 500 MHz spectrometers. High resolution mass spectra (HRMS) were determined on Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF) and electrospray ionization mass spectrometry (ESI-MS). Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. TGA-DTA measurements from 30 °C to 600 °C were carried out on a Shimadzu DTG-60 instrument under dry nitrogen flow with a heating rate of 10 °C/min. Jasco V-570 UV-vis spectrophotometer was utilized to measure the solution and thin-film absorption spectra, while a Hitachi (F4500) spectrophotometer was used to record the solution and solid state fluorescence spectra at 25°C. Fluorescence quantum yields and fluorescence lifetimes were measured with a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus QY and the compact fluorescence lifetime spectrometer C11367 of Hamamatsu, respectively. PL images were recorded with an Olympus research inverted system microscope equipped with a CCD camera; a mercury lampequipped with a band pass filter (λ = 330-380 nm) was utilized as the excitation source. Cyclic voltammograms were measured on computer controlled CHI660C instruments at room temperature; the measurements were performed in a conventional three-electrode cell using a Pt working electrode, a Pt counter electrode, and a Ag/AgCl (saturated KCl) reference electrode, and n-Bu_4NPF_6 (0.1 M) as the supporting electrolyte with a scan rate of 100 $mV \cdot s^{-1}$. To calibrate the redox potentials, the cyclic voltammogram of ferrocene was measured under the same conditions. Single crystals of **TTCTTC** and **TTTCTTTC** was cultivated by slowly cooling their hot solutions in toluene. The diffraction data of single crystals were collected on a Rigaku Saturn diffractometer with a CCD area detector. All calculations were performed with the SHELXS-97 programs. Crystallographic data for the structure reported in this paper were deposited in the Cambridge Crystallographic Data Centre (CCDC: 1963694 for compound **TTCTTC**, 1975874 for compound **TTTCTTTC**). X-ray diffraction (XRD) patterns of the thin films were carried out in the reflection mode at room temperature using a 2 kW Rigaku X-ray diffraction system.

2. TGA analysis

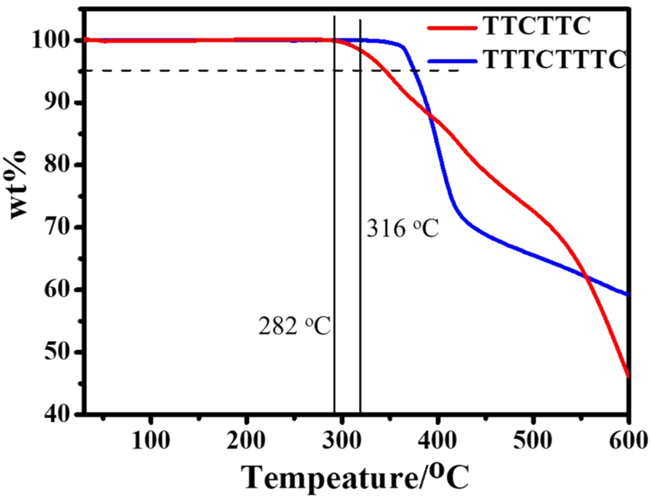

Figure S1. TGA curves of **TTCTTC** and **TTTCTTTC** from 30-600 ^{o}C.

3. X-ray crystallographic data of TTCTTC and TTTCTTTC.

Table S1. X-ray crystallographic data of **TTCTTC** and **TTTCTTTC**

Compound	**TTCTTC**	**TTTCTTTC**
CCDC No.	1963694	1975874
Empirical formula	$C_{38}H_{40}O_2S_4$	$C_{42}H_{40}O_2S_6$
Formula weight	656.94	769.10
Temperature	170.00(11) K	170.00(12) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions	a = 5.34500(10) Å	a = 8.1600(3) Å
	α = 101.923(2) °	α = 87.738(3) °
	b = 8.3039(2) Å	b = 8.4682(4) Å
	β = 93.255(2) °	β = 87.241(3) °
	c = 18.8962(4) Å	c = 13.9854(5) Å
	γ = 98.322(2) °	γ = 71.942(4) °
Volume	808.70(3) $Å^3$	916.0(3) $Å^3$
Z, Calculated density	1, 1.349 Mg/m^3	1, 1.392 Mg/m^3
Absorption coefficient	2.959 mm^{-1}	3.731
F(000)	348	404
Crystal size	0.2 x 0.05 x 0.05 mm^3	0.23 × 0.07 × 0.01
Theta range for data collection	4.798 to 150.886°	6.33 to 151.146°
Limiting indices	-6≤h≤5, -10≤k≤10, -23≤l≤23	-10 ≤ h ≤ 10, -8 ≤ k ≤ 10, -17 ≤ l ≤ 17
Reflections collected/unique	9092/3194 [R(int) = 0.0514, R_{sigma} = 0.0489]	11695/3633 [R_{int} = 0.0561, R_{sigma} = 0.0488]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.82621	-
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	6059 / 134 / 508	3633/0/228
Goodness-of-fit on F2	1.051	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1057	R_1 = 0.0897, wR_2 = 0.2433
R indices (all data)	R1 = 0.0630, wR2 = 0.1185	R_1 = 0.0992, wR_2 = 0.2565
Largest diff. peak and hole	0.41 and -0.38 e.$Å^{-3}$	1.26 and -0.55 e.$Å^{-3}$

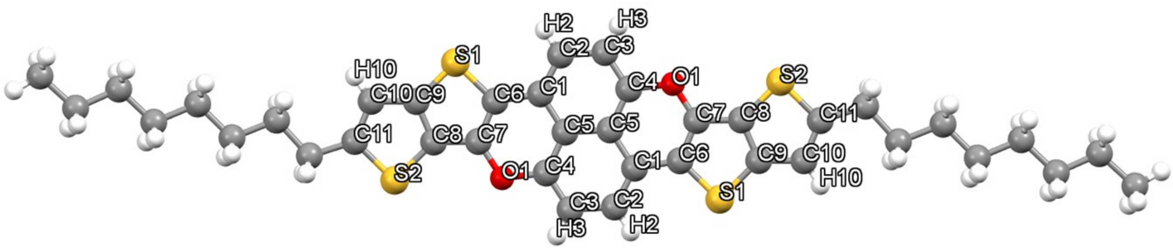

Figure S2. Molecular structure of **TTCTTC**.

Table S2. Selected bond lengths of **TTCTTC**

Bond lengths from crystal structure		Bond lengths from the optimized structure	
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
S1-C6	1.741	S1-C6	1.764
S1-C9	1.733	S1-C9	1.753
S2-C8	1.719	S2-C8	1.743
S2-C11	1.752	S2-C11	1.776
O1-C4	1.398	O1-C4	1.385
O1-C7	1.370	O1-C7	1.364
C1-C2	1.374	C1-C2	1.388
C1-C5a	1.430	C1-C5a	1.434
C1-C6^{i}	1.447	C1-C6^{i}	1.447
C2-C3	1.401	C2-C3	1.408
C3-C4	1.369	C3-C4	1.380
C4-C5	1.413	C4-C5	1.422
C5-C5a	1.417	C5-C5a	1.424
C6-C7	1.368	C6-C7	1.377
C7-C8	1.411	C7-C8	1.417
C8-C9	1.385	C8-C9	1.388
C9-C10	1.423	C9-C10	1.425
C10-C11	1.361	C10-C11	1.371

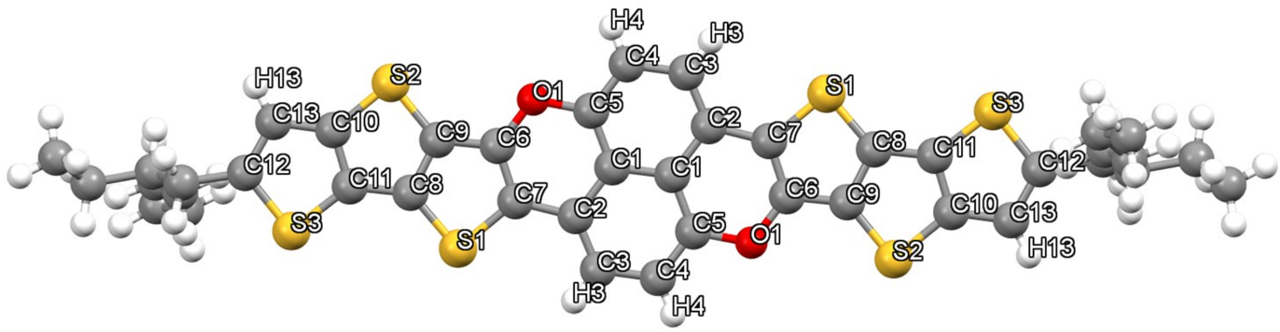

Figure S3. Molecular structure of **TTTCTTTC**.

