2-(Azulen-1-yl)-4,6-diphenyl Substituted Six-membered Heteroaromatics

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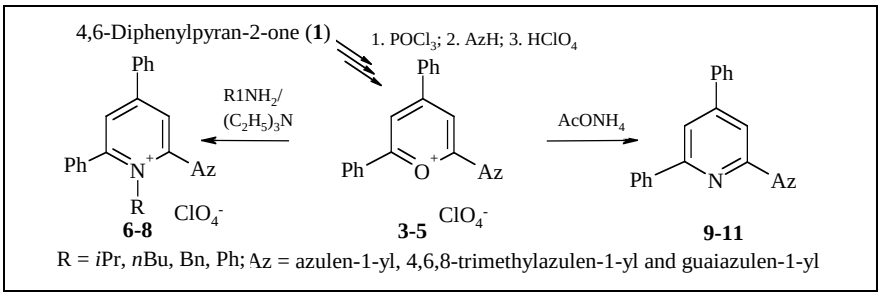

2-(Azulen-1-yl)-4,6-diphenyl substituted pyranylium salts, pyridinium salts and pyridines were efficiently synthesized and the new obtained compounds were completely characterized. Comparative structural analysis between these compounds and their corresponding isomers that contain the azulen-1-yl moiety in the 4-position of the heterocycle, were carried out. These studies are based on calculated dihedral angles formed between central heterocycle and the aromatic substituents and on the obtained electronic and NMR spectra. Due to the restriction in the rotation around azulenyl-pyridinium bond produced by the quaternary nitrogen substituent, in the herein reported pyridinium salts, the substitution groups of the quaternary nitrogen atom are prochiral. This property leads to the non-equivalence of *gem*-protons or *gem*–methyl groups of N-substituents in the ^{1}H nmr spectra of the synthesized pyridinium salts.

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INTRODUCTION

In recent years it has become apparent that the azulen-1-yl moiety can serve as a stabilizing group for electron deficient molecules as, for example, ionic or neutral heterocycles. Our recent works has emphasized the stabilizing influence of the azulen-1-yl group on pyranylium [1] and pyridinium [2a] salts as well as on pyridine [2b] when it is attached in the 4-position of these heterocycles. Besides the interest for generation of these compounds, which are valuable synthones in other synthesis, the interdependence between molecular structure and some of their properties represented another interesting point of our research. Thus, for 4-(azulen-1-yl)-2,6-dimethyl-pyridinium salts when the nitrogen was quaternized by isopropyl we have observed a difference between chemical shift of the methyl protons at C-2 and C-6 positions. Moreover, different δ_H for the heterocyclic protons, 3-H and 5-H, have been also registered [3]. We now turn our attention on the 2-(azulen-1-yl) substituted heterocycles where the azulenyl group is placed in the neighborhood of the heteroatom. We report herein the synthesis of 2-(azulen-1-yl)-4,6-diphenyl substituted pyranylium and pyridinium salts as well as of the corresponding pyridines. There are several pathways for the synthesis of azulenyl-substituted heterocycles either by coupling of suitable substituted azulenes and heterocycles [4] or starting from pyranones [1,2]. We also focus our attention on the correlation between structure and behavior of the synthesized compounds in order to compare the obtained results with the reported data for isomers with the azulen-1yl group in the 4-position of the heterocycles.

RESULTS AND DISCUSSION

Synthesis. The synthesis of 2-(azulen-1-yl) substituted pyranylium salts was carried out following a similar route to that used for the generation of corresponding 4-substituted isomers (Scheme 1) [1]. The first step of the synthesis pathway consists in halogenation of 4,6-diphenyl-pyran-2-one, **1** [5], using $POCl_3$.

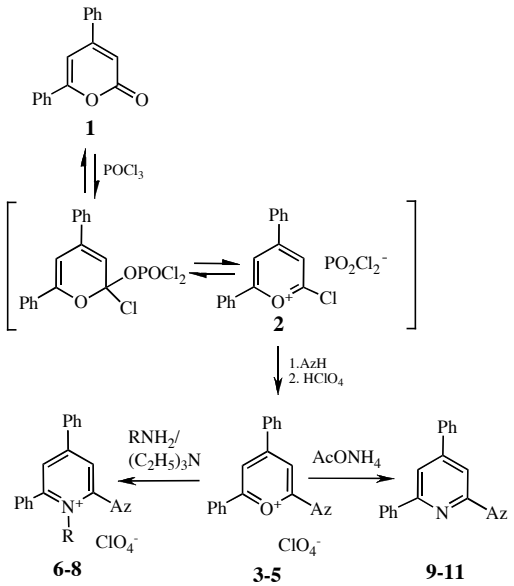
Table 1

Net charges at carbonyl group of diphenyl-pyranones

Compound	2-pyranone		4-pyranone	
Atom	C(2)	O	C(4)	O
Net Charge	0.334	-0.301	0.295	-0.313

The calculated net charges [6] on the atoms of carbonyl group in pyran-2 and 4-ones (Table 1) showed a smaller polarization of this group in pyran-2-one, which is hence less reactive. Therefore, in order to shift the equilibrium toward the addition product, an excess of $POCl_3$ must be used. Nevertheless, this excess is limited (2:1 ratio was used) by the sensitivity of azulenes to $POCl_3$ and by the difficult isolation of perchlorate in the final step of reaction.

Scheme 1



3,6,9 Az = azulen-1-yl,
4,7,10 Az = 4,6,8-trimethylazulen-1-yl,
5,8,11 Az = guaiazulen-1-il

R = *i*Pr, *n*Bu, Bn, Ph

Subsequently, 2-cloropyranylium salt, **2**, reacts *in situ* [7] with azulene in a nucleophilic reaction [8] followed by anion exchange with perchloric acid. Unfortunately, the reaction yields were severe diminished (35-45 %, Table 2) at the purification of the products by column chromatography due to the slight solubility of pyranylium perchlorates **3**-**5**.

The pyridinium salts were obtained generally in good yields from the pyranylium salts in two-steps reaction [2a]. The ring opening which requires a basic medium was accomplished using equimolar amounts of RNH_2 and NEt_3. The cyclization of the intermediate to form the pyridinium ring, in the second step of reaction, has occurred in the presence of 2 moles of acetic acid *per* mole of amine. The reaction time was usually 1 hour for the first step and two days for the second reaction step. The yields were good in the case of n-butylamine, isopropylamine and benzylamine whereas aniline reacted more difficultly and in lower yields.

Pyridine derivatives are easily synthesized by reaction of pyranylium salts with excess of ammonium acetate (10 equivalents) [2b]. Similar yields for synthesis of pyranylium salts, **3** or **4**, and for the corresponding pyridines, **9** or **10**, prove that, the reaction pyranylium salts → pyridines occurs almost quantitatively.

Approach to molecular geometry calculation. The value of dihedral angles α formed between the plane of the heterocycle and the planes of its aromatic substituents, mainly with the azulen-1-yl moiety, strongly influences the charge distribution and the magnetic field anisotropy in the obtained compounds **3-11** as well as in the corresponding compounds **12** with azulen-1-yl moiety in 4-position represented in Scheme 2. Therefore, we consider it interesting to correlate the calculated [9] dihedral angles with the electronic and NMR spectra of these compounds.

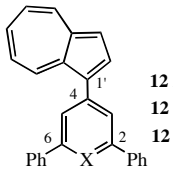
Table 2.

Yields (η) for the synthesis of 2-(azulen-1-yl) substituted 4,6-diphenyl-pyranylium and pyridinium perchlorates and of corresponding pyridines

Pyranylium salt		Pyridine[a]		Pyridinium salts[b]	
Comp	η (%)	Comp.	η (%)	Comp.	η (%)
3	36	**9**	42	**6***i*Pr	100
				6*n*Bu	100
				6Bn	69
				6Ph	26
4	44	**10**	43	**7***n*Bu	79
				7Bn	57
5	45	**11**	23	**8***n*Bu	70
				8Bn	70
				8Ph	34

[a]The yields were calculated starting from pyranone. [b]The yields were calculated starting from pyranylium salts.

