Supporting Information

5,5'-Bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4'*H*-[3,3'-bi(1,2,6-thiadiazine)]-4,4'-dione

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S1. Cyclic Voltammetry

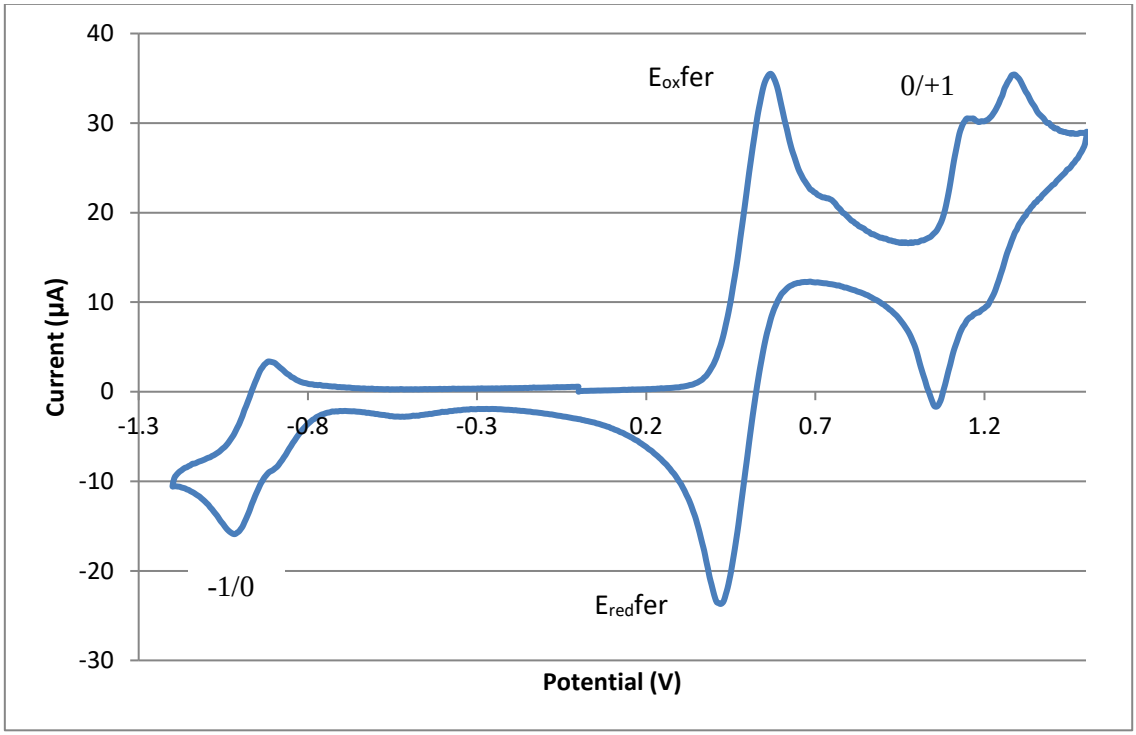


Figure S1. Cyclic voltammogram of bithiadiazinone **7**. The voltammogram was run in a 1.0 mM solution of compound **7** in dry (over CaH_2), HPLC grade DCM containing $TBAPF_6$ (0.1 M) as an electrolyte. A three-electrode electrochemical cell was used with a glassy carbon disk as working electrode (ø 3 mm), Pt wire as counter electron and Ag/AgCl (1.0 M KCl) as reference electrode. Scan rate 50 $mV \cdot s^{-1}$. Temp. = 20 °C. Fc/Fc^+ (E_{Fc/Fc^+} = 0.475 V *vs.* SCE)[1] was used as an internal reference.

