Azulene-substituted Pyranylium Salts. Syntheses and Products Characterization

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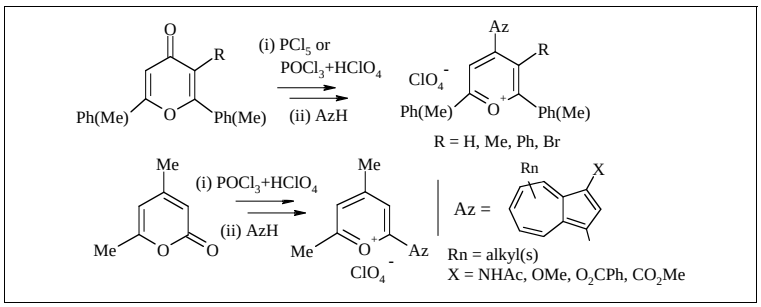

The synthesis of 4-azulene-substituted 2,6-diphenyl- and 2,6-dimethyl-pyranylium salts and 2-azulene-substituted 4,6-dimethyl-pyranylium salts by nucleophilic substitution at pyranylium moiety with various azulenes was studied. The starting materials for 2,6-diphenyl derivatives were 4 chlorinated pyranylium salts. They were obtained by the halogenation with PCl_5 of corresponding pyranones and were used either *in situ* or after separation. For the synthesis of dimethyl derivatives the corresponding pyranones were treated with $POCl_3$ and the resulted intermediate was reacted *in situ* with azulene. In the aim to study the influence of dihedral angle between azulene and pyranylium planes on the recorded spectra, both moieties were adequately substituted. The obtained results were in accord with the calculated values.

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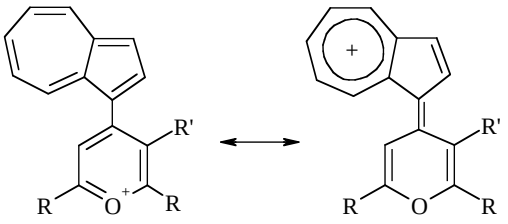
Introduction.

Generally, the pyranylium salts which present interesting properties that make them able to be used in various purposes (*e.g.*, as for detection of nucleic acids [1], in cancer therapy by selective irradiation [2], or dye sensitized photopolimerization) [3] are stabilized by substitution with electron donating (or releasing) groups. At the same time, due to their high electric moment, these compounds could also present valuable electrical or optical properties (as nonlinear optical properties). The ability of azulen-1-yl group to donate an electron pair forming the stable azulenylium cations is well known, therefore such a moiety situated in 2- or 4-position towards the oxonium center of pyranylium ring can stabilize this ring (Scheme 1) conferring interesting synthetic, structural and technical features to the generated salts. Consequently, we have enlarged our interest concerning the aromatic heterocyclic compounds containing azulene moiety [4] on azulene substituted pyranylium salts. The ability to use the pyranylium salts as synthones for building other varied molecules stimulated also our interest for this investigation.

Scheme 1



One of the more used ways for pyranylium ring syntheses consists in the condensation of carbonylic compounds [5] with the generation of chalcone as intermediate [6]. The extended electron delocalization in azulenic chalcone however, drastically limits the possibility of the subsequent condensation. The protocols described for the synthesis of 4-(azulen-1-yl) 2,6-diphenyl-pyranylium salt [7,8,9], the sole reported azulenyl-pyranylium system, started from the previous pyranylium salts. Despite the good claimed reaction yields [10], the obtained products are characterized only by melting points, elemental analysis and sometimes infrared spectra.

