Dipolar NLO chromophores bearing diazine rings as π-conjugated linkers

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Summary

Experimental details for X-ray analysis

A translucent red block-like specimen of $C_{36}H_{23}NO_2S_2$*0.5 CH_2Cl_2, approximate dimensions 0.091 mm × 0.163 mm × 0.263 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 1.22 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 90854 reflections to a maximum θ angle of 27.54° (0.77 Å resolution), of which 6631 were independent (average redundancy 13.701, completeness = 99.6 %, R_{int} = 12.23 %, R_{sig} = 4.30 %) and 4939 (74.48 %) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.7933(5) Å, b = 9.9953(5) Å, c = 15.9261(8) Å, α = 99.293(2)°, β = 91.403(2)°, γ = 109.660(2)°, volume = 1443.59(13) $Å^3$, are based upon the refinement of the XYZ-centroids of 9959 reflections above 20 σ(I) with 4.69° < 2θ < 54.91°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.947. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9220 and 0.9720.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{36.50}H_{24}ClNO_2S_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 396 variables converged at R1 = 5.38 %, for the observed data and wR2 = 12.44 % for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 1.087 $e^-/Å^3$ and the largest hole was −1.122 $e^-/Å^3$ with an RMS deviation of 0.073 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.399 g/cm^3 and F(000), 630 e^-.

Table S1. Sample and crystal data for **3d.**

Identification code	fb170227S1	
Chemical formula	$C_{36.50}H_{24}ClNO_2S_2$	
Formula weight	608.14 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.091 x 0.163 x 0.263 mm	
Crystal habit	translucent red block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.7933(5) Å	α = 99.293(2)°
	b = 9.9953(5) Å	β = 91.403(2)°
	c = 15.9261(8) Å	γ = 109.660(2)°
Volume	1443.59(13) $Å^3$	
Z	2	
Density (calculated)	1.399 g/cm^3	
Absorption coefficient	0.313 mm^{-1}	
F(000)	630	

Table S2. Data collection and structure refinement for **3d.**

Theta range for data collection	2.20 to 27.54°
Index ranges	–12<=h<=12, –12<=k<=12, –20<=l<=20
Reflections collected	90854
Independent reflections	6631 [R(int) = 0.1223]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9720 and 0.9220
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6631 / 20 / 396
Goodness-of-fit on F^2	1.051
Final R indices	4939 data; I>2σ(I) R1 = 0.0538, wR2 = 0.1112
	all data R1 = 0.0841, wR2 = 0.1244
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0426P)^2+1.9457P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.087 and -1.122 eÅ^{-3}
R.M.S. deviation from mean	0.073 eÅ^{-3}

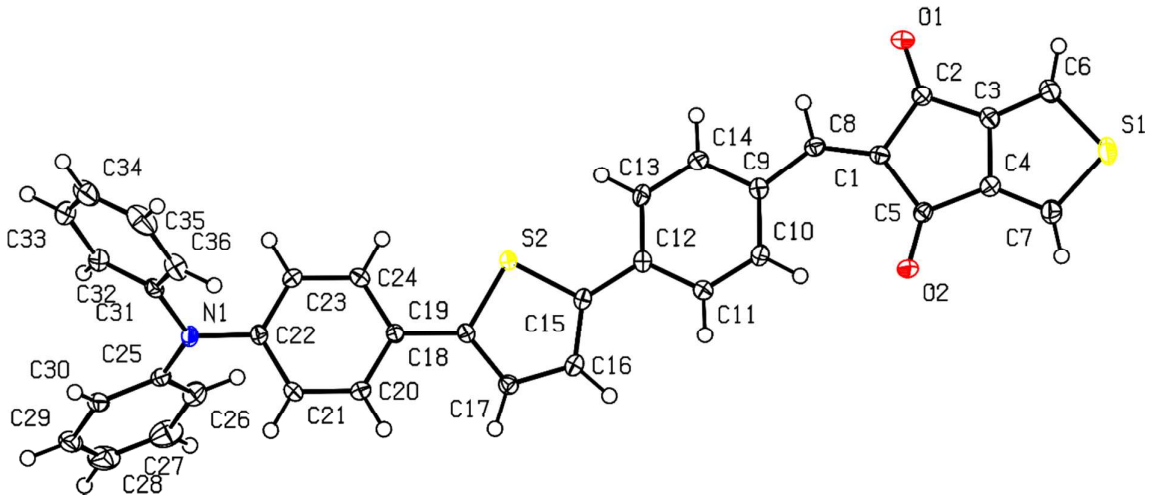

Figure S1. ORTEP representations of molecule **3d** (150 K, R = 0.05, CCDC 1549497). Thermal elipsoids are shown with 50% probability level.

Electrochemistry

Electrochemical measurements of chromophores **1–4** were performed with a home-designed 3-electrodes cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine redox potential values. The potential of the cell was controlled by an μAUTOLAB PSTAT 100 potentiostat monitored by a computer. Anhydrous "extra-dry" dichloromethane was used as received and kept under N_2. The potential were reported versus ferrocene as standard using a scan rate of 0.1 V/s. NBu_4BF_4 salt was added as supporting electrolyte.

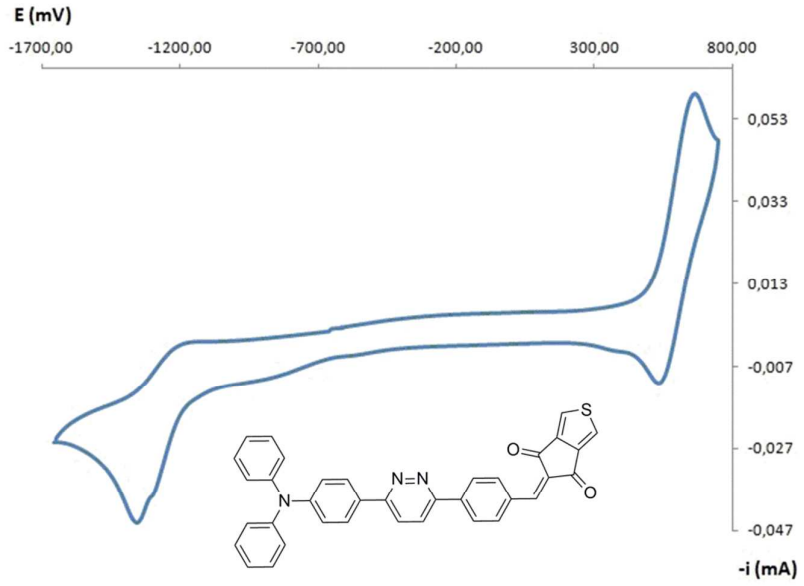

Figure S2. Representative CV curve of the oxidation and reduction of chromophore **1a** at Pt electrode vs. Fc in CH_2Cl_2 containing 0.1 M Bu_4NBF_4.

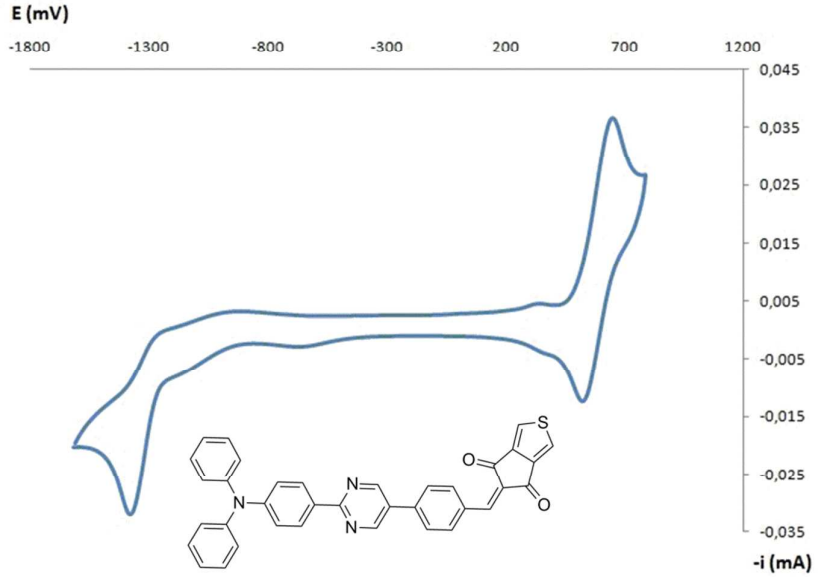

Figure S3. Representative CV curve of the oxidation and reduction of chromophore **2b** at Pt electrode vs. Fc in CH_2Cl_2 containing 0.1 M Bu_4NBF_4.

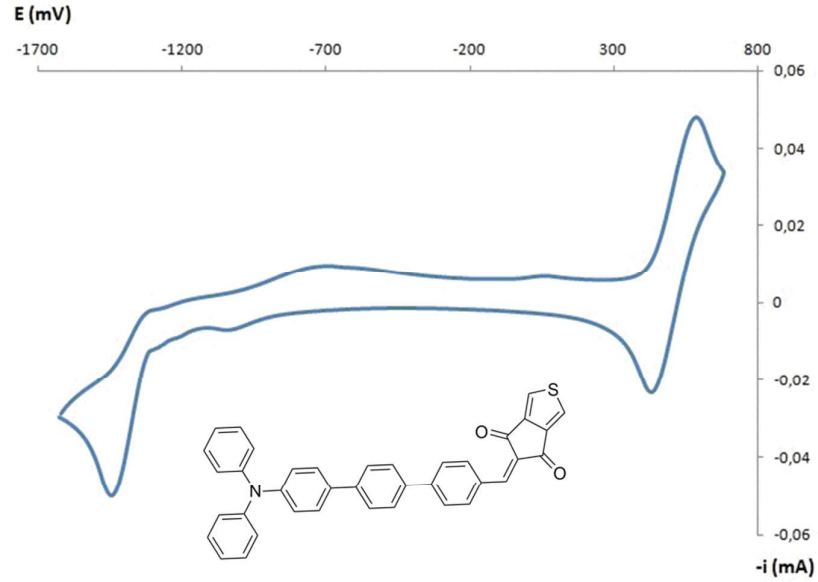

Figure S4. Representative CV curve of the oxidation and reduction of chromophore **3a** at Pt electrode vs. Fc in CH_2Cl_2 containing 0.1 M Bu_4NBF_4.

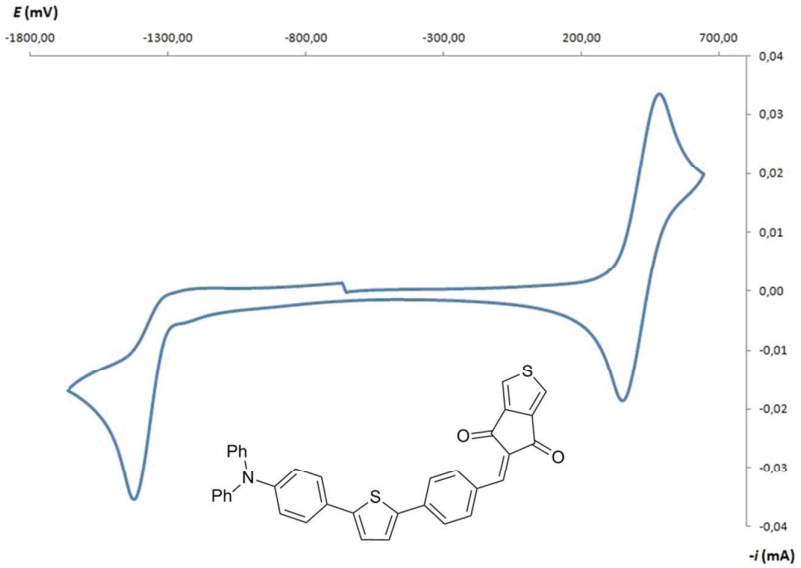

Figure S5. Representative CV curve of the oxidation and reduction of chromophore **3d** at Pt electrode vs. Fc in CH_2Cl_2 containing 0.1 M Bu_4NBF_4.

Absorption properties

Table S3. Optical data of chromophores **1**–**4** in various solvents.

Chromophore	$\lambda/\varepsilon_{max}$CHCl$_3$	$\lambda/\varepsilon_{max}$toluene	$\lambda/\varepsilon_{max}$MeOH
1a	442/20900	440/23500	≈425(sh)
1b	449/36100	450/39000	≈430(sh)
1c	454/25500	450/27800	≈425(sh)
2a	443/29800	436/28300	≈430(sh)
2b	450/25800	450/25500	≈430(sh)
2c	451/38100	445/41200	≈435(sh)
2d	459/33100	455/36200	≈420(sh)
3a	444(sh)/21700	440/24100	≈425(sh)
3b	470/42200	464/46100	455/44800
3c	459/41300	455/46600	442/43500
3d	506/36500	496/39800	487/39800
4a	505/46300	494/36100	495/36700
4b	490/25900	477/28300	470/21225

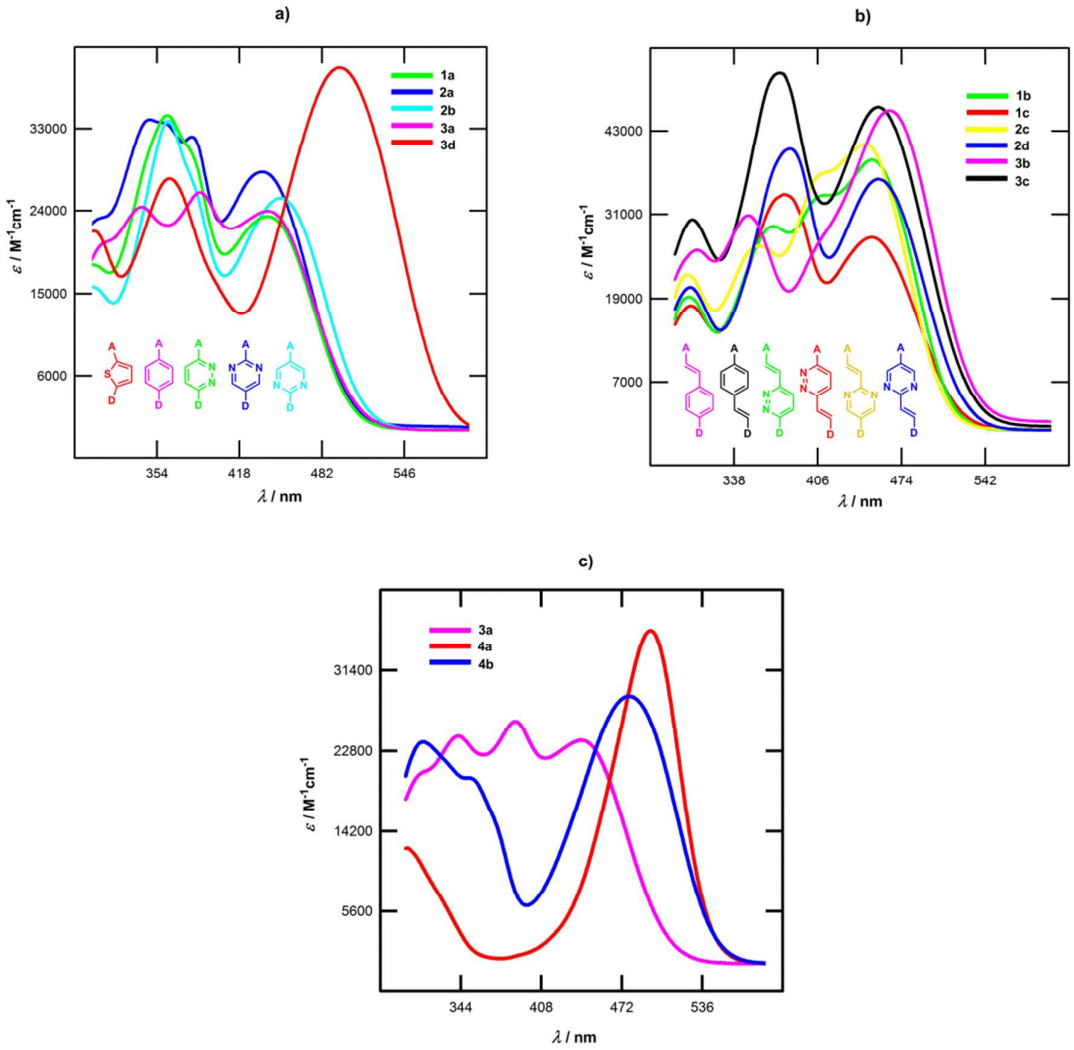

Figure S6. UV-Vis absorption spectra of chromophores **1–4** measured in toluene at ≈ 10^{-5} M.

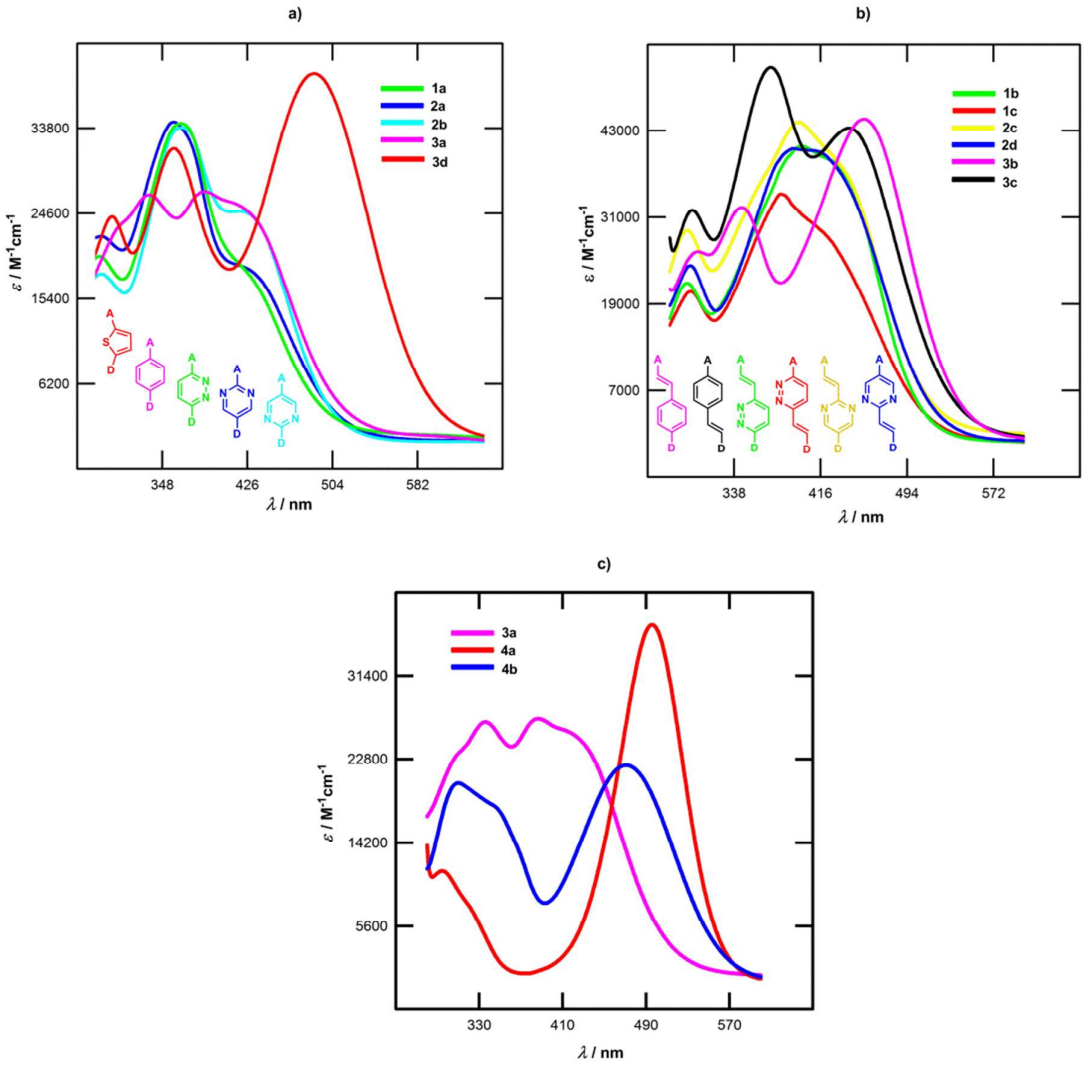

Figure S7. UV-Vis absorption spectra of chromophores **1–4** measured in MeOH at ≈ 10^{-5} M.

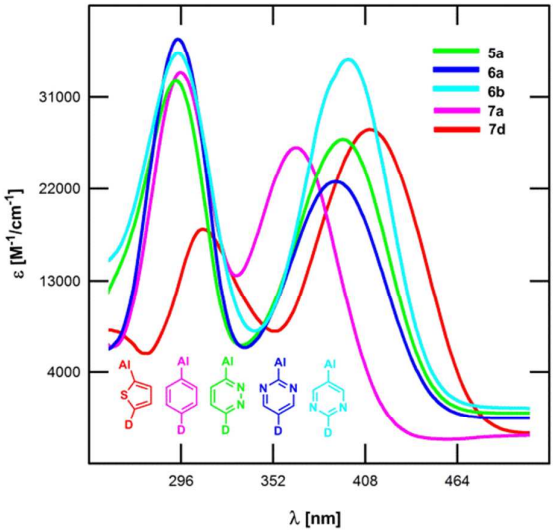

Figure S8. UV-Vis absorption spectra of basic aldehydes **5a, 6a–6b, 7a** and **7d** measured in CH_3Cl at $\approx 10^{-5}$ M.

Emission properties

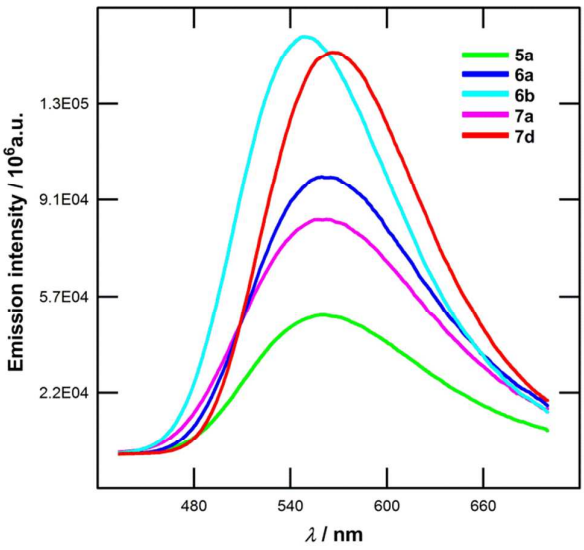

Figure S9. Emission spectra of basic aldehydes **5a**, **6a**–**6b**, **7a** and **7d** in $CHCl_3$**.**

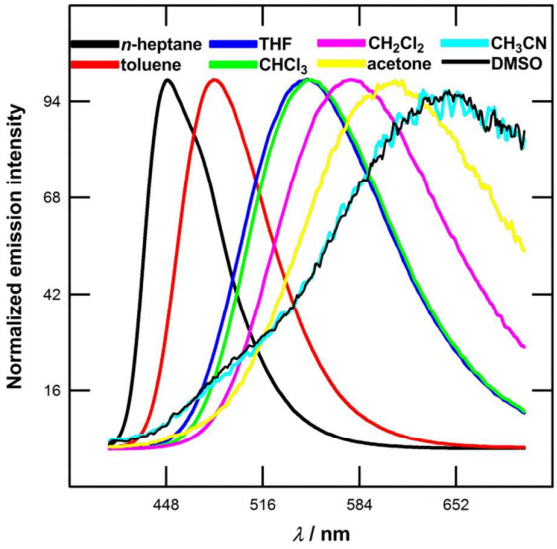

Figure S10. Normalized emission spectra of representative aldehyde **6b** in various aprotic solvents.

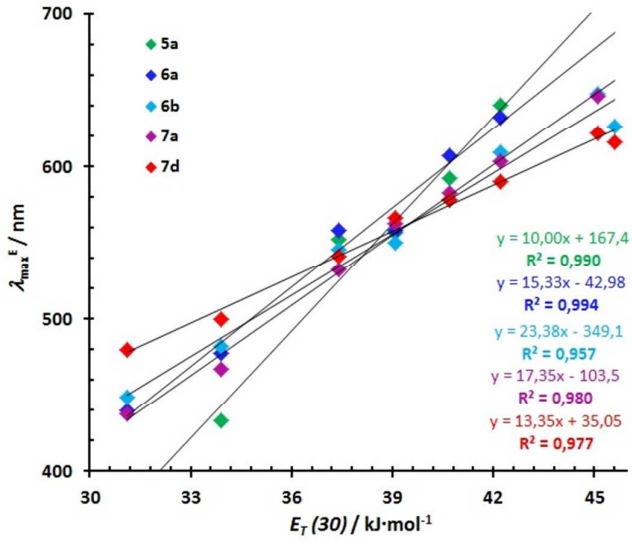

Figure S11. Emission maxima (λ_{em}) as a function of the Dimroth-Reichardt polarity parameter E_T *(30)* for selected aldehydes.

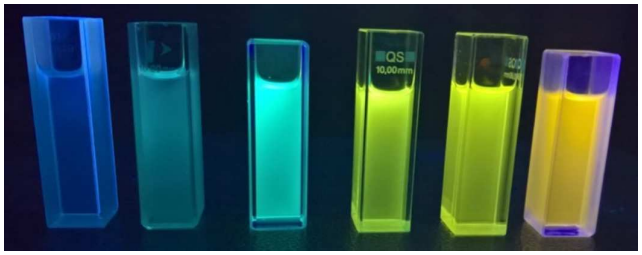

Figure S12. Fluorescence color changes of **6b** in various solvents (from left to right: heptane, toluene, 1,4-dioxane, THF, $CHCl_3$, and CH_2Cl_2). Picture was taken in the dark upon irradiation with a hand-held UV lamp (λ_{exc} = 366 nm).

Differential scanning calorimetry

Thermal properties of chromophores **1–4** were investigated by DSC measurements.