Table S3. Selected bond lengths of **TTTCTTTC.**

Bond lengths from crystal structure		**Bond lengths from the optimized structure**	
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
S1-C7	1.742	S1-C7	1.754
S1-C8	1.718	S1-C8	1.749
S2-C9	1.725	S2-C9	1.756
S2-C10	1.743	S2-C10	1.754
S3-C11	1.721	S3-C11	1.742
S3-C12	1.744	S3-C12	1.769
O1-C5	1.388	O1-C5	1.386
O1-C6	1.367	O1-C6	1.363
C1-C2	1.429	C1-C2	1.434
C1-C5	1.413	C1-C5	1.422
C2-C3	1.361	C2-C3	1.388
C3-C4	1.412	C3-C4	1.408
C1-C1a	1.416	C1-C1a	1.424
C4-C5	1.369	C4-C5	1.388
C2-C7	1.454	C2-C7	1.446
C6-C7	1.358	C6-C7	1.377
C6-C9	1.419	C6-C9	1.415
C8-C9	1.388	C8-C9	1.393
C8-C11	1.430	C8-C11	1.419
C10-C11	1.375	C10-C11	1.394
C12-C13	1.368	C12-C13	1.373

4. DFT calculations

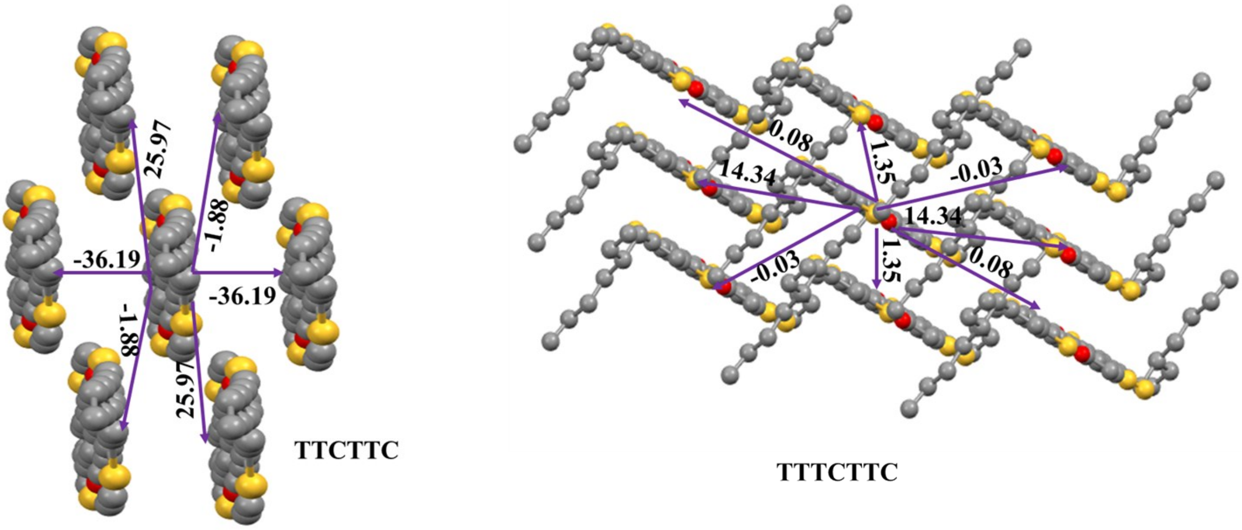

Figure S4. Calculated transfer integrals (meV) of **TTCTTC** and **TTTCTTTC** by using the popular long-range functional ωB97XD with optimized ω=0.00168 and 6-31G(d) basis set.

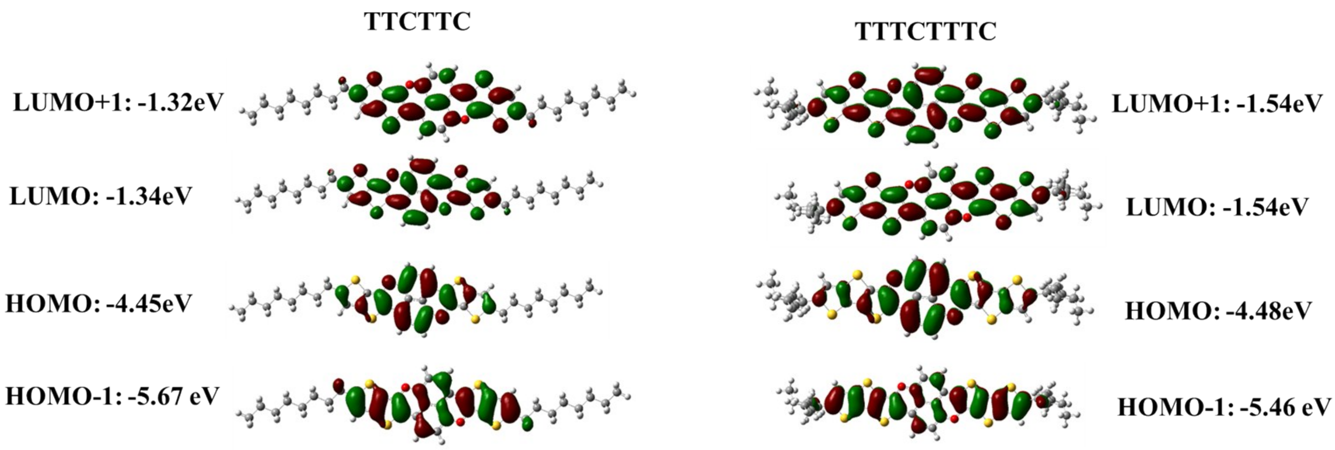

Figure S5. Energy levels of **TTCTTC** and **TTTCTTTC** calculated at PCM-B3LYP/6-31G(d) level.

Table S4. The electronic transitions with transition energy lower than 4.3803 eV (280nm) and the oscillator strengths (*f*) with their values larger than 0.01 at PCM-B3LYP/6-31G(d) level.

	TTCTTC	**TTTCTTTC**
$S_0 \rightarrow S_2$	**2.69 eV (461.1nm)** ***f*=0.7906** **HOMO→LUMO**	**2.53 eV (490.9nm)** ***f*=1.0733** **HOMO→LUMO+1**
$S_0 \rightarrow S_3$	3.32 eV (373.9nm) *f*=0.0917	3.28 eV (378.5nm) *f*=0.0881

$S_0 \rightarrow S_4$	3.84 eV (323.0nm) f=0.0693	**3.55 eV (349.3 nm)** $\boldsymbol{f}$**=1.3688** **HOMO-1→LUMO**
$S_0 \rightarrow S_6$	**3.95 eV (313.8nm)** $\boldsymbol{f}$**=1.0662** **HOMO-1→LUMO+1**	3.66 eV (340.1nm) f=0.0062

5. Fluorescence spectra of TTCTTC and TTTCTTTC in solutions and solid states

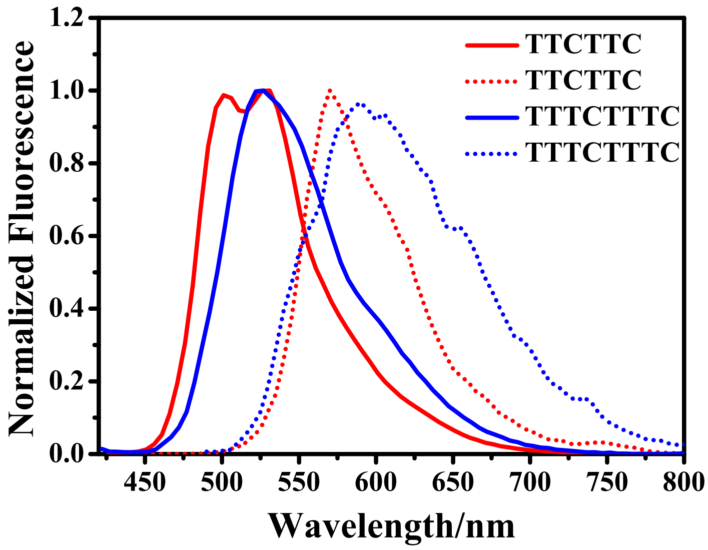

Figure S6. Fluorescence spectra of **TTCTTC** and **TTTCTTTC** in solutions (solid line) and solid states (dotted line).

Table S5. Photoluminescence data of **TTCTTC** and **TTTCTTTC** in solutions and solid states

Compd.	Solution			Solid State		
	PL $\lambda_{em.}$(nm)	Φ^a (%)	<τ>^{b} (ns)	PL $\lambda_{em.}$ (nm)	Φ^a (%)	<τ>^{b} (ns)
TTCTTC	503, 529	13.8	3.56	571	**16.5**	1.64
TTTCTTTC	526	13.6	3.35	587	1.5	1.26

[a] The quantum yields in solutions (10 μM in CH_2Cl_2) and in the solid states were measured with the Hamamatsu spectrometer C11347 Quantaurus-QY. [b] Fluorescence lifetimes in solutions (10 μM in CH_2Cl_2) and in the solid state were measured with the Hamamatsu spectrometer C11367.