S2. UV-vis Spectrum of Bithiadiazinone 7

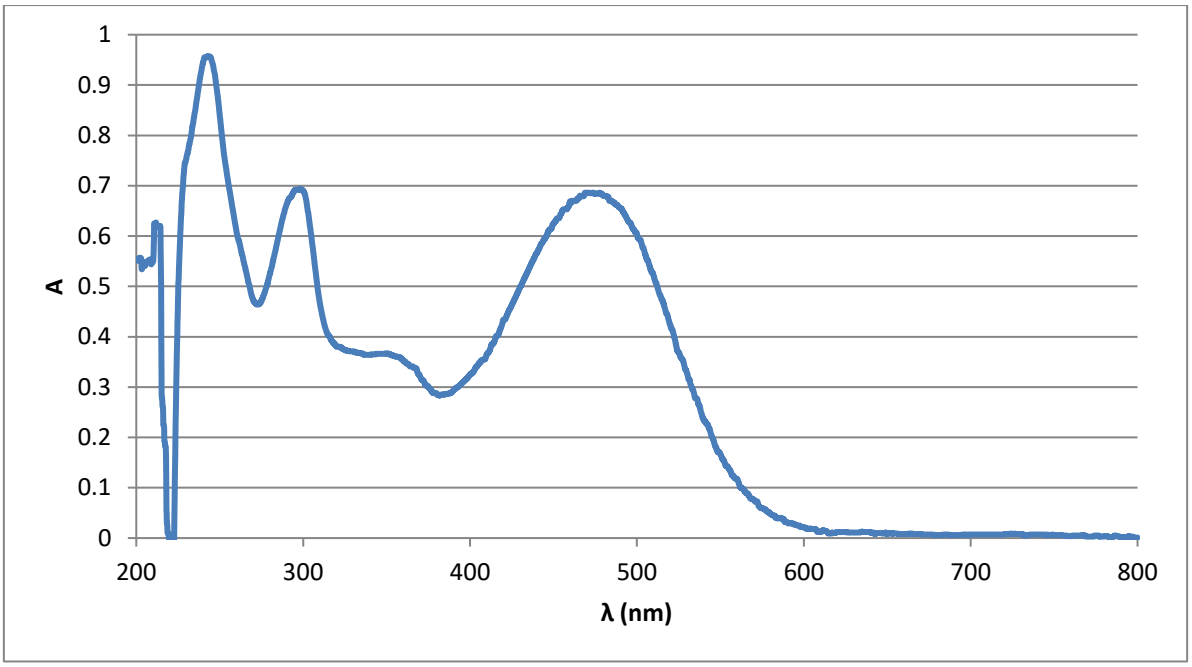


Figure S2. UV-vis absorption spectrum of bithiadiazinone **7** in CH_2Cl_2 at 0.008 mM. Peaks: 243 nm (log ε 5.08), 298 (4.94), 349 (4.66) and 472 (4.93).

