

Supplementary material for the article:

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Supplementary material

Solvent, structural, quantum chemical study and antioxidative activity of symmetrical 1-methyl-2,6-bis[2-(substituted phenyl)ethenyl]pyridinium iodides

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Materials and characterization methods

All commercially available chemical: 2,6-diaminopyridine, Methyl iodide, 1,1-diphenyl-2-picryldrazil (DPPH), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), Benzaldehyde, 2-naphthyl benzaldehyde, 4-methylbenzaldehyde, 3-methylbenzaldehyde, 4-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, 2,6-dichlorobenzaldehyde, 2-chloro-6-fluorobenzaldehyde, 4-dimethylaminobenzaldehyde, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde were purchased from Sigma-Aldrich. 1-methyl-2,6-dimethylpyridinium iodide was synthesized from the literature.[1] All solvent were of reagent purity and used without further purification.

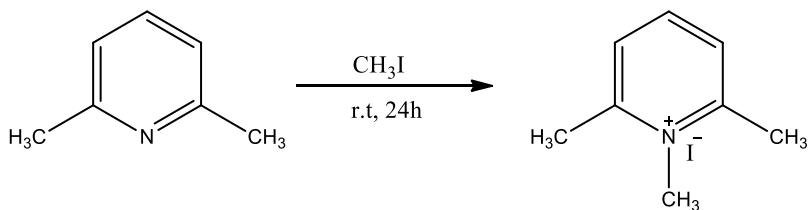
^1H and ^{13}C NMR spectra were recorded at room temperature in a deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) using Varian Gemini 200 spectrometer. The Chemicals shifts are expressed in ppm value referenced to the trimethylsilane (TMS) as a standard in the ^1H and ^{13}C NMR spectra. The description of NMR chemical shift are as follow: s-singlet, d-doublet, t-triplet, m-multiplet, dd-double doublet and br.m.ovlp.-broad multiplet overlapping coupling constants J are expressed in Hz.

Fourier Transform Infrared spectra of samples were recorded on er FTIR BOMEM MB series (Hartmann & Braun), in the range $4000\text{-}500\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} in the form of KBr pellets.

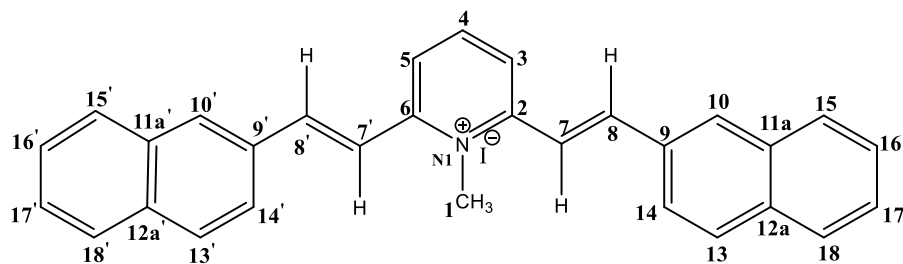
The UV absorption spectra were measured in range of $200\text{-}600\text{ nm}$ in twenty one solvent of different polarity using Shimadzu 1700 UV/vis spectrophotometer. All UV spectra were recorded at concentration of solvent $5 \times 10^{-5}\text{ mol dm}^{-3}$ and temperature 25°C . Three measurements were performed, and the mean value is presented. Elemental analysis (C, H, N) was performed using a VARIO EL III Elemental analyzer.

Synthesis of 1-methyl-2,6-dimethylpyridinium iodide

The mixture of 2,6-dimethylpyridine (2,6-Lutidine) (0,025 mol) and methyl-iodide (0.125 mol) was stirred at room temperature for 24 h, Scheme S1. After that, the product was filtered and recrystallized repeatedly from ethanol [1].



Scheme S1. Synthesis of 1-methyl-2,6-dimethylpyridinium iodide



Scheme S2 Numbering of compound 1-Methyl-2,6-Bis[2-(2-naphthyl)-ethenyl]pyridinium iodide (**2**)

Table S1 Solvent parameters used in Kamlet–Taft equation[2]

Solvent	π^*	β	α
1 1-methyl-2-pyrrolidinone (NMP)	0.92	0.77	0.00
2 1-propanol (1-PrOH)	0.48	0.84	0.98
3 2-methyl-1-propanol (iBuOH)	0.40	0.84	0.79
4 2-methyl-2-butanol (t-AmOH)	0.40	0.93	0.28
5 2-propanol (iPrOH)	0.48	0.95	0.76
6 Acetone	0.71	0.43	0.08
7 Acetonitrile (AcN)	0.75	0.40	0.19
8 Anisole	0.73	0.32	0.00
9 1-butanol (1-BuOH)	0.47	0.84	0.76
10 Dioxane	0.55	0.37	0.00
11 <i>N,N</i> -Dimethylformamide (DMF)	0.88	0.69	0.00
12 Dimethyl sulfoxide (DMSO)	1.00	0.76	0.00
13 Ethanol (EtOH)	0.54	0.75	0.86
14 Ethyl acetate (EtAc)	0.55	0.45	0.00
15 Formamide (F)	0.97	0.48	0.71
16 Chloroform (TCM)	0.58	0.10	0.20
17 Methanol (MeOH)	0.60	0.66	0.98
18 <i>N,N</i> -dimethylacetamide (DMA)	0.88	0.76	0.00
19 <i>N</i> -methylformamide (NMF)	0.90	0.80	0.62
20 Tetrahydrofuran(THF)	0.51	0.54	0.00

Table S2. Solvent parameters used in Catalán equation [3]

Solvent	SP	SdP	SB	SA	
1	1-methyl-2-pyrrolidinone	0,812	0,959	0,613	0,024
2	1-propanol	0,658	0,748	0,782	0,367
3	2-methyl-1-propanol	0,657	0,684	0,828	0,311
4	2-methyl-2-butanol	-	-	-	-
5	2-propanol	0,633	0,808	0,830	0,283
6	Acetone	0,651	0,907	0,475	0.000
7	Acetonitrile	0,645	0,974	0,286	0,044
8	Anisole	0,820	0,543	0,299	0,084
9	1-butanol	0,674	0,655	0,809	0,341
10	Dioxane	0,737	0,312	0,444	0.000
11	<i>N,N</i> -Dimethylformamide	0,759	0,977	0,613	0,031
12	Dimethyl sulfoxide	0,830	1.000	0,647	0,072
13	Ethanol	0,633	0,783	0,658	0,400
14	Ethyl acetate	0,656	0,603	0,542	0.000
15	Formamide	0,814	1,006	0,414	0,549
16	Chloroform	0,783	0,614	0,071	0,047
17	Methanol	0,608	0,904	0,545	0,605
18	<i>N,N</i> -dimethylacetamid	0,763	0,987	0,650	0,028
19	<i>N</i> -methylformamide	0.814	1.007	0.414	0.549
20	Tetrahydrofuran	0,714	0,634	0,591	0.000

