Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Rational Design of Phenothiazine (PTz) and Ethylenedioxythiophene (EDOT) Based Donor-Acceptor Compounds with a Molecular Aggregation Breaker for Solid State Emission in Red and NIR region

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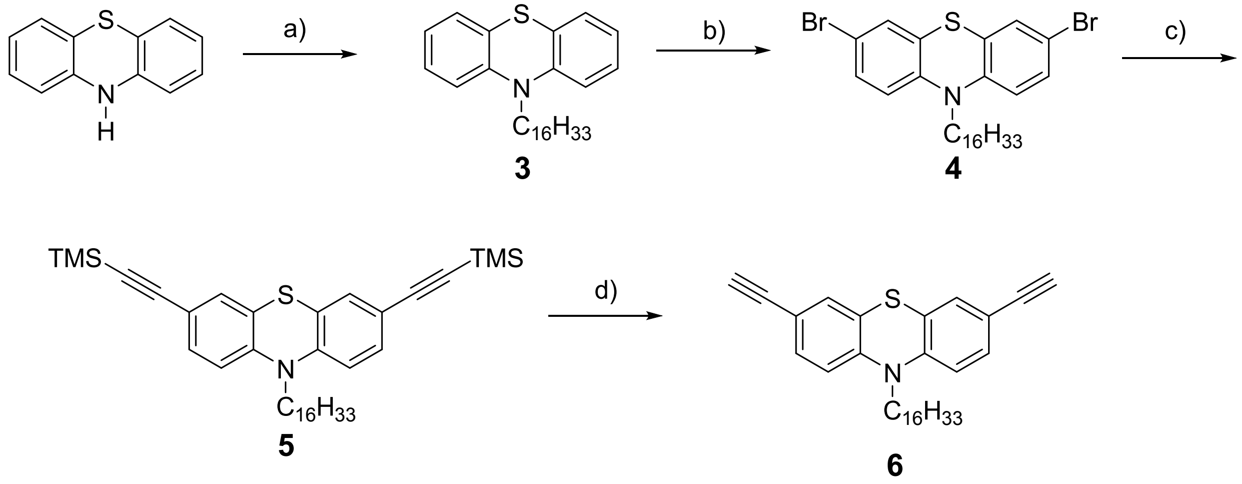
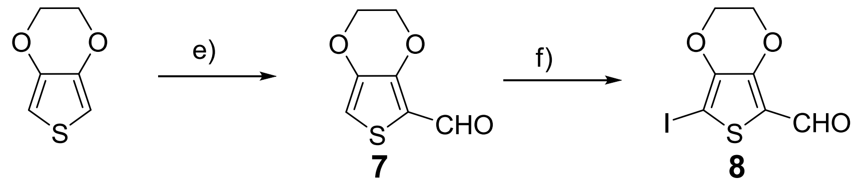
Scheme S1. Synthesis intermediates.



a) $C_{16}H_{33}Br$, KOH, DMSO, RT, Overnight, 95 %, b) Br_2, AcOH, RT, 12 h, 88 %, c) TMS-Acetylne, Pd(II), CuI, PPh_3, DIPA/ THF (1:1), 70 °C, 18 h, 65 %, d) K_2CO_3, THF:MeOH (1:1), RT, 6 h, 87 %.



e) DMF/$POCl_3$, 1,2-dichloroethane, 80 °C, overnight, 87 %, f) NIS, THF:AcOH (1:1), RT, Overnight, 81 %.

References:

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2) M. Jessing, M. Brandt, K. J. Jensen, J. B. Christensen, U. Boas, *J. Org. Chem.* **2006,** *71,* 6734.
3) X. Zhao, M. R. Pinto, L. M. Hardison, J. Mwaura, J. Muller, H. Jiang, D. Witker, V. D. Kleiman, J. R. Reynolds, K. S. Schanze, *Macromolecules,* **2006**, *39*, 6355.
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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. Gaussian 09 Revisions A.02, Gaussian Inc. Wallingford CT 2009.

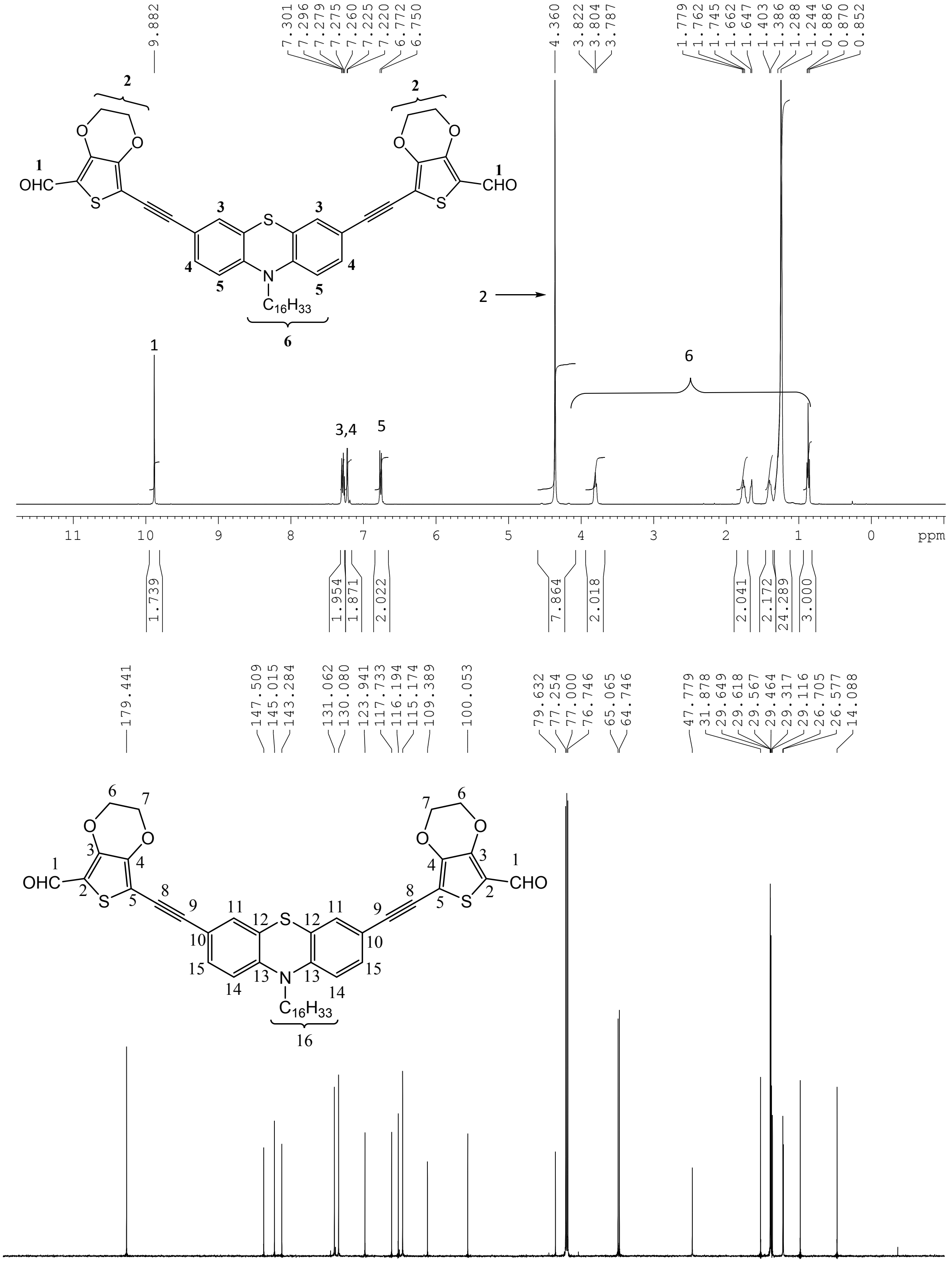
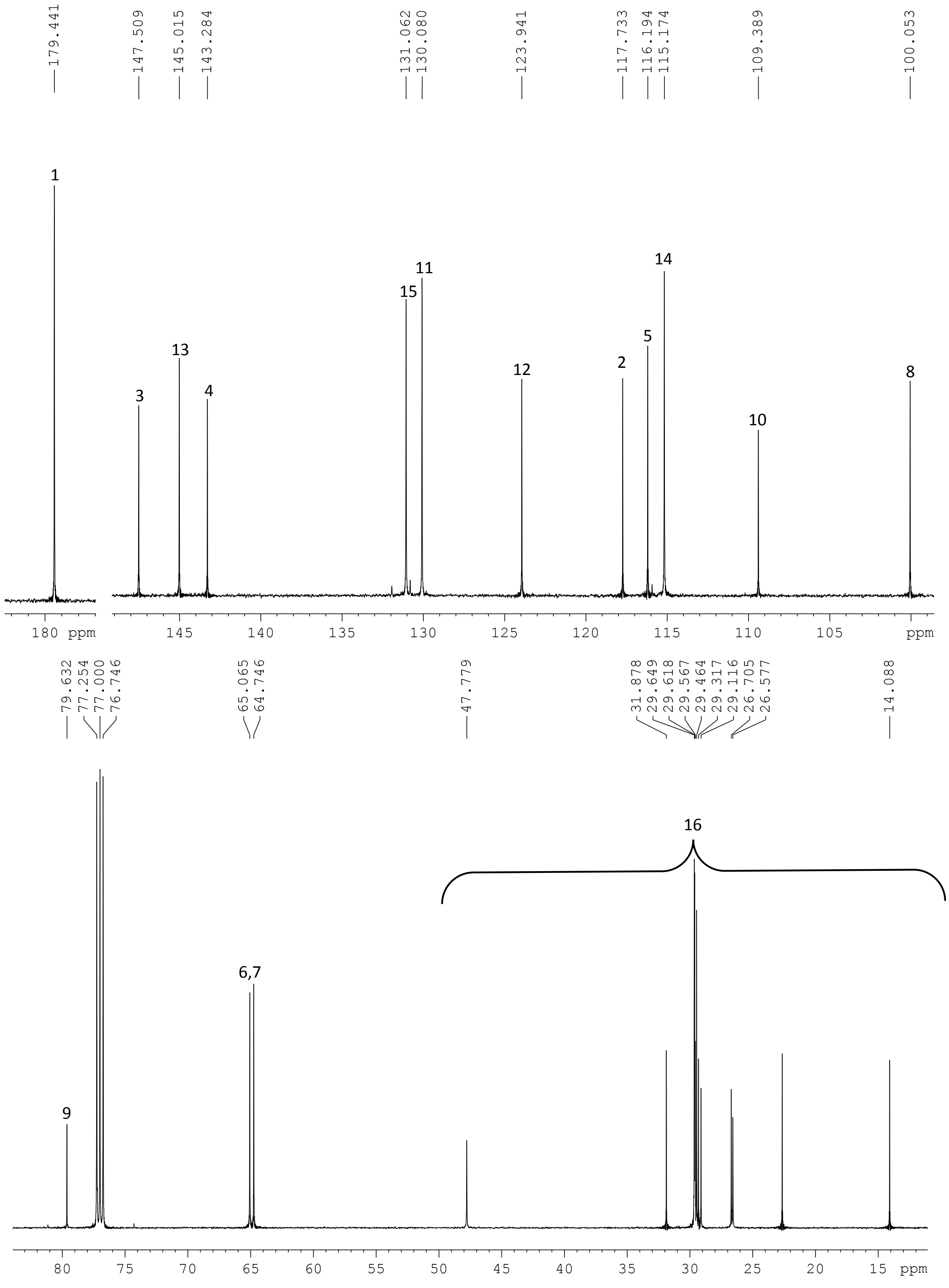


