Azulene-substituted Pyridines and Pyridinium Salts. Synthesis and Structure. 2. Azulene-substituted Pyridinium salts

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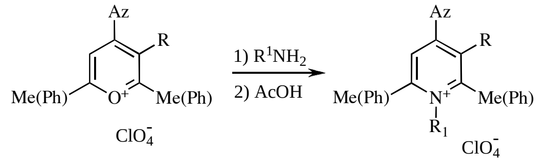

Az = unsubstituted or substituted azulen-1-yl
R = H or Me, Ph
R^1 = Me, Bu, *i*Pr, Bn, Ph, *t*Bu

4-Azulen-1-yl substituted 2,6-dimethyl-and 2,6-diphenyl-pyridinium salts are obtained in yields between 50 % and 100 % in the reaction of corresponding 4-azulen-1-yl-pyranylim salts and various amines. The effects of amine structure and of substitution in the heterocycle or at azulene moieties on the synthesis have been investigated. The uv-vis and NMR spectra of reaction products are examined and discussed in correlation with their structure.

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INTRODUCTION

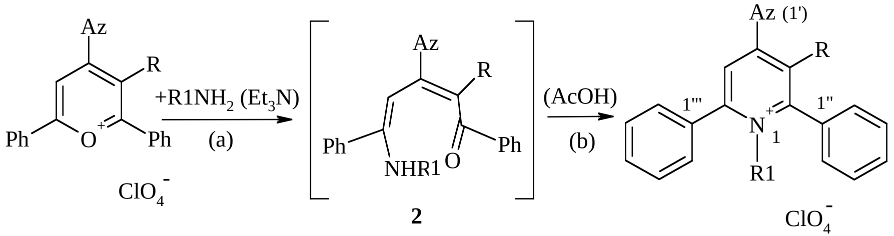
In our previous study focused on the substitution of oxygen atom in 4-azulen-1-yl-pyranylium salts by nitrogen, we have reported the synthesis of pyridine compounds [1]. The next step of the study, presented in this paper, consists of the synthesis of pyridinium salts starting from 2,6-diphenyl- or 2,6-dimethyl-substituted 4-azulen-1-yl-pyranylium salts. The salts arising from oxygen substitution allow us to investigate the influence of N-substituents on both structure and some properties of the obtained compounds. The presence of positive charge in these compounds, as in the corresponding pyranylium salts [2], changes the charge density over the whole structure, *vis a vis* the uncharged pyridines, affording salts with a high intensity of push-pull effect. Therefore, we consider that interesting conclusions can be drawn from comparison of pyridine, pyridinium salts and pyranylium salts.

RESULTS AND DISCUSSION

A. Synthesis of pyridinium salts. For the preparation of N-substituted pyridinium salts we have adapted one of the most widely used methods, namely the treatment of pyranylium salt with an amine [3a]. In the reaction development two steps can be distinguished, the pyranylium ring opening (step a in Scheme 1) with the generation of an enamine, in the presence of a tertiary amine and the ring closure with water elimination, promoted by acetic acid, wherein the pyridinium system is obtained (step b).

After several preliminary attempts we have found that the best experimental protocol required an equimolar

Scheme 1



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1 R = H
8 R = Me; Az = azulen-1-yl;
9 R = Ph; Az = azulen-1-yl

3 R = H
10 R = Me, R1 = Bu, Az = azulen-1-yl
11 R = Ph, R1 = Bu, Az = azulen-1-yl

The numbers of compounds **3** when Az is unsubstituted or substituted and R1 = Me, Bu, *i*Pr, Bn, Ph or *t*Bu are shown in Table 1.

mixture of amine and triethylamine for each mole of pyranylium salt for reaction step (a) along with 2 equivalents of acetic acid for the step (b). The obtained 2,6-diphenyl-pyridinium salts and the reaction conditions are reported in Scheme 1 and Table 1 and for the corresponding 2,6-dimethyl derivatives in Scheme 2 and Table 2.

The yields for the first series of compounds are over 80 % and for the last one between 50 and 80 %. For the generation of N-methyl-pyridinium salts, methylammonium chloride was used instead of volatile methylamine, and to the reaction mixture one equivalent of potassium acetate was added as buffer. The obtained yields exceeded 50%.

The ring opening, step (a), occurred quickly (about 30 minutes) and independently of the used pyranylium salt or even of amine. However the closure of generated enamines, step (b), strongly depended on the pyranylium substituents and on the amine structure.

Table 1

Synthesis of 4-Azulen-1-yl-2,6-diphenyl-pyridinium perchlorates

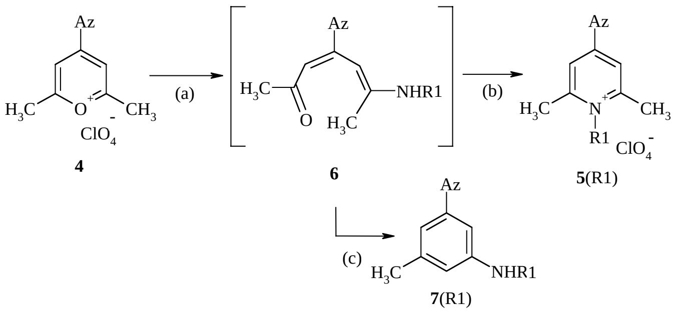
Comp.	Az Subst.	R1	R	Reaction time (days)[a]	Yield (%)
3a	H	Bu	H	2	100
3b	3-Me	Bu	H	2	84
3c	4,8-Me_2	Bu	H	2	85
3d	4,6,8-Me_3	Bu	H	2	100
3e	5-*i*Pr,3,8-Me_2	Bu	H	1	81
3f	2-*t*Bu, 6-Me	Bu	H	1	80
3g[b]	H	Me	H	2	63
3h	H	*i*Pr	H	1	86[c]
3i	H	Bn	H	1	85
3j	H	Ph	H	1	93[d]
3k	H	*t*Bu	H	2	trace
10	H	Bu	Me	1	67
11	H	Bu	Ph	1	85

[a] For step (b); for step (a) the reaction time was 1 hour. [b] Starting from pyranylium salt and N-methylammonium chloride; reaction time 2 days. [c] After 3 days yield was 81 %. [d] After 6 days yield was 94 %.

As shown by the experimental data, the strong electron donating character of azulene hinders to some extent the intermediate reactivity as compared with other substituents, *e.g.* phenyl [3a]+[3b]. The ring closure, (step b), for the 2,6-diphenyl derivatives occurred with more difficulty than that for 2,6-dimethyl compounds because the steric hindrance produced by the tendency of aromatic rings to conform co-planar in the products. Due to this difference, 1-2 days were necessary for the closure of 2,6-diphenyl intermediates **2** (Table 1) and only 1/4h-24h were enough for 2,6-dimethyl intermediates **6**.

For the synthesis of 2,6-dimethyl-pyridinium derivatives, **5**, other difficulties were encountered due to the generation of anilines **7** as by-products (Scheme 2). The aniline results from the intramolecular condensation of the highly reactive methyl groups, path (c) in Scheme 2. This ring closure seems thermodynamically more favorable in comparison with the pyridinium ring closure, mostly when crowded amines were used. Similar intermolecular condensation at methyl groups produced some amount of tar, lowering the yield in 2,6-dimethyl-pyridinium salts.

Scheme 2



Az substituents (in **4**, **5** or **7**) = H (**a**); 4,6,8-Me_3 (**d**); 2-tBu,6-Me (**f**)
R1 (in **4** and **5**) = Me; *i*Pr; Bn; Ph
R1 (in **7**) = *i*Pr

Taking into account the steric and electronic effects of substituent in $R1NH_2$ the reactivity of amines used must decrease in order $BnNH_2$ > $BuNH_2$ > $iPrNH_2$ > $PhNH_2$ >> $tBuNH_2$ [4]. Nevertheless, as it results from Tables 1 and 2, the generation of pyridinium salts, starting from 4-pyranylium salts seems to be only slightly influenced by amine excepting when *t*$BuNH_2$ was used as reagent. For this amine, the reaction with 2,6-diphenyl derivatives produced traces of **3k** together with a large amount of open compound 3-azulen-1-yl-1,5-diphenyl-pent-2-ene-1,5-dione, **12**, deriving from hydrolysis of the intermediate enamine. Using 2,6-dimethyl derivatives only traces of N-*t*Bu-aniline **7**(*t*Bu) were detected in the mass spectra of the reaction mixture.

Table 2

Synthesis of 4-azulen-1-yl-2,6-dimethyl-pyridinium perchlorates (**5**), and 3-azulen-1-yl-5-methylanilines (**7**).[a]

Comp.	Az Subst.	R1	Reaction Time[b]	Yield (%)
5a	H	Me[c]	1 day	55
		*i*Pr	90 min	50 + **7a**(*i*Pr) in 25 %
		Ph	1 day	58
		Bn	15 min	79
5d	4,6,8-Me_3	Me[a]	1 day	50
		*i*Pr	90 min	67 + **7d**(*i*Pr) in 9 %
		Ph	1 day	60
		Bn	15 min	72
5f	2*t*-Bu,6-Me	*i*Pr	90 min	56 + **7f**(*i*Pr) in 5 %
		Ph	1 day	49
		Bn	15 min	64

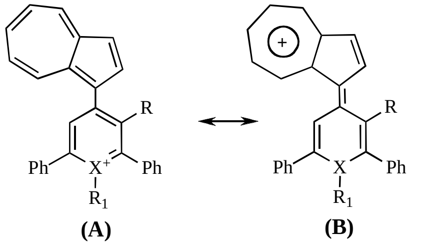
[a] Traces of anilines **7** were generated in almost all reactions of pyranylium salts with amines (only mass spectra were recorded when small amount of anilines was obtained). [b] The first reaction step occurred in 30 minutes.

While the separation and purification of 2,6-diphenyl-pyridinium salts can be accomplished by column chromatography, the same operation with the corresponding dimethyl products occurred with severe decomposition on the column. For the last compounds only dissolution and precipitation could be used with loss of the products, however. The substitution at azulene moiety seems to have a little importance in the reaction development.

B. Comparison between the influence of structural features on spectra of pyridinium salts and on corresponding pyridines and pyranylium salts. *NMR-spectra analysis*. Although the NMR spectra of 2,4,6-triaryl-pyranylium and 2,4,6-triaryl-pyridinium salts were studied extensively and the correlation between the structure of salts and their ^{1}H and ^{13}C chemical shifts are well explained [5], no such research has been reported when aryl is an azulene moiety. Therefore, we report here some considerations about the peculiarities of NMR spectra for pyridines and pyridinium salts substituted by an azulene, with particular focus on comparing their chemical shifts with those previously obtained for the corresponding pyranylium salts [2].