Scheme 2



	Dihedral angle, α		
	(Az-Het)	(2Ph-Het)	(6Ph-Het)
12 X = N	39°	15°	4°
12 X = O^+	24°	20°	0°
12 X = N^+-Me	29°	62°	62°

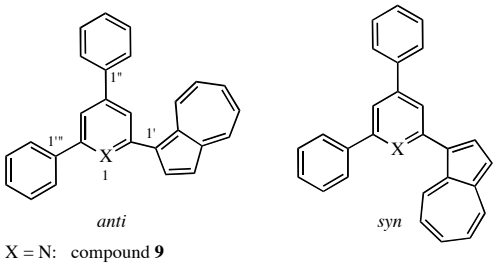
[ClO_4^- for X = O^+ or N^+-R]

12 X = O^+, N^+-R or N

For the compounds **12**, due to the negligible steric interaction between the azulenic proton 2'-H and 8'-H and the heterocycle protons, the dihedral angle $\alpha_{(Az\text{-}Het)}$ is decisively influenced by the push-pull interaction between an efficient electron donor and a good acceptor group, namely, azulene-1-yl and heterocycle moieties. Thus, it can be concluded that a higher electron conjugation leads to a smaller $\alpha_{(Az\text{-}Het)}$. This assumption is supported by the increase of $\alpha_{(Az\text{-}Het)}$ values in series **12** (X = O^+) ≈ **12** (X = N^+-Me) << **12** (X = N) as it is outlined in Scheme 2.

While in the compounds **12** both *ortho* positions relative to azulen-1-yl are substituted by hydrogen atoms, in the series **3-11** one position is substituted by hydrogen the other represents the heteroatom. As shown in Scheme 3, for these compounds two arrangements of azulene-1-yl and heterocycle moieties are possible, namely *syn* and *anti*, each with their own steric requirements. Hence, for comparison we have calculated the dihedral angles for both series of isomers as is shown in Table 3.

Scheme 3



X = N: compound **9**
X = O^+: compound **3**
X = N^+-R: compounds **6**

Table 3

Dihedral angles for 4-(azulen-1-yl)-4,6-diphenyl substituted pyridine and pyranylium and pyridinium cations

Heterocycle	α (°)		
	Az-Het	6Ph-Het	4Ph-Het
Pyridine **9** *sin*	35	42	41
9 *anti*	43	42	40
Pyranylium **3** *sin*	5	33	35
3 *anti*	21	25	34
1-*n*Bu pyridinium			
6Bu *sin*	51	54	20
6Bu *anti*	42	51	29

As a general rule, for pyranylium salts and pyridines the isomer *syn* is preferred because a free space is offered by the unsubstituted heteroatom to the seven-membered azulenic ring. Interaction between the strong positive charge of pyranylium oxygen with azulene-1-yl moiety reduces the angle $\alpha_{(Az\text{-}Het)}$ close to coplanarity. Strong steric strain for azulene group appears at the nitrogen quaternization in pyridinium salts. This is reflected in the high values of $\alpha_{(Az\text{-}Het)}$ as well as of $\alpha_{(6Ph\text{-}Het)}$. In this case the *anti* isomer is favored because the seven-membered ring is removed from the occupied space by the nitrogen substituent. Considerations on the influence of the nitrogen substituent in pyridinium salts upon compounds properties will be discussed in a special section.

Electronic spectra. Correlations between the dihedral angle $\alpha_{(Az\text{-}Het)}$ and the A and B bands of the recorded UV-Vis spectra for 4-(azulen-1-yl) substituted compounds **12** and for the corresponding 2-(azulen-1-yl) isomers **9**, **3** and **6***n*Bu are outlined in Table 4. Both A and B bands are intense and well structured for the majority of the analyzed compounds.

Table 4

Calculated dihedral angles and the recorded A and B band in the UV-Vis spectra

		12 X			**9**	**3**	**6***n*Bu
		N	O^+	N^+Me	(*syn*)	(*syn*)	(*anti*)
α(°)		39	24	29	35	5	42
λ_{max}	**B**	313sh	387	333	306	348	301
(log ε)	band	(4.32)	(4.17)	(4.12)	(4.22)	(4.33)	(4.39)
				344			
				(4.10)			
λ_{max}	**A**	370	530	434	373	525	419
(log ε)	band	(3.93)	(4.36)	(4.39)	(3.92)	(4.03)	(3.55)
					378		
					(3.93)		

While the wavelengths of A band are almost the same for the similar compounds of the two series, the B-band wavelength are higher shifted for compounds **12** by comparison with the isomers with azulen-1-yl at C-2 of heterocycle. Nevertheless, for both series of compounds, the wavelengths decrease in order X = O^+ > X = N^+*n*Bu > X = N. This corresponds just to the decrease of push-pull efficiency of the electronic system at the increase in $\alpha_{(Az\text{-}Het)}$ values. The slight hypsochromic shift observed in the case of the compound **6***n*Bu can be explained by the highest values of $\alpha_{(Az\text{-}Het)}$ and $\alpha_{(6Ph\text{-}Het)}$ which diminish the conjugation between the central heterocycle and 2- and 6-substituents.

The presence of the alkyl groups at azulene moiety in pyranylium salts causes an increase of $\alpha_{(Az\text{-}Het)}$ value, therefore on might anticipate a decrease in conjugation between the two moieties followed by a hypsochromic shift. However, the better stabilization of the positive charge on the seven-membered azulene ring, due to the inductive effect of alkyl groups, reduces the energy gap between HOMO and LUMO of the entire molecule. As a consequence, instead the attempted hypsochromic shift a bathochromic effect on the band A [10] is observed which increases in series **3** < **4** < **5** (Table 5). A bathochromic shift in pyridinium salts was also observed at the nitrogen quaternization with phenyl group instead of alkyl (Table 5). This is a consequence of the lower inductive effect of phenyl and, at the same time, of the more extended aromatic system.

The almost identical wavelengths recorded for the A band of pyridinium salts **6** (R = *i*Pr) and **6** (R = *n*Bu) arise from similar steric and inductive effects of the two groups.

Table 5

Recorded A band in the UV-Vis spectra for 2-azulen-1-yl substituted compounds **3-6**

	3	**4**	**5**	**6***i*Pr	**6***n*Bu	**6**Ph
λ_{max}	525	541	557	417	419	435
(logε)	(4.03)	(4.23)	(4.10)	(3.54)	(3.55)	(3.72)

Proton NMR spectra. ***Aromatic protons.*** The correlation between chemical shifts, δ, and the structure for 2,4,6-triarylpyridinium and triarylpyranylium salts was extensively studied [11]. In our recent paper we have also discussed some peculiarities observed in the NMR spectra of compounds **12** [1,2]. During our investigations we have shown that two main factors are determinant for the chemical shifts of protons for compounds **12**. These factors are the electronic push-pull effect azulene →

heterocycle and the change in anisotropy of magnetic field generated by aromatic substituents and heterocycle moiety according to the dihedral angle formed by their planes. Therefore, we consider useful to compare the obtained ^{1}H-NMR data for the compounds **12** and their 2-(azulen-1-yl)-substituted isomers.

electron density on seven-membered ring expectedly affects the protons substituted at this moiety, which are more deshielded. At the same time, the steric interference acts on 2'-H and to some extent on 8'-H. It is somehow surprising that the chemical shifts of the last two protons for the pyridinium salt **6** are placed close or even lower

Table 6

Chemical shifts of the aromatic protons in azulen-1yl substituted heterocycles (δ_H in ppm)

Compound	3-H and or 5-H	2'-H	3'-H	4'-H	5'-H	6'-H	7'-H	8'-H
Azulene[a]	-	7.81	7.30	8.23	7.05	7.45	7.05	8.23
12 X = N[a]	7.95	8.18	7.53	8.44	7.28	7.72	7.29	8.71
12 X = N$^+$-*n*Bu[b]	8.32	8.59	7.66	8.74	7.68	8.03	7.68	9.15
12 X = O$^+$[b]	8.83	8.92	7.77	8.89	8.03	8.31	8.14	9.57
9[a]	7.89 (5-H), 7.97 (3-H)	8.45	m[c]	8.44	7.29	7.73	7.43	9.96
10[a]	7.68 (5-H), 7.89 (3-H)	7.82	m[c]	-	7.08	-	7.12	-
6 *n*Bu[b]	8.33 (5-H), 8.42 (3-H)	8.46	7.71	8.70	7.61	8.02	7.61	8.78
7 *n*Bu[b]	8.42 (5-H), 8.57 (3-H)	7.98	7.63	-	7.43[d] (7.45)	-	7.45[d] (7.43)	-
3[b]	8.59 (5-H), 8.88 (3-H)	9.02	7.75	8.94	8.07[d] (8.17)	8.34	8.17[d] (8.07)	9.76
4[b]	8.71 (5-H), 8.73 (3-H)	8.56	7.63	-	7.88[d] (7.89)	-	7.89[d] (7.88)	-

[a]In $CDCl_3$. [b]In acetone-d_6. [c]The signal is a part from a multiplet for more protons. [d]The correct atribution for 5'- and 7'-H signals failed.