Figure S1. ^{1}H and ^{13}C NMR spectra of **1**

Expansion of ^{13}C NMR spectrum of **1**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147.509
145.015
143.284
131.062
130.080
123.941
117.733
116.194
115.174
109.389
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1
15
11
14
5
13
3
4
12
2
8
10
180 ppm
145
140
135
130
125
120
115
110
105
100 ppm
79.632
77.254
77.000
76.746
65.065
64.746
47.779
31.878
29.649
29.618
29.567
29.464
29.317
29.116
26.705
26.577
14.088
16
6,7
9
80
75
70
65
60
55
50
45
40
35
30
25
20
15 ppm

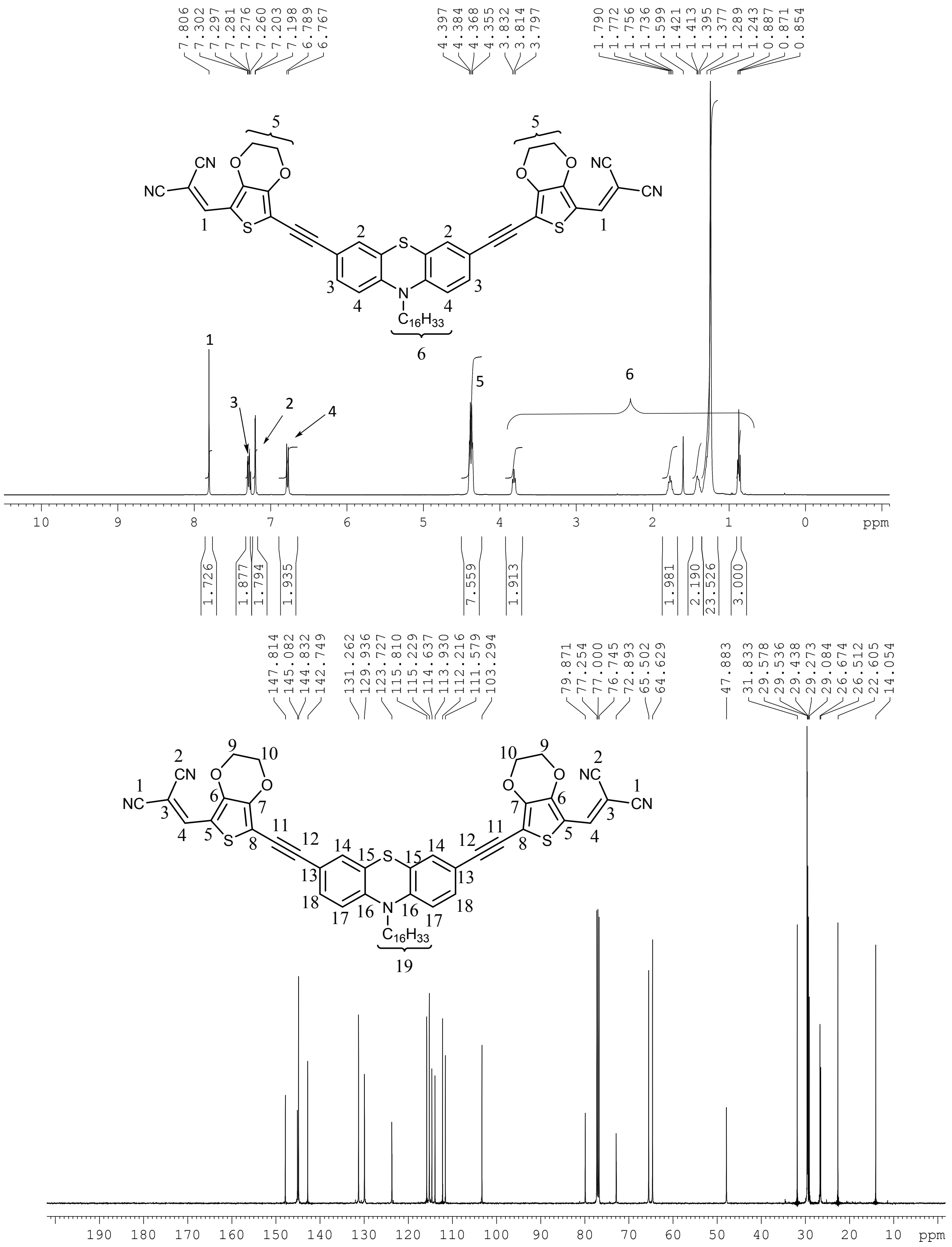
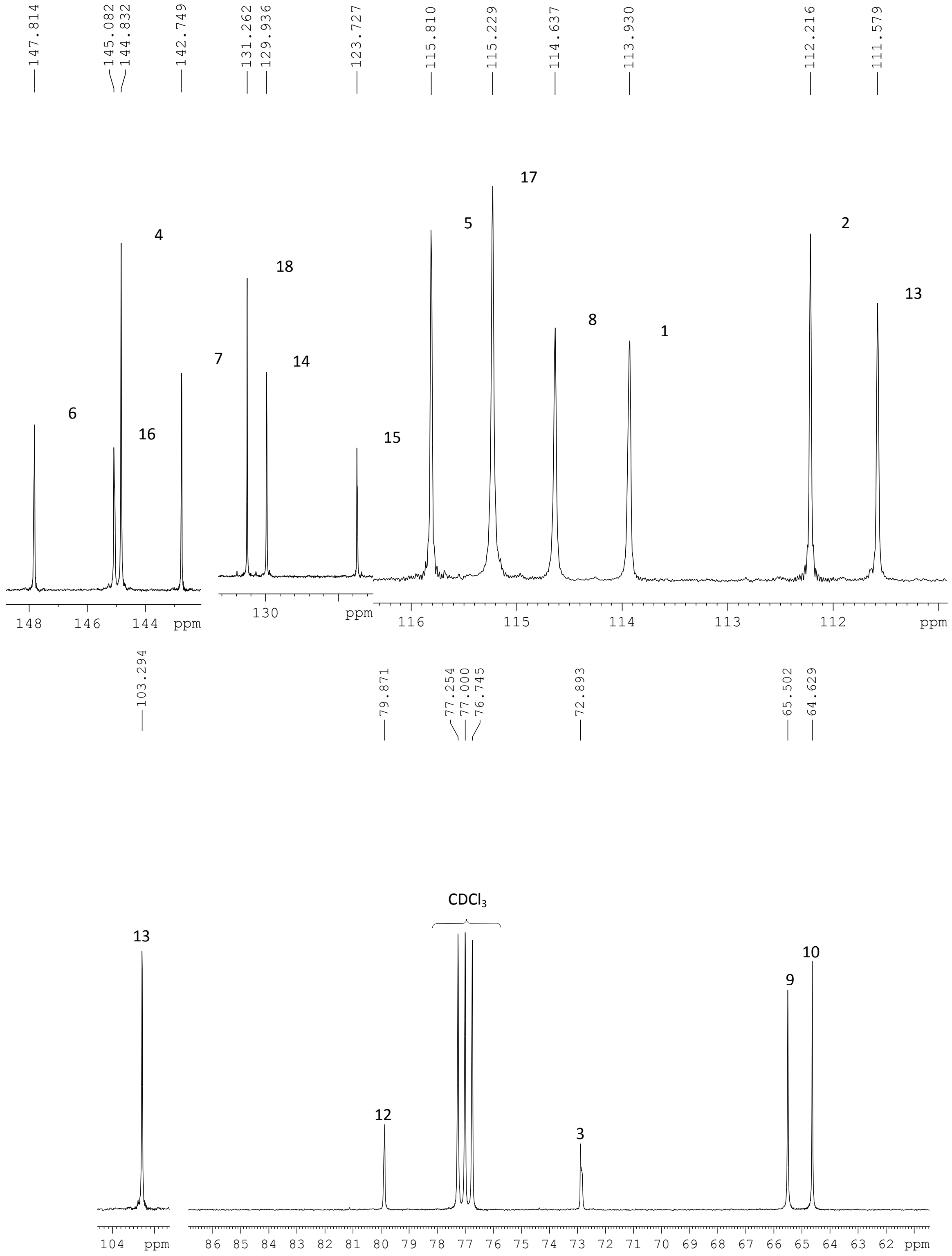
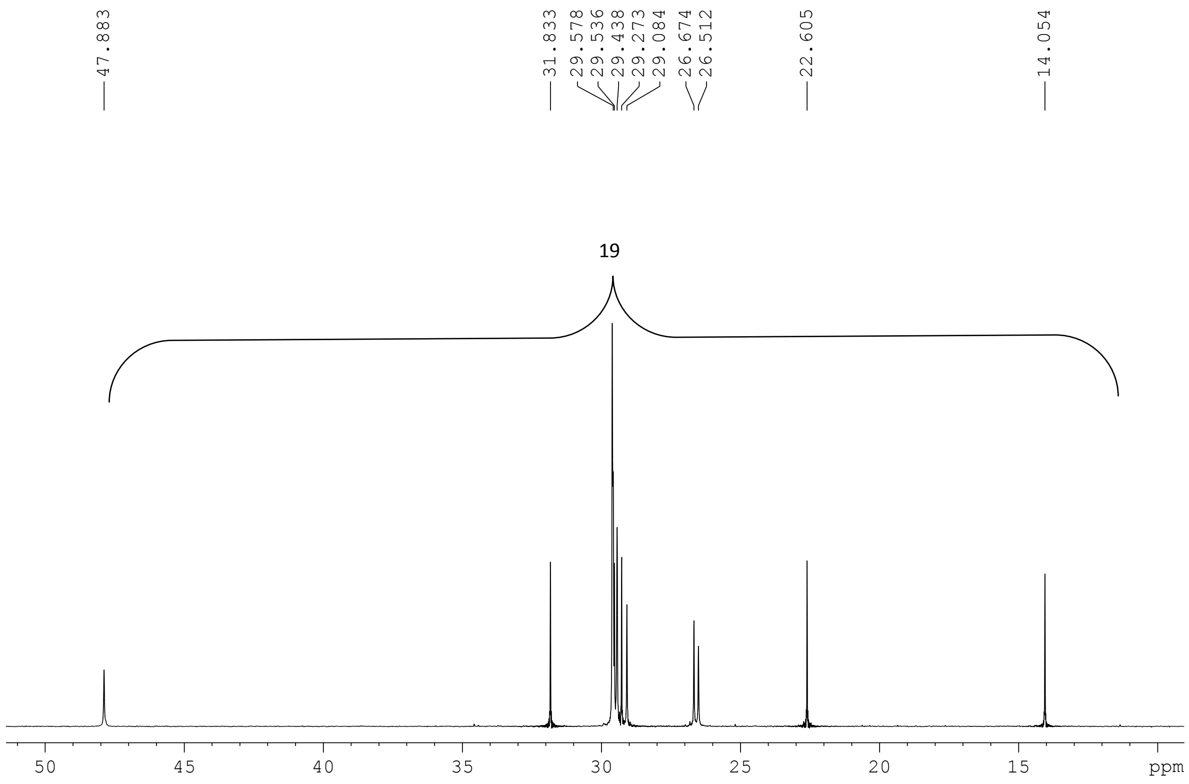