From the analysis of the most important contributing resonance structures (A) and (B) of 4-azulen-1-yl substituted charged heterocycles (Scheme 3), some previous hypotheses regarding the charge distribution and, therefore, the spectral properties of these classes of compounds can be advanced. The contribution of "tropylium" structure (B) decreases the charge density at the azulene moiety, mainly at the seven membered ring, enhancing its "aromaticity". At the same time, the influence exerted by the positive charge of heteroatom on the heterocyclic protons and carbon atoms is diminished. The co-planarity ensures the highest conjugation between the two connected moieties and at a dihedral angle of 90^{o} this property is completely missing, thus the contribution of structure (B) is absent. In order to evaluate the contribution of conjugation we have calculated the dihedral angle between the azulene and heterocycle moieties for some of the studied compounds [6]. Although the obtained values must be regarded with prudence due to the limits of used method, several qualitative observations can be drawn. All obtained values of the dihedral angles for out-of-plane forms of pyridinium salts are a little higher than those for pyranylium salts, possibly due to the better conjugation in the last salts. The presence of substituent R at C3 in the heterocycle or the substitution of azulene at the position 2' or 8' increases the dihedral angle therefore the conjugation between the two cycles decreases.

Scheme 3



X = N; R1 = alkyl or aryl
X = O unsubstitued

Recently we have shown that some of these suppositions regarding NMR spectra are confirmed for pyranylium salts [2]. Therefore, we have desired to establish the general validity of advanced hypotheses comparing the chemical shifts found for these salts with those for the corresponding pyridines, **13** and **14,** (Scheme 4) or pyridinium salts (Table 4). In the course of this comparison we have also included the chemical shifts of 1-phenyl-azulene, **12**, and 2,4,6-triphenyl-pyridinium salts **15** [7].

Table 3

Calculated dihedral angle between azulene and heterocycle moieties[a]

Az Substituent	Heterocyclic substituents	Dihedral angle (^{0}) For pyranylium salts	For pyridinium salts [b]
H	2,6-Ph$_2$	24	29
H	2,6-Ph$_2$-3-Me	38	42
H	2,6-Ph$_2$-3-Ph	41	52
4,6,8-Me$_3$	2,6-Ph$_2$	39	40
2-tBu-6-Me	2,6-Ph$_2$	50	56
H	2,6-Me$_2$	22	28
4,6,8-Me$_3$	2,6-Me$_2$	41	48
2-*t*Bu-6-Me	2,6-Me$_2$	45	54

[a] All values are calculated for N-Me pyridinium salts. [b] For 4-azulen-1-yl-2,6-diphenylpyridine the dihedral angle = 45 ^{0}.

The deshielding of azulene protons increases in series 1-phenylazulene < pyridines < pyridinium salts < pyranylim salts, *e.g*. **12** < **13**Ph < **3a** < **1a** or **12 < 13**Me < **5a** < **4a**; usually the azulene protons 4'-, 6'- and 8'-H are more deshielded (Table 4). The observed order follows, generally, the decrease in dihedral angle between the connected moieties and reflects the increase in their conjugation. The differences are not so accentuated for the 2,6-dimethyl series possibly due to the leveling inductive effect of the methyl groups which stabilize the positive charge at the heteroatom. At the same time the C3-substitution of heterocyclic ring (compound **10**) [8] or the presence of alkyl groups at C2' or C8' of azulene (compounds **3c-f**) increases the dihedral angle diminishing the conjugation**.** As a result, an upfield displacement of all azulene protons is produced. It is interesting to note that with the increase in dihedral angle the magnetic field of heterocycle changes in direction disturbing mainly the azulenic protons 2'- and 8'-H. Thus the proton 2'-H in compounds **13**Ph and **3a** without a substituent at C3 is deshielded by ≈ 0.2 ppm compared to the methyl-substituted compounds **14** and **10**, and the proton 8'-H is even more deshielded, with ≈ 0.5 ppm. More changed seems to be the direction of the heterocycle magnetic field when the azulene is substituted at C2' with *t*Bu group; in this case the order of chemical shifts for 4'-H and 8'-H is reversed compared to those of other compounds from the studied series.

Next we considered to what extent the chemical shifts for heterocyclic 3-H and 5-H depend on the conjugative and anisotropic effect of azulene moiety, on the influence of the substituents in 2 and 6 positions, and on the nature of N$^+$-substituent. Comparing the chemical shifts of 3- and 5-H for triphenyl derivative **15** (7.95 ppm in $CDCl_3$+TFA) [5] with those for compounds **3** (between 8.14 and 8.49 ppm), it is easy to see the large anisotropic influence of the azulene moiety (Table 5). The inductive and/or anisotropic effects of the two pyridinium methyl or phenyl substituents act differently; therefore, the heterocycle protons for **5** are shielded compared to **3**. As previously noted, the presence of alkyl or benzyl groups bonded to the ammonium center can stabilize the positive charge compared with phenyl, therefore for the first compounds the heterocycle protons are shielded.

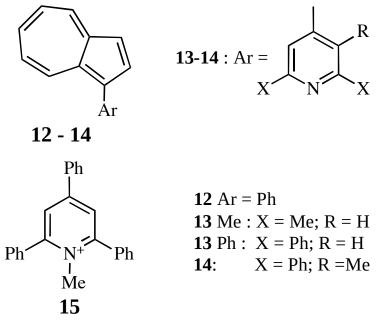
Table 4

Proton chemical shifts for azulene in 1-aryl substituted azulenes

Compd.	Azulene protons (δ in ppm)						
	2'-H	3'-H	4'-H	5'-H	6'-H	7'-H	8'-H
3a[a]	8.59	7.66	8.74	7.68	8.03	7.68	9.15
1a[a]	8.92	7.77	8.89	8.03	8.31	8.14	9.57
13Ph[c]	8.18	7.53	8.44	7.28	7.72	7.29	8.71
10[a]	8.22	7.63	8.55	7.51	7.92	7.55	8.67
14[c]	7.99	7.50	8.42	7.24	7.65	7.19	8.21
5a R1= Me[b]	8.40	7.61	8.66	7.58	7.99	7.63	8.94
4a[b]	8.45	7.51	8.65	7.77	8.07	7.80	9.12
13Me[c]	7.95	7.36	8.30	7.15	7.57	7.17	8.52
Azulene[c]	7.81	7.30	8.23	7.05	7.45	7.05	8.23
12[c,]	8.02	7.43	8.34	7.14	7.58	7.14	8.55

[a] In acetone-d_6. [b] In DMSO-d_6. [c] In $CDCl_3$

Scheme 4



12 - 14

15

12 Ar = Ph
13 Me : X = Me; R = H
13 Ph : X = Ph; R = H
14: X = Ph; R =Me

C. Roussel, A. T. Balaban *et al.* [9] established that some groups, like *i*Pr substituted at 1-position of pyridinium ring, can induce the non equivalency of chemical shifts for protons 3-H and 5-H due to the eclipsed conformation of this group towards the plane of heterocycle. Therefore, another target of this research was to establish if the N-substitution with *i*Pr plays the same role for our salts. As it can be seen in Table 5, the protons 3-H and 5-H really become non-equivalent for 2,6-dimethyl compounds **5a**(*i*Pr), **5d**(*i*Pr) and **5f**(*i*Pr). Moreover, the different chemical shifts for 2 and 6-methyl groups in these compounds were also observed due the rigid conformation of *i*Pr group. However, this phenomenon was not observed for 2,6-diphenyl compound **3h,** possibly due to the leveling effect of the strong magnetic field generated by the neighbouring phenyl groups.

From the ^{13}C NMR spectra, described in the experimental section, a similar influence of the structure on chemical shifts can be observed, albeit to a smaller extent.

Table 5

Chemical shifts of pyridinium protons (2H) in 4-azulen-1-yl-pyridinium perchlorates 2,6-diphenyl- and 2,6-dimethyl-substituted

R1							
Me	Bu[a]		*i*Pr		*t*Bu	Bn	Ph
3g	**3a**		**3h**		**3k**	**3i**	**3j**
8.33	8.32		8.20		8.14	8.40	8.49
5a	-	**5a**	**5d**	**5f**	-	**5a**	**5a**
(Me)		(*i*Pr)	(*i*Pr)	(*i*Pr)		(Bn)	(Ph)
8.14	-	8.06	7.44	7.87	-	8.31	8.39
		and	and	and			
		8.08[b]	7.41[b]	7.90[b]			

[a]Chemical shift for 5-H in **10** δ = 8.02 ppm. [b]Each signal for 1H; for 2- and 6-CH_3 protons δ (in ppm; each signal for 3H) for **5a**(*i*Pr) = 2.84 and 2.90, **5d**(*i*Pr) = 2.90 and 2.95 and **5f**(*i*Pr) = 2.95 and 3.00.

UV-Viz-spectra analysis. With the increase of overall polarization as a consequence of more and more advanced π-electron delocalization, the increase of both bathochromic and hypsochromic effects in the order pyridines, pyridinium salts, pyranylium salts results from the uv-vis spectra (Table 6).

Table 6

UV-Viz absorption of 4-azulen-1-yl-2,6-diphenyl-heterocycles

Comp.	L1(log ε)	L2(log ε)	L3(log ε)	L4(log ε)	L5(log ε)
1a	218 (4.35)	257 (4.35)	280 (4.41)	382 (4.15)	517 (4.36)
3a	217 (4.40)	233 (4.49)	286 (4.35)	326(4.12) 343(4.08)	434 (4.35)
13Ph	217 (4.46)	243 (4.53)	279 (4.46)	300(4.40) 313sh (4.32)	370 (3.93)

Any structure change that involves another distribution of π-electrons in molecules affects the electronic spectra of the compounds, mainly in the visible range. Thus the alkyl substitution on the azulene moiety stabilizes the tropylium like structure (B) (Scheme 3) in order **3e** (with 5*i*Pr,3,8-Me_2) > **3d** (with 4,6,8-Me_3) > **3c** (with 4,8-Me_2) > **3f** (with 2-tBu,6-Me) > **3a** and produces a bathochromic displacement (despite the slight increase in the dihedral angle between azulene and heterocycle). At the same time, the presence of the two methyl groups at pyridinium induces a hypsochromic effect, as compared to the corresponding compound with two phenyl groups. While the salts with electron releasing groups (Me, Bu, *i*Pr) at pyridinium nitrogen absorb at longer wave lengths, the N-substitution with deficient electron groups (phenyl, benzyl) generates a contrary effect.