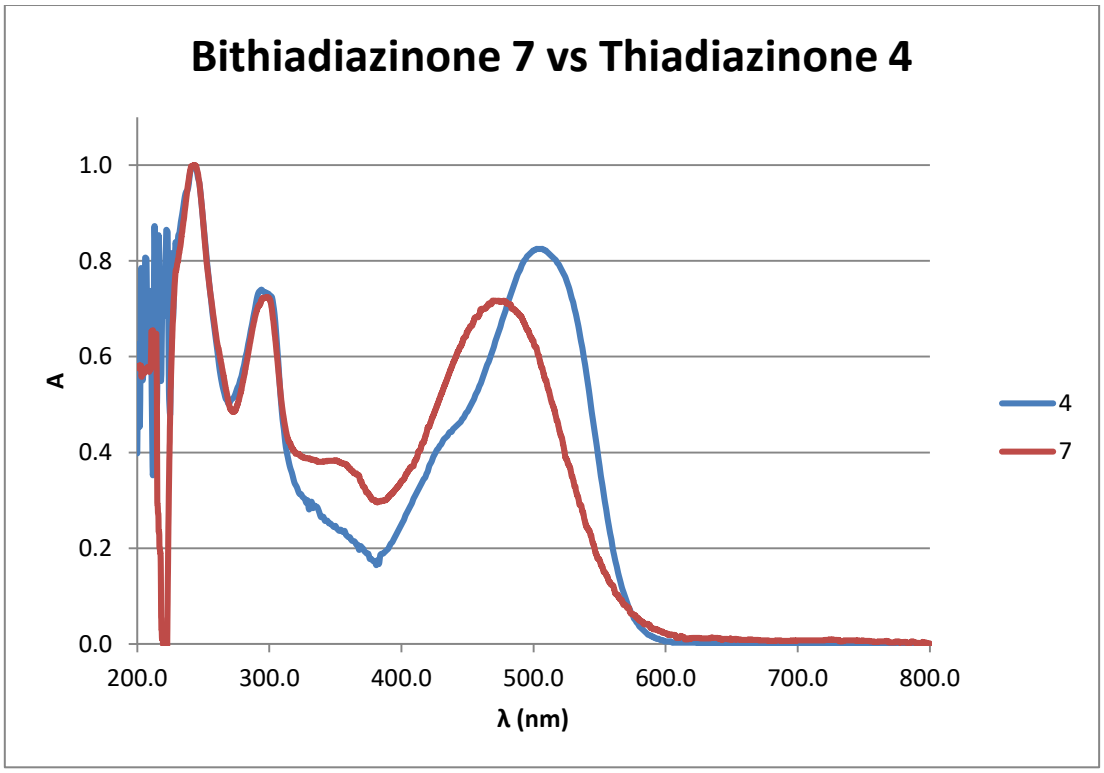


Figure S3. UV-vis absorption spectra of compounds **7** (bithiadiazinone) and **4** (mono-thiadiazinone) in CH_2Cl_2. Concentrations at 0.008 mM.

S3. Computational Data

S3.1 Computational methods

The geometries of the closed-shell singlet states of 5,5'-bis[5-(9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4'*H*-[3,3'-bi(1,2,6-thiadiazine)]-4,4'-dione (**10**) that has the same structure as bithiadiazine **7** excluding the decyl alkyl groups were fully optimized and analytical second derivatives were computed using vibrational analysis to confirm each stationary point to be a minimum by yielding zero imaginary frequencies. The reliable hybrid MPW1PW91 method[2] was employed for all the calculations with the 6-31G, 6-311G, 6-311G(d), 6-311G(d,p) and 6-311G(2d) basis sets. All the above computations were performed using the Gaussian 03 suite of programs.[3]

S3.2 Atom Coordinates at RMPW1PW91/6-311G(d) Level of Theory

*5,5'-Bis[5-(9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4'*H*-[3,3'-bi(1,2,6-thiadiazine)]-4,4'-dione (**10**)*

C(1)	-2.899648	2.646780	0.513755
C(2)	-1.559793	2.723359	-0.127377
N(1)	-1.021024	4.836906	1.040455
N(2)	-3.349840	3.588966	1.301724
O(1)	-1.173252	1.935152	-0.971332
S(1)	-2.504321	4.912596	1.710717
C(3)	0.689832	3.841922	-0.284201
C(4)	1.559560	2.722973	0.126999
C(5)	2.899593	2.646669	-0.513796
N(3)	1.021238	4.837181	-1.039862
N(4)	3.349974	3.589135	-1.301322
S(2)	2.504524	4.912861	-1.710145
O(2)	1.172973	1.934675	0.970847
C(6)	-0.689826	3.841935	0.284327
C(7)	-3.763026	1.517756	0.268172
C(8)	-3.564462	0.397423	-0.511159
S(3)	-5.320339	1.460434	1.043929
C(9)	-4.646348	-0.498336	-0.470031