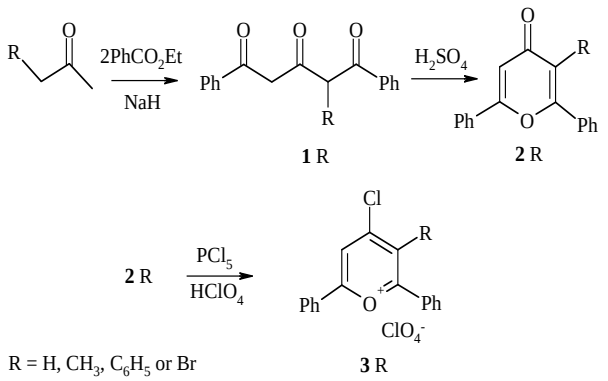
In this paper we report the synthesis of 2- and 4-azulene substituted pyranylium salts starting from the corresponding diphenyl or dimethyl-pyranones and the investigations concerning the salts structure. Besides the presence of methyl or phenyl in 2 and 6 positions of 4-azulenyl-pyranylium salts, we considered that the 3-substituted compounds are very interesting due to free rotation hindrance around the azulene-pyranylium bond which could generate the molecule chirality.

Results and Discussion.

Azulen-1-yl substituted diphenyl-pyranylium salts. The synthesis of 4-(azulen-1-yl)-2,6-diphenyl-pyranylium salts, **6**, started with the synthesis of corresponding pyranone and their 3-substituted derivatives, **2** R (Scheme 2) [11]. In the next step, chloropyranylium salts, **3** R, were obtained [12], separated and purified.

The nucleophilic substitution of an efficient leaving group or hydrogen at C-4 in pyranylium salts was largely investigated [5b].

Scheme 2



Thus, the substitution of chlorine (in 2 or 4 position) with azulenic compounds takes place in two steps: (i) the coupling of azulene with chloropyranylium salt when the intermediate **5** (Scheme 3), well stabilized by the tropylium structure, is formed and (ii) the elimination of hydrochloric acid with the regeneration of the aromatic pyranylium moiety.

In a recent paper about the reaction mechanism between 4-halogenated pyranylium salts and aromatic amines, Berberova and co-workers [13] suppose that before coupling a single electron transfer takes place from the nucleophile towards pyranylium. This transfer can be favorable when azulenes are used as nucleophile due to their low oxidation potential and also to their property to easily form radical-cations [14].

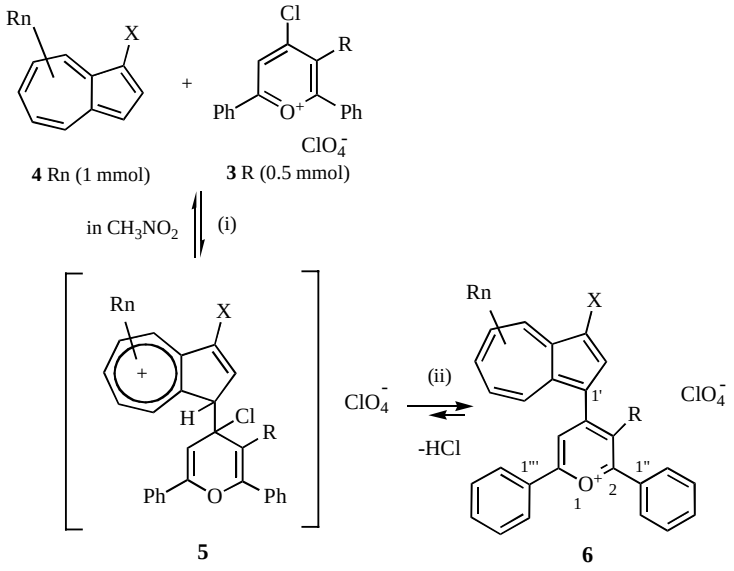
While step (i) is favored by electron releasing substituents at azulenes, efficient electron withdrawing groups, like NO_2 or CO_2Me, increase the oxidation potential of azulenes and also lower their nucleophilic capacity. As a consequence, the substitution occurred in very small yields; at the same time, some side reactions are promoted. For example, when methyl (azulen-1-yl)-carboxylate, **4** Rn = H; X = CO_2Me, was used as nucleophile, two pyranylium salts were formed, substituted at 4-position with 3-carbomethoxyazulen-1-yl, **6** R = Rn = H; X = CO_2Me or with azulen-1-yl **6** R = Rn = X = H (in ratio 2:1). Strong activating groups, as methoxy, induce the destruction of azulenic ring during the reaction. The best yields are obtained with alkylated azulenes, such as 4,6,8-trimethyl-azulene or 4,8-dimethyl-azulene, due to their increased stabilizing power in the intermediate **5**. When 1,3-di(*t*-butyl)-azulene reacts with 4-chloro-2,6-diphenyl-pyranylium salt, one *t*-Bu group is replaced by pyranylium moiety.