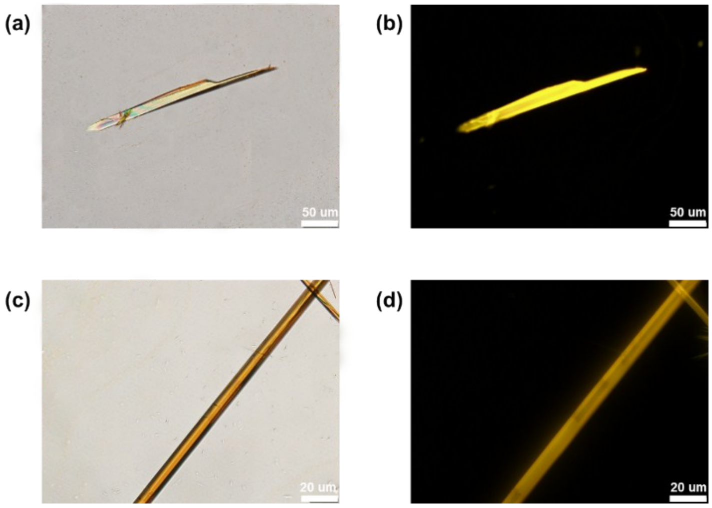

Figure S7. The microscope (a, c) and fluorescence microscope (b, d) (λ_{ex} = 330-380 nm) images of **TTCTTC** and **TTTCTTTC** crystals, respectively.

6. ESR spectra of TTCTTC and TTTCTTTC in the presence of CF_3COOH

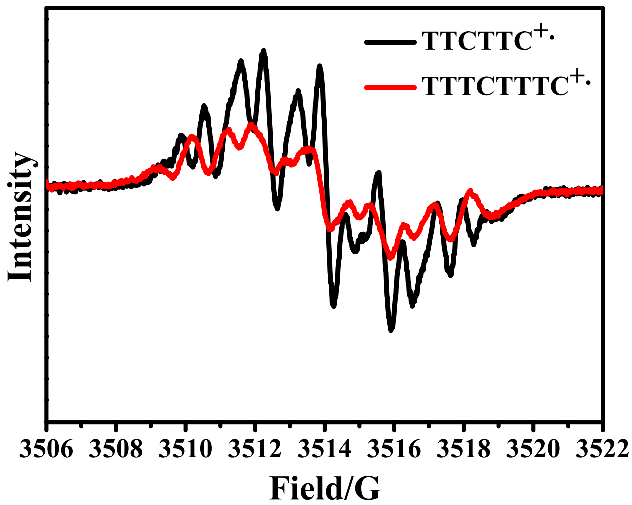

Figure S8. ESR spectra of CH_2Cl_2 solution of **TTCTTC** and **TTTCTTTC** in the presence of 1%wt TFA (CF_3COOH).

7. UV-vis-NIR spectra of TTCTTC and TTTCTTTC after electrochemical oxidation

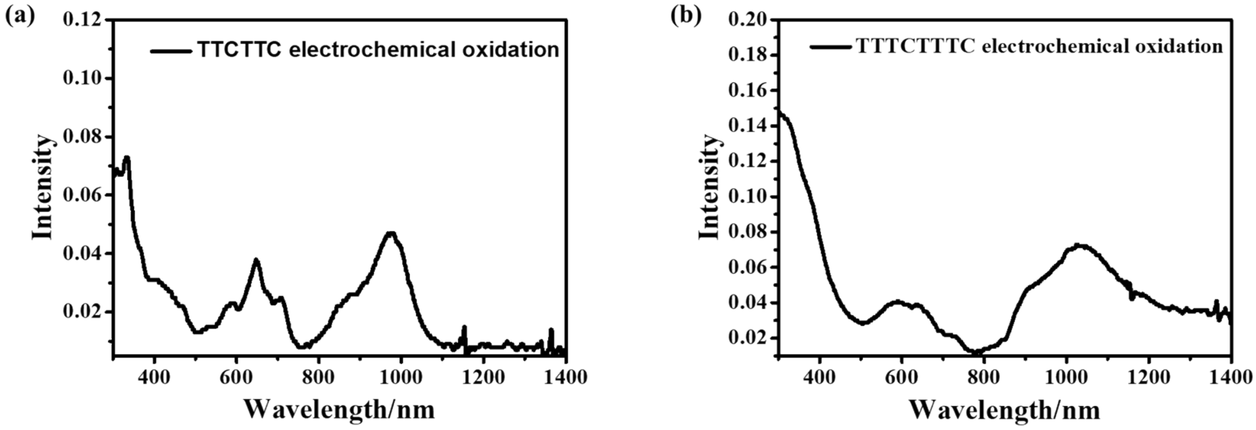

Figure S9. The UV-vis-NIR spectra of solutions of **TTCTTC** (a, 10 μM) and **TTTCTTTC** (b, 10 μM) after electrochemical oxidation. The spectroelectrochemical experiments were carried out in 1 mm spectroelectrochemical cell containing platinum minigrid working electrode, Pt counter electrode and Ag/AgCl reference electrode. The spectra were recorded after the solutions were applied an oxidation potential at +0.6 V (vs Ag/AgCl) for 30 min.

8. Transfer and output curves of OFETs with thin films of TTCTTC and TTTCTTTC

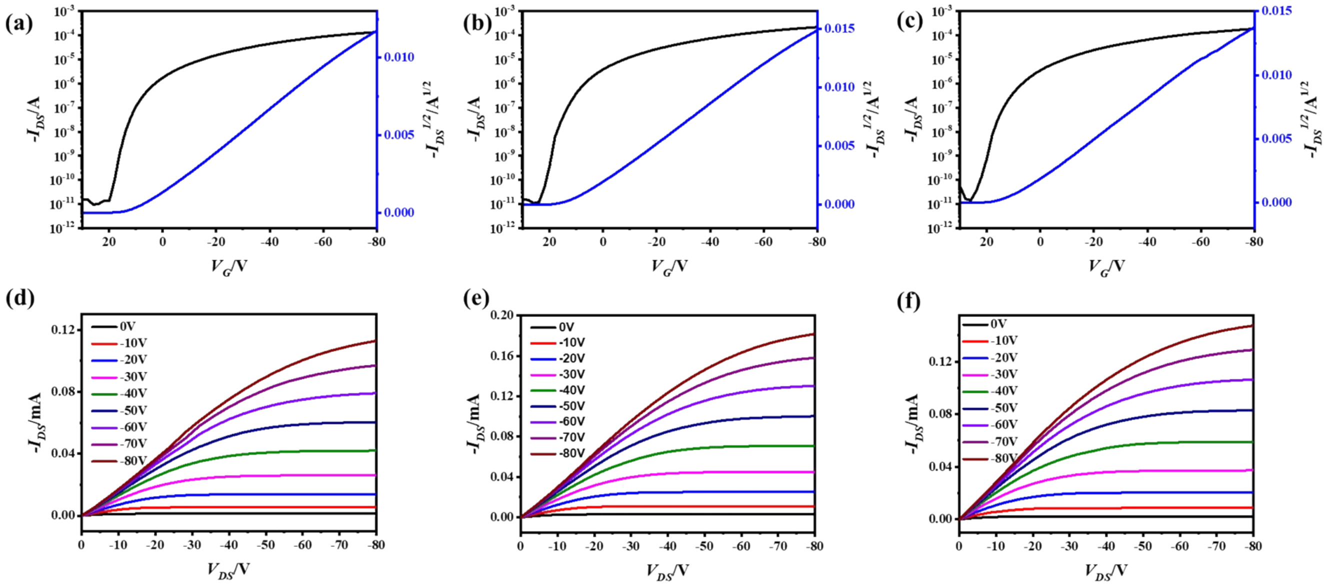

Figure S10. Transfer (a, b and c) and output (d, e and f) characteristics of OFETs with thin films of **TTCTTC** deposited on OTS-modified SiO_2/Si substrate at 25 °C (a and d), 50 °C (b and e) and 90 °C (c and f).