H(1)	-2.657854	0.243390	-1.074833
C(10)	-5.682028	-0.075478	0.333373
H(2)	-4.654763	-1.448498	-0.987789
C(11)	3.762941	1.517587	-0.268371
C(12)	3.564200	0.396972	0.510508
S(4)	5.320468	1.460592	-1.043721
C(13)	4.646140	-0.498723	0.469383
H(3)	2.657439	0.242703	1.073870
C(14)	5.682032	-0.075540	-0.333577
H(4)	4.654451	-1.449062	0.986817
C(15)	-6.949280	-0.751902	0.595503
C(16)	-7.619561	-0.583323	1.824313
C(17)	-7.507699	-1.584962	-0.375541
C(18)	-8.814740	-1.219436	2.100885
H(5)	-7.173892	0.046391	2.585964
C(19)	-8.705089	-2.240920	-0.119725
H(6)	-7.018858	-1.695304	-1.336753
C(20)	-9.352726	-2.050597	1.122946
H(7)	-9.305781	-1.076846	3.056983
C(21)	-9.534346	-3.143626	-0.883686
C(22)	-10.642821	-3.461204	-0.067637
C(23)	-9.440702	-3.703031	-2.157012
C(24)	-11.648818	-4.319764	-0.498294
C(25)	-10.439515	-4.558420	-2.591899
H(8)	-8.598264	-3.472558	-2.799934
C(26)	-11.530332	-4.861375	-1.768617
H(9)	-12.497046	-4.559774	0.133352

H(10)	-10.378767	-4.999532	-3.579980
H(11)	-12.299922	-5.533902	-2.130572
C(27)	6.949392	-0.751813	-0.595572
C(28)	7.620017	-0.582784	-1.824133
C(29)	7.507574	-1.585173	0.375349
C(30)	8.815307	-1.218743	-2.100578
H(12)	7.174534	0.047166	-2.585699
C(31)	8.705070	-2.240986	0.119653
H(13)	7.018463	-1.695867	1.336384
C(32)	9.353054	-2.050209	-1.122767
H(14)	9.306614	-1.075805	-3.056487
C(33)	9.534153	-3.143911	0.883546
C(34)	10.642877	-3.461158	0.067706
C(35)	9.440170	-3.703757	2.156653
C(36)	11.648792	-4.319816	0.498358
C(37)	10.438899	-4.559246	2.591534
H(15)	8.597537	-3.473544	2.799412
C(38)	11.529967	-4.861867	1.768461
H(16)	12.497213	-4.559568	-0.133126
H(17)	10.377889	-5.000700	3.579446
H(18)	12.299486	-5.534480	2.130408
N(5)	-10.509381	-2.792333	1.132060
N(6)	10.509749	-2.791884	-1.131801
H(19)	-11.163556	-2.833375	1.891578
H(20)	11.164144	-2.832635	-1.891145

S3.3 Computed properties

Table S1. Computational ground state energy values of bithiadiazinone **7** as calculated with DFT at the RMPW1PW91 Level of theory.

Basis set	**HOMO** (eV)	**LUMO** (eV)	$\Delta E_{\text{HOMO-LUMO}}$ (eV)
631G	-5.73	-2.93	2.80
6311G	-5.92	-3.06	2.86
6311G(d)	-5.78	-2.44	3.35
6311G(d,p)	-5.79	-2.41	3.35
6311G(2d)	-5.72	-2.41	3.31

Table S2. Main excited states of bithiadiazinone **7** as derived from TD-DFT data at the RB3LYP Level of theory.

Basis set	**Excited state**	**Transition**	**Energy (eV)**	λ_{max} (nm)	***f***
631G	S1	HOMO-1→LUMO (22%) HOMO→LUMO+1 (26%)	2.287	542	0.0555
	S2	HOMO-1→LUMO+1 (19%) HOMO→LUMO (30%)	2.288	542	0.0693
6311G	S1	HOMO-1→LUMO (22%) HOMO→LUMO+1 (26%)	2.345	529	0.0598
	S2	HOMO-1→LUMO+1 (22%) HOMO→LUMO (29%)	2.348	528	0.0737
6311G(d)	S1	HOMO→LUMO (41%)	2.677	463	0.7424
	S2	HOMO→LUMO+1 (46%)	2.693	460	0.0678
6311G(d,p)	S1	HOMO→LUMO (38%)	2.811	441	0.9698
	S2	HOMO→LUMO+1 (40%)	2.880	431	0.1504
6311G(2d)	S1	HOMO→LUMO (47%)	2.618	474	0.9278
	S2	HOMO→LUMO+1 (44%)	2.755	450	0.0340

Table S3. Computational ground and excited state energy values of bithiadiazinone **7** as calculated with DFT at the RMPW1PW91 and TD-DFT at the RB3LYP Level of theory respectively.