Figure S2. ^{1}H and ^{13}C NMR spectra of **2**

Expansion of ^{13}C NMR spectrum of **2**




47.883
31.833
29.578
29.536
29.438
29.273
29.084
26.674
26.512
22.605
14.054
19
50
45
40
35
30
25
20
15
ppm

DEPT NMR spectra of compounds 1 and 2:

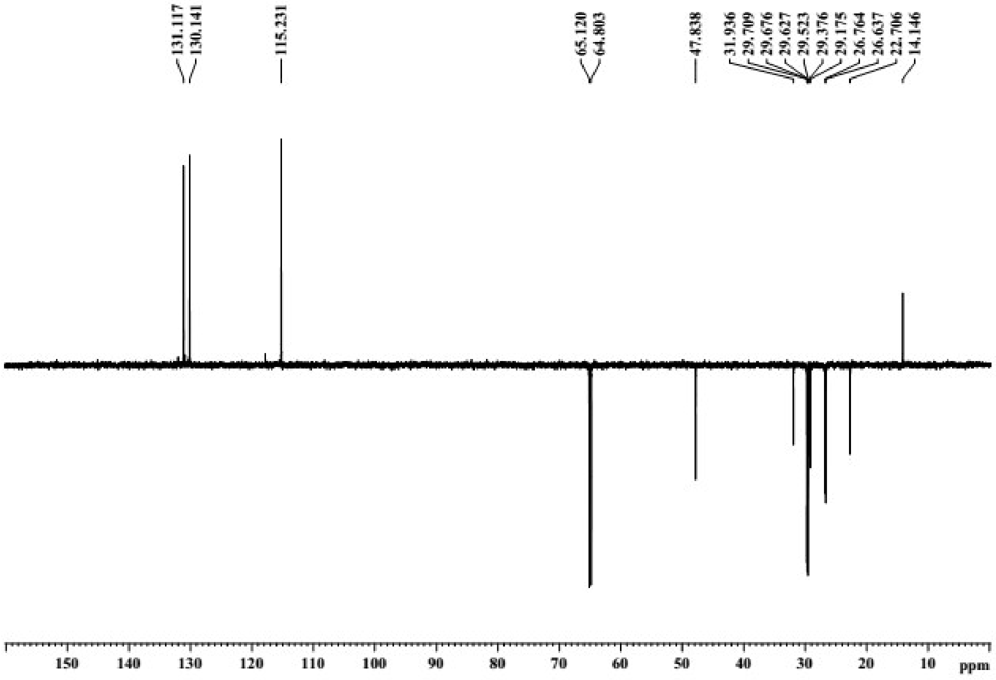


Figure S3. DEPT spectrum of compound **1**

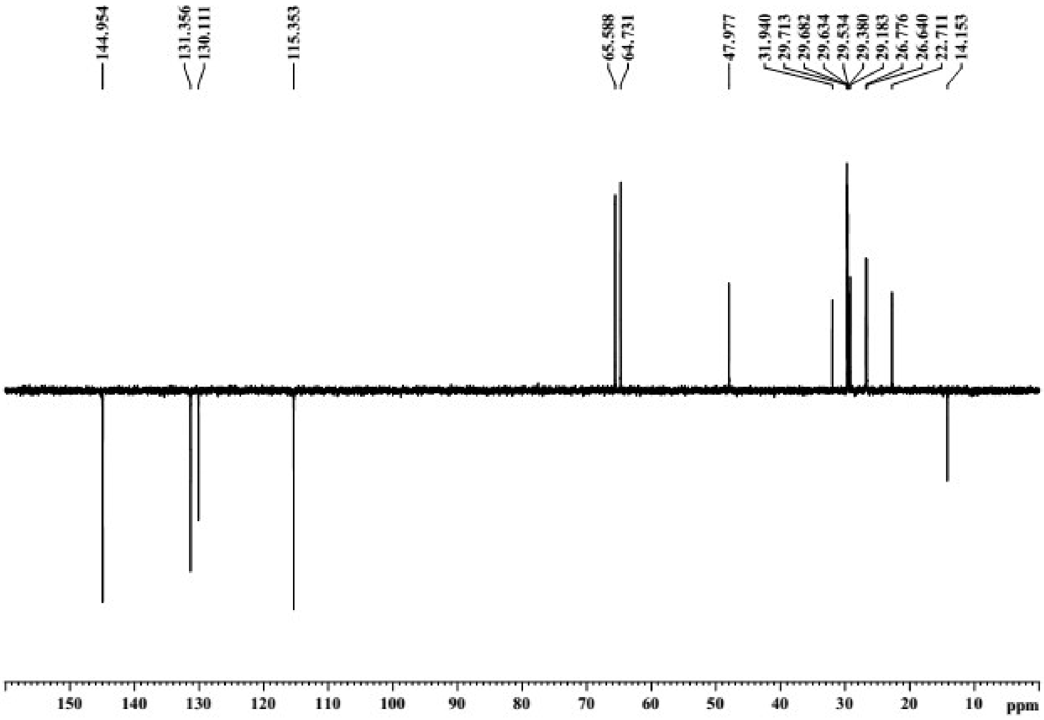
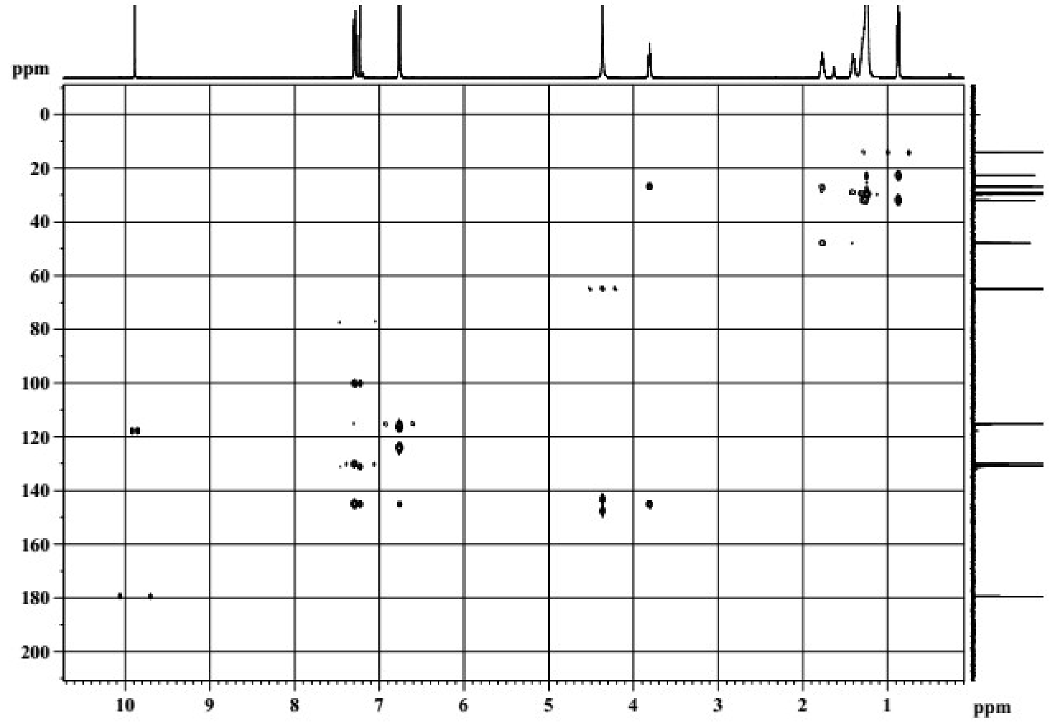