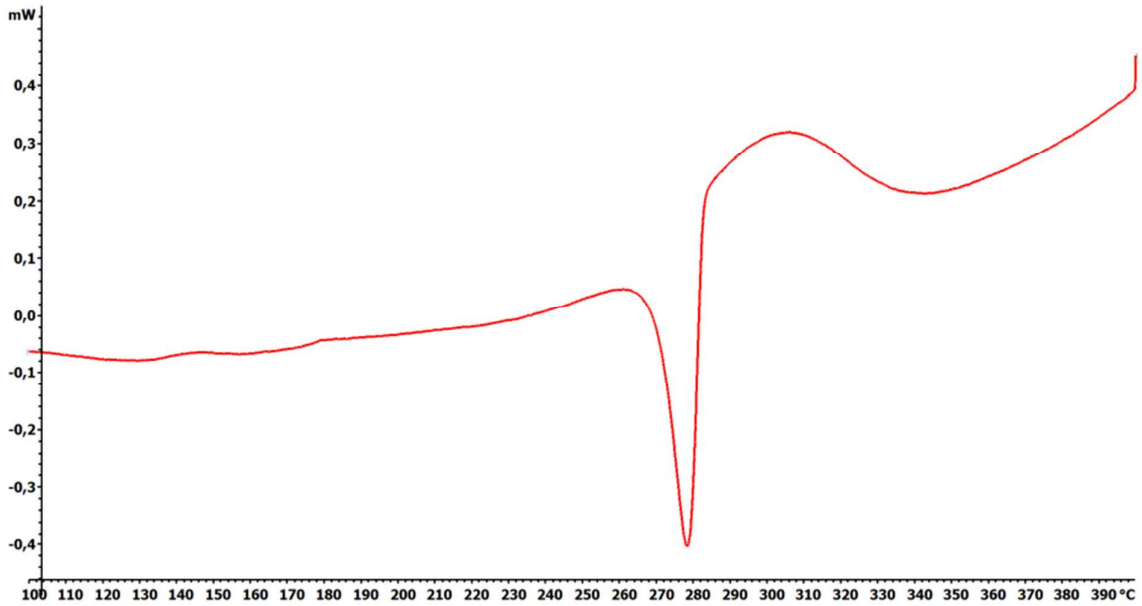

Figure S13. DSC curve of chromophore **1a.**

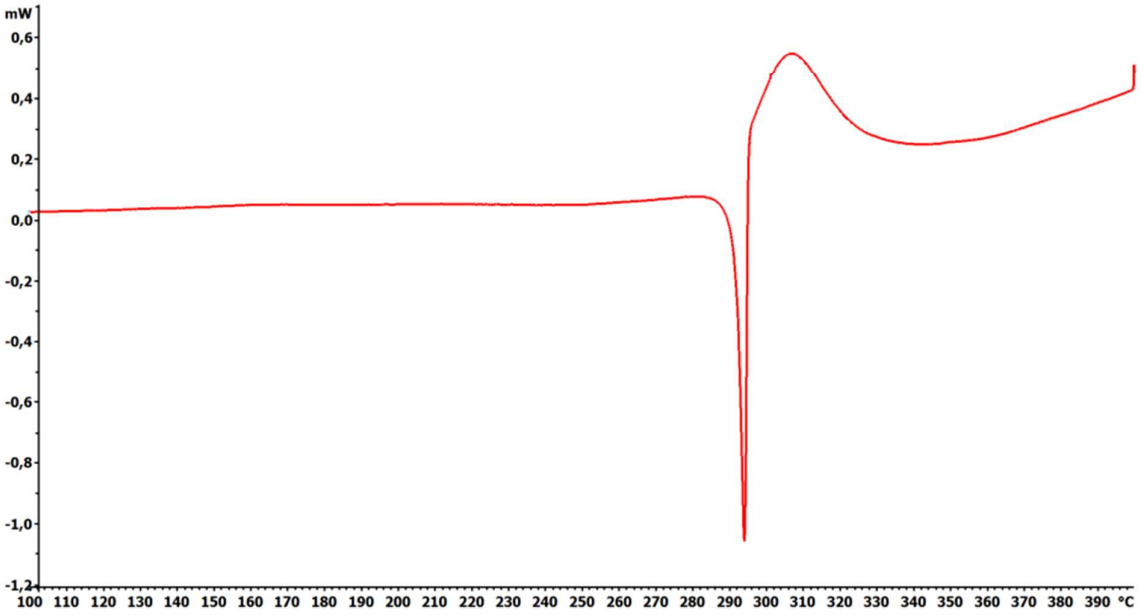

Figure S14. DSC curve of chromophore **1b.**

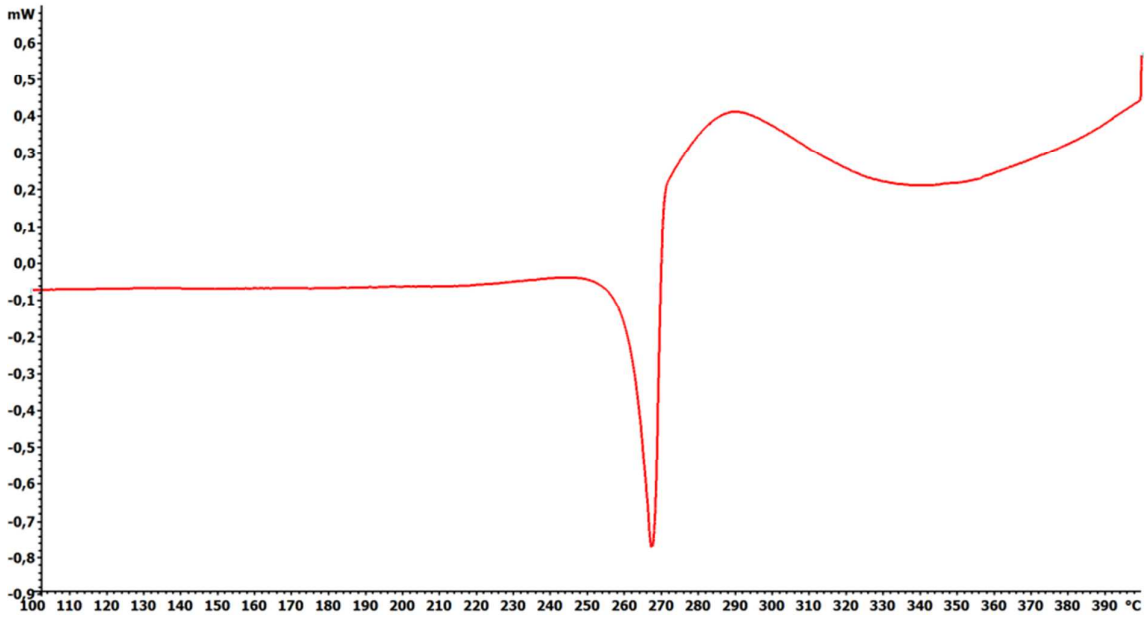

Figure S15. DSC curve of chromophore **1c.**

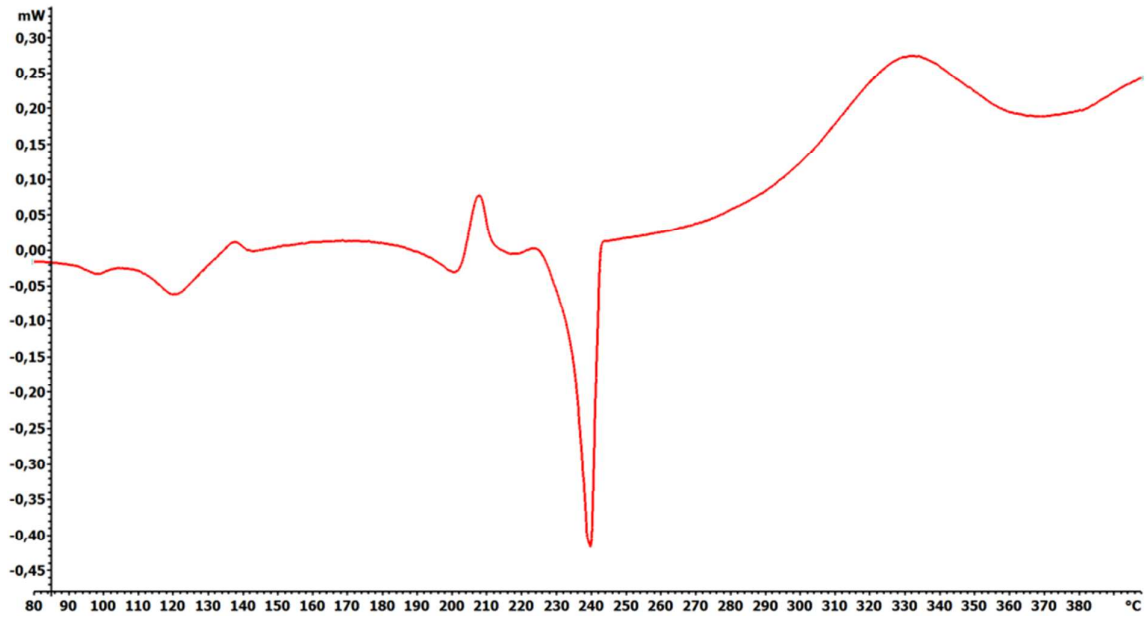

Figure S16. DSC curve of chromophore **2a.**

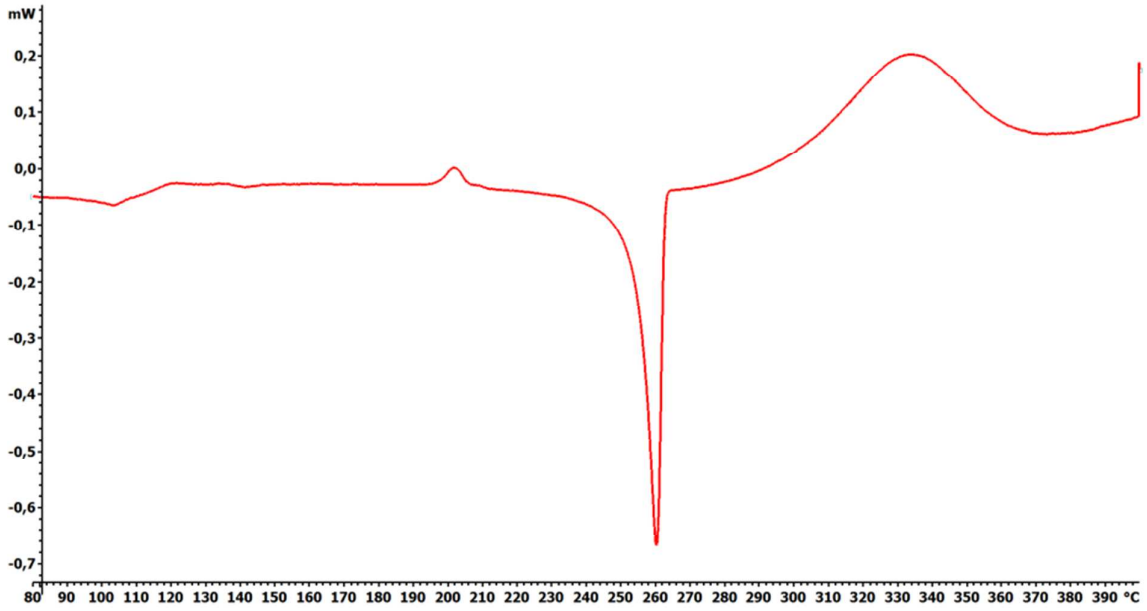

Figure S17. DSC curve of chromophore **2b.**

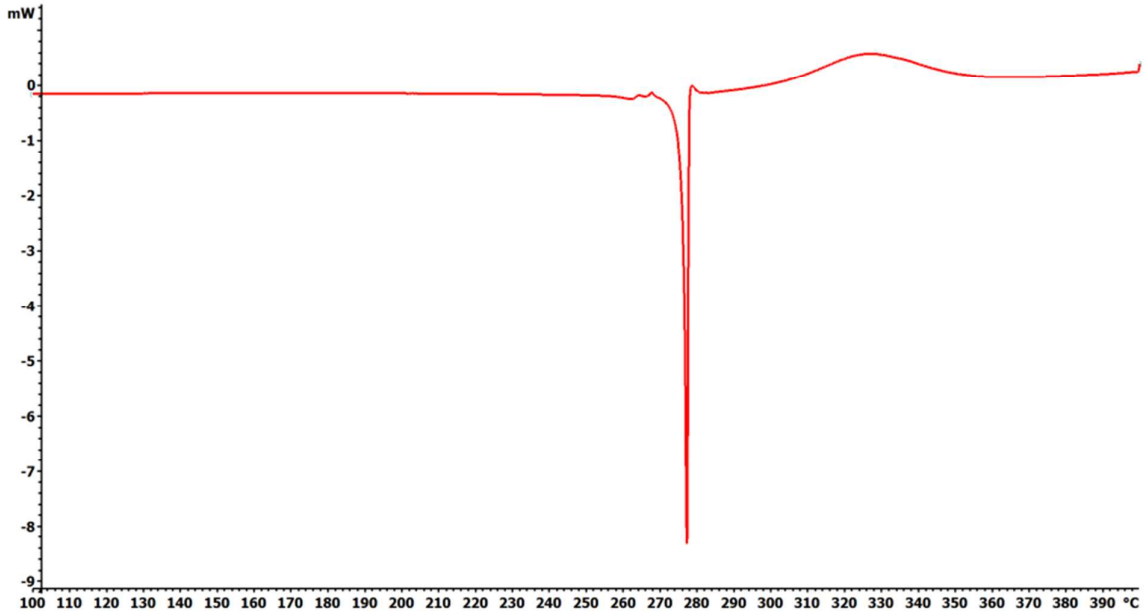

Figure S18. DSC curve of chromophore **2c.**

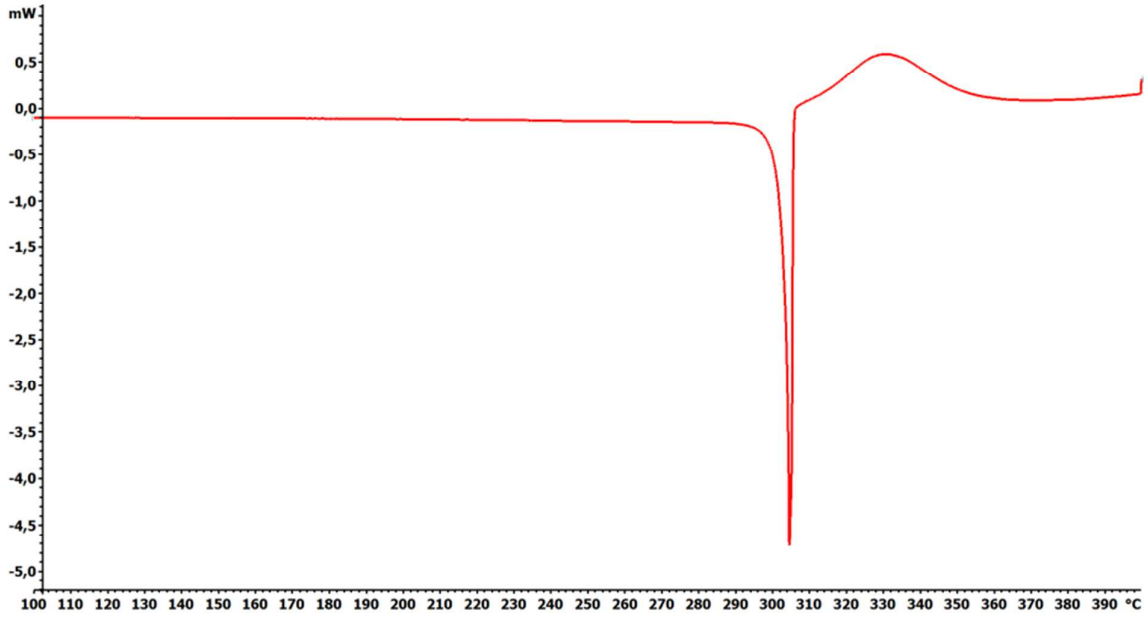

Figure S19. DSC curve of chromophore **2d.**

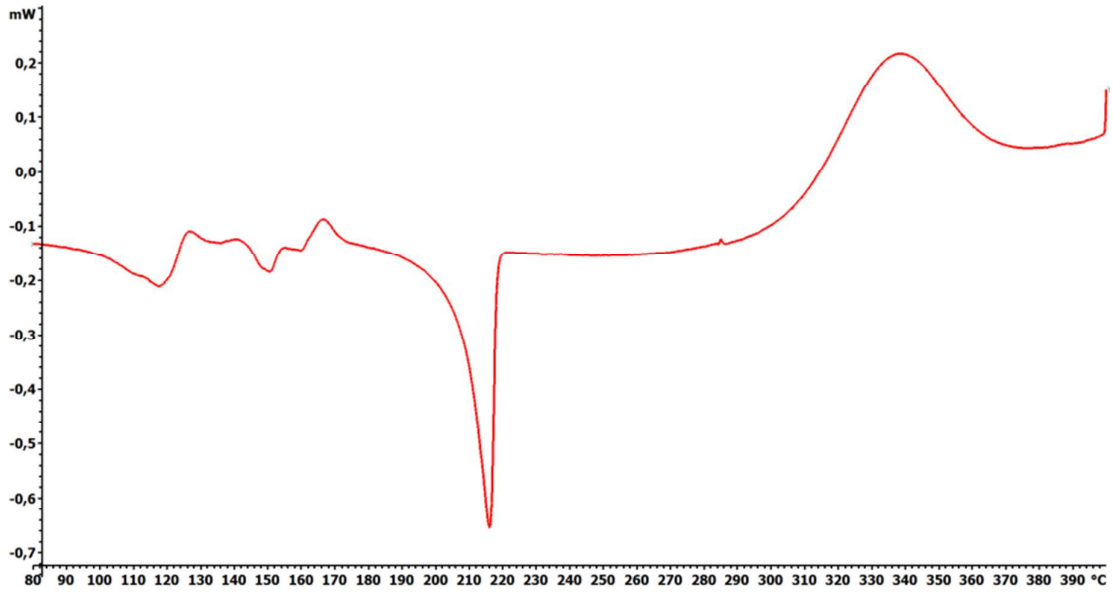

Figure S20. DSC curve of chromophore **3a.**

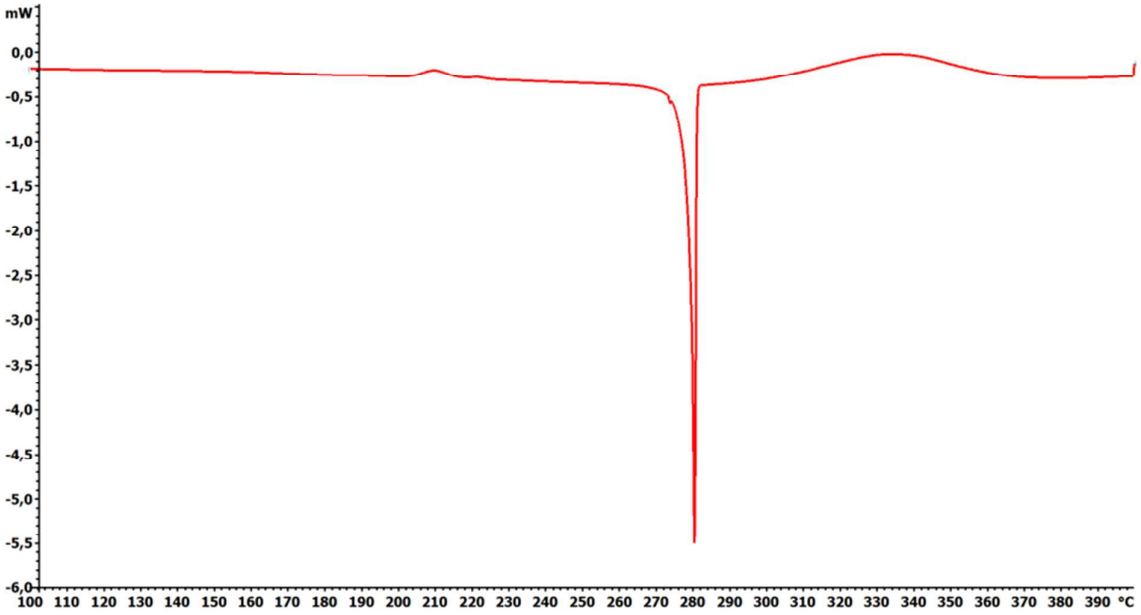

Figure S21. DSC curve of chromophore **3b.**

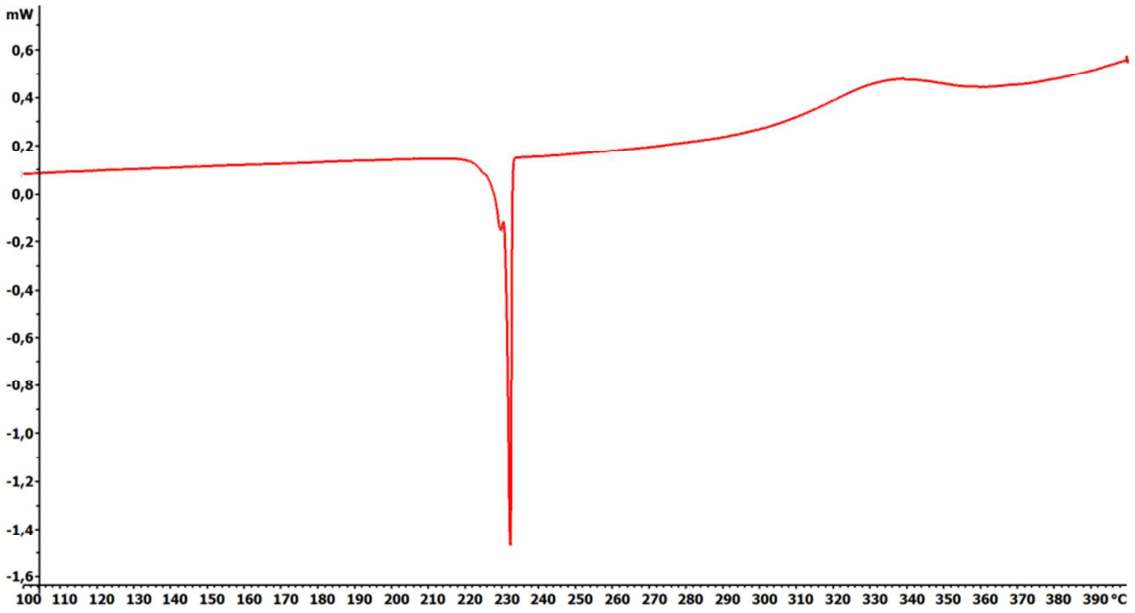

Figure S22. DSC curve of chromophore **3c.**

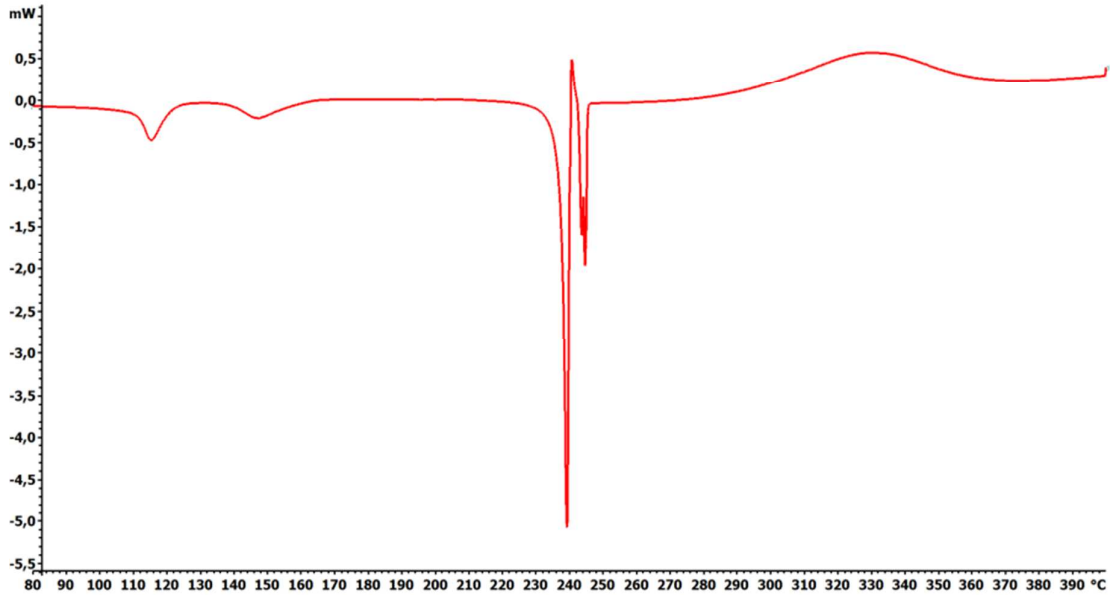

Figure 23. DSC curve of chromophore **3d.**

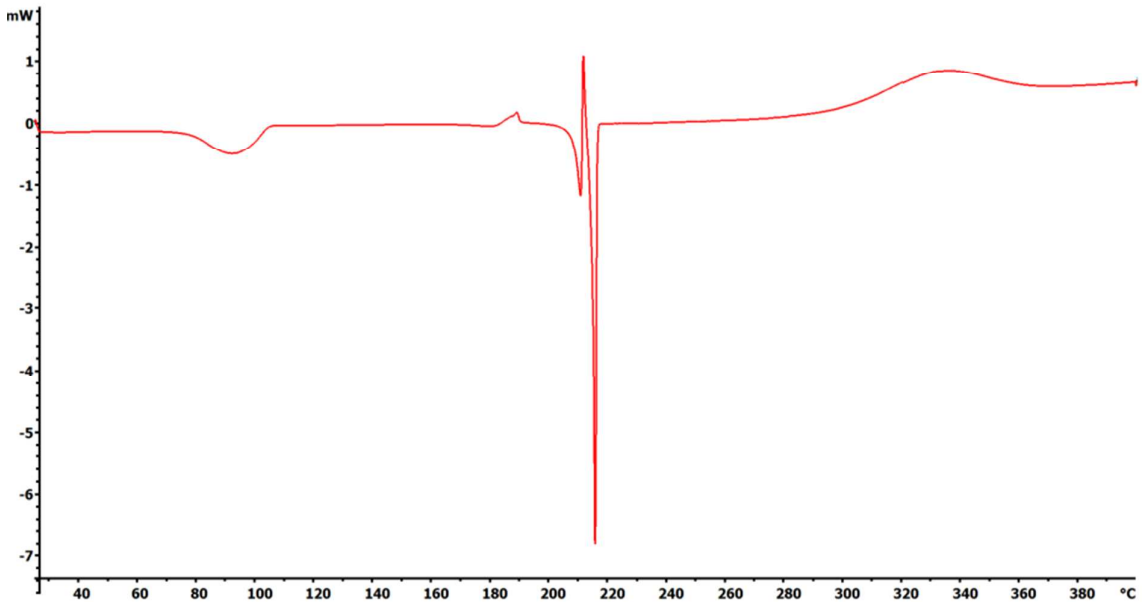

Figure S24. DSC curve of chromophore **4a.**

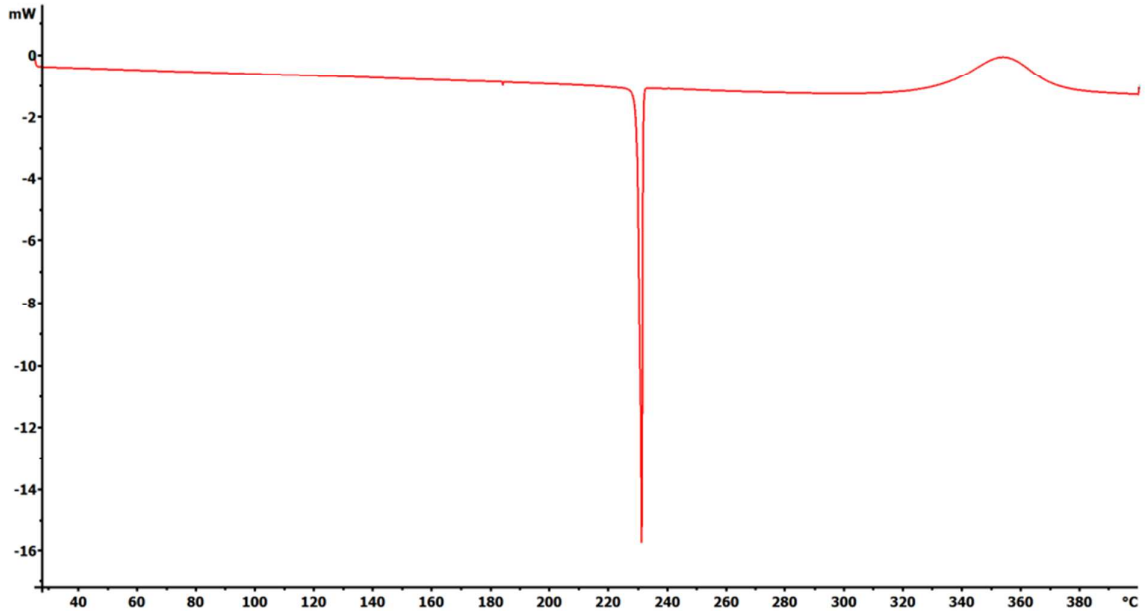

Figure S25. DSC curve of chromophore **4b.**

DFT calculations

All calculations were carried out in Gaussian 09W package at the DFT level of theory. The initial geometry optimizations were carried out by the PM3 method implemented in program ArgusLab and subsequently by the DFT B3LYP method using the 6-311G++(2d,f,p) basic set. The energies of the HOMO and LUMO (E_{HOMO} and E_{LUMO}), their differences (ΔE) and ground state dipole moments (μ) and first hyperpolarizabilities β were calculated by the DFT B3LYP/6-311++G(2d,f,p) method.

The following HOMO and LUMO localizations in molecules **1–4** were derived from the calculations using PM7 method implemented in MOPAC2016 program. The visualizations have been performed in program OPchem.

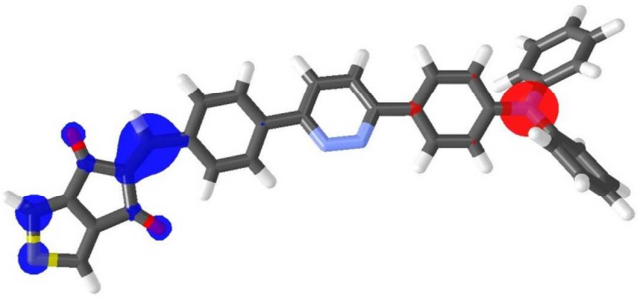

Figure S26. HOMO (red) and LUMO (blue) localizations in chromophores **1a**.

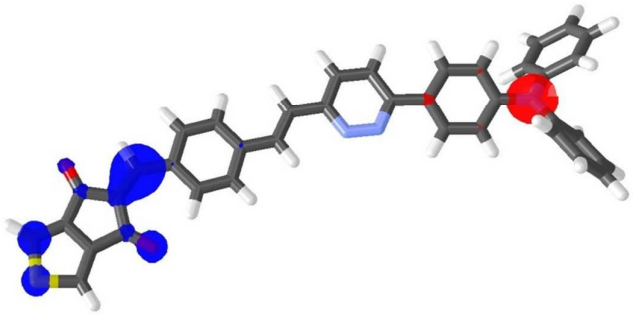

Figure S27. HOMO (red) and LUMO (blue) localizations in chromophores **1b**.

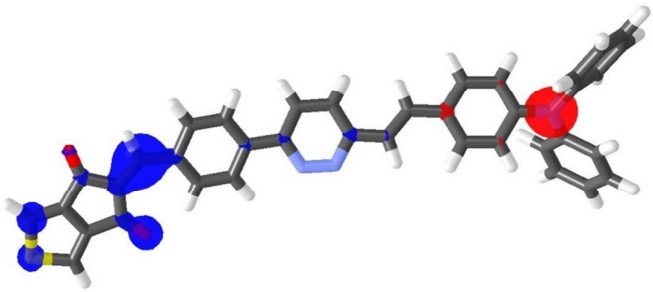

Figure S28. HOMO (red) and LUMO (blue) localizations in chromophores **1c**.

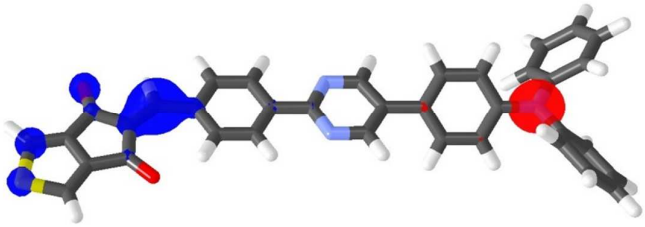

Figure S29. HOMO (red) and LUMO (blue) localizations in chromophores **2a**.

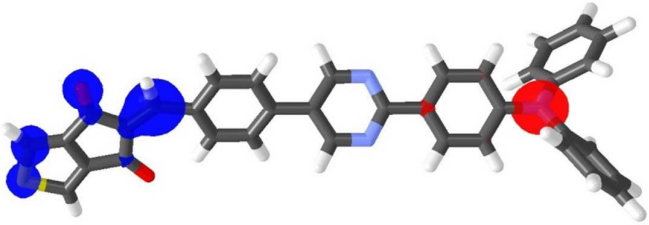

Figure S30. HOMO (red) and LUMO (blue) localizations in chromophores **2b**.

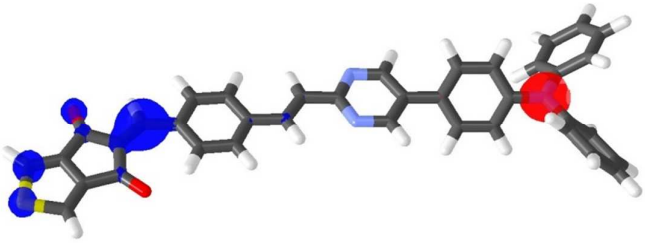

Figure S31. HOMO (red) and LUMO (blue) localizations in chromophores **2c**.

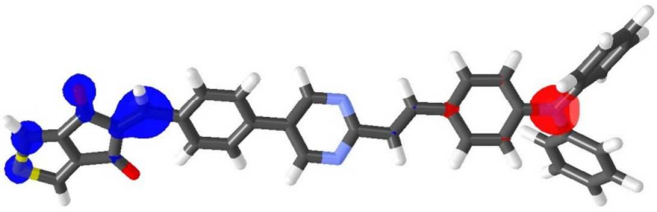

Figure S32. HOMO (red) and LUMO (blue) localizations in chromophores **2d**.

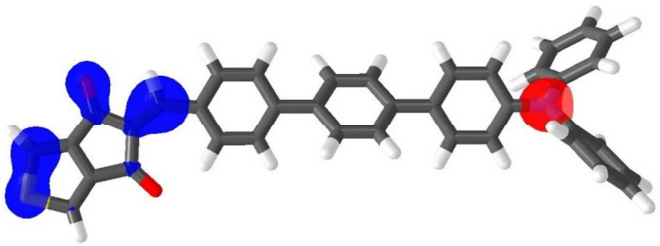

Figure S33. HOMO (red) and LUMO (blue) localizations in chromophores **3a**.

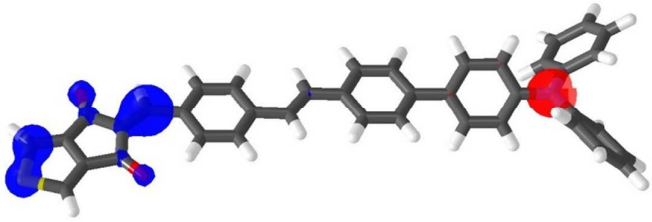

Figure S34. HOMO (red) and LUMO (blue) localizations in chromophores **3b**.

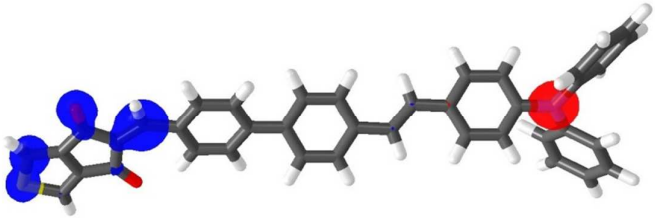

Figure S35. HOMO (red) and LUMO (blue) localizations in chromophores **3c**.

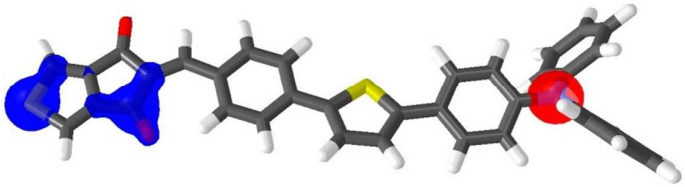

Figure S36. HOMO (red) and LUMO (blue) localizations in chromophores **3d**.

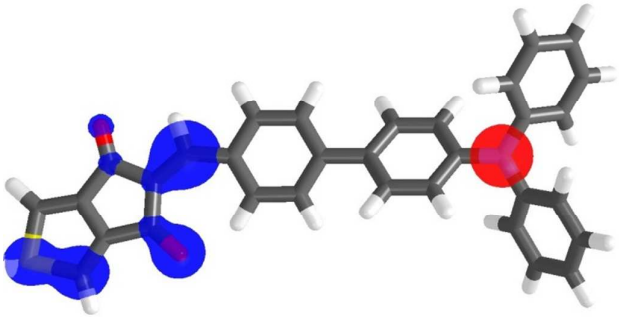

Figure S37. HOMO (red) and LUMO (blue) localizations in chromophores **4a**.

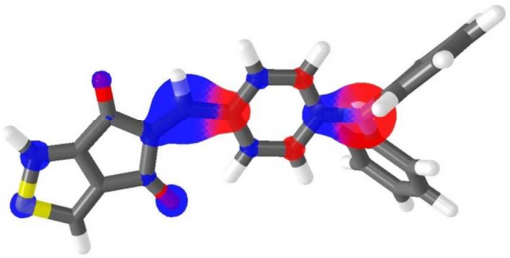

Figure S38. HOMO (red) and LUMO (blue) localizations in chromophores **4b**.

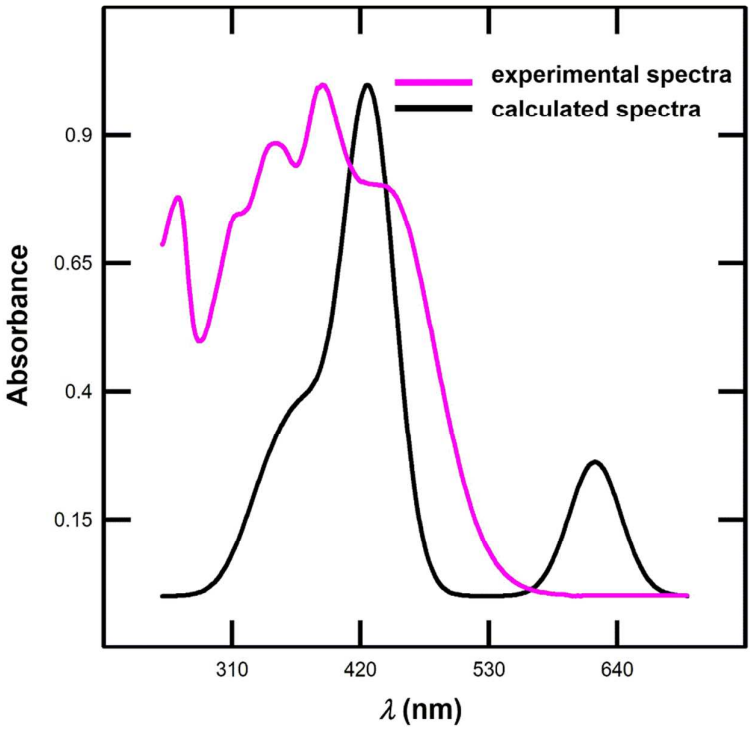

Figure S39. Comparison of the TD-DFT calculated and experimental spectra for representative chromophore **3a** in $CHCl_3$.

Table S4. Cartesian coordinates of compounds **1-c** on B3LYP/6-311++G(2d,f,p) level.

		1a					**1b**					**1c**		
N[a]		x	y	z	N[a]		x	y	z	N[a]		x	y	z
1	C	19.4169	-16.0239	0.24325	1	C	19.9834	-18.4310	-0.58279	1	C	19.8531	-18.6741	-1.16042
2	C	19.3750	-17.4023	0.30606	2	C	19.8732	-19.8050	-0.50487	2	C	19.8590	-20.0504	-1.24430
3	C	20.4533	-18.1765	-0.14705	3	C	20.8692	-20.6381	-1.03487	3	C	20.9265	-20.8015	-0.72480
4	C	21.5720	-17.5093	-0.66332	4	C	21.9775	-20.0343	-1.64318	4	C	21.9874	-20.1106	-0.12642
5	C	21.6106	-16.1281	-0.70997	5	C	22.0859	-18.6573	-1.70478	5	C	21.9750	-18.7301	-0.05679
6	C	20.5385	-15.3497	-0.25823	6	C	21.0961	-17.8199	-1.17700	6	C	20.9117	-17.9696	-0.56361
7	C	20.5639	-13.8780	-0.30534	7	C	21.1960	-16.3520	-1.23850	7	C	20.0829	-14.1981	-0.73402
8	N	20.4120	-19.5814	-0.08968	8	N	20.7577	-22.0391	-0.96274	8	N	20.9283	-22.2057	-0.80841
9	C	21.5976	-20.3291	0.14861	9	C	21.9164	-22.8474	-0.80622	9	C	22.1474	-22.9169	-0.98122
10	C	19.1853	-20.2765	-0.27682	10	C	19.4854	-22.6678	-1.05247	10	C	19.7122	-22.9359	-0.70859
11	C	18.3187	-19.9248	-1.31503	11	C	18.5615	-22.2710	-2.02294	11	C	18.7716	-22.6214	0.27591
12	C	17.1243	-20.6084	-1.49133	12	C	17.3224	-22.8899	-2.10409	12	C	17.5870	-23.3382	0.36640
13	C	16.7825	-21.6610	-0.64995	13	C	16.9905	-23.9222	-1.23412	13	C	17.3281	-24.3873	-0.50818
14	C	17.6471	-22.0196	0.37762	14	C	17.9111	-24.3259	-0.27412	14	C	18.2664	-24.7091	-1.48205
15	C	18.8362	-21.3309	0.57052	15	C	19.1464	-23.7017	-0.17606	15	C	19.4466	-23.9874	-1.58940
16	C	21.8841	-21.4620	-0.61719	16	C	22.0843	-23.9987	-1.57998	16	C	22.4157	-24.0547	-0.21626
17	C	23.0334	-22.2003	-0.37281	17	C	23.2082	-24.7957	-1.41503	17	C	23.5984	-24.7575	-0.39779
18	C	23.9205	-21.8156	0.62574	18	C	24.1872	-24.4529	-0.48973	18	C	24.5364	-24.3317	-1.33092
19	C	23.6410	-20.6859	1.38646	19	C	24.0258	-23.3053	0.27831	19	C	24.2749	-23.1965	-2.09000
20	C	22.4865	-19.9510	1.15865	20	C	22.8978	-22.5112	0.13040	20	C	23.0882	-22.4969	-1.92547
21	C	21.7386	-13.1333	-0.48963	21	C	22.3883	-15.6721	-1.52789	21	C	21.1401	-13.4802	-0.15207
22	C	21.6463	-11.7662	-0.53143	22	C	22.3608	-14.3018	-1.57100	22	C	21.0537	-12.1145	-0.11134
23	C	20.3826	-11.1788	-0.38062	23	C	21.1480	-13.6500	-1.31001	23	C	19.9160	-11.5003	-0.65852
24	N	19.3007	-11.9419	-0.17103	24	N	20.0419	-14.3545	-1.01519	24	N	18.9322	-12.2403	-1.18896
25	N	19.3863	-13.2520	-0.13799	25	N	20.0659	-15.6643	-0.98556	25	N	19.0077	-13.5508	-1.22739
26	C	20.1592	-9.71877	-0.41369	26	C	19.7623	-10.0601	-1.11986	26	C	19.7171	-10.0370	-0.67529
27	C	21.1096	-8.84256	-0.95285	27	C	20.8068	-9.16049	-1.39646	27	C	20.7792	-9.14731	-0.46823
28	C	20.8815	-7.48149	-0.96919	28	C	20.5839	-7.80263	-1.39437	28	C	20.5674	-7.78376	-0.48339
29	C	19.6968	-6.92901	-0.44748	29	C	19.3104	-7.26025	-1.11722	29	C	19.2873	-7.24141	-0.70356
30	C	18.7412	-7.81412	0.08651	30	C	18.2640	-8.15878	-0.84032	30	C	18.2242	-8.13897	-0.91867
31	C	18.9715	-9.17508	0.09675	31	C	18.4949	-9.51968	-0.84432	31	C	18.4412	-9.50193	-0.90692
32	C	19.5659	-5.49127	-0.51287	32	C	19.1949	-5.82247	-1.14292	32	C	19.1812	-5.80040	-0.69308
33	C	18.6235	-4.59518	-0.13050	33	C	18.1876	-4.93634	-0.93986	33	C	18.1700	-4.91137	-0.85065
34	C	18.8958	-3.13732	-0.39527	34	C	18.5085	-3.47104	-1.06819	34	C	18.5068	-3.44576	-0.76189
35	C	17.7159	-2.40404	0.11953	35	C	17.2407	-2.75280	-0.79799	35	C	17.2301	-2.72278	-0.96822
36	C	16.7843	-3.32859	0.66173	36	C	16.2138	-3.69455	-0.52369	36	C	16.1828	-3.66064	-1.16863
37	C	17.2919	-4.71996	0.53698	37	C	16.7416	-5.08219	-0.59649	37	C	16.7041	-5.05122	-1.10686
38	C	17.3080	-1.10756	0.20330	38	C	16.8206	-1.45868	-0.74688	38	C	16.8162	-1.42634	-1.01355
39	S	15.7581	-1.02912	0.95939	39	S	15.1398	-1.40357	-0.35604	39	S	15.1161	-1.36448	-1.30679
40	C	15.6623	-2.74060	1.16119	40	C	15.0064	-3.12208	-0.26234	40	C	14.9660	-3.08294	-1.36763
41	O	16.7084	-5.71574	0.91466	41	O	16.0906	-6.09055	-0.40773	41	O	16.0370	-6.05680	-1.24235
42	O	19.8819	-2.67180	-0.92198	42	O	19.5864	-2.98889	-1.33771	42	O	19.6014	-2.96786	-0.56192
43	H	18.5791	-15.4397	0.59785	43	C	21.0509	-12.1960	-1.33961	43	C	20.0204	-15.6443	-0.85620
44	H	18.5021	-17.8927	0.71587	44	C	19.9233	-11.5051	-1.10437	44	C	20.9552	-16.5207	-0.45037
45	H	22.4089	-18.0821	-1.03970	45	H	21.9757	-11.6776	-1.57255	45	H	19.1058	-15.9856	-1.32773
46	H	22.4841	-15.6574	-1.14370	46	H	19.0326	-12.0819	-0.87754	46	H	21.8578	-16.1395	0.02042
47	H	18.5857	-19.1137	-1.98033	47	H	19.2086	-17.8013	-0.16818	47	H	19.0149	-18.1341	-1.58251
48	H	16.4630	-20.3233	-2.30089	48	H	19.0106	-20.2459	-0.02330	48	H	19.0339	-20.5612	-1.72248
49	H	15.8523	-22.1962	-0.79402	49	H	22.7504	-20.6529	-2.07917	49	H	22.8200	-20.6633	0.28778
50	H	17.3902	-22.8345	1.04405	50	H	22.9465	-18.2367	-2.20988	50	H	22.8069	-18.2214	0.41830
51	H	19.5018	-21.6071	1.37830	51	H	18.8194	-21.4756	-2.71046	51	H	18.9743	-21.8140	0.96785
52	H	21.2005	-21.7604	-1.40169	52	H	16.6172	-22.5702	-2.86202	52	H	16.8680	-23.0822	1.13550
53	H	23.2412	-23.0761	-0.97602	53	H	16.0247	-24.4070	-1.30402	53	H	16.4053	-24.9486	-0.43099
54	H	24.8191	-22.3909	0.81068	54	H	17.6631	-25.1254	0.41390	54	H	18.0747	-25.5211	-2.17350
55	H	24.3190	-20.3806	2.17468	55	H	19.8563	-24.0128	0.57967	55	H	20.1699	-24.2351	-2.35574
56	H	22.2660	-19.0803	1.76294	56	H	21.3288	-24.2647	-2.30819	56	H	21.6920	-24.3849	0.51796
57	H	22.7013	-13.6200	-0.56874	57	H	23.3234	-25.6849	-2.02338	57	H	23.7917	-25.6378	0.20372
58	H	22.5349	-11.1600	-0.64574	58	H	25.0655	-25.0742	-0.36695	58	H	25.4607	-24.8793	-1.46658
59	H	22.0253	-9.22400	-1.38581	59	H	24.7765	-23.0317	1.01027	59	H	24.9934	-22.8591	-2.82762
60	H	21.6263	-6.82065	-1.39743	60	H	22.7697	-21.6263	0.74062	60	H	22.8830	-21.6216	-2.52841
61	H	17.8230	-7.41478	0.49192	61	H	23.3117	-16.2099	-1.69545	61	H	21.9986	-13.9907	0.26473
62	H	18.2309	-9.84928	0.50332	62	H	23.2542	-13.7283	-1.78938	62	H	21.8367	-11.5289	0.35133
63	H	20.4206	-4.99784	-0.97636	63	H	21.8005	-9.53014	-1.61491	63	H	21.7849	-9.51730	-0.31686
64	H	17.8096	-0.21129	-0.12471	64	H	21.4035	-7.12677	-1.61040	64	H	21.4037	-7.11209	-0.32795
65	H	14.8026	-3.19643	1.62550	65	H	17.2791	-7.77059	-0.62486	65	H	17.2323	-7.74769	-1.09137
					66	H	17.6763	-10.1968	-0.62872	66	H	17.6213	-10.1851	-1.07772
					67	H	20.1303	-5.31488	-1.38005	67	H	20.1316	-5.29606	-0.51692
					68	H	17.3804	-0.55192	-0.91073	68	H	17.3906	-0.52157	-0.89577
					69	H	14.0656	-3.59244	-0.02531	69	H	14.0100	-3.54975	-1.54285

[a]Atomic number

Table S5. Cartesian coordinates of compounds **2a-c** on B3LYP/6-311++G(2d,f,p) level.