CONCLUSION

The results of this paper constitute a detailed examination of the synthesis of 1-substituted pyridinium salts with an azulene moiety at 4-position. Starting from the pyranylium salts and amines, the pyridinium salts were obtained in yields from 50 % to 100 %. The high electron donating aptitude of azulene, together with the good withdrawing effect of the charged heteroatom, ensures a valuable push-pull property of the obtained compounds. The charge displacement produced by this property as well as the effect of the dihedral angle between the two connected moieties on the NMR and electronic spectra were carefully analyzed. The experimental results confirm the good agreement between the calculated dihedral angles and spectral properties of the compounds. The comparative analysis of the structure of pyranylium salts, pyridinium salts, and pyridines illustrates the existent differences between the spectroscopic characteristics of the compounds belonging to these three series. The interesting behaviour of some compounds upon change of the substituent(s) in the azulenyl-pyridinium or even azulenyl-pyranylium salts has motivated us to continue this research by the study of their atropisomerism and possible enantiomerism. The research on the synthesis and properties of pyridines and pyridinium salts with azulene in other positions is also in progress.

EXPERIMENTAL

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B; uv-vis spectra: Specord UV-VIS-spectrometer Zeiss Jena.; ^{1}H- and ^{13}C-NMR: Bruker ARX 500 (^{1}H: 500 MHz, ^{13}C: 125.75 MHz) and Bruker Avance DRX4 (^{1}H: 400 MHz, ^{13}C: 100.62 MHz) spectrometers, chemical shifts (δ) are expressed in ppm, and *J* values are given in Hz, TMS was used as internal standard in DMSO-d_6, acetone-d_6 and $CDCl_3$, the signals were assigned on the basis of COSY, HETCOR and HMBC experiments; mass spectra: JEOL JMS-DX303 spectrometer coupled to analytical gas-chromatograph Shimadzu GC-14B with a DB-1 capillary column and C-R6A integrator and Finnigan MAT 311-A/100 MS; for the spectra recording in solid state: Carlo Erba QMD 1000 (EI+, 70 eV). Column chromatography: silica gel [70-230 mesh (ASTM)]. Dichloromethane (DCM) was distilled over CaH_2, and diethyl ether was conserved on NaOH and freshly distilled on $LiAlH_4$. The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06). The numbering of atom positions, used for the pyridinium salts characterization, is described in Scheme 1 and 2. For the salts **3** when R = H positions 1" = 1"'. Pyranylium perchlorates are obtained as described in literature [2].

Procedure for the preparation of the pyridinium salts. Under inert atmosphere (to avoid the air humidity), pyranylium perchlorate (1 mmol), corresponding amine (1 mmol), and triethylamine (1 mmol) were dissolved in DCM (40 ml) with magnetically stirring, at room temperature, and the stirring was continued for 30-60 min depending on the used salt (Table 1 and 2). Then acetic acid (2 mmol) was added and the reaction mixture was stirred at room temperature for a period showed in Table 1 and 2. For the 2,6-dimethyl-pyridinium salts, to the reaction mixture ethyl ether was added to induce salt precipitation. Then, the salts were filtered, and from the filtrate the generated aniline was separated by column chromatography on silica gel with a mixture of *n*-pentane:DCM = 5:1. The analytical pure 2,6-dimethyl-pyridinium salts were obtained by re-precipitation with ethyl ether from a solution in DCM. For 2,6-diphenyl-pyridinium salts, after the solvent vaporization, the products were separated from the residue by column chromatography on silica gel with DCM and ethanol (from 0 to 5%). The obtained compounds and the yields are reported in Table 1 and 2.

Procedure for the preparation of N-methyl-pyridinium salts. Methylammonium chloride (1 mmol) and potassium acetate (1 eq.) were dissolved in DCM (50 ml/mmol) and magnetically stirred for 30 min. at room temperature. Then the pyranylium salt (1 mmol) was added, and the stirring was continued over night. The next day, after solvent removal, the 2,6-diphenyl derivatives were separated by column chromatography as previously described. 2,6-Dimethyl derivatives were precipitated with ethyl ether directly from the reaction mixture. The filtered residue was again dissolved in DCM and washed three times with water for removal of KCl. Then the organic layer was dried and the DCM was vaporized. The obtained compounds and the yields are reported in Table 1 and 2.

4-(Azulen-1-yl)-1-butyl-2,6-diphenyl-pyridinium perchlorate, (3a). This compound was obtained as brown crystals; mp 103-4 °C; uv-vis (MeOH, λ_{max}, log ε): 223 (4.44), 234 (4.50), 283 (4.36), 333 (4.10), 344 (4.10), 434 (4.39) nm; ^{1}H nmr (acetone-d_6): δ 0.48 (t, J = 7.2 Hz, 3 H, CH_3), 0.85-0.95 (m, 2 H, CH_3CH_2), 1.50-1.62 (m[10], 2 H, $CH_2CH_2CH_2$), 4.50-4.52 (m, 2 H, NCH_2), 7.66 (d, J = 4.0 Hz, 1 H, 3'-H), 7.68 (t, J = 10.0 Hz, 2 H, 5'-H, 7'-H), 7.74-7.76 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.93-7.96 (m, 4 H, 2"-H, 6"-H), 8.03 (t, J = 9.9 Hz, 1 H, 6'-H), 8.32 (s, 2 H, 3-H, 5-H), 8.59 (d, J = 4.4 Hz, 1 H, 2'-H), 8.74 (d, J = 9.6 Hz, 1 H, 4'-H), 9.15 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 13.67 (CH_3), 20.58 (CH_3CH_2), 33.03 ($CH_2CH_2CH_2$), 55.38 (NCH_2), 122.1 (C3'), 125.5 (C1'), 128.4 (C3, C5), 129.7 (C5'), 130.1 (C7'), 130.8 (C2", C3", C5", C6"), 132.5 (C4"), 137.8 (C8'), 140.0 (C3a'), 140.5 (C2'), 141.0 (C4'), 142.3 (C6'), 148.0 (C8a'), 153.9 (C4), 157.3 (C2, C6) ppm; ms [EI]: m/z 414 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{31}H_{28}ClNO_4}$: C, 72.49; H, 5.50; N, 2.73; Cl, 6.81. Found: C, 72,35; H, 5,78; N, 2.61; Cl, 6.89.

1-Butyl-4-(3-methyl-azulen-1-yl)- 2,6-diphenyl-pyridinium perchlorate, (3b). This compound was obtained as brown crystals; mp 86 ºC; uv-vis (MeOH, λ_{max}, log ε): 222 (4.39), 237 (4.46), 288 (4.41), 347 (4.17), 455 (4.33) nm; ^{1}H nmr (acetone-d_6): δ 0.45 (t, J = 7.2 Hz, 3 H, $\mathrm{CH_3}$), 0.85-0.95 (m, 2 H, $\mathrm{CH_3C}H_2$), 1.48-1.60 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.66 (s, 3 H, 3'-Me), 4.40-4.50 (m, 2 H, $\mathrm{NC}H_2$), 7.55 (t, J = 10.0 Hz, 1 H, 5'-H), 7.57 (t, J = 10.0 Hz, 1 H, 7'-H), 7.71-7.72 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.90-7.97 (m, 5 H, 6'-H, 2"-H, 6"-H), 8.21 (s, 2 H, 3-H, 5-H), 8.40 (s, 1 H, 2'-H), 8.55 (d, J = 9.6 Hz, 1 H, 4'-H), 9.00 (d, J = 9.6 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 11.75 (3'-Me), 12.12 ($\mathrm{CH_3}$), 19.01 ($\mathrm{CH_3}C\mathrm{H_2}$), 31.46 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 53.70 ($\mathrm{N}C\mathrm{H_2}$), 121.4 (C1'), 126.5 (C3, C5), 127.0 (C7'), 128.1 (C5'), 128.4 (C3'), 129.2 (C2", C6"), 129.3 (C3", C5"), 130.9 (C4"), 135.7 (C1"), 135.9 (C8'), 136.3 (C4'), 138.9 (C3a'), 139.5 (C2'), 140.5 (C6'), 143.1 (C8a'), 151.3 (C4), 155.5 (C2, C6) ppm; ms (15 eV): m/z 428 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{32}H_{30}ClNO_4}$: C, 72.79; H, 5.73; N, 2.65; Cl, 6.71. Found: C, 72.75; H, 5.86; N, 2.58; Cl, 6.66.

1-Butyl-4-(4,8-dimethyl-azulen-1-yl)-2,6-diphenyl-pyridinium perchlorate, (3c). This compound was obtained as brown crystals; mp 93 ºC; uv-vis (MeOH, λ_{max}, log ε): 219 (4.33), 232 (4.33), 246 (4.41), 292 (4.29), 343 (4.00), 446 (4.17) nm; ^{1}H nmr (acetone-d_6): δ 0.46 (t, J = 7.4 Hz, 3 H, $\mathrm{CH_3}$), 0.82-0.93 (m, 2 H, $\mathrm{CH_3C}H_2$), 1.51-1.62 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.87 (s, 3 H, 4'-Me), 2.98 (s, 3 H, 8'-Me), 4.42-4.50 (m, 2 H, $\mathrm{NCH_2}$), 7.49 (d, J = 10.8 Hz, 1 H, 5'-H), 7.52 (d, J = 10.8 Hz, 1 H, 7'-H), 7.55 (d, J = 4.4 Hz, 1 H, 3'-H), 7.70-7.71 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.76 (t, J = 10.2 Hz, 1 H, 6'-H), 7.88-7.90 (m, 4 H, 2"-H, 6"-H), 7.95 (s, 2 H, 3-H, 5-H), 8.17 (d, J = 4.4 Hz, 1 H, 2'-H) ppm; ^{13}C nmr (acetone-d_6): 12.11 ($C\mathrm{H_3CH_2}$), 19.03 ($\mathrm{CH_3}C\mathrm{H_2}$), 24.45 (8'-Me), 29.1 (4'-Me), 31.49 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 53.85 ($\mathrm{N}C\mathrm{H_2}$), 117.1 (C3'), 125.3 (C1'), 128.7 (C3, C5), 129.1 (C2", C6"), 129.2 (C3", C5"), 129.5 (C7'), 130.9 (C5', C4"), 133.5 (C1"), 135.6 (C3a'), 136.9 (C6'), 139.4 (C2'), 143.2 (C8a'), 148.8 (C8'), 149.6 (C4'), 154.5 (C4), 154.8 (C2, C6) ppm; ms (15 eV): m/z 442 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{33}H_{32}ClNO_4}$: C, 73.12; H, 5.95; N, 2.58; Cl, 6.54. Found: C, 73.05; H, 5.89; N, 2.53; Cl, 6.48.