The reaction between halogenated pyranylium perchlorate and azulenes occurred in nitromethane at 100 °C for 1 hour and the product was precipitated with ether. Two equivalents of azulenic compound are needed in the reaction: one as the substitution reagent and the second as a base for the elimination of hydrochloric acid in the second reaction step. The supplementary azulene could be replaced by one equivalent of tertiary amines, however in this case decomposition was observed at the work-up of reaction mixture. Because some amount of unreacted chloropyraylium salt contaminated the reaction product, the separation by column chromatography on silica gel was necessary for all salts **6**, excepting when R = Br that decomposed on column. Generally, some amount of unreacted azulene was separated on the column (under 10%). The generation of salts **6** was accomplished also using $POCl_3$ in the first reaction step however in lower yields.

Azulen-1-yl substituted dimethyl-pyranylium salts. The intermediate generated when 2,6-dimethyl-pyranone reacted with PCl_5 crystallized after a long period of time and only partially, therefore we tried to use the resulting mixture without separation for condensation with azulenes, however with unsatisfactory yields. Good results were however obtained when dimethyl-pyranones were treated with $POCl_3$ in nitromethane [15]. To this reaction mixture, azulene and perchloric acid were added (the time between the two additions is reported in Scheme 4) and the mixture was heated until the evolution of HCl was no longer observed. The reaction of 2,4-dimethyl-pyranone, **10**, occurred slowly and in more severe conditions than for the 2,6 isomer, **7**.

After cooling, the pyranylium salt was precipitated with diethyl ether and was crystallized from isopropyl alcohol. The absence of halogenated pyranylium salt in the reaction mixture together with the products **9** or **11** as well as the sequence in which the reagents are added suggests the avoidance of this intermediate. We suppose that in the reaction of pyranone with $POCl_3$ the addition intermediate **8** was obtained (Scheme 4) followed by substitution of the dichlorophosphate group with azulene, HCl elimination and finally, anion exchange. In the aim to enhance the product solubility, perchloric acid was replaced by tetrafluoroboric acid and terafluoroborates were thus obtained in similar yields, unfortunately without improvement of this property.

Scheme 3



The yield (%) of nucleophilic substitution at **3** with **4**

R = X = H

Rn	H	3'-Me	6'-Me	3'-tBu[a]	4',8'-Me$_2$	4',6',8'-Me$_3$	2'-tBu,6'-Me	5'-iPr,3',8'-Me$_2$
Yield in **6**	73[b]	60	51	39	79	90[c]	59	54[d]

[a]Starting from 1,3-di tBu-azulene. [b]Lit.[7] 51%. [c]Lit.[7] 45%. [d]Lit.[7] 42%.

Rn = R = H

X	NHAc	OMe	OOCPh	COOMe[a]	PhN=N	CHO	NO_2
Yield in **6**	38	44	22	10	0	0	traces

[a]The product **6** R = Rn = X = H was also formed in yield ~5 %.