The deshielding effect of 3-H, placed between phenyl and azulen-1-yl groups is stronger by comparison with 5-H, as it was expected. It is not surprising that by alkylation of azulene-1-yl moiety the signals for 3-H and 5-H of all compounds **12** are upfield shifted as a consequence of the increase in $\alpha_{(Az\text{-}Het)}$. For isomers with (azulen-1-yl) in 2-position, both protons of the pyridinium ring are deshielded, whereas a shielding of the ring protons results in the case of pyridines. The high $\alpha_{(Az\text{-}Het)}$ value reduces to some extent the conjugation between pyridinium ring and azulene-1-yl moiety in position 2. As a consequence, the electron density on the heterocycle is lowered and determines the slight observed deshielding effect of its two protons. It might be assumed that the more intense deshielding of the pyranylium protons is due to the enhanced positive charge on the ring and this is really true for the proton at the 5-position. However, the proton at 3-position is upfield shifted possibly because the change in the direction of azulene magnetic field with the increase in $\alpha_{(Az\text{-}Het)}$ value.

The deshielding of heterocycle protons of both 2- and 4-(azulen-1-yl) substituted pyridinium salts follows the same order for the significance of R, namely, *i*Pr < Bu < Bn < Ph, accordingly to the inductive effect of nitrogen substituent (Table 7).

Substitution of azulene at C-1' with one of the studied heterocycles (coupled in 2- or 4-position) deshields all azulene protons according to the molecular charge distribution and steric factors (Table 6). Thus, the lower than the values for pyridine **9** whereas the other azulene-1-yl protons are deshielded. We believe that this is consistent with the higher value of $\alpha_{(Az\text{-}Het)}$ in pyridinium salts which modifies the magnetic field mainly for 2'- and 8'-H located closely to the heterocycle ring.

R protons in pyridinium salts. As we have pointed out, our early results indicated a slight anisotropy for 2- and 6-methyl protons as well as for 3- and 5-H in the case of 4-(azulene-1-yl)-2,6-dimethyl-1-isopropylpyranilium salt. The last protons are however equivalent when R = nBu or Bn. These findings are consistent with the high steric interference between 2 and 6 methyl substituents and *iPr* group which adopts an eclipsed conformation towards the heterocycle plane [2a,3b]. It was somewhat surprising that, for the similar 2,6-diphenyl-pyridinium salts **12** even when R = *i*Pr, the anisotropy disappears. On might assume that the high dihedral angles (62°) between phenyls and heterocycle planes minimize the steric interference imposed to *i*Pr group allowing its free rotation.

Table 7

The influence of nitrogen quaternization of 2- and 4-(azulen-1-yl)-diphenyl pyridinium salts on 5- and 7-H (δ in ppm)

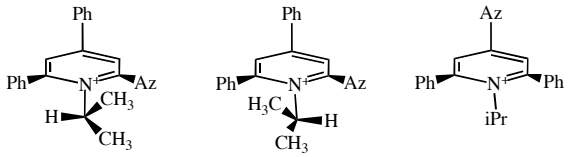
Position of azulen-1-yl group	Nitrogen substituent iPr	nBu	Bn	Ph
2	8.23/8.32	8.33/8.42	8.43/8.56	8.54/8.68
4	8.20	8.32	8.40	8.49

For the compound **6***i*Pr two conformers A1 and A2 are possible as it is represented in Scheme 4. High values of both $\alpha_{(Az\text{-}Het)}$ and $\alpha_{(6Ph\text{-}Het)}$ for compounds **6**-**8** (Table 3) allow the free rotation around N^+-alkyl bond and explain the non-existence of these conformers. Contrary to what is observed for the compound **12** N^+-*i*Pr, where the methyls of the *i*Pr group are equivalent, for **6***i*Pr a difference of 0.19 ppm in δ_H values of the methyl groups was observed.

While in salts **12** the heterocycle is symmetrically substituted and around the azulene-pyridinium bond a free rotation is allowed, in the compounds **6**-**8** the isopropyl group is prochiral due to the molecular asymmetry generated by the rotational restriction around the azulene - pyridinium bond produced by the substituent at the quaternary nitrogen. This explains the $\Delta\delta_H$ between the methyl groups.

The $\Delta\delta_H$ of 0.18 ppm between AB doublets of methylene protons in salt **6**Bn is consistent with the fact that these protons are diastereotopic.

Scheme 4



6*i*Pr (A1) **6***i*Pr (A2) **12** X = N^+*i*Pr

6*i*Pr: 2 d, δ_H 1.25 and 1.44 ppm, ^3J = 7.2 Hz, each for 3H, 2C<u>H</u>$_3$ and hept, δ_H 5.26, ^3J = 7.2 Hz, for 1H, $(CH_3)_2C\underline{H}$

12 X = **N^+***i*Pr: d, δ_H 1.44 ppm, ^3J = 7.2 Hz, 6H, 2C<u>H</u>$_3$ and hept, δ_H 5.18 ppm, J = 7.2 Hz, for 1H, $(CH_3)_2C\underline{H}$

Prochirality of butyl group in **6***n*Bu made also diastereotopic the protons of methylene linked to nitrogen, $(CH_2)_\alpha$. They couple each other with a high *gem*-coupling constant and are also coupled with their neighboring methylene protons. These last protons are, in turn, magnetically non-equivalent therefore the multiplicity of $(CH_2)_\alpha$ signal becomes $d_{AB}dd$ with ^2J = 13.6 Hz, ^3J = 10.8 Hz, ^3J = 5.6 Hz [12]. It is interesting to observe that the last two values indicate a rather rigid conformation for the $(CH_2)_\beta$-$(CH_2)_\alpha$ fragment. The rule that the effect of prochirality decreases with the distance from the center of asymmetry [13] is true also for the *n*-butyl chain of compounds **6**-**8***n*Bu. In this case $\Delta\delta_H$ for pairs of diastereotopic methylene protons decrease with the distance to heterocycle (for **6***n*Bu, $\Delta\delta_H$ in ppm: $(CH_2)_\alpha$ = 0.20; $(CH_2)_\beta$ = 0.09; $(CH_2)_\gamma$ = 0.01). It is important to note that for all pyridinium salts, the value of $\Delta\delta_H$ decrease with the increase of temperature until signals coalescence [14].

CONCLUSIONS

We have obtained and characterized three classes of 2-(azulen-1-yl)-4,6-diphenyl-heterocycles namely, pyranylium and pyridinium salts and pyridine, respectively. In order to carry out a comparative structural analysis between these compounds and their corresponding isomers with azulen-1-yl moiety in the 4 position of the heterocycle we have calculated dihedral angles between the planes of the central heterocycle and the aromatic substituents. The dihedral angle determines the intensity of the push-pull effect between the heterocycle and the aromatic groups as well as the direction of the magnetic fields generated by the aromatic ring current. This fact is well reflected in the electronic and ^{1}H-NMR spectra of both isomer series. Perhaps the most interesting result from this contribution can be associated to the behavior in magnetic field of the substituents at nitrogen in pyridinium salts with azulenyl group in 2-position, compounds **6**-**8**. In these compounds the substituent at quaternary nitrogen is prochiral due to the molecular asymmetry generated by the rotational restriction around azulene-pyridinium bond produced just by the neighborhood of nitrogen substituent. This property generates the magnetically non-equivalence of *geminal* protons or methyl groups of R in the ^{1}H-NMR spectra of salts **6**-**8**. One may wonder how the above presented structural conclusions, based mainly from spectral data, are in accord with the structural compound features which will be given by the crystal structure analysis. It is expected that the crystallographic packing interactions will change the compounds environment and will reduce their freedom degrees comparatively to the behavior in the NMR solution. This viewpoint of the research is in progress.