1-Butyl-4-(4,6,8-trimethyl-azulen-1-yl)-2,6-diphenyl-pyridinium perchlorate, (3d) This compound was obtained as brown crystals; mp 89 ºC; uv-vis (MeOH, λ_{max}, log ε): 220 (4.35), 231 (4.35), 247 (4.44), 292 (4.32), 349 (4.07), 450 (4.25) nm; ^{1}H nmr (acetone-d_6): δ 0.45 (t, J = 7.4 Hz, 3 H, $\mathrm{CH_3}$), 0.85-0.95 (m, 2 H, $\mathrm{CH_3C}H_2$), 1.50-1.61 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.67 (s, 3 H, 6'-Me), 2.92 (s, 3 H, 4'-Me), 3.04 (s, 3 H, 8'-Me), 4.39-4.55 (m, 2 H, $\mathrm{NC}H_2$), 7.44 (s, 1 H, 5'-H), 7.45 (d, J = 4.0 Hz, 1 H, 3'-H), 7.47 (s, 1 H, 7'-H), 7.70-7.72 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.80-7.95 (m, 4 H, 2"-H, 6"-H), 7.89 (s, 2 H, 3-H, 5-H), 8.04 (d, J = 4.4 Hz, 1 H, 2'-H) ppm; ^{13}C nmr (acetone-d_6); δ 12.12 ($C\mathrm{H_3CH_2}$), 19.04 ($\mathrm{CH_3}C\mathrm{H_2}$), 24.75 (8'-Me), 27.36 (6'-Me), 29.1 (4'-Me), 31.47 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 53.75 ($\mathrm{N}C\mathrm{H_2}$), 117.2 (C3'), 125.3 (C1'), 128.4 (C3, C5), 129.2 (C2", C3", C5", C6"), 130.8 (C4"), 131.3 (C7'), 132.3 (C5'), 133.5 (C1"), 134.5 (C3a'), 138.1 (C2'), 142.0 (C8a'), 147.6 (C8'), 148.3 (C4'), 148.8 (C6'), 154.4 (C4), 154.7 (C2, C6) ppm; ms (15 eV): m/z 456 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{34}H_{34}ClNO_4}$: C, 73.44; H, 6.16; N, 2.52; Cl, 6.38. Found: C, 73.35; H, 6.13; N, 2.50; Cl, 6.28.

1-Butyl-2,6-diphenyl-4-(5-*iso*-propyl-3,8-dimethyl-azulen-1-yl)-pyridinium perchlorate, (3e). This compound was obtained as brown crystals; mp 107 ºC; uv-vis (MeOH, λ_{max}, log ε): 219 (4.28), 231 (4.28), 246 (4.39), 296 (4.28), 351 (4.02), 475 (4.26) nm; ^{1}H nmr (acetone-d_6): δ 0.47 (t, J = 7.2 Hz, 3 H, $\mathrm{CH_3}$), 0.83-0.93 (m, 2 H, $\mathrm{CH_3C}H_2$), 1.40 (d, J = 6.8 Hz, 6 H, $\mathrm{C}H_3\mathrm{CH}$), 1.53-1.60 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.66 (s, 3 H, 3'-Me), 2.84 (s, 3 H, 8'-Me), 3.26 (hept, J = 6.8 Hz, 1 H, $\mathrm{(CH_3)_2C}H$), 4.45-4.49 (m, 2 H, $\mathrm{NC}H_2$), 7.48 (d, J = 10.8 Hz, 7'-H), 7.71-7.74 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.81 (dd, J = 10.8, 2.0 Hz, 1 H, 6'-H), 7.89 (s, 2 H, 3-H, 5-H), 7.90-7.92 (m, 4 H, 2"-H, 6"-H), 8.10 (s, 1 H, 2'-H), 8.45 (d, J = 2.0 Hz, 1 H, 4'-H) ppm. ^{13}C nmr (acetone-d_6): δ 13.53 (3'-Me), 13.67 ($C\mathrm{H_3CH_2}$), 20.57 ($\mathrm{CH_3}C\mathrm{H_2}$), 25.34 ($C\mathrm{H_3CH}$), 29.88 (8'-Me), 33.04 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 39.27 ($\mathrm{(CH_3)_2}C\mathrm{H}$), 55.19 ($\mathrm{N}C\mathrm{H_2}$), 123.6 (C1'), 128.6 (C3'), 129.9 (C3, C5), 130.7 (C2", C6"), 130.8 (C3", C5"), 132.4 (C4"), 133.3 (C7'), 135.2 (C1"), 136.2 (C4'), 137.8 (C3a'), 138.3 (C6'), 142.5 (C2'), 144.0 (C8a'), 147.7 (C5'), 148.9 (C8'), 155.2 (C4), 157.3 (C2, C6) ppm; ms (15 eV): m/z 484 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{36}H_{38}ClNO_4}$: C, 74.02; H, 6.56; N, 2.40; Cl, 6.07. Found: C, 74,06; H, 6,63; N, 2.35; Cl, 6.15.

1-Butyl-4-(2-*tert*-butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-pyridinium perchlorate, (3f). This compound was obtained as brown crystals; mp 103 ºC; uv-vis (MeOH, λ_{max}, log ε): 222 (4.42), 235 (4.43), 291 (4.34), 346 (3.85), 442 (3.85) nm; ^{1}H nmr (acetone-d_6): δ 0.49 (t, J = 7.2 Hz, 3 H, $\mathrm{CH_3}$), 0.87-0.97 (m, 2 H, $\mathrm{CH_3C}H_2$), 1.45 (s, 9 H, tBu), 1.62-1.69 (m, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.64 (s, 3 H, 6'-Me), 4.61-4.64 (m, 2 H, $\mathrm{NCH_2}$), 7.26 (d, J = 10.4 Hz, 1 H, 7'-H), 7.31 (d, J = 10.0 Hz, 1 H, 5'-H), 7.44 (s, 1 H, 3'-H), 7.71-7.73 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.93-7.96 (m, 4 H, 2"-H, 6"-H), 8.04 (d, J = 9.6 Hz, 1 H, 4'-H), 8.05 (s, 2 H, 3-H, 5-H), 8.32 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 13.65 ($C\mathrm{H_3CH_2}$), 20.62 ($\mathrm{CH_3}C\mathrm{H_2}$), 28.59 (6'-Me), 32.88 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 33.57 ($Me_3\mathrm{C}$), 36.08 ($\mathrm{Me_3}C$), 56.33 ($\mathrm{N}C\mathrm{H_2}$), 118.1 (C3'), 123.6 (C1'), 127.6 (C3, C5), 128.0 (C5'), 128.3 (C7'), 130.7 (C2", C6"), 130.8 (C3", C5"), 132.6 (C4"), 133.5 (C1"), 137.5 (C8'), 139.7 (C3a'), 140.6 (C4'), 148.0 (C8a'), 151.3 (C6'), 156.8 (C4), 159.6 (C2, C6), 161.1 (C2') ppm; ms (15 eV): m/z 484 [M$^+$, 100]. *Anal.* Calcd. for $\mathrm{C_{36}H_{38}ClNO_4}$: C, 74.02; H, 6.56; N, 2.40; Cl, 6.07. Found: C, 73,95; H, 6,68; N, 2.34; Cl, 6.16.

4-(Azulen-1-yl)-2,6-diphenyl-1-methyl-pyridinium perchlorate, (3g). This compound was obtained as brown crystals; mp 86 ºC; uv-vis (MeOH, λ_{max}, log ε): 217 (4.40), 233 (4.49), 286 (4.35), 326 (4.12), 343 (4.08), 434 (4.35) nm; ^{1}H nmr (acetone-d_6): δ 3.99 (s, 3 H, NMe), 7.66 (d, J = 4.0 Hz, 1 H, 3'-H), 7.67 (t, J = 10.0 Hz, 1 H, 5'-H), 7.69 (t, J = 10.0 Hz, 1 H, 7'-H), 7.71-7.76 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.93-7.96 (m, 4 H, 2"-H, 6"-H), 8.03 (t, J = 9.9 Hz, 1 H, 6'-H), 8.33 (s, 2 H, 3-H, 5-H), 8.59 (d, J = 4.4 Hz, 1 H, 2'-H), 8.73 (d, J = 9.6 Hz, 1 H, 4'-H), 9.14 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 46.21 (N*Me*), 121.9 (C3'), 124.8 (C1'), 127.6 (C3, C5), 129.5 (C5'), 129.7 (C7'), 130.8 (C2", C6"), 130.9 (C3", C5"), 132.6 (C4"), 137.7 (C8'), 139.8 (C3a'), 140.4 (C2'), 140.9 (C4'), 142.2 (C6'), 147.6 (C8a'), 135.2 (C1"), 153.5 (C4), 157.9 (C2, C6) ppm; ms [EI]: m/z 372 [M$^+$, 100].*Anal.* Calcd. for $\mathrm{C_{28}H_{22}ClNO_4}$: C, 71.32; H, 4.71; N, 2.97; Cl, 7.42. Found: C, 71,26; H, 4,88; N, 2.86; Cl, 7.50.