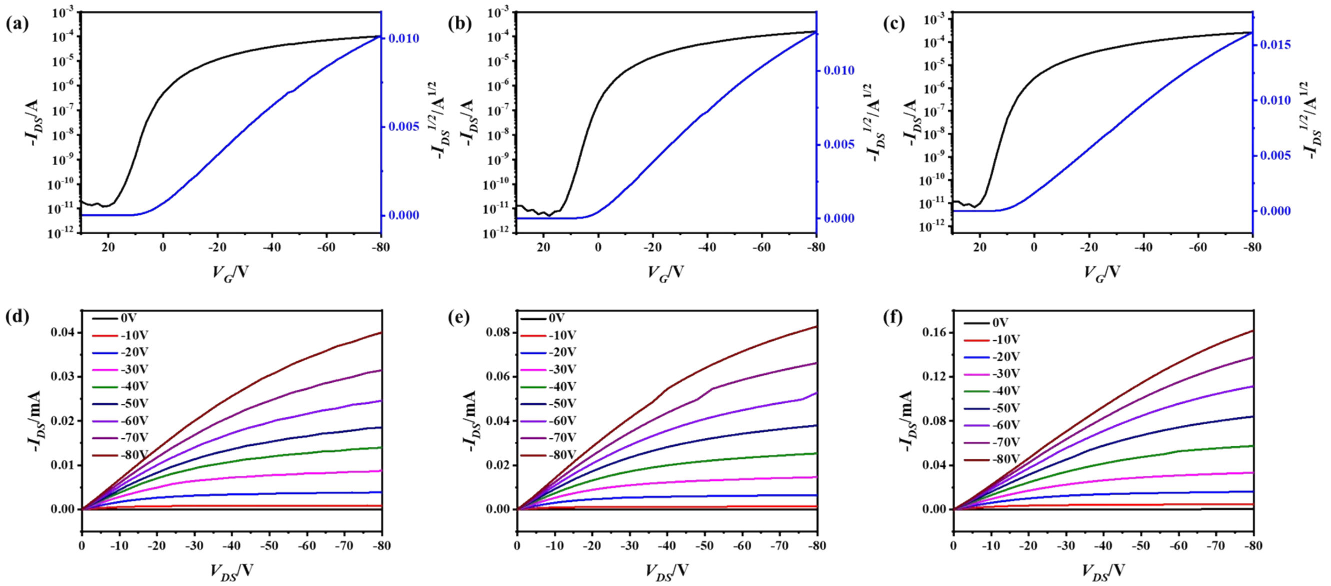

Figure S11. Transfer (a, b and c) and output (d, e and f) characteristics of OFETs with thin films of **TTTCTTTC** deposited on OTS-modified SiO_2/Si substrate at 25 °C (a and d), 50 °C (b and e) and 90 °C (c and f).

Table S6. The performance data for OFETs with thin films of **TTCTTC** and **TTTCTTTC**

Compd.	Substrate temp. (°C)	μ_{max} [$cm^2 V^{-1} s^{-1}$]	$\mu_{average}$[a] [$cm^2 V^{-1} s^{-1}$]	On/off ratio	Threshold (V)
TTCTTC	90	0.26	0.20	$1x10^7$	10 V
	50	0.39	0.25	$2x10^7$	13 V
	25	0.31	0.19	$1x10^7$	9 V
TTTCTTTC	90	0.031	0.017	$2x10^7$	7 V
	50	0.025	0.013	$2x10^7$	2 V
	25	0.016	0.008	$5x10^7$	3 V

[a] based on 10 devices

9. XRD patterns of TTCTTC and TTTCTTTC films deposited at different temperatures

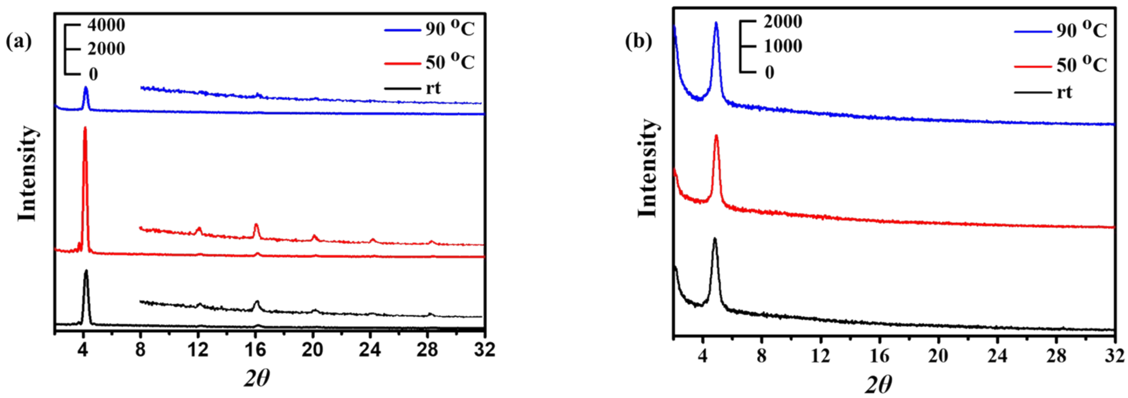

Figure S12. XRD patterns of thin-films of **TTCTTC** (a) and **TTTCTTTC** (b) deposited on OTS-modified SiO_2/Si substrates at different temperatures (a, 25 °C; b, 50 °C; c, 90 °C).

10. AFM images of TTCTTC deposited at different temperatures

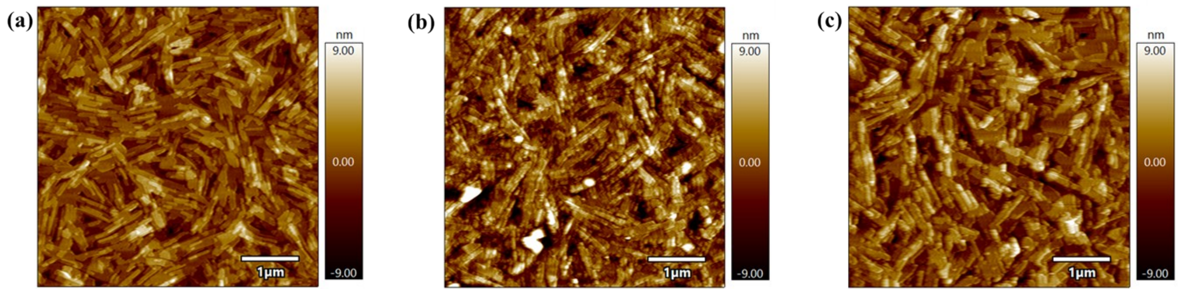

Figure S13. AFM height images of thin-films of **TTCTTC** deposited on OTS-modified SiO_2/Si substrates at different temperatures (a, 25 °C; b, 50 °C; c, 90 °C).

11. AFM images of TTTCTTTC deposited at different temperatures

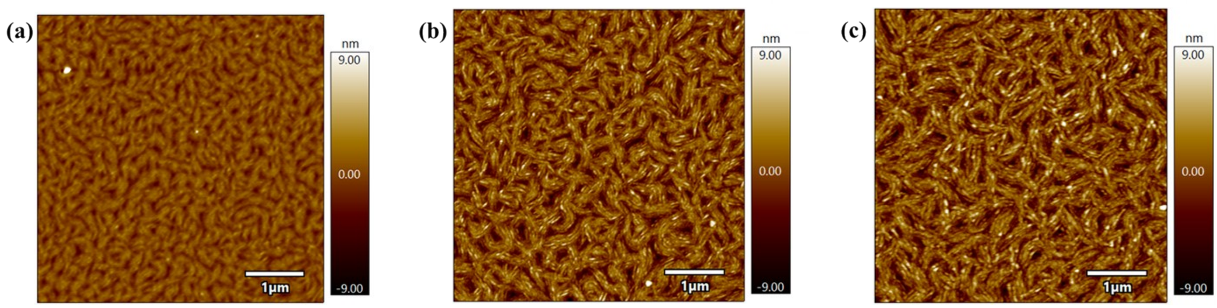

Figure S14. AFM height images of thin-films of **TTTCTTTC** deposited on OTS-modified SiO_2/Si substrates at different temperatures (a, 25 °C; b, 50 °C; c, 90 °C).

12. References

[1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

13. NMR Spectra.

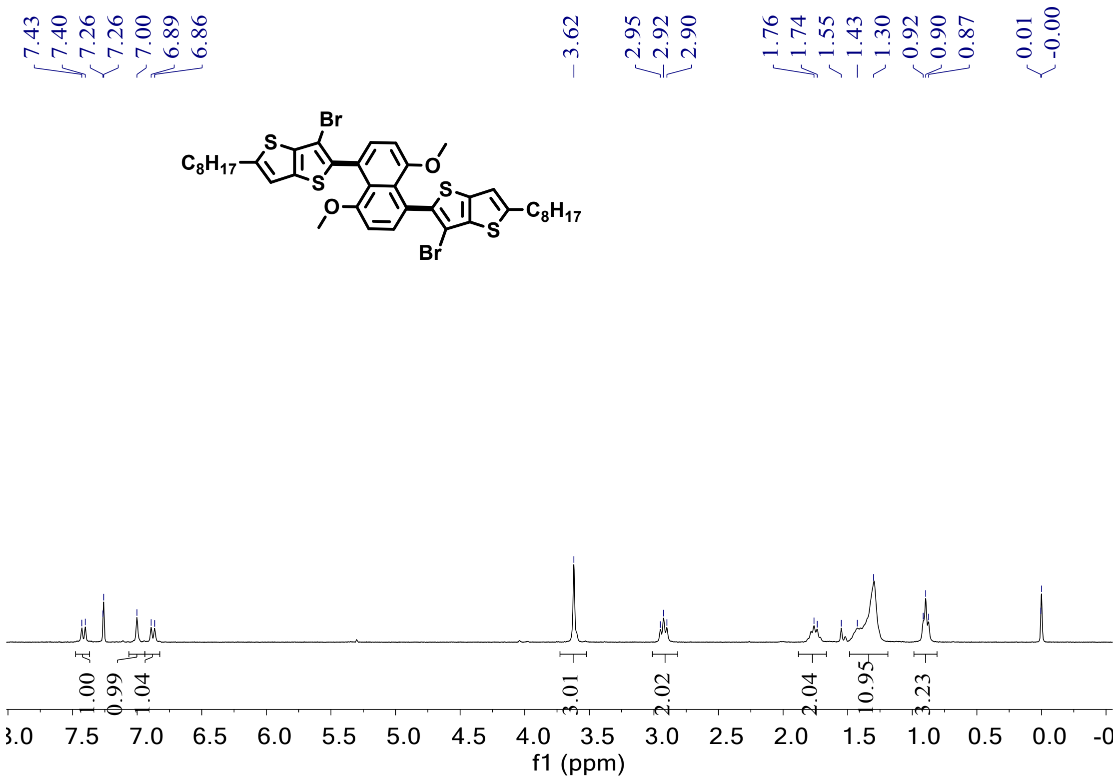

Figure S15. ^{1}H NMR spectrum of **3a** in $CDCl_3$ (25°C).