EXPERIMENTAL

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. UV-Vis spectra in methanol: Varian Cary 100 spectrophotometer. ^{1}H and ^{13}C nmr: Bruker Avance DRX4 (^{1}H nmr: 400 MHz, ^{13}C nmr: 100.62 MHz), δ are expressed in ppm J in Hz, TMS was used as internal standard in acetone-d_6 and $CDCl_3$ at the room temperature; COSY and HETCOR correlation experiments were used for the structure assignment (the numbering for the compounds is indicated in the Schemes). 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. 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 $LiAlH_4$.

General Procedures for Synthesis.

Synthesis of 4,6-diphenyl-pyranylium salts substituted in 2-position with (azulen-1-yl) moieties. 4,6-Diphenyl-pyran-2-

one [4] (0.1 mmol) and freshly distilled $POCl_3$ (0.2 mmol) were dissolved in nitromethane (~ 2 mL). The stirred reaction mixture was heated at 60 °C for 6 hour. Then, it was cooled at room temperature and azulenic compound (0.2 mmol) was added to the mixture. The stirring was continued over night. Finally, an excess of perchloric acid 70 % was added and the temperature was raised to 70-80 °C when an evolvement of HCl was observed. After cooling down, the pyranylium salts were precipitated in ether and separated by filtration. The solid was chromatographed on silica gel column with benzene-acetone (from 0 % to 100 % acetone) as eluent. If unreacted azulene derivatives are present in the reaction mixture, they were eluted first. Then, a brown material, mainly pyranone, was separated and finally the pyranylium salt was collected (the yields are reported in Table 2).

Synthesis of 4,6-diphenyl-pyridines substituted in 2-position with (azulen-1-yl) moieties. Pyranylium perchlorate (without purification) was refluxed in ethanol with ammonium acetate (molar ratio perchlorate:acetate = 1:10) for one hour. The solvent was evaporated under vacuum and the residue dissolved in a small amount of DCM and washed with water. The organic layer was dried (over Na_2SO_4) and the solvent was removed under vacuum. The chromatography on silica-gel using *n*-pentane-DCM (from 0 % to 100 % DCM) as eluent afforded the pure pyridines (the yields are reported in Table 2) as blue or green solutions.

Synthesis of 4,6-diphenyl-pyridinium salts substituted in 2-position with (azulen-1-yl) moieties. Under inert atmosphere (for avoiding air moisture), pure pyranylium perchlorate (1 mmol), amine, RNH_2, (1 mmol) and triethylamine (1 mmol) were dissolved in DCM (40 mL) with magnetically stirring, at room temperature. The stirring was continued for 30-60 minutes. Then, acetic acid (2 mmol) was added and the reaction mixture was stirred for 48 hours at room temperature. The solvent was evaporated under vacuum and the products were separated from the obtained tar on silica gel with DCM and ethanol (from 0 % to 5% ethanol). The separated salts (the yields are reported in Table 2) are usually brown in solution.

Product Characterization.

2-(Azulen-1-yl)-4,6-diphenyl-pyranylium perchlorate, 3. Dark brown crystals, (red in solution), mp 280 °C; uv (MeOH), λ_{max} (log ε): 216 (4.33), 247 (4.35), 285 (4.30), 327 (4.31), 348 (4.33), 525 (4.03); ^{1}H nmr (acetone-d_6): δ 7.72-7.80 (m, 2H, 3"-H, 5"-H), 7.75 (d, J = 5.0, 1H, 3'-H), 7.80-7.89 (m, 4H, 4"-H, 3"'-H, 4"'-H, 5"'-H), 8.07 (t, J = 10.0 Hz, 1H, 5'(or 7')-H), 8.17 (t, J = 10.0 Hz, 1H, 7'(or 5')-H), 8.34 (t, J = 10.0 Hz, 1H, 6'-H) 8.43 (d, J = 7.6 Hz, 2H, 2"-H, 6"-H), 8.50 (dd, J = 8.0, 1.6 Hz, 2H, 2"'-H, 6"'), 8.59 (d, J = 1.6 Hz, 1H, 5-H), 8.88 (d, J = 1.6 Hz, 1H, 3-H), 8.94 (d, J = 10.0 Hz, 1H, 4'-H), 9.02 (d, J = 4.4 Hz, 1H, 2'-H), 9.76 (d, J = 10.0 Hz, 1H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 113.1 (C5), 118.0 (C3), 124.9 (C3'), 129.3 (C2"', C6"'), 130.4 (C2", C6"), 131.4 (C3"', C5"'), 131.6 (C3", C5"), 134.6 (C5'), 134.8 (C7'), 135.2 (C1"', C1'), 135.3 (C4"'), 135.4 (C4"), 135.7 (C1"), 140.2 (C8'), 142.0 (C2'), 142.1 (C3a'), 142.5 (C4'), 144.4 (C6'), 151.9 (C8a'), 162.4 (C4), 169.5 (C6), 171.5 (C2) ppm; ms (ESI): 359 (M^+, 100%). *Anal.* Calcd. for $C_{27}H_{19}O_5Cl$: C, 70.67; H, 4.17. Found: C, 70.53; H, 4.35.

4,6-Diphenyl-2-(4,6,8-trimethyl-azulen-1-yl)-pyranylium perchlorate, 4. Dark brown crystals (violet in solution), mp 185 °C; uv (MeOH), λ_{max} (log ε): 216 (4.33), 244 (4.47), 333 (4.47), 385 (3.88), 541(4.23). ^{1}H nmr (acetone-d_6): 2.85 (s, 3H, Az-Me), 2.97 (s, 3H, Az-Me), 3.07 (s, 3H, Az-Me), 7.63 (d, J = 4.8 Hz, 1H, 3'-H), 7.73-7.87 (m, 6H, 3"-H, 4"-H, 5"-H 3"'-H, 4"'-H, 5"'-H), 7.88 (s, 1H, 5'-H or 7'-H) 7.89 (s, 1H, 7'-H or 5'-H), 8.38 (dd, J = 7.6, 1.4 Hz, 2H, 2"-H, 6"-H), 8.44 (dd, J = 7.2, 1.4 Hz, 2H, 2"'-H, 6"'-H), 8.56 (d, J = 4.8 Hz, 1H, 2'-H), 8.71 (d, J = 1.2 Hz, 1H, 5-H), 8.73 (s, 1H, 3-H) ppm; ^{13}C nmr (acetone-d_6): δ 25.89 (Az-Me), 28.28 (Az-Me), 29.27 (Az-Me), 118.0 (C3), 112.0 (C5), 124.9 (C3'), 128.4 (C2", C6"), 129.8 (C2"', C6"'), 130.7 (CH), 130.9 (CH), 134.7 (CH), 134.9 (CH), 135.2 (Cq), 135.5 (Cq), 136.6 (CH), 136.8 (CH), 137.8 (Cq), 140.3 (C2'), 146.6 (Cq), 150.5 (Cq), 151.3 (Cq), 162.3 (C4), 169.0 (C6), 171.0 (C2) ppm; ms (ESI): 401 (M^+, 100%). *Anal.* Calcd. for $C_{30}H_{25}O_5Cl$: C, 71.93; H, 5.03;. Found: C, 71.95; H, 5.06.