4-(Azulen-1-yl)-2,6-diphenyl-1-(*iso*-propyl)-pyridinium perchlorate, (3h). This compound was obtained as brown crystals; mp 89 ºC; uv-vis (MeOH, λ_{max}, log ε): 222 (4.15), 235 (4.23), 284 (4.12), 333 (3.86), 345 (3.91), 443 (4.17) nm; ^{1}H nmr (acetone-d$_6$): δ 1.44 (t, J = 7.2 Hz, 6 H, CH$_3$), 5.18 (t, J = 7.2 Hz, 1 H, NCH), 7.63 (d, J = 4.0 Hz, 1 H, 3'-H), 7.66 (t, J = 10.0 Hz, 2 H, 5'-H, 7'-H), 7.72-7.75 (m, 6 H, 3"-H, 4"-H, 5"-H), 7.89-7.93 (m, 4 H, 2"-H, 6"-H), 8.01 (t, J = 9.9 Hz, 1 H, 6'-H), 8.20 (s, 2 H, 3-H, 5-H), 8.52 (d, J = 4.4 Hz, 1 H, 2'-H), 8.72 (d, J = 9.6 Hz, 1 H, 4'-H), 9.09 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d$_6$): δ 24.42 (Me), 63.55 (N*C*H), 122.1 (C3'), 124.6 (C1'), 128.4 (C3, C5), 129.7 (C5'), 130.1 (C7'), 130.3 (C2", C6"),131.3 (C3", C5"), 132.3 (C4"), 136.1 (C1"), 137.7 (C8'), 140.1 (C3a'), 140.5 (C2'), 140.9 (C4'), 142.3 (C6'), 147.8 (C8a'), 152.5 (C4), 158.2 (C2, C6) ppm; ms (20 eV) m/z 400 [M$^+$, 10], 358 (M-iPr, 100). *Anal.* Calcd. for C$_{30}$H$_{26}$ClNO$_4$: C, 72.12; H, 5.25; N, 2.81; Cl, 7.01. Found: C, 72,21; H, 5,34; N, 2.72; Cl, 7.09.

4-(Azulen-1-yl)-1-benzyl-2,6-diphenyl-pyridinium perchlorate, (3i). This compound was obtained as brown crystals; mp 260 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 215 (4.42), 234 (4.42), 287 (4.26), 336 (4.03), 345 (4.03), 443 (4.32) nm; ^{1}H nmr (acetone-d$_6$) (benzyl atoms X'''): δ 5.82 (s, 2 H, NC*H*$_2$), 6.50 (dt, J = 7.2, 1.2 Hz, 2 H, 2'''-H, 6'''-H), 7.18 (tt, J = 7.2, 1.2 Hz, 2 H, 3'''-H, 5'''-H), 7.22 (tt, J = 7.2, 1.2 Hz, 1 H, 4'''-H), 7.59 (tt, J = 7.2, 1.2 Hz, 4 H, 3"-H, 5"-H), 7.63 (tt, J = 7.2, 1.2 Hz, 2 H, 4"-H), 7.68 (d, J = 4.0 Hz, 1 H, 3'-H), 7.73 (t, J = 10.2 Hz, 1 H, 5'-H), 7.74 (t, J = 10.2 Hz, 1 H, 7'-H), 7.79 (dt, J = 7.2, 1.2 Hz, 4 H, 2"-H, 6"-H), 8.06 (t, J = 9.9 Hz, 1 H, 6'-H), 8.40 (s, 2 H, 3-H, 5-H), 8.64 (d, J = 4.4 Hz, 1 H, 2'-H), 8.76 (d, J = 9.6 Hz, 1 H, 4'-H), 9.22 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d$_6$) δ 59.05 (N*C*H$_2$), 122.3 (C3'), 124.6 (C1'), 127.8 (C2''', C6'''), 128.3 (C3, C5), 129.6 (C4'''), 130.1 (C1'''), 130.3 (C3''', C5'''), 130.4 (C5'), 130.6 (C7', C3", C5"), 130.8 (C2", C6"), 132.4 (C4"), 135.0 (C1"), 138.0 (C8'), 140.5 (C3a'), 140.7 (C2'), 141.0 (C4'), 142.4 (C6'), 148.2 (C8a'), 154.0 (C4), 158.0 (C2, C6) ppm; ms [EI] m/z 448 [M$^+$, 100].*Anal.* Calcd. for C$_{34}$H$_{26}$ClNO$_4$: C, 74.52; H, 4.78; N, 2.56; Cl, 6.47. Found: C, 74.43; H, 4,85; N, 2.48; Cl, 6.57.

4-(Azulen-1-yl)-1,2,6-triphenyl-pyridinium perchlorate, (3j). This compound was obtained as brown crystals; mp 234 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 223 (4.40), 235 (4.44), 285 (4.31), 331 (4.10), 343 (4.13), 442 (4.39) nm; ^{1}H nmr (acetone-d$_6$) (N-phenyl atoms X'''): δ 7.70 (d, J = 4.0 Hz, 1 H, 3'-H), 7.72 (t, J = 10.0 Hz, 1 H, 5'-H or 7'-H), 7.73 (t, J = 10.0 Hz, 1 H, 7'-H or 5'-H), 7.25-7.29 (m, 3 H, 4"-H, 4'''-H), 7.37-7.45 (m, 6 H, 2"-H, 6"-H, 3'''-H, 5'''-H), 7.55-7.59 (m, 6 H, 3"-H, 5"-H, 2'''-H, 6'''-H), 8.07 (t, J = 10.0 Hz, 1 H, 6'-H), 8.49 (s, 2 H, 3-H, 5-H), 8.68 (d, J = 4.4 Hz, 1 H, 2'-H), 8.78 (d, J = 9.6 Hz, 1 H, 4'-H), 9.23 (d, J = 10.0 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d$_6$): δ 122.3 (C3'), 124.6 (C1'), 127.3 (C3, C5), 127.6 (C2''', C6'''), 129.8 (C2", C6"), 130.0 (C3''', C5'''), 130.4 (C5'), 130.6 (C7'), 131.4 (C3", C5", C4'''), 131.5 (C4"), 135.2 (C1"), 137.9 (C8'), 140.2 (C3a'), 140.7 (C2'), 140.9 (C1'''), 141.1 (C4'), 142.4 (C6'), 148.3 (C8a'), 154.6 (C4), 157.4 (C2, C6) ppm; ms [EI]: m/z 434 [M$^+$, 100]. *Anal.* Calcd. for C$_{33}$H$_{24}$ClNO$_4$: C, 74.22; H, 4.53; N, 2.62; Cl, 6.64. Found: C, 74.35; H, 4,62; N, 2.70; Cl, 6.71.

4-(Azulen-1-yl)-1-(*tert*-butyl)-2,6-diphenyl-pyridinium perchlorate, (3k). This compound was obtained in such a small amount that only mass spectrum was recorded; ms (30 eV): (m/z, %): 414 [M$^+$, 23], 358 (M-tBu, 100).

4-(Azulen-1-yl)-1-butyl-2,6-diphenyl-3-methyl-pyridinium perchlorate, (10). This compound was obtained as brown crystals; mp 82 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 233 (4.49), 278 (4.49), 329 sh (3.94), 422 (4.11) nm; ^{1}H nmr (acetone-d$_6$): δ 0.46 (t, J = 7.2 Hz, 3 H, CH$_3$), 0.83-0.93 (m, 2 H, CH$_3$C*H*$_2$), 1.63-1.70 (m, 2 H, CH$_2$C*H*$_2$CH$_2$), 2.17 (s, 3 H, 3-Me), 4.37-4.41 (m, 2 H, NC*H*$_2$), 7.51 (t, J = 9.8 Hz, 1 H, 5'-H), 7.55 (t, J = 9.2 Hz, 1 H, 7'-H), 7.65 (d, J = 4.0 Hz, 1 H, 3'-H), 7.67-7.69 (m, 3 H, 3'''-H, 4'''-H, 5'''-H), 7.75-7.90 (m, 7 H, 2"-H, 3"-H, 4"-H, 5"-H, 6"-H, 2'''-H, 6'''-H), 7.95 (t, J = 9.6 Hz, 1 H, 6'-H), 8.05 (s, 1 H, 5-H), 8.24 (d, J = 4.0 Hz, 1 H, 2'-H), 8.56 (d, J = 10.0 Hz, 1 H, 4'-H), 8.69 (d, J = 9.2 Hz, 1 H, 8'-H) ppm; ^{13}C-nmr (acetone-d$_6$); δ 12.15 (*C*H$_3$CH$_2$), 13.56 (CH$_3$), 20.69 (CH$_3$*C*H$_2$), 33.10 (CH$_2$*C*H$_2$CH$_2$), 56.66 (N*C*H$_2$), 120.4 (C3'), 125.6 (C1'), 127.9 (C5', C7'), 130.3 (*C*H), 130.7 (*C*H), 130.8 (*C*H), 131.3 (*C*H), 132.2 (C5), 132.3 (*C*H), 134.4 (C$_q$), 134.8 (C$_q$), 137.6 (C8'), 137.7 (C3), 139.4 (C$_q$), 140.0 (C2'), 140.4 (C4'), 141.4 (C6'), 144.9 (C$_q$), 153.7 (C4), 153.9 (C2), 155.7 (C6) ppm; ms (15 eV): m/z 428 [M$^+$, 100]. *Anal.* Calcd. for C$_{32}$H$_{30}$ClNO$_4$: C, 72.79; H, 5.73; N, 2.65; Cl, 6.71. Found: C, 72.76; H, 5.68; N, 2.65; Cl, 6.69.

4-(Azulen-1-yl)-1-butyl-2,3,6-triphenyl-pyridinium perchlorate, (11). This compound was obtained as brown crystals; mp 125 ºC. uv-vis (MeOH, λ$_{max}$, log ε): 223 (4.43), 235 (4.47), 282 (4.43), 343 (3.89), 437 (4.18) nm; ^{1}H nmr (acetone-d$_6$): δ 0.45 (t, J = 7.2 Hz, 3 H, CH$_3$), 0.80-0.90 (m, 2 H, CH$_3$C*H*$_2$), 1.65-1.75 (m, 2 H, CH$_2$C*H*$_2$CH$_2$), 4.39-4.44 (m, 2 H, NCH$_2$), 7.04-7.06 (m, 3 H, 3'''-H, 4'''-H, 5'''-H), 7.12 (dd, J = 7.8 Hz, J = 1.8 Hz, 2 H, 2'''-H, 6'''-H), 7.23 (d, J = 4.4 Hz, 1 H, 3'-H), 7.38 (d, J = 4.0 Hz, 1 H, 2'-H), 7.44-7.45 (m, 3 H, 3"-H, 4"-H, 5"-H), 7.48 (t, J = 10.0 Hz, 2 H, 5'-H, 7'-H), 7.67-7.69 (m, 2 H, 2^{IV}-H, 6^{IV}-H), 7.72-7.74 (m, 3 H, 3^{IV}-H, 4^{IV}-H, 5^{IV}-H), 7.87 (t, J = 9.9 Hz, 1 H, 6'-H), 7.97-7.99 (m, 2 H, 2"-H, 6"-H), 8.16 (s, 1 H, 5-H), 8.49 (d, J = 9.6 Hz, 1 H, 4'-H), 8.85 (d, J = 9.6 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (acetone-d$_6$): δ 13.55 (*C*H$_3$), 20.70 (CH$_3$*C*H$_2$), 33.06 (CH$_2$*C*H$_2$CH$_2$), 56.63 (*C*H$_2$N), 120.1 (C3'), 125.7 (C1'), 128.0 (C5'), 128.2 (C7'), 129.3 (C4^{IV}), 129.4 (C3^{IV}, C5^{IV}), 130.0 (C3", C5"), 130.6 (C2", C6"), 130.8 (C2''', C6'''), 131.5 (C3''', C5'''), 132.2 (C2^{IV}, C6^{IV}), 132.3 (C$_q$), 132.3 (C5), 132.4 (C4'''), 132.3 (C4"), 134.9 (C$_q$), 137.3 (C$_q$), 137.4 (C$_q$), 139.5 (C$_q$), 139.9 (C4'), 140.3 (C2'), 141.3 (C6'), 142.3 (C3), 144.9 (Cq), 154.7 (C4), 155.4 (C6), 156.9 (C2) ppm; ms (15 eV): m/z 490 [M$^+$, 100]. *Anal.* Calcd. for C$_{37}$H$_{32}$ClNO$_4$: C, 75.36; H, 5.47; N, 2.38; Cl, 5.93. Found: C, 75.42; H, 5,65; N, 2.25; Cl, 6.02.