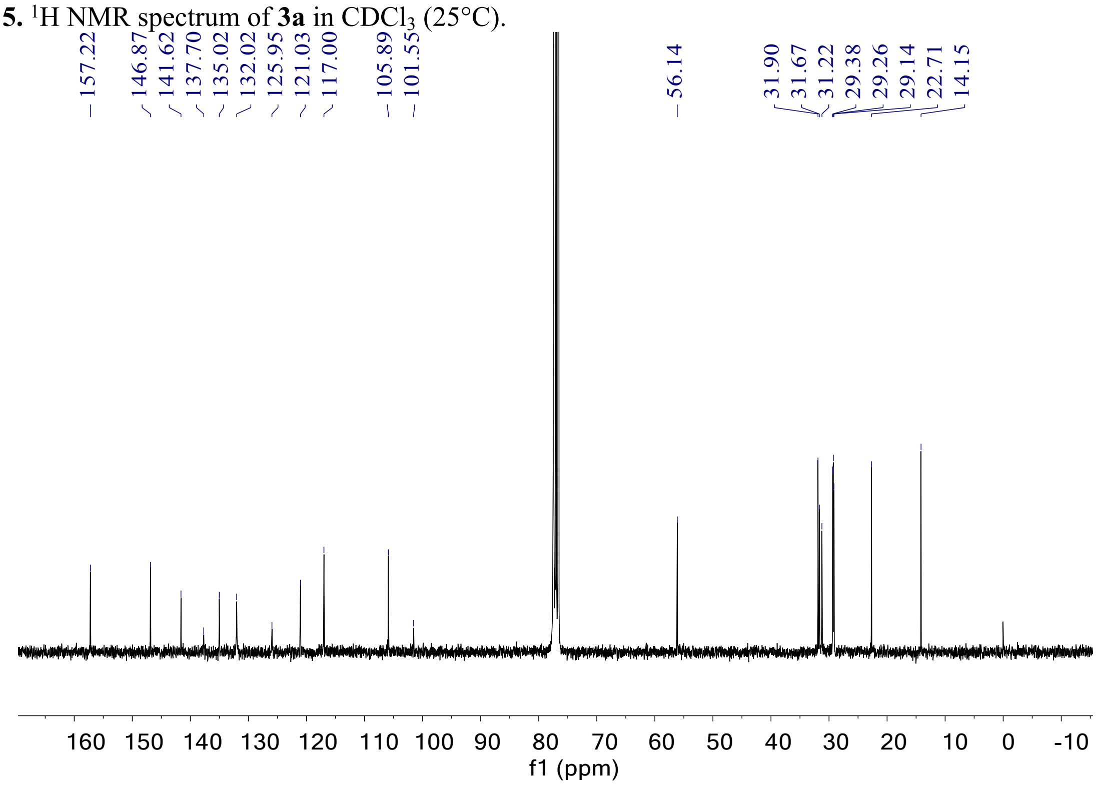

Figure S16. ^{13}C NMR spectrum of **3a** in $CDCl_3$ (25°C).

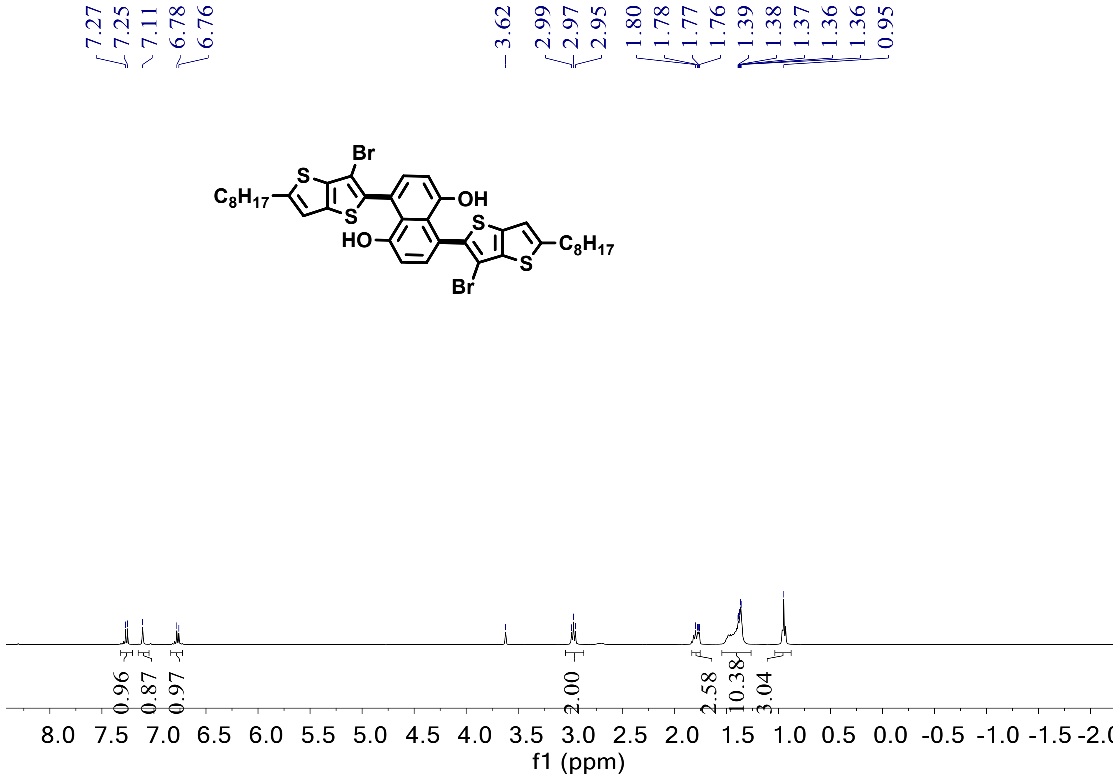

Figure S17. ^{1}H NMR spectrum of **3b** in $[D_8]$THF (25°C).

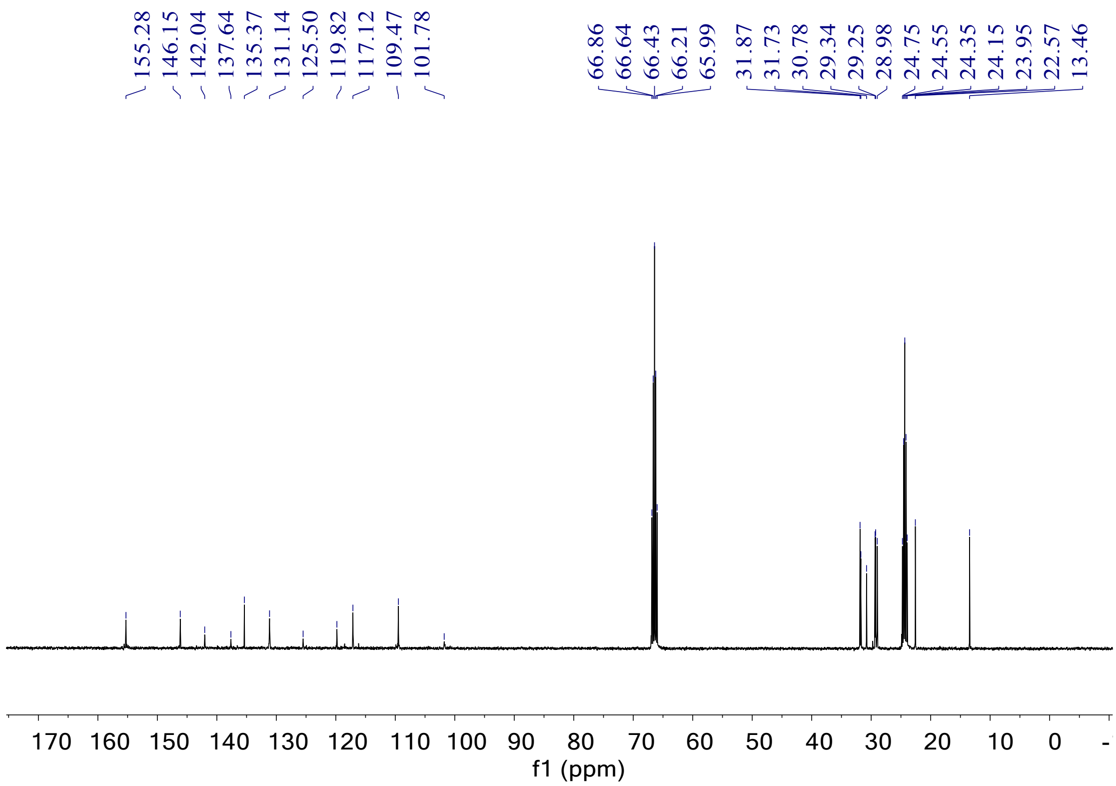

Figure S18. ^{13}C NMR spectrum of **3b** in $[D_8]$THF (25°C).