		2a					**2b**					**2c**		
N[a]		x	y	z	N[a]		x	y	z	N[a]		x	y	z
1	C	19.2564	-16.5548	0.55730	1	C	19.0291	-16.5614	0.10414	1	C	19.7874	-18.7298	-0.24465
2	C	19.3334	-17.9354	0.56089	2	C	19.1371	-17.9359	0.18229	2	C	19.8014	-20.1126	-0.24214
3	C	20.3539	-18.5982	-0.13369	3	C	20.3474	-18.5777	-0.12010	3	C	20.7894	-20.8204	-0.93878
4	C	21.2931	-17.8206	-0.82384	4	C	21.4424	-17.7866	-0.49861	4	C	21.7618	-20.0861	-1.62989
5	C	21.2148	-16.4401	-0.81109	5	C	21.3289	-16.4121	-0.56740	5	C	21.7464	-18.7034	-1.61631
6	C	20.1947	-15.7699	-0.12435	6	C	20.1212	-15.7697	-0.27019	6	C	20.7593	-17.9875	-0.92731
7	C	20.1126	-14.3023	-0.11914	7	C	20.0031	-14.3066	-0.34941	7	C	20.7448	-16.5178	-0.92077
8	N	20.4332	-20.0038	-0.13800	8	N	20.4601	-19.9782	-0.04579	8	N	20.8047	-22.2289	-0.94419
9	C	21.6974	-20.6539	-0.14636	9	C	21.6828	-20.5847	0.35299	9	C	22.0385	-22.9345	-0.94398
10	C	19.2498	-20.7917	-0.13384	10	C	19.3537	-20.8108	-0.36887	10	C	19.5867	-22.9614	-0.95005
11	C	18.1823	-20.4777	-0.97945	11	C	18.5891	-20.5664	-1.51287	11	C	18.5381	-22.5927	-1.79737
12	C	17.0304	-21.2512	-0.96968	12	C	17.5122	-21.3844	-1.82281	12	C	17.3515	-23.3118	-1.79692
13	C	16.9293	-22.3565	-0.13259	13	C	17.1900	-22.4657	-1.01047	13	C	17.1957	-24.4167	-0.96772
14	C	17.9931	-22.6775	0.70244	14	C	17.9546	-22.7174	0.12269	14	C	18.2402	-24.7921	-0.13105
15	C	19.1425	-21.9000	0.71023	15	C	19.0240	-21.8951	0.44811	15	C	19.4244	-24.0691	-0.11380
16	C	21.9273	-21.7397	-0.99511	16	C	22.1902	-21.6796	-0.35089	16	C	22.2252	-24.0314	-1.78932
17	C	23.1567	-22.3832	-0.99168	17	C	23.3747	-22.2815	0.04941	17	C	23.4252	-24.7281	-1.77787
18	C	24.1790	-21.9483	-0.15634	18	C	24.0781	-21.7954	1.14530	18	C	24.4612	-24.3366	-0.93792
19	C	23.9556	-20.8647	0.68551	19	C	23.5787	-20.7027	1.84480	19	C	24.2810	-23.2423	-0.09965
20	C	22.7241	-20.2256	0.69963	20	C	22.3873	-20.1047	1.46034	20	C	23.0787	-22.5497	-0.09347
21	C	21.2424	-13.4771	-0.11926	21	N	21.0885	-13.6044	-0.71593	21	C	21.9103	-15.7453	-0.92491
22	N	21.1790	-12.1546	-0.12020	22	C	20.9707	-12.2893	-0.78452	22	N	21.9090	-14.4198	-0.92525
23	C	19.9615	-11.5954	-0.10962	23	C	19.7840	-11.6058	-0.49837	23	C	20.7131	-13.8089	-0.91055
24	N	18.8140	-12.2865	-0.10334	24	C	18.7202	-12.4354	-0.12735	24	N	19.5320	-14.4481	-0.89996
25	C	18.8980	-13.6078	-0.11356	25	N	18.8161	-13.7519	-0.05115	25	C	19.5598	-15.7695	-0.91011
26	C	19.8797	-10.1190	-0.10456	26	C	19.6649	-10.1434	-0.58091	26	C	19.5825	-10.1292	-0.89474
27	C	21.0446	-9.34339	-0.10001	27	C	20.3643	-9.41542	-1.55382	27	C	20.7265	-9.31242	-0.89490
28	C	20.9604	-7.96673	-0.09535	28	C	20.2478	-8.04236	-1.62525	28	C	20.6094	-7.94127	-0.89090
29	C	19.7159	-7.30554	-0.09522	29	C	19.4278	-7.32553	-0.73291	29	C	19.3495	-7.30436	-0.88651
30	C	18.5502	-8.09409	-0.09983	30	C	18.7261	-8.05754	0.24230	30	C	18.2039	-8.12063	-0.88620
31	C	18.6374	-9.47240	-0.10431	31	C	18.8481	-9.43150	0.31038	31	C	18.3289	-9.49539	-0.89017
32	C	19.7484	-5.86071	-0.09036	32	C	19.3786	-5.89090	-0.89918	32	C	19.3489	-5.86151	-0.88266
33	C	18.8136	-4.87863	-0.08908	33	C	18.7427	-4.87419	-0.26752	33	C	18.3897	-4.90181	-0.87826
34	C	19.2980	-3.45224	-0.08358	34	C	18.9765	-3.47652	-0.77940	34	C	18.8383	-3.46457	-0.87543
35	C	18.0793	-2.60924	-0.08373	35	C	18.1691	-2.58694	0.08756	35	C	17.5987	-2.65240	-0.87147
36	C	16.9291	-3.44181	-0.08885	36	C	17.4880	-3.36587	1.06036	36	C	16.4699	-3.51397	-0.87162
37	C	17.3190	-4.87634	-0.09228	37	C	17.8038	-4.80803	0.89317	37	C	16.8967	-4.93777	-0.87546
38	C	17.7888	-1.27897	-0.08035	38	C	17.9203	-1.25195	0.18740	38	C	17.2745	-1.33005	-0.86786
39	S	16.0772	-1.05350	-0.08357	39	S	16.8344	-0.95504	1.49614	39	S	15.5576	-1.14794	-0.86474
40	C	15.7566	-2.74955	-0.08943	40	C	16.7174	-2.62744	1.90609	40	C	15.2802	-2.85179	-0.86827
41	O	16.5449	-5.81218	-0.09679	41	O	17.3648	-5.70695	1.58265	41	O	16.1469	-5.89394	-0.87685
42	O	20.4508	-3.08135	-0.07983	42	O	19.6821	-3.15872	-1.71060	42	O	19.9816	-3.06514	-0.87631
43	H	18.4728	-16.0759	1.13219	43	H	18.0937	-16.0758	0.34644	43	C	20.7341	-12.3507	-0.90636
44	H	18.6053	-18.5113	1.11656	44	H	18.2824	-18.5253	0.48592	44	C	19.6332	-11.5829	-0.89891
45	H	22.0808	-18.3076	-1.38317	45	H	22.3828	-18.2608	-0.74518	45	H	21.7309	-11.9271	-0.91082
46	H	21.9395	-15.8726	-1.38267	46	H	22.1769	-15.8119	-0.86763	46	H	18.6756	-12.0938	-0.89608
47	H	18.2614	-19.6264	-1.64341	47	H	18.8436	-19.7331	-2.15508	47	H	19.0273	-18.2162	0.33196
48	H	16.2122	-20.9950	-1.63225	48	H	16.9297	-21.1818	-2.71371	48	H	19.0487	-20.6554	0.31412
49	H	16.0314	-22.9619	-0.13216	49	H	16.3526	-23.1058	-1.25866	49	H	22.5257	-20.6083	-2.19055
50	H	17.9256	-23.5333	1.36348	50	H	17.7113	-23.5537	0.76733	50	H	22.4951	-18.1689	-2.18870
51	H	19.9646	-22.1483	1.36920	51	H	19.6109	-22.0893	1.33668	51	H	18.6592	-21.7417	-2.45526
52	H	21.1374	-22.0762	-1.65435	52	H	21.6505	-22.0555	-1.21065	52	H	16.5487	-23.0135	-2.46075
53	H	23.3189	-23.2234	-1.65637	53	H	23.7553	-23.1293	-0.50776	53	H	16.2707	-24.9797	-0.97457
54	H	25.1391	-22.4490	-0.16016	54	H	25.0052	-22.2638	1.45184	54	H	18.1304	-25.6482	0.52409
55	H	24.7407	-20.5211	1.34847	55	H	24.1127	-20.3189	2.70603	55	H	20.2313	-24.3597	0.54664
56	H	22.5509	-19.3912	1.36724	56	H	21.9960	-19.2618	2.01550	56	H	21.4250	-24.3343	-2.45236
57	H	22.2384	-13.9108	-0.09982	57	H	21.8677	-11.7402	-1.05849	57	H	23.5539	-25.5760	-2.44008
58	H	17.9563	-14.1492	-0.13631	58	H	17.7448	-12.0108	0.09446	58	H	25.3984	-24.8790	-0.93559
59	H	22.0041	-9.84108	-0.09990	59	H	20.9810	-9.93568	-2.27600	59	H	25.0769	-22.9317	0.56671
60	H	21.8689	-7.37535	-0.09157	60	H	20.7909	-7.50031	-2.39080	60	H	22.9389	-21.7069	0.57132
61	H	17.5856	-7.60807	-0.10000	61	H	18.0967	-7.53026	0.94453	61	H	22.8853	-16.2243	-0.90887
62	H	17.7402	-10.0755	-0.10809	62	H	18.3188	-9.96548	1.09006	62	H	18.5962	-16.2713	-0.92895
63	H	20.7582	-5.44952	-0.08701	63	H	19.9939	-5.52725	-1.72256	63	H	21.7123	-9.75898	-0.89801
64	H	18.4582	-0.43373	-0.07628	64	H	18.2985	-0.43995	-0.41269	64	H	21.5041	-7.32930	-0.89106
65	H	14.7447	-3.12191	-0.09287	65	H	16.1005	-2.95436	2.72773	65	H	17.2274	-7.65854	-0.88284
										66	H	17.4351	-10.1088	-0.88988
										67	H	20.3483	-5.42588	-0.88347
										68	H	17.9223	-0.46812	-0.86691
										69	H	14.2781	-3.24979	-0.86759

[a]Atomic number

Table S6. Cartesian coordinates of compounds **2d** and **3a-b** on B3LYP/6-311++G(2d,f,p) level.

2d

N[a]		x	y	z
1	C	19.6248	-18.7902	-1.41843
2	C	19.7631	-20.1621	-1.42141
3	C	20.8313	-20.7808	-0.75061
4	C	21.7540	-19.9642	-0.08511
5	C	21.6102	-18.5895	-0.09701
6	C	20.5445	-17.9598	-0.75636
7	C	19.4758	-14.2921	-1.19564
8	N	20.9695	-22.1811	-0.75324
9	C	22.2597	-22.7785	-0.76309
10	C	19.8214	-23.0191	-0.73459
11	C	18.7564	-22.7488	0.12904
12	C	17.6391	-23.5714	0.14128
13	C	17.5711	-24.6825	-0.69138
14	C	18.6331	-24.9598	-1.54442
15	C	19.7475	-24.1337	-1.57409
16	C	22.5481	-23.8507	0.08487
17	C	23.8027	-24.4433	0.06242
18	C	24.7918	-23.9700	-0.79182
19	C	24.5097	-22.8996	-1.63306
20	C	23.2533	-22.3113	-1.62778
21	N	20.4679	-13.6545	-0.54629
22	C	20.4116	-12.3367	-0.49809
23	C	19.3850	-11.5847	-1.08536
24	C	18.4102	-12.3502	-1.73349
25	N	18.4412	-13.6720	-1.79387
26	C	19.3385	-10.1177	-1.02526
27	C	20.5152	-9.35523	-1.04679
28	C	20.4636	-7.97769	-0.98963
29	C	19.2379	-7.28919	-0.91002
30	C	18.0579	-8.05532	-0.88927
31	C	18.1156	-9.43386	-0.94460
32	C	19.3005	-5.84685	-0.85677
33	C	18.3858	-4.85008	-0.77113
34	C	18.8955	-3.43277	-0.74071
35	C	17.6936	-2.57162	-0.64521
36	C	16.5301	-3.38540	-0.61812
37	C	16.8938	-4.82411	-0.69391
38	C	17.4270	-1.23797	-0.57862
39	S	15.7220	-0.98593	-0.48142
40	C	15.3715	-2.67511	-0.53063
41	O	16.1051	-5.74822	-0.69045
42	O	20.0535	-3.08196	-0.78597
43	C	19.4921	-15.7430	-1.27459
44	C	20.4479	-16.5120	-0.72422
45	H	18.6570	-16.1645	-1.82027
46	H	21.2415	-15.9961	-0.19194
47	H	18.7932	-18.3522	-1.95622
48	H	19.0450	-20.7727	-1.95254
49	H	22.5823	-20.4148	0.44508
50	H	22.3342	-17.9789	0.43112
51	H	18.8102	-21.8925	0.78898
52	H	16.8222	-23.3484	0.81731
53	H	16.7003	-25.3260	-0.67480
54	H	18.5909	-25.8196	-2.20245
55	H	20.5678	-24.3480	-2.24712
56	H	21.7840	-24.2167	0.75859
57	H	24.0106	-25.2735	0.72691
58	H	25.7716	-24.4310	-0.80303
59	H	25.2688	-22.5264	-2.31029
60	H	23.0346	-21.4863	-2.29369
61	H	21.2066	-11.8408	0.05274
62	H	17.5820	-11.8658	-2.24376
63	H	21.4750	-9.84827	-1.13784
64	H	21.3854	-7.40806	-1.01626
65	H	17.1045	-7.55167	-0.81989
66	H	17.1924	-9.99812	-0.89703
67	H	20.3171	-5.45419	-0.89229
68	H	18.1103	-0.40397	-0.58042
69	H	14.3545	-3.03107	-0.49279

3a

N[a]		x	y	z
1	C	19.1820	-16.5831	0.37663
2	C	19.2681	-17.9629	0.43279
3	C	20.3622	-18.6341	-0.12499
4	C	21.3660	-17.8694	-0.73036
5	C	21.2778	-16.4890	-0.76645
6	C	20.1838	-15.8077	-0.21947
7	C	20.0904	-14.3350	-0.26924
8	N	20.4506	-20.0428	-0.07851
9	C	21.7049	-20.6739	0.13172
10	C	19.2860	-20.8379	-0.24309
11	C	18.3477	-20.5306	-1.23298
12	C	17.2094	-21.3089	-1.38600
13	C	16.9933	-22.4134	-0.56996
14	C	17.9285	-22.7277	0.40932
15	C	19.0617	-21.9456	0.57971
16	C	22.0689	-21.7954	-0.61923
17	C	23.2903	-22.4173	-0.40377
18	C	24.1751	-21.9265	0.54938
19	C	23.8196	-20.8075	1.29370
20	C	22.5937	-20.1888	1.09579
21	C	21.2301	-13.5282	-0.15998
22	C	21.1432	-12.1479	-0.21100
23	C	19.9103	-11.5023	-0.36508
24	C	18.7696	-12.3074	-0.46976
25	C	18.8584	-13.6879	-0.42745
26	C	19.8164	-10.0305	-0.41579
27	C	20.8267	-9.25957	-1.00817
28	C	20.7321	-7.88395	-1.05376
29	C	19.6258	-7.20316	-0.50957
30	C	18.6124	-7.97678	0.08601
31	C	18.7135	-9.35334	0.12639
32	C	19.6295	-5.76324	-0.61204
33	C	18.7898	-4.77063	-0.22502
34	C	19.1892	-3.35369	-0.54017
35	C	18.1018	-2.49775	-0.00947
36	C	17.1064	-3.31549	0.58785
37	C	17.4770	-4.75152	0.48643
38	C	17.8212	-1.16682	0.05020
39	S	16.3121	-0.92183	0.85262
40	C	16.0626	-2.61114	1.10571
41	O	16.8142	-5.67741	0.91071
42	O	20.1957	-2.99708	-1.11171
43	H	18.3358	-16.0941	0.84419
44	H	18.4873	-18.5307	0.92173
45	H	22.2140	-18.3659	-1.18368
46	H	22.0579	-15.9298	-1.26902
47	H	18.5165	-19.6796	-1.88026
48	H	16.4934	-21.0567	-2.15928
49	H	16.1069	-23.0225	-0.69632
50	H	17.7704	-23.5821	1.05677
51	H	19.7808	-22.1892	1.35119
52	H	21.3888	-22.1761	-1.37031
53	H	23.5563	-23.2852	-0.99564
54	H	25.1301	-22.4108	0.71092
55	H	24.4956	-20.4187	2.04618
56	H	22.3173	-19.3258	1.68778
57	H	22.1964	-13.9900	0.00205
58	H	22.0437	-11.5584	-0.08864
59	H	17.8023	-11.8460	-0.62636
60	H	17.9589	-14.2779	-0.55331
61	H	21.6786	-9.75005	-1.46209
62	H	21.5209	-7.31010	-1.52677
63	H	17.7570	-7.47936	0.51956
64	H	17.9317	-9.92091	0.61560
65	H	20.5100	-5.36584	-1.11751
66	H	18.3936	-0.33092	-0.31877
67	H	15.1802	-2.97111	1.60997

3b

N[a]		x	y	z
1	C	19.7325	-18.7960	-0.29312
2	C	19.7902	-20.1782	-0.28621
3	C	20.7849	-20.8561	-1.00057
4	C	21.7198	-20.0950	-1.71192
5	C	21.6629	-18.7128	-1.69858
6	C	20.6677	-18.0240	-0.99386
7	C	20.6080	-16.5500	-0.98956
8	N	20.8435	-22.2666	-1.00370
9	C	22.0986	-22.9302	-0.98018
10	C	19.6480	-23.0322	-1.03063
11	C	18.5945	-22.6780	-1.87867
12	C	17.4275	-23.4280	-1.89792
13	C	17.2950	-24.5501	-1.08797
14	C	18.3438	-24.9107	-0.25006
15	C	19.5083	-24.1572	-0.21287
16	C	22.3310	-24.0363	-1.80281
17	C	23.5542	-24.6904	-1.76924
18	C	24.5699	-24.2473	-0.93006
19	C	24.3449	-23.1437	-0.11519
20	C	23.1195	-22.4933	-0.13086
21	C	21.7712	-15.7720	-1.02254
22	C	21.7087	-14.3900	-1.01947
23	C	20.4836	-13.7089	-0.98274
24	C	19.3176	-14.4905	-0.94890
25	C	19.3805	-15.8696	-0.95255
26	C	19.4313	-9.98181	-0.96316
27	C	20.6074	-9.21001	-0.97454
28	C	20.5473	-7.83557	-0.97452
29	C	19.3161	-7.14436	-0.96320
30	C	18.1382	-7.91431	-0.95141
31	C	18.2061	-9.29219	-0.95127
32	C	19.3753	-5.70474	-0.96437
33	C	18.4563	-4.70487	-0.95687
34	C	18.9640	-3.28870	-0.96212
35	C	17.7590	-2.42520	-0.95264
36	C	16.5957	-3.23945	-0.94228
37	C	16.9645	-4.67985	-0.94418
38	C	17.4898	-1.09072	-0.95143
39	S	15.7817	-0.83756	-0.93742
40	C	15.4345	-2.52890	-0.93317
41	O	16.1754	-5.60440	-0.93678
42	O	20.1229	-2.93607	-0.97209
43	C	20.4857	-12.2530	-0.98188
44	C	19.4174	-11.4361	-0.96278
45	H	21.4774	-11.8103	-1.00108
46	H	18.4241	-11.8742	-0.94671
47	H	18.9675	-18.3040	0.29535
48	H	19.0658	-20.7433	0.28568
49	H	22.4880	-20.5956	-2.28668
50	H	22.3841	-18.1562	-2.28482
51	H	18.6966	-21.8130	-2.52145
52	H	16.6215	-23.1397	-2.56241
53	H	16.3852	-25.1370	-1.11023
54	H	18.2524	-25.7794	0.39122
55	H	20.3174	-24.4371	0.44945
56	H	21.5476	-24.3797	-2.46614
57	H	23.7171	-25.5457	-2.41432
58	H	25.5254	-24.7566	-0.91061
59	H	25.1245	-22.7921	0.55034
60	H	22.9462	-21.6426	0.51562
61	H	22.7392	-16.2579	-1.02212
62	H	22.6290	-13.8164	-1.03606
63	H	18.3457	-14.0137	-0.92875
64	H	18.4587	-16.4383	-0.95476
65	H	21.5759	-9.69299	-0.98271
66	H	21.4673	-7.26221	-0.98319
67	H	17.1814	-7.41260	-0.94252
68	H	17.2856	-9.86531	-0.94210
69	H	20.3918	-5.31064	-0.97349
70	H	18.1725	-0.25623	-0.95779
71	H	14.4169	-2.88514	-0.92442

[a]Atomic number

Table S7. Cartesian coordinates of compounds **3c-d** and **4a** on B3LYP/6-311++G(2d,f,p) level.

3c

N[a]		x	y	z
1	C	19.6742	-21.9157	-1.33491
2	C	19.7631	-23.2925	-1.35839
3	C	20.7921	-23.9608	-0.67723
4	C	21.7297	-23.1899	0.01802
5	C	21.6377	-21.8098	0.02472
6	C	20.6086	-21.1292	-0.64139
7	C	19.5894	-17.4094	-1.03793
8	N	20.8789	-25.3683	-0.70044
9	C	22.1467	-26.0076	-0.74479
10	C	19.7002	-26.1597	-0.66801
11	C	18.6522	-25.8416	0.20081
12	C	17.5020	-26.6172	0.22496
13	C	17.3819	-27.7291	-0.60076
14	C	18.4258	-28.0539	-1.45937
15	C	19.5731	-27.2748	-1.50135
16	C	22.4113	-27.1134	0.06800
17	C	23.6460	-27.7442	0.01298
18	C	24.6406	-27.2773	-0.83839
19	C	24.3832	-26.1736	-1.64372
20	C	23.1463	-25.5465	-1.60634
21	C	20.6000	-16.6243	-0.45914
22	C	20.5117	-15.2469	-0.43340
23	C	19.4081	-14.5716	-0.97714
24	C	18.3982	-15.3508	-1.55330
25	C	18.4909	-16.7306	-1.58581
26	C	19.3183	-13.1007	-0.94443
27	C	20.4658	-12.3005	-1.04759
28	C	20.3743	-10.9245	-1.01830
29	C	19.1340	-10.2708	-0.88185
30	C	17.9826	-11.0733	-0.77689
31	C	18.0817	-12.4499	-0.80932
32	C	19.1542	-8.82813	-0.86176
33	C	18.2153	-7.85575	-0.74326
34	C	18.6824	-6.42511	-0.77133
35	C	17.4623	-5.59654	-0.62355
36	C	16.3278	-6.44312	-0.51253
37	C	16.7313	-7.87236	-0.58037
38	C	17.1598	-4.27028	-0.56846
39	S	15.4560	-4.06558	-0.37742
40	C	15.1552	-5.76556	-0.37222
41	O	15.9715	-8.81832	-0.51262
42	O	19.8246	-6.04015	-0.89063
43	C	19.6234	-18.8654	-1.09794
44	C	20.5648	-19.6749	-0.58343
45	H	18.8713	-21.4421	-1.88605
46	H	19.0345	-23.8677	-1.91448
47	H	22.5314	-23.6792	0.55539
48	H	22.3756	-21.2374	0.57627
49	H	18.7454	-24.9849	0.85579
50	H	16.6999	-26.3569	0.90545
51	H	16.4854	-28.3360	-0.57474
52	H	18.3437	-28.9144	-2.11285
53	H	20.3783	-27.5265	-2.17951
54	H	21.6440	-27.4751	0.74038
55	H	23.8344	-28.5998	0.65057
56	H	25.6050	-27.7684	-0.87472
57	H	25.1463	-25.8040	-2.31843
58	H	22.9473	-24.6953	-2.24480
59	H	21.4682	-17.0979	-0.01865
60	H	21.3006	-14.6788	0.04440
61	H	17.5430	-14.8677	-2.00948
62	H	17.6975	-17.3048	-2.05131
63	H	21.4338	-12.7661	-1.18244
64	H	21.2746	-10.3278	-1.11133
65	H	17.0192	-10.5982	-0.66153
66	H	17.1814	-13.0412	-0.69786
67	H	20.1542	-8.40593	-0.96436
68	H	17.8163	-3.41700	-0.62675
69	H	14.1533	-6.15030	-0.26814
70	H	18.7777	-19.3104	-1.61418
71	H	21.3992	-19.2271	-0.05091

3d

N[a]		x	y	z
1	C	11.5993	-1.67704	-0.56523
2	C	10.9355	-2.47164	0.36220
3	C	11.2537	-3.81566	0.49520
4	C	12.2371	-4.39120	-0.31389
5	C	12.8959	-3.59144	-1.25198
6	C	12.5824	-2.24483	-1.36758
7	N	12.5545	-5.77074	-0.18865
8	C	13.8982	-6.19413	-0.17876
9	C	11.5020	-6.71829	-0.07322
10	C	10.3756	-6.62753	-0.89541
11	C	9.34269	-7.54573	-0.77235
12	C	9.41993	-8.57543	0.15822
13	C	10.5415	-8.67231	0.97382
14	C	11.5720	-7.74926	0.86808
15	C	14.2787	-7.40090	-0.78129
16	C	15.5969	-7.81382	-0.76927
17	C	16.6013	-7.04632	-0.16131
18	C	16.2119	-5.83832	0.43314
19	C	14.8944	-5.42056	0.43015
20	C	17.9864	-7.50218	-0.15455
21	C	18.4681	-8.78617	-0.27175
22	C	19.8721	-8.87368	-0.23146
23	C	20.5046	-7.66062	-0.07948
24	S	19.3136	-6.38804	-0.00109
25	C	21.9291	-7.38526	0.01040
26	C	22.8740	-8.34863	-0.38917
27	C	24.2292	-8.11423	-0.30543
28	C	24.7186	-6.88566	0.18136
29	C	23.7711	-5.91970	0.57472
30	C	22.4170	-6.15993	0.49455
31	C	26.1085	-6.53007	0.31018
32	C	27.2879	-7.14998	0.04647
33	C	27.6440	-8.49128	-0.50084
34	C	29.1303	-8.52202	-0.52964
35	C	29.6653	-7.30096	-0.04077
36	C	28.5553	-6.39445	0.33866
37	C	30.0812	-9.42126	-0.90440
38	S	31.6530	-8.75295	-0.65076
39	C	31.0261	-7.26391	-0.04059
40	O	28.6414	-5.27413	0.79166
41	O	26.9183	-9.39809	-0.86000
42	H	11.3526	-0.62711	-0.66246
43	H	10.1709	-2.04097	0.99791
44	H	10.7408	-4.42766	1.22604
45	H	13.6531	-4.03113	-1.88848
46	H	13.1019	-1.63918	-2.10066
47	H	10.3148	-5.83353	-1.62861
48	H	8.47674	-7.46132	-1.41821
49	H	8.61454	-9.29373	0.24783
50	H	10.6110	-9.46455	1.70984
51	H	12.4368	-7.82149	1.51519
52	H	13.5318	-8.00870	-1.27469
53	H	15.8608	-8.73398	-1.27572
54	H	16.9506	-5.22818	0.93958
55	H	14.6267	-4.49048	0.91370
56	H	17.8218	-9.64932	-0.34968
57	H	20.4058	-9.81259	-0.27818
58	H	22.5331	-9.29316	-0.79301
59	H	24.9327	-8.87089	-0.62182
60	H	24.1204	-4.96694	0.95583
61	H	21.7232	-5.39743	0.82680
62	H	26.2662	-5.52933	0.71319
63	H	29.9602	-10.4146	-1.30562
64	H	31.6878	-6.47242	0.27286

4a

N[a]		x	y	z
1	N	14.4219	-8.04982	-0.46676
2	C	15.8261	-7.93908	-0.47370
3	C	13.6087	-6.88500	-0.42401
4	C	13.8011	-9.32773	-0.50196
5	C	18.6528	-7.71634	-0.48773
6	C	17.8415	-6.77490	-1.13513
7	C	18.0052	-8.77243	0.16716
8	C	16.4633	-6.88390	-1.13940
9	C	16.6271	-8.88079	0.18516
10	C	11.6874	-5.64274	-1.19930
11	C	12.4889	-6.77416	-1.25259
12	C	11.9949	-4.59966	-0.33351
13	C	13.1115	-4.70396	0.48806
14	C	13.9093	-5.83851	0.45233
15	C	14.2531	-10.3149	-1.38213
16	C	13.6428	-11.5606	-1.41046
17	C	12.5650	-11.8382	-0.57740
18	C	12.7211	-9.61220	0.33801
19	C	12.1067	-10.8554	0.29226
20	C	20.1211	-7.60091	-0.49563
21	C	22.9498	-7.36784	-0.51099
22	C	22.1289	-6.22433	-0.51681
23	C	22.3146	-8.62524	-0.49721
24	C	20.7541	-6.34735	-0.50925
25	C	20.9403	-8.74025	-0.48967
26	C	24.3920	-7.36362	-0.51868
27	C	25.3506	-6.40260	-0.52299
28	C	25.3113	-4.91071	-0.52120
29	C	26.7345	-4.48021	-0.52771
30	C	27.5982	-5.60722	-0.53314
31	C	26.7877	-6.84848	-0.53043
32	C	27.3942	-3.28930	-0.52958
33	S	29.0989	-3.56308	-0.53819
34	C	28.9198	-5.28062	-0.53923
35	O	24.3539	-4.16203	-0.51579
36	O	27.1904	-7.99097	-0.53350
37	H	18.3002	-5.96275	-1.68562
38	H	18.5906	-9.50171	0.71373
39	H	15.8693	-6.15302	-1.67190
40	H	16.1600	-9.69482	0.72346
41	H	10.8232	-5.57236	-1.84907
42	H	12.2509	-7.57946	-1.93565
43	H	11.3707	-3.71548	-0.29852
44	H	13.3579	-3.90213	1.17396
45	H	14.7699	-5.92024	1.10389
46	H	15.0832	-10.0995	-2.04262
47	H	14.0047	-12.3144	-2.09966
48	H	12.0868	-12.8093	-0.60662
49	H	12.3666	-8.85360	1.02401
50	H	11.2709	-11.0599	0.95086
51	H	22.5892	-5.24686	-0.51731
52	H	22.9248	-9.52127	-0.50308
53	H	20.1504	-5.44873	-0.48346
54	H	20.4898	-9.72449	-0.51023
55	H	24.8296	-8.36229	-0.52097
56	H	26.9943	-2.28802	-0.52646
57	H	29.7830	-5.92669	-0.54415

[a]Atomic number

Table S8. Cartesian coordinates of compounds **4b** on B3LYP/6-311++G(2d,f,p) level.

		4b		
N[a]		x	y	z
1	C	15.7206	-4.85644	0.88536
2	C	15.7586	-5.89137	-0.05132
3	C	14.5986	-4.04596	0.98397
4	C	14.6527	-6.10843	-0.87472
5	C	13.4971	-4.26539	0.16449
6	C	13.5289	-5.30208	-0.76076
7	N	16.9036	-6.73537	-0.15292
8	C	16.6967	-8.14650	-0.16547
9	C	18.1878	-6.19581	-0.24341
10	C	20.8018	-5.10752	-0.42340
11	C	19.6701	-4.40037	-0.88071
12	C	20.5784	-6.38489	0.13122
13	C	18.3989	-4.92014	-0.79750
14	C	19.3093	-6.91137	0.21733
15	C	17.3027	-8.94448	-1.13786
16	C	17.0876	-10.3152	-1.14802
17	C	16.2556	-10.9045	-0.20288
18	C	15.8640	-8.74031	0.78426
19	C	15.6429	-10.1101	0.75900
20	C	22.0788	-4.46707	-0.56318
21	C	23.3632	-4.79915	-0.25826
22	C	24.4390	-3.80644	-0.59018
23	C	25.7147	-4.42947	-0.15871
24	C	25.4479	-5.70817	0.39777
25	C	23.9885	-5.99703	0.36566
26	C	27.0351	-4.10025	-0.15934
27	S	27.9602	-5.38379	0.53521
28	C	26.5641	-6.35966	0.82413
29	O	23.4694	-7.01696	0.77897
30	O	24.2901	-2.71930	-1.10579
31	H	16.5722	-4.69279	1.53340
32	H	14.5812	-3.24702	1.71552
33	H	14.6788	-6.91135	-1.60038
34	H	12.6206	-3.63501	0.24818
35	H	12.6775	-5.48021	-1.40661
36	H	19.8094	-3.42084	-1.32414
37	H	21.4222	-6.94778	0.50469
38	H	17.5587	-4.35160	-1.17140
39	H	19.1700	-7.88815	0.66002
40	H	17.9415	-8.48595	-1.88188
41	H	17.5640	-10.9235	-1.90743
42	H	16.0854	-11.9739	-0.21693
43	H	15.3922	-8.12378	1.53871
44	H	14.9958	-10.5592	1.50285
45	H	22.0233	-3.47967	-1.02252
46	H	27.5153	-3.20333	-0.51639
47	H	26.6537	-7.33216	1.28101

[a]Atomic number

Table S9. Computed total energies of compounds **1–4** on B3LYP/6-311++G(2d,f,p) level in vacuum.

Compound	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**	**3c**	**3d**	**4a**	**4b**
E_{total} **×10^4 (eV)**	-5.71	-5.92	-5.92	-5.71	-5.71	-5.92	-5.92	-5.62	-5.84	-5.84	-6.50	-5.00	-4.37

Correlations

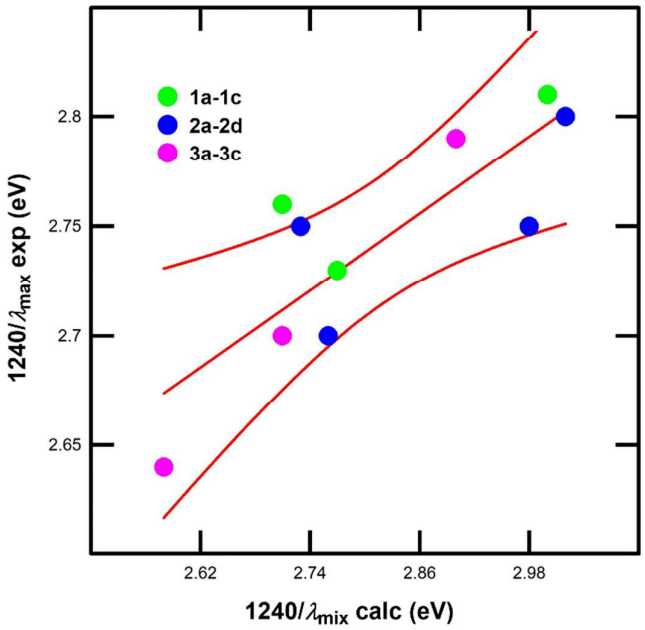

Figure S40. Correlation of the optical absorption ($1240/\lambda_{max}$) and TD-DFT calculated ($1240/\lambda_{mix}$) gaps in $CHCl_3$ (R = 0.83); **3d**, **4a–b** were excluded as outliers.

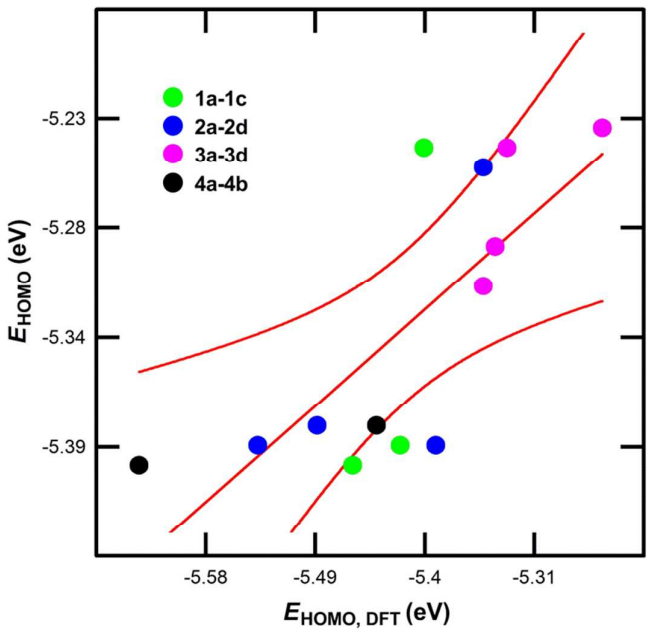

Figure S41. Correlation of the electrochemical and calculated HOMO energies (R = 0.76).

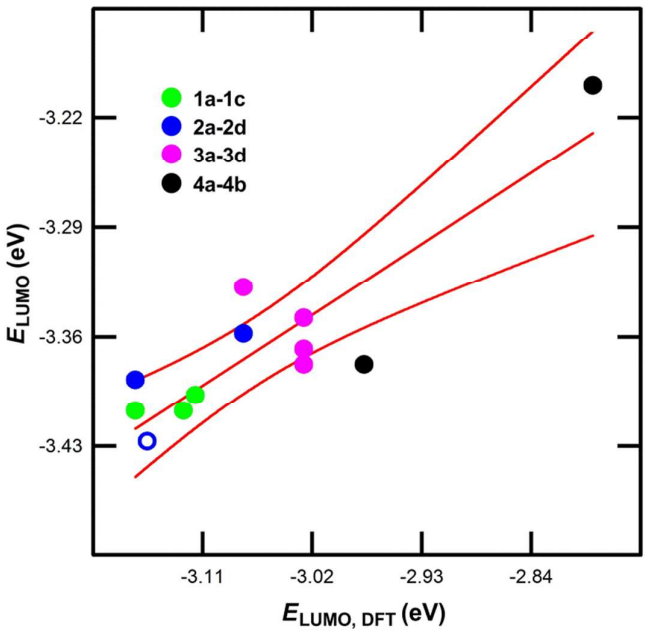

Figure S42. Correlation of the electrochemical and calculated LUMO energies (R = 0.89).

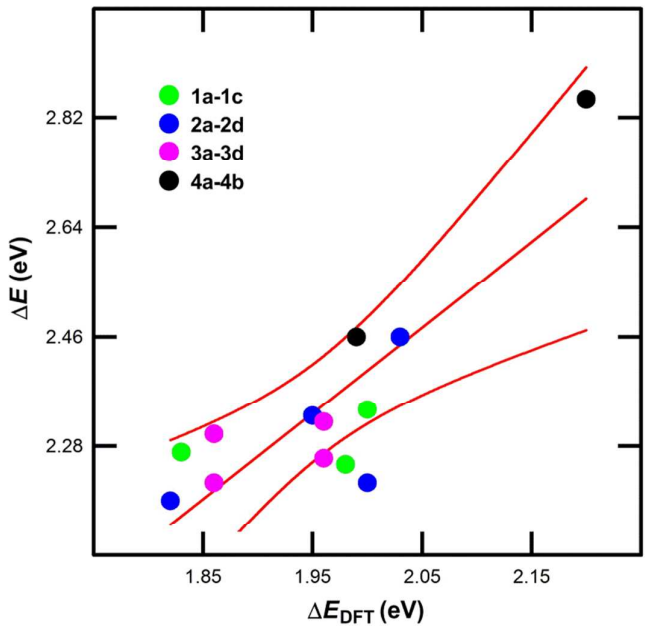

Figure S43. Correlation of the electrochemical (ΔE) and calculated (ΔE_{DFT}) gaps (R = 0.82).