3-Azulen-1-yl-1,5-diphenyl-pent-2-ene-1,5-dione, (12). This compound was obtained as brown oil; ^{1}H nmr (CDCl$_3$): δ 5.05 (s, 2 H, CH$_2$), 7.25 (t, J= 9.6 Hz, 1 H, 5-H), 7.30 (t, J = 10.0 Hz, 1 H, 7-H), 7.37 (d, J = 3.6 Hz, 1 H, 3-H), 7.44 (t, J = 7.6 Hz, 2 H, *m*-Ph$_1$), 7.44 (s, 1 H, CH=), 7.46 (t, J = 7.6 Hz, 2 H, *m*-Ph$_5$), 7.50-7.58 (m, 2 H, *p*-Ph$_1$, *p*-Ph$_5$), 7.66 (t, J = 10.0 Hz, 1 H, 6-H), 7.97 (d, J = 4.0 Hz, 1 H, 2-H), 7.98 (d, J = 7.2 Hz, 2 H, *o*-Ph$_1$), 8.07 (d, J = 7.2 Hz, 2 H, *o*-Ph$_5$), 8.34 (d, J = 9.6 Hz, 1 H, 4-H), 8.83 (d, J = 10 Hz, 1 H, 8-H) ppm; ^{13}C-NMR (CDCl$_3$): 45.59 (*C*H$_2$CO), 118.3 (C3), 123.8 (*C*H=), 124.8 (C5), 125.3 (C7), 128.2 (*o*-Ph$_1$), 128.3 (*o*-Ph$_5$), 128.5 (*m*-Ph$_1$), 128.6 (*m*-Ph$_5$), 132.3 (*p*-Ph$_1$), 132.9 (*p*-Ph$_5$), 136.2 (C8), 136.5 (C2), 136.8 (C1-Ph$_5$), 137.3 (C3a), 137.9 (C4) 139.5, 139.7 (C6), 139.7 (C1-Ph$_1$), 143.2 (C8a), 149.7 (*C*=), 190.2 (*C*O=), 196.5 (*C*O) ppm; ms (15 eV): m/z: 377 [M$^+$+1, 85], 359 (100).

4-(Azulen-1-yl)-1,2,6-trimethyl-pyridinium perchlorate, (5a(Me)). This compound was obtained as dark green crystals; mp > 260 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 234 (4.29), 275 sh (4.24), 284 (4.24), 336 (4.00), 408 (4.02) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.82 (s, 6 H, 2-Me, 6-Me), 3.99 (s, 3 H, N*Me*), 7.58 (t, J = 9.8 Hz, 1 H, 5'-H), 7.61 (d, J = 4.0 Hz, 1 H, 3'-H), 7.63 (t, J = 10.0 Hz, 1 H, 7'-H), 7.99 (t, J = 9.8 Hz, 1 H, 6'-H), 8.14 (s, 2 H, 3-H, 5-H), 8.40 (d, J = 4.0 Hz, 1 H, 2'-H), 8.66 (d, J = 9.6 Hz, 1 H, 4'-H), 8.94 (d, J = 9.6 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 21.4 (2-Me, 6-Me), 55.00 (N*Me*), 120.0 (C3'), 123.0 (C1'), 124.8 (C3, C5), 127.5 (C7'), 127.9 (C5'), 136.3 (C8'), 137.2 (C3a'), 138.5 (C2'), 139.4 (C4'), 140.7 (C6'), 144.9 (C8a'), 150.4 (C4), 154.9 (C2, C6) ppm; ms (ESI): m/z 248 [M$^+$, 100]. *Anal.* Calcd. for C$_{18}$H$_{18}$ClNO$_4$: C, 62.16; H, 5.22; N, 4.03; Cl, 10.19. Found: C, 62.03; H, 5.29; N, 4.05; Cl, 10.11.

4-(Azulen-1-yl)-2,6-dimethyl-1-(*iso*-propyl)-pyridinium perchlorate, (5a(*i*Pr)). This compound was obtained as dark green crystals; mp 257-259 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 234 (4.28), 275 (4.24), 282 sh (4.19), 331 (4.02), 339 (4.03), 415 (4.26) nm; ^{1}H nmr (DMSO-d$_6$): δ 1.62 (d, ^{J} = 7.0 Hz, 6 H, *Me$_2$*CH), 2.84 and 2.90 (2s, 2x3 H, 2-Me and 6-Me), 5.28 (hept, J = 7.1 Hz, 1 H, Me$_2$*CH*), 7.51 (t, J = 9.5 Hz, 1 H, 5'-H), 7.53 (d, J = 4.0 Hz, 1 H, 3'-H), 7.55 (t, J = 9.9 Hz, 1 H, 7'-H), 7.91 (t, J = 9.8 Hz, 1 H, 6'-H), 8.06 and 8.08 (2s, 2x1 H, 3-H and 5-H), 8.33 (d, J = 4.2 Hz, 1 H, 2'-H), 8.58 (d, J = 9.4 Hz, 1 H, 4'-H), 8.87 (d, J = 9.8 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 20.7 (*Me$_2$*CH), 22.5 (2-Me, 6-Me), 57.4 (Me$_2$*CH*), 120.2 (C3'), 122.8 (C1'), 127.7 (C3, C5), 128.2 (C5', C7'), 136.7 (C8'), 137.5 (C3a'), 138.7 (C2'), 139.6 (C4'), 140.9 (C6'), 145.3 (C8a'), 150.4 (C4), 155.0 (C2, C6) ppm; ms (ESI): m/z 276 [M$^+$, 100]. *Anal.* Calcd. for C$_{20}$H$_{22}$ClNO$_4$: C, 63.91; H, 5.90; N, 3.73; Cl, 9.43. Found: C, 63.84; H, 6.10; N, 3.95; Cl, 9.25.

4-(Azulen-1-yl)-2,6-dimethyl-1-phenyl-pyridinium perchlorate, (5a(Ph)). This compound was obtained as brown crystals; mp > 260 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 217 (4.05), 234 (4.13), 276 (4.08), 339 (3.82), 424 (4.06) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.40 (s, 6 H, 2-Me, 6-Me), 7.63-7,79 (m, 8H, 3'-H, 5'-H, 7'-H, 2"-H, 3"-H, 4"-H, 5"-H and 6"-H), 8.06 (t, J = 9.6 Hz, 1 H, 6'-H), 8.39 (s, 2 H, 3-H, 5-H), 8.52 (d, J = 4.0 Hz, 1 H, 2'-H), 8.73 (d, J = 9.6 Hz, 1 H, 4'-H), 9.08 (d, J = 9.6 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 21.7 (2-Me, 6-Me), 120.1, 126.2, 127.8, 128.2, 130.7 and 130.9 (C3', C5', C7', C2", C3", C4", C5"and C6"), 122.9 (C$_q$), 123.7 (C3, C5), 136.5 (C8'), 137.8 (C$_q$), 138.5 (C2'), 138.6 (C$_q$), 139.4 (C4'), 140.8 (C6'), 145.3 (C$_q$), 154.4 (C2, C4, C6) ppm; ms (ESI): m/z 310 [M$^+$, 100]. *Anal.* Calcd. for C$_{23}$H$_{20}$ClNO$_4$: C, 67.40; H, 4.92; N, 3.42; Cl, 8.65. Found: C, 67.27; H, 5.11; N, 3.54; Cl, 8.49.

4-(Azulen-1-yl)-1-benzyl-2,6-dimethyl-pyridinium perchlorate, (5a(Bn)). This compound was obtained as dark green crystals; mp 127-130 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 217 (4.23), 235 (4.28), 275 (4.23), 283 sh (4.18), 330 (3.97), 340 (4.05), 424 (4.24) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.79 (s, 6 H, 2-Me, 6-Me), 5.86 (s, 2 H, N*CH$_2$*), 7.16 (d, J = 7.2 Hz, 2 H, 2"-H, 6"-H), 7.41 (tt, J = 7.4, 1.2 Hz, 1 H, 4"-H), 7.46 (tt, J = 7.4, 1.2 Hz, 2 H, 3"-H, 5"-H), 7.63 (t, J = 9.9 Hz, 1 H, 5'-H), 7.65 (d, J = 4.2 Hz, 1 H, 3'-H), 7.68 (t, J = 9.9 Hz, 1 H, 7'-H), 8.04 (t, J = 9.9 Hz, 1 H, 6'-H), 8.31 (s, 2 H, 3-H, 5-H), 8.48 (d, J = 4.2 Hz, 1 H, 2'-H), 8.71 (d, J = 9.4 Hz, 1 H, 4'-H), 9.07 (d, J = 9.8 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 21.2 (2-Me, 6-Me), 54.5 (N*CH$_2$*), 120.4 (C3'), 123.1 (C1'), 125.5 (C3, C5), 125.9 (C2", C6"), 128.0 (C5'), 128.4 (C7'), 128.5 (C4"), 129.7 (C3", C5"), 133.5 (C1"), 136.9 (C8'), 137.8 (C3a'), 139.0 (C2'), 139.7 (C4'), 141.1 (C6'), 145.5 (C8a'), 151.4 (C4), 155.0 (C2, C6) ppm; ms (ESI): m/z 276 [M$^+$, 100]. *Anal.* Calcd. for C$_{24}$H$_{22}$ClNO$_4$: C, 68.00; H, 5.23; N, 3.30; Cl, 8.36. Found: C, 67,83; H, 5.32; N, 3.26; Cl, 8.40.