Figure S4. DEPT NMR spectrum of compound **2**

2D NMR spectra of compounds 1and 2



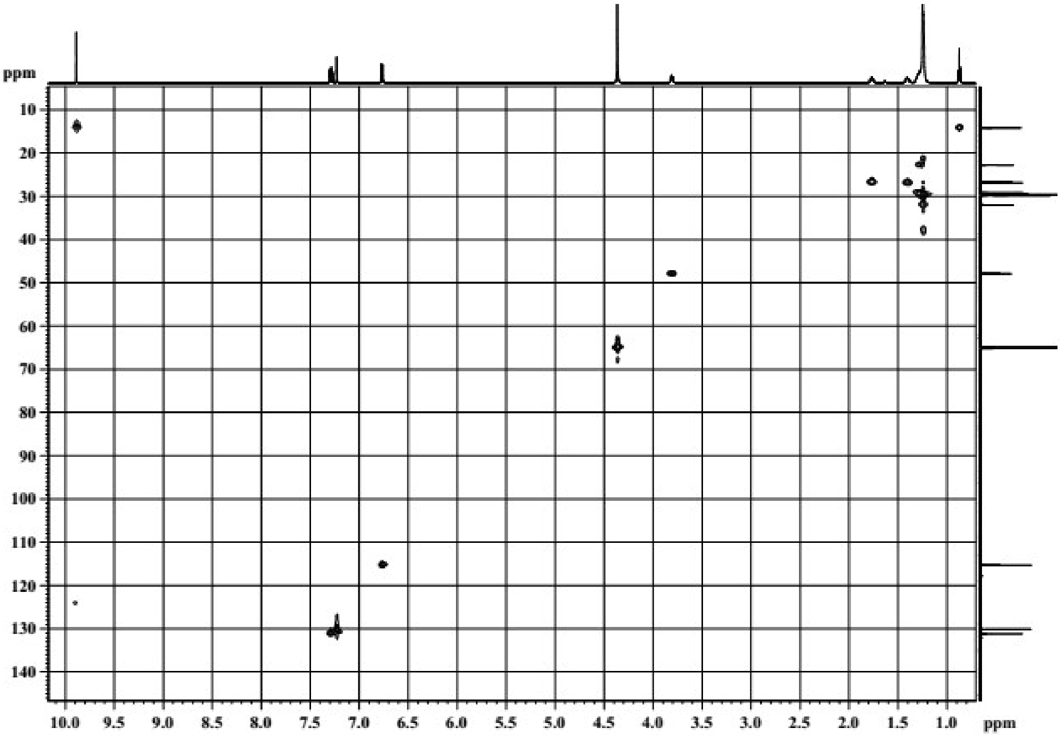
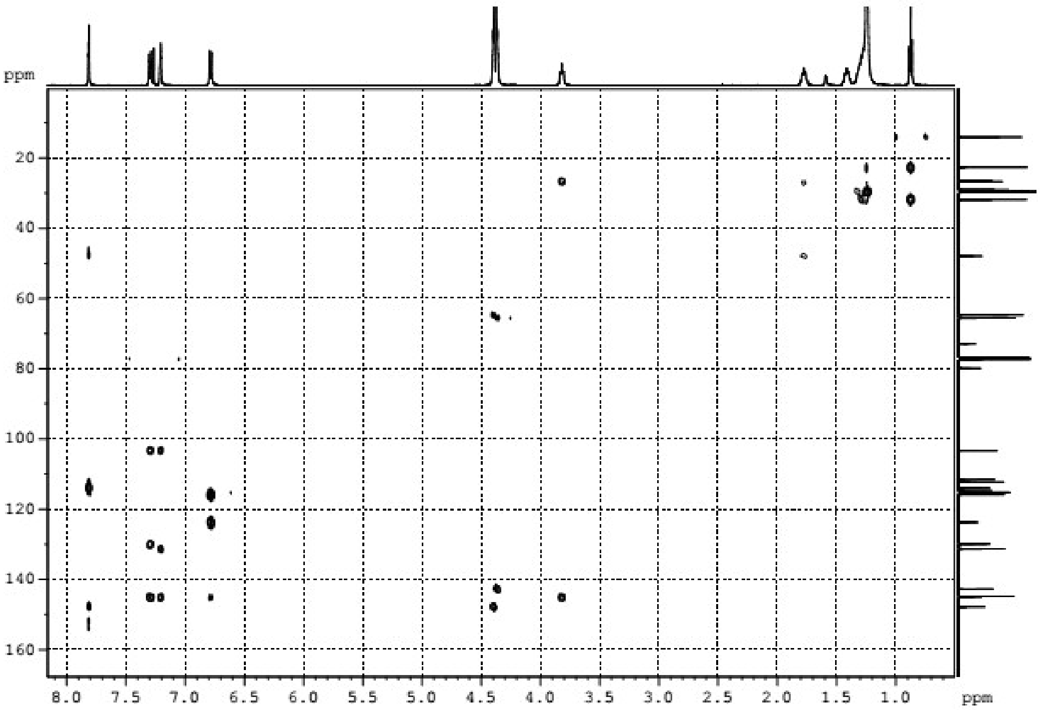


Figure S5. HMBC and HSQC NMR spectra of compound **1**



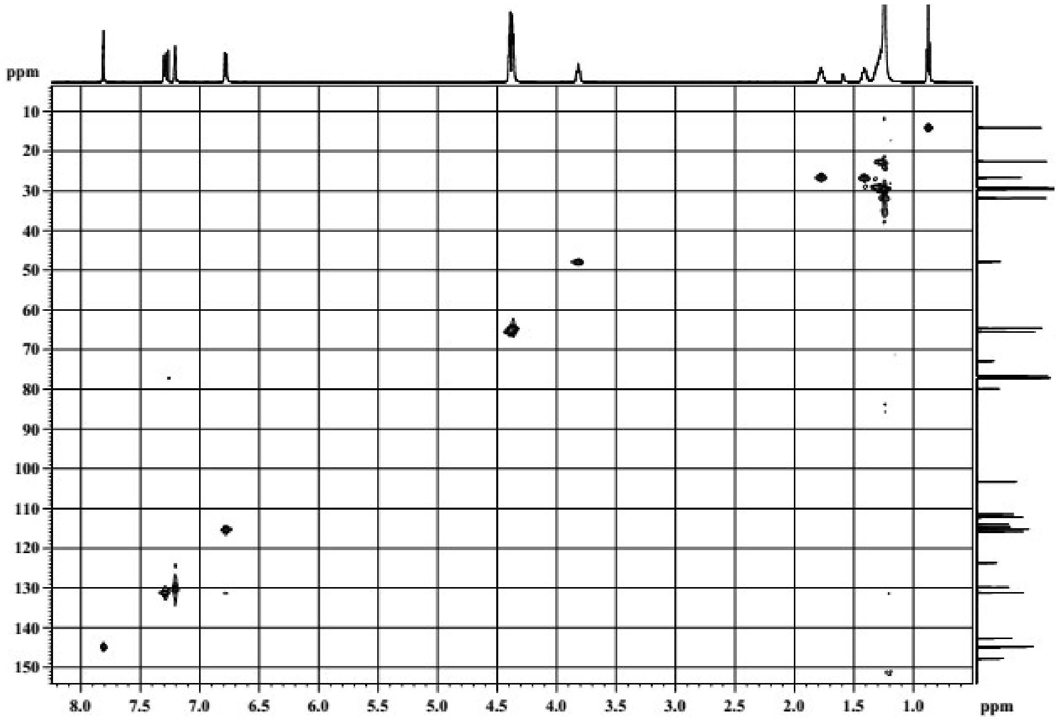


Figure S6. HMBC and HSQC NMR spectra of compound **2**

MALDI Spectra of compounds 1and 2:

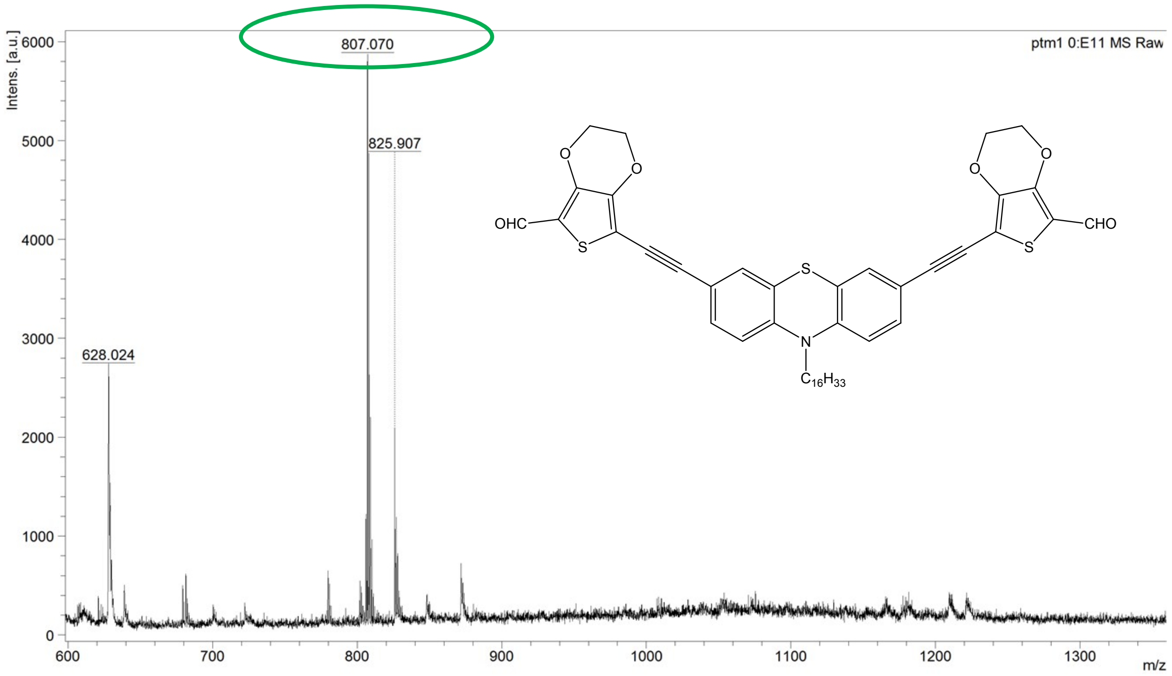


Figure S7. MALDI mass spectrum of compound **1**

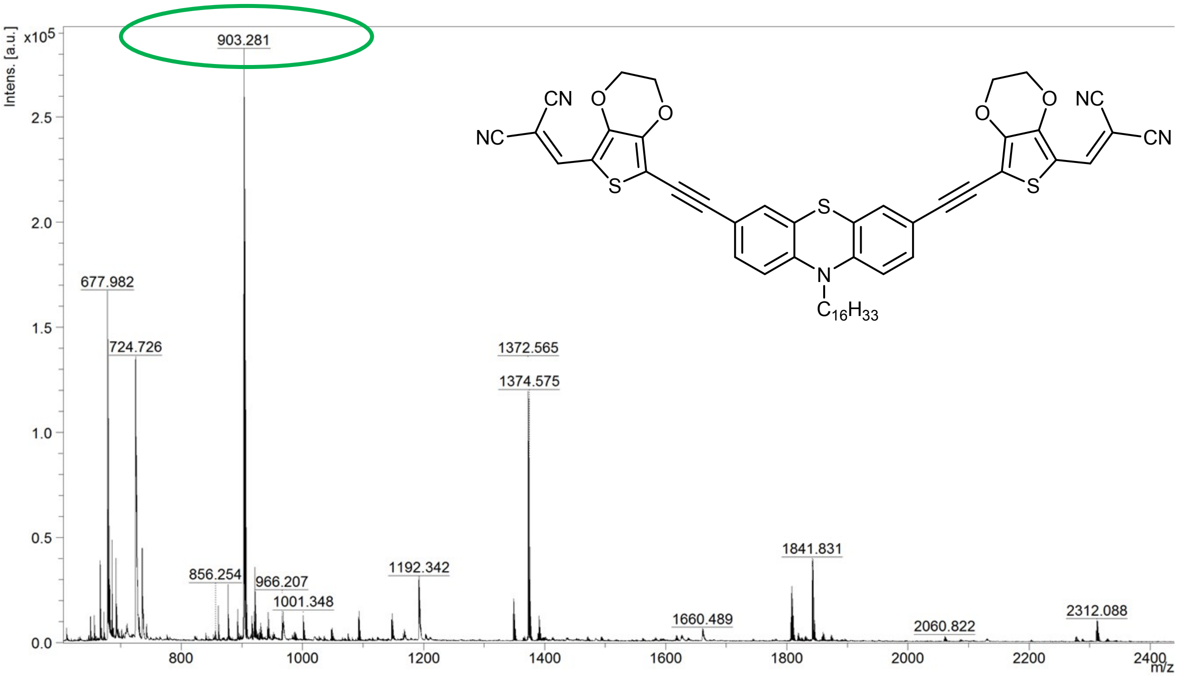


Figure S8. MALDI mass spectrum of compound **2**

Data of X-ray crystallographic analysis of compound 1:

CCDC–921593 contains the supplementary crystallographic data for **1**.
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Empirical formula	$C_{46}H_{49}NO_6S_3$	
Formula weight	808.04	
Temperature	298(2) K	
Wavelength	0.71073 A	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.3262(3) Å	α = 100.032(3)^{o}
	b = 13.1770(9) Å	β = 92.318(2)^{o}
	c = 34.470(2) Å	γ = 95.724(3)^{o}
Volume	2366.2(3) $Å^3$	
Z	2	
Calculated density	1.134 g/cm^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	856	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	0.60 to 25.00^{o}	
Limiting indices	-6<=h<=5, -15<=k<=15, -40<=l<=40	
Reflections collected	21926	
Independent reflections	7690 [R(int) = 0.0408]	
Completeness to theta = 25.00	92.0 %	
Absorption correction	None	
Max. and min. transmission	0.9706 and 0.9516	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7690 / 0 / 506	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0793, wR2 = 0.2482	
R indices (all data)	R1 = 0.1416, wR2 = 0.2921	
Largest diff. peak and hole	0.743 and -0.322 $e.A^{-3}$	

Comparison of powder XRD of 1 in various forms:

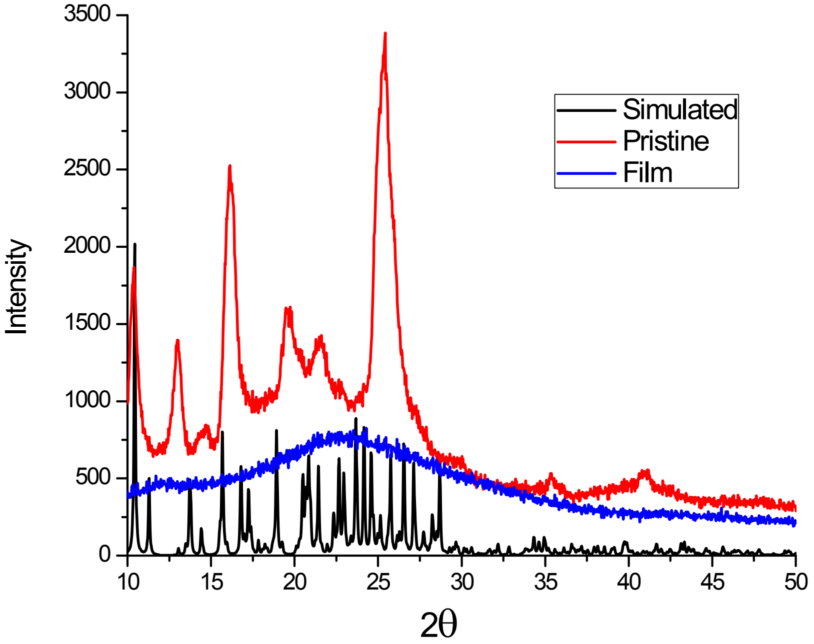


Figure S9. Powder XRD pattern of compound **1** in crystal (red line), powder (blue line) and thin film form (violet) compared with the simulated data obtained from SXRD

Powder XRD pattern of the compounds 1 and 2:

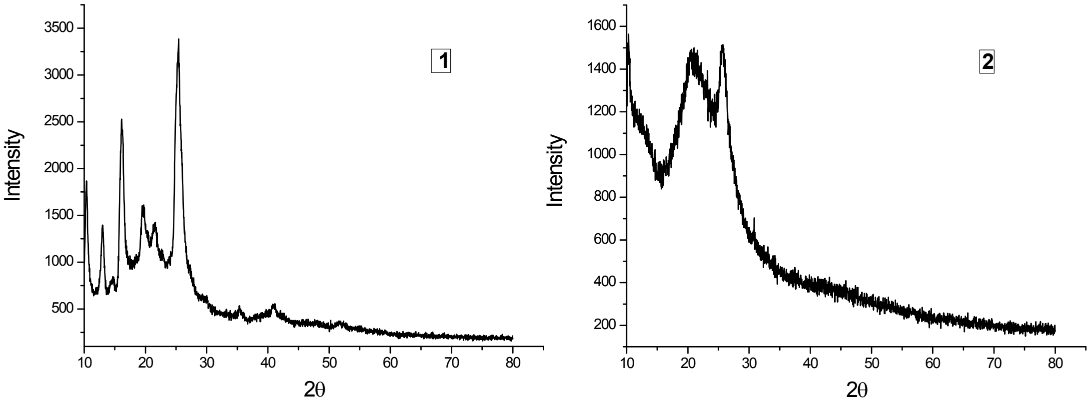


Figure S10. Powder XRD Pattern of compounds **1** and **2**

^{1}H NMR analysis of Acetone included crystals of 1

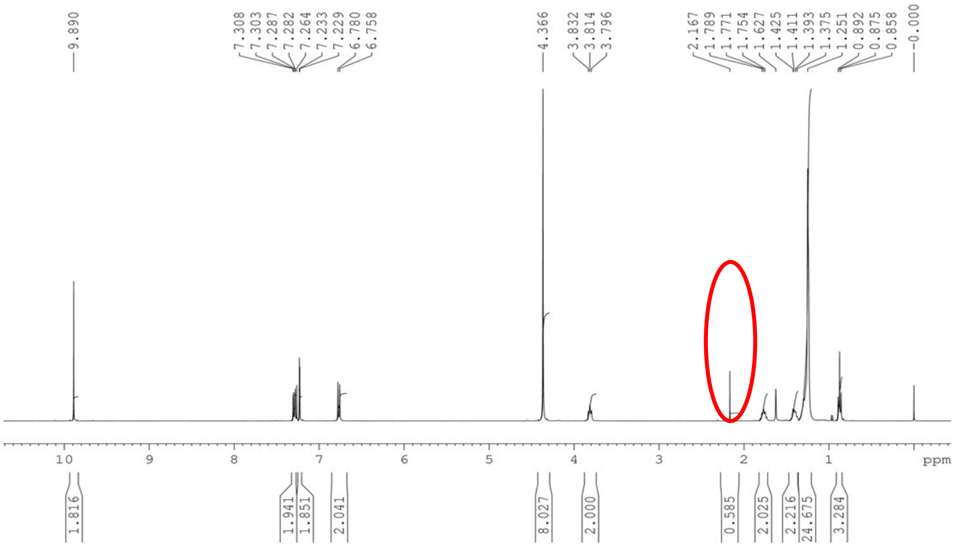


Figure S11. ^{1}H NMR spectrum of **1** as crystallized **(**acetone at 2.1 ppm)