Table S3. Hammett substituent parameters [4]

Substituent	σ_p	Substituent	σ_p	Substituent	σ_p
H	0	3-OH	0.12	4- <i>N,N</i> (CH ₃) ₂	-0.83
2-naphthyl	-	4-F	0.06	4-NO ₂	0.78
4-CH ₃	-0.17	4-Cl	0.23	4-OCH ₃	-0.27
3-CH ₃	-0.07	2,6-diCl	0.80	3,4-(OCH ₃) ₂	-0.15
4-OH	-0.37	2-Cl, 6-F	0.65	3,4,5-(OCH ₃) ₃	-0.03

Results of the characterization of 1-Methyl-2,6-bis[2-(substituted phenyl)ethenyl]pyridinium iodides

1-Methyl-2,6-bis[2-(substituted phenyl)ethenyl]pyridinium iodides were obtained by condensation of 1-methyl-2,6-dimethylpyridinium iodide (0.01 mol) in methanol (40 ml) with various aromatic aldehydes (0.02 mol) under reflux for 2 hours with addition one drop of piperidine. After that, the reaction mixture was cooled to room temperature and the product was filtered. The obtained crystalline products were purified by crystalliation from a suitable solvent.

1-Methyl-2,6-bis[2-(phenyl)ethenyl]pyridinium iodide(I)[5]

Yellow crystals; Yield: 78%; m.p. 254 °C; ¹H NMR (200 MHz, DMSO-*d*₆, δ / ppm): 4.28 (3H, s, =N⁺-CH₃), 7.47-7.49 (4H, *d*, CH₂=CH₂ and pyridine), 7.62-7.27 (6H, *dd*, *J*=30.3 Hz, *J*=15.9 Hz, CH₂=CH₂ and C₆H₄), 7.848-7.872 (4H, *d*, *J*=7.2 Hz, C₆H₄), 8.26-8.29 (2H *m*, C₆H₄), 8.39-8.44 (1H *t*, *J*=7.8 Hz, pyridine); ¹³C NMR (DMSO *d*₆): δ 41.97, 119.09, 124.02, 128.40, 128.91, 130.39, 134.87, 142.22, 143.11, 149.88, 153.10

1-Methyl-2,6-bis[2-(4-hydroxyphenyl)ethenyl]pyridinium iodide (5)[1]

Red crystalline compound; Yield 31 %; m.p. >300 °C; IR (KBr, cm⁻¹): 3441 (O-H stretching of aromatic alcohols), 2934 (=N⁺-CH₃ stretching), 2805(C-H stretching of -CH₃ group attached to nitrogen), 1660, 1603, 1591, 1562, 1514, (C=C stretching of aromatic ring), 1483 (C=C antisymmetric stretching of aromatic ring), 1392, 1391, 1324, 1268, 1231(C-N stretching of pyridine), 1171, 1102 (C-OH stretching), 940, 834 (=CH out of plane deformation of trans alkenes); ¹H-NMR (200 MHz, DMSO-*d*₆, δ / ppm):4.24 (3H, s, -NCH₃), 6.87 (4H, *d*, *J* = 9.0 Hz, C₆H₄), 7.42 (2H, *d*, *J* = 15.6 Hz, CH₂=CH₂), 7.66-7.74 (6H, *m*, C₆H₄ and CH₂=CH₂), 8.17 (2H, *d*, *J* = 7.2 Hz, pyridine), 8.32 (1H, *t*, *J* = 7.2 Hz, pyridine); ¹³C-NMR(50 MHz, DMSO-*d*₆, δ / ppm): 115.4 (-NCH₃), 116.2 (C₁₁), 122.6 (C₇), 126.2 (C₃) (C₅), 130.8 (C₁₀) C₁₂), 142.5 (C₁₄), 142.7 (C₈), 153.8 (C₄), 160.7 (C₂), 162.5 (C₁₃).

1-Methyl-2,6-bis[2-(4-dimethylaminophenyl)ethenyl]pyridinium iodide (II) [6]

Black crystals Yield: 65%, m.p. 204.5-205.2°C, Elem. Anal. Calcd. for C₂₆H₃₀IN₃ (*M*_w = 511.44 g mol⁻¹): C, 61.06; H, 5.91; N, 8.22; %, Found: C, 60.99; H, 5.98; N, 8.17, %; ¹H-NMR (200 MHz, DMSO-*d*₆, δ / ppm):3.02 (12H, s, 4-NCH₃), 4.18 (3H, s, -NCH₃), 6.78 (4H, *d*, *J* = 8.8 Hz, C₆H₂), 7.32 (2H, *d*³, *J* = 16.0 Hz, CH₂=CH₂), 7.65-7.71 (6H, *m*, 2CH=CH₂ and C₆H₂), 8.08 (2H, *d*, *J* = 8.1 Hz, pyridine), 8.00 (1H, *t* *J* = 8.1 Hz, pyridine); ¹³C-NMR(50 MHz, DMSO-*d*₆, δ / ppm): 42.1 (4-NCH₃), 43.4 (N-CH₃), 114.2 (C₁₀), (C₁₁), 115.2 (C₉).

NMR spectra

1-Methyl-2,6-bis[2-(2,6-dichlorophenyl)ethenyl]pyridinium iodide (**9**)