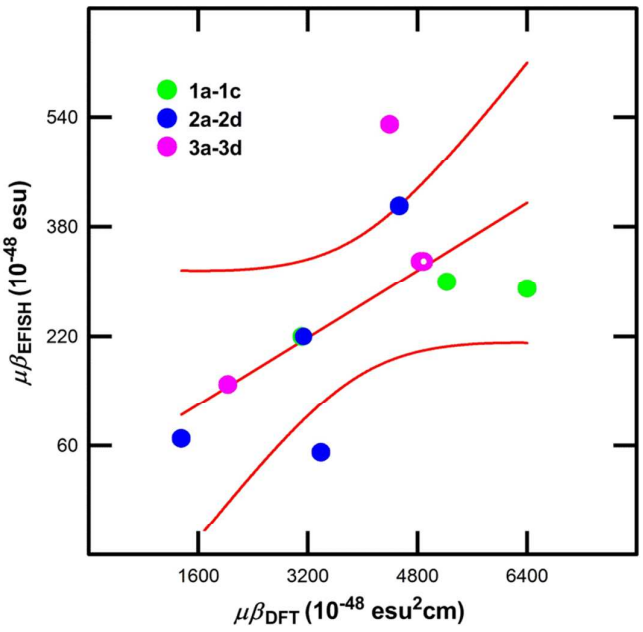

Figure S44. Correlation of the experimental ($\mu\beta_{EFISH}$) and calculated ($\mu\beta_{DFT}$) NLO $\mu\beta$ coefficients (R = 0.64).

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^{1}H and ^{13}C NMR spectra

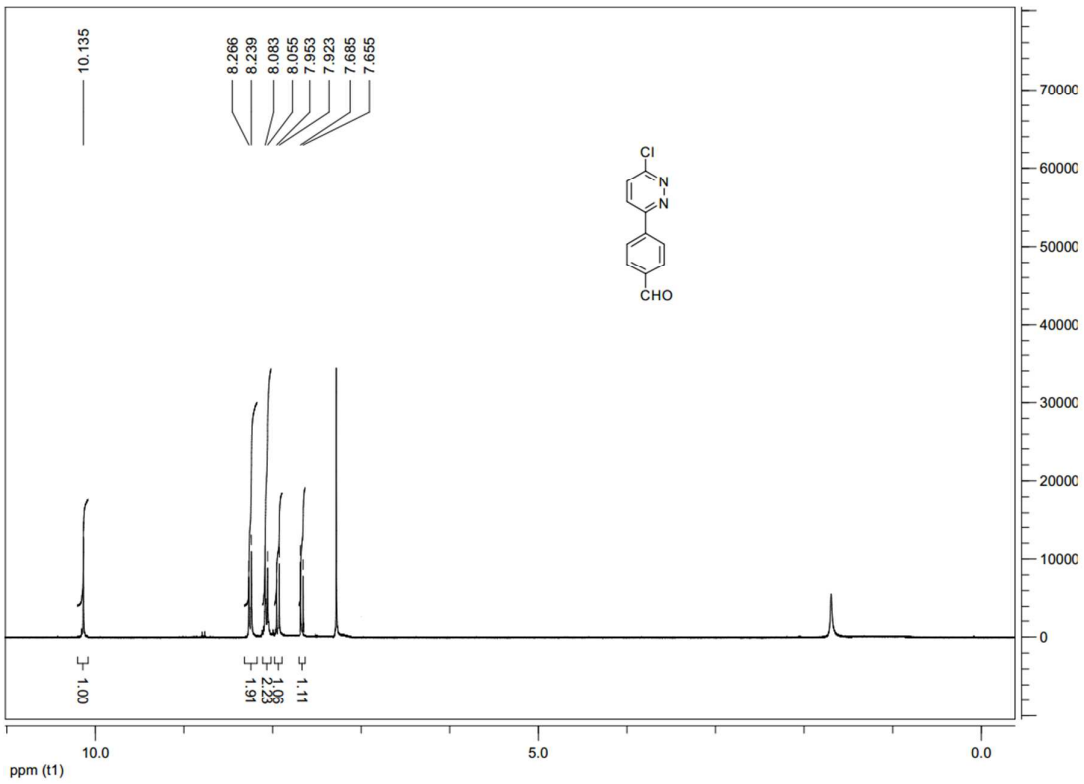

Figure S45. ^{1}H NMR spectrum of compound **14** (300 MHz, $CDCl_3$, 25 °C).

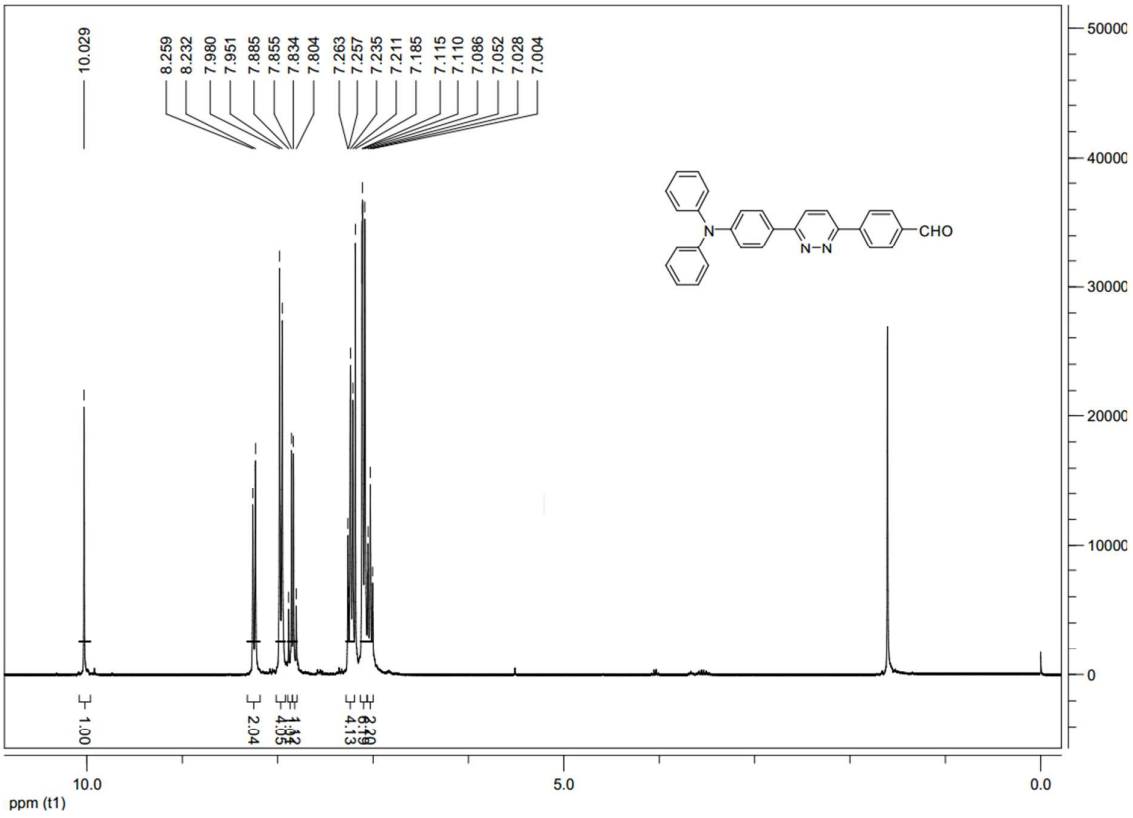

Figure S46. ^{1}H NMR spectrum of compound **5a** (300 MHz, $CDCl_3$, 25 °C).

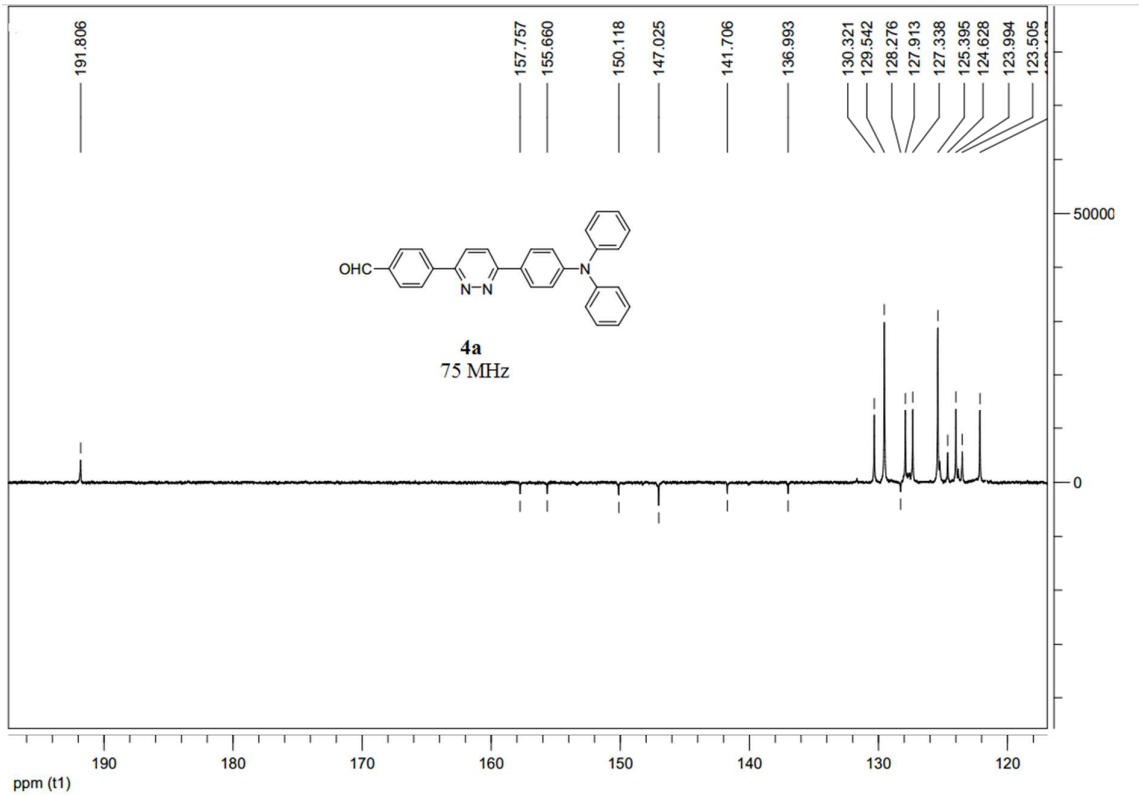

Figure S47. ^{13}C NMR spectrum of compound **5a** (75 MHz, $CDCl_3$, 25 °C).

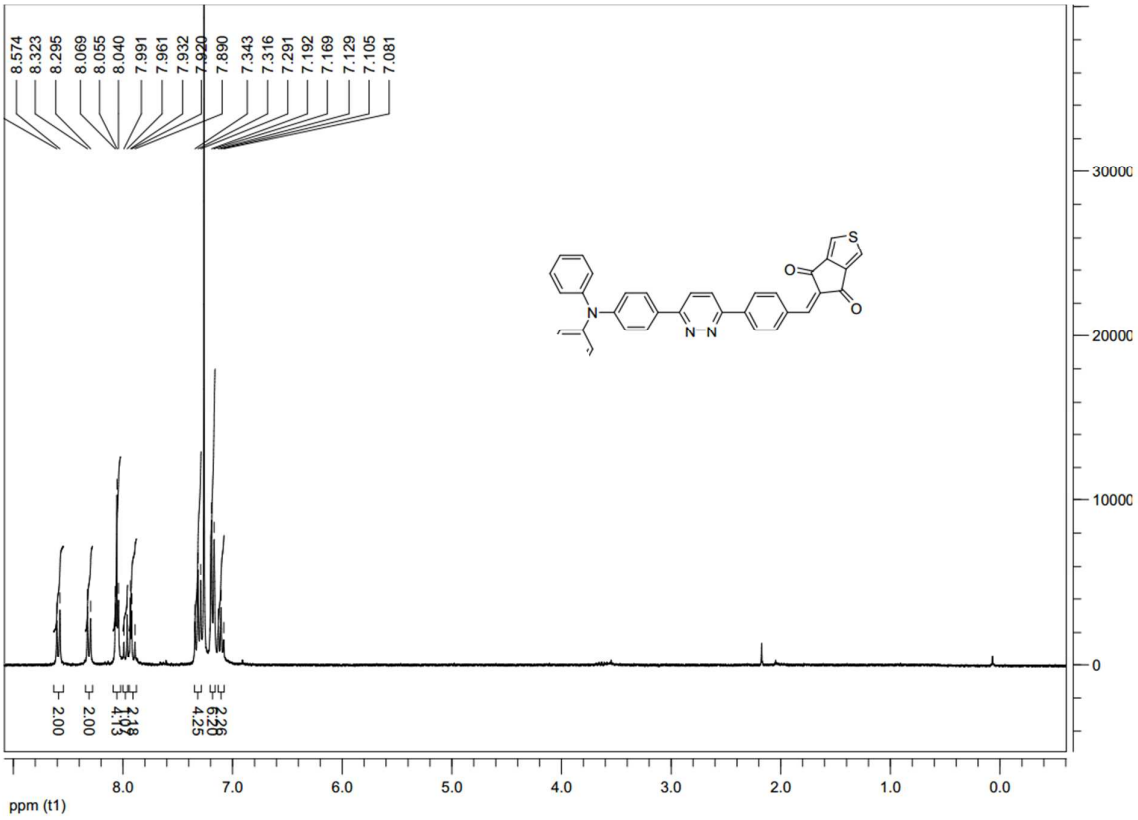

Figure S48. ^{1}H NMR spectrum of compound **1a** (300 MHz, $CDCl_3$, 25 °C).

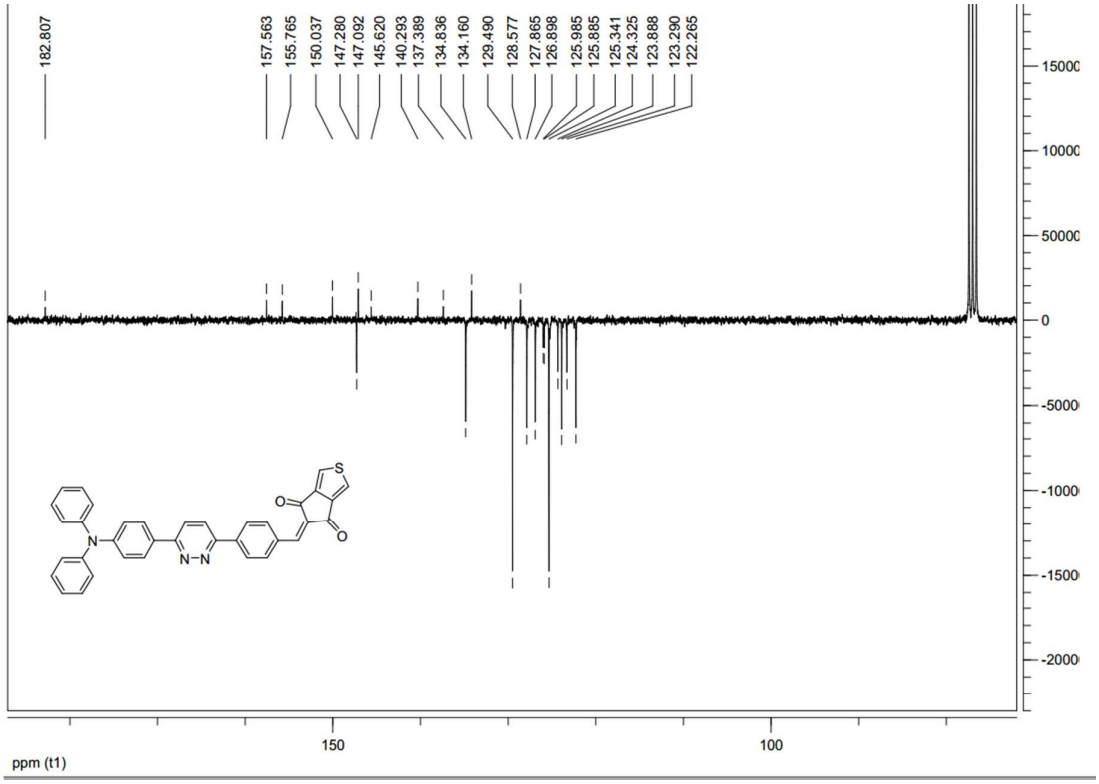

Figure S49. ^{13}C NMR spectrum of compound **1a** (75 MHz, $CDCl_3$, 25 °C).

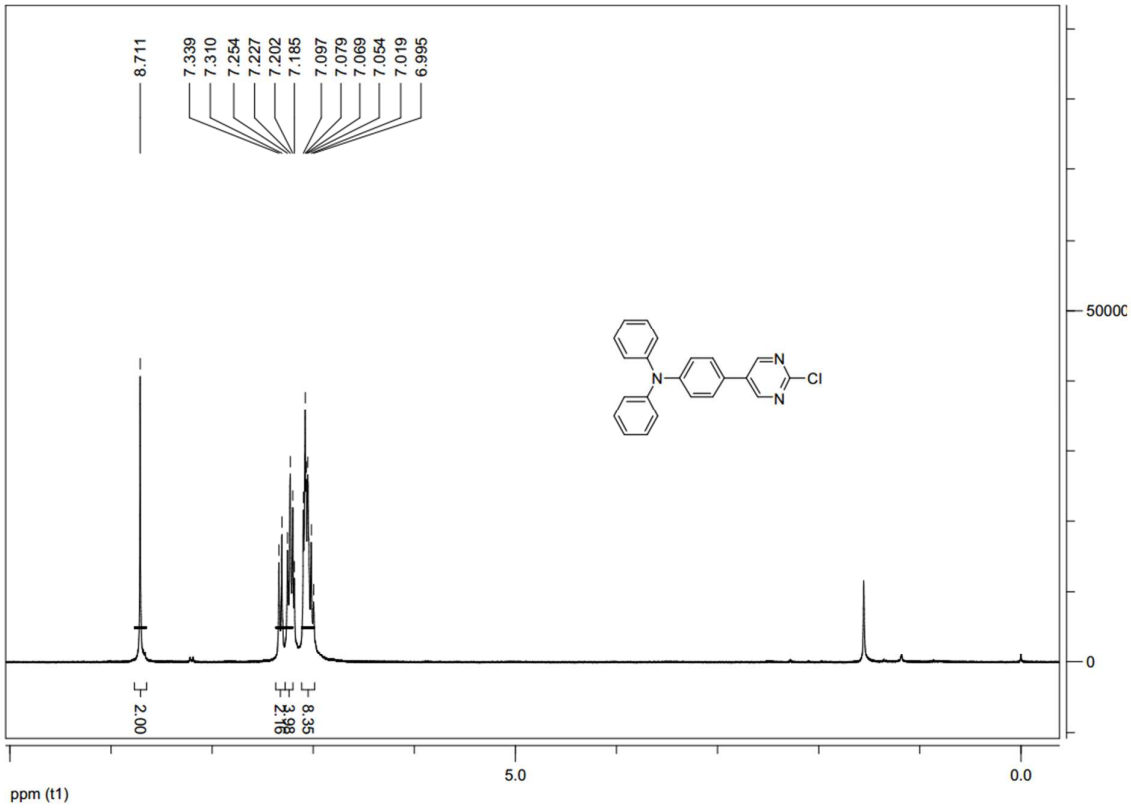

Figure S50. ^{1}H NMR spectrum of compound **17** (300 MHz, $CDCl_3$, 25 °C).

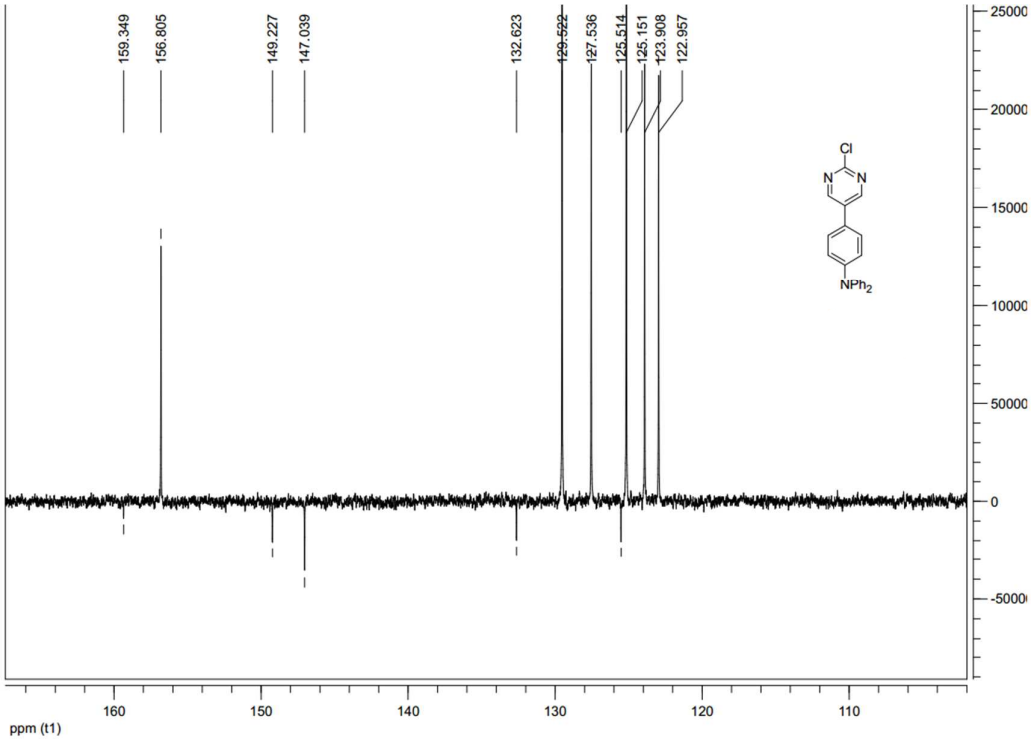

Figure S51. ^{13}C NMR spectrum of compound **17** (75 MHz, $CDCl_3$, 25 °C).

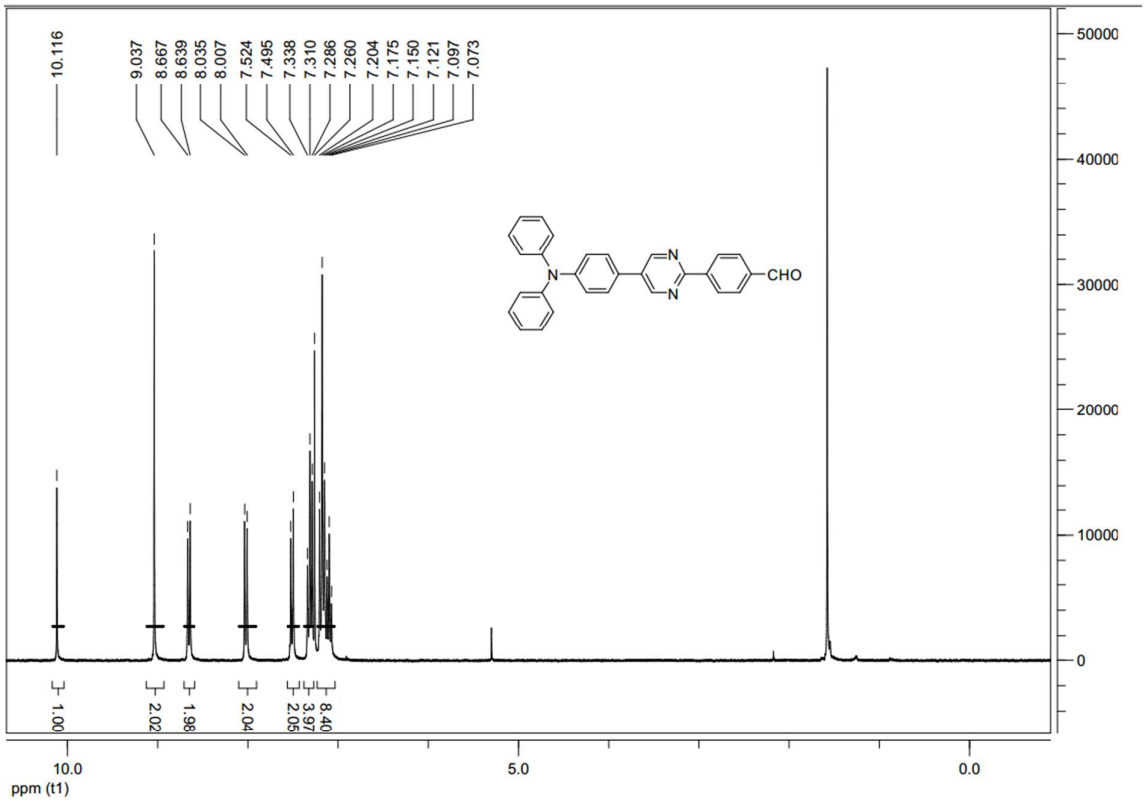

Figure S50. ^{1}H NMR spectrum of compound **6a** (300 MHz, $CDCl_3$, 25 °C).

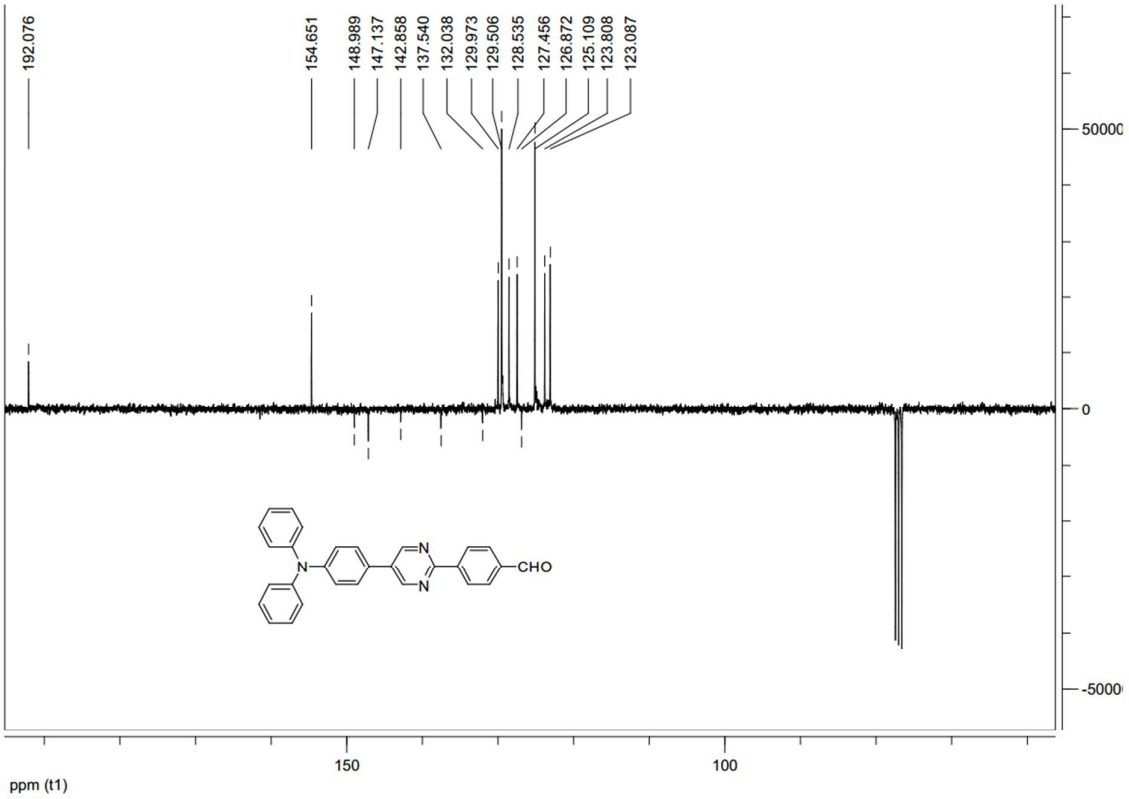

Figure S51. ^{13}C NMR spectrum of compound **6a** (75 MHz, $CDCl_3$, 25 °C).

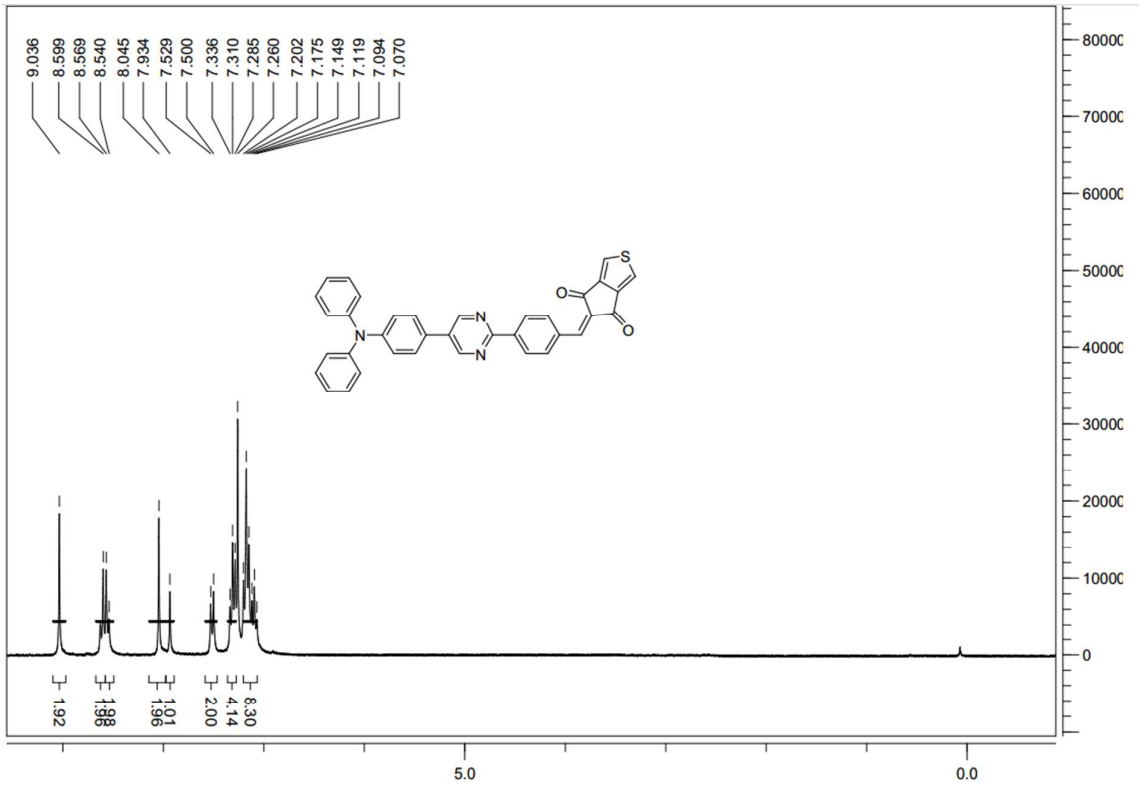

Figure S52. ^{1}H NMR spectrum of compound **2a** (300 MHz, $CDCl_3$, 25 °C).

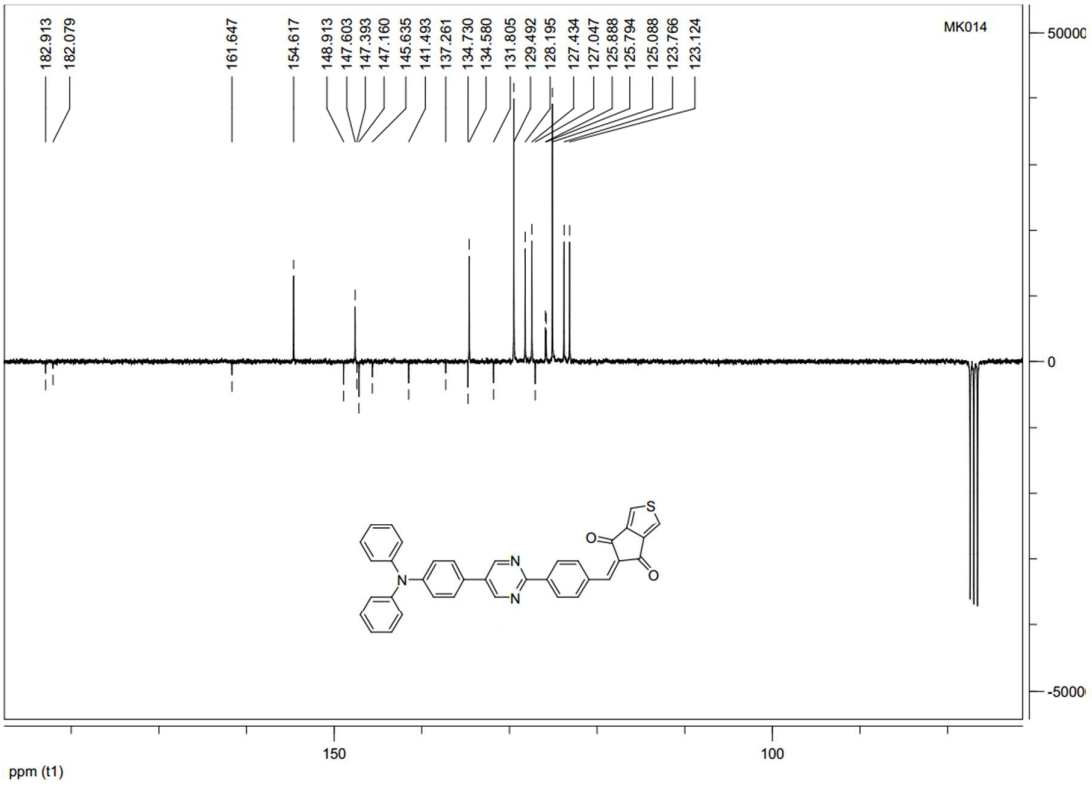

Figure S53. ^{13}C NMR spectrum of compound **2a** (75 MHz, $CDCl_3$, 25 °C).

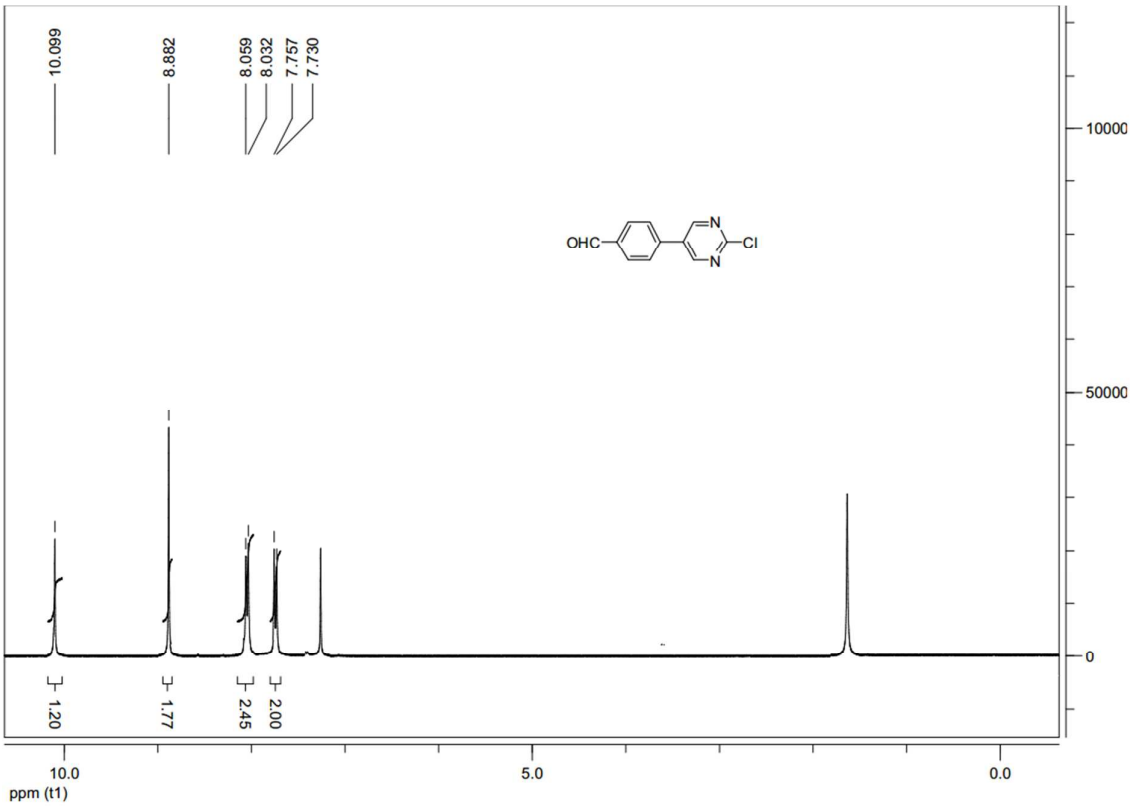

Figure S54. ^{1}H NMR spectrum of compound **18** (300 MHz, $CDCl_3$, 25 °C).

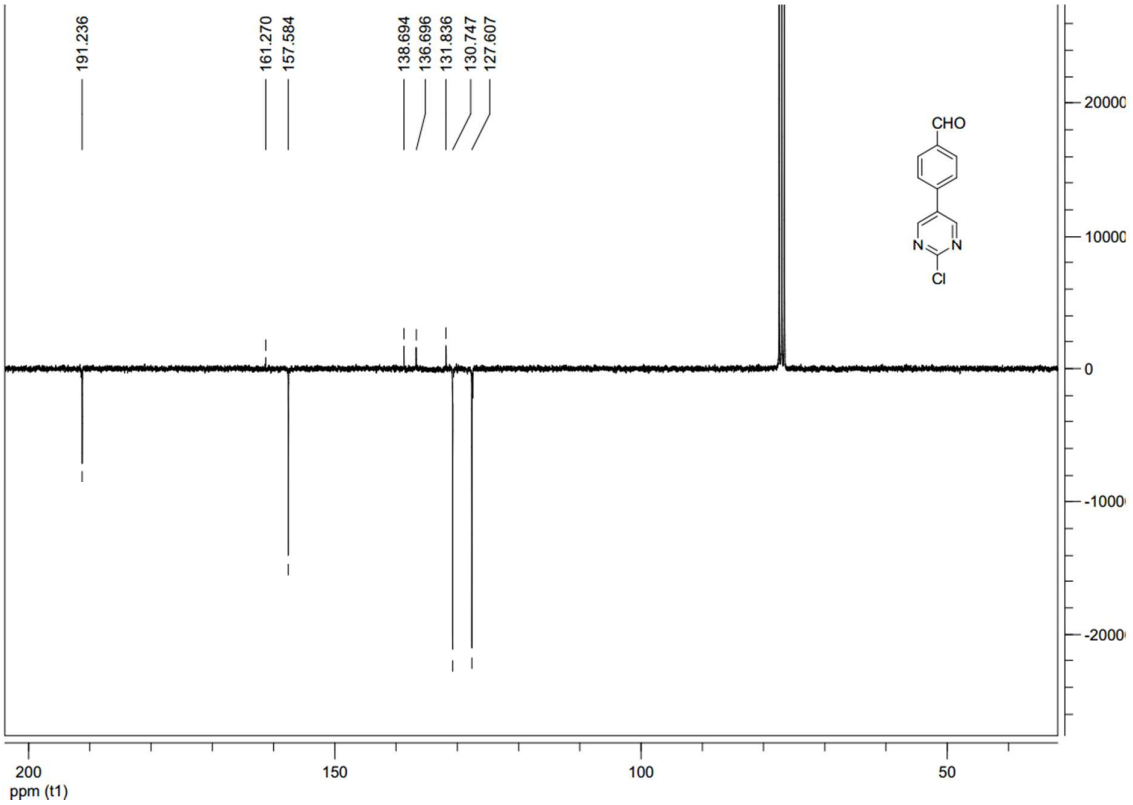

Figure S55. ^{13}C NMR spectrum of compound **18** (75 MHz, $CDCl_3$, 25 °C).