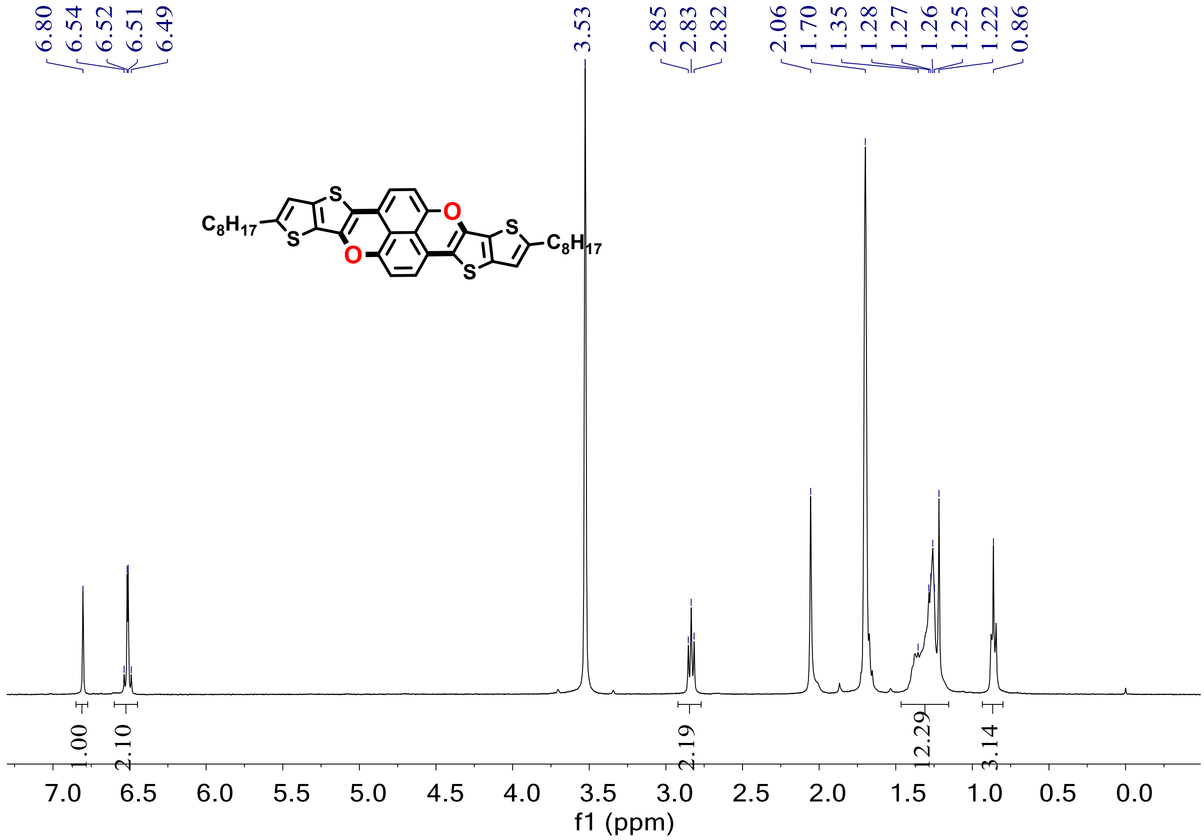

Figure S19. ^{1}H NMR spectrum of **TTCTTC** in $[D_8]THF/CS_2$ v/v = 1:4 (25°C).

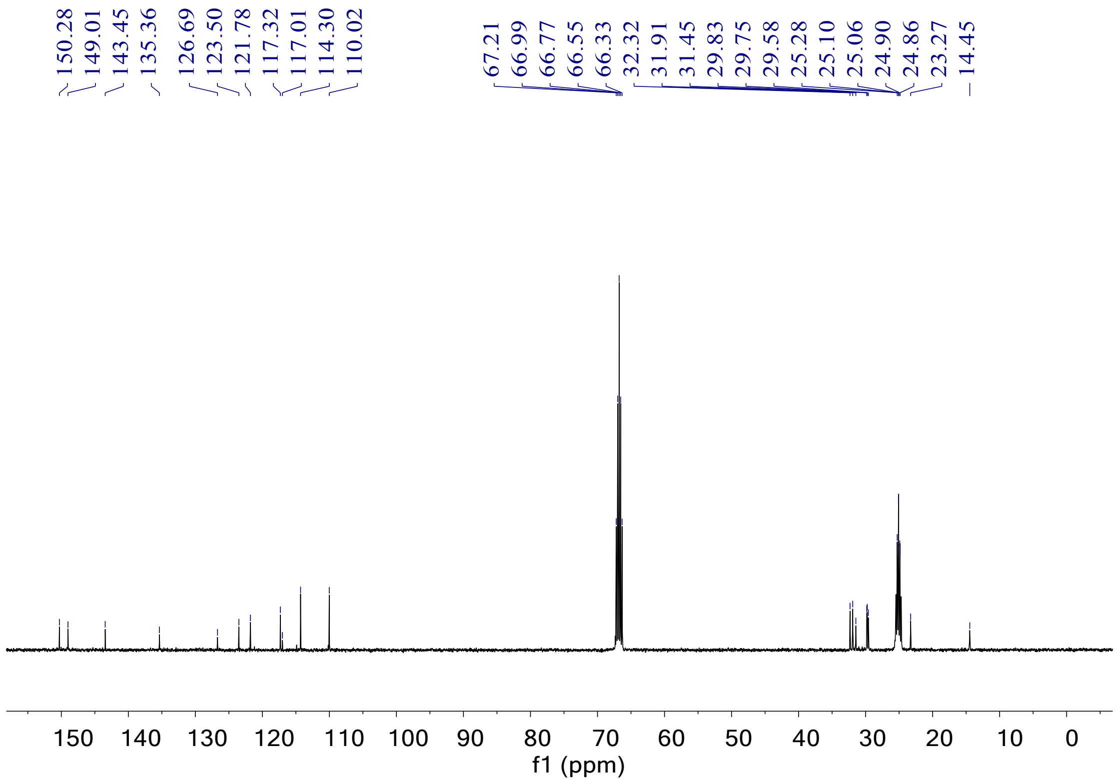

Figure S20. ^{13}C NMR spectrum of **TTCTTC** in $[D_8]THF/CS_2$ v/v = 1:4 (25°C).

