Electronic Supplementary Information

Dithieno[3,2-*b*:2′,3′-*d*]pyrrole based, NIR absorbing, solution processable, small molecule donor for efficient bulk heterojunction solar cells.

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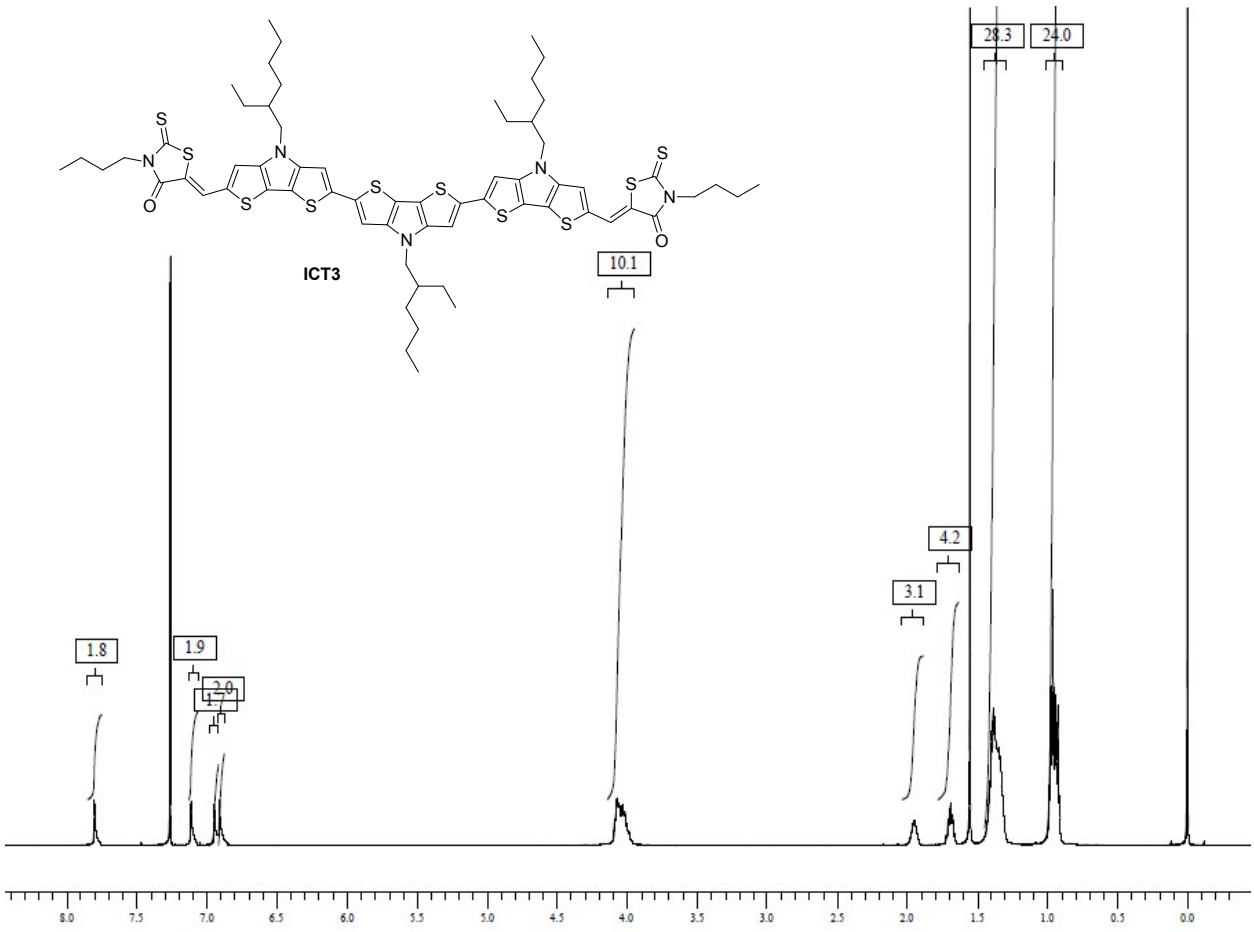