X = H

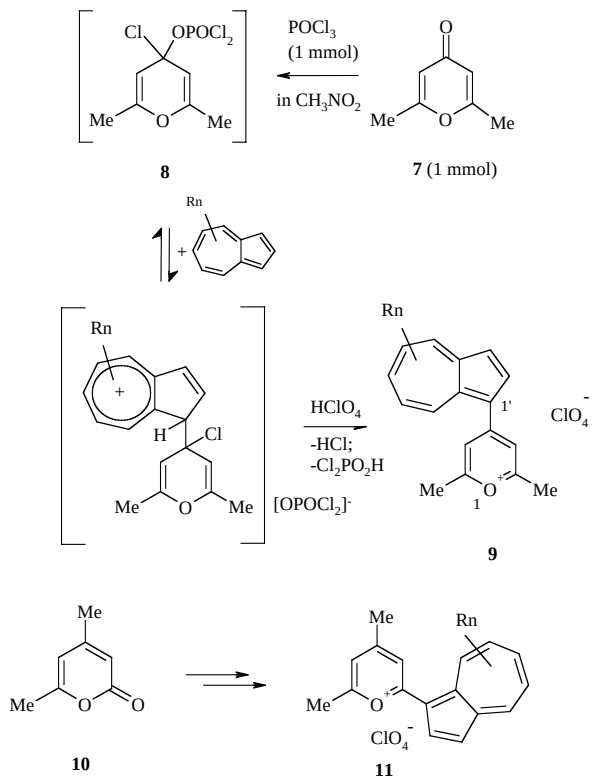
Rn	H			4',6',8'-Me$_3$			5'-iPr,3',8'-Me$_2$			2'-tBu,6'-Me		
R	Me	Ph	Br	Me	Ph	Br	Me	Ph	Br	Me	Ph	Br
Yield in **6**	63	65	53	79	78	72	90	90	63	83	58	-

Structure of azulen-1-yl pyranylium salts. A biphenyl-like isomerism of azulenyl pyranylium salts can be predicted due to the short distance, (C_{Az}-C_{Py}), between the two moieties mainly when the system has bulky groups substituted in the proper positions. A useful tool for structure assignment was considered the computation (with MOPAC and PCMODEL method) [16] of the dihedral angle, (α), and (C_{Az}-C_{Py}) bond length and also of the energy barrier to rotation (racemization); the calculated values are given in Table 1 and 2. Assuming that better conjugation results from shorter bond lengths, the calculated values for C_{Az}-C_{Py} length indicate that the conjugation between 4-pyranylium and 1-azulene is stronger than that with benzene or 1-naphthalene. The increase of the angle α in order azulene < phenyl < naphthyl results from the greater electron donating character of the azulenyl moiety, which stabilizes the positive charge of the 4-pyranylium moiety.

The stronger decrease in electron density at azulenic seven-membered ring in comparison with 1-phenyl-azulene is consistent with the obtained NMR data. As expected, the calculated parameters (Table 1) show the smallest steric hindrance for **13** where azulene couples at C(2') and the highest for the coupling at C(4') as in **14**.

At the substitution with Me at C(2') or C(3) in **12** the effect on α and C_{Az}-C_{Py} is similar (Table 2), however smaller than that produced by the presence of this group at (C8') and mainly by the bulky *t*-Bu group at (C2'). Despite the sensible difference in energy barrier depending on the substituents at C(3), the values for α and C_{Az}-C_{Py} are slightly influenced by the nature of substituents. The calculated parameters seem to be sensible to the electronic requirement of the substituents at C(3'); thus, whereas the withdrawing groups lower α and stretch C_{Az}-C_{Py} length comparing with the unsubstituted salt (Table 1), the effect of donors is unimportant.

Scheme 4

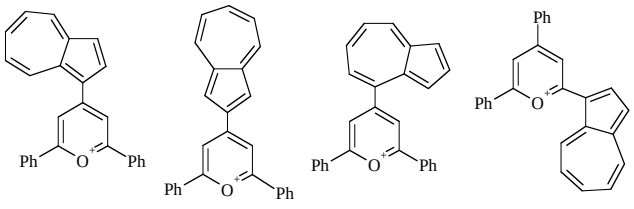


The yield (%) of nucleophilic substitution at **7** or **10** with azulenes

Rn	H	4',6',8'-Me_3	5'-iPr,3',8'-Me_2	2'-tBu,6'-Me
Yield in **9**/ reaction time	94/15 min	98/3 h	55/4 h	80/4 h

Rn	H	4',6',8'-Me_3	5'-iPr,3',8'-Me_2	2'-tBu,6'-Me
Yield in **11**/ reaction time	9/40 min	15/75 min	9/75 min	17/2 h

Scheme 5



As shown in Tables 1 and 2, the calculated energy barrier of compounds is near to that necessary for the free rotation around C_{Az}-C_{Py} bond at room temperature. Since the atropisomerism is also present in the basic structures, *e.g.* **12**, **14** or **15**, detectible or measurable enantiomerism for adequately substituted compounds could be expected; the presence of the substituents at C(3) seems to be the most favorable.