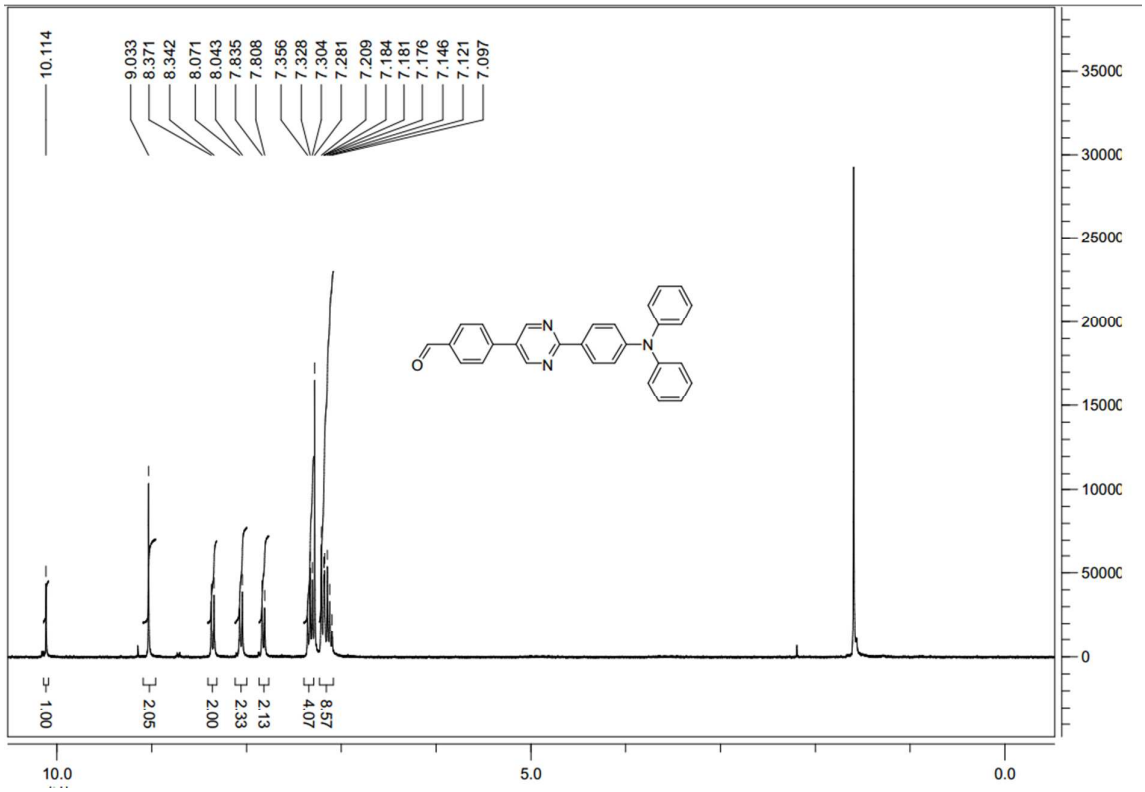

Figure S56. ^{1}H NMR spectrum of compound **6b** (300 MHz, $CDCl_3$, 25 °C).

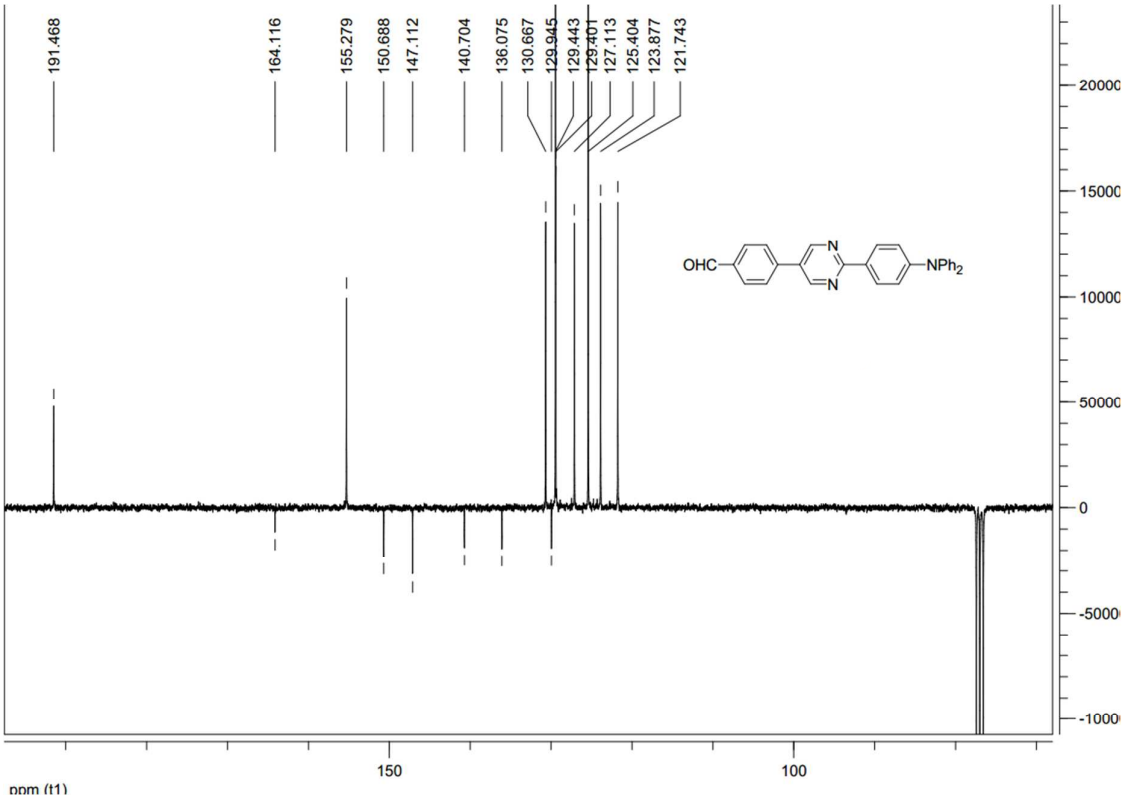

Figure S57. ^{13}C NMR spectrum of compound **6b** (75 MHz, $CDCl_3$, 25 °C).

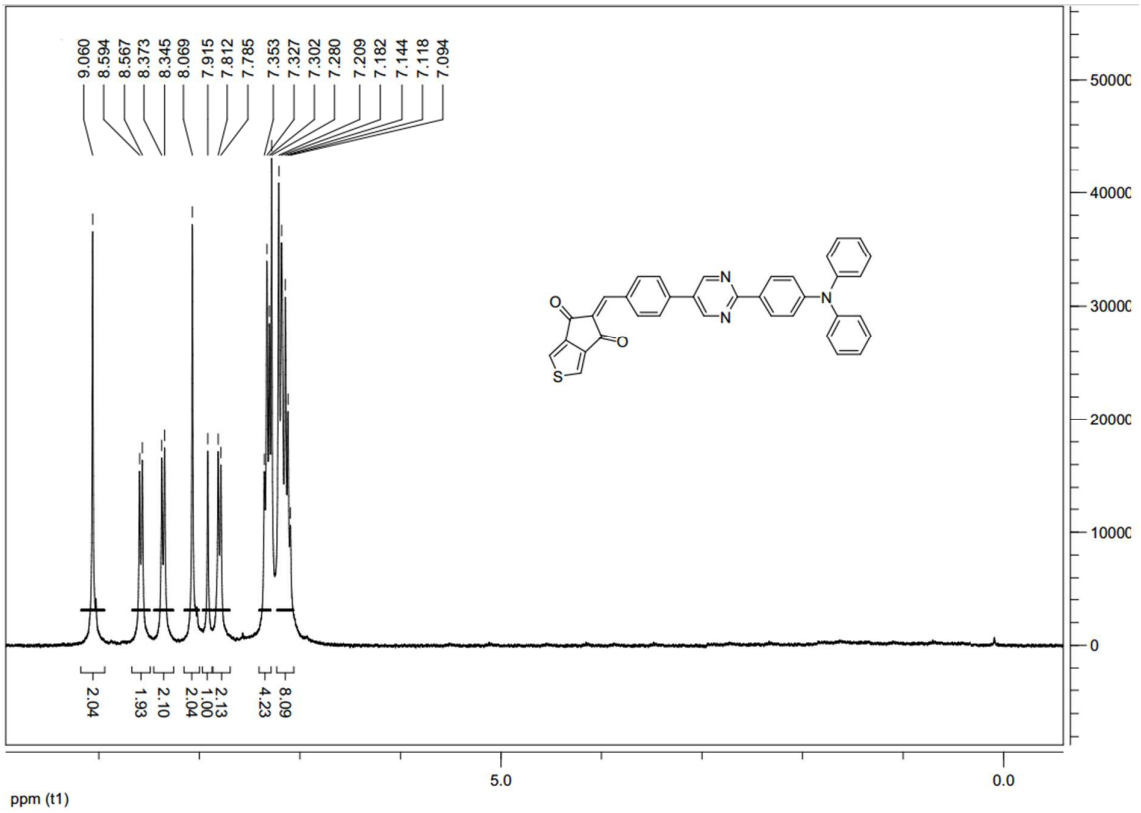

Figure S60. ^{1}H NMR spectrum of compound **2b** (300 MHz, $CDCl_3$, 25 °C).

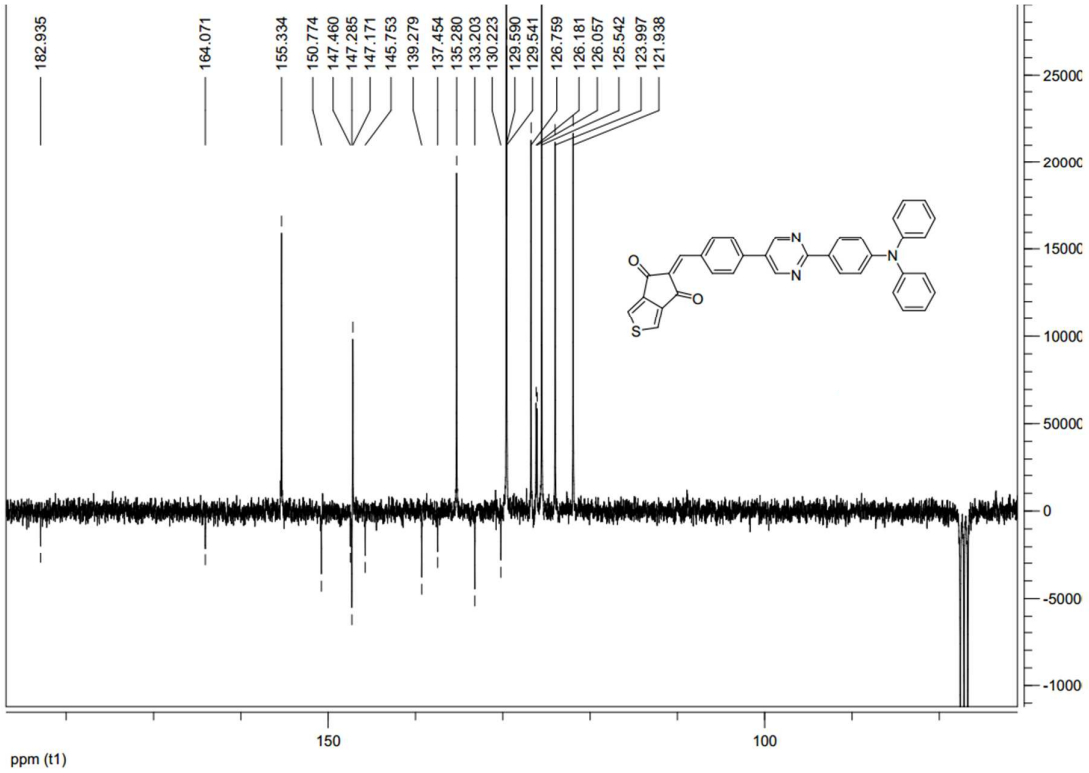

Figure S61. ^{13}C NMR spectrum of compound **2b** (75 MHz, $CDCl_3$, 25 °C).

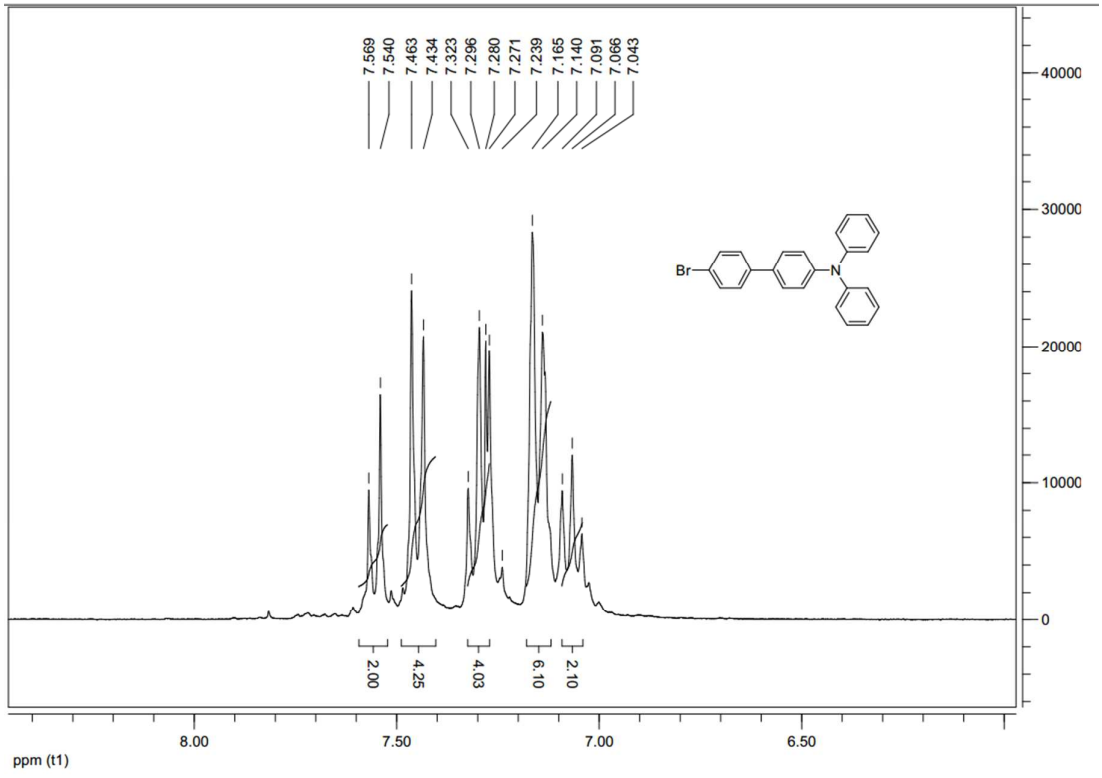

Figure S58. ^{1}H NMR spectrum of compound **20** (300 MHz, $CDCl_3$, 25 °C).

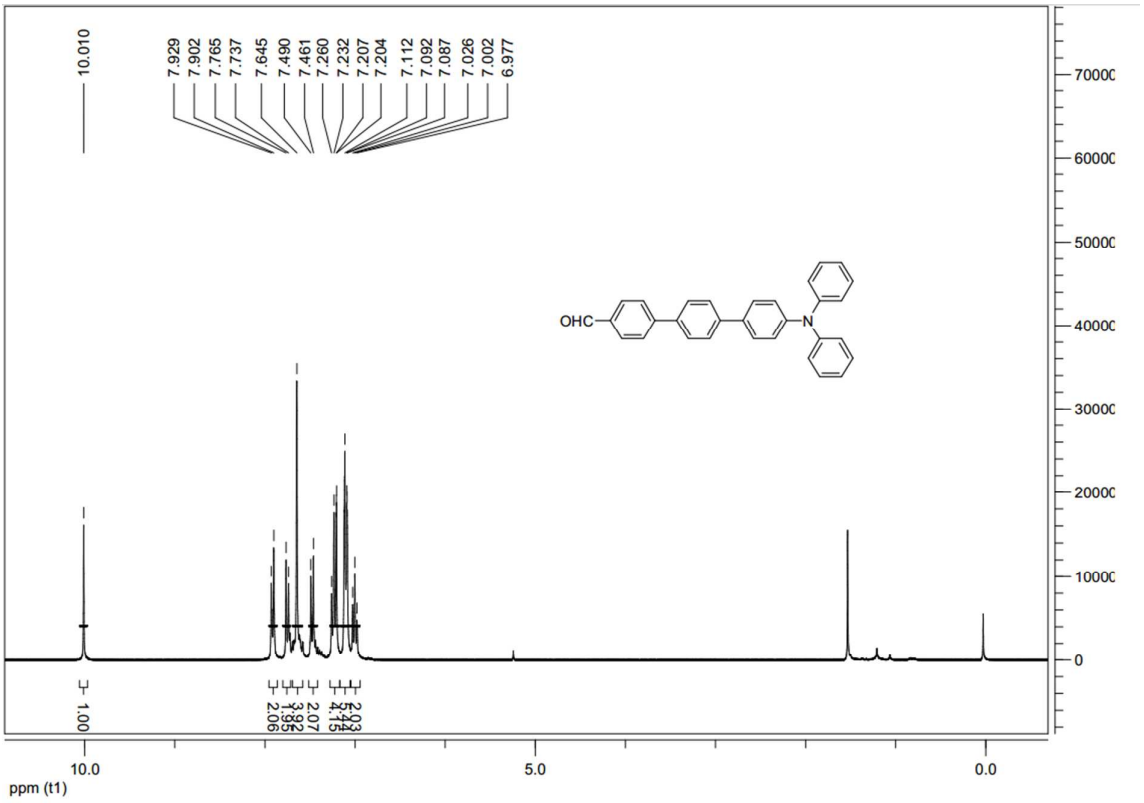

Figure S59. ^{1}H NMR spectrum of compound **7a** (300 MHz, $CDCl_3$, 25 °C).

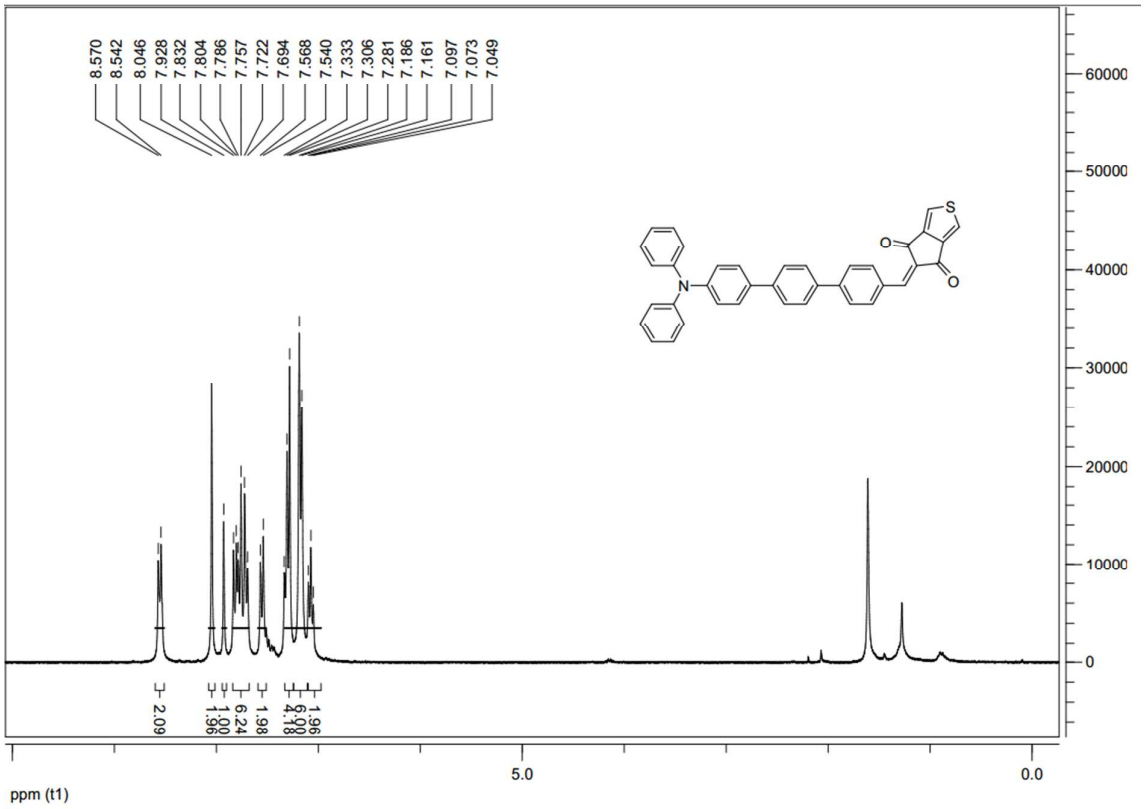

Figure S60. ^{1}H NMR spectrum of compound **3a** (300 MHz, $CDCl_3$, 25 °C).

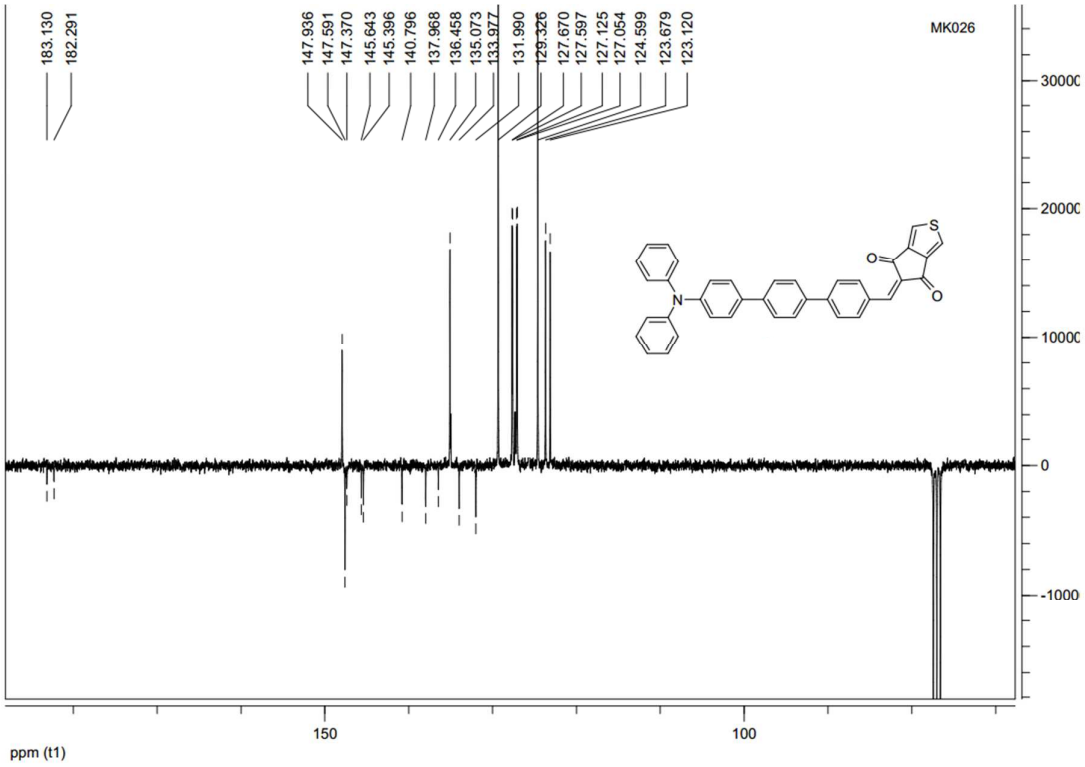

Figure S61. ^{13}C NMR spectrum of compound **3a** (75 MHz, $CDCl_3$, 25 °C).

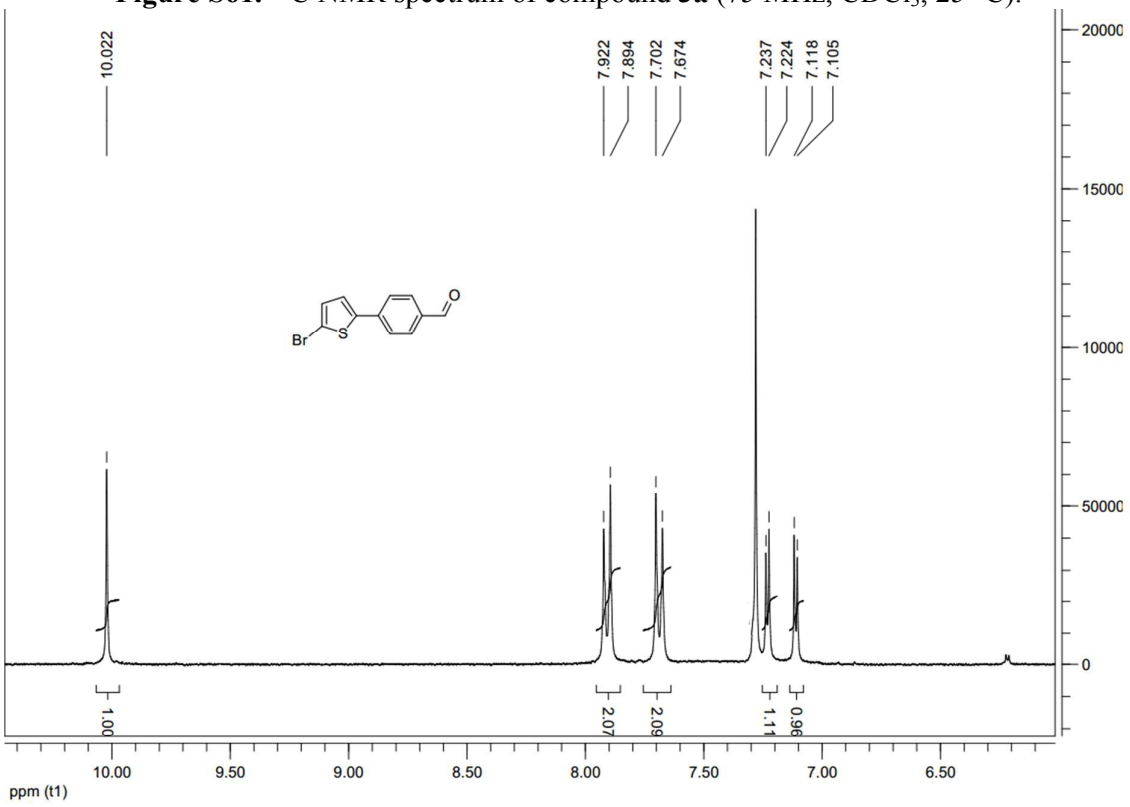

Figure S62. ^{1}H NMR spectrum of compound **22** (300 MHz, $CDCl_3$, 25 °C).

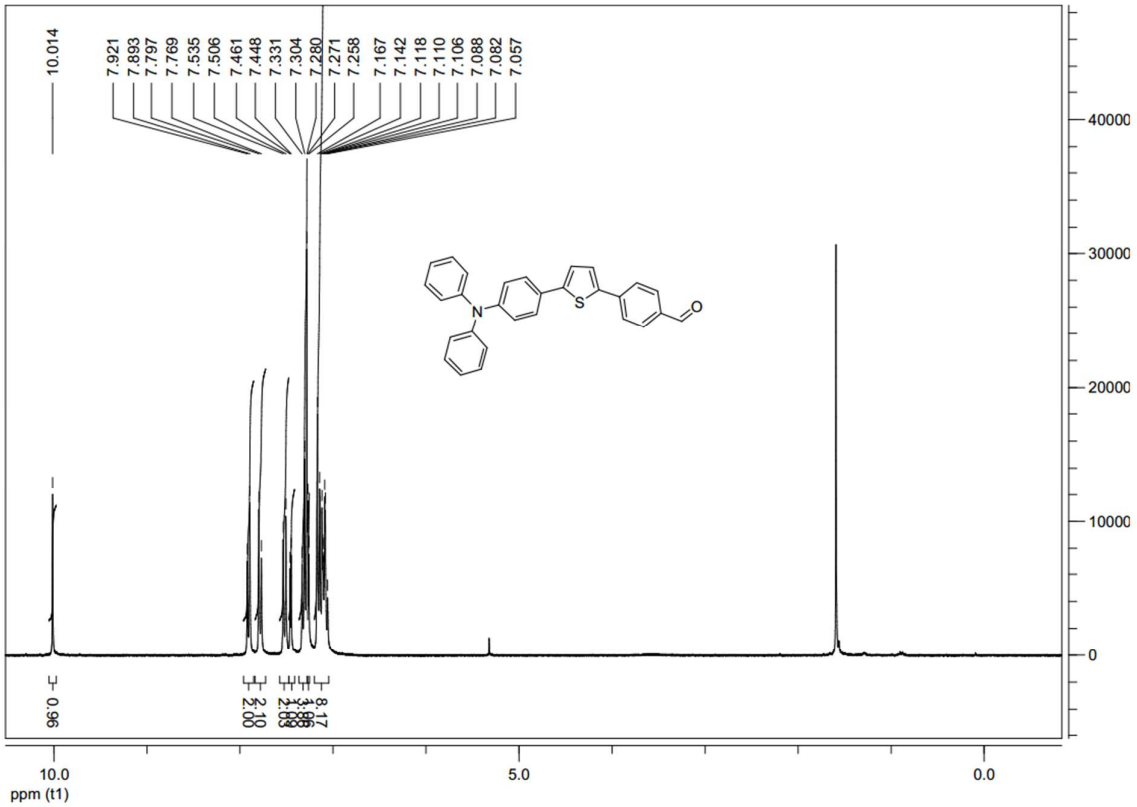

Figure S63. ^{1}H NMR spectrum of compound **7d** (300 MHz, $CDCl_3$, 25 °C).

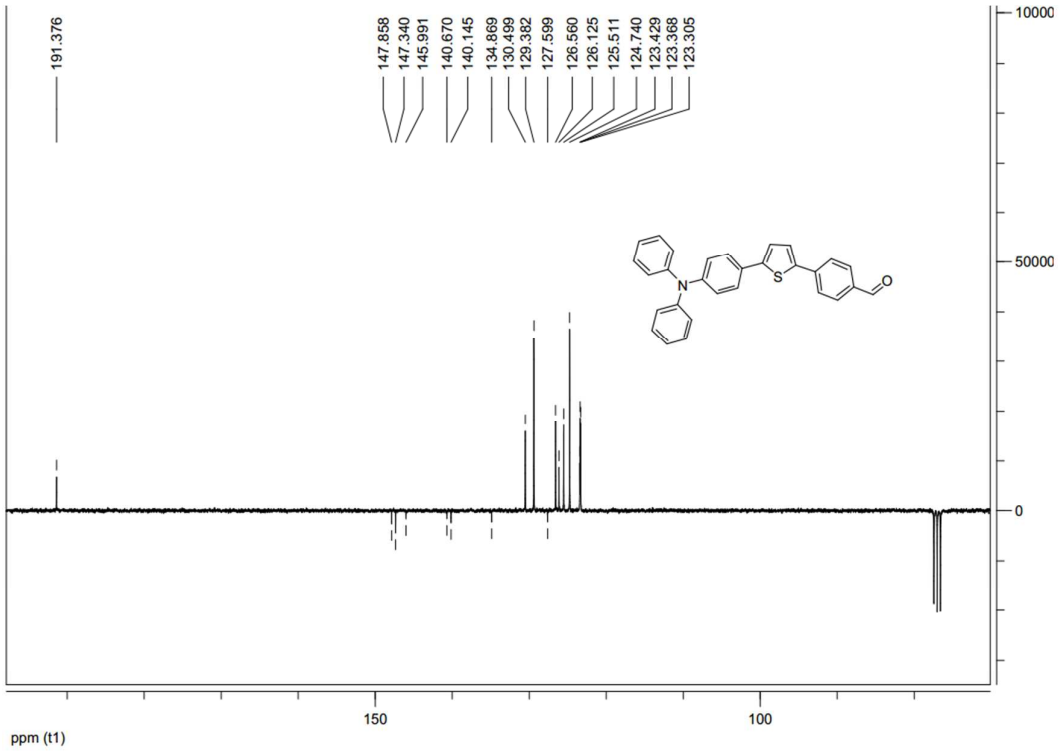

Figure S64. ^{13}C NMR spectrum of compound **7d** (75 MHz, $CDCl_3$, 25 °C).

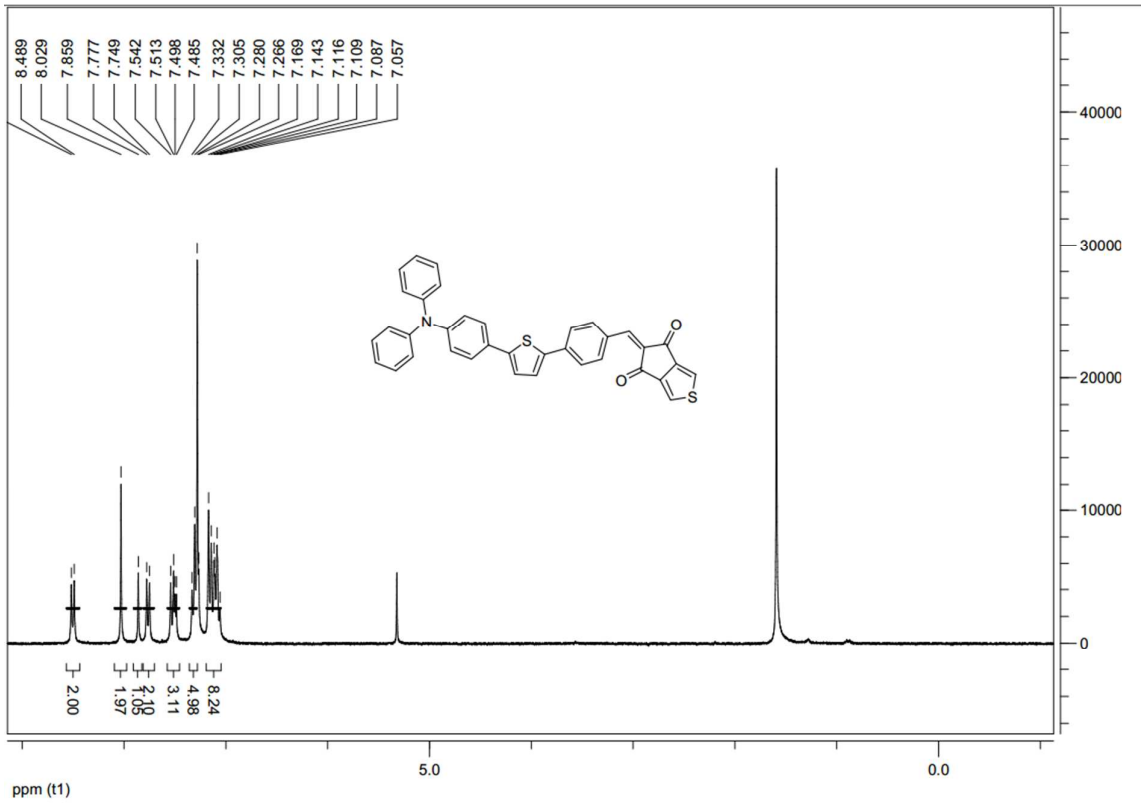

Figure S65. ^{1}H NMR spectrum of compound **3d** (300 MHz, $CDCl_3$, 25 °C).

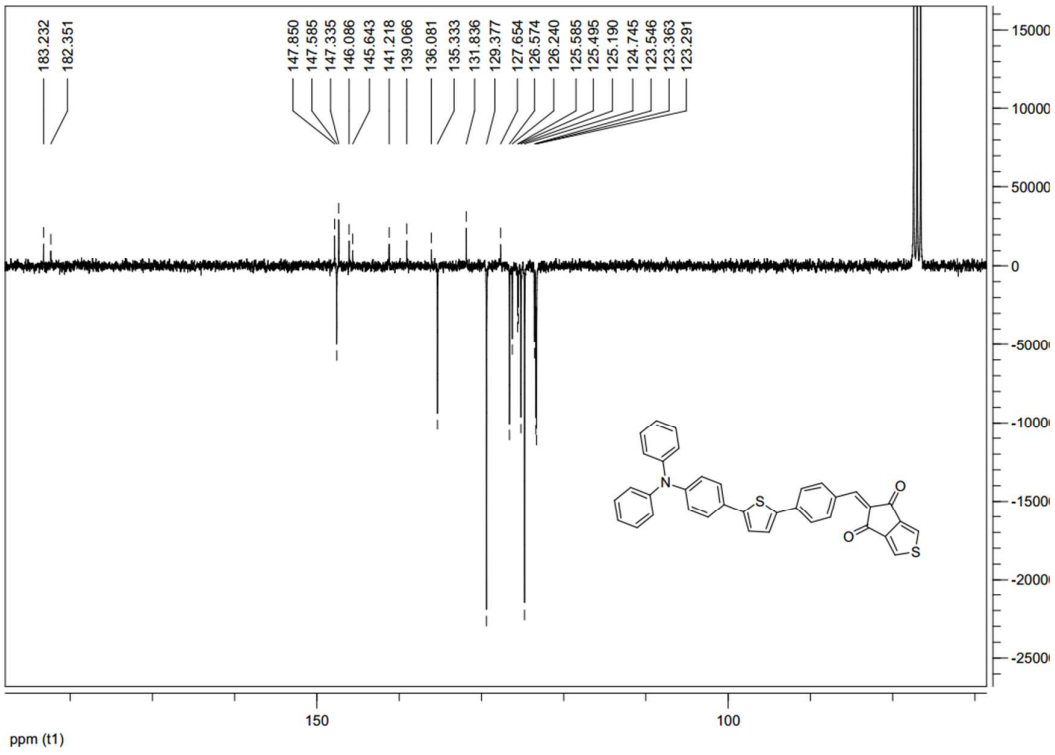

Figure S70. ^{13}C NMR spectrum of compound **3d** (75 MHz, $CDCl_3$, 25 °C).