Fig. S1. ^{1}H NMR spectrum of **ICT3**

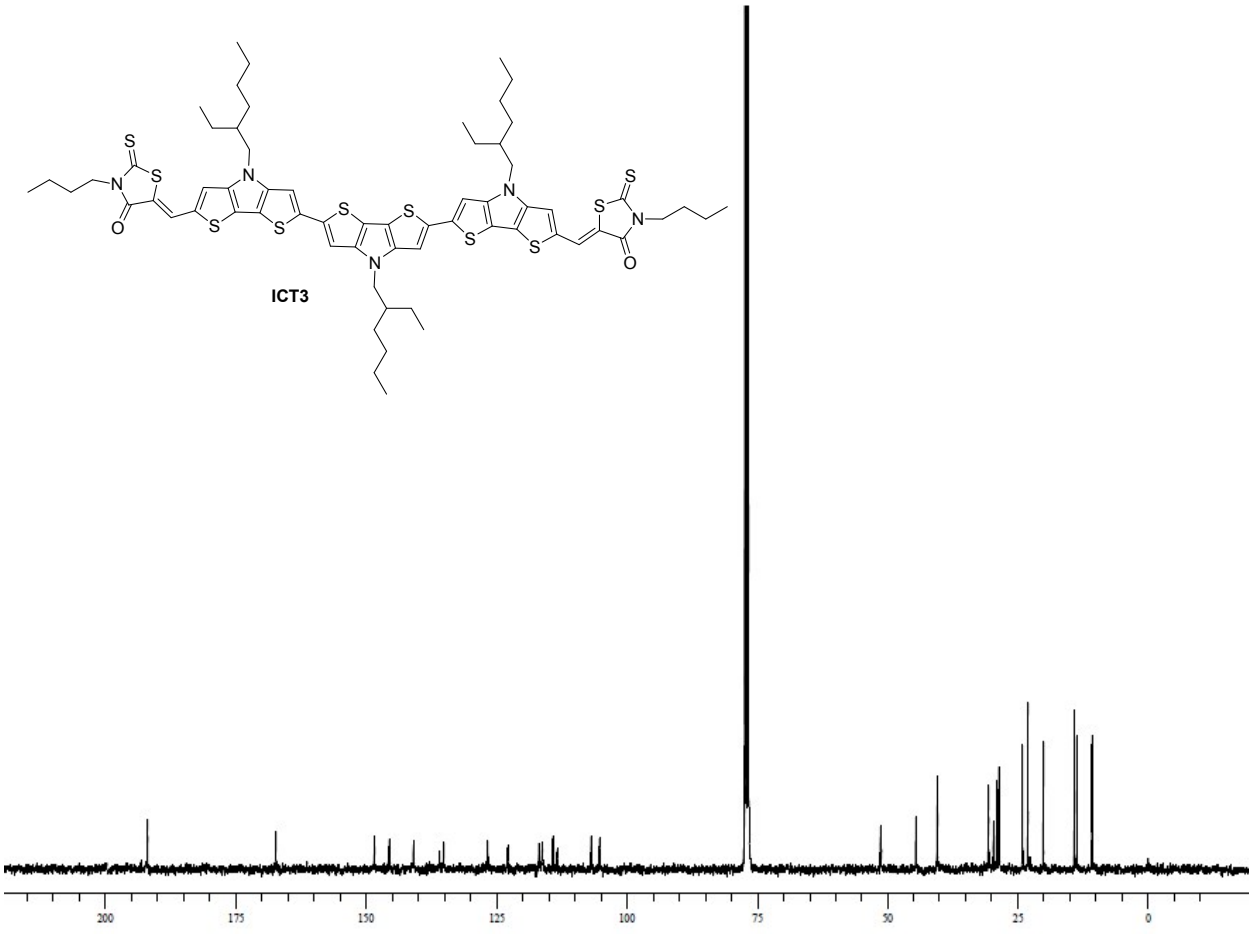


Fig. S2. ^{13}C NMR spectrum of **ICT3**

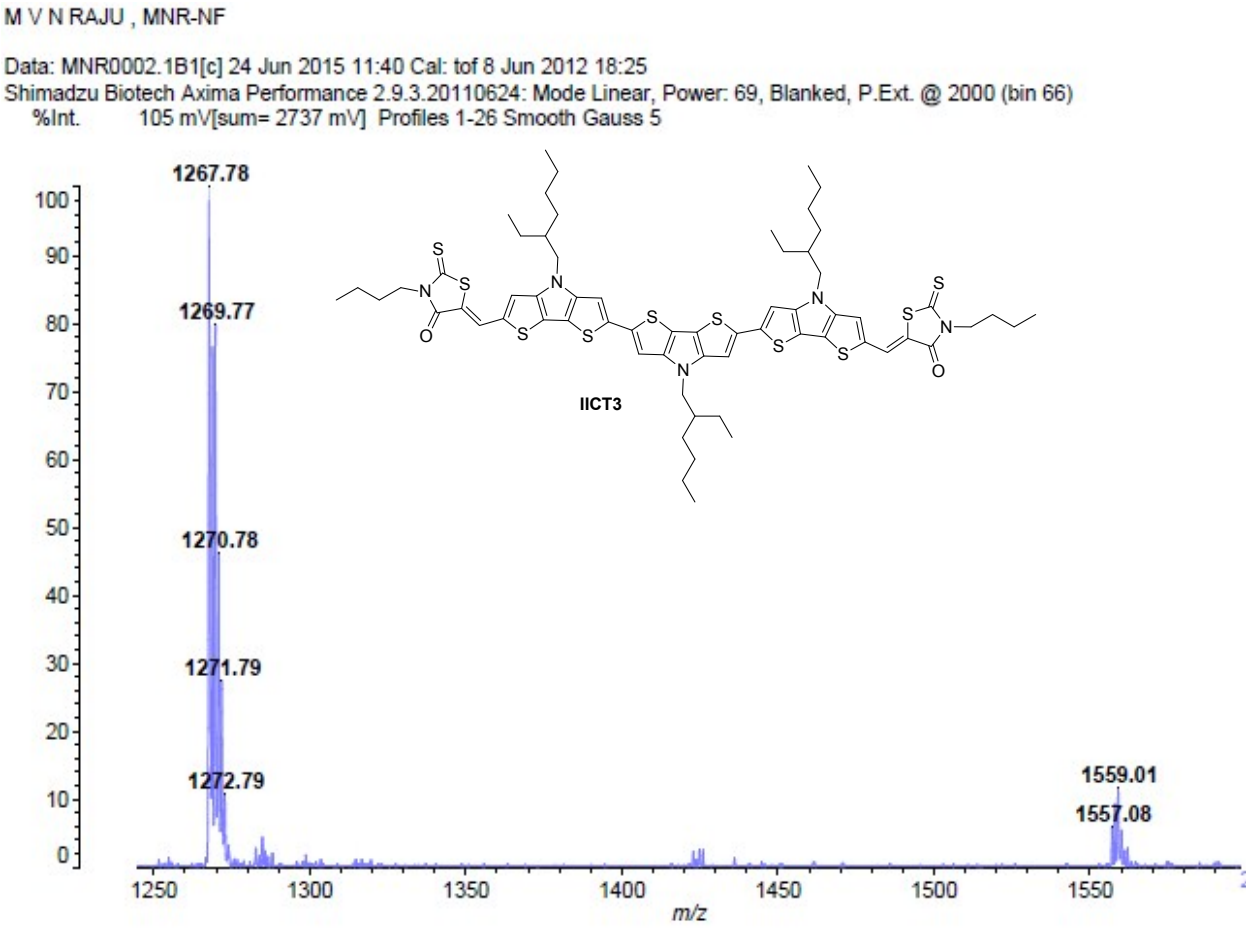
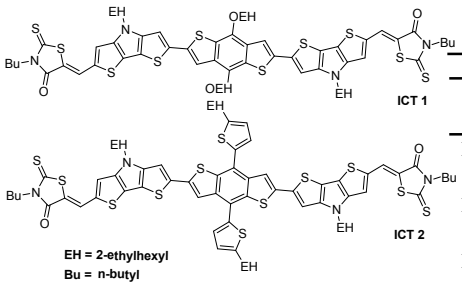


Fig. S3. MALDI-MS spectrum of **ICT3**



Material Code	λ_{max} (nm)[a]	ξ (x 10^5 mol^{-1} cm^{-1})[a]	λ_{max} (nm)[b]	E_{o-o} (eV)[c]	E_g^{opt} (eV)[d]	E_{ox} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)[e]
ICT1	586	1.71	604	1.96	1.68	0.29	-5.39	-3.43
ICT2	594	1.65	608	2.02	1.63	0.38	-5.48	-3.46

Active layer	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)	R_s (Ωcm^2)	R_{sh} (Ω cm^2)
ICT1:PC_{71}BM (as cast)	6.84	0.92	0.44	2.77	24.06	510
ICT2:PC_{71}BM (as cast)	7.26	0.96	0.47	3.27	22.16	564
ICT1:PC_{71}BM (TSA)	10.15	0.87	0.58	5.12	12.92	686
ICT2:PC_{71}BM (TSA)	10.68	0.92	0.60	5.90	9.08	746

[a]in dilute chloroform solution (10 μM), [b]in thin film cast from chloroform solution, [c]estimated from intersection of absorption and emission spectra in chloroform solution, [d]estimated from $E_g^{opt}=1240/\lambda_{onset}$, λ_{onset} is onset absorption wavelength in thin film, [e]$E_{LUMO}= E_{HOMO}-E_{o-o}$.

Fig. S4. Chemical structures of **ICT1** and **ICT2** and their photophysical, electrochemical and photovoltaic data

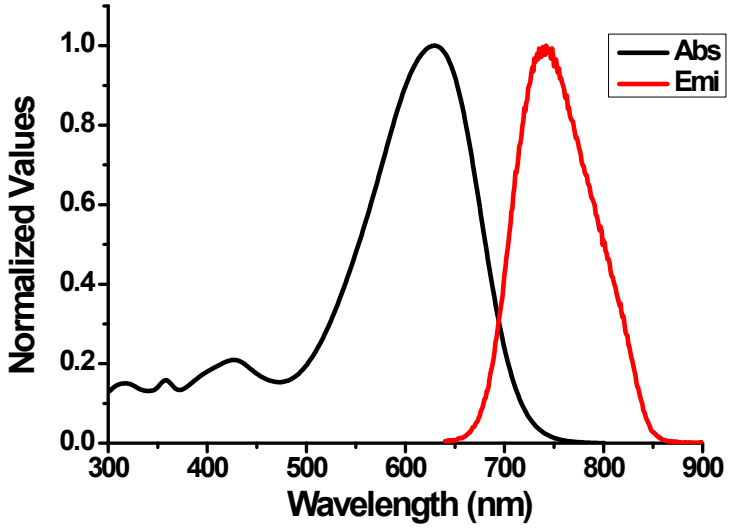


Fig. S5. Absorption and fluorescence spectra of **ICT3** (10 μM) measured in chloroform solution.

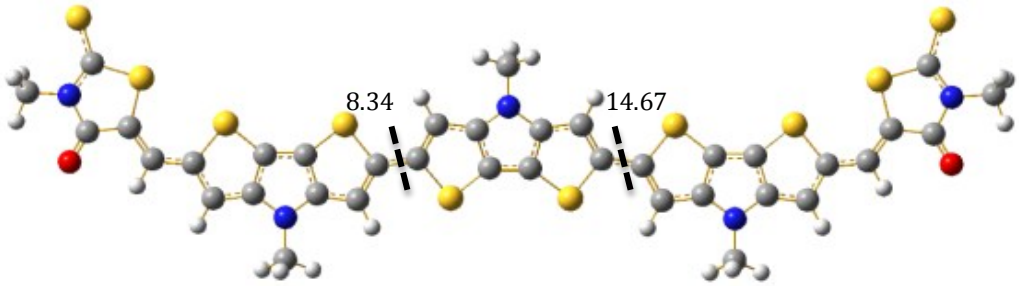


Fig. S6. Optimized structure of **ICT3**.

Table S1 Calculated properties of **ICT3** at M06/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength *f*, the wavelength maxima, the major contribution (%)to the first excited state and the dipole moment μ_g (D).[a]

Molecule	**HOMO (eV)**	**LUMO (eV)**	**HLG (eV)**	**λ (nm)**	***OG* (eV)**	***f***	**Major contribution (%)**	**μ_g [a] (D)**
ICT3	-5.1	-2.69	2.41	628	1.974	3.520	H -1→ L+1(4%) H → L (95%)	9.07
	-5.04	*-2.71*	*2.33*	*676*	*1.834*	*3.707*	*H -1→ L+1(4%)* *H → L (93%)*	*12.27*

[a] values given in *Italic font* are the values obtained in the solvent phase CF.

Table S2 Calculated properties of **ICT3** at B3LYP/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength *f*, the wavelength maxima, the major contribution (%)to the first excited state and the dipole moment μ_g (D).[a]

Molecule	**HOMO (eV)**	**LUMO (eV)**	**HLG (eV)**	**λ (nm)**	**OG**	***f***	**Major contribution (%)**	**μ_g [b] (D)**
ICT3	-4.82	-2.76	2.06	664	1.867	3.291	H → L (99%)	9.72
	-4.75	*-2.76*	*1.97*	*724*	*1.712*	*3.484*	*H → L (98%)*	*13.15*

[a] values given in *Italic font* are the values obtained in the solvent phase CF.