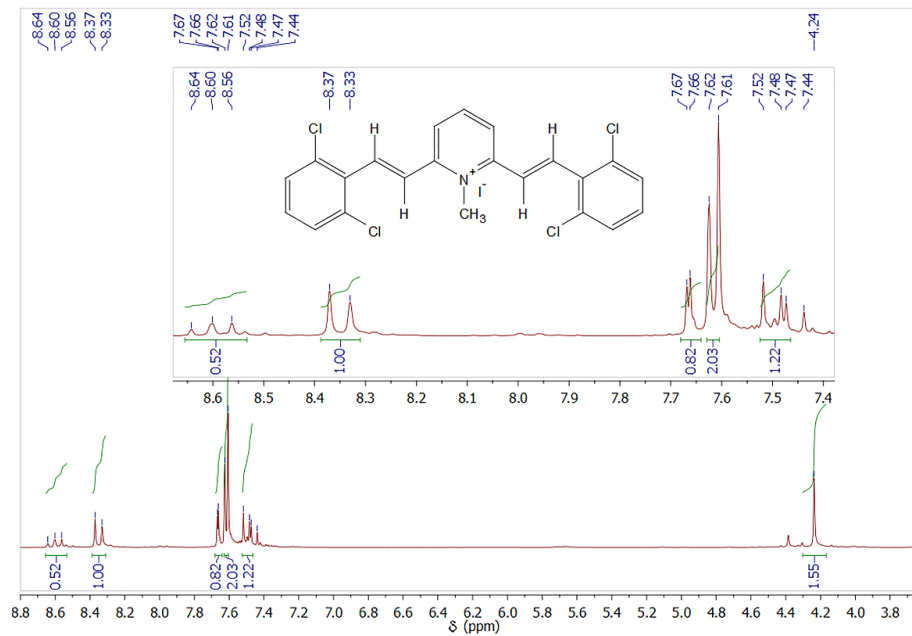


Fig. S1. ¹H NMR spectrum of **9** in DMSO-d₆ recorded at 298 K

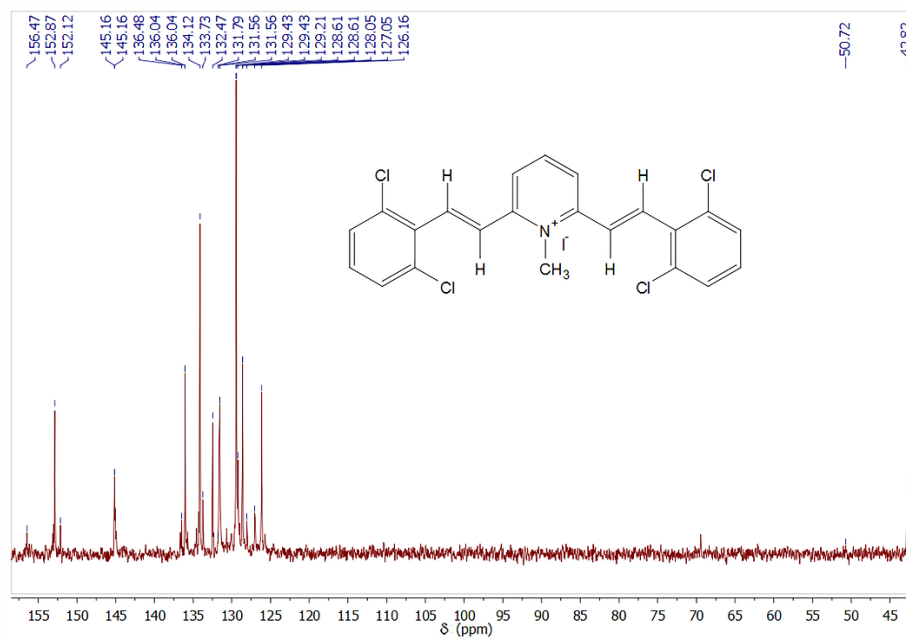


Fig. S2. ¹³C NMR spectrum of **9** in DMSO-d₆ recorded at 298 K

1-Methyl-2,6-bis[2-(3,4-dimethoxy phenyl)ethenyl]pyridinium iodide (14)