2-(5-Isopropyl-3,8-dimethyl-azulen-1-yl)-4,6-diphenyl-pyranylium perchlorate, 5. Dark brown crystals (blue in solution), mp 164 °C; uv (MeOH), λ_{max} (log ε): 217 (4.34), 238 (4.36), 332 (4.31), 351 (4.25), 394 (3.98), 557 (4.10). ^{1}H nmr (acetone-d_6): δ 1.49 (d, J = 6.8 Hz, 6H, *Me*$_2$CH), 2.73 (s, 3H, Me(3')), 2.99 (s, 3H, Me(8')), 3.43 (hept, J = 6.8 Hz, 1H, Me$_2$C*H*), 7.72-7.86 (m, 6H, 3"-H, 4"-H, 5"-H, 3"'-H, 4"'-H, 5"'-H), 7.96 (d_{AB}, J = 10.8 Hz, 2H, 7'-H), 8.16 (d_{AB}d, J = 10.8, 2.0 Hz, 1H, 6'-H), 8.38 (dt, J = 8.0, 1.2 Hz, 2H, 2"-H, 6"-H), 8.44 (dt, J = 8.0, 1.2 Hz, 2H, 2"'-H, 6"'-H), 8.57 (s, 1H, 2'-H), 8.63 (s, 2H, 3-H, 5-H), 8.67 (d, J = 2.0 Hz, 1H, 4'-H) ppm; ^{13}C nmr (acetone-d_6): δ 13.6 (Az-Me(3')), 25.5 (*C*HMe$_2$), 29.0 (Az-Me(8')), 39.6 (CH(*C*H$_3$)$_2$), 111.3 (C5), 118.8 (C3'), 128.6 (C2", C6"), 130.8 (C2"', C6"'), 131.2 (CH), 131.3 (CH), 131.6 (C3), 135.0 (CH), 135.2 (CH), 135.5 (Cq), 135.8 (Cq), 137.3 (C7'), 137.8 (C4'), 140.0 (C6'), 142.6 (C2'), 143.0 (Cq), 146.3 (Cq), 151.0 (Cq), 154.5 (Cq), 162.0 (C4), 168.3 (C6), 170.5 (C2) ppm; ms (ESI): 429 (M^+, 100%). *Anal.* Calcd. for $C_{32}H_{29}O_5Cl$: C, 72.65; H, 5.53. Found: C, 72.60; H, 5.63.

2-(Azulen-1-yl)-1-isopropyl-4,6-diphenyl-pyridinium perchlorate, 6*i*Pr. Brown crystals, mp 108 °C; uv (MeOH), λ_{max} (log ε):232 (4.26), 282 (4.41), 301 (4.29), 417 (3.54); ^{1}H nmr (acetone-d_6): δ 1.25 (d, J = 7.2 Hz, 3H, C*H*$_3$CH), 1.44 (d, J = 7.2 Hz, 3H, C*H*$_3$CH), 5.26 (hept, J = 7.2 Hz, 2H, (CH$_3$)$_2$C*H*), 7.52 (t, J = 9.9 Hz, 1H, 5'-H or 7')-H), 7.55 (t, J = 9.6 Hz, 1H, 7'-H or 5'-H), 7.56-7.61 (m, 3H, 3"'-H, 4"'-H, 5"'-H), 7.66 (d, J = 4.0 Hz, 1H, 3'-H), 7.68-7.73 (m, 3H, 3"-H, 4"-H, 5"-H), 7.86-7.92 (m, 2H, 2"-H, 6"-H), 7.96 (t, J = 9.9 Hz, 1H, 6'-H), 8.09 (d, J = 7.0 Hz, 2H, 2"'-H, 6"'-H), 8.23 (d, J = 2.3 Hz, 1H, 5-H), 8.31 (d, J = 2.4 Hz, 1H, 3-H), 8.32 (d, J = 4.2 Hz, 1H, 2'-H), 8.60 (d, J = 9.8 Hz, 1H, 4'-H), 8.75 (d, J = 9.5 Hz, 1H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 23.02 (CH*Me*), 23.99 (CH*Me*), 63.56 (Me$_2$*C*H), 118.6 (C3'), 121.5 (C1'), 127.1 (C5', C7'), 128.1 (C5), 129.2 (C2"', C6"'), 130.2 (C3), 130.3 (CH), 130.4 (C2", C6"), 130.5 (CH), 131.5 (CH), 132.8 (CH), 134.6 (Cq), 135.2 (Cq), 137.4 (C8'), 139.4 (Cq), 139.6 (C2'), 140.1 (C4'), 140.8 (C6'), 142.9 (Cq), 154.3 (C2), 155.2 (C4), 158.8 (C6) ppm; ms (ESI): 402 (M^+, 100%). *Anal.* Calcd. for $C_{30}H_{26}ClNO_4$: C, 72.12; H, 5.25; N, 2.81. Found: C, 72.21; H, 5.34; N, 2.72.

2-(Azulen-1-yl)-1-(but-1-yl)-4,6-diphenyl-pyridinium perchlorate, 6*n*Bu. Brown crystals, mp 101 °C, uv (MeOH), λ_{max} (log ε): 231 (4.26), 281 (4.38), 301 (4.29), 419 (3.55); ^{1}H nmr (acetone-d_6): δ 0.29 (t, ^{3}J = 7.2 Hz, 3H, Bu-C*H*$_3$), 0.73 (sext, J = 7.2 Hz, 1H, Bu–(C*H*$_2$)$_\gamma$), 0.74 (sext, J = 7.2 Hz, 1H, Bu–(C*H*$_2$)$_\gamma$), 1.27-1.39 (m, 1H, Bu–(C*H*$_2$)$_\beta$), 1.46-1.58 (m, 1H, Bu–(C*H*$_2$)$_\beta$), 4.46-4.54 (m, 1H, Bu–(C*H*$_2$)$_\alpha$), 4.76-4.84 (m, 1H, Bu–(C*H*$_2$)$_\alpha$), 7.59-7.69 (m, 3H, 4"-H, 3"'-H, 5"'-H), 7.61 (t, J = 6.8 Hz, 1H, 5'-H or 7'-H), 7.64 (t, J = 9.6 Hz, 1H, 7'-H or 5'-H), 7.71 (d, J = 4.4 Hz, 1H, 3'-H), 7.73-7.77 (m, 3H, 4"'-H, 3"-H, 5"-H), 7.97-8.01

(m, 2H, 2"-H, 6"-H), 8.02 (t, J = 9.6 Hz, 1H, 6'-H), 8.16 (dd, J = 8.0, 1.2 Hz, 2H, 2"'-H, 6"'-H), 8.33 (d, J = 2.4 Hz, 1H, 5-H), 8.42 (d, J = 2.4 Hz, 1H, 3-H), 8.46 (d, J = 4.8 Hz, 1H, 2'-H), 8.70 (d, J = 9.6 Hz, 1H, 4'-H), 8.78 (d, J = 9.6 Hz, 1H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 13.57 (Bu-*C*H$_3$), 20.38 (Bu–(*C*H$_2$)$_\gamma$), 32.92 (Bu–(*C*H$_2$)$_\beta$), 56.52 (Bu–(*C*H$_2$)$_\alpha$), 120.0 (C3'), 121.2 (C1'), 127.4 (C3), 128.1 (C5' or 7'), 128.3 (C7'or 5'), 129.7 (C5), 129.9 (C2"', C6"'), 130.7 (C3"', C5"'), 130.8 (C2", C6"), 131.2 (C3", C5"), 132.4 (C4"'), 133.6 (C4"), 135.1 (C$_q$), 135.6 (C$_q$), 137.5 (C4'), 139.5 (C2'), 139.8 (C$_q$), 140.8 (C8'), 141.7 (C6'), 144.1 (C$_q$), 155.0 (C2), 156.0 (C6), 158.5 (C4) ppm; ms (ESI): 414 (M$^+$, 100%). *Anal.* Calcd. for $C_{31}H_{28}ClNO_4$: C, 72.49; H, 5.50; N, 2.73. Found: C, 72.35; H, 5.78; N, 2.61.