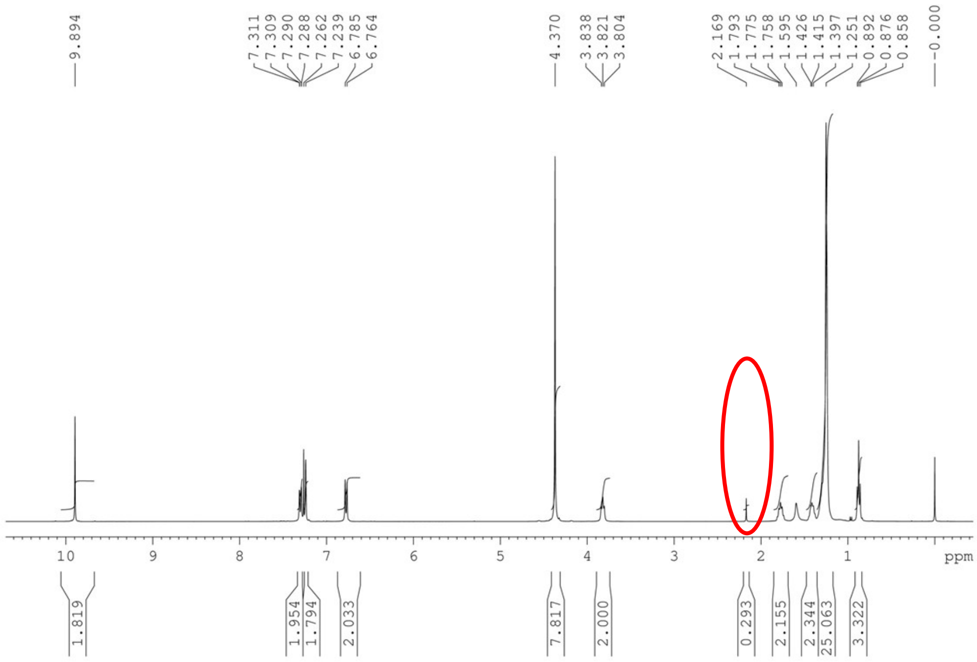


Figure S12. ^{1}H NMR spectrum of **1** after heating at 70 ^{0}C for 10 minutes (amount of acetone at 2.1 ppm is reduced)

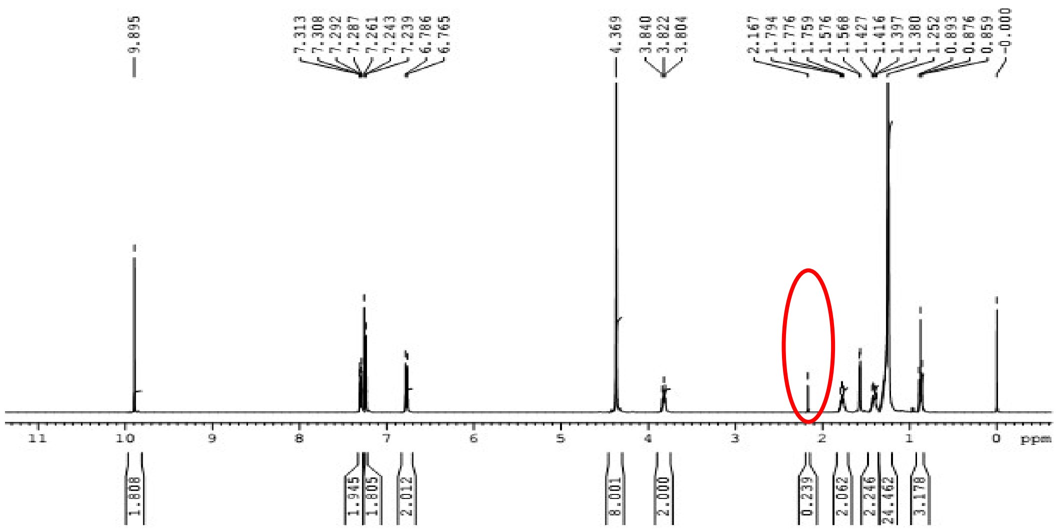


Figure S13. ^{1}H NMR spectrum of **1** after heating at 70 ^{0}C for 20 minutes (amount of acetone at 2.1 ppm is reduced further)

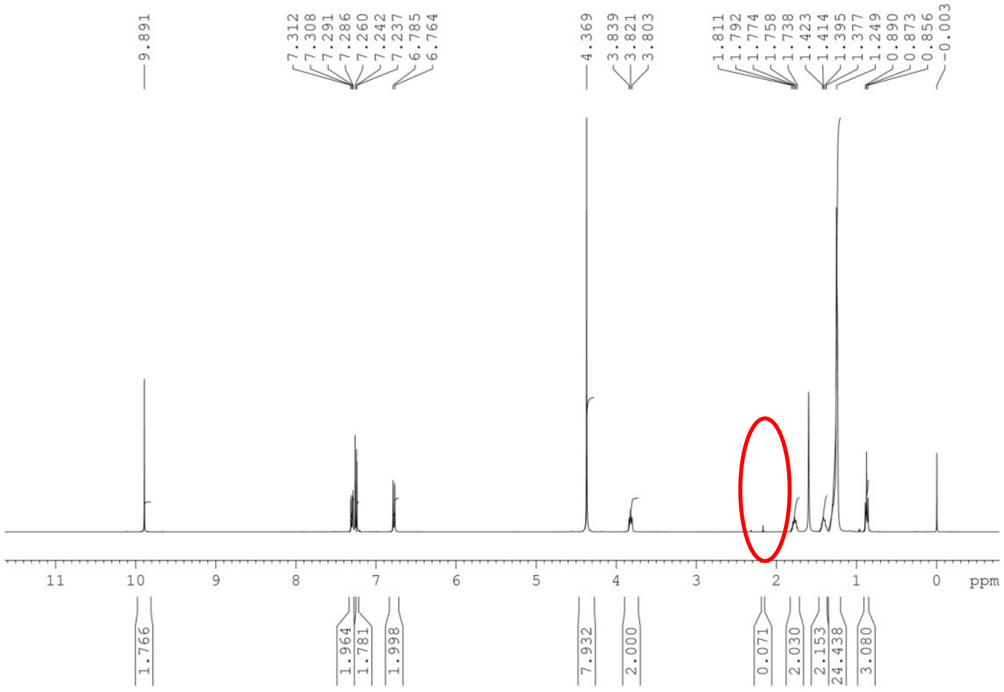


Figure S14. ^{1}H NMR spectrum of **1** after grinding well (acetone peak at 2.1 ppm is reduced even further)

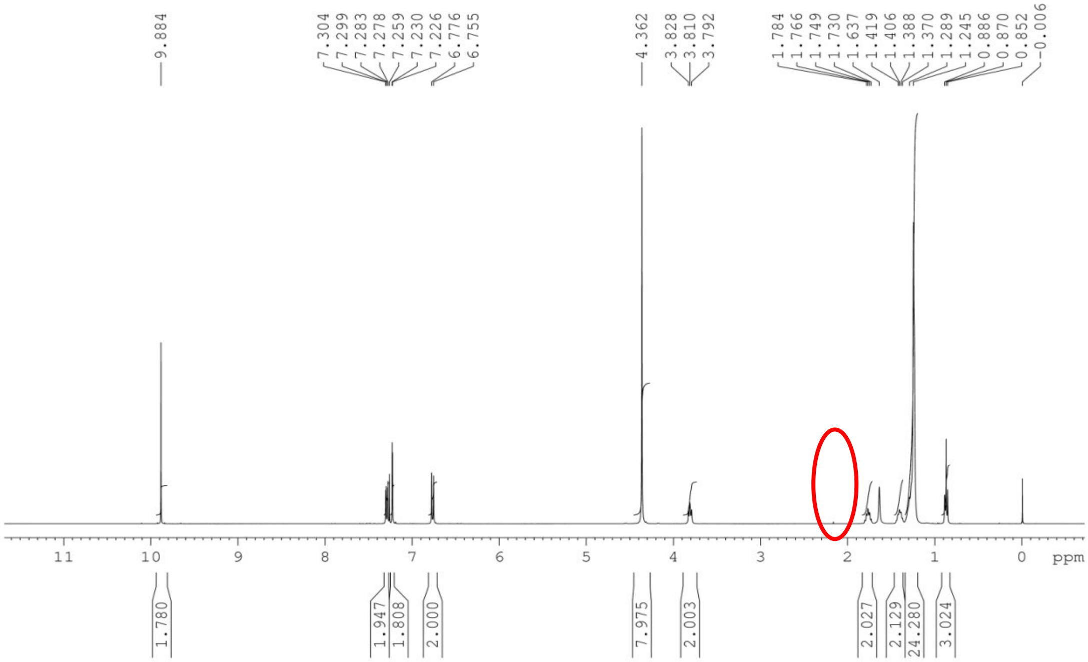


Figure S15. ^{1}H NMR spectrum of **1** after grinding well and heating for 30 minutes (acetone at 2.1 ppm is nearly disappeared)