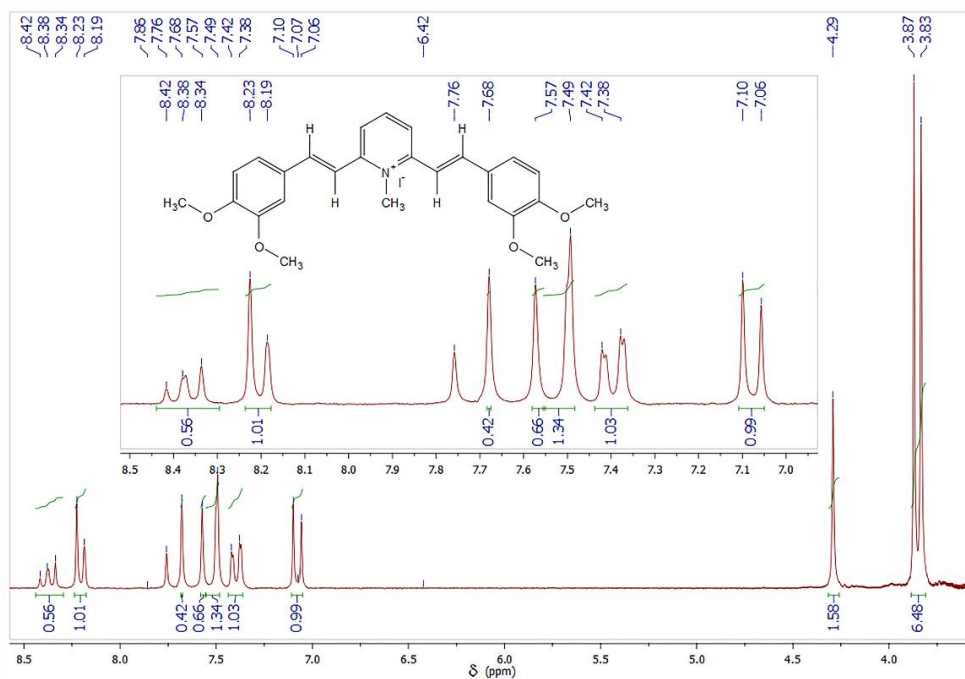


Fig. S3. ¹H NMR spectrum of **14** in DMSO-d₆ recorded at 298 K

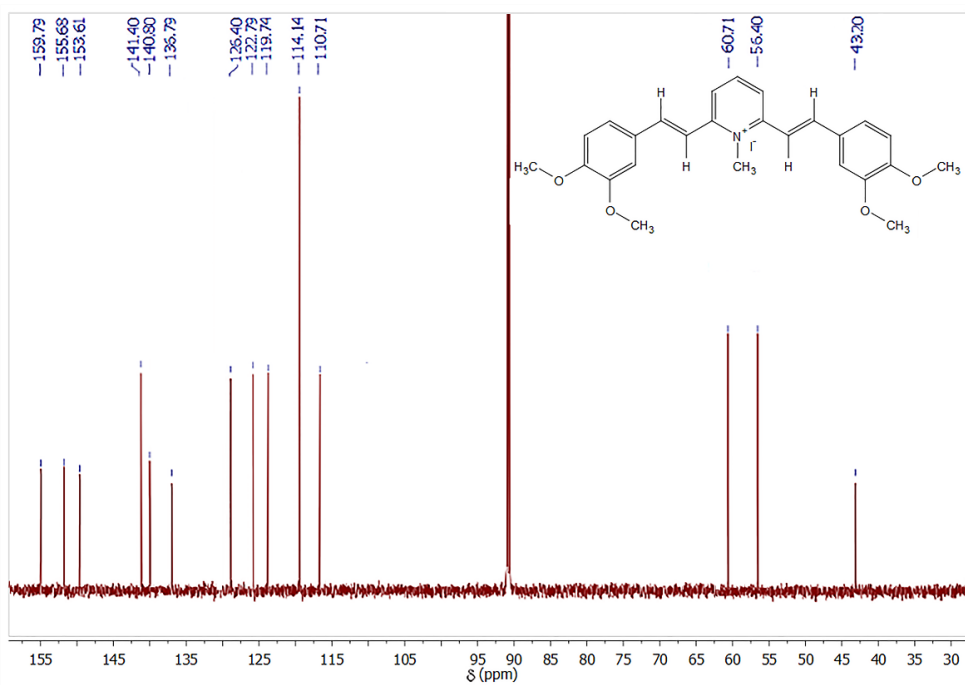


Fig. S4. ¹³C NMR spectrum of **14** in DMSO-d₆ recorded at 298 K

Geometry optimization and TD-DFT calculations

Table S4 Geometrical data for the most stable *s-trans/s-trans* isomer of compounds **1-15** obtained by the use of B3LYP/Def2TZVP method.

Compound/parameter	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Bond distance (Å)															
C1-N1	1.476	1.475	1.475	1.476	1.474	1.476	1.476	1.476	1.479	1.478	1.471	1.478	1.474	1.472	1.473
N1-C2(N1-C6)	1.378	1.380	1.379	1.378	1.381	1.378	1.379	1.379	1.375	1.376	1.384	1.376	1.381	1.382	1.381
C2-C7(C6-C7')	1.450	1.448	1.448	1.450	1.446	1.451	1.450	1.450	1.457	1.454	1.441	1.454	1.446	1.445	1.446
C7-C8(C7'-C8')	1.350	1.353	1.352	1.351	1.354	1.350	1.351	1.351	1.345	1.350	1.360	1.348	1.355	1.356	1.355
C8-C9(C8'-C9')	1.450	1.445	1.447	1.450	1.442	1.452	1.448	1.448	1.459	1.452	1.433	1.455	1.441	1.440	1.443
C12-C15(C12'-C15')			1.501												
C11-C15(C11'-C15')				1.505											
C11-O(C11'-O)						1.356								1.356	1.354
C12-O(C12'-O)					1.348								1.341	1.343	1.349
C13-O(C13'-O)															1.356
C12-F(C12'-F)							1.336								
C10-F(C10'-F)										1.346					
C10-Cl (C10'-Cl)									1.745						
C12-Cl(C12'-Cl)								1.729							
C14-Cl(C14'-Cl)									1.748	1.743					
C12-N2(C12'-N2')											1.359	1.483			
Bond angles (θ)															
C1-N1-C2(C1-N1-C6)	118.8	118.7	118.7	118.7	118.7	118.8	118.8	118.8	118.8	118.8	118.6	118.8	118.7	118.7	118.7
N1-C2-C7(N1-C6-C7')	119.4	119.4	119.4	119.4	119.4	119.4	119.4	119.4	118.9	119.0	119.4	119.3	119.4	119.4	119.4
C2-C7-C8(C6-C7'-C8')	123.5	123.7	123.5	123.5	123.4	123.3	123.5	123.5	122.6	122.2	123.8	123.4	123.6	123.6	123.5
C7-C8-C9(C7'-C8'-C9')	127.6	127.4	127.7	127.5	128.0	127.4	127.7	127.6	129.0	130.9	128.1	127.3	128.0	128.2	128.0
Dihedral angles															
α	10.7	11.2	11.0	10.8	11.2	10.7	10.9	10.9	9.9	10.3	11.9	10.4	11.3	11.8	11.6
β	152.6	154.5	153.5	152.7	154.4	152.2	152.9	153.0	151.1	151.5	157.4	151.0	154.7	155.3	154.8
γ	177.0	176.7	176.9	176.9	176.7	177.0	176.9	176.9	176.6	177.5	176.3	177.1	176.7	176.2	176.6

Solvatochromism of the studied compounds: multi-parameter correlations

Table S5 Absorption frequencies of studied compounds in the selected solvent