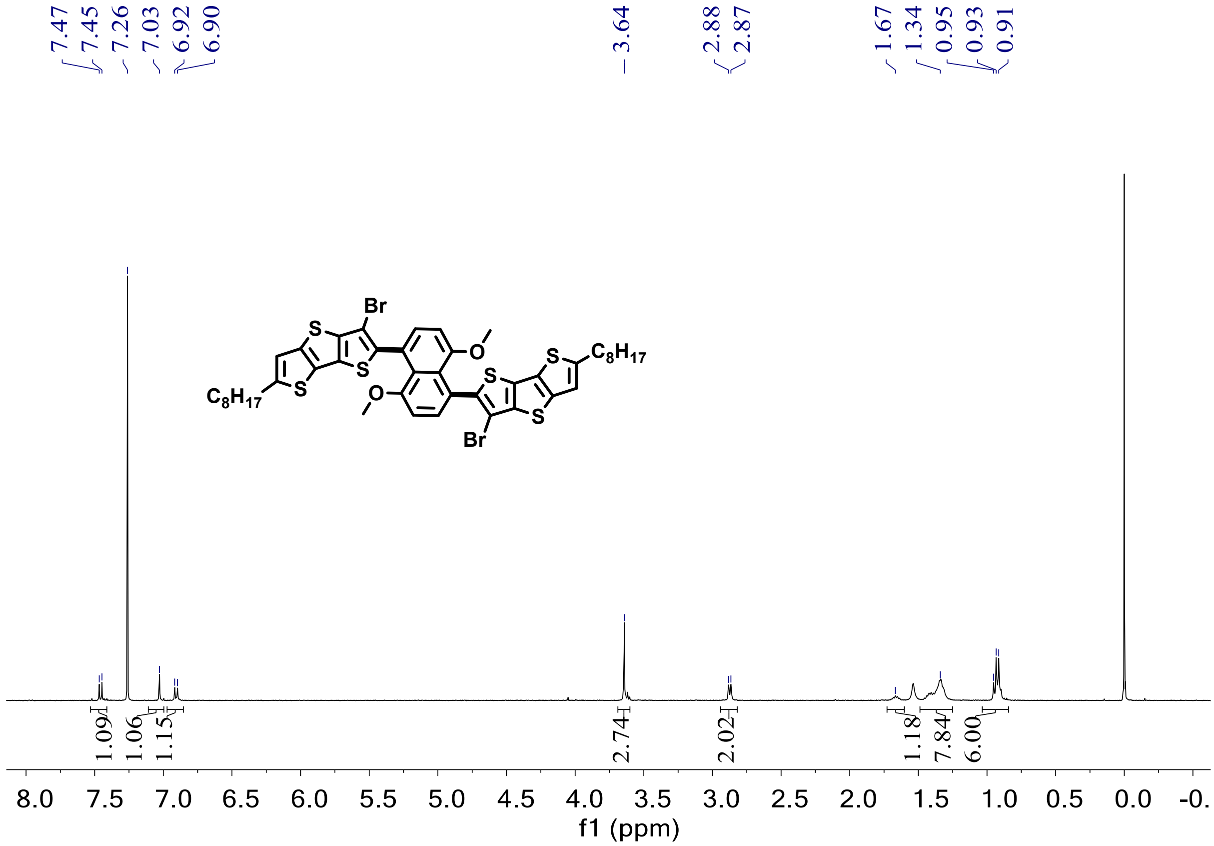

Figure S21. ^{1}H NMR spectrum of **4a** in $CDCl_3$ (25°C).

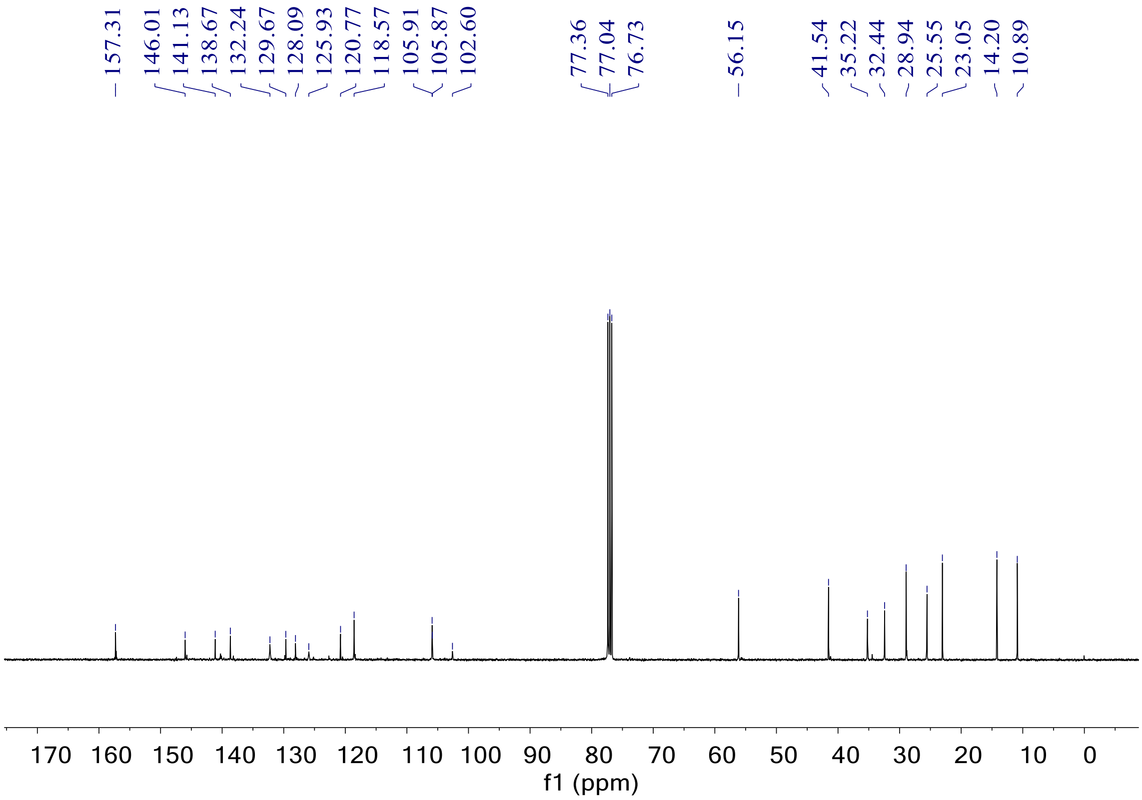

Figure S22. ^{13}C NMR spectrum of **4a** in $CDCl_3$ (25°C).

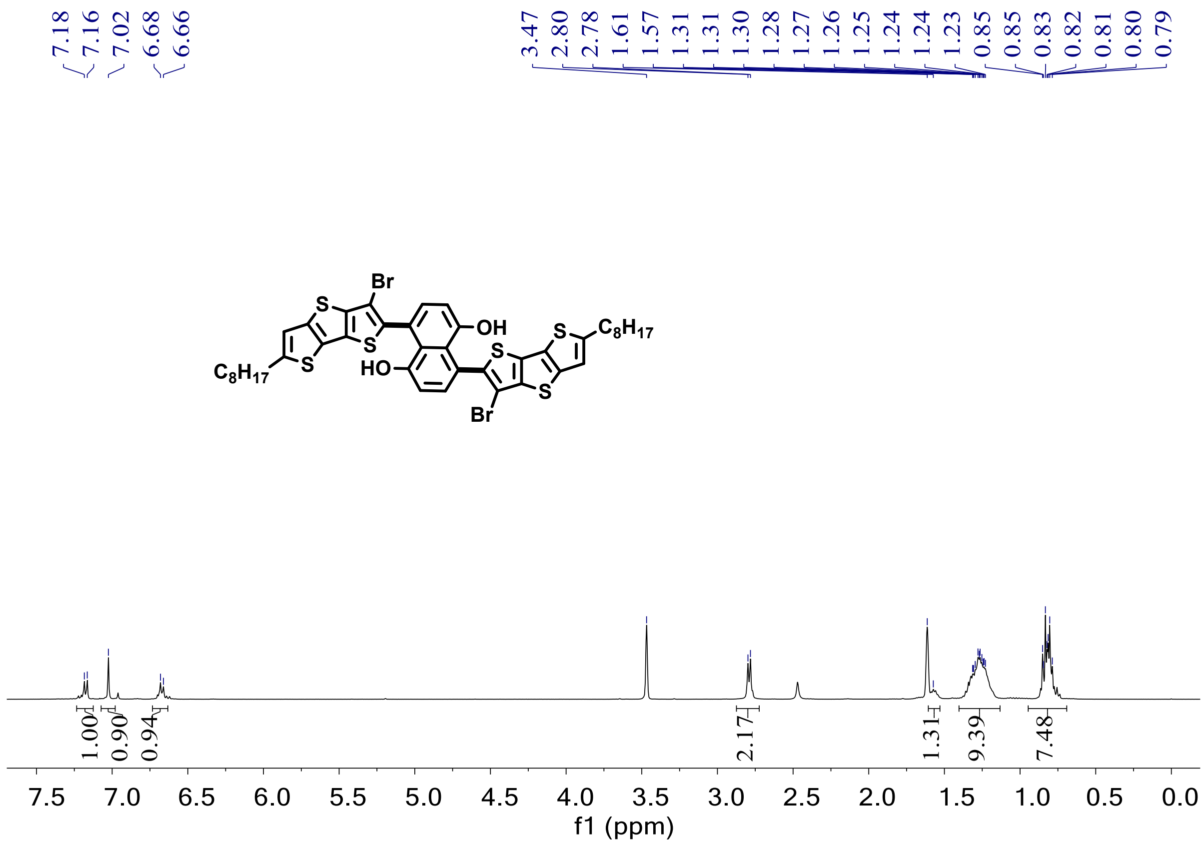

Figure S23. ^{1}H NMR spectrum of **4b** in [D$_8$]THF (25°C).