Table S3 Calculated properties of **ICT3** at PBE/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength *f*, the wavelength maxima, the major contribution (%)to the first excited state and the dipole moment μ_g (D).[a]

Molecule	**HOMO (eV)**	**LUMO (eV)**	**HLG (eV)**	**λ (nm)**	**OG (eV)**	***f***	**Major contribution(%)**	**μ_g (D)**
ICT3	-4.82	-2.76	2.06	839	1.4770	1.975	H -1→ L+1 (6%) H→L+2 (3%) H → L (91%)	9.70

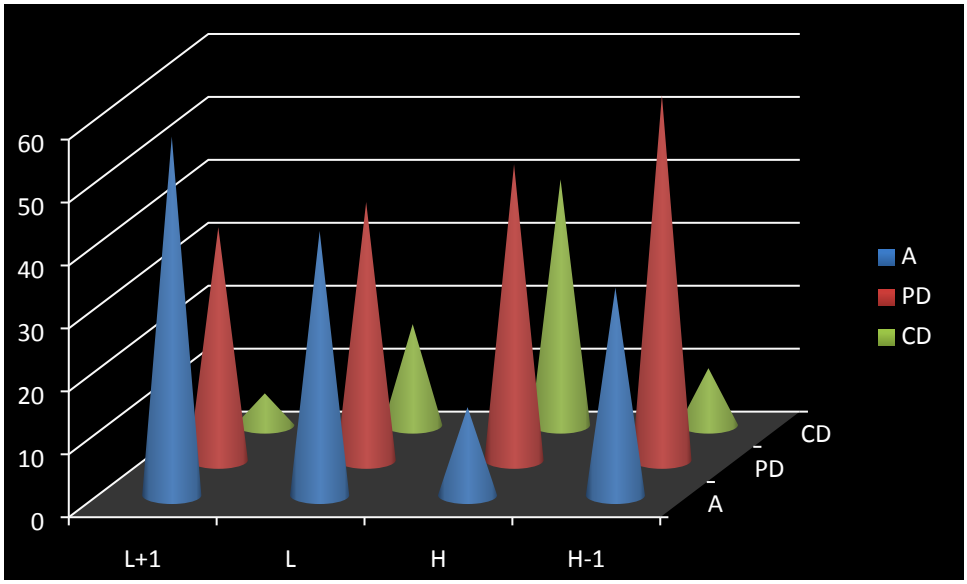


Fig. S7. Graphical representation of percentage contribution of different moieties of **ICT3**.

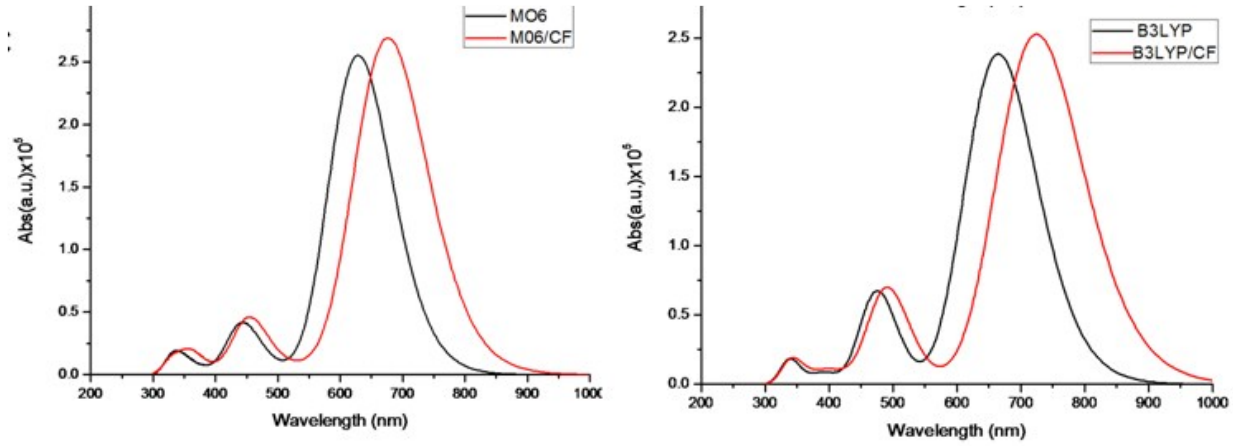


Fig. S8. Simulated UV-Vis Absorption spectra of **ICT3** using M06 and B3LYP in gas phase and solvent chloroform (CF)