Solvent/ Comp.	$\nu_{\max} \times 10^{-3} \text{ (cm}^{-1}\text{)}$														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1-Methyl-2-pyrrolidone (NMP)	26.52	27.35	26.62	27.05	24.86	25.67	21.64	26.44	29.64	30.98	19.99	27.91	24.88	23.87	24.47
1-Propanol (1-PrOH)	26.66	27.68	26.29	26.83	24.25	25.67	21.22	26.98	29.37	31.28	19.36	28.54	25.17	23.83	24.66
2-methyl-1-propanol (iBuOH)	26.63	27.42	26.20	26.84	24.38	25.94	21.19	26.94	29.48	31.21	19.34	28.39	25.26	23.79	24.67
2-methyl-2-butanol (t-AmOH)	26.63	27.38	26.29	27.00	24.65	25.72	21.48	26.84	29.43	31.18	19.71	28.15	25.64	23.81	24.56
2-propanol (iPrOH)	26.75	27.84	26.28	26.94	24.91	25.59	21.33	26.99	29.84	31.32	20.00	28.66	25.09	23.82	24.64
Acetone	26.78	27.77	26.47	27.31	26.13	26.17	21.48	26.77	29.63	29.99	20.10	27.85	25.31	23.75	24.51
Acetonitrile (AcN)	26.66	26.89	26.52	27.11	26.44	26.38	21.82	26.98	29.58	31.14	20.34	27.94	25.25	23.91	24.49
Anisole	26.47	26.66	25.92	26.69	25.68	26.78	21.13	26.61	29.61	29.79	18.98	28.64	24.85	22.80	24.26
1-Butanol (1-BuOH)	26.61	27.47	26.26	26.89	24.46	25.98	21.16	26.89	29.40	31.29	19.12	28.58	25.50	23.81	24.55
1,4-Dioxane	26.01	27.28	26.52	27.25	24.86	26.47	21.79	26.52	29.64	30.84	20.07	27.99	25.37	23.71	24.53
<i>N,N</i> -dimethylformamide (DMF)	26.78	27.99	26.65	27.24	24.99	25.67	21.61	26.92	29.63	30.99	20.10	27.35	25.08	23.72	24.64
Dimethyl sulfoxide (DMSO)	26.88	27.92	26.59	27.13	24.95	26.25	21.58	26.89	29.59	31.04	20.02	27.58	25.04	23.73	24.69
Ethanol (EtOH)	26.86	27.05	26.29	26.86	24.59	26.20	21.48	26.94	29.57	31.21	20.02	28.64	25.06	23.83	24.68
Ethylacetate (EtAc)	26.03	27.67	26.51	27.25	24.30	25.59	21.80	26.75	29.80	30.02	19.99	27.75	25.31	23.74	24.52
Formamide (F)	26.80	27.47	26.23	26.95	24.61	26.29	21.73	26.94	29.45	31.25	19.86	28.53	25.04	23.79	24.79
Chloroform (TCM)	26.47	26.87	25.96	26.97	26.52	26.66	21.72	26.75	29.72	30.86	19.00	28.15	24.88	22.80	24.24
Methanol (MeOH)	26.81	27.66	26.11	26.95	24.84	26.07	21.39	26.99	29.70	31.16	20.16	28.55	25.05	23.77	24.69
<i>N,N</i> -dimethylacetamide (DMA)	26.65	27.16	26.55	27.05	24.72	26.21	21.58	26.43	29.64	30.89	19.62	28.72	24.90	23.86	24.51
<i>N</i> -methylformamide (NMF)	26.80	27.32	26.38	26.93	24.58	25.85	21.55	26.96	29.69	31.58	19.94	28.64	24.96	23.82	24.71
Tetrahydrofuran (THF)	26.84	26.95	26.63	27.10	24.29	25.58	21.82	26.59	29.63	30.86	20.00	28.22	25.29	23.71	24.40