Table 1

Influence of the coupling positions between azulenyl and diphenyl-pyranylium moieties on dihedral angle α (°), C_{Az}-C_{Py} length (Å) and energy barrier for the biphenyl-like isomerism (kJ/mol).

Calculated parameters	azulenyl pyranylium cation			
	12	**13**	**14**	**15**
α	24.4[a]	2.6	49.1	2.2
C_{Az}-C_{Py} length	1.402	1.419	1.469	1.405
Energy barrier[b]	75	68	81	71

[a]For 2,4,6-triphenyl-pyranylium salts α (phenyl at C-4)-(pyranylium) = 32.0 °, C_{Ph}-C_{Py} = 1.448 Å and energy barrier, 43 kJ/mol; for 4-(naphth-1-yl)-2,6-diphenyl-pyranylium α (naphtha-1-yl)-(pyranylium) = 45,6 °, C_{Nf}-C_{Py} = 1.452 Å and energy barrier 67 kJ/mol. [b]The calculated energy barriers must be regarded with care and only as a comparison between the studied compounds.

Table 2

Dihedral angle α (°), C_{Az}-C_{Py} length (Å) and energy barrier (kJ/mol) for 4-(azulen-1'-yl)-2,6 diphenyl-pyranylium system substituted at 2', 3 and 3'-positions.

Compound	Calculated parameters		
6	A	C_{Az}-C_{Py} length	Energy barrier
C(2')-Me	32.5	1.407	74
C(2')- tBu	62.3	1.431	77[a]
C(8')-Me	57.1	1.427	79
C(3)-Me	38.1	1.413	81
C(3)-Ph	40.9	1.417	100
C(3)-Br	36.2	1.406	98
C(3')-OMe	26.6	1.406	-[b]
C(3')-OAc	24.2	1.395	-[b]
C(3')-NO_2	19.9	1.416	-[b]

[a]The calculated energy barrier seems to be doubtful. [b]The values are irrelevant.

Finally, the calculated data for 2-(azulen-1-yl)-substituted pyranylium system **15**, (Table 1) indicate that despite the very small values of α, the other two parameters are comparable with those of corresponding 4-(azulen-1-yl)- substituted system, **12**.

Correlation between the structure and some characterization data of pyranylium salts. The color of molecular chromophores changes with the consistent increase of angle α between the two moieties when bulky substituents are present. Unfortunately, the slight solubility of synthesized salts and the low performance of the used UV/VIS device do not allowed us to undertake a careful study [17].

The NMR spectra of 2,4,6-triarylpyranylium salts were extensively studied by several authors [18] however no work reported the spectra of azulenyl-substituted pyranylium salts. It seems that the explanation for the lack

in information about the spectra of these salts is their poor solubility in the usual NMR solvents. Favored by the use of more performing NMR devices, we have analyzed in what manner the proton chemical shifts are controlled by the reciprocal influence between azulenyl and pyranylium moieties in the synthesized salts. Different solvents were used at the recording of NMR spectra depending on the solubility of obtained salts. For the more soluble salts NMR spectra were recorded in all used solvents ($CDCl_3$, DMSO-d_6 and acetone-d_6) and the results showed that the chemical shifts are not dramatically changed by the solvent changing. Therefore our attempt to compare the chemical shifts of studied salts in different solvents seems to be correct. Even in the most favorable conditions we have encountered difficulties mainly for ^{13}C NMR spectra recording and therefore the assignment of some carbon signals failed. Table 3 shows the ^1H NMR spectra for some compounds.