2-(Azulen-1-yl)-1-benzyl-4,6-diphenyl-pyridinium perchlorate, 6Bn. Brown crystals, mp 98 °C; uv (MeOH), λ$_{max}$ (log ε): 233 (4.36), 285 (4.30), 305 (4.21), 430 (3.58); ^{1}H nmr (acetone-d_6): δ 5.84 (d$_{AB}$, J = 16.0 Hz, 1H, Ph-C*H*$_2$), 6.02 (d$_{AB}$, J = 16.0 Hz, 1H, Ph-C*H*$_2$), 6.56 (dd, J = 8.0, 2.0 Hz, 2H, 2^{IV}-H, 6^{IV}-H), 6.92-7.01 (m, 3H, 3^{IV}-H, 4^{IV}-H, 5^{IV}-H), 7.48 (t, J = 9.6 Hz, 1H, 5'(or 7')-H), 7.55-7.73 (m, 8H, 3'-H, 7'(or 5')-H, 3"'-H, 4"'-H, 5"'-H, 3"-H, 4"-H, 5"-H), 7.78 (dd, J = 7.2 Hz, ^{4}J = 1.2 Hz, 2H, 2"-H, 6"-H), 7.93 (t, J = 9.8 Hz, 1H, 6'-H), 8.23 (dd, J = 8.0, 1.2 Hz, 2H, 2"'-H, 6"'-H), 8.32 (d, J = 4.0 Hz, 1H, 2'-H), 8.43 (d, J = 2.4 Hz, 1H, 5-H), 8.51 (d, J = 9.2 Hz, 1H, 4'-H), 8.56 (d, J = 2.4 Hz, 1H, 3-H), 8.68 (d, J = 9.6 Hz, 1H, 8'-H) ppm; ^{13}C nmr (acetone-d_6): δ 59.65 (Ph*C*H$_2$), 119.5 (C3'), 120.6 (C1'), 126.6 (C4^{IV}), 126.9 (C2^{IV}, C6^{IV}), 127.6 (C5), 127.7 (C5'), 128.7 (C3), 129.0 (C7'), 129.3 (C2"', C6"'), 129.4 (C2", C6"), 130.0 (C3", C5", C3"', C5"'), 130.6 (C3^{IV}, C5^{IV}), 131.8 (C4"'), 133.2 (C4"), 134.4 (C$_q$), 134.8 (C$_q$), 135.3 (C$_q$), 136.6 (C8'), 138.5 (C2'), 139.1 (C$_q$), 140.1 (C4'), 141.0 (C6'), 143.8 (C$_q$), 155.2 (C2), 156.2 (C6), 158.8 (C4) ppm; ms (ESI): 448 (M$^+$, 100%). *Anal.* Calcd. for $C_{34}H_{26}ClNO_4$: C, 74.52; H, 4.78; N, 2.56. Found: C, 74.43; H, 4,85; N, 2.48.

2-(Azulen-1-yl)-1,4,6-triphenyl-pyridinium perchlorate, 6Ph. Brown crystals, mp 123 °C; uv (MeOH), λ$_{max}$ (log ε): 233 (4.36), 284 (4.41), 311 (4.34), 435 (3.72); ^{1}H nmr (acetone-d_6): δ 7.15-7.26 (m, 3H, aromatics), 7.31 (d, J = 4.0 Hz, 1H, 3'-H), 7.38-7.47 (m, 4H, aromatics), 7.52-7.61 (m, 5'-H, 7'-H and 3H aromatics), 7.62 (d, J = 4.4 Hz, 1H, 2'-H), 7.71 (tt, 1H, J = 7.2, 1.4 Hz, 4"'-H) 7.72 (t, 2H, J = 8.0 Hz, 3"'-H, 5"'-H), 7.97 (t, J = 9.8 Hz, 1H, 6'-H), 8.30 (dt, J = 8.0, 1.4 Hz, 2H, 2"'-H, 6"'-H), 8.54 (d, J = 2.0 Hz, 1H, 5-H), 8.58 (d, J = 9.6 Hz, 1H, 4'-H), 8.68 (d, J = 2.0 Hz, 1H, 3-H), 8.84 (d, J = 10.0 Hz, 1H, 8'-H) ppm; ^{13}C nmr (acetone-d_6) [15]: δ 118.9 (CH), 120.8 (Cq), 125.6 (C5), 127.4 (CH), 127.5 (CH), 128.1 (C3), 129.1 (CH), 129.4 (CH), 129.6 (CH), 130.6 (CH), 130.7 (CH), 130.9 (CH), 134.5 (Cq), 135.1 (Cq), 136.9 (CH), 139.4 (CH), 139.7 (CH), 140.7 (CH), 140.8 (Cq), 143.3 (Cq), 154.7 (Cq), 156.6 (Cq), 158.1 (Cq) ppm; ms (ESI): 434 (M$^+$, 100%). *Anal.* Calcd. for $C_{33}H_{24}ClNO_4$: C, 74.22; H, 4.53; N, 2.62. Found: C, 74.35; H, 4.62; N, 2.70.

1-(But-1-yl)-4,6-diphenyl-2-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, 7*n*Bu. Brown crystals, mp 144 °C; uv (MeOH), λ$_{max}$ (log ε): 221 (4.38), 242 (4.41), 294 (4.48), 357 (3.80), 451 (3.59); ^{1}H nmr (acetone-d_6): δ 0.32 (t, J = 7.2 Hz, 3H, Bu-C*H*$_3$), 0.72 (sext, J = 7.2 Hz, 2H, Bu–(C*H*$_2$)$_\gamma$), 1.49-1.55 (m, 2H, Bu–(C*H*$_2$)$_\beta$), 2.65 (s, 3H, Az-Me(8')), 2.73 (s, 3H, Az-Me(6')), 3.03 (s, 3H, Az-Me(4')), 4.34 (d$_{AB}$dd, J = 13.4, 10.5, 5.8 Hz, 1H, Bu–(C*H*$_2$)$_\alpha$), 4.63 (d$_{AB}$dd, J = 13.4, 10.5, 6.0 Hz, 1H, Bu–(C*H*$_2$)$_\alpha$), 7.43 (s, 1H, 5'-H or 7'-H), 7.45 (s, 1H, 7'-H or 5'-H), 7.56-7.60 (m, 1H, 4"-H), 7.63 (d, J = 4.0 Hz, 1H, 3'-H), 7.67 (t, J = 7.2 Hz, 2H, 3"'-H, 5"'-H), 7.69 (t, J = 7.2 Hz, 1H, 4"'-H), 7.72-7.78 (m, 2H, 3"-H, 5"-H), 7.89-7.94 (m, 2H, 2"-H, 6"-H), 7.98 (d, J = 4.0 Hz, 1H, 2'-H), 8.23 (dd, J = 7.6, 1.4 Hz, 2H, 2"'-H, 6"'-H), 8.42 (d, J = 2.0 Hz, 1H, 5-H), 8.57 (d, J = 2.4 Hz, 1H, 3-H) ppm; ^{13}C nmr (acetone-d_6): δ 13.48 (Bu-*C*H$_3$), 20.59 (Bu–(*C*H$_2$)$_\gamma$), 26.58 (Az-Me(6')), 28.82 (Az-Me(8')), 29.27 (Az-Me(4')), 32.42 (Bu–(*C*H$_2$)$_\beta$), 56.20 (Bu–(*C*H$_2$)$_\alpha$), 118.0 (C3'), 120.7 (C1'), 127.6 (C5), 129.5 (C3), 130.0 (C2"', C6"'), 130.6 (C4"), 130.8 (C2", C6"), 130.9 (C3", C5"), 131.3 (C3"', C5"'), 131.6 (C4"'), 132.6 (C5'), 132.9 (C7'), 134.5 (C$_q$), 134.6 (C$_q$), 134.7 (C$_q$), 137.7 (C2'), 140.3 (C$_q$), 148.6 (C8'), 150.2 (C4'), 151.0 (C6'), 155.5 (C6), 157.6 (C4), 159.3 (C2) ppm; ms (ESI, m/z, %): 456 (M$^+$, 100). *Anal.* Calcd. for $C_{34}H_{34}ClNO_4$: C, 73.44; H, 6.16; N, 2.52. Found: C, 73.35; H, 6.13; N, 2.50.