Basis set	**Ground state**			**Excited state (HOMO→LUMO)**		
	HOMO (eV)	**LUMO** (eV)	$\Delta E_{\text{HOMO-LUMO}}$ (eV)	**Excitation energy** (eV)	λ_{max} (nm)	**LUMO excited** (eV)
631G	-5.73	-2.93	2.80	2.29	542	-3.45
6311G	-5.92	-3.06	2.86	2.35	528	-3.57
6311G(d)	-5.78	-2.44	3.35	2.68	463	-3.11
6311G(d,p)	-5.79	-2.41	3.35	2.81	441	-2.98
6311G(2d)	-5.72	-2.41	3.31	2.62	474	-3.10

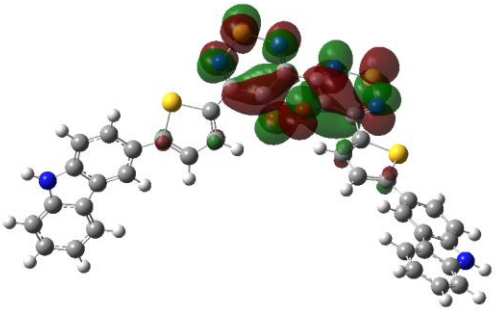
An examination of the computational data reveals that the ground state optimization HOMO energy values tend to approach the experimental electrochemical HOMO value of -5.69 eV as the basis set is increased with the best value being -5.72 eV with the 6311G(2d) basis set. In contrast, the excited states derived from TD-DFT data show an increase of the optical band gap energies (E_g^{opt}) as the basis set is increased; the best fit with the experimental values (E_g^{opt} 2.17 eV) was with the 631G basis set.

S3.4 Molecular Orbitals

Figure S4. Molecular orbitals for the singlet ground state of bithiadiazinone **7** as calculated with DFT RMPW1PW91/6-31G.

LUMO+1

E=-2.9255 eV



LUMO

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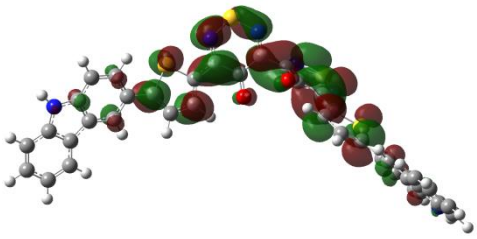
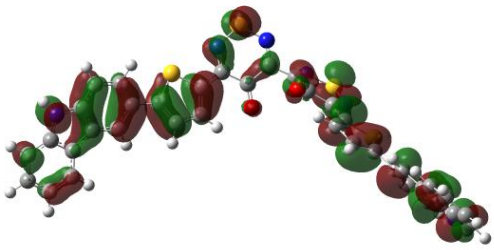