Two effects govern the chemical shifts of azulenic protons: the azulene conjugation with good electron-withdrawing pyranylium moiety that strongly deshielded all azulenic protons comparing with neutral 1-phenyl-azulene [20], or 4-(azulen-1-yl)-2,6-diphenylpyridine, [21] and the different position of protons towards pyranylium magnetic field. The pyranylium magnetic field acts mainly toward the protons at C(2'), C(7') and C(8') as reflected by their higher deshielding. The smallest modification, as expected, is observed for the proton at C(3'). The comparison between the chemical shift of proton at C(3/5) in pyranylium ring for 2,4,6-triphenyl-pyranylium perchlorate (9.17 ppm) [18] and for the perchlorate of 4-(azulen-1-yl)-2,6,-diphenylpyranylium, **6** Rn = R = X = H, (8.83 ppm) clearly shows the increase in electron density at pyranylium moiety by the more efficient conjugation with azulene, as predicted by calculations.

Table 3
^1H NMR spectra of substituted azulenic compounds (chemical shifts in ppm)

H[a]	Compound Az-H	1-PhAz[b]	4-(Azulen-1-yl)-2,6-diphenyl Pyridine[b]	**6**(R = X = H)[c] Rn H	Rn 4',6',8'-Me_3	Rn 2'-tBu, 6'-Me	**6**(Rn=H X= H)[c] R Me	**9**[d] Rn H	Rn 4',6',8'-Me_3[b]	Rn 2'-tBu, 6'-Me
3 and 5	-	-	7.95	8.83[e]	8.40	8.78	8.80, (C5)-H	8.06	7.76	8.08
2'	7.81	8.02	8.18	8.92	8.51	1.59, tBu	8.55	8.45	8.23	1.44, tBu
3'	7.30	7.43	7.53	7.77	7.57	7.67	7.78	7.51	7.49	7.55
4'	8.23	8.34	8.44	8.89	3.01, Me	8.52	8.86	8.65	2.92, Me	8.07
5'	7.05	7.14	7.28	8.03	7.88	7.57	7.88	7.77	7.82	7.38
6'	7.45	7.58	7.45	8.31	2.82, Me	2.73, Me	8.20	8.07	2.79, Me	2.68, Me
7'	7.05	7.14	7.29	8.14	7.90	7.48	7.93	7.80	7.82	7.47
8'	8.23	8.55	8.71	9.57	3.04, Me	8.41	9.03	9.12	2.98, Me	8.43
Other H	-	-	-	-	-	-	2.71, 3 Me	2.56, 2,6-Me_2	2.83, 2,6-Me_2	2.91, 2,6-Me_2

[a]For position numbering see Scheme 1 and 2. [b]In $CDCl_3$. [c]In acetone-d_6. [d]In DMSO-d_6.

Deuterium exchange between deuterated acetone and even dimethylsulfoxide, used as solvents, and the methyl protons of 2,6-dimethyl-pyranylium salts was observed over a time varying from several hours to several days [19]. A similar exchange was also observed with the proton at 3-position in azulenic moiety, however much more slowly.

From the calculated values (Table 2), the substitution at C(2') in azulene or at C(3) in pyranylium increase the angle α in salts **6** and **9** and reduces the conjugation between the two moieties. Therefore the electron density must increase at azulenic moiety [22] and decrease at pyranylium comparing with unsubstituted derivatives. The proton chemical shifts shown in Table 3 are

consistent with this assumption. Thus, the presence at C(2') of *t*-Bu in salts **6** or **9** generally shielded azulenic protons and deshielded the pyranylium ones (even methyl protons at C(2/6) in pyranylium are deshielded). The shielding is more evident for the proton at C(8') comparing with those at (C4') (possibly due to the more efficient intervention of pyranylium magnetic field on (C8')-H).

The shielding effect on all protons produced by azulenic methyl groups in compounds **6** Rn = 4',6',8' Me_3 and **9** Rn = 4',6',8' Me_3 could be explained by the inductive effect of these groups. The same effect and with smaller intensity observed for the compound with only two methyl groups, **6** Rn = 4',8' Me_2, is in agreement with our supposition.