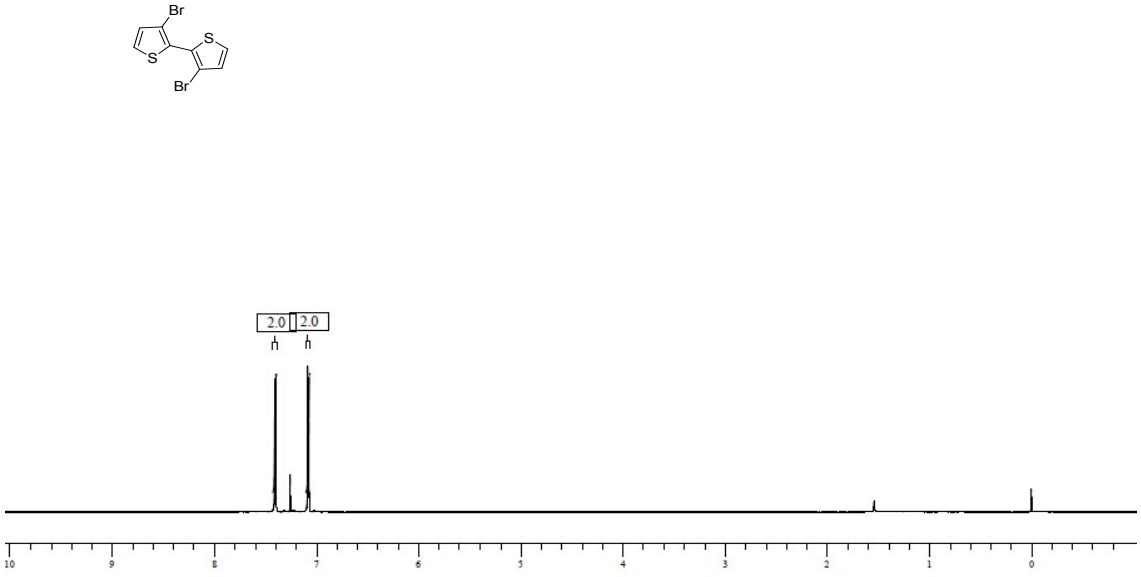


Fig. S9. ^{1}H NMR spectrum of **1**

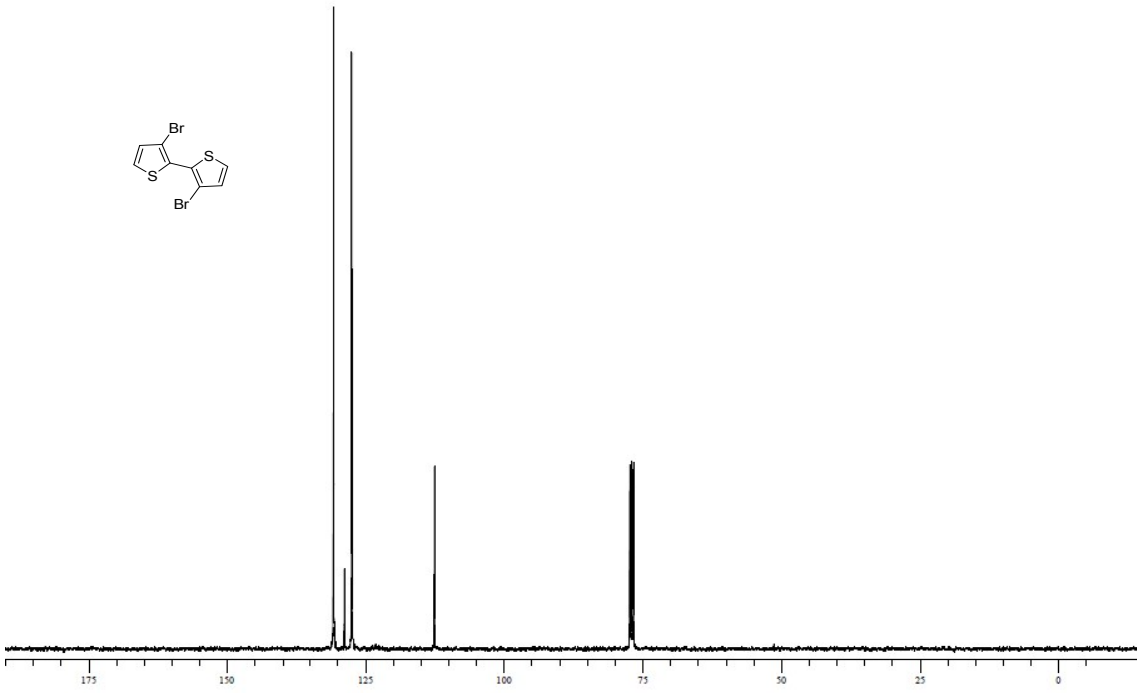


Fig. S10. ^{13}C NMR spectrum of **1**

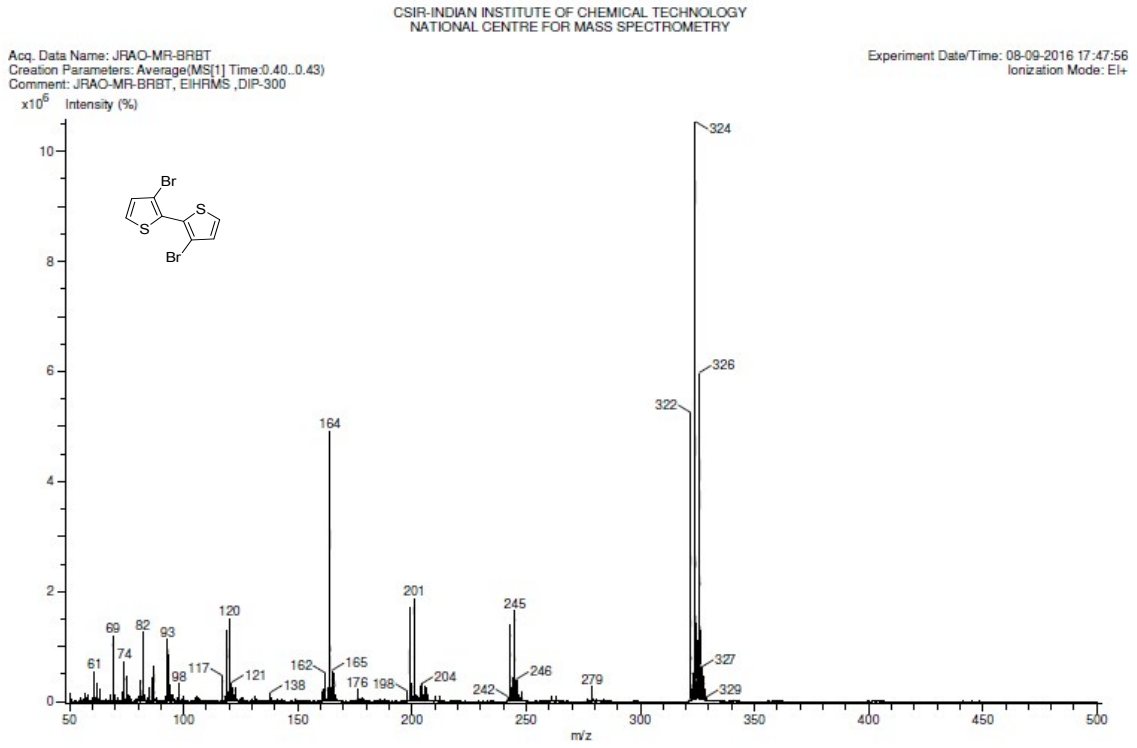


Fig. S11. EI-MS spectrum of **1**

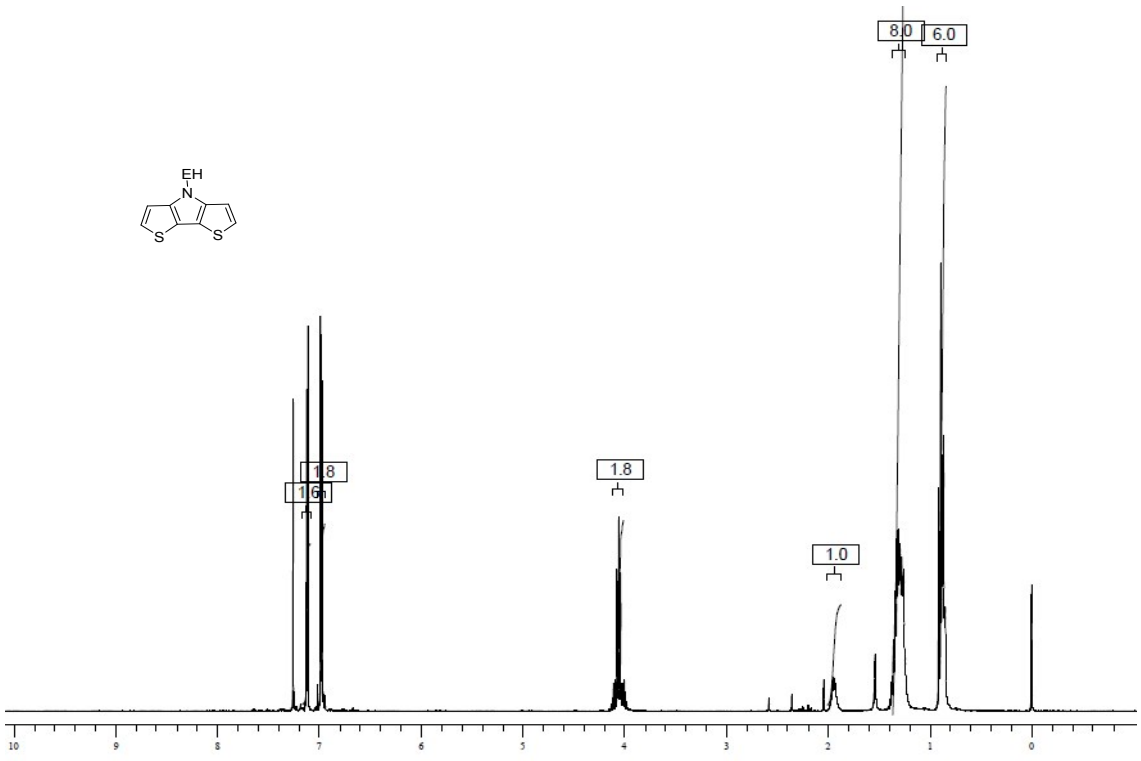


Fig. S12. ^{1}H NMR spectrum of **2**