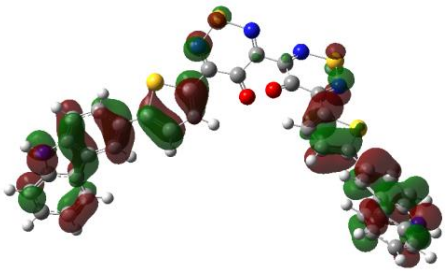
HOMO

E=-5.7334 eV



HOMO+1

E=-5.7538 eV



S4. References

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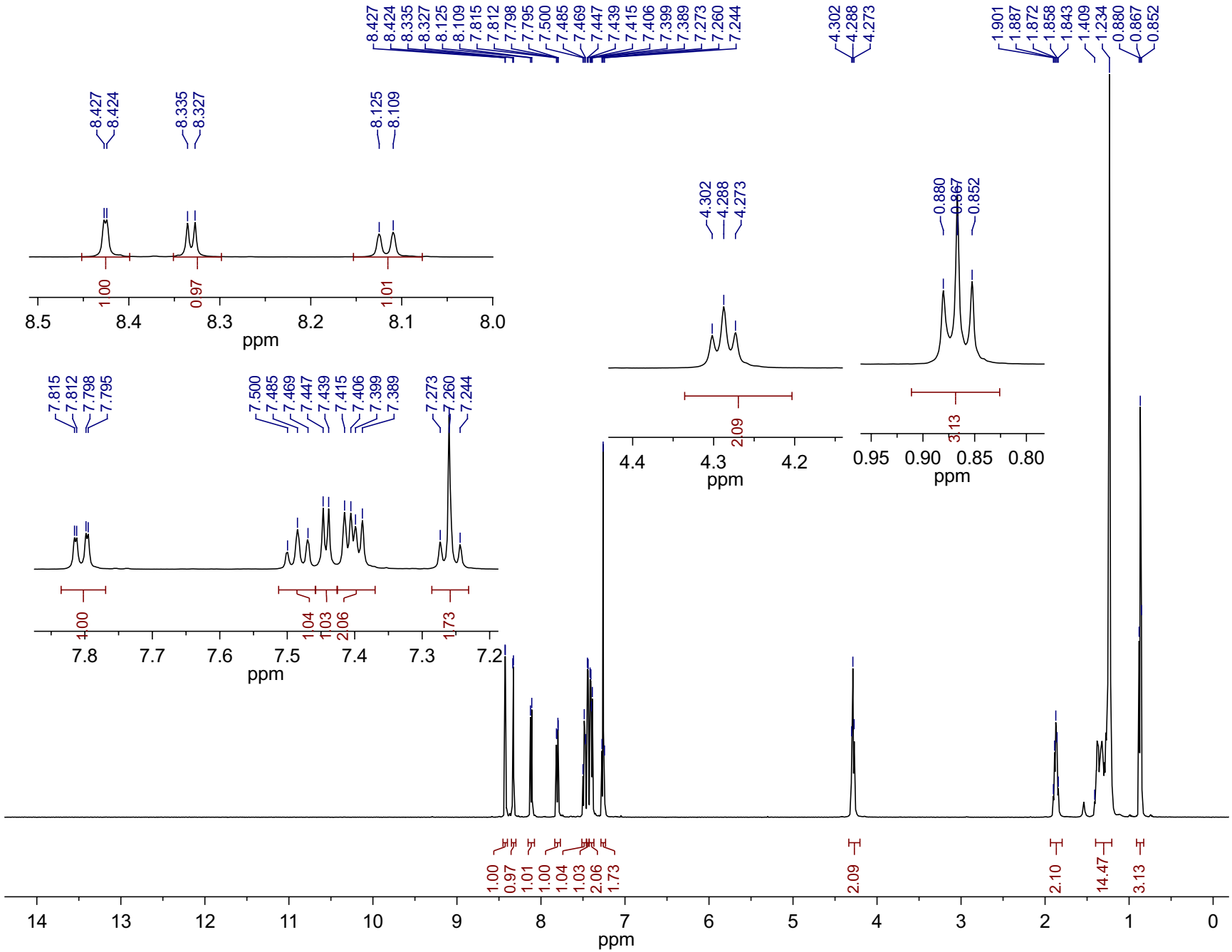
S5. ^{1}H and ^{13}C NMR Spectra of Bithiadiazinone 7

^{1}H NMR of 5,5'-Bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4'*H*-[3,3'-bi(1,2,6-thiadiazine)]-4,4'-dione (**7**)