1-Benzyl-4,6-diphenyl-2-(4,6,8-trimethyl-azulen-1-yl)-pyridinium perchlorate, 7Bn. brown crystals, mp 105 °C; uv (MeOH), λ$_{max}$ (log ε): 227 (4.35), 241 (4.36), 296 (4.44), 342sh (3.86), 439 (3.68); ^{1}H nmr (acetone-d_6): δ 2.60 (s, 3H, Me(8')), 2.73 (s, 3H, Me(6')), 2.99 (s, 3H, Me(4')), 5.75 (d$_{AB}$, J = 16.0 Hz, 1H, Ph-C*H*), 5.93 (d$_{AB}$, J = 15.6 Hz, 1H, Ph–C*H*), 6.56 (d, J = 7.6 Hz, 2H, 2^{IV}-H, 6^{IV}-H), 7.08 (t, J = 7.6 Hz, 2H, 3^{IV}-H, 5^{IV}-H), 7.18 (t, J = 7.6 Hz, 1H, 4^{IV}-H), 7.44 (s, 1H, 5'-H or 7'-H), 7.49 (d, J = 4.4 Hz, 1H, 3'-H), 7.52 (s, 1H, 7'-H or 5'-H), 7.60-7.78 (m, 8H, 5H for 4-Ph and 3"'-H, 4"'-H, 5"'-H), 7.87 (d, J = 4.4 Hz, 1H, 2'-H), 8.28 (dd, J = 7.8, 1.4 Hz, 2H, 2"'-H, 6"'-H), 8.50 (d, J = 2.4 Hz, 1H, 5-H), 8.65 (d, J = 2.4 Hz, 1H, 3-H) ppm; ^{13}C nmr (acetone-d_6) [16]: δ 26.56 (Az-Me(6')), 28.82 (Az-Me(8')), 29.24 (Az-Me(4')), 50.19 (Ph*C*H$_2$), 118.1 (CH), 120.9 (Cq), 127.7 (C5), 128.1 (CH), 129.5 (C3), 129.7 (CH), 130.1 (CH), 130.5 (CH), 130.7 (CH), 130.8 (CH), 131.3 (CH), 131.8 (CH), 133.1 (CH), 132.5 (CH), 134.1 (Cq), 134.6 (Cq), 134.9 (Cq), 135.5 (CH), 137.8 (C2'), 140.8 (Cq), 148.7(C8'), 150.3 (C4'), 151.1 (C6'), 153.3 (Cq), 158.2 (Cq), 159.6 (Cq) ppm; ms (ESI, m/z, %): 490 (M$^+$, 100). *Anal.* Calcd. for $C_{37}H_{32}ClNO_4$: C, 75.31; H, 5.47; N, 2.37. Found: C, 75.40; H, 5.64; N, 2.45.

1-(But-1-yl)-2-(5-isopropyl-3,8-dimethyl-azulen-1-yl)-4,6-diphenyl-pyridinium perchlorate, 8*n*Bu. Brown crystals, mp 118 °C; uv (MeOH), λ$_{max}$ (log ε): 225 (4.31), 242 (4.36), 294 (4.42), 356 sh (3.73), 455 (3.46); ^{1}H nmr (acetone-d_6): δ 0.33 (t, J = 7.4 Hz, 3H, Bu-C*H*$_3$), 0.75 (sext, J = 7.2 Hz, 2H, Bu–(C*H*$_2$)$_\gamma$), 1.44 (d, J = 6.8 Hz, 6H, *Me*$_2$CH), 1.47-1.59 (m, 2H, Bu–(C*H*$_2$)$_\beta$), 2.64 (s, 3H, Az-Me$_8$), 2.76 (s, 3H, Az-Me$_3$), 3.29 (hept, J = 6.8 Hz, 1H, Me$_2$C*H*), 4.41 (d$_{AB}$dd, J = 13.6, 10.8, 5.6 Hz, 1H, Bu–(C*H*$_2$)$_\alpha$), 4.69 (d$_{AB}$dd, J = 13.6, 10.8, 5.6 Hz, 1H, Bu–(C*H*$_2$)$_\alpha$), 7.43 (d, J = 10.4 Hz, 1H, 7'-H), 7.66 (t, J = 6.8 Hz, 2H, 3"'-H, 5"'-H), 7.69 (t, J = 6.8 Hz, 1H, 4"'-H), 7.73-7.78 (m, 3H, 3"-H, 4"-H, 5"-H), 7.82 (dd, J = 10.8, 2.0 Hz, 1H, 6'-H), 7.92-7.94 (m, 2H, 2"-H, 6"-H), 8.01 (s, 1H, 2'-H), 8.23 (dt, J = 8.0, 1.6 Hz 2H, 2"'-H, 6"'-H), 8.42 (d, J= 2.0 Hz, 1H, 5-H), 8.55 (d, J = 2.4 Hz, 1H, 3-H), 8.58 (d, J = 2.4 Hz, 1H, 4'-H) ppm; ^{13}C nmr (acetone-d_6) [13]: δ 13.50 (Bu-*C*H$_3$), 13.60 (Az-Me(3')), 20.58 (Bu–(*C*H$_2$)$_\gamma$), 25.48 (*Me*$_2$CH), 27.98 (Az-Me(8')), 32.41 (Bu–(*C*H$_2$)$_\beta$), 39.40 (Me$_2$*C*H), 56.20 (Bu–(*C*H$_2$)$_\alpha$), 127.6 (Cq), 117.8 (C1'), 127.5 (C5), 129.8 (C3), 130.0 (C2"', C6"'), 130.8 (C2", C6"), 130.9 (C3", C5"), 131.3 (C3"', C5"'), 131.6 (C4"'), 132.6 (C7'), 133.9 (C4"), 134.8 (Cq), 134.8 (Cq), 136.0 (Cq), 137.4 (C4'), 138.7 (C6'), 140.6 (C2'), 140.8 (Cq), 145.7 (Cq), 147.2 (Cq), 155.1 (C6), 157.6 (C4), 159.3 (C2) ppm; ms (ESI, m/z, %): 484 (M$^+$, 100). *Anal.* Calcd. for $C_{36}H_{38}ClNO_4$: C, 74.02; H, 6.56; N, 2.40. Found: C, 74,06; H, 6,63; N, 2.35.

1-Benzyl-2-(5-isopropyl-3,8-dimethyl-azulen-1-yl)-4,6-diphenyl-pyridinium perchlorate, 8Bn. Brown crystals, mp 121

°C; uv (MeOH), λ_{max} (log ε): 219 (4.35), 243 (4.36), 294 (4.39), 347sh (3.85), 467 (3.44). ^{1}H nmr (acetone-d_6): δ 1.43 (d, J = 6.8 Hz, 6H, *Me*$_2$CH), 2.55 (s, 3H, Me(8')), 2.65 (s, 3H, Me(3')), 3.25-3.35 (m, 1H, Me$_2$C*H*), 5.77 (d_{AB}, J = 15.6 Hz, 1H, Ph–C*H*), 5.97 (d_{AB}, J = 15.6 Hz, 1H, Ph–C*H*), 6.54 (d, J = 7.6 Hz, 2H, 2^{IV}-H, 6^{IV}-H), 7.07 (t, J = 7.6 Hz, 2H, 3^{IV}-H, 5^{IV}-H), 7.17 (t, J = 7.6 Hz, 1H, 4^{IV}-H), 7.40 (d, J = 10.4 Hz, 2H, 7'-H), 7.61-7.73 (m, 6H, 3"-H, 4"-H, 5"-H, 3"'-H, 4"'-H, 5"'-H), 7.68 (dt, J = 6.8, 2.0 Hz, 2H, 2"-H, 6"-H), 7.81 (dd, J = 10.8, 2.0 Hz, 1H, 6'-H), 7.86 (s, 1H, 2'-H), 8.27 (dt, J = 8.0, 1.6 Hz, 2H, 2"'-H, 6"'-H), 8.48 (d, J = 2.2 Hz, 1H, 5-H), 8.53 (d, J = 2.0 Hz, 1H, 4'-H), 8.61 (d, J = 2.4 Hz, 1H, 3-H) ppm; ^{13}C nmr (acetone-d_6) [14]: δ 13.54 (Me)3')), 25.42 (*Me*$_2$CH), 27.96 (Me(8')), 39.45 (Me$_2$*C*H), 60.00 (PhCH$_2$), 118.3 (CH), 127.4 (C5), 127.7 (Cq), 128.3 (C2^{IV}, C6^{IV}), 129.7 (C4^{IV}), 129.8 (C3), 130.0 (C3^{IV}, C5^{IV}), 130.1 (CH), 130.8 (CH), 130.9 (CH), 131.3 (CH), 131.9 (CH), 132.1 (C7'), 134.1 (CH), 134.9 (CH), 135.3 (Cq), 136.5 (Cq), 137.3 (C4'), 138.7 (C6'), 140.7 (C2'), 140.8 (Cq), 146.2 (Cq), 147.8 (C8'), 158.2 (C6), 158.6 (C4), 159.3 (C2) ppm; ms (ESI, m/z, %): 518 (M$^+$, 100). *Anal.* Calcd. for $C_{39}H_{36}ClNO_4$: C, 75.78; H, 5.87; N, 2.27. Found: C, 75.86; H, 5.66; N, 2.32.