Nature of molecular orbital: TD-DFT study

Table S6. Calculated energies of the HOMO and LUMO orbitals and E_{gap} for *s-trans/s-trans* isomer of the investigated compounds **1-15** in DMSO.

Molecule	HOMO, eV	LUMO, eV	E_{gap} , eV
1	-7.6987	-1.9657	5.7330
2	-7.3667	-2.0199	5.3468
3	-7.5002	-1.9135	5.5866
4	-7.6484	-1.9436	5.7048
5	-7.2515	-1.8441	5.4074
6	-7.6626	-1.9775	5.6851
7	-7.6414	-1.9597	5.6817
8	-7.6663	-2.0440	5.6223
9	-8.0700	-2.0936	5.9764
10	-7.9354	-2.1096	5.8258
11	-6.5176	-1.6938	4.8239
12	-8.1247	-2.4459	5.6788
13	-7.1859	-1.8420	5.3439
14	-7.0743	-1.8838	5.1904
15	-7.1792	-1.9174	5.2618

Bond length and occupying coefficient for quantifying the push-pull effect in studied compounds

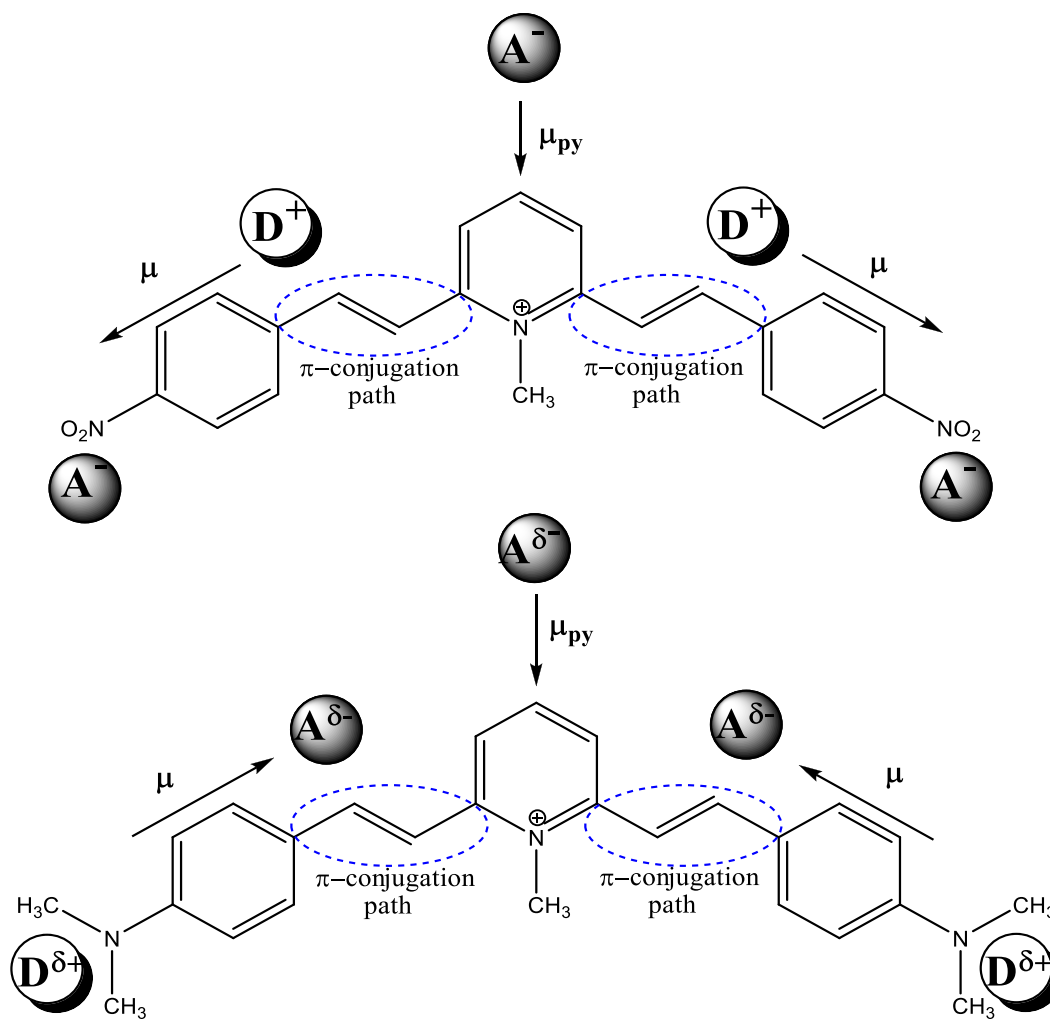


Fig. S5. Presentation of the contribution of local dipole moments

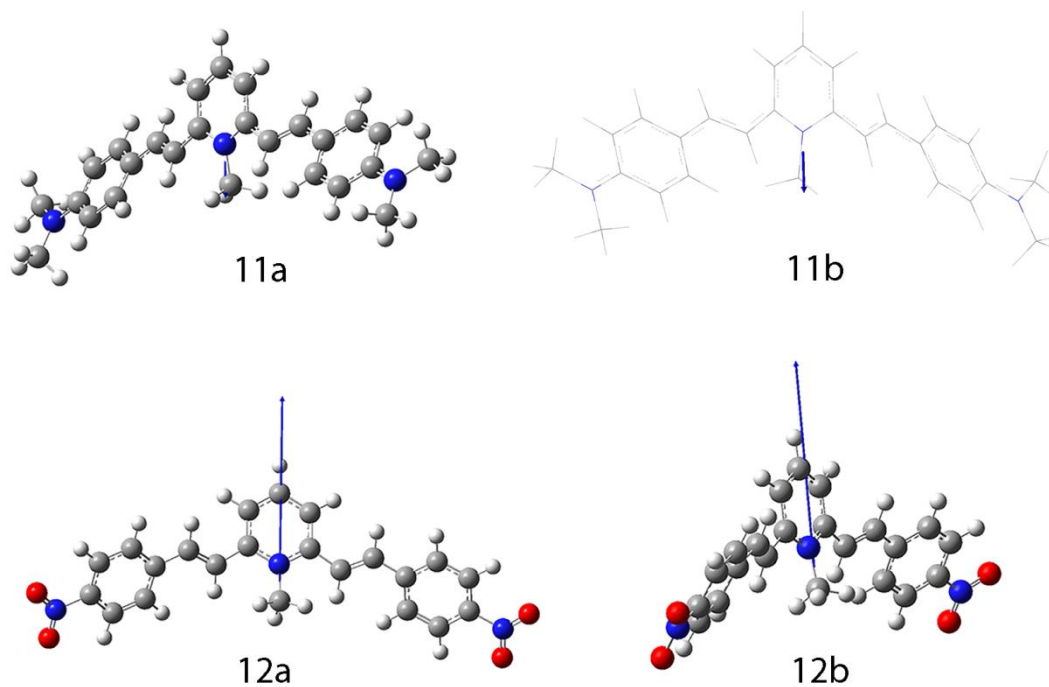


Fig.S6. Calculated summary vectors for compounds with the strongest electron donating (11) and accepting (12) substituents

Chemical shift differences $\Delta\delta$ for quantifying the push-pull effect

Table S7. Selected ^{13}C NMR chemical shifts (δ , ppm) and $\Delta\delta_{\text{C7-C8}}$ values of **1-15**

Compound	δ_{C7}	δ_{C8}	$\Delta\delta_{\text{C7-C8}}$
1	124.02	134.87	10.85
2	124.50	134.60	10.1
3	124.3	134.5	10.2
4	124.25	134.7	10.45
5	122.6	142.7	20.1
6	124.43	136.61	12.18
7	124.28	141.43	17.15
8	124.31	139.48	15.17
9	126.16	136.48	10.32
10	128.12	137.52	9.4
11	123.6	145.2	21.6
12	124.6	132.8	8.2
13	126.3	141.71	15.41
14	126.4	141.21	14.81
15	126.35	140.65	14.3

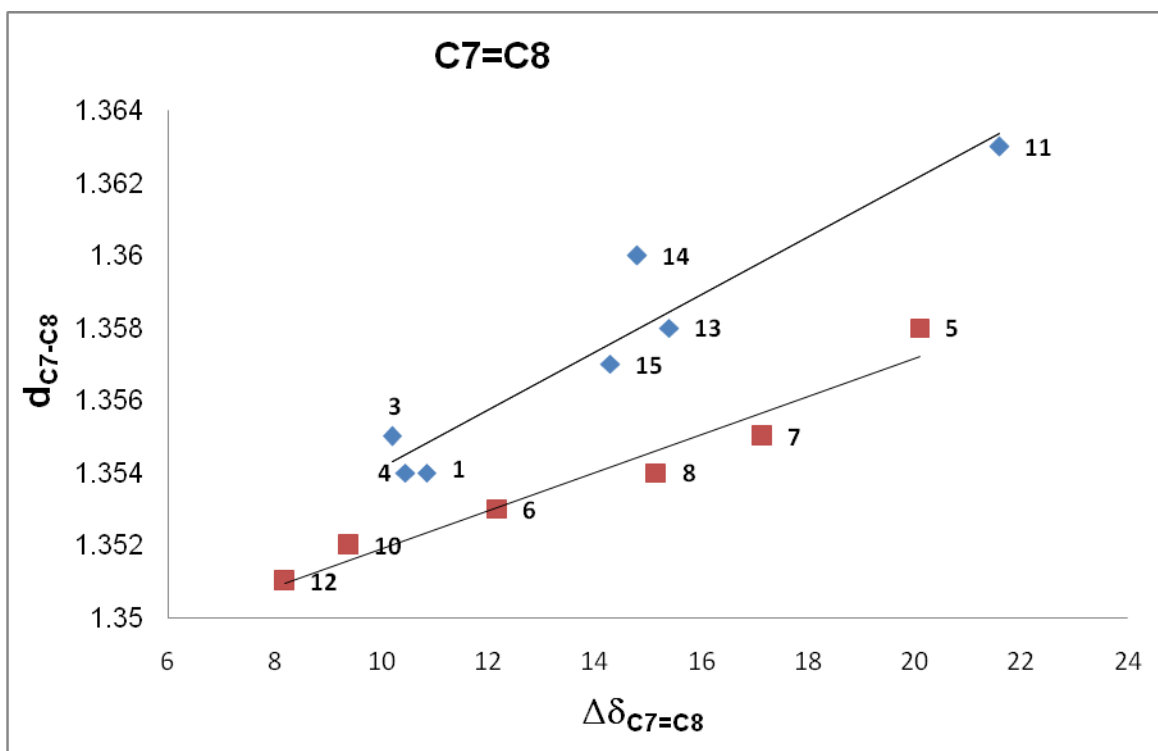


Fig. S7. The concept of the correlation of $d(C_7=C_8)$ versus $\Delta\delta_{C_7=C_8}$ used for the evaluation of push-pull effect