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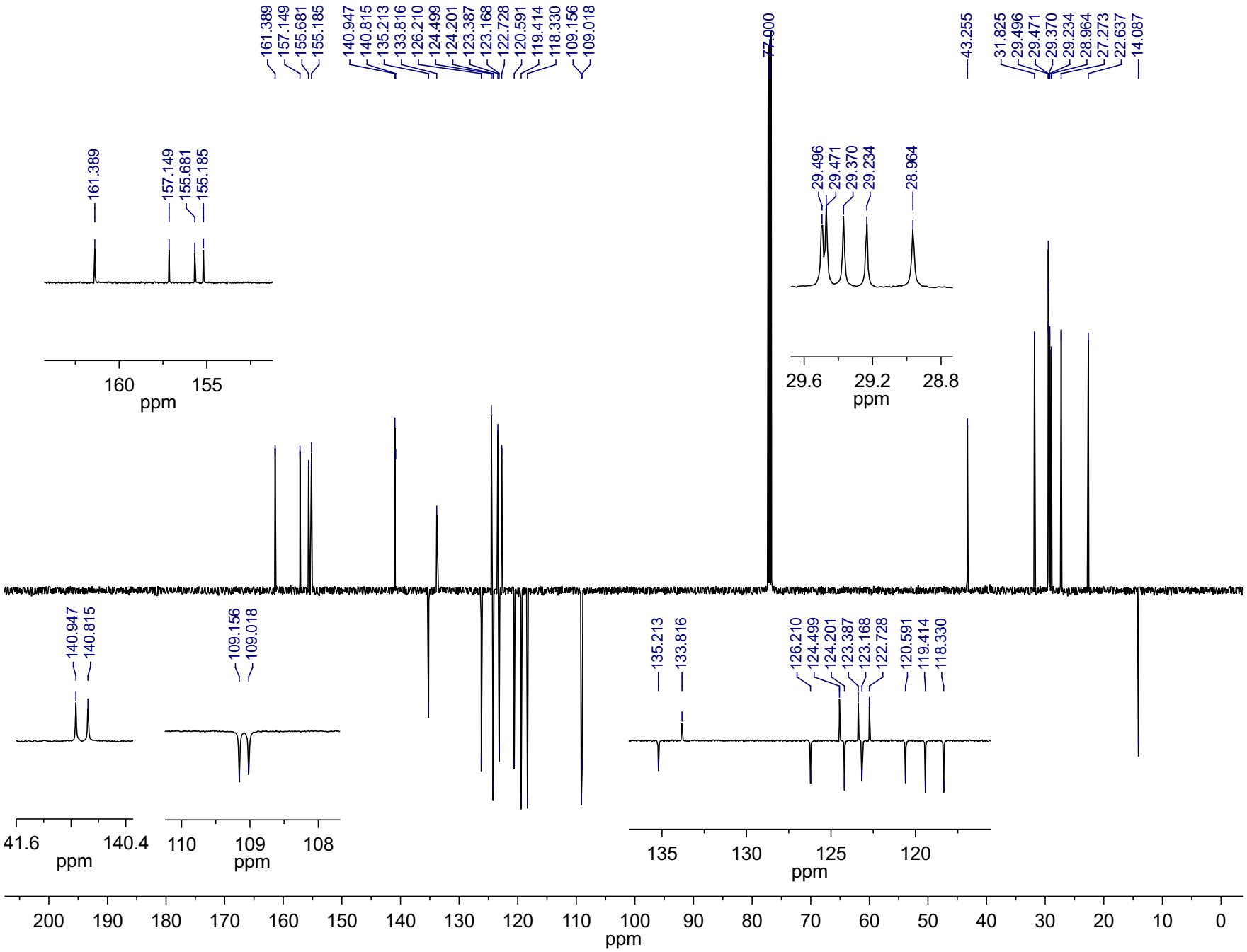
^{13}C NMR of 5,5'-Bis[5-(9-decyl-9*H*-carbazol-3-yl)thien-2-yl]-4*H*,4'*H*-[3,3'-bi(1,2,6-thiadiazine)]-4,4'-dione (**7**)



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