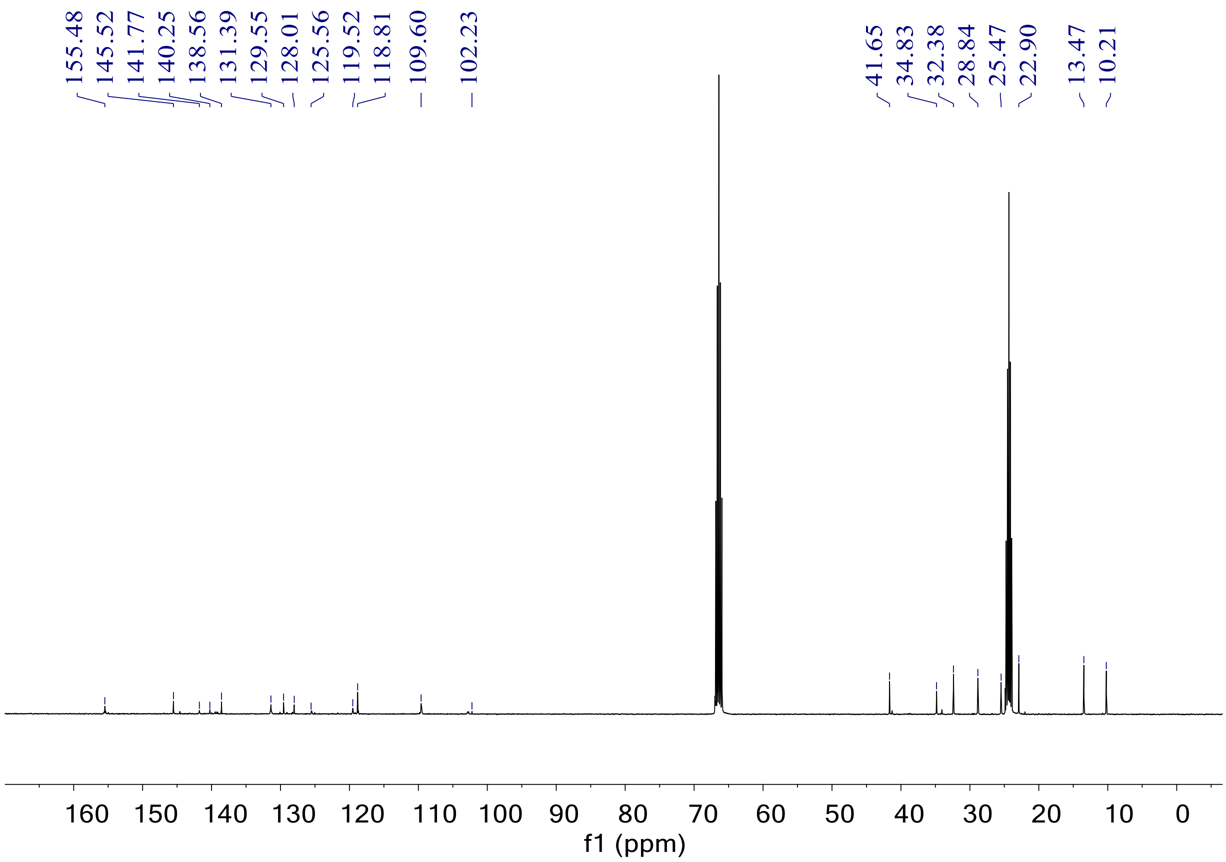

Figure S24. ^{13}C NMR spectrum of **4b** in [D$_8$]THF (25°C).

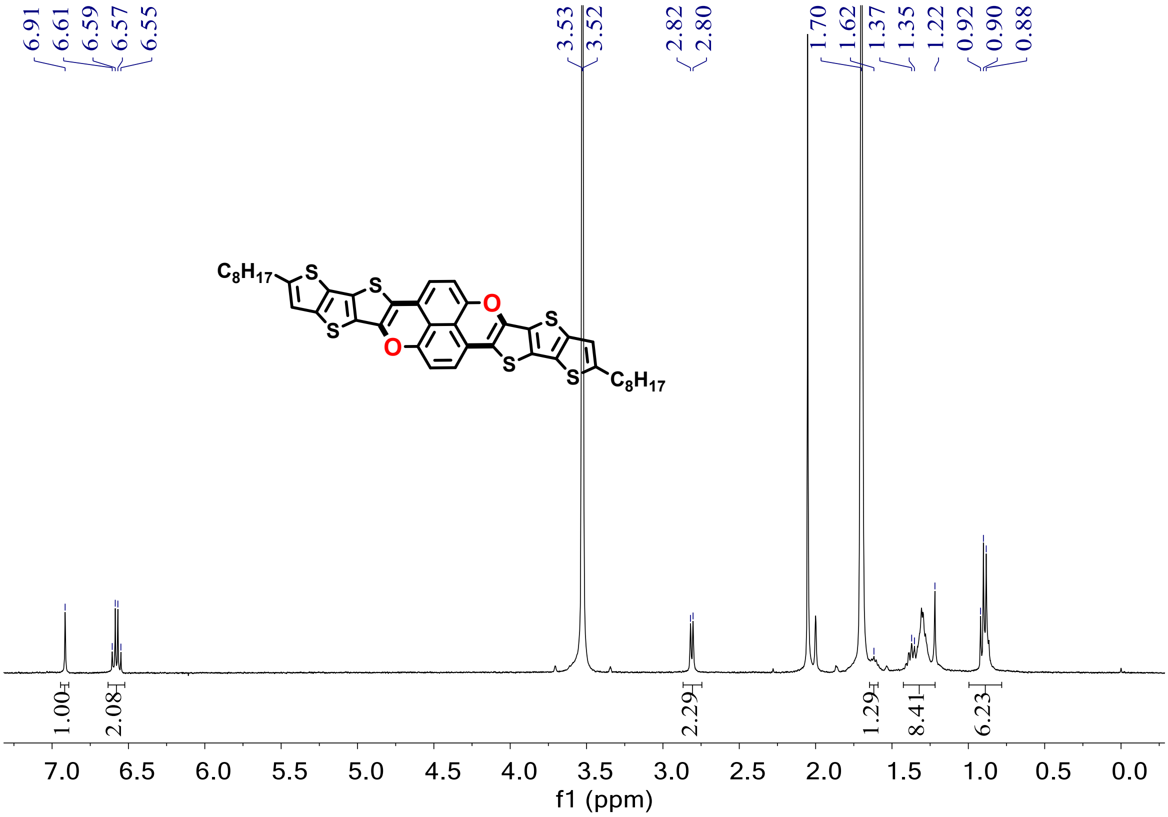

Figure S25. ^{1}H NMR spectrum of **TTTCTTTC** in [D_8]THF/CS_2 v/v = 1:4 (25°C).

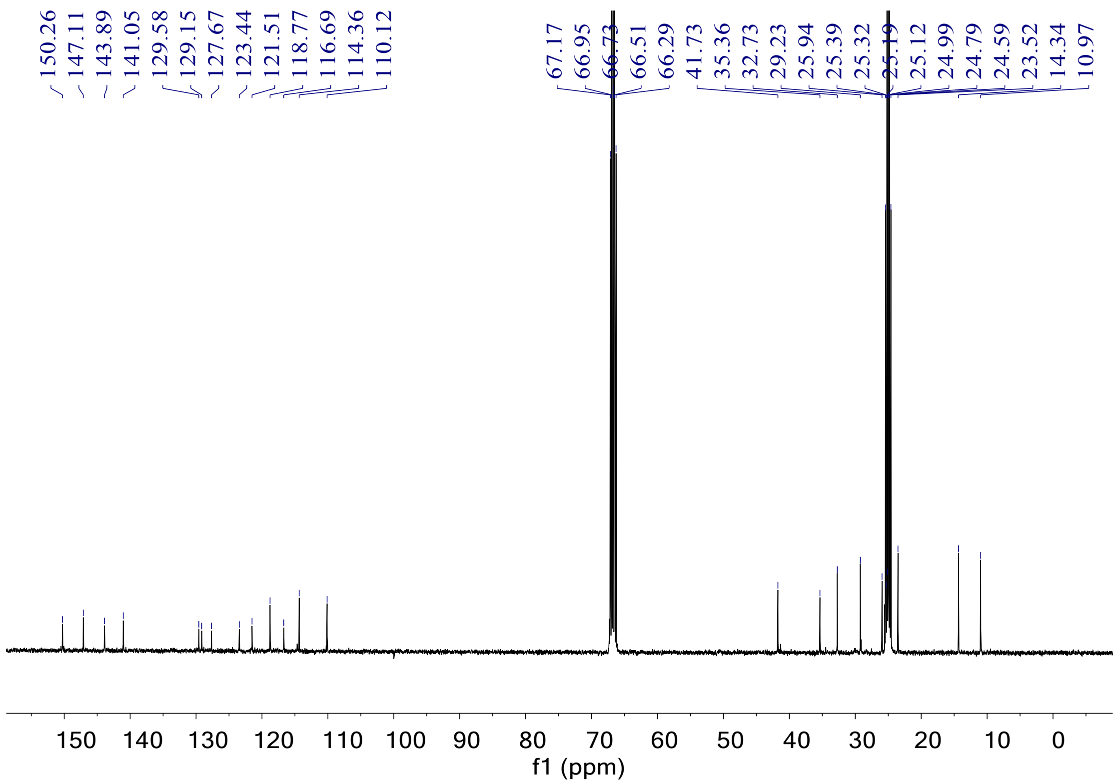

Figure S26. ^{13}C NMR spectrum of **TTTCTTTC** in [D_8]THF/CS_2 v/v = 1:4 (25°C).