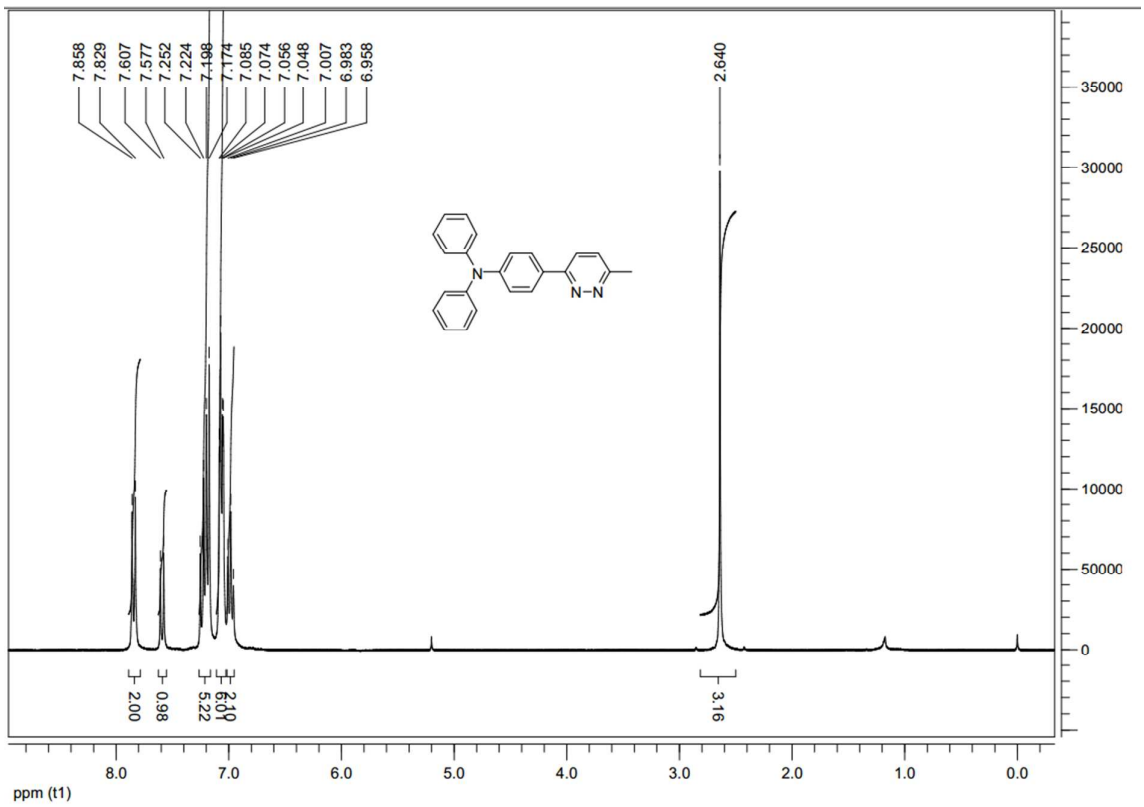

Figure S71. ^{1}H NMR spectrum of compound **24** (300 MHz, $CDCl_3$, 25 °C).

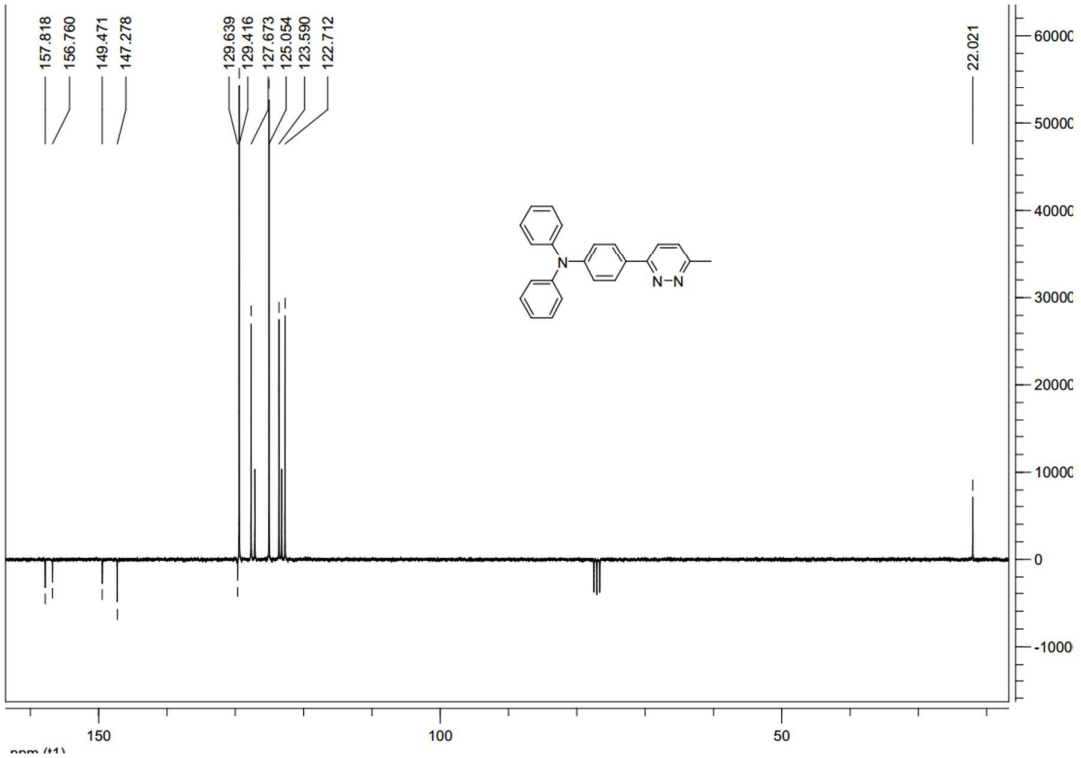

Figure S72. ^{13}C NMR spectrum of compound **24** (75 MHz, $CDCl_3$, 25 °C).

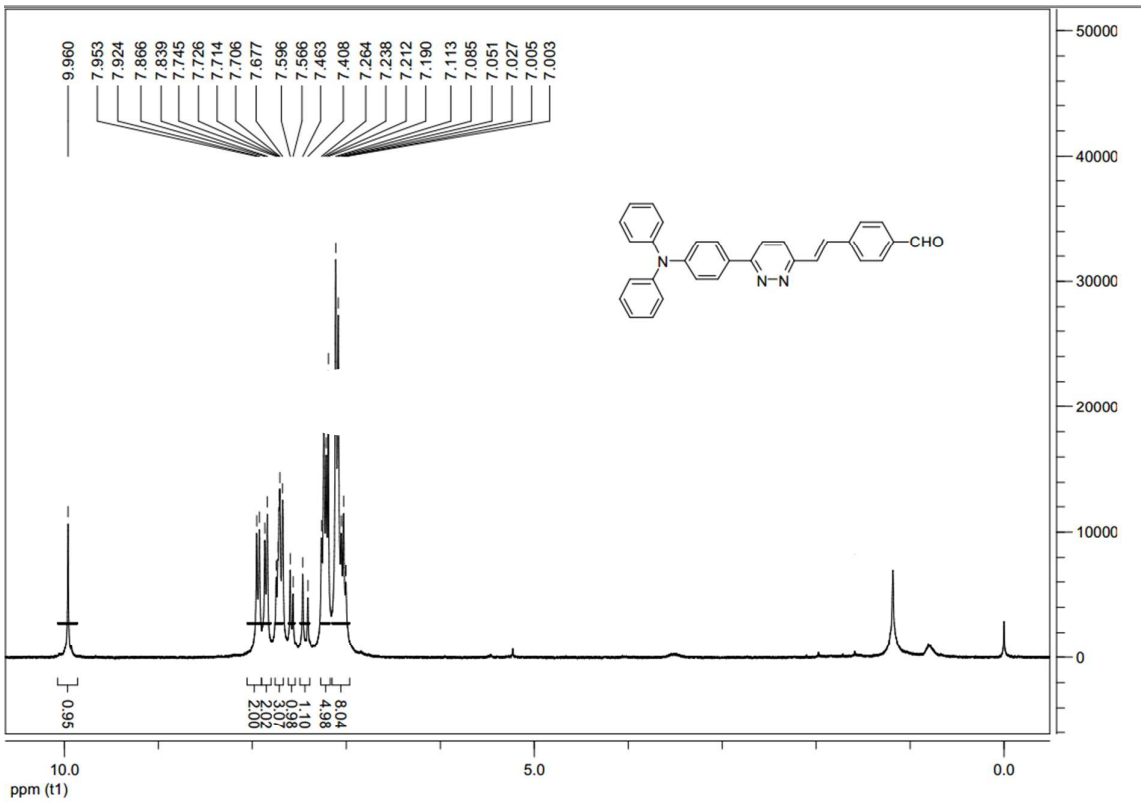

Figure S73. ^{1}H NMR spectrum of compound **5b** (300 MHz, $CDCl_3$, 25 °C).

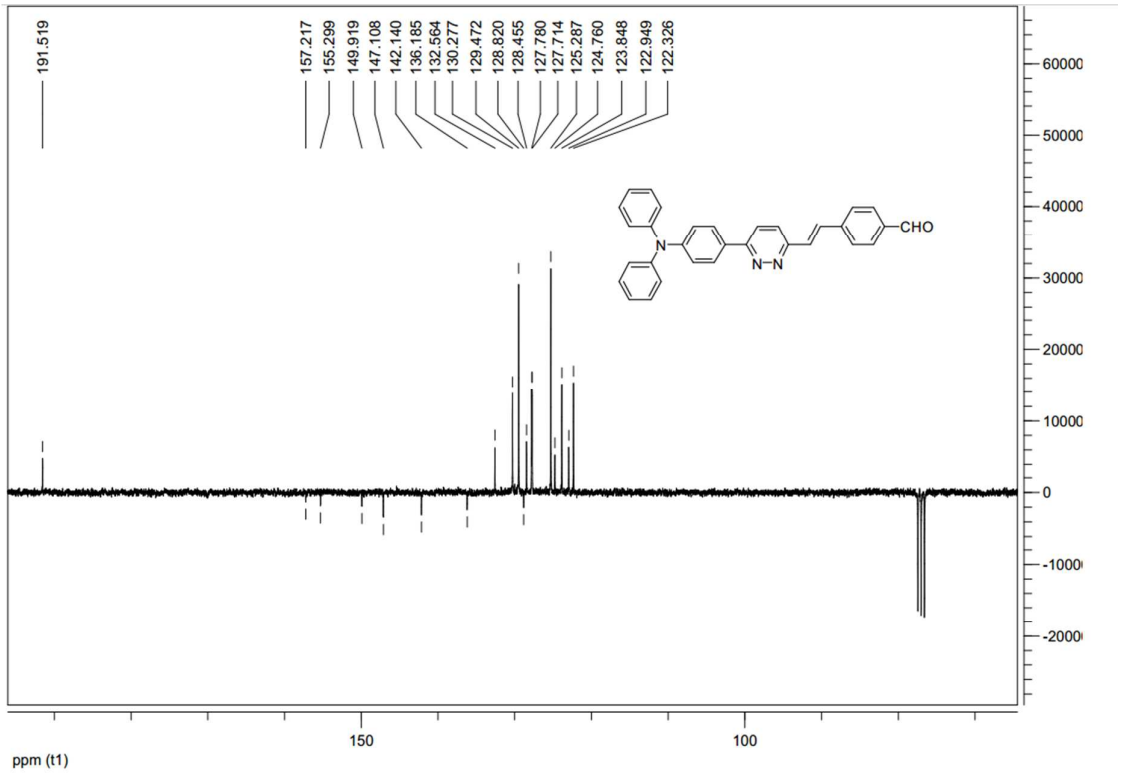

Figure S66. ^{13}C NMR spectrum of compound **5b** (75 MHz, $CDCl_3$, 25 °C).

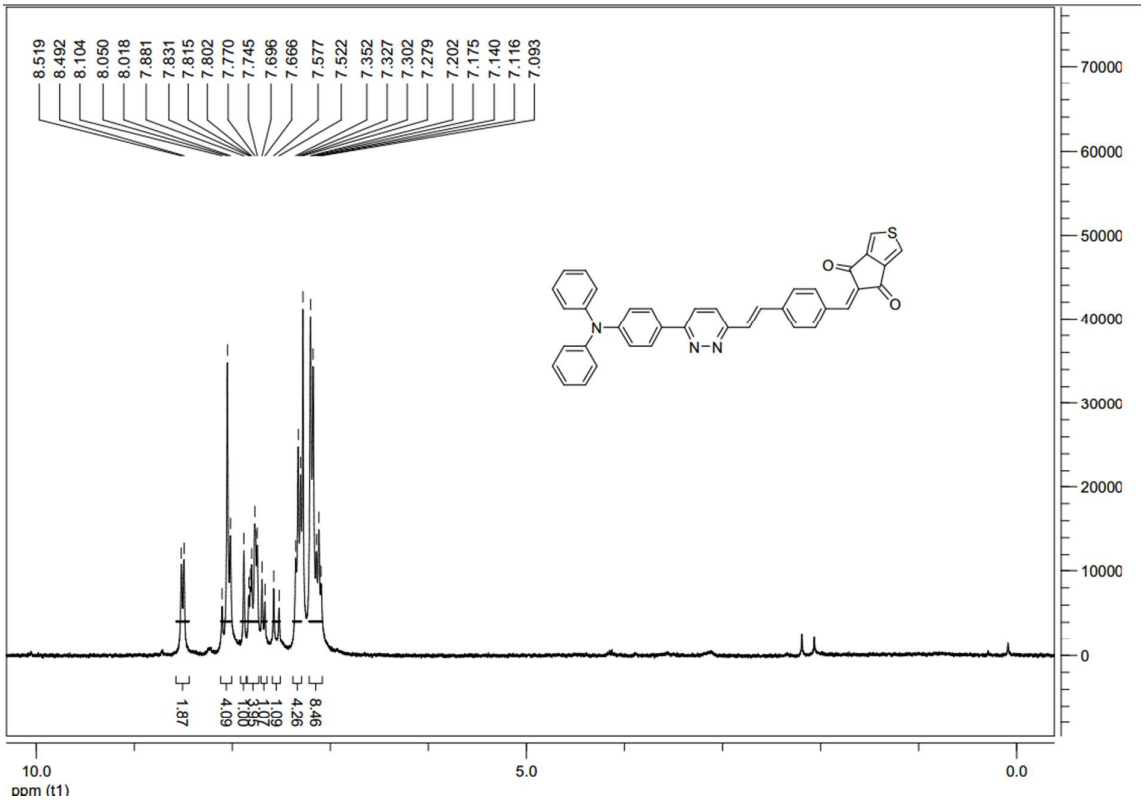

Figure S67. ^{1}H NMR spectrum of compound **1b** (300 MHz, $CDCl_3$, 25 °C).

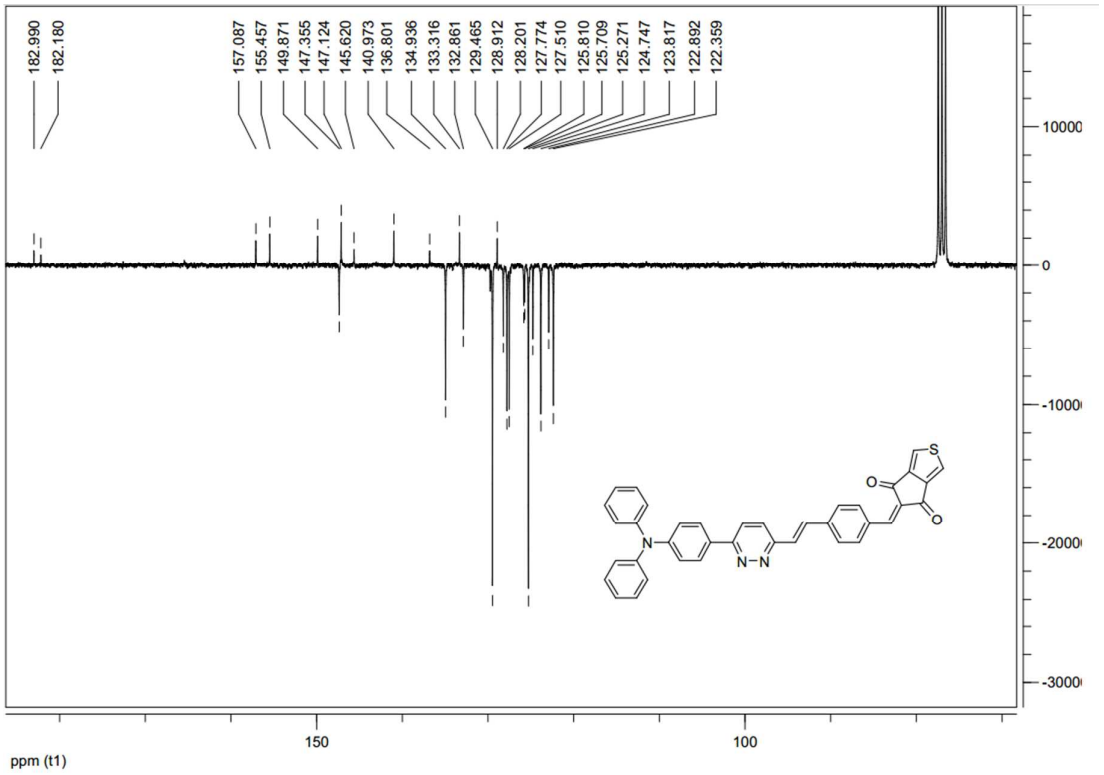

Figure S68. ^{13}C NMR spectrum of compound **1b** (75 MHz, $CDCl_3$, 25 °C).

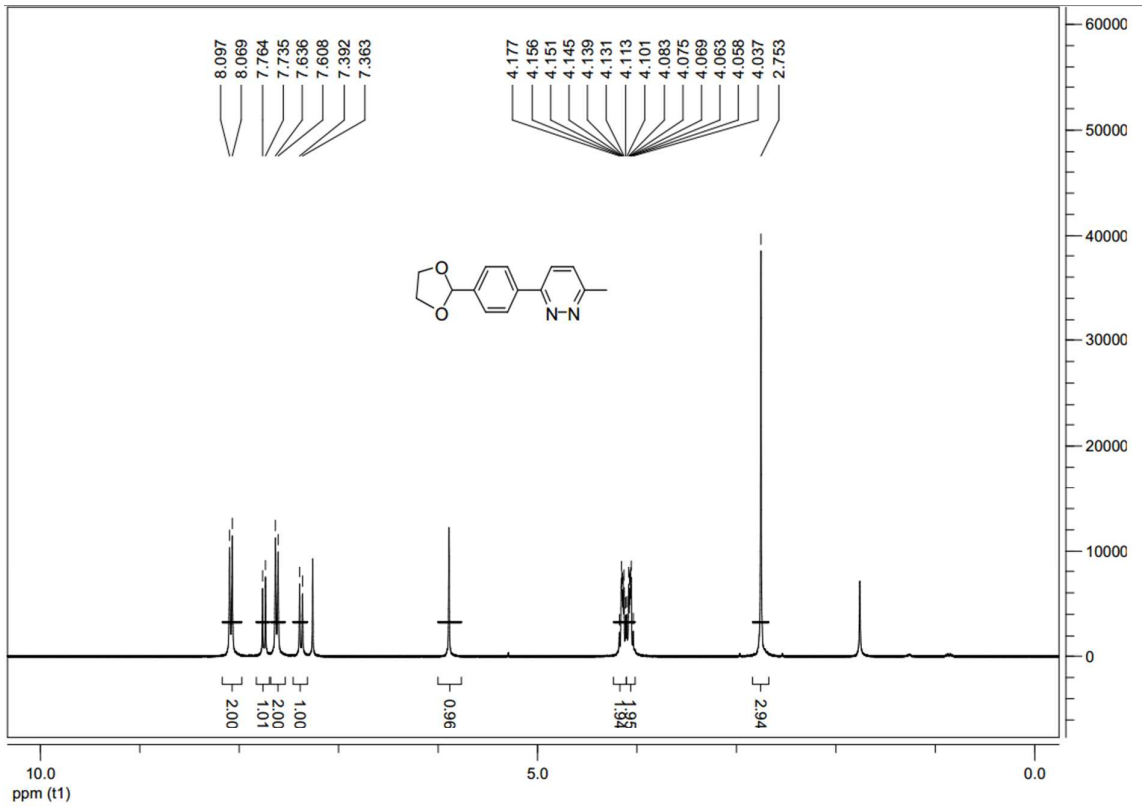

Figure S69. ^{1}H NMR spectrum of compound **27** (300 MHz, $CDCl_3$, 25 °C).

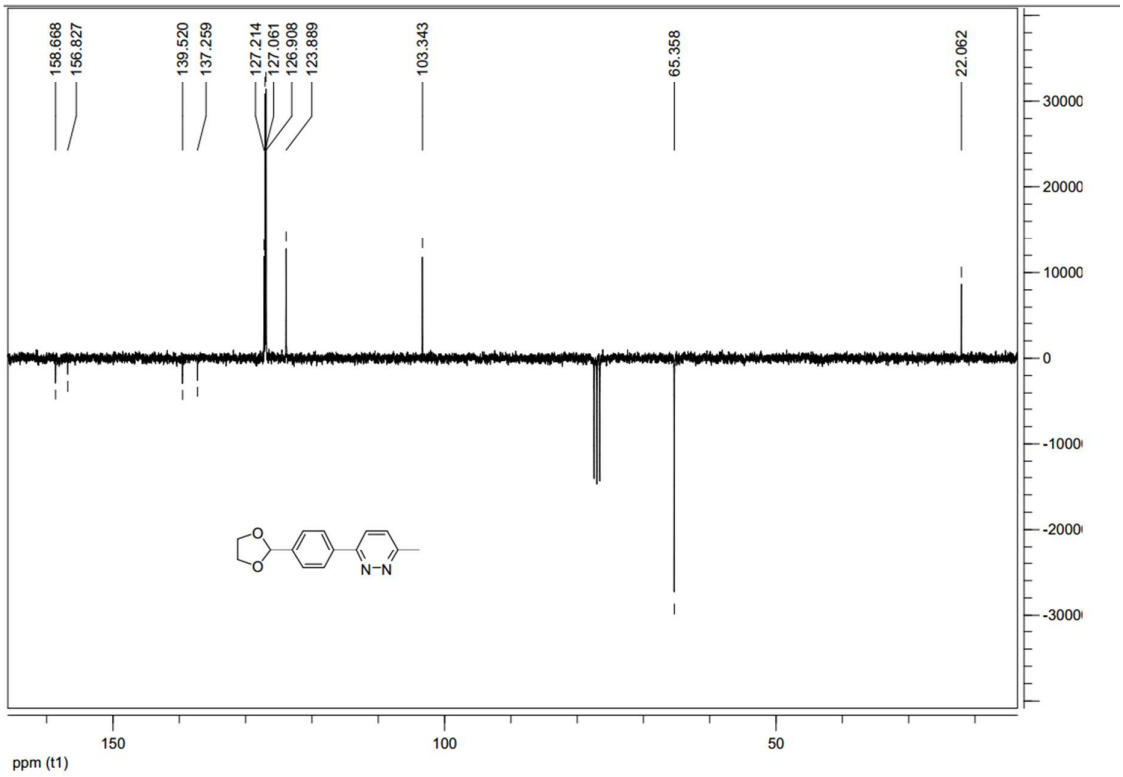

Figure S78. ^{13}C NMR spectrum of compound **27** (75 MHz, $CDCl_3$, 25 °C).

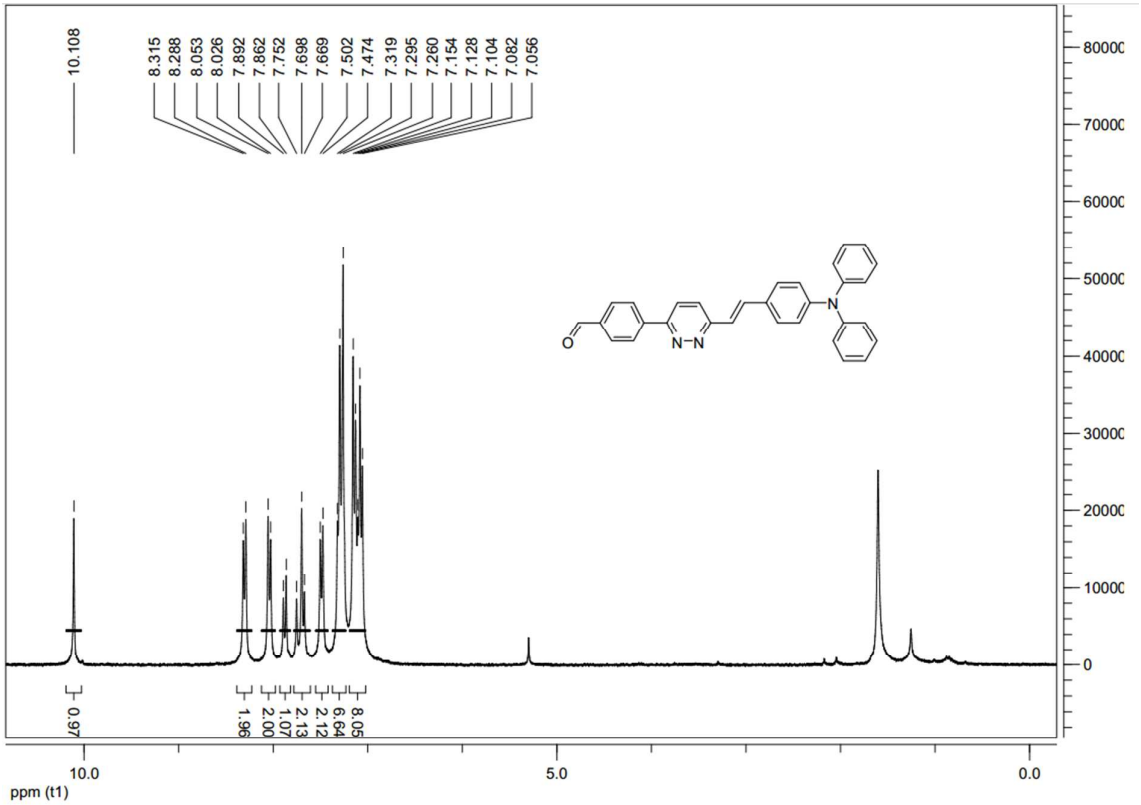

Figure S70. ^{1}H NMR spectrum of compound **5c** (300 MHz, $CDCl_3$, 25 °C).

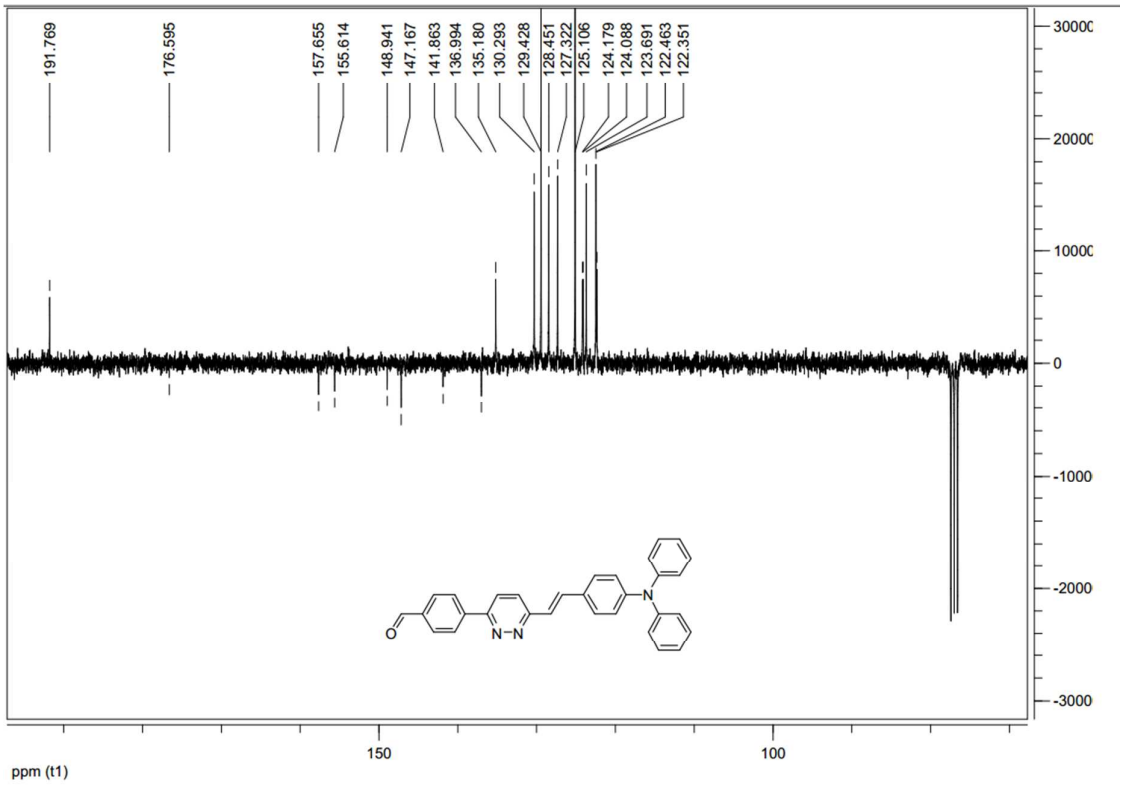

Figure S80. ^{13}C NMR spectrum of compound **5c** (75 MHz, $CDCl_3$, 25 °C).

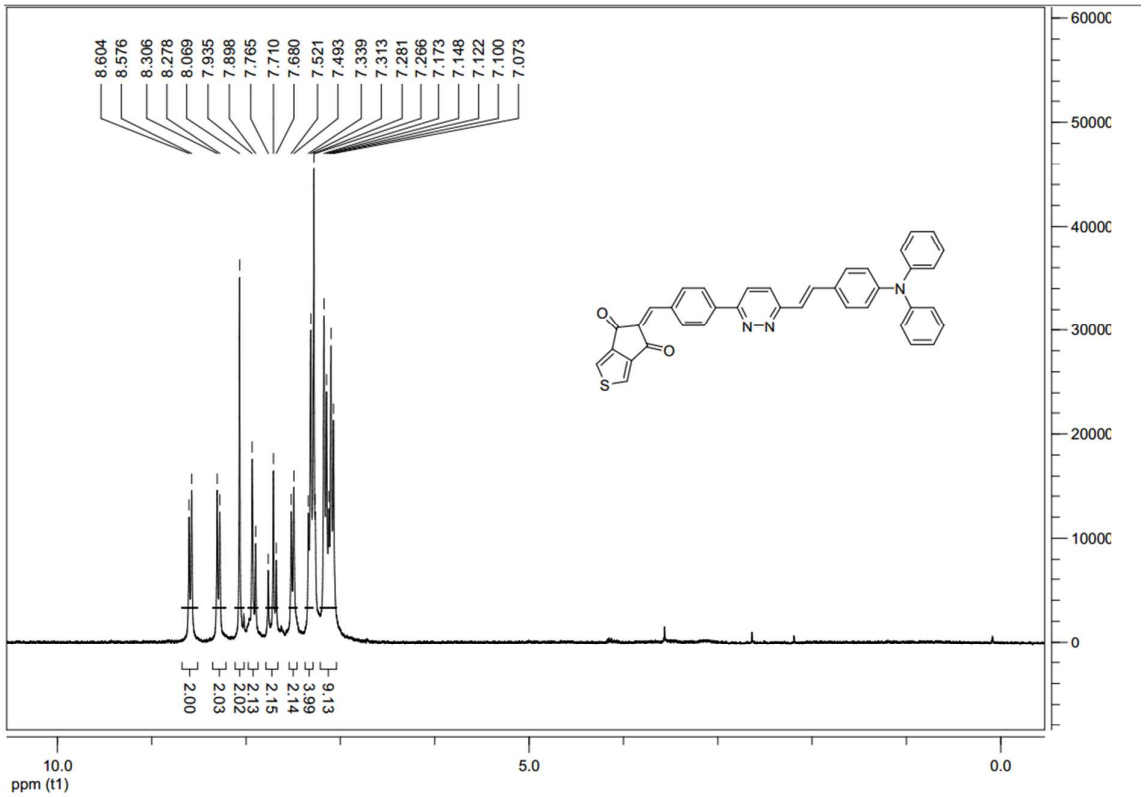

Figure S81. ^{1}H NMR spectrum of compound **1c** (300 MHz, $CDCl_3$, 25 °C).

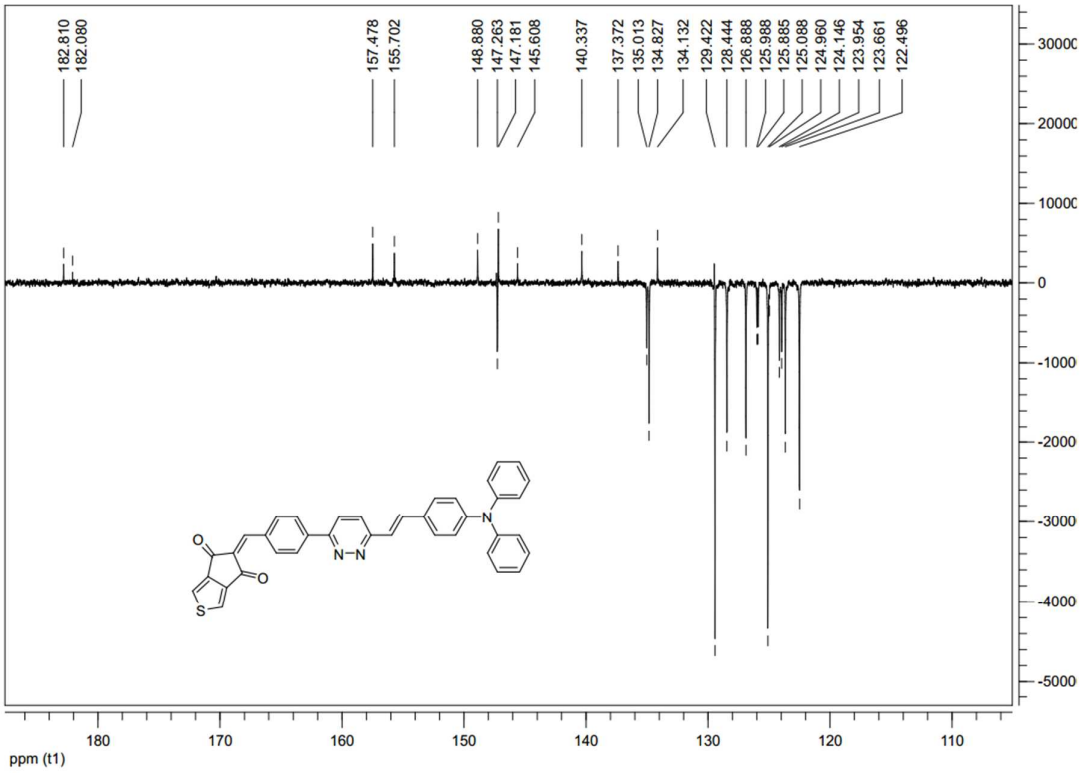

Figure S82. ^{13}C NMR spectrum of compound **1c** (300 MHz, $CDCl_3$, 25 °C).

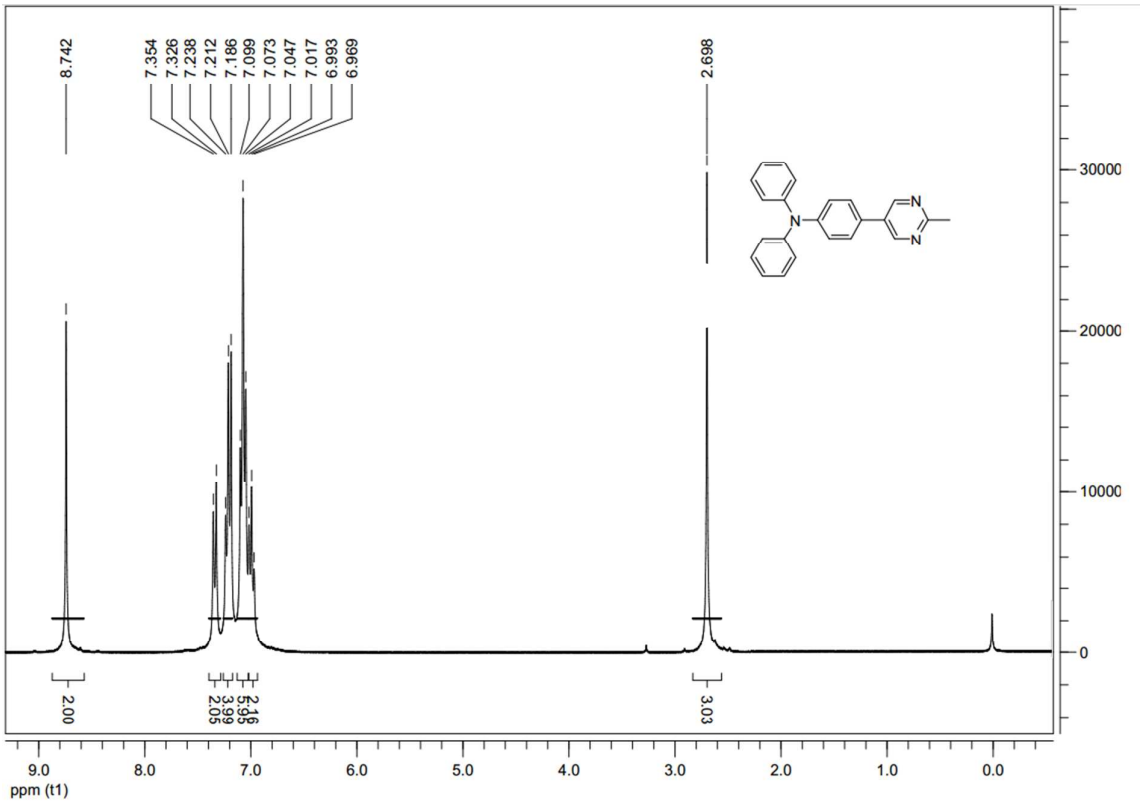

Figure S83. ^{1}H NMR spectrum of compound **30** (300 MHz, $CDCl_3$, 25 °C).