Liner free energy relationships (LFER) analysis of NMR data

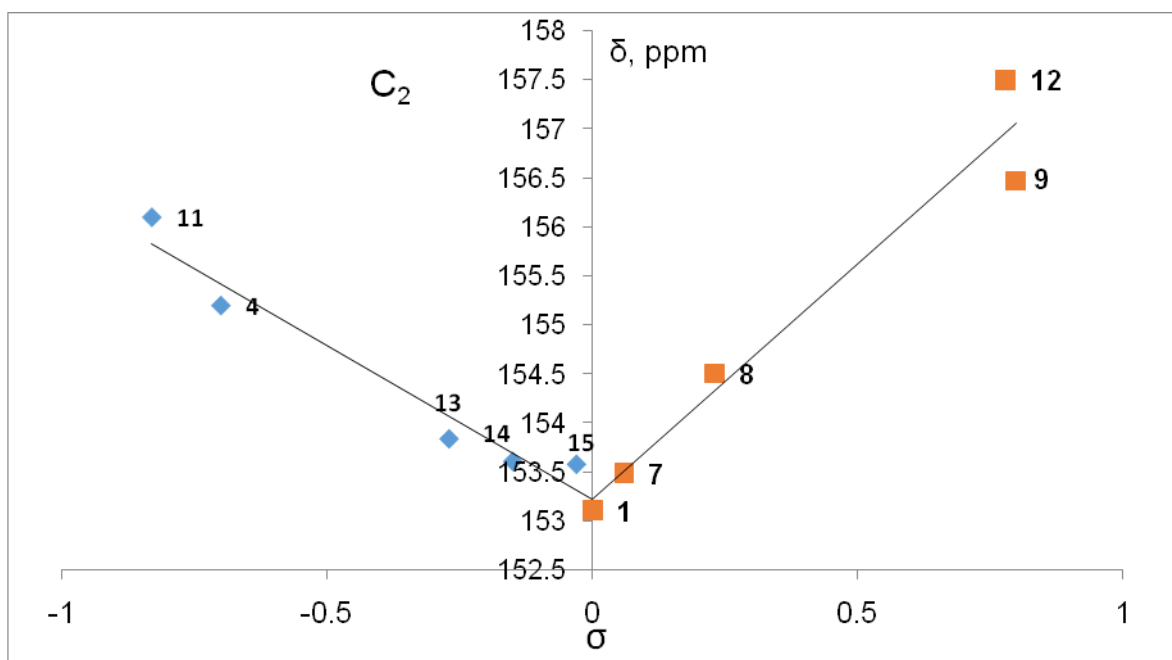


Fig.S8. Correlations of ^{13}C NMR chemical shifts of C₂ carbon for investigated compounds

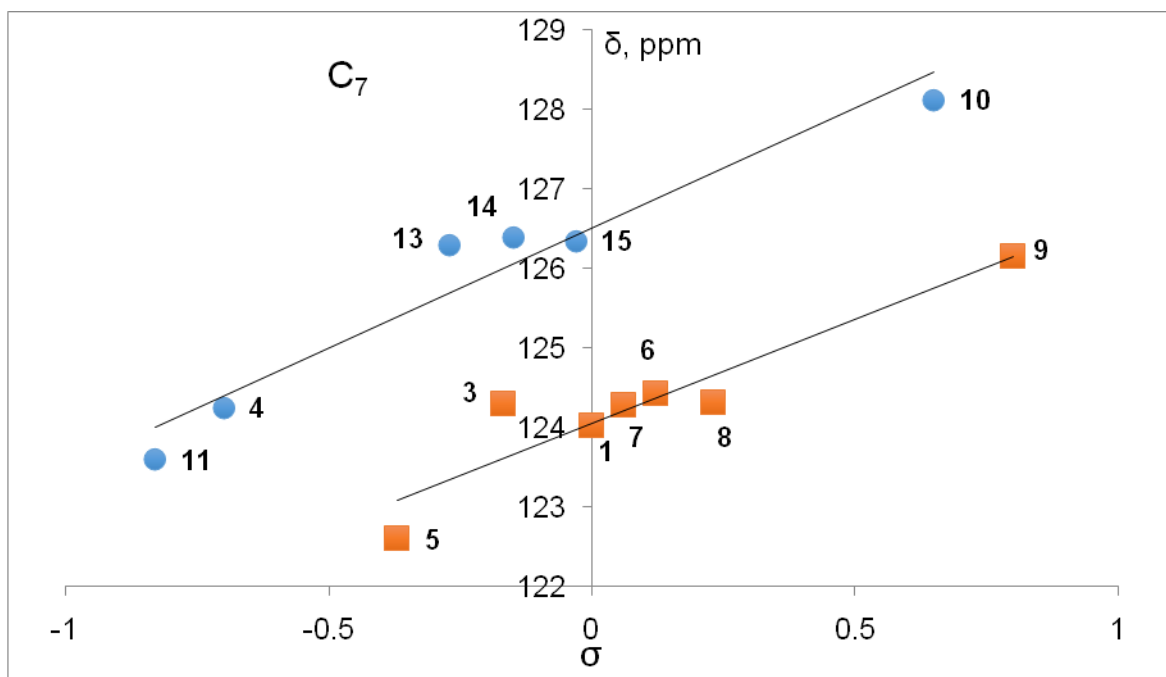


Fig.S9. Correlations of ^{13}C NMR chemical shifts of C₇ carbon for investigated compounds

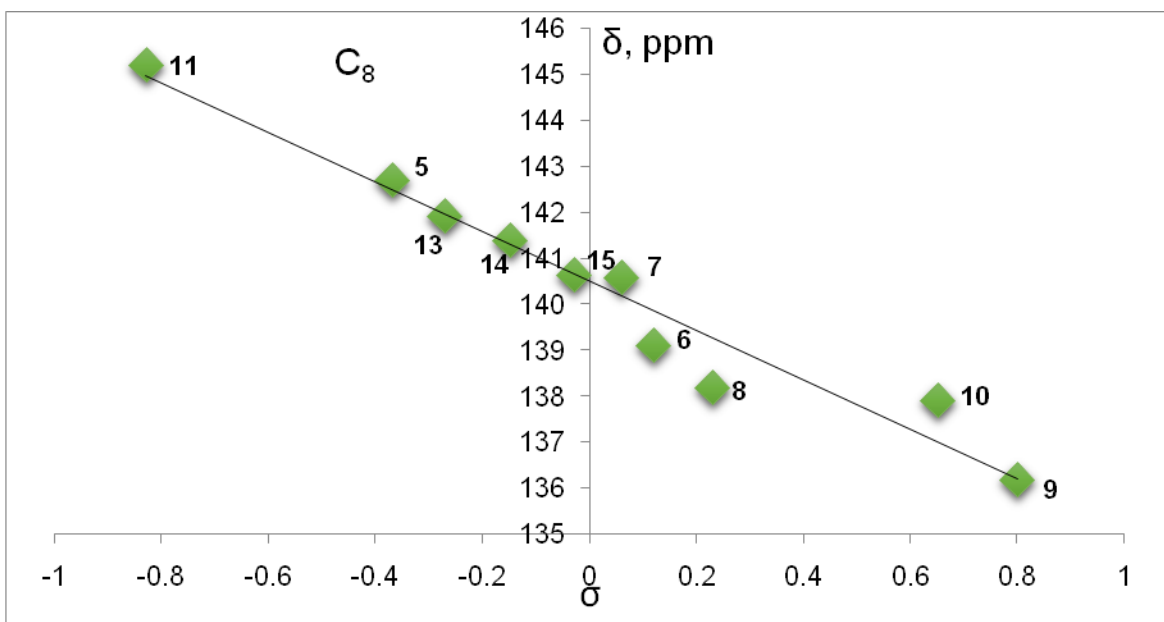


Fig.S10. Correlations of ^{13}C NMR chemical shifts of C8 carbon for investigated compounds