1,2,6-Trimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, (5d(Me)). This compound was obtained as brown crystals; mp 139-141 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 245 (4.26), 293 (4.22), 344 (3.90), 422 (3.94) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.60 (s, 3 H, 4'-Me), 2.66 (s, 3 H, 6'-Me), 2.78 (s, 6 H, 2-Me, 6-Me), 2.89 (s, 3 H, 8'-Me), 3.99 (s, 3 H, N*Me*), 7.37 (s, 1 H, 5'-H), 7.41 (s, 1 H, 7'-H), 7.42 (d, J = 4.4 Hz, 1 H, 3'-H), 7.80 (bs, 3 H, 2'-H, 3-H, 5-H); ^{13}C nmr (DMSO-d$_6$): δ 21.2 (2-Me, 6-Me), 25.3 (8'-Me), 27.9 (6'-Me), 29.4 (4'-Me), 39.1 (N*Me*), 116.7 (C3'), 125.6 and 125.7 (C1' and C 3a'), 126.5 (C3, C5), 130.3 (C7'), 131.5 (C5'), 137.3 (C2'), 140.3 (C8a'), 147.4 (C8'), 148.0 (C4'), 148.5 (C6'), 153.7 (C2, C6), 154.3 (C4); ms (ESI): m/z 290 [M$^+$, 100]. *Anal.* Calcd. for C$_{21}$H$_{24}$ClNO$_4$: C, 64.69; H, 6.20; N, 3.59; Cl, 9.09. Found: C, 64.67; H, 6.30; N, 3.69; Cl, 9.25.

2,6-Dimethyl-1-(*iso*-propyl)-4-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, (5d(*i*Pr)). This compound was obtained as brown crystals; mp 112-115 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 217 (4.11), 246 (4.32), 286 sh (4.20), 293 (4.22), 343 (4.01), 425 (4.07) nm; ^{1}H nmr (DMSO-d$_6$): δ 1.68 (d, ^{J} = 6.8 Hz, 6 H, *Me$_2$*CH), 2.62, 2.67 and 2.89 (3s, 3x3 H, 4'-Me, 6'-Me and 8'-Me), 2.87 and 2.93 (2s, 2x3 H, 2-Me and 6-Me), 5.37 (hept, J = 6.8 Hz, 1 H, Me$_2$*CH*), 7.38 (s, 1 H, 5'-H), 7.42 (s, 1 H, 7'-H), 7.43 (d, J = 4.0 Hz, 1 H, 3'-H), 7.76 and 7.78 (2s, 2x1 H, 3-H and 5-H), 7.83 (d, J = 3.6 Hz, 1 H, 2'-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 20.3 (*Me$_2$*CH), 22.0 (2-Me, 6-Me), 25.1, 27.7 and 29.3 (4'-Me,6'-Me and 8'-Me), 57.1 (Me$_2$*CH*), 116.6 (C3'), 125.5 (C$_q$), 127.9 (C3 and C5), 128.9 (C$_q$), 130.3 (C7'), 131.4 (C5'), 137.2 (C2'), 140.3(C$_q$), 147.2 (C$_q$), 147.9 (C$_q$), 148.2 (C$_q$), 153.5 (C$_q$), 153.7 (C2, C6) ppm; ms (ESI): m/z 318 [M$^+$, 100]. *Anal.* Calcd. for C$_{23}$H$_{28}$ClNO$_4$: C, 66.10; H, 6.75; N, 3.35; Cl, 8.48. Found: C, 65.93; H, 6.67; N, 3.41; Cl, 8.59.

2,6-Dimethyl-1-phenyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, (5d(Ph)). This compound was obtained as brown crystals; mp 134-135 ºC; uv (MeOH, λ$_{max}$, log ε): 245 (4.57), 283 sh (4.45), 293 (4.47), 343 (4.19), 436 (4.24) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.36 (s, 6 H, 2-Me, 6-Me), 2.70 (s, 3 H, 4'-Me), 2.76 (s, 3 H, 6'-Me), 2.93 (s, 3 H, 8'-Me), 7.47 (s, 1 H, 5'-H), 7.48 (s, 1 H, 7'-H), 7.49 (d, J = 4.0 Hz, 1 H, 3'-H), 7.70 (d, J = 8.0 Hz, 2 H, 2"-H, 6"-H), 7.71 (t, J = 7.6 Hz, 1 H, 4"-H), 7.75 (t, J = 7.6 Hz, 2 H, 3"-H, 5"-H), 7.94 (d, J = 4.4 Hz, 1 H, 2'-H), 8.02 (s, 2 H, 3-H, 5-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 21.5 (2-Me, 6-Me), 25.1 (8'-Me), 27.7 (4'-Me), 29.5 (6'-Me), 116.8 (C3'), 125.3 (C$_q$), 125.5 (C4"), 125.7 (C3, C5), 126.2 (C2", C6"), 130.7 (C3", C5"), 130.8 (C7'), 131.8 (C5'), 135.6 (C$_q$), 137.5 (C2'), 137.6 (C$_q$), 140.8 (C$_q$), 147.2 (C8'), 148.2 (C6'), 148.4 (C4'), 155.2 (C2, C6), 155.3 (C4) ppm; ms (ESI): m/z 352 [M$^+$, 100]. *Anal.* Calcd. for C$_{26}$H$_{26}$ClNO$_4$: C, 69.10; H, 5.80; N, 3.10; Cl, 7.84. Found: C, 69.22; H, 5.92; N, 3.20; Cl, 7.91.

1-Benzyl-2,6-dimethyl-4-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, (5d(Bn)). This compound was obtained as brown crystals; mp 154-156 ºC; uv-vis (MeOH, λ$_{max}$, log ε): 214 (4.26), 247 (4.38), 278sh (4.43), 294 (4.27), 345 (4.08), 433 (4.16) nm; ^{1}H nmr (DMSO-d$_6$): δ 2.68, 2.69 and 2.92 (3s, 3x3 H, 4'-Me, 6'-Me and 8'-Me), 2.74 (s, 6 H, 2-Me, 6-Me), 5.84 (s, 2 H, N*CH$_2$*), 7.11 (d, J = 7.2 Hz, 2 H, 2"-H, 6"-H), 7.38-7.84 (m, 6 H, 3'-H, 5'-H, 7'-H, 3"-H, 4"-H and 5"-H), 7.92 (d, J = 4.6 Hz, 1 H, 2'-H), 7.95 (s, 2 H, 3-H, 5-H) ppm; ^{13}C nmr (DMSO-d$_6$): δ 20.2 (2-Me, 6-Me), 25.1, 27.7 and 29.3 (4'-Me, 6'-Me and 8'-Me), 54.1 (N*CH$_2$*), 116.8, 128.2, 129.4, 130.6 and 131.7 (*C*H for C3', C5', C7', C3", C4" and C5"), 125.2 (C$_q$), 125.5 (C2", C6"), 127.0 (C3, C5), 133.1 (C$_q$), 133.3 (C$_q$), 137.5 (C2'), 140.7 (C$_q$), 147.3 (C$_q$), 147.9 (C$_q$), 148.4 (C$_q$), 153.5 (C$_q$), 154.7 (C2, C6) ppm; ms (ESI): m/z 366 [M$^+$, 100]. *Anal.* Calcd. for C$_{27}$H$_{28}$ClNO$_4$: C, 69.60; H, 6.06; N, 3.01; Cl, 7.61. Found: C, 69.79; H, 5.89; N, 3.14; Cl, 7.48.

4-(2-*tert*-Butyl-6-methyl-azulen-1-yl)-2,6-dimethyl-1-(*iso*-propyl)-pyridinium perchlorate, (5f(*i*Pr)). This compound was obtained as brown crystals; mp 156-157 ºC; uv-vis (MeOH,

λ_{max}, log ε): 234 (4.31), 287 (4.73), 337 (3.75), 347 (3.75), 407 (3.73) nm; ^{1}H nmr (DMSO-d_6): δ 1.35 (s, 9H, *Me*$_3$C), 1.77 (d, J = 6.8 Hz, 6 H, *Me*$_2$CH), 2.62 (s, 3 H, 6'-Me), 2.95 and 3.00 (2s, 2x3 H, 2-Me and 6-Me), 5.49 (hept, J = 6.8 Hz, 1 H, Me$_2$*CH*), 7.15 (d, J = 10.0 Hz, 1 H, 7'-H), 7.28 (d, J = 10.0 Hz, 1 H, 5'-H), 7.42 (s, 1 H, 3'-H), 7.66 (d, J = 10.0 Hz, 1 H, 8'-H), 7.87 and 7.90 (2s, 2x1 H, 3-H and 5-H), 8.33 (d, J = 10.0 Hz, 1 H, 4'-H) ppm; ^{13}C nmr (DMSO-d_6): δ 20.2 (*Me*$_2$CH), 22.0 (2-Me, 6-Me), 27.4 (6'-Me), 32.2 (*Me*$_3$C), 34.4 (Me$_3$*C*), 58.1 (Me$_2$*CH*), 115.9 (C3'), 122.2 (C1'), 125.9 (C7'), 126.0 (C5'), 131.3 and 132.3 (C3 and C5), 133.3 (C8'), 135.9 (C4'), 137.2 (C8a'), 138.0 (C3a'), 149.3 (C6'), 154.5 (C2,C6), 155.9 (C4) , 158.8 (C2') ppm; ms (ESI): m/z 346 [M$^+$, 100]. *Anal.* Calcd. for $C_{25}H_{32}ClNO_4$: C, 67.33; H, 7.23; N, 3.14; Cl, 7.95. Found: C, 67.22; H, 7.12; N, 3.21; Cl, 7.80.