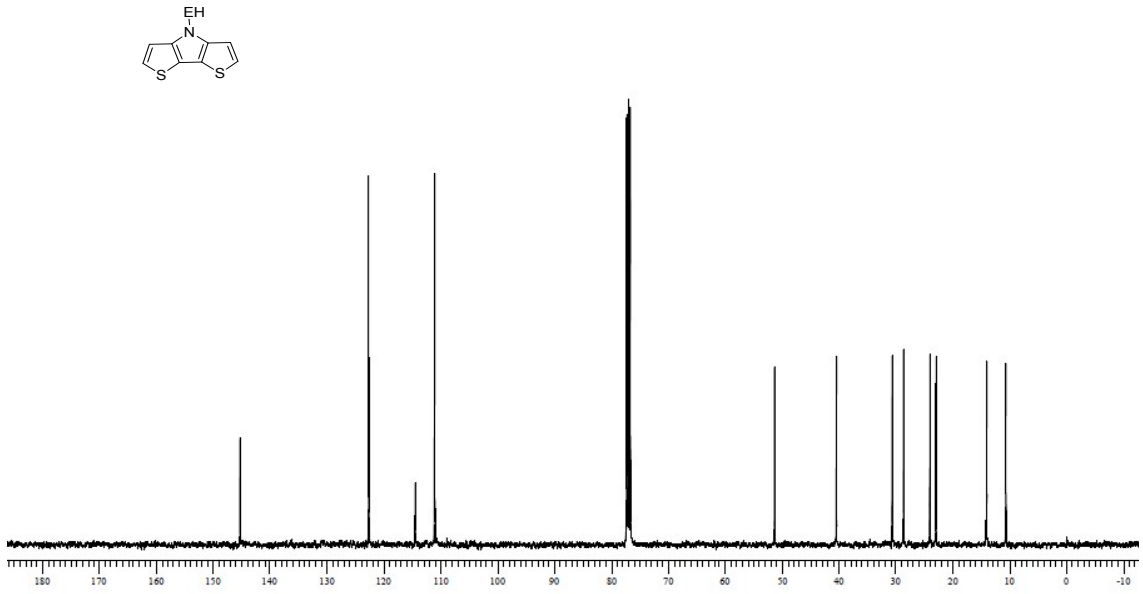


Fig. S13. ^{13}C NMR spectrum of **2**

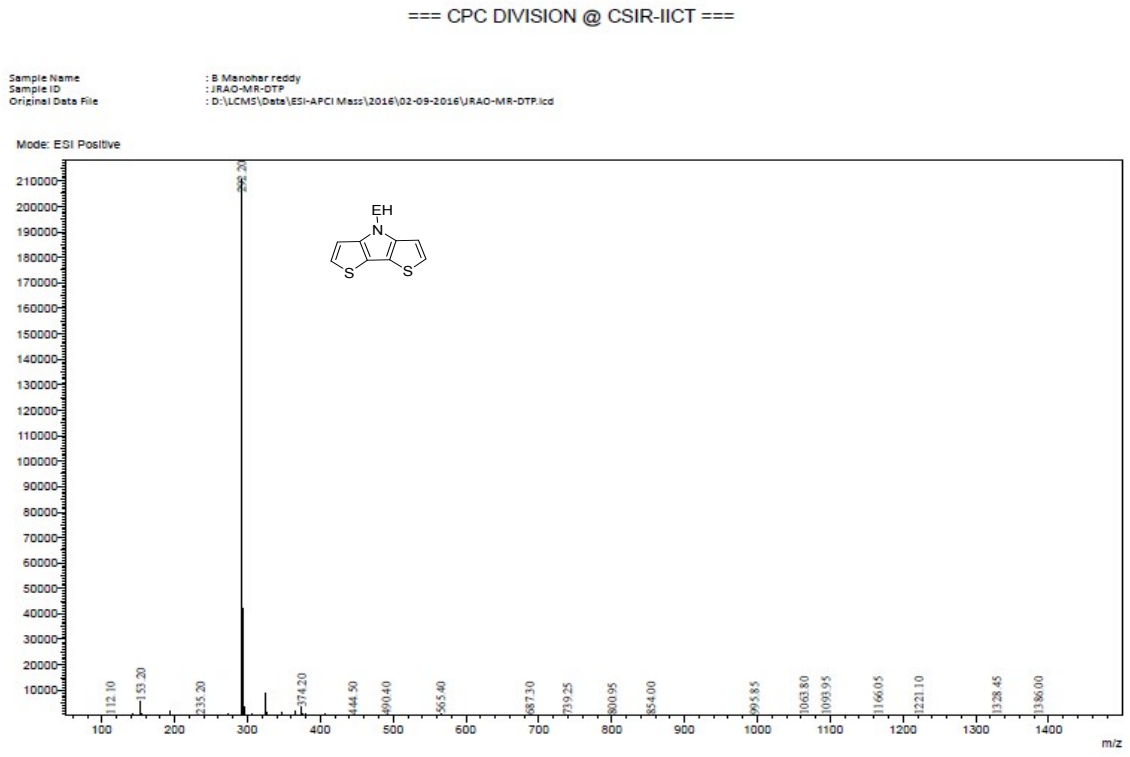


Fig. S14. ESI-MS spectrum of **2**

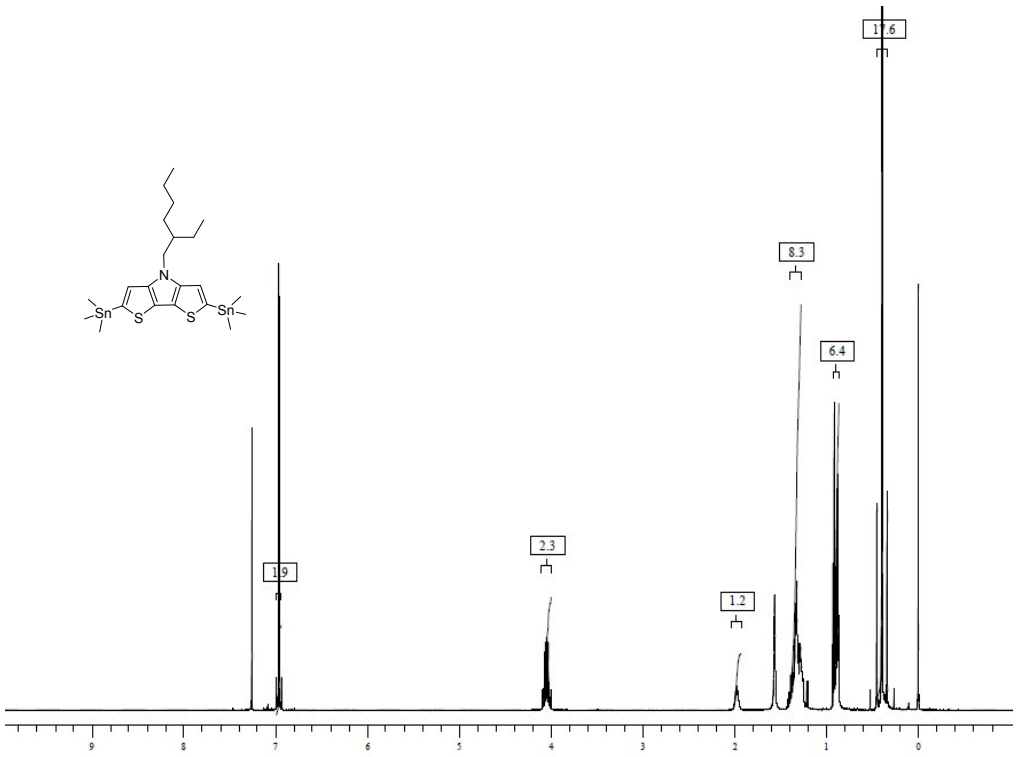


Fig. S15. ^{1}H NMR spectrum of **3**

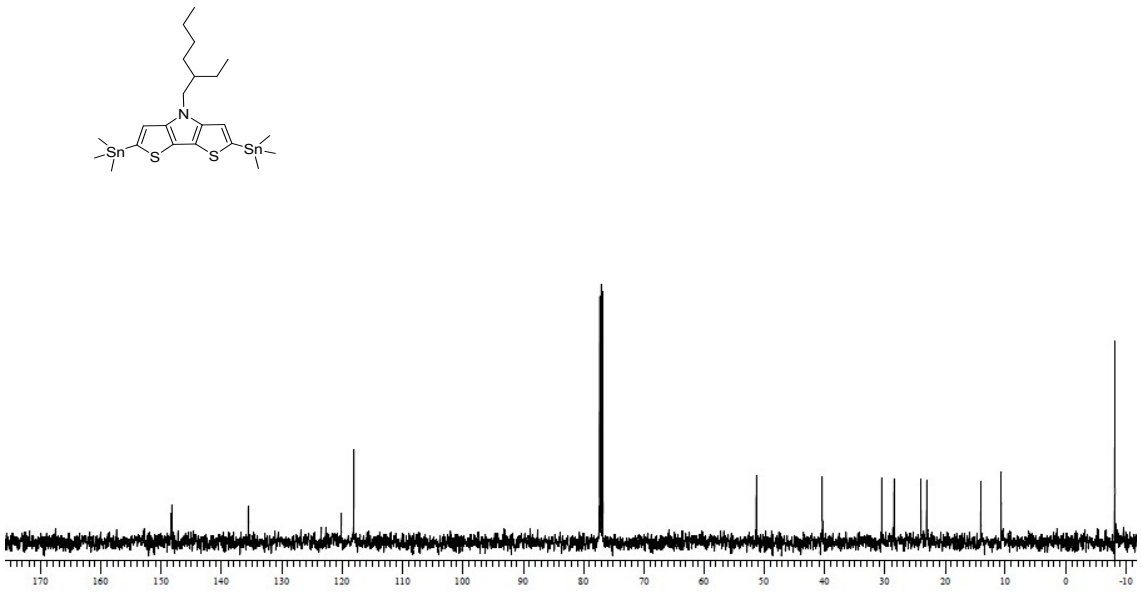