As expected, the substitution with Me at C(3) in pyranylium moiety, **6** R = Me, shields all azulenic protons (Table 3). The other substituents, Br or Ph, at the same position acts by inductive, conjugative and also by magnetic influence determining a difficult spectra knowledge.

Due to the strong charge delocalization at the substitution of azulene with pyranylium, as in compounds **6**, **9** and **11**, an important deshielding of all carbon atoms is observed, opposite to the reduced effect when azulene is coupled with phenyl or even with milder electron withdrawing heterocycles, such as pyridines or thiophene. The most influenced are C(5), C(7) and C(8a) for which the shielding surpasses 12 ppm.

Conclusions.

The investigated sequence of reactions represents a convenient and efficient route to (azulen-1-yl)-pyranylium salts. Taking into account the specific reactions of pyranylium salts, several other synthetic pathways could be imagined starting from the obtained salts for the generation of azulenic compounds in which the pyranylium ring is changed or conserved. The synthesis and characterization of a large and various number of pyranylium salts opened the door for us to the study new azulenic compounds such as substituted pyridines or pyridinium salts and, also, substituted benzene. The results will be reported in due course. Another future target consists in the investigation of atropisomerism of the pyranylium salts by comparison with the same properties of corresponding pyridines and pyridinium salts.

EXPERIMENTAL

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. Some difficulties were encountered at the elemental analysis due to tendency of perchlorates to violent decomposing. ^{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 $CDCl_3$ as solvents; the signals were assigned on the basis of COSY, HETCOR and HMBC experiments; IR: Beckmann IR 5A. Mass spectra were recorded on 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) device was used. Column chromatography: silica gel [70-230 mesh (ASTM)]. The low volatility of the compounds raised some problems for mass spectra recording [23]. Dichloromethane (DCM) was distilled over CaH_2, ethyl acetate was distilled over Na_2CO_3 and diethyl ether was conserved on NaOH and freshly distilled on $LiAlH_4$. UV spectra in methanol or dioxane: Specord UV-Vis spectrometer (C. Zeiss Jena). The nomenclature was obtained by use of the ACD/I-Lab web service (ACD/IUPAC Name Free 7.06). The slight solubility of studied pyranylium salts (*e.g.* in acetone or nitromethane) and their limited stability in nucleophilic solvents (*e.g.* dimethylformamide or methanol) creates difficulties in NMR and UV/Vis spectra recording. For the numbering of the positions in compounds see Schemes 3 and 4.

Starting reagents.

The protocols described in literature were used for the synthesis of 2,6-diphenyl-4*H*-pyran-4-one, [24] 3-bromo-2,6-diphenyl-4*H*-pyran-4-one [12], 3-methyl-2,6-diphenyl-4*H*-pyran-4-one and 2,3,6-triphenyl-4*H*-pyran-4-one [11] and for the halogenation to corresponding 4-chloropyrylium perchlorates [7]. The 2,6-dimethyl-4*H*-pyran-4-one and 4,6-dimethyl-2*H*-pyran-2-one were commercially available.

General Procedure for Synthesis of 4-(Azulen-1-yl)-2,6-diphenyl-pyranylium perchlorates, **6**.

The azulenic compound (0.2 mmol) and 2,6-diphenyl-4-chloro-pyranylium perchlorate (0.1 mmol) were added in nitromethane (~ 2 mL) and the reaction mixture was stirred at 100 °C for 1 hour and then cooled at room temperature (the reaction time for 2-*t*-butyl-6-methyl-azulene was 2.5 hours). When the product was precipitated with ether, as described in literature [7], it contains a variable amount of unreacted chloro-pyranylium salt that altered the elemental analysis. Therefore, the nitromethane was evaporated at reduced pressure and the residue was purified by column chromatography on silica gel. The unreacted azulene was eluted using benzene; then, chloro-pyranylium salts followed by azulenyl-pyranylium products were eluted with benzene/acetone 3/2 (v). Finally, the traces of product, possibly remained absorbed on the column, were removed using acetone with 1-2 drops of perchloric acid. After the solvent removing at reduced pressure, the residue was dissolved in a small amount of acetone containing 1-2 drops of perchloric acid and product was precipitated with ether, was filtered and washed on filter with ether. When methyl 1-azulene-carboxylate was used as starting reagent, elimination of CO_2Me group can occur in some extent; therefore several column separations were necessary in order to obtain pure azulenyl-