2-(5-Isopropyl-3,8-dimethyl-azulen-1-yl)-1,4,6-triphenyl-pyridinium perchlorate, 8Ph. Brown crystals, mp 122 °C; uv (MeOH), λ_{max} (log ε): 218 (4.40), 255 (4.36), 285 (4.44), 342 (3.70), 472 (3.55); ^{1}H nmr (acetone-d_6): δ 1.38 (d, J = 6.8 Hz, 6H, *Me*$_2$CH), 2.48 (s, 3H, Me(8')), 2.83 (s, 3H, Me(3')), 3.27-3.39 (m, 1H, Me$_2$C*H*), 7.40 (m, 5H, Ph(4)), 7.41 (d, J = 10.4 Hz, 2H, 7'-H), 7.76 (t, J = 6.8 Hz, 1H, 4"-H), 7.71 (t, J = 6.8 Hz, 2H, 3"'-H, 5"'-H), 7.71 (t, J = 6.8 Hz, 1H, 4"'-H), 7.62-7.72 (m, 3H, 3"-H, 4"-H, 5"-H), 7.62 (dd, J =6.8, 2.0 Hz, 2H, 2"-H, 6"-H), 7.74 (dd, J = 10.8, 2.0 Hz, 1H, 6'-H), 8.14 (s, 1H, 2'-H), 8.31 (dd, J = 8.0, 1.6 Hz, 2H, 2"'-H, 6"'-H), 8.33 (d, J = 2.4 Hz, 1H, 4'-H), 8.57 (d_{AB}, J = 2.0 Hz, 1H, 5-H), 8.60 (d_{AB}, J = 2.4 Hz, 1H, 3-H); ms (ESI, m/z, %): 504 (M$^+$, 100) [17]. *Anal.* Calcd. for $C_{38}H_{34}ClNO_4$: C, 75.55; H, 5.67; N, 2.32. Found: C, 75.48; H, 5.78; N, 2.28.

2-(Azulen-1-yl)-4,6-diphenyl-pyridine, 9: blue crystals, mp 131 °C; uv (MeOH), λ_{max} (log ε): 217 (4.26), 246 (4.40), 305 (4.30), 373 (3.92), 378 (3.93); ^{1}H nmr ($CDCl_3$): δ 7.29 (t, J = 9.6 Hz, 1H, 5'-H), 7.43 (t, J = 9.6 Hz, 1H, 7'-H), 7.51 (d, J = 4.0 Hz, 1H, 3'-H), 7.43-7.63 (m, 7H, 3'-H, 3"-H, 4"-H, 5"-H, 3"'-H, 4"'-H, 5"'-H), 7.73 (t, J = 9.8 Hz, 1H, 6'-H), 7.83 (d, J = 8.0 Hz, 2H, 2"'-H, 6"'-H), 7.89 (s, 1H, 5-H), 7.97 (s, 1H, 3-H), 8.31 (d, J = 7.6 Hz, 2H, 2"-H, 6"-H), 8.45 (d, J = 4.8 Hz, 1H, 2'-H), 8.44 (d, J = 10.0 Hz, 1H, 4'-H), 9.96 (d, J = 10.0 Hz, 1H, 8'-H) ppm; ^{13}C nmr ($CDCl_3$): δ 115.3 (C3), 117.9 (CH), 119.6 (C5), 124.2 (C5'), 125.2 (C7'), 127.0 (C2", C6"), 127.1 (C2"', C6"'), 128.1 (Cq), 128.7 (CH), 128.8 (CH), 129.0 (CH), 136.6 (C´q), 137.0 (C2'), 137.5 (C4'), 138.2 (C8'), 138.6 (C6'), 139.3 (Cq), 140.0 (Cq), 143.4 (Cq), 149.7 (C4), 156.8 (C2), 157.2 (C6) ppm; ms (ESI): 358 (M$^+$+1, 100%). *Anal.* Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N 3.92. Found C, 90.64; H, 5.40; N 3.94.

2,4-Diphenyl-6-(4,6,8-trimethyl-azulen-1-yl)-pyridine, 10. Viscous dark brown oil (violet in solution). uv (MeOH), λ_{max} (log ε): 217 (4.26), 227 (4.49), 299 (4.23), 372 (3.57), 378 (3.54); ^{1}H nmr ($CDCl_3$): δ 2.63 (s, 3H, Me(6')), 2.64 (s, 3H, Me(4')), 2.94 (s, 3H, Me(8')), 7.08 (s, 1H, 5'-H), 7.12 (s, 1H, 7'-H), 7.40 (d, J = 4.0 Hz, 1H, 3'-H) 7.42 (t, J = 6.8 Hz, 1H, 4"'-H), 7.46-7.48 (m, 5H, 3"-H, 4"-H, 5"-H, 3"'-H, 5"'-H), 7.68 (d, J = 1.2 Hz, 1H, 5-H), 7.77 (dt, J = 8.0, 1.2 Hz, 2H, 2"-H, 6"-H), 7.82 (d, J = 4.0 Hz, 1H, 2'-H),7.89 (d, J = 1.2 Hz, 1H, 3-H), 8.16 (dt, J = 8.0, 1.2 Hz, 2H, 2"'-H, 6"'-H) ppm; ^{13}C nmr (acetone-d_6): δ 28.10 (Az-Me(6')), 28.29 (Az-Me(8')), 29.71 (Az-Me(4')), 116.0 (C3), 120.2 (C5), 127.2 (C2", C6"), 127.3 (C2"', C6"'), 128.7 (CH), 128.9 (CH), 129.0 (C5'), 129.1 (CH), 129.2 (CH), 129.3 (C7'), 131.5 (Cq), 131.8 (Cq), 137.8 (C2'), 138.3 (Cq), 138.8 (Cq), 147.6 (C8'), 148.5 (C4'), 148.7 (C6'), 149.2 (C4), 156.8 (C6), 159.7 (C2) ppm; ms (ESI): 400 (M$^+$+1, 100%). *Anal.* Calcd. for $C_{30}H_{25}N$: C, 90.19; H, 6.31; N 3.51, found C, 90.14; H, 6.36; N 3.51.

2-(5-Isopropyl-3,8-dimethyl-azulen-1-yl)-4,6-diphenyl-pyridine, 11. Viscous dark brown oil (green in solution); uv (MeOH), λ_{max} (log ε): 217 (4.26), 253 (4.49), 305 (4.16), 372 (3.70), 379 (3.70); ^{1}H nmr ($CDCl_3$): δ 1.49 (d, J = 6.8 Hz, 6H, *Me*$_2$CH), 2.60 (s, 3H, Me(3')), 2.69 (s, 3H, Me(8')), 3.11 (heptet, J = 6.8 Hz, 1H, Me$_2$C*H*), 7.04 (d, J = 10.8 Hz, 2H, 7'-H), 7.37-7.55 (m, 7H, 6'-H, 3"-H, 4"-H, 5"-H, 3"'-H, 4"'-H, 5"'-H), 7.66 (d, J = 1.2 Hz, 1H, 5-H), 7.76 (d, J = 8.0 Hz, 2H, 2"-H, 6"-H), 7.83 (s, 1H, 2'-H), 7.88 (d, J = 1.2 Hz, 1H, 3-H), 8.18 (d, J = 8.0 Hz, 2H, 2"'-H, 6"'-H), 8.25 (d, J = 1.4 Hz, 1H, 4'-H) ppm; ^{13}C nmr ($CDCl_3$): δ 12.90 (Az-Me(3')), 24.67 (*Me*$_2$CH), 28.17 (Az-Me(8')), 37.93 (Me$_2$*C*H), 115.4 (C3), 122.2 (C5), 124.4 (CH), 127.0 (Cq), 127.1 (C2", C6"), 127.2 (C2"', C6"'), 127.6 (C7'), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH)), 132.7 (Cq), 135.0 (C6'), 138.7 (Cq), 138.9 (Cq), 140.2 (Cq), 140.5 (C2'), 140.7 (C5'), 148.1 (C4'), 148.2 (C8'), 148.4 (C4), 156.4 (C6), 159.8 (C2) ppm; ms (ESI): 428 (M$^+$+1, 100%). *Anal.* Calcd. for $C_{32}H_{29}N$: C, 89.89; H, 6.84; N 3.28, found C, 89.85; H, 6.86; N 3.29.

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[15] Correct attribution for ^{13}C chemical shifts was hindered by the close values of aromatic signals both in ^1H- and ^{13}C-NMR spectra.

[16] The correct signal attributions for all ^{13}C failed due to the small solubility of salts in NMR solvents.

[17] The small amount of obtained compound hindered the ^{13}C nmr recording.