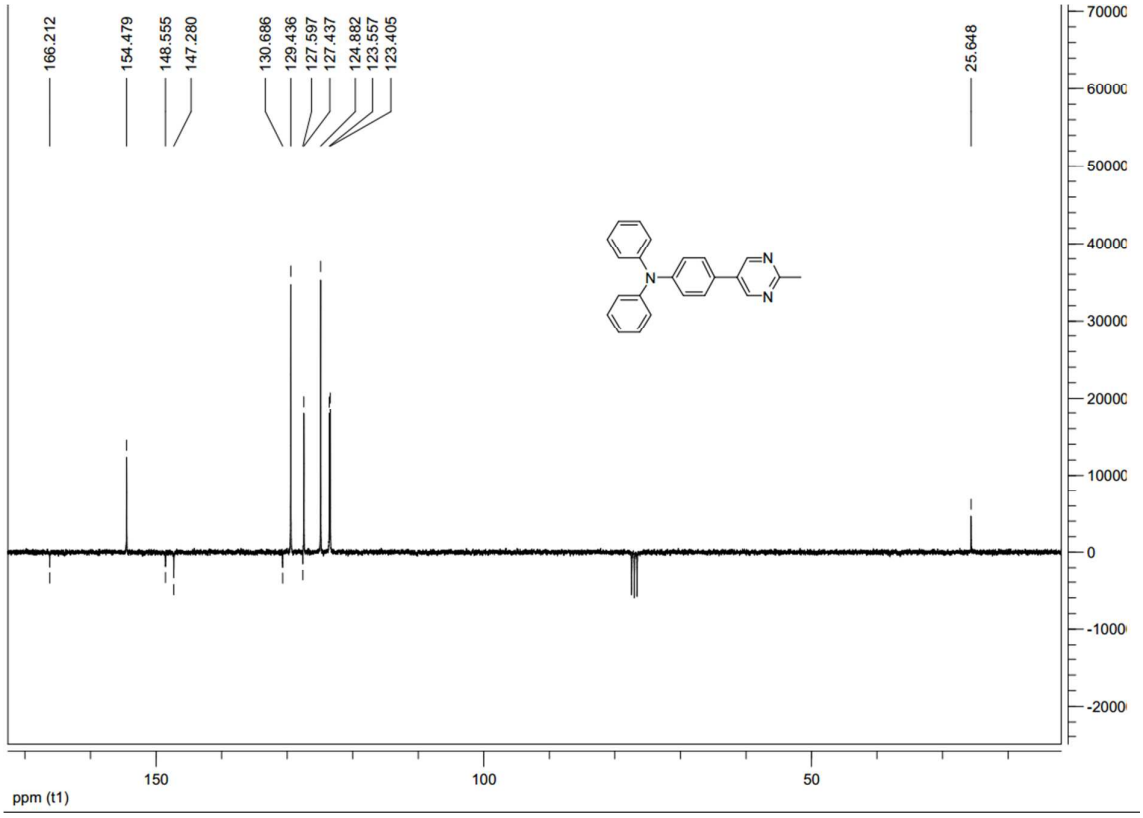

Figure S84. ^{13}C NMR spectrum of compound **30** (75 MHz, $CDCl_3$, 25 °C).

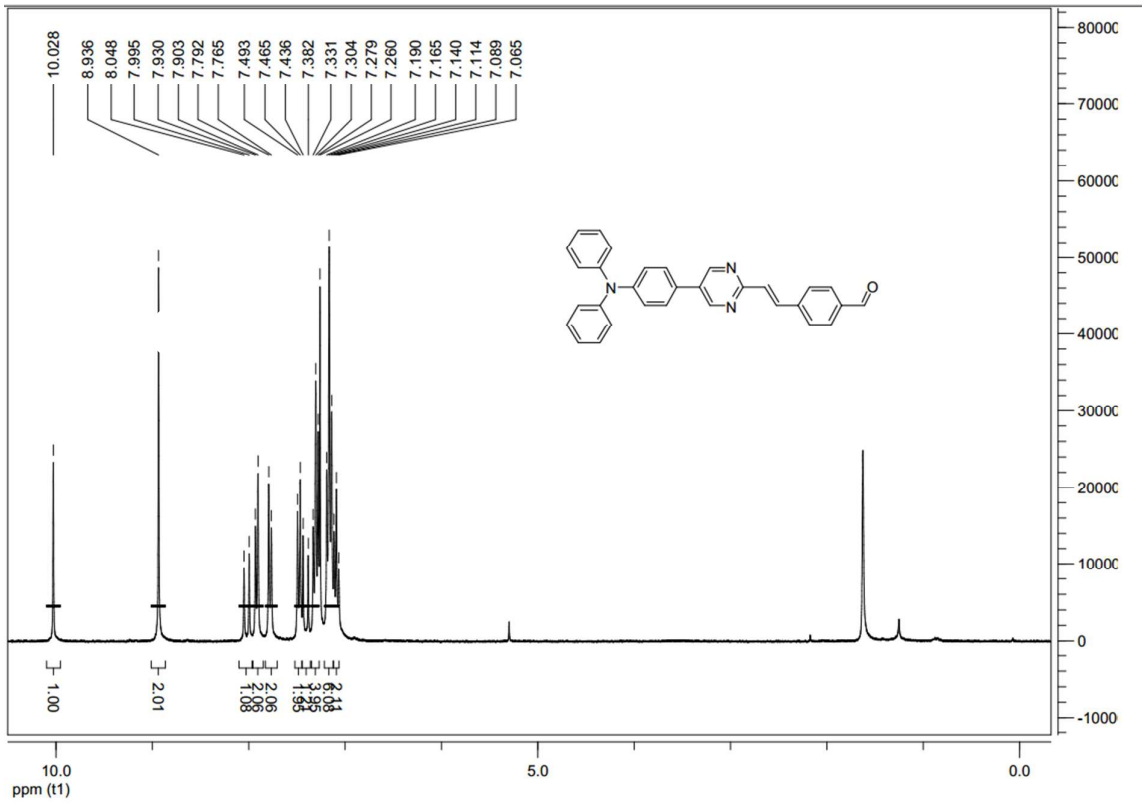

Figure S71. ^{1}H NMR spectrum of compound **6c** (300 MHz, $CDCl_3$, 25 °C).

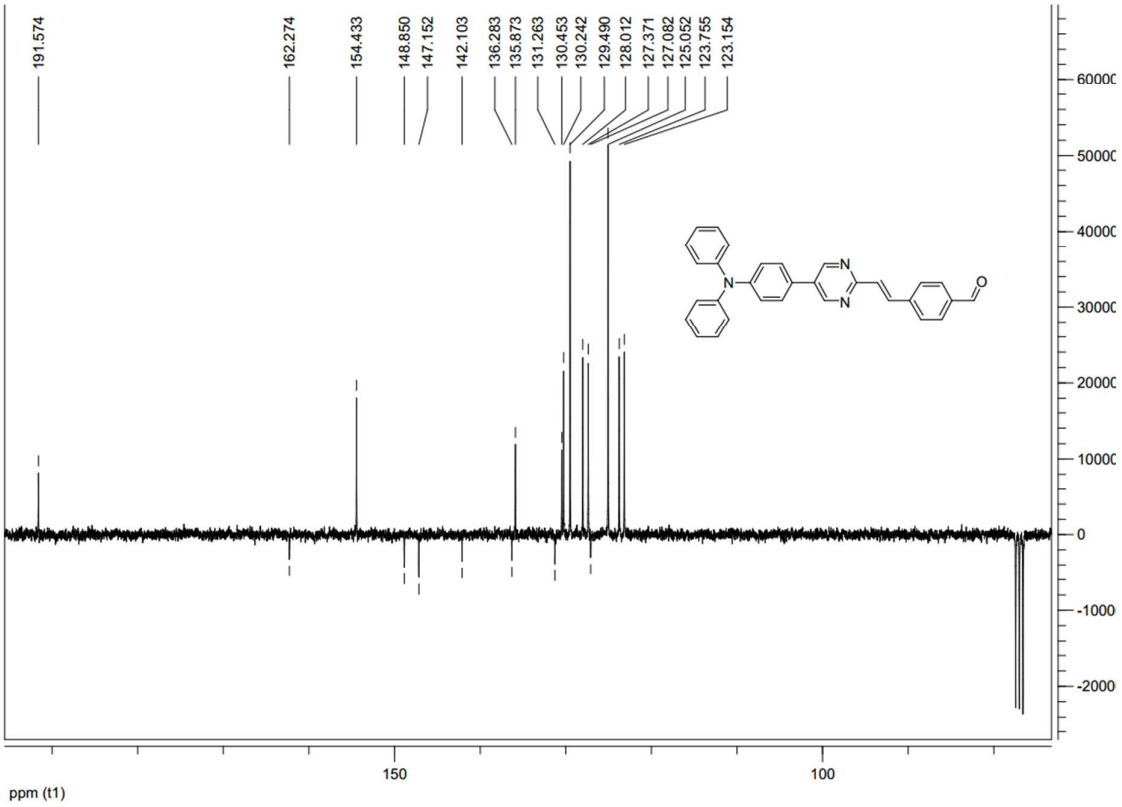

Figure S72. ^{13}C NMR spectrum of compound **6c** (75 MHz, $CDCl_3$, 25 °C).

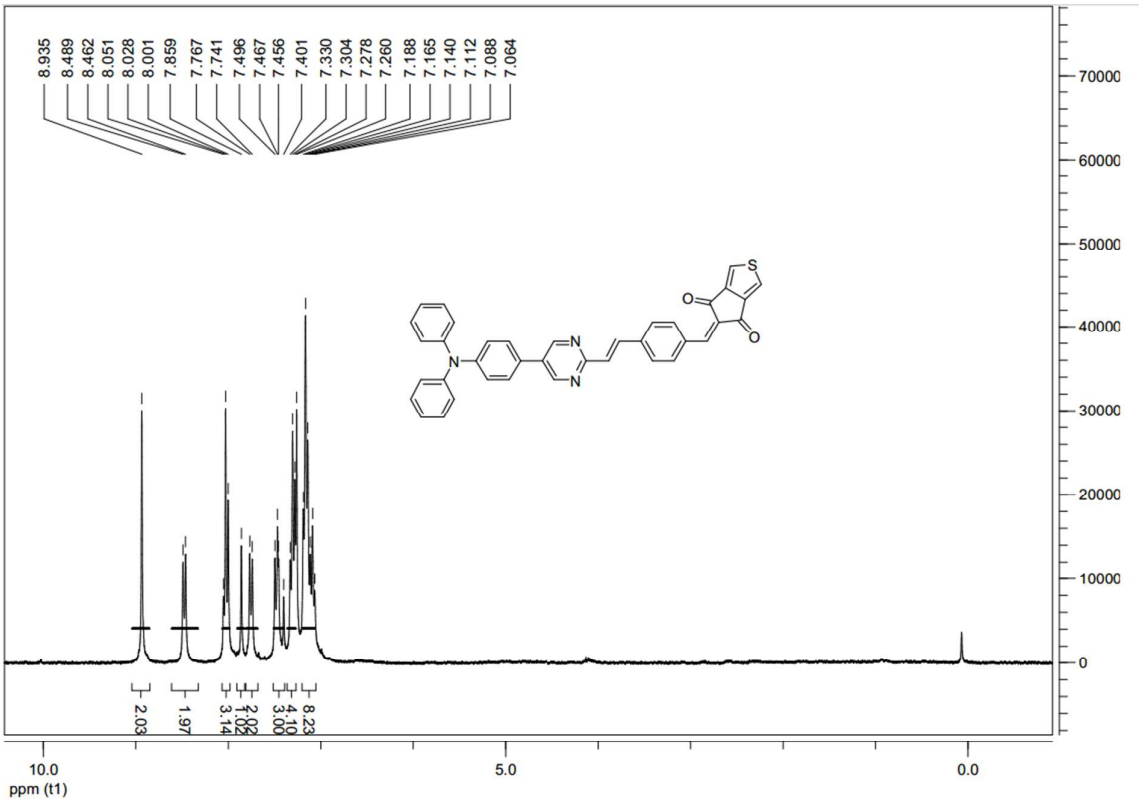

Figure S73. ^{1}H NMR spectrum of compound **2c** (300 MHz, $CDCl_3$, 25 °C).

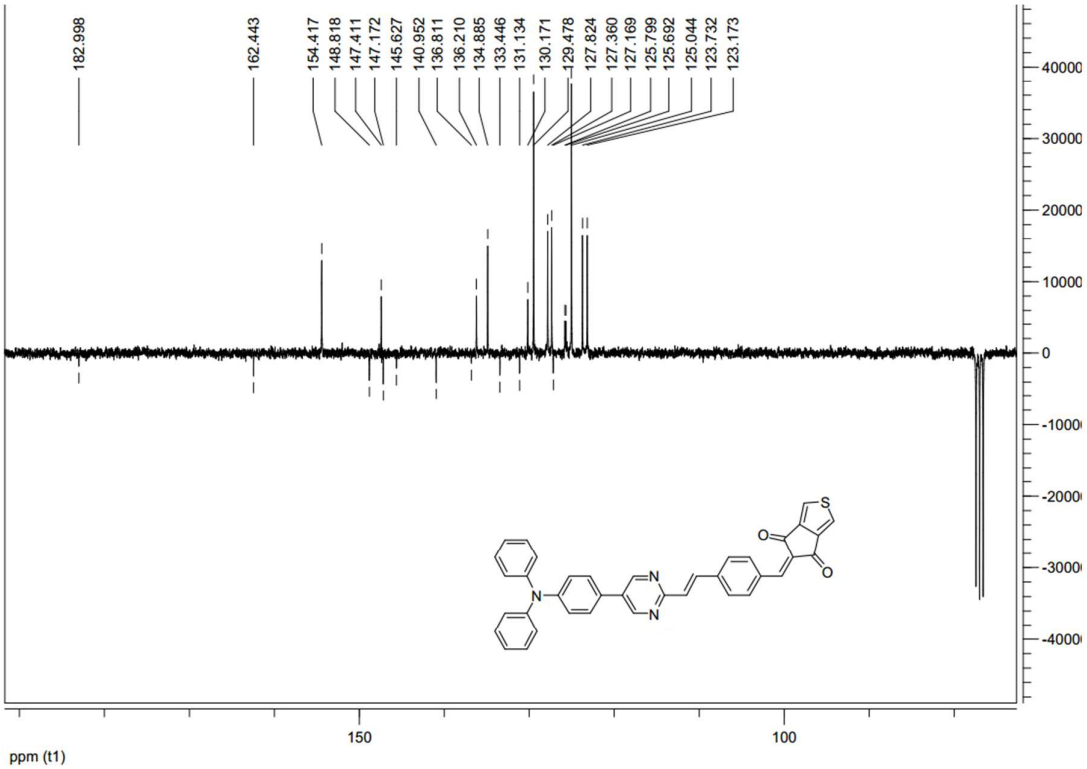

Figure S74. ^{13}C NMR spectrum of compound **2c** (75 MHz, $CDCl_3$, 25 °C).

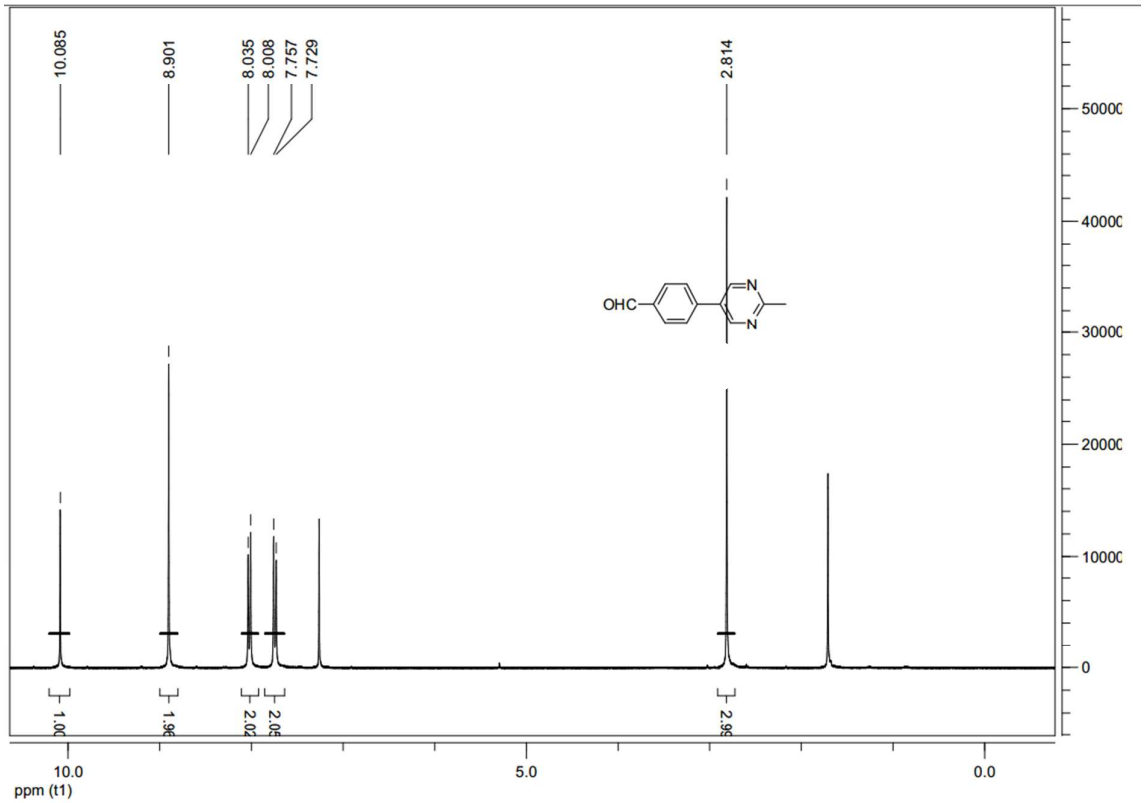

Figure S75. ^{1}H NMR spectrum of compound **31** (300 MHz, $CDCl_3$, 25 °C).

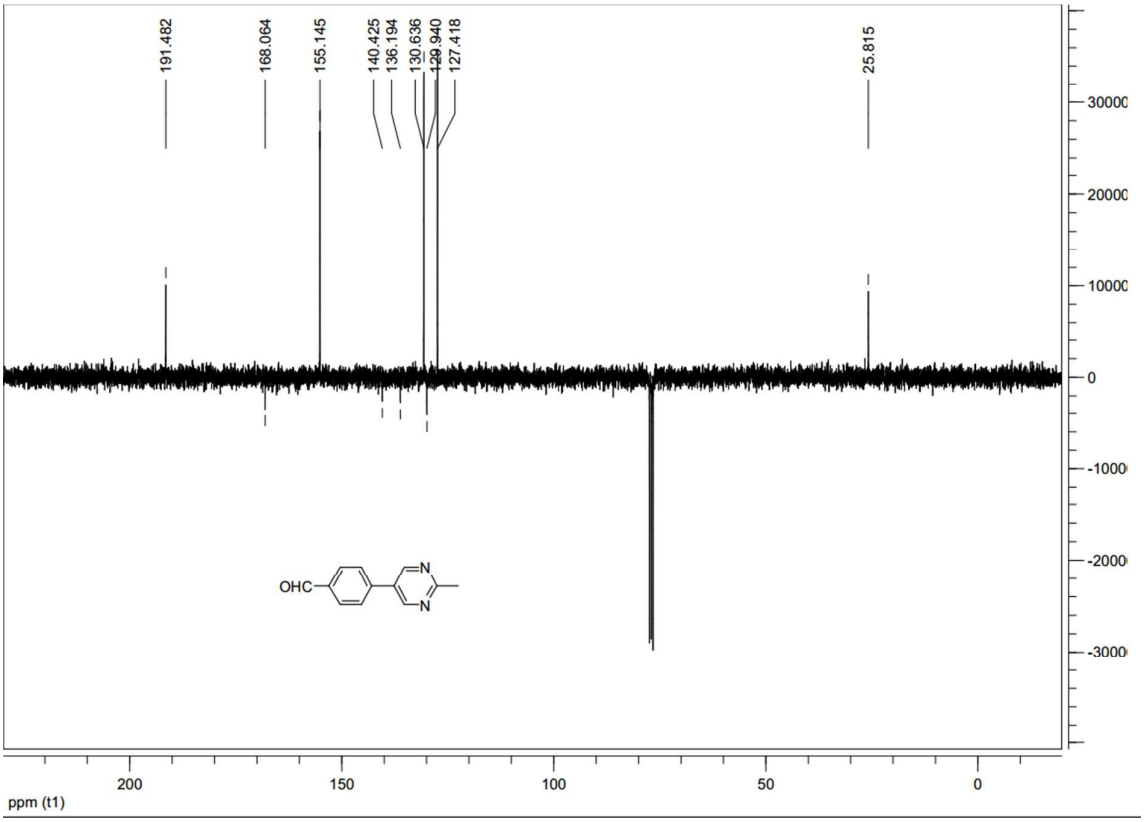

Figure S90. ^{13}C NMR spectrum of compound **31** (75 MHz, $CDCl_3$, 25 °C).

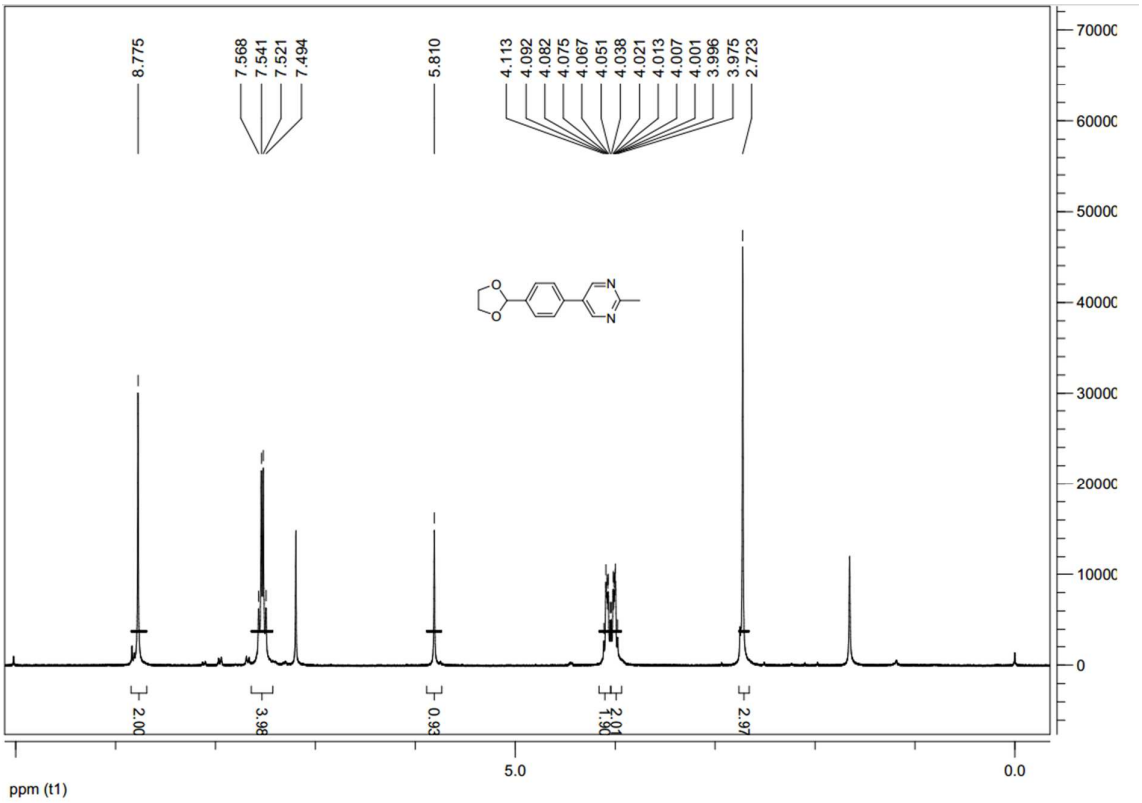

Figure S91. ^{1}H NMR spectrum of compound **32** (300 MHz, $CDCl_3$, 25 °C).

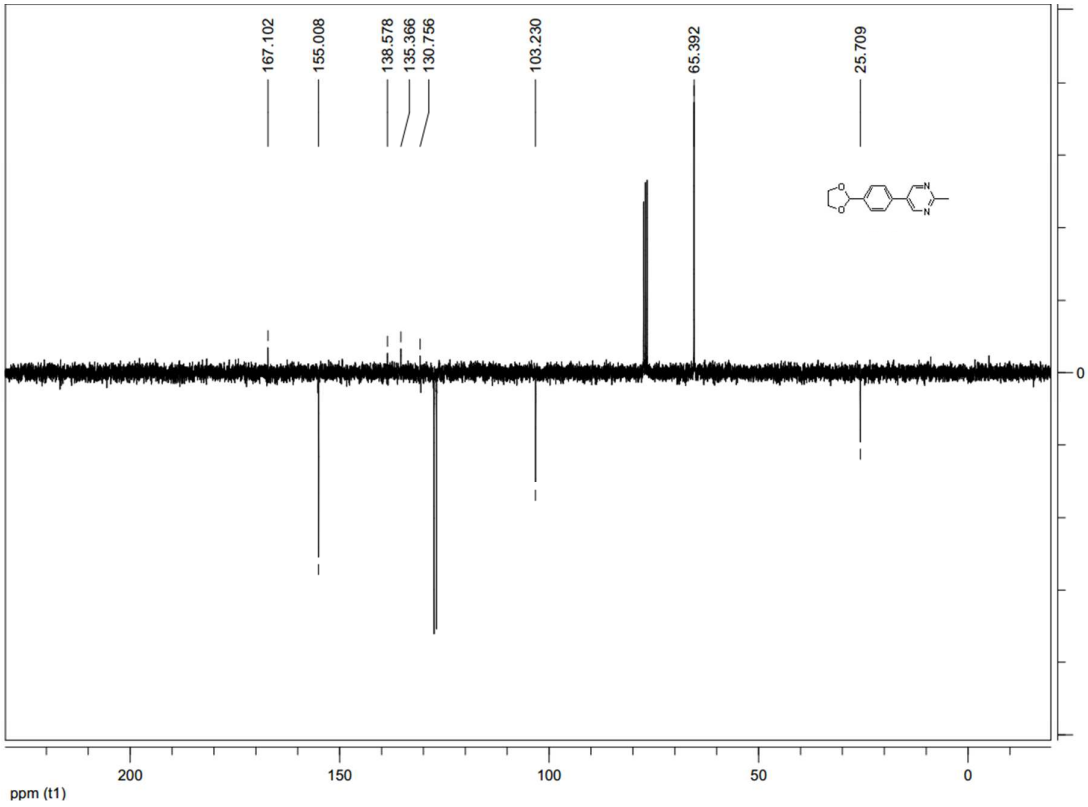

Figure S92. ^{13}C NMR spectrum of compound **32** (75 MHz, $CDCl_3$, 25 °C).

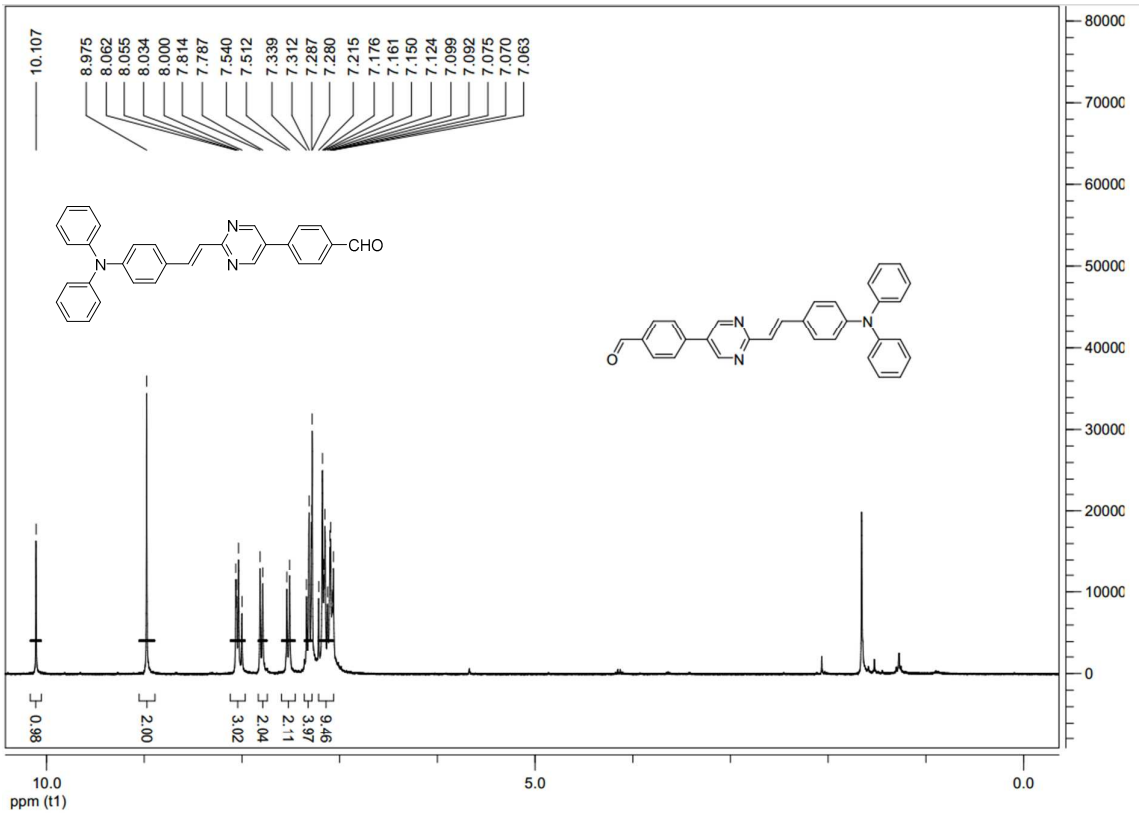

Figure S93. ^{1}H NMR spectrum of compound **6d** (300 MHz, $CDCl_3$, 25 °C).

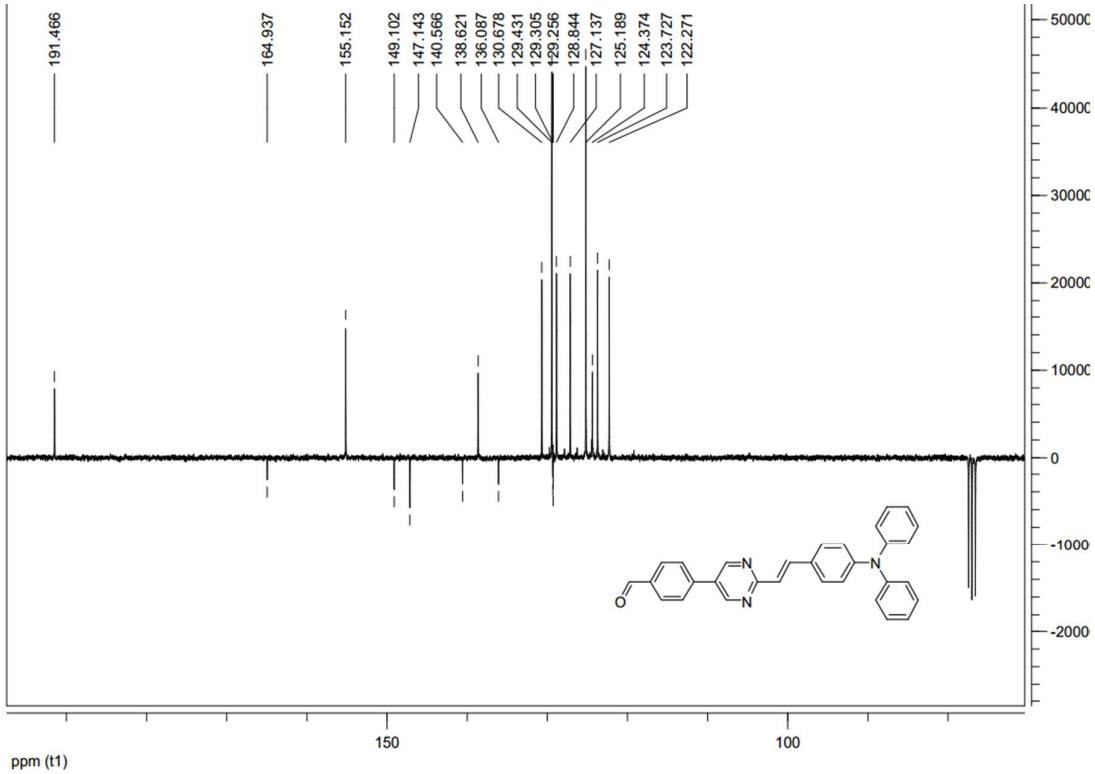

Figure S94. ^{13}C NMR spectrum of compound **6d** (75 MHz, $CDCl_3$, 25 °C).

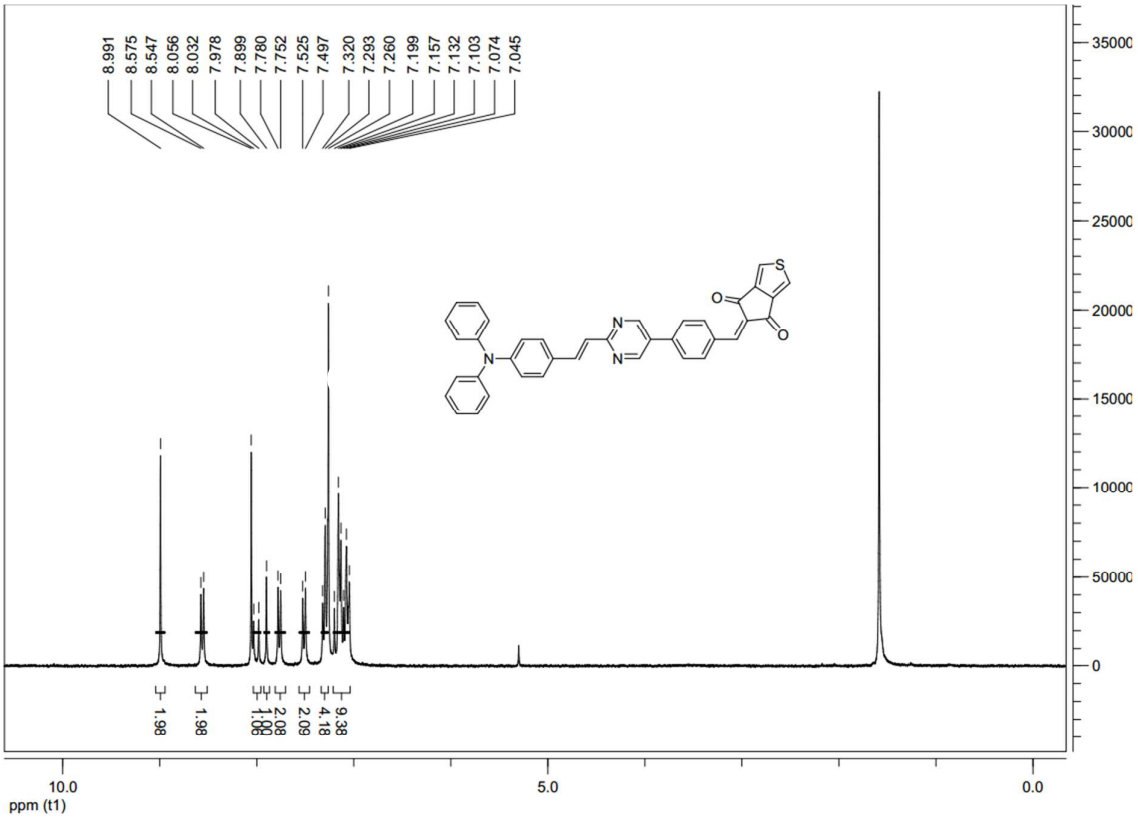

Figure S76. ^{1}H NMR spectrum of compound **2d** (300 MHz, $CDCl_3$, 25 °C).

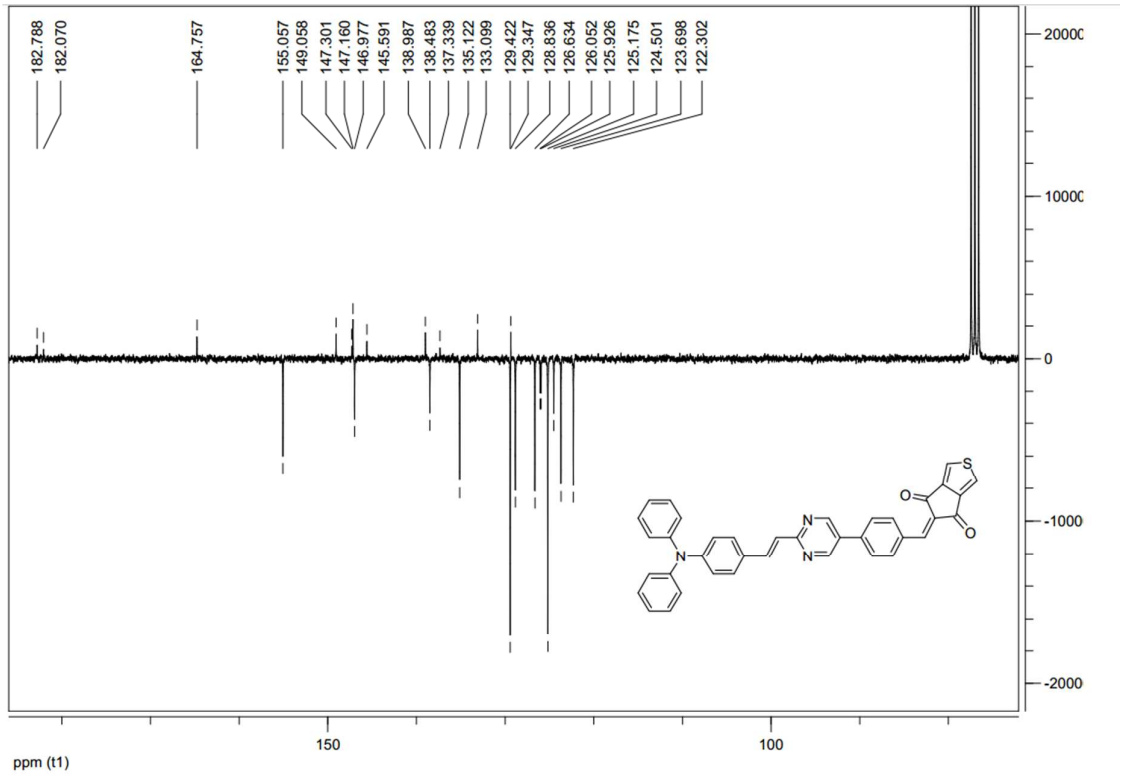

Figure S77. ^{13}C NMR spectrum of compound **2d** (75 MHz, $CDCl_3$, 25 °C).