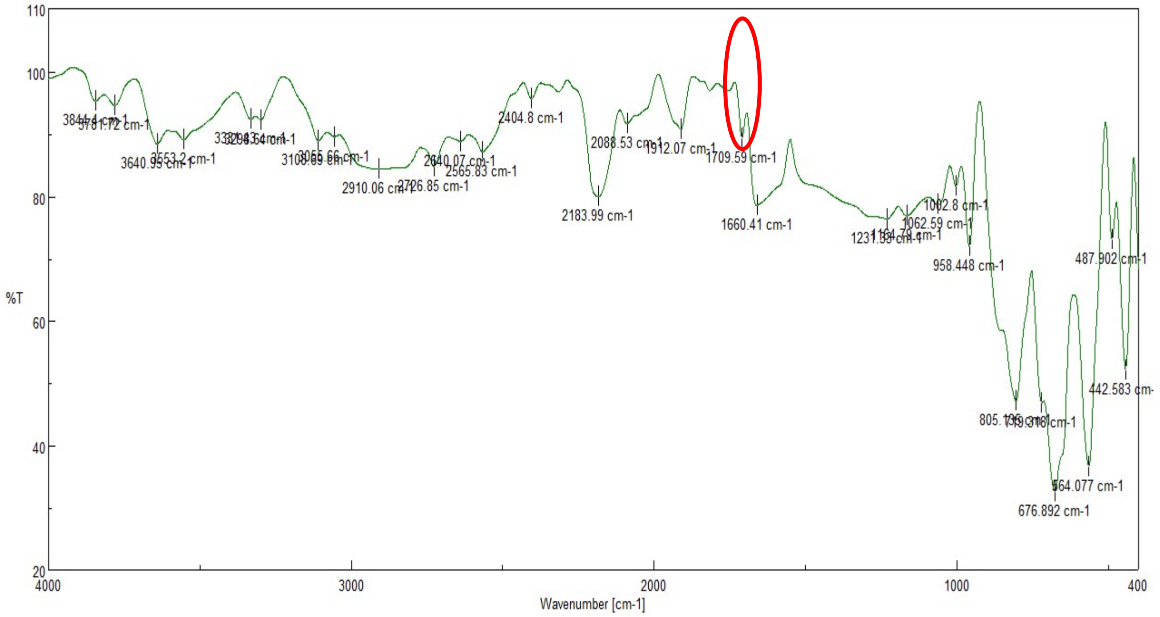


Figure S16. IR spectrum of compound **1** as crystallized

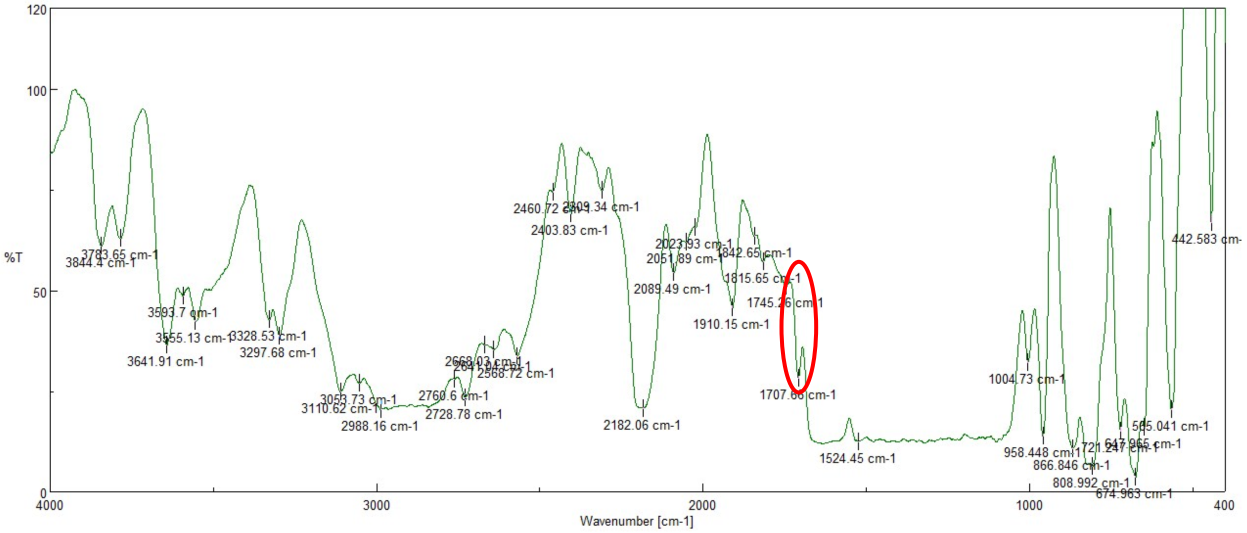


Figure S17. IR spectrum of compound **1** slightly ground

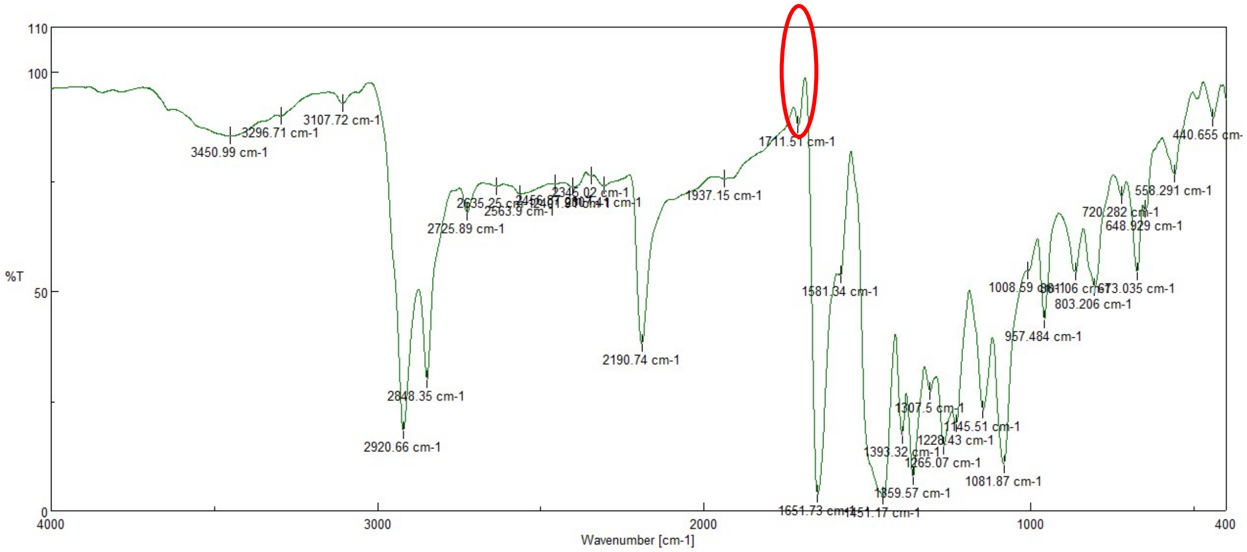


Figure S18. IR spectrum of compound **1** slightly ground with KBr

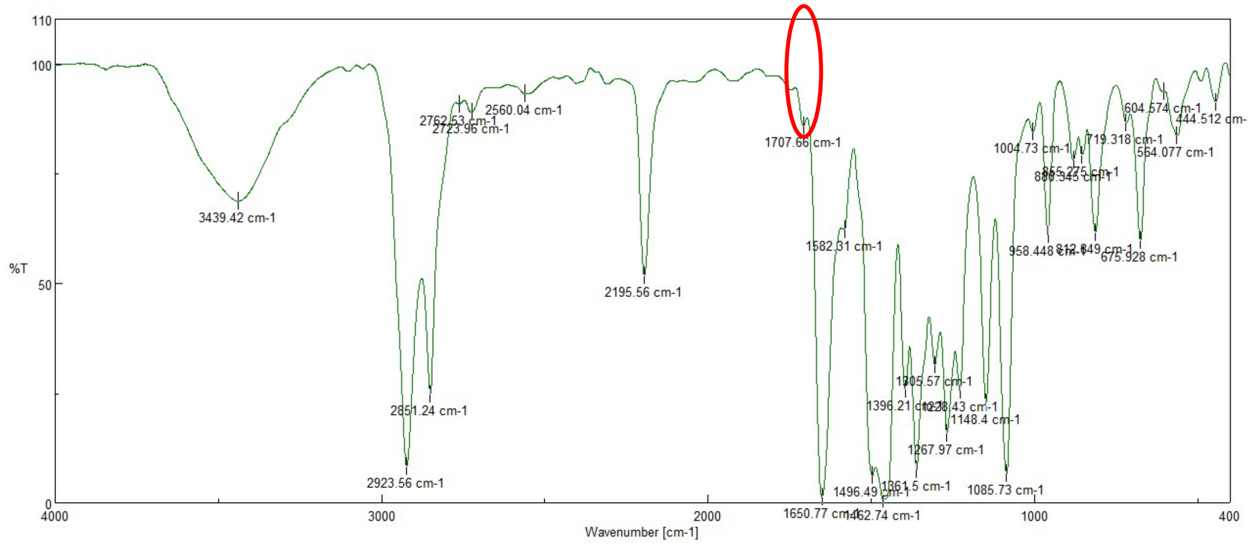


Figure S19. IR spectrum of compound **1** strongly ground with KBr

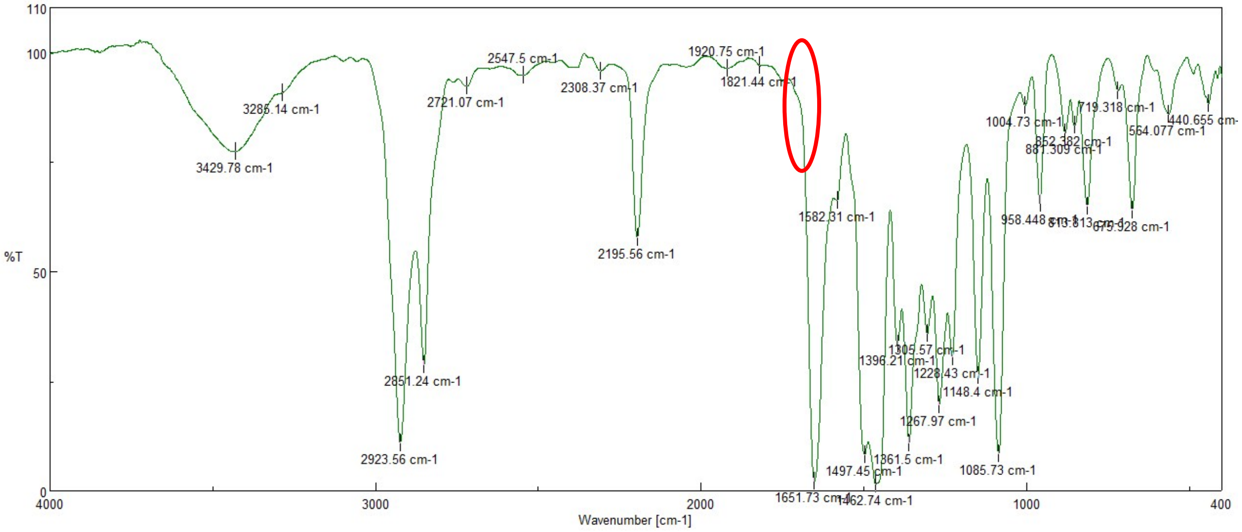


Figure S20. IR spectrum of compound **1** strongly ground with KBr and heated for 30 minutes

Differential scanning calorimetry analysis of acetone included crystals of 1:

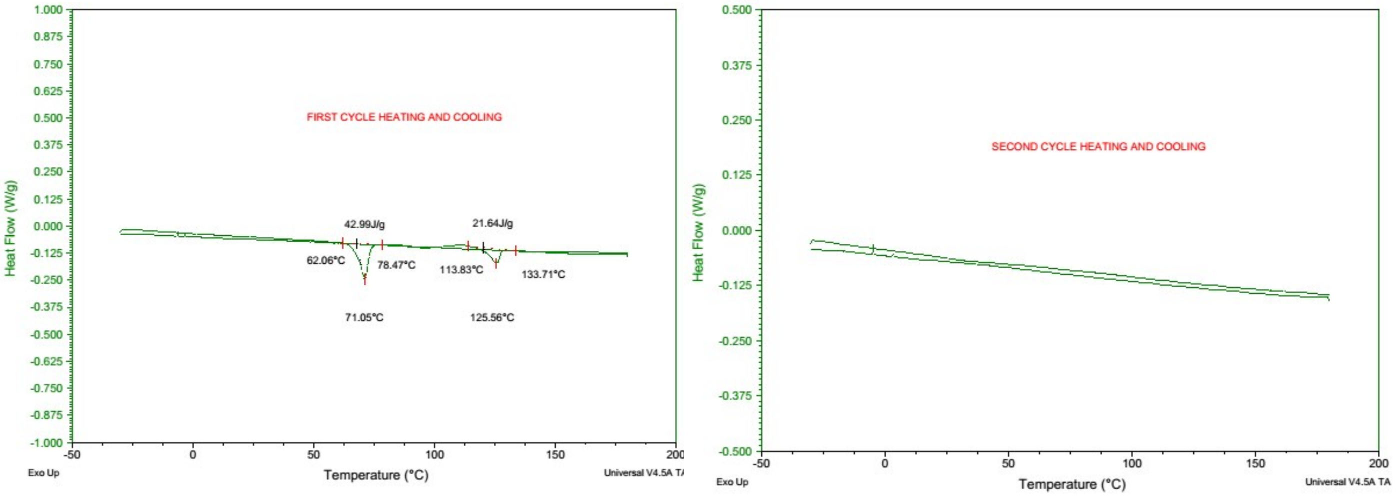


Figure S21. Differential scanning calorimetry traces of compounds **1** in single crystal form in the first cycle of heating at 1 ^{0}C / min followed by cooling at 1 ^{0}C / min and second cycle of heating and cooling at 1 ^{0}C / min

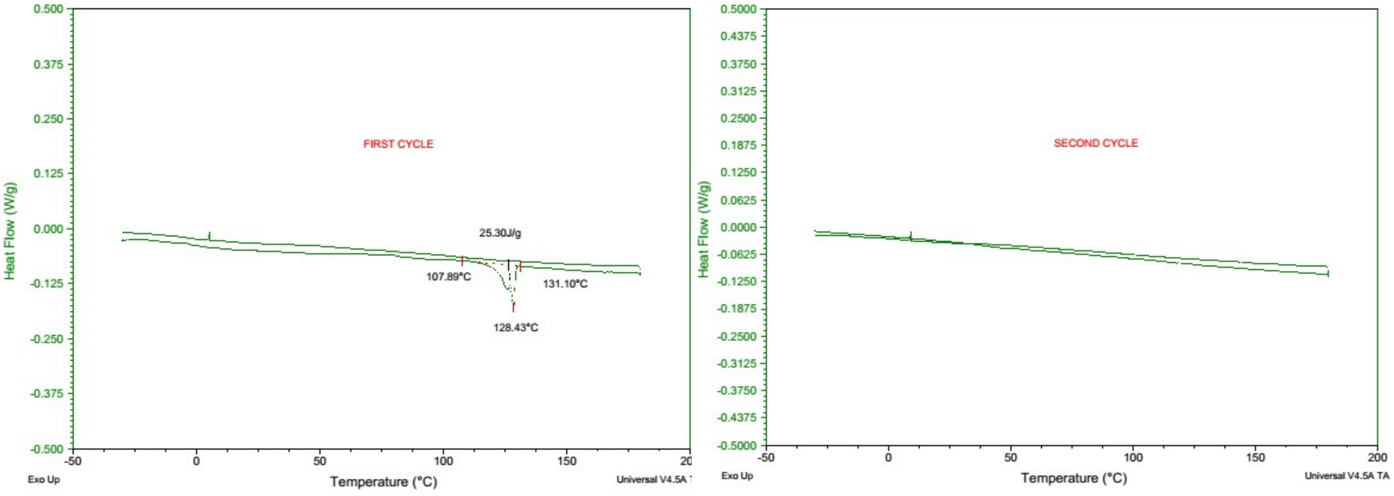


Figure S22. Differential scanning calorimetry traces of compounds **1** in the as synthesized form in the first cycle of heating at 1 ^{0}C / min followed by cooling at 1 ^{0}C / min and second cycle of heating and cooling at 1 ^{0}C / min.

Thermogravimetric analysis (TGA) traces of compounds 1 and 2:

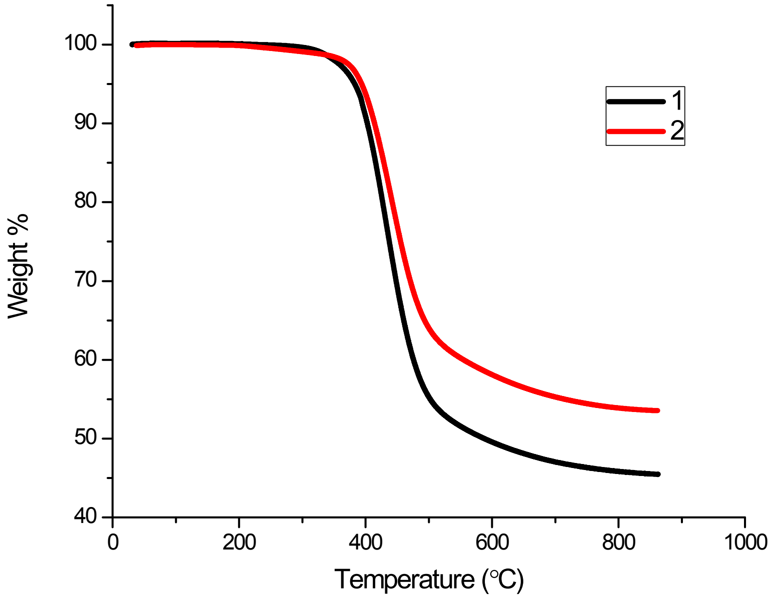


Figure S23. Thermogravimetric analysis traces of compounds **1** and **2**

***Table S1.* Thermal properties of 1 and 2**.

Cmpd	**1**	**2**
M_p[°C][a]	128	100
T_d[°C][b]	383	394

[a] determined using a melting point apparatus. [b] *T*d: decomposition temperature at which the compound loses 5% of the weight as determined by TGA at a heating rate of 5 °C / min.

UV-visible absorption and fluorescence measurement of 1 and 2 in thin film form dispersed in polystyrene (PS) matrix

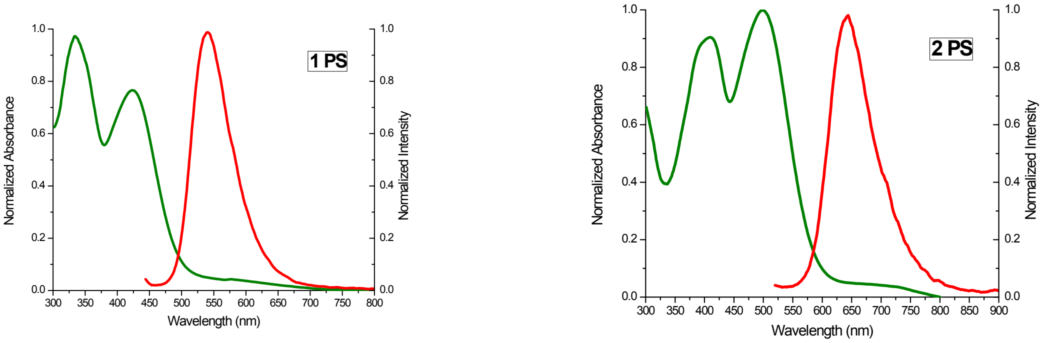


Figure S24. UV-visible and fluorescence spectra of aldehyde **1** (left) and dicyanovinyl compound **2** (right) in thin film form dispersed in PS matrix.

Preparation of doped polystyrene (PS) films:
The sample was dissolved in a saturated PS benzene solution (0.1 mg/mL). The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 1000 rpm for 30 seconds. The PS film was dried under reduced pressure at 50 °C for 1 h.

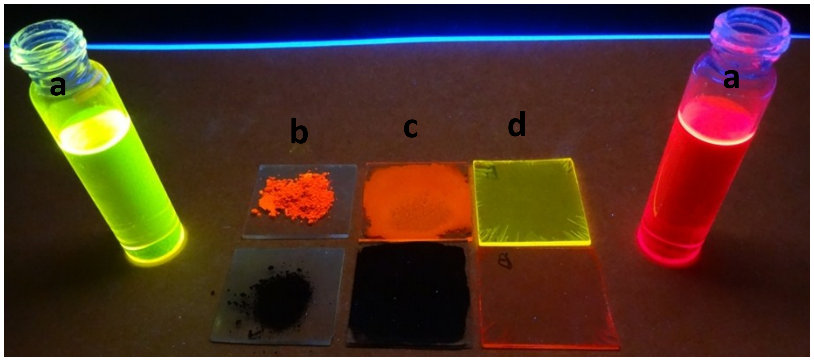


Figure S25. **1** and **2** *a)* in toluene (left vial, **1**; right vial, **2**). b) as powder. c) drop cast film. d) doped in PS film (Top row, **1**; bottom row, **2**)

CV Measurement: Cyclic voltammetry (CV) was performed on a CHI 660D electrochemical analyzer. The CV cell consisted of Glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. A DCM solution of a sample with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4PF_6) as supporting electrolyte were used for the measurement at a scan rate of 50 mV/s. The solvent (DCM) was degassed with nitrogen for 15 minutes before making the solution of the compound prior to each experiment.

***Table S2*. Computational data of compounds 1 and 2**

Cpd	Exp wavelength [nm]	Exp Excitation Energy (eV)	Calc. wavelength [nm]	Calc. Excitation Energy (eV)	Transition configuration (coefficient)	Oscillator strength (*f*)
1	500 (abs edge)	2.48	473	2.62	214 → 215 (0.69889) [HOMO → LUMO]	0.9487
	419 (abs maximum)	2.95	368	3.36	213 → 216 (0.68591) [HOMO-1 → LUMO+1]	0.7640
2	584 (abs edge)	2.12	568	2.18	238 → 239 (0.70124) [HOMO → LUMO]	1.1880
	493 (abs maximum)	2.51	438	2.83	237 → 240 (0.66884) [HOMO-1 → LUMO+1]	0.7494