1-(Benzyl)-4-(2-*tert*-butyl-6-methyl-azulen-1-yl)-2,6-dimethylpyridinium perchlorate, (5f(Bn)). This compound was obtained as brown crystals; mp 115-116 ºC; uv-vis (MeOH, λ_{max}, log ε): 216 (4.12), 234 (4.18), 285 (4.43), 336 (3.62), 345 (3.64), 356 (3.56), 419 (3.56) nm; ^{1}H nmr (DMSO-d_6): δ 1.37 (s, 9H, *Me*$_3$C), 2.64 (s, 3 H, 6'-Me), 2.80 (s, 6 H, 2-Me, 6-Me), 5.97 (s, 2 H, N*CH*$_2$), 7.19 (d, J = 7.6 Hz, 2 H, 2"-H, 6"-H), 7.21 (d, J = 10.0 Hz, 1 H, 7'-H), 7.30 (d, J = 10.0 Hz, 1 H, 5'-H), 7.44 (t, J = 7.6 Hz, 1 H, 4"-H), 7.45 (s, 1 H, 3'-H), 7.51 (t, J = 7.4 Hz, 2 H, 3"-H, 5"-H), 7.76 (d, J = 10.0 Hz, 1 H, 8'-H), 8.06 (s, 2 H, 3-H, 5-H), 8.35 (d, J = 10.0 Hz, 1 H, 4'-H) ppm; ^{13}C nmr (DMSO-d_6): δ 20.8 (2-Me, 6-Me), 27.5 (6'-Me), 32.3 (*Me*$_3$C), 34.5 (Me$_3$*C*), 55.0 (N*CH*$_2$), 116.1 (C3'), 122.3 (C1'), 125.6 (C7', C2", C6"), 126.2 (C5'), 128.3 (C4"), 129.5 (C3", C5"), 130.6 (C3, C5), 132.6 (C1"), 133.5 (C8'), 136.0 (C4'), 137.2 (C8a'), 138.1 (C3a'), 149.5 (C6'), 154.8 (C2,C6), 157.3 (C4), 158.9 (C2') ppm; ms (ESI): m/z 394 [M$^+$, 100]. *Anal.* Calcd. for $C_{29}H_{32}ClNO_4$: C, 70.51; H, 6.53; N, 2.84; Cl, 7.18. Found: C, 70.39; H, 6.59; N, 2.81; Cl, 7.11.

4-(2-*tert*-butyl-6-methyl-azulen-1-yl)-2,6-dimethyl-1-phenylpyridinium perchlorate, (5f(Ph)). This compound was obtained as brown oil; uv-vis (MeOH, λ_{max}, log ε): 231 (4.33), 287 (4.57), 333 (3.89), 346 (3.63), 357 (3.55), 424 (3.52) nm; ^{1}H nmr (DMSO-d_6): δ 1.42 (s, 9H, *Me*$_3$C), 2.42 (s, 6 H, 2-Me, 6-Me), 2.65 (s, 3 H, 6'-Me) 7.20 (d, J = 10.4 Hz, 1 H, 7'-H), 7.31 (d, J = 10.0 Hz, 1 H, 5'-H), 7.46 (s, 1 H, 3'-H), 7.80 (d, J = 10.0 Hz, 1 H, 8'-H), 7.74-7.84 (m, 5 H, 2"-H, 3"-H, 4"-H, 5"-H and 6"-H), 8.10 (s, 2 H, 3-H, 5-H), 8.36 (d, J = 10.0 Hz, 1 H, 4'-H) ppm; ^{13}C nmr (DMSO-d_6): δ 21.8 (2-Me, 6-Me), 27.5 (6'-Me), 32.4 (*Me*$_3$C), 34.5 (Me$_3$*C*), 116.1 (C3'), 122.7 (C1'), 126.1 (C7'), 126.3 (C5'), 129.4 (C3, C5), 126.0, 130.8, 131.1, 133.5 (*C*H for C8', C2", C3", C4", C5" and C6"), 136.1 (C4'), 137.4 (C8a'), 138.2 (C3a'), 138.6 (C1"), 149.6 (C6'), 154.5 (C2,C6), 158.0 (C4), 159.0 (C2') ppm; ms (ESI): m/z 380 [M$^+$, 100]. *Anal.* Calcd. for $C_{28}H_{30}ClNO_4$: C, 70.06; H, 6.30; N, 2.92; Cl, 7.39. Found: C, 70.16; H, 6.32; N, 2.91; Cl, 7.36.

***N*-(3-Azulen-1-yl-5-methylphenyl)-N-*iso*-propylamine, (7a(*i*Pr)).** This compound was obtained as blue oil; uv (MeOH,λ_{max}, log ε): 237 (4.44), 287 (4.47), 362 (3.77), 556 (2.27) nm; ^{1}H nmr (CDCl$_3$): δ 1.24 (d, J = 6.4 Hz, 6 H, *Me*$_2$CH), 2.36 (s, 3 H, 5-Me), 3.68 (hept, J = 6.2 Hz, 1 H, *CH*Me$_2$), 6.42 (s, 1 H, 6-H), 6.65 (s, 1 H, 2-H), 6.76 (s, 1 H, 4-H), 7.10 (t, J = 9.8 Hz, 1 H, 5'-H), 7.11 (t, J = 9.6 Hz, 1 H, 7'-H), 7.40 (d, J = 4.0 Hz, 1 H, 3'-H), 7.55 (t, J = 10.0 Hz, 1 H, 6'-H), 7.99 (d, J = 4.0 Hz, 1 H, 2'-H), 8.31 (d, J = 9.4 Hz, 1 H, 4'-H), 8.61 (d, J = 9.6 Hz, 1 H, 8'-H) ppm; ^{13}C nmr (CDCl$_3$): δ 21.7 (5-Me), 23.1 (*Me*$_2$CH), 44.3 (*CH*Me$_2$), 111.8 (C2), 112.3 (C6), 117.2 (C3'), 119.8 (C4), 122.7 (C7'), 122.9 (C5'), 132.1 (C3), 135.2 (C1'), 135.9 (C8'), 137.0 (C4'), 137.1 (C2'), 138.0 (C6'), 138.3 (C3a'), 139.2 (C5), 141.5 (C8a'), 147.7 (C1) ppm; ms (ESI): m/z 276 [M$^+$+1, 100]. *Anal.* Calcd. for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N 5.09. Found: C, 87.18; H, 7.71; N 5.11.

***N*-*iso*-Propyl-*N*-[3-(4,6,8-trimethyl-azulen-1-yl)-5-methylphenyl]-amine, (7d(*i*Pr)).** This compound was obtained as violet oil; uv-vis (MeOH, λ_{max}, log ε): 216 (4.36), 247 (4.46), 296 (4.53), 347 (3.74), 369 (3.50) nm; ^{1}H nmr (CDCl$_3$): δ 1.19 (d, J = 6.4 Hz, 6 H, *Me*$_2$CH), 2.26 (s, 3 H, 5-Me), 2.47 (s, 3 H, 4'-Me), 2.55 (s, 3 H, 6'-Me), 2.84 (s, 3 H, 8'-Me), 3.59 (hept, J = 6.4 Hz, 1 H, *CH*Me$_2$), 6.46 (bs, 1 H, 6-H), 6.50 (bs, 1 H, 2-H), 6.57 (bs, 1 H, 4-H), 6.90 (s, 1 H, 5'-H), 6.97 (s, 1 H, 7'-H), 7.29 (d, J = 4.0 Hz, 1 H, 3'-H), 7.51(d, J = 4.0 Hz, 1 H, 2'-H) ppm; ^{13}C nmr (CDCl$_3$): δ 21.4 (5-Me), 22.5 (*Me*$_2$CH), 25.4 (8'-Me), 28.2 (6'-Me), 28.3 (4'-Me), 44.5 (*CH*Me$_2$), 113.3 (C2), 113.8 (C6), 114.6 (C3'), 119.8 (C4), 126.6 (C7'), 128.5 (C5'), 131.0 (C3), 133.0 (C1'), 135.9 (C2'), 136.8 (C3a'), 137.7 (C5), 139.8 (C8a'), 143.0 (C1), 145.4 (C6'), 145.9 (C8'), 147.5 (C4') ppm; ; ms (ESI): m/z 318 [M$^+$+1, 100]. *Anal.* Calcd. for $C_{23}H_{27}N$: C, 87.02; H, 8.57; N 4.41. Found: C, 86.97; H, 8.60; N 4.43.

***N*-*iso*-Propyl-*N*-[3-(2-t-butyl-6-methyl-azulen-1-yl)-5-methylphenyl]-amine, (7f(*i*Pr)).** This compound was obtained as violet oil; uv-vis (MeOH, λ_{max}, log ε): 216 (4.36), 240 (4.33), 287 (4.70), 291 (4.74), 337 (3.71), 351 (3.73), 417 (3.45) nm; ^{1}H nmr (CDCl$_3$): δ 1.19 and 1.21 (d and d, J = 6.0, 6.4 Hz, 3 H and 3 H, *Me*$_2$CH) [11], 1.36 (s, 9 H, *Me*$_3$C), 2.32 (s, 3 H, 5-Me), 2.57 (s, 3 H, 6'-Me), 3.61 (hept, J = 6.4 Hz, 1 H, *CH*Me$_2$), 6.42 (s, 1 H, 6-H), 6.45 (s, 1 H, 2-H), 6.51 (s, 1 H, 4-H), 6.89 (d, J = 10.4 Hz, 1 H, 5'-H), 6.99 (d, J = 9.6 Hz, 1 H, 7'-H), 7.27 (s, 1 H, 3'-H), 7.66 (d, J = 10.4 Hz, 1 H, 8'-H), 8.08 (d, J = 10.0 Hz, 1 H, 4'-H) ppm; ^{13}C nmr (CDCl$_3$): δ 21.6 (5-Me), 23.2 (*Me*$_2$CH), 27.9 (6'-Me), 31.8 (*Me*$_3$C), 34.7 (Me$_3$*C*), 44.3 (*CH*Me$_2$), 113.0 (C2), 114.4 (C6), 114.6 (C3'), 122.5 (C4), 123.9 (C7'), 124.0 (C5'), 130.6 (C3), 133.1 (C1'), 133.8 (C8'), 134.2 (C4'), 137.2 (C8a'), 137.7 (C5), 138.0 (C3a'), 146.6 (C1), 147.2 (C6'), 159.3 (C2') ppm; ms (ESI): m/z 346 [M$^+$+1, 100]. *Anal.* Calcd. for $C_{25}H_{31}N$: C, 86.90; H, 9.04; N 4.05. Found: C, 86.94; H, 9.01; N 4.04.

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[10] Instead of the expected triplet and quintet for the signals of the two methylene groups: N^+-CH_2-CH_2- a more complicated multiplicity of these signals are present possible due to the hinder of rotation around N^+-C bond despite the difficulty to accept that explanation. This observation as well as other structural aspects regarding the above studied series of compounds will be approached in the future.

[11] Until now we did not have an explanation for the multiplicity of the signal for the $(CH_3)_2CH$ group in compound **7f**(*i*Pr).