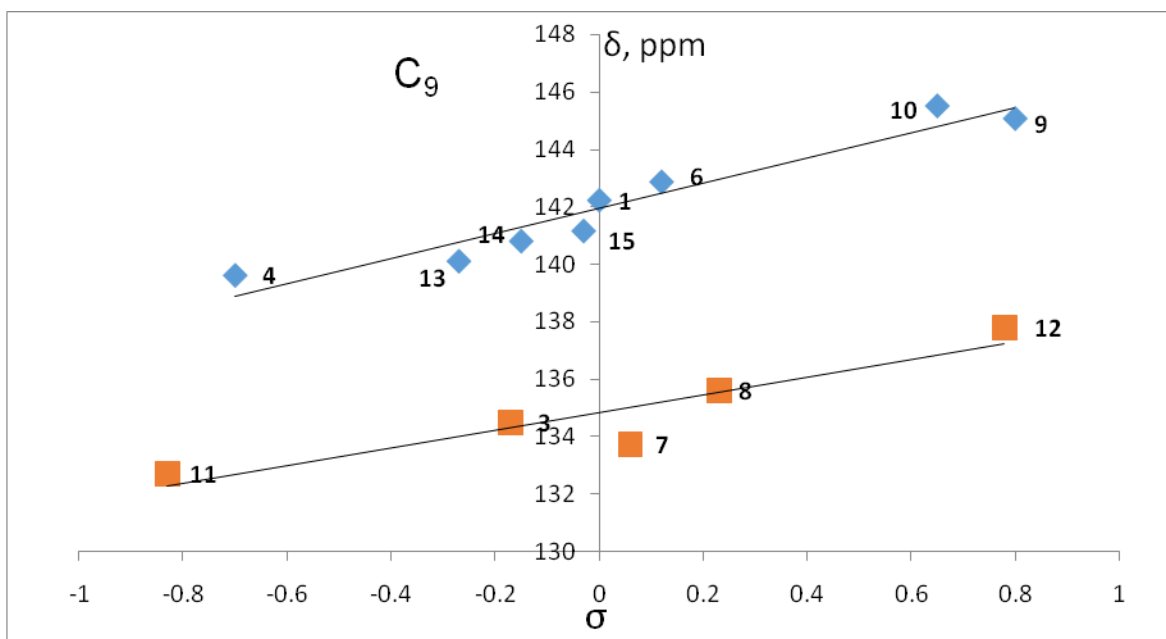


Fig.S11. Correlations of ^{13}C NMR chemical shifts of C9 carbon for investigated compounds

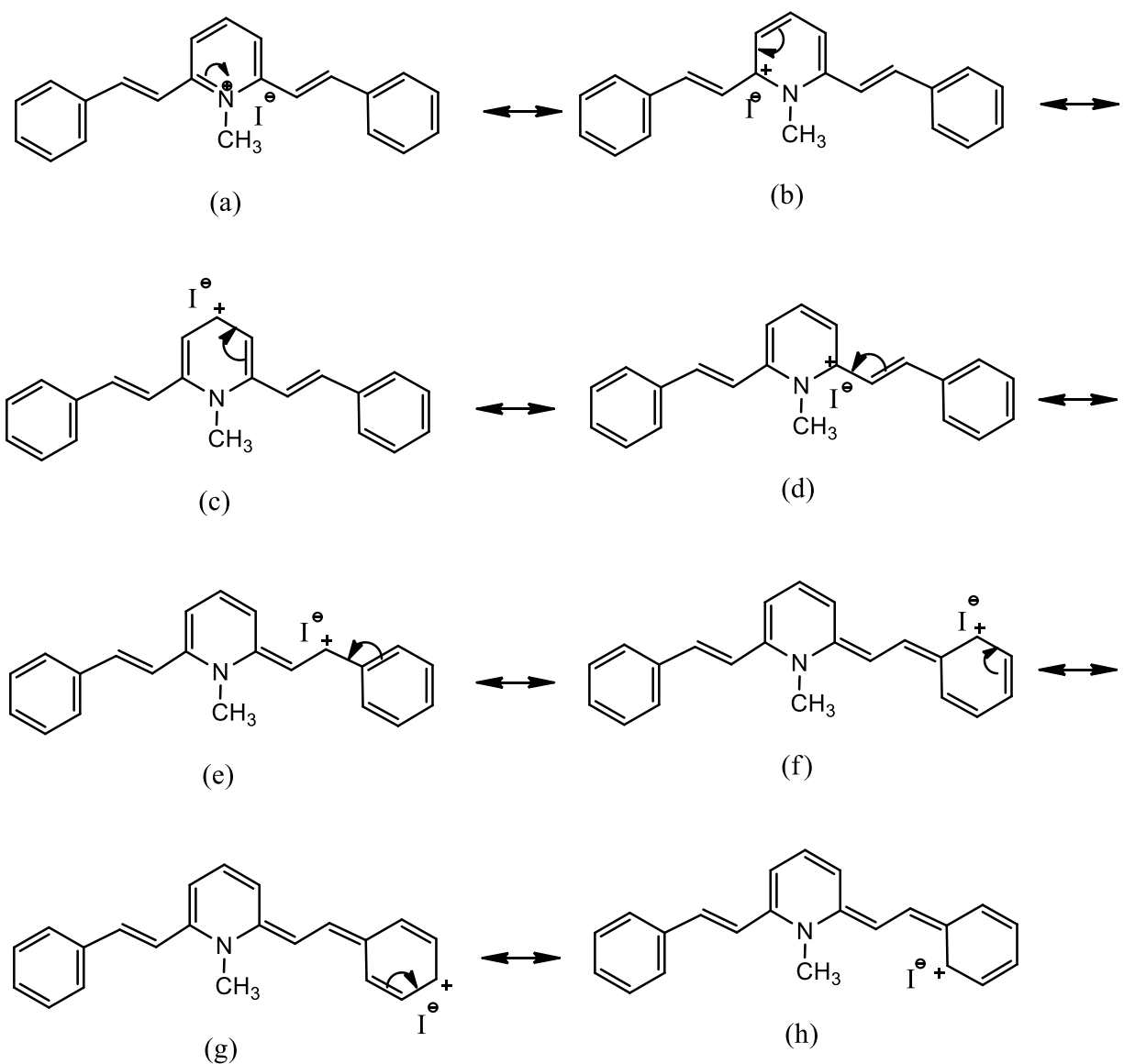


Fig.S12 Resonance structures of investigated compound given as example for unsubstituted compound **1**

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