Fig. S16. ^{13}C NMR spectrum of **3**

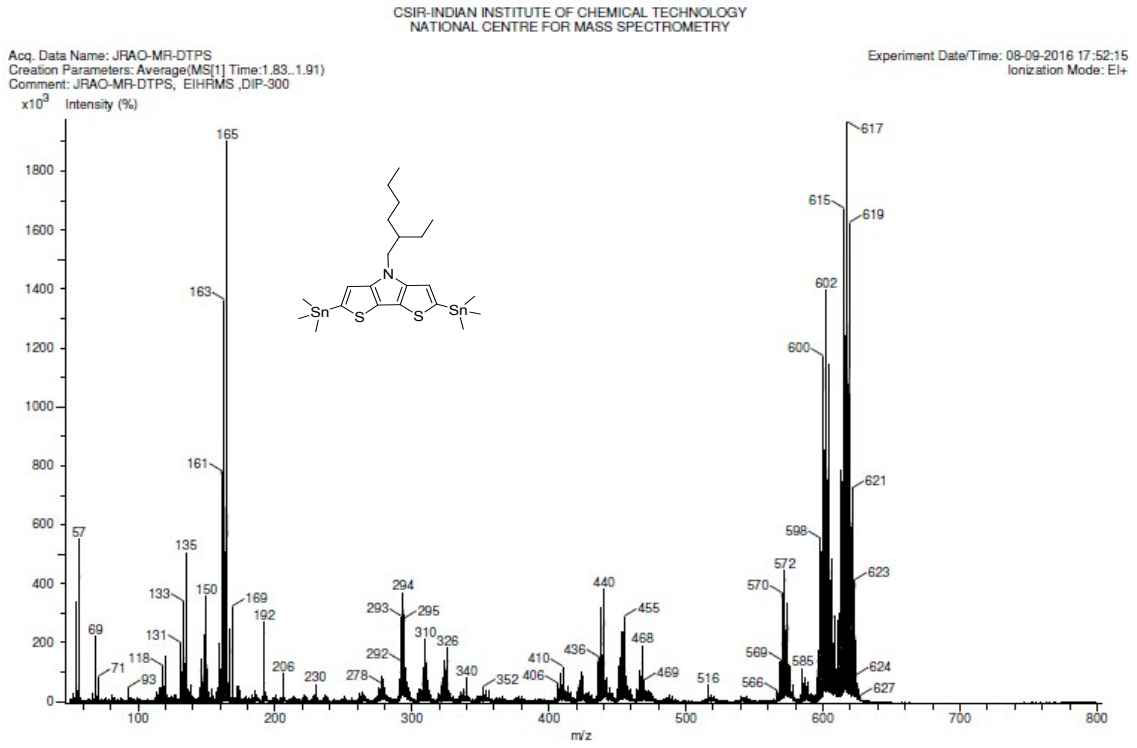


Fig. S17. EI-MS spectrum of **3**

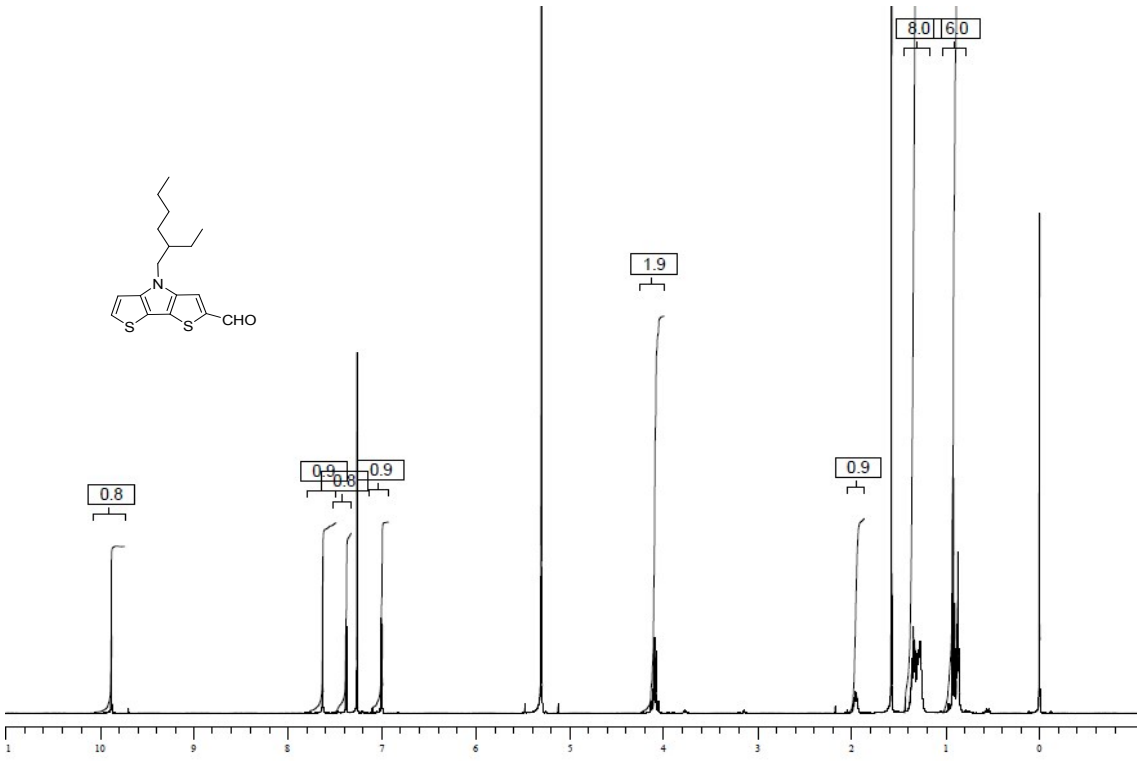


Fig. S18. ^{1}H NMR spectrum of **4**

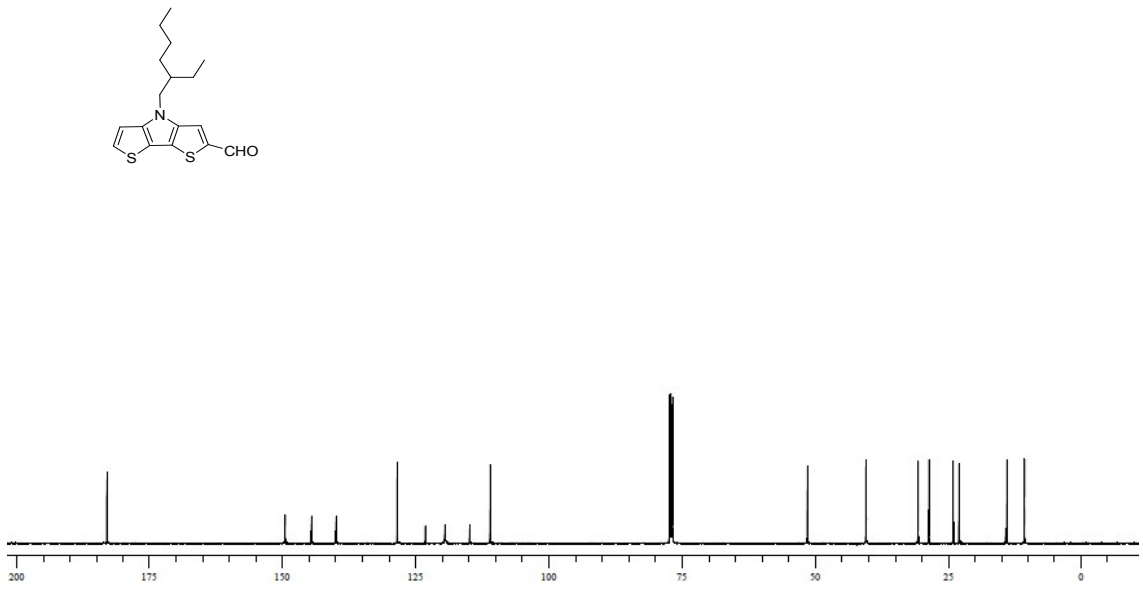


Fig. S19. ^{13}C NMR spectrum of **4**

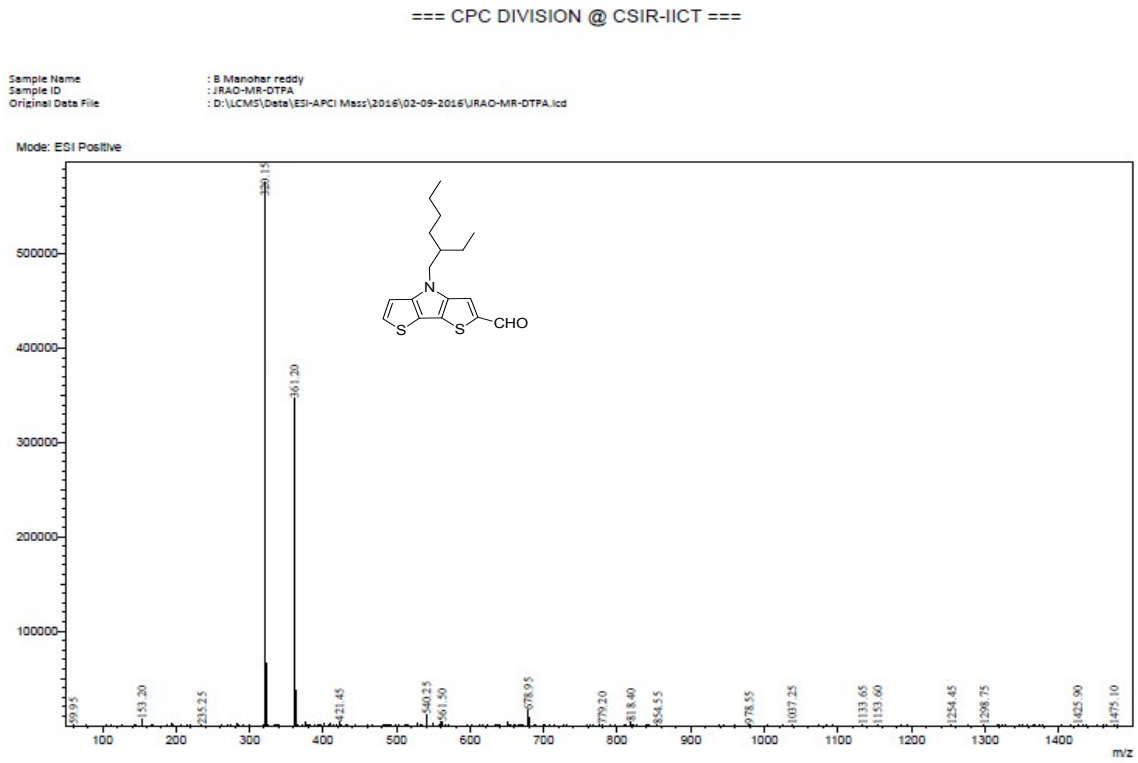