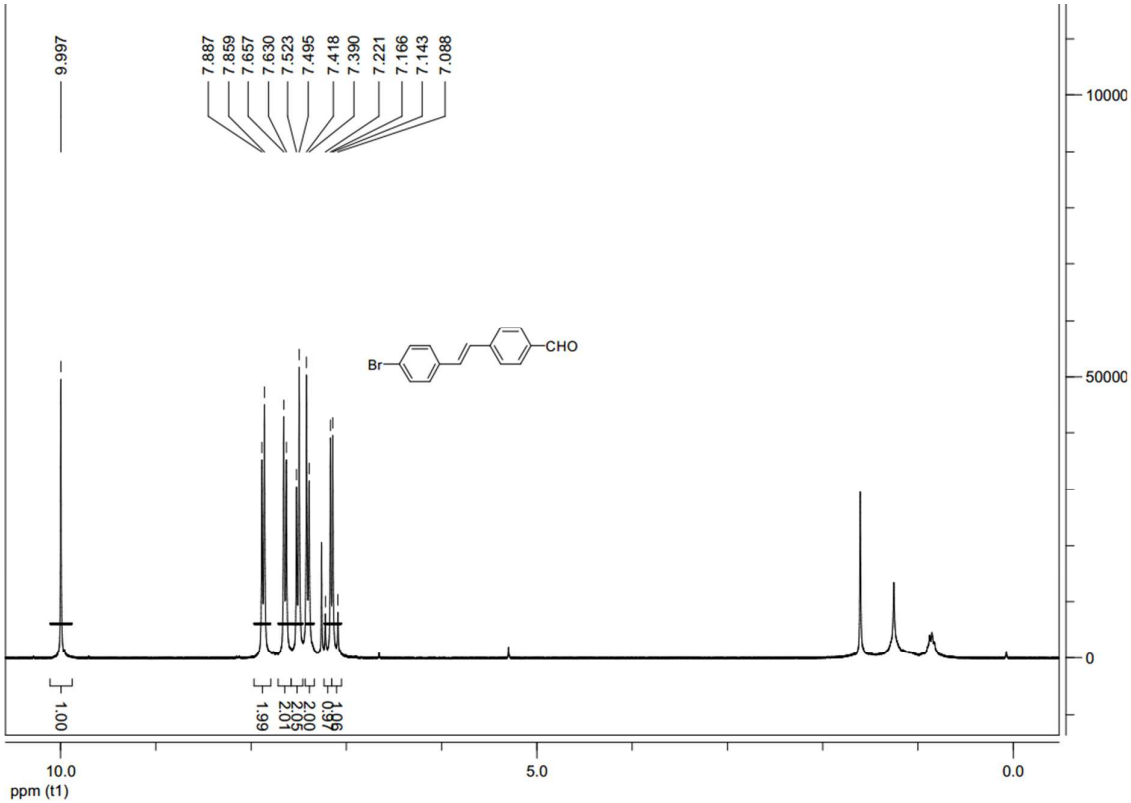

Figure S78. ^{1}H NMR spectrum of compound **35** (300 MHz, $CDCl_3$, 25 °C).

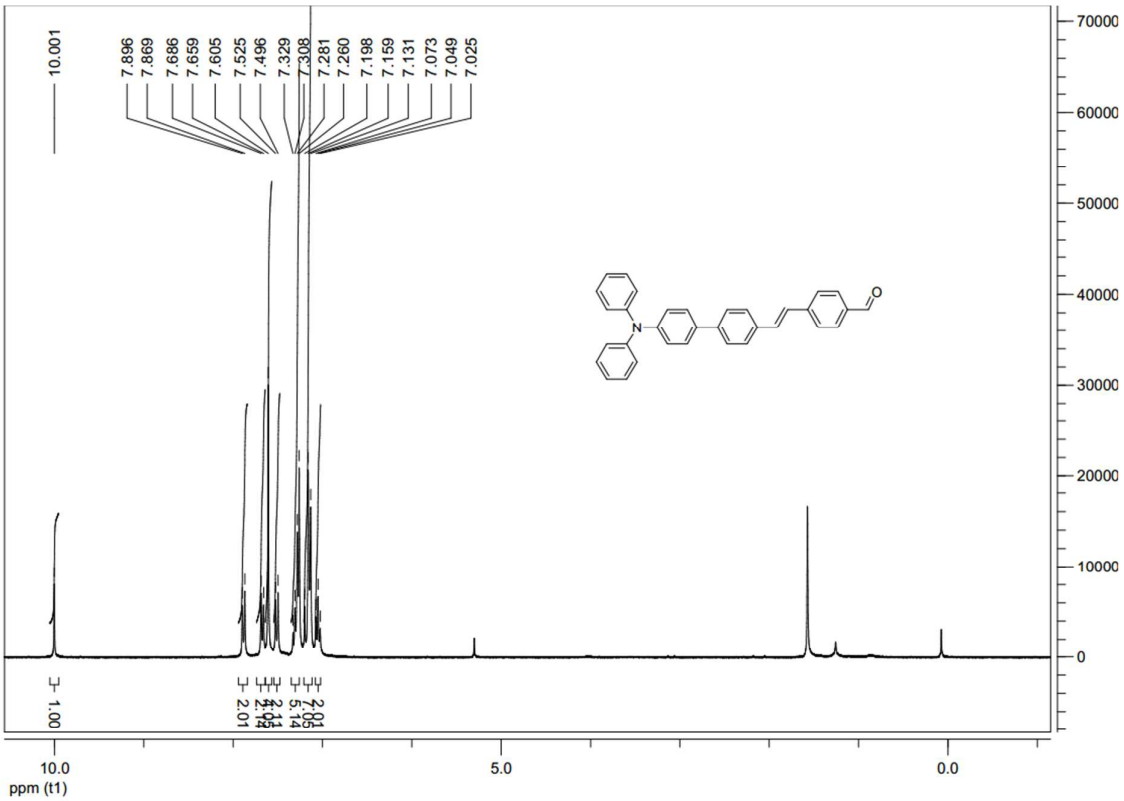

Figure S79. ^{1}H NMR spectrum of compound **7b** (300 MHz, $CDCl_3$, 25 °C).

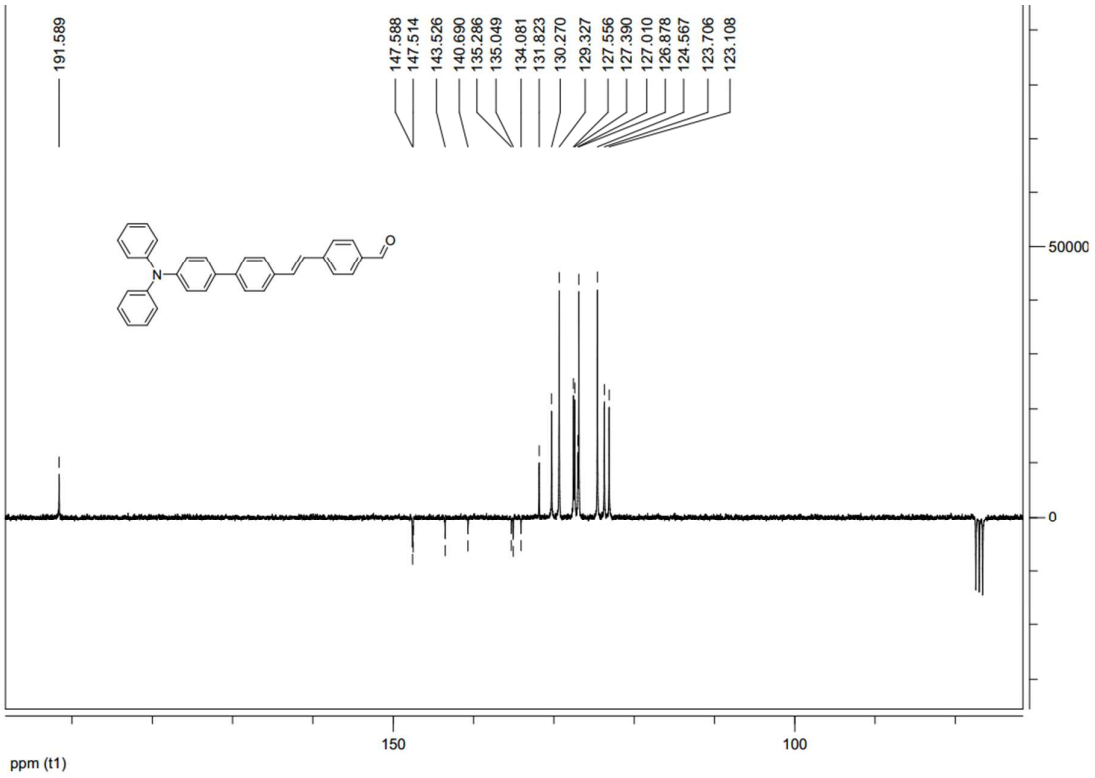

Figure S80. ^{13}C NMR spectrum of compound **7b** (75 MHz, $CDCl_3$, 25 °C).

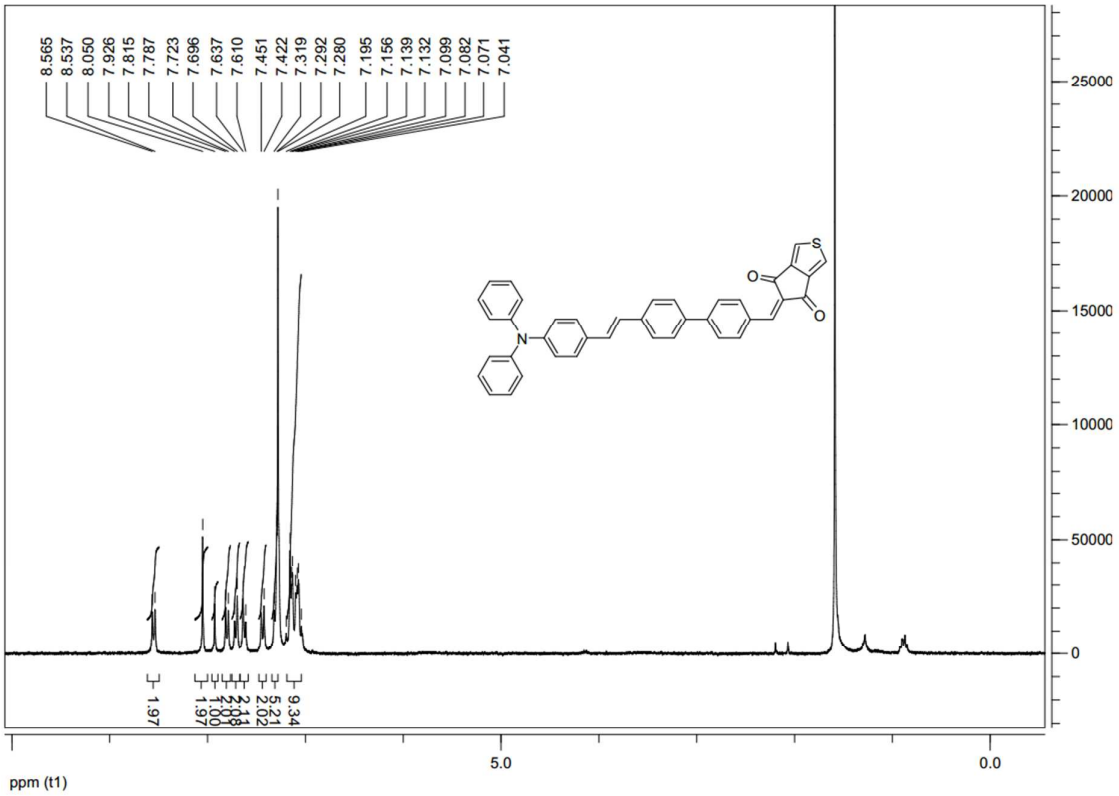

Figure S100. ^{1}H NMR spectrum of compound **3b** (300 MHz, $CDCl_3$, 25 °C).

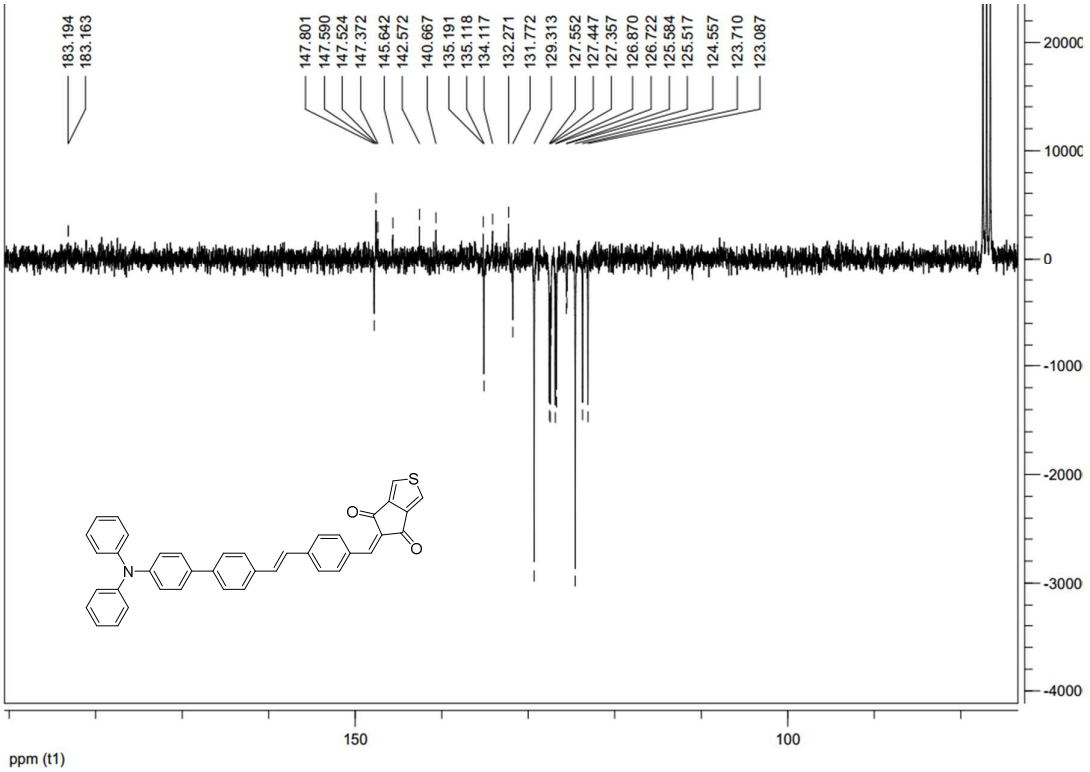

Figure S81. ^{13}C NMR spectrum of compound **3b** (75 MHz, $CDCl_3$, 25 °C).

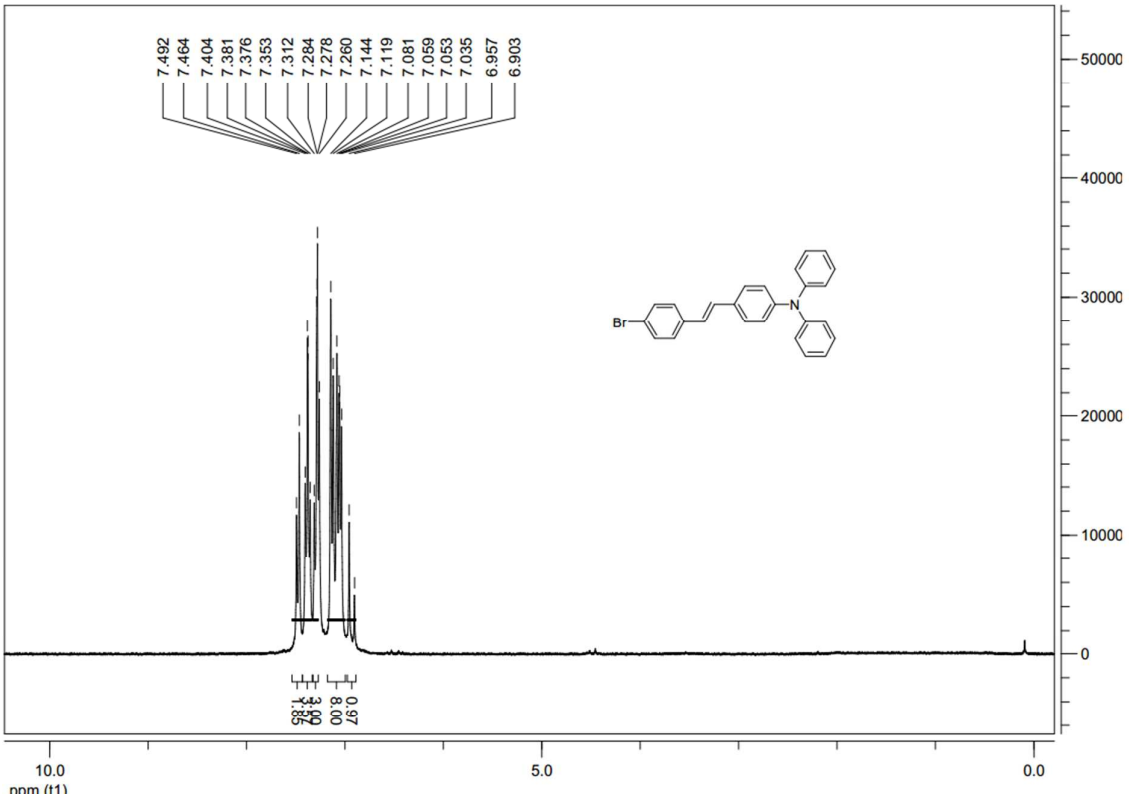

Figure S102. ^{1}H NMR spectrum of compound **36** (300 MHz, $CDCl_3$, 25 °C).

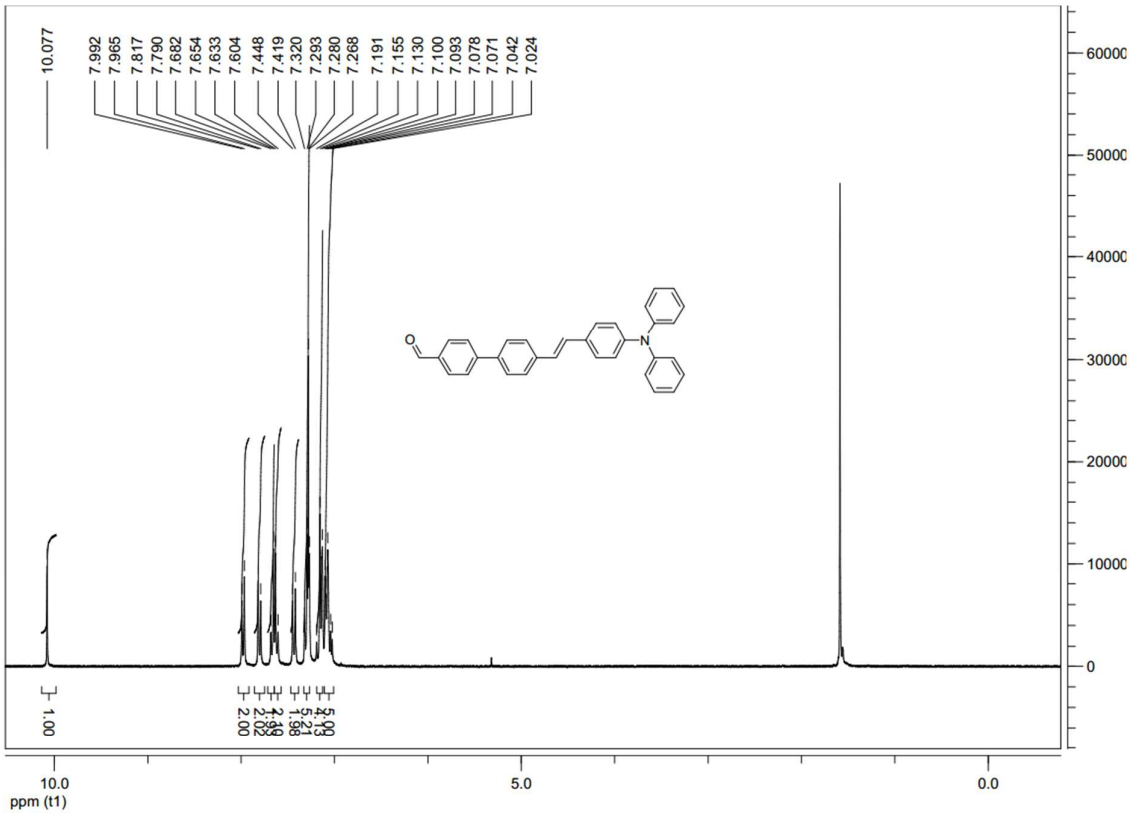

Figure S103. ^{1}H NMR spectrum of compound **7c** (300 MHz, $CDCl_3$, 25 °C).

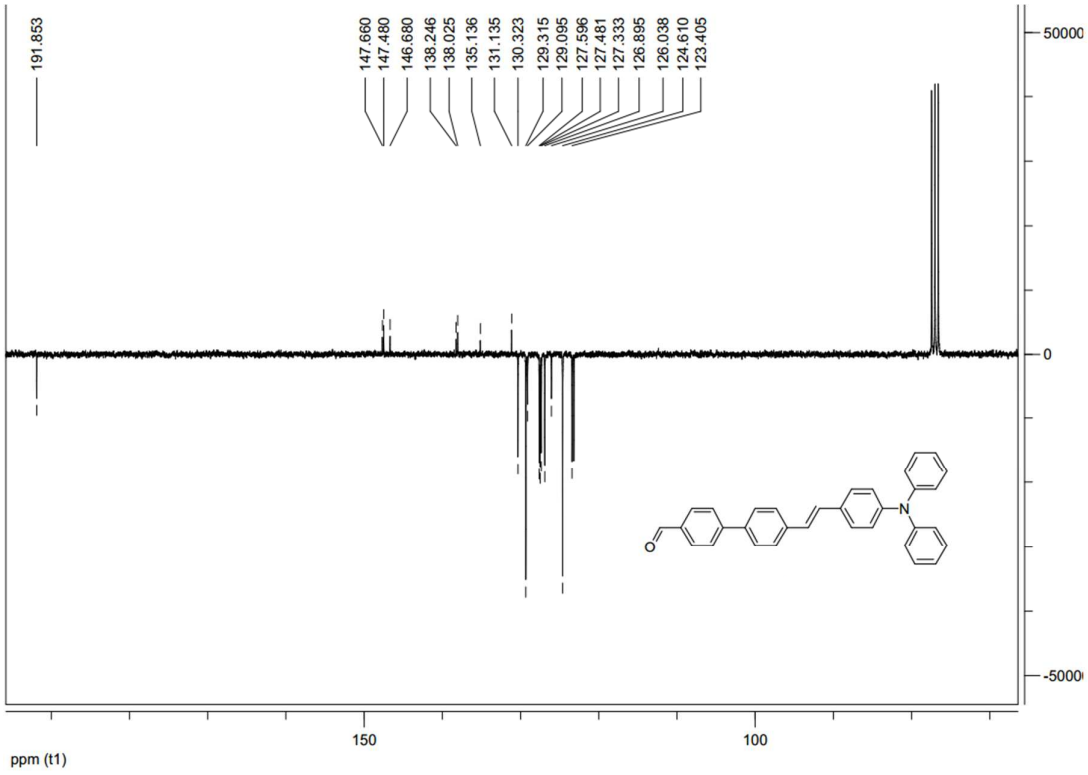

Figure S104. ^{13}C NMR spectrum of compound **7c** (75 MHz, $CDCl_3$, 25 °C).

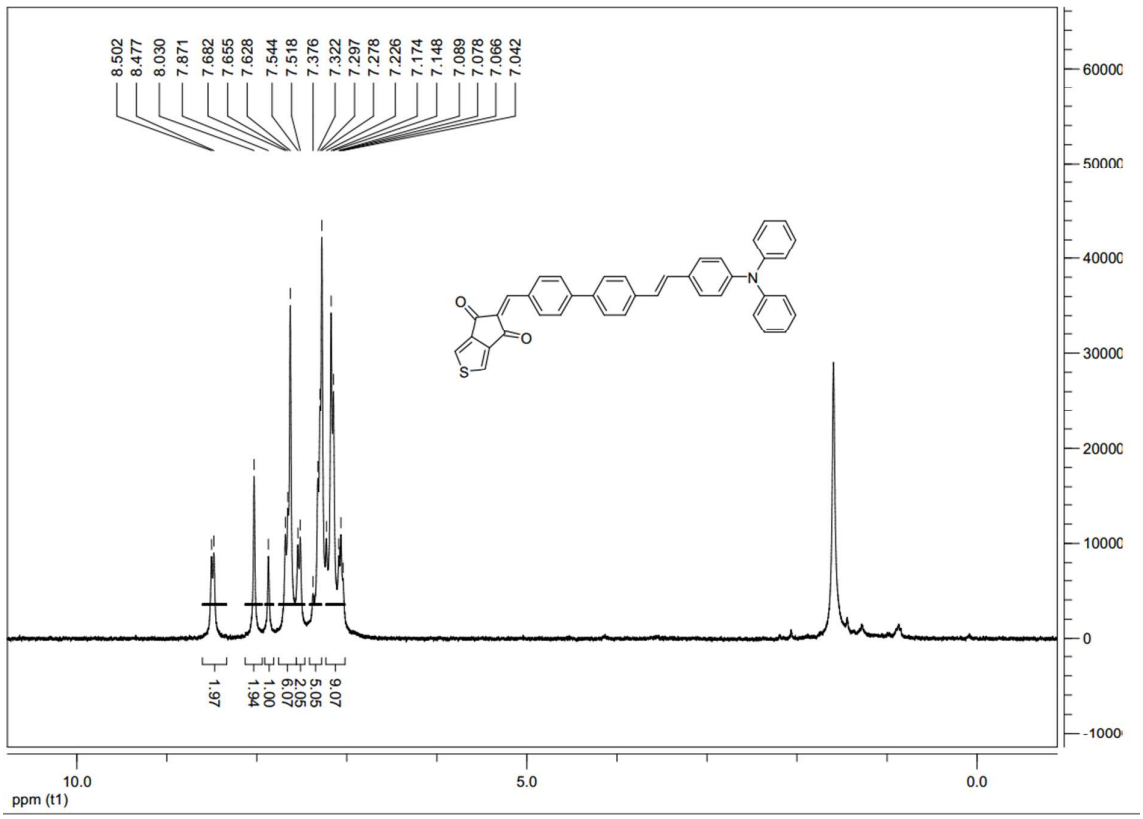

Figure S82. ^{1}H NMR spectrum of compound **3c** (300 MHz, $CDCl_3$, 25 °C).

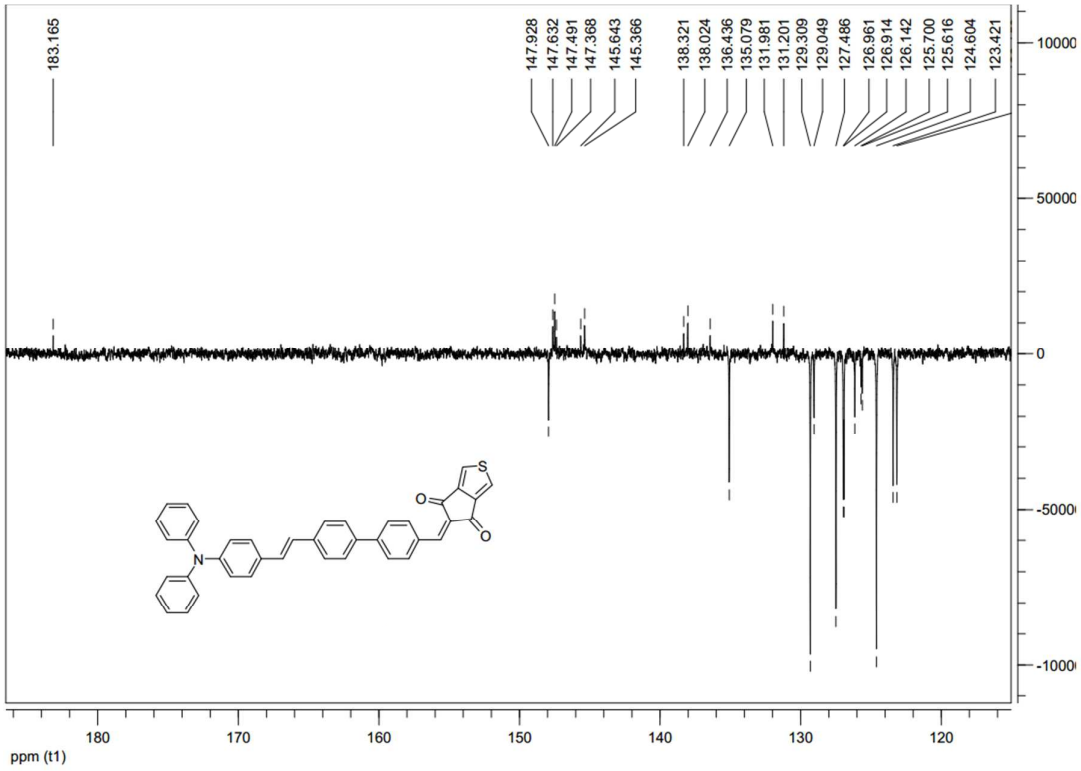

Figure S83. ^{13}C NMR spectrum of compound **3c** (75 MHz, $CDCl_3$, 25 °C).

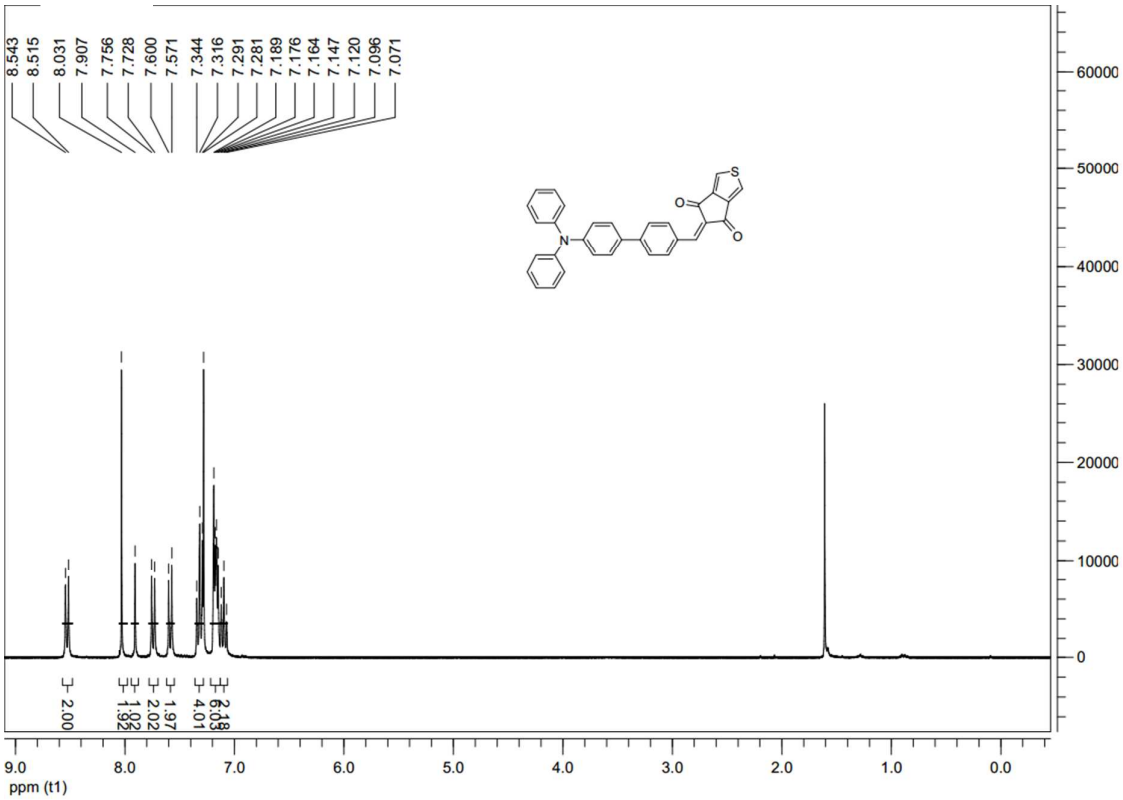

Figure S84. ^{1}H NMR spectrum of compound **4a** (300 MHz, $CDCl_3$, 25 °C).

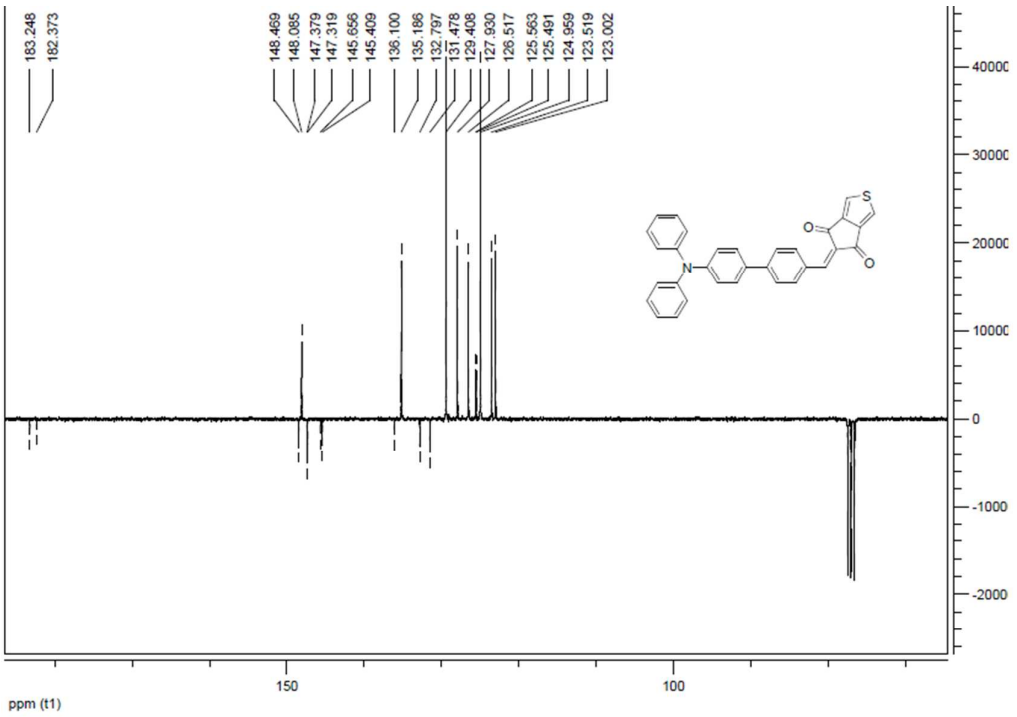

Figure S85. ^{13}C NMR spectrum of compound **4a** (75 MHz, $CDCl_3$, 25 °C).

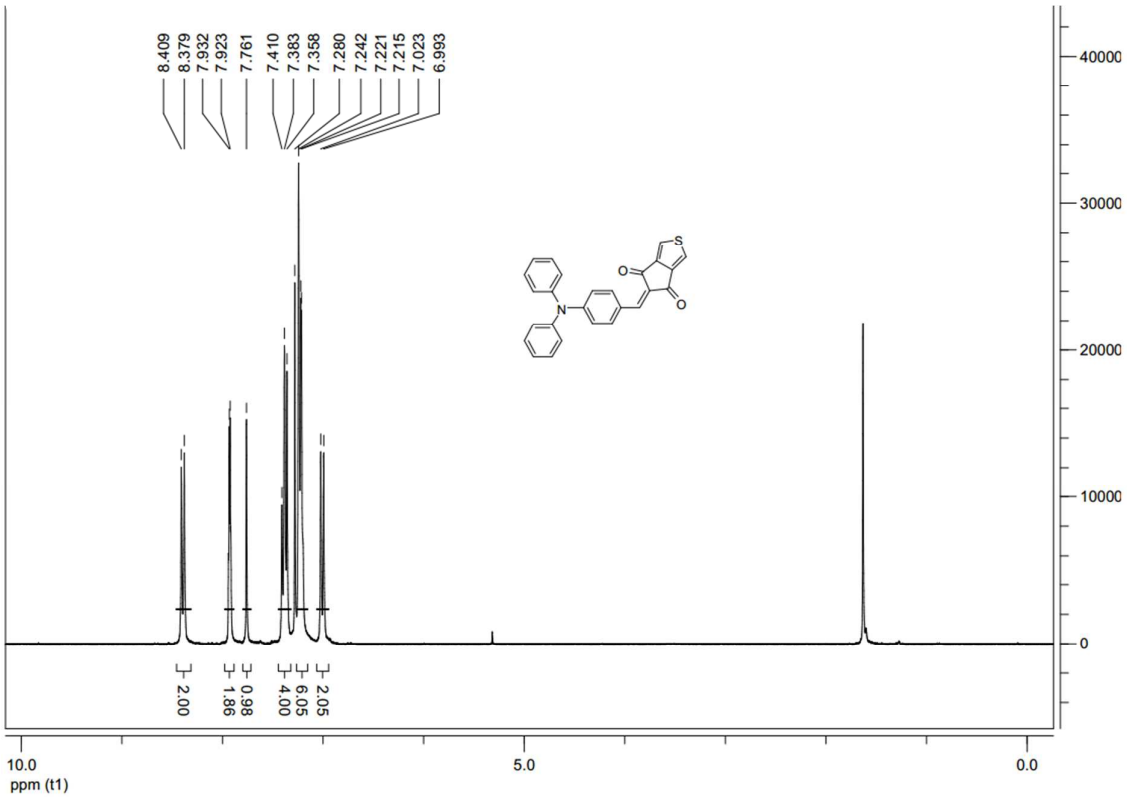

Figure S86. ^{1}H NMR spectrum of compound **4b** (300 MHz, $CDCl_3$, 25 °C).

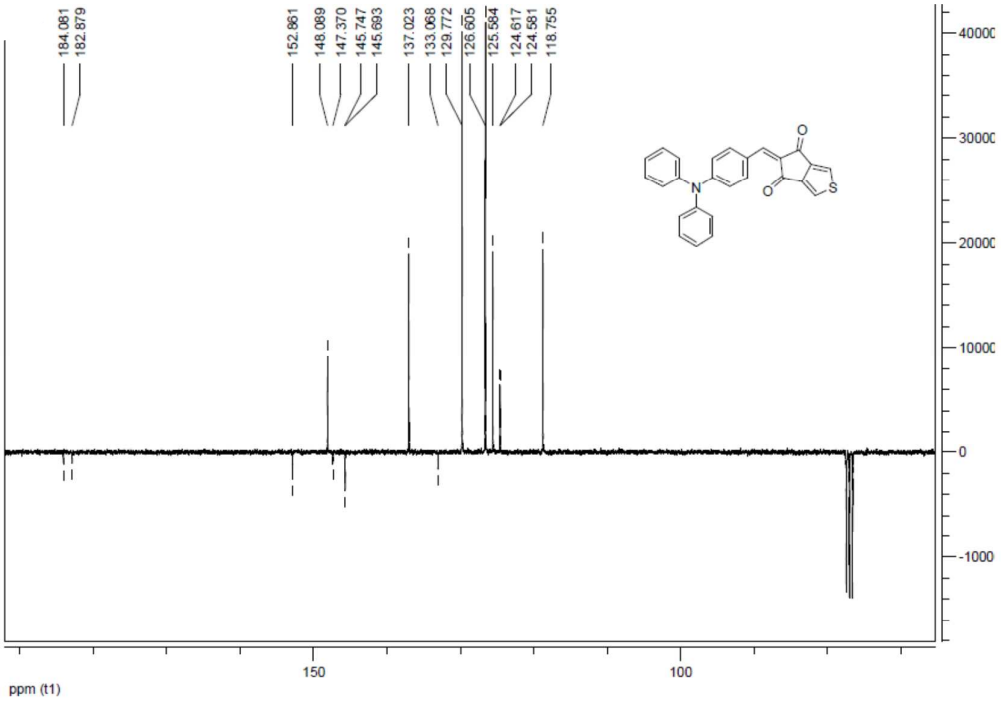

Figure S87. ^{13}C NMR spectrum of compound **4b** (75 MHz, $CDCl_3$, 25 °C).