Fig. S20. ESI-MS spectrum of **4**

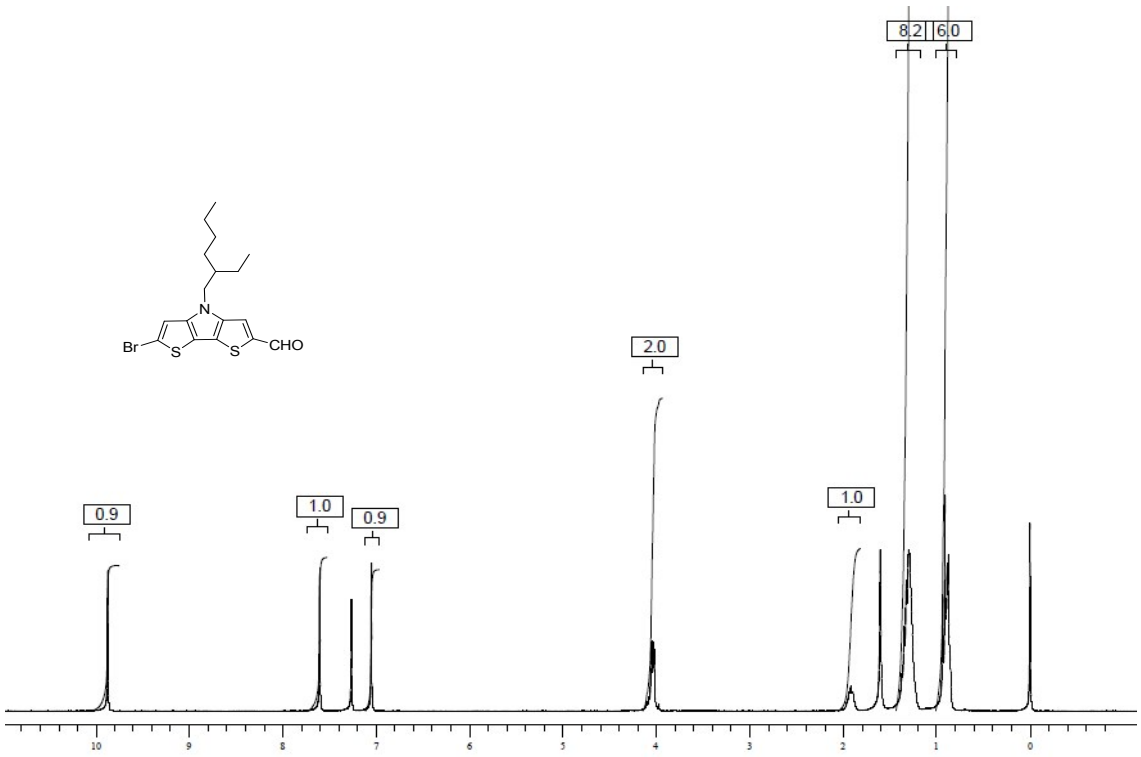


Fig. S21. ^{1}H NMR spectrum of **5**

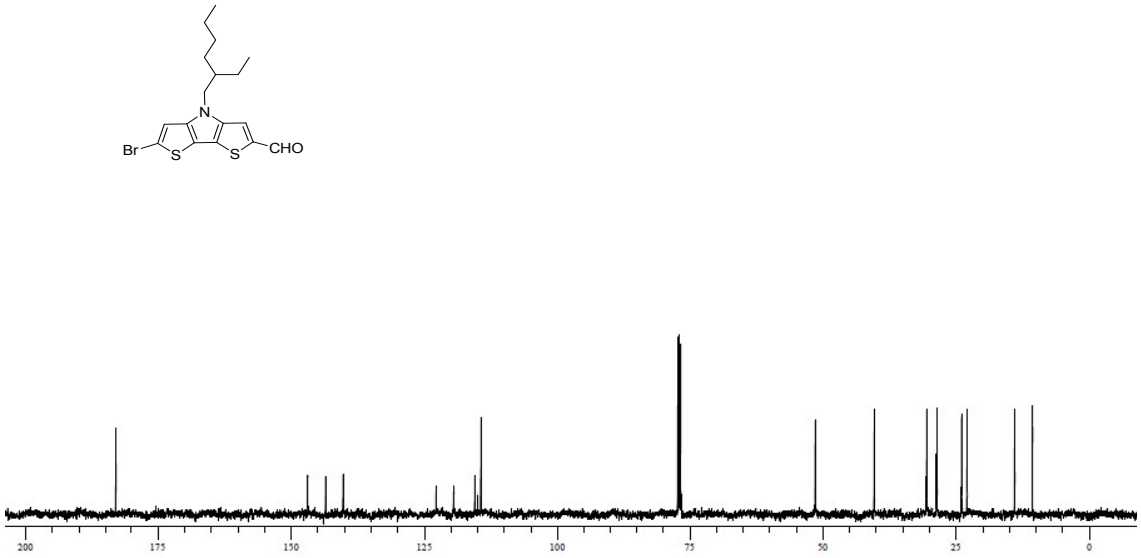


Fig. S22. ^{13}C NMR spectrum of **5**

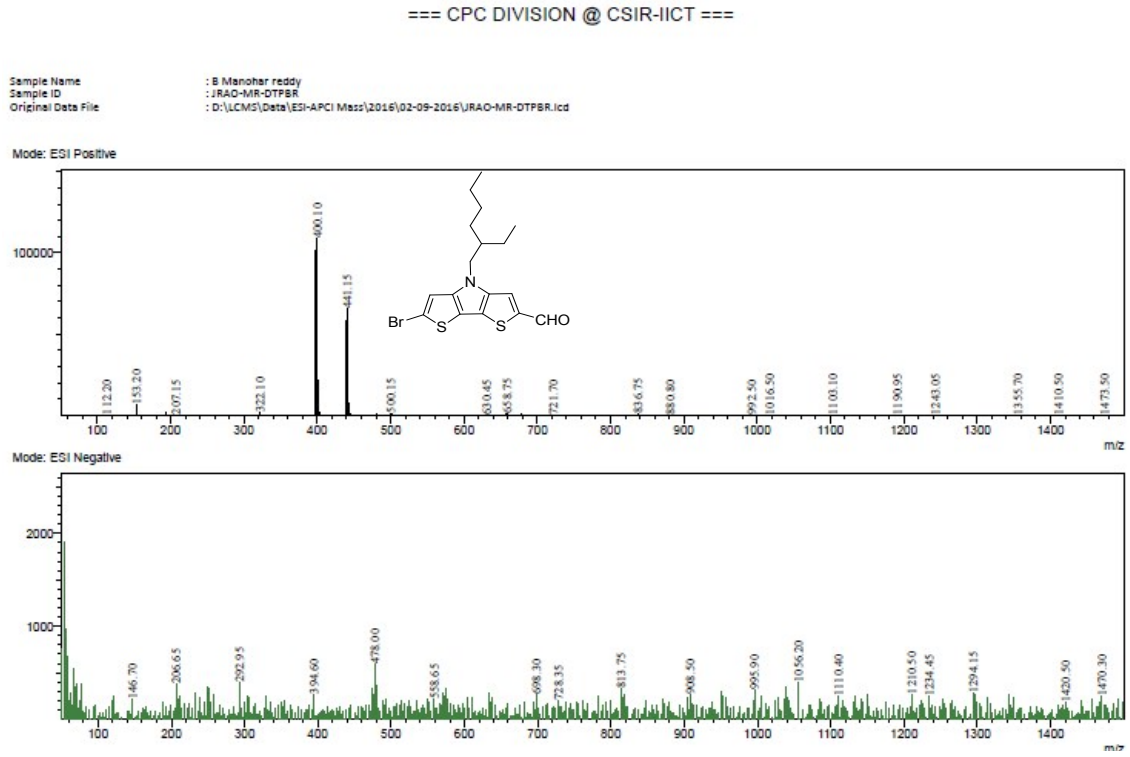


Fig. S23. ESI-MS spectrum of **5**

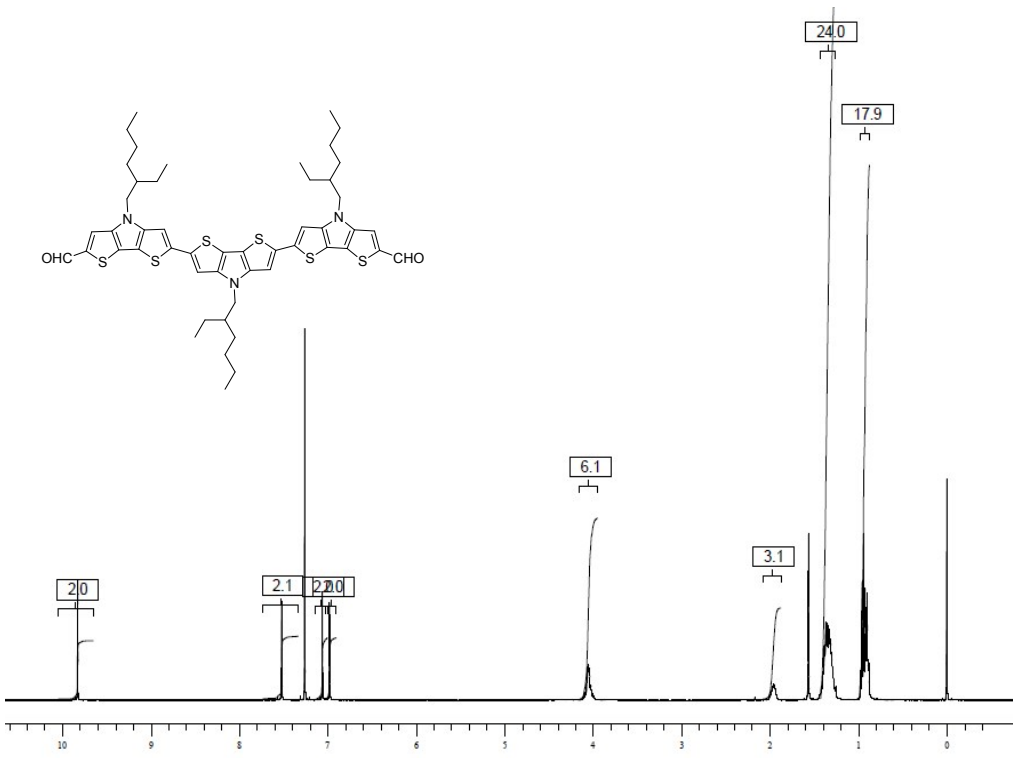


Fig. S24. ^{1}H NMR spectrum of **6**

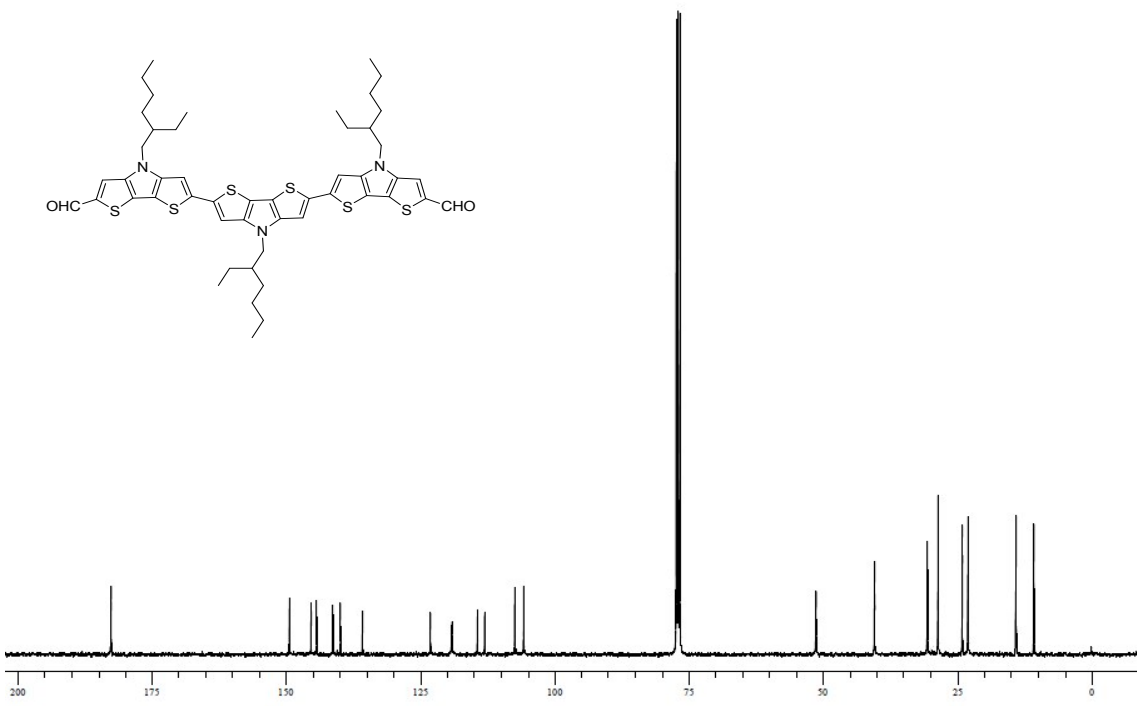


Fig. S25. ^{13}C NMR spectrum of **6**

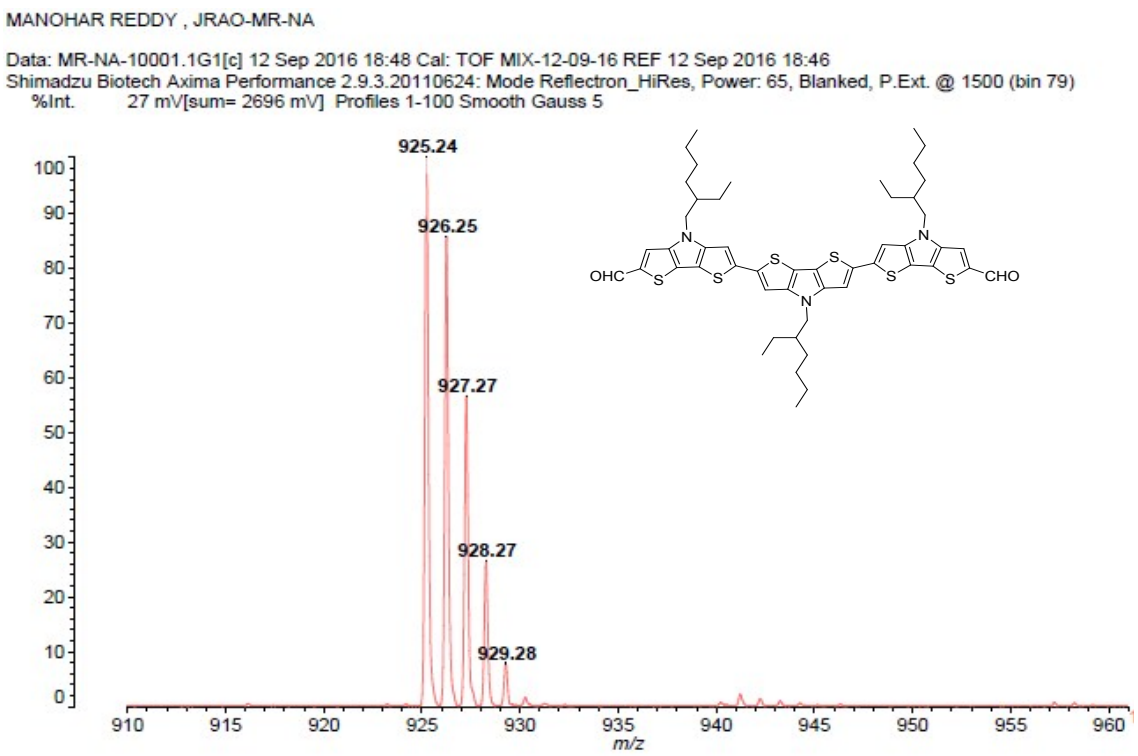


Fig. S26. ESI-MS spectrum of **6**

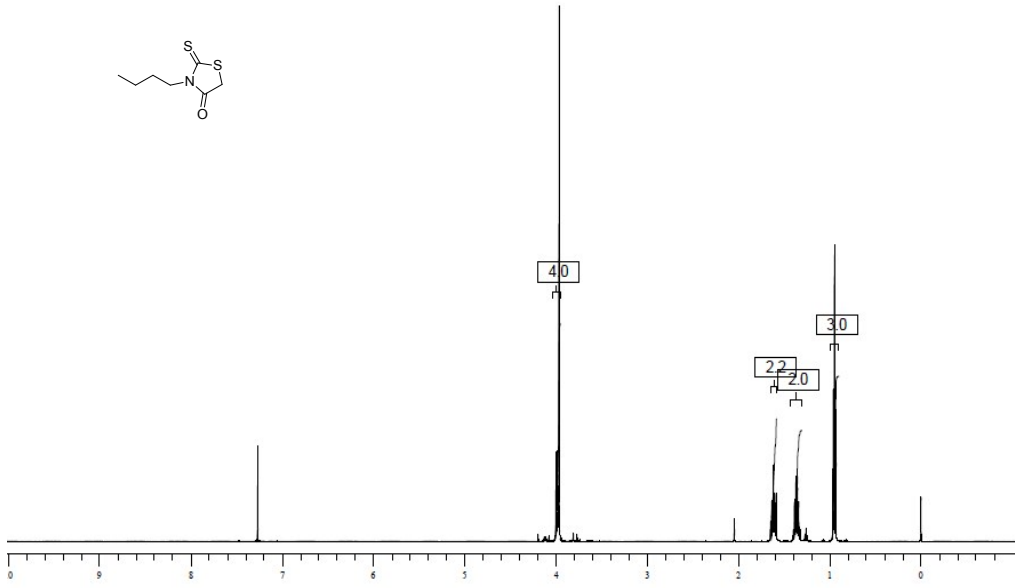


Fig. S27. ^{1}H NMR spectrum of *n*-butyl rhodanine