pyrylium salts. Because elimination of HBr from 3-bromo-substituted pyranylium salts occurs during chromatography, precipitation with ether from the nitromethane solution was used for purification. After the first adding of ethyl ether, an oily residue was separated which was repeatedly washed with ether until a crystalline product was formed. The resulted azulenyl-pyranilium salts **6** and the obtained yields are reported in Scheme 3.

General Procedure for Synthesis of 4-(Azulen-1-yl)-2,6-dimethyl- and 2-(azulen-1-yl)-4,6-dimethyl pyranylium salts, **9** and **11**.

The dimethyl-pyranone (0.1 mmol) and freshly distilled $POCl_3$ (0.1 mmol) were disolved in nitromethane (~ 2 mL). Starting from **1** R = Me, R = H the reaction mixture was stirred under inert atmosphere one hour. Starting from the pyranone **10** the reaction mixture was heated at 60 °C for 6 hour and at room temperature over night. To the obtained mixture, azulenic compound (0.1 mmol) was added and the stirring was continued for the time shown in Scheme 4. Then, perchloric acid (0.1 mmol) was added and the temperature was raised to 70-80 °C when an evolvement of HCl was observed. After 20 min of heating, the reaction mixture was cooled and poured in ether. The pyranylium salts **9** were thus separated and were crystallized from 2-propanol. For the 2-azulenyl-pyranylium salts **11** the product purification depended on the nature of azulenic substituent. For Rn = 4',6',8'-Me_3 the solid salt obtained by ether precipitation was extracted in acetone with 2 drops of perchloric acid. The resulted product after solvent removing was analytical pure. The solid precipitated for **11** Rn = H was extracted twice with 2-propanol at reflux to obtain the analytical sample. For **11** Rn = 5'-*i*-Pr,3',8'-Me_2 or **11** Rn = 2'-*t*-Bu,6'-Me at the precipitation a viscous oil was separated. The first salt was purified by two extractions with ethanol at reflux and the solvent elimination (the impurities such as the salt are very soluble in 2-propanol). All attempts for the crystallization of the last salt failed. After several triturations with ether, however, the elemental analysis of remained salt was satisfactory. The obtained azulenyl-pyranilium salts **9** and **11** and the resulted yields are reported in Scheme 4.

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4-(Azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = X =H).

Brown powder, red (in acetone), m. p. 250 °C (lit 250-1)[7]; uv-vis (MeOH): λ_{max} (log ε) 221 (4.35), 257 (4.35), 295 (4.41), 387 (4.17), 530 (4.36); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.76 (d, 1 H, 3'-H, *J* = 4.4 Hz), 7.77 (t, 4 H, 3"-H, 5"-H, *J* = 7.0 Hz), 7.81 (t, 2 H, 4"-H, *J* = 7.0 Hz), 8.03 (t, 1 H, 5'-H, *J* = 9.8 Hz), 8.14 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.31 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.50 (d, 4 H, 2"-H, 6"-H, *J* = 8.2 Hz), 8.83 (s, 2 H, 3-H, 5-H), 8.89 (d, 1 H, 4'-H, *J* = 9.9 Hz), 8.92 (d, 1 H, 2'-H, *J* = 4.4 Hz), 9.57 (d, 1 H, 8'-H, *J* = 9.6 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 114.4 (C-3, C-5), 124.9 (C-3'), 125.4 (C-1'), 128.9 (C-2", C-6"), 130.7 (C-3", C-5"), 130.9 (C-1"), 134.0 (C-5'), 134.1 (C-7'), 134.8 (C-4"), 141.4 (C-8'), 143.9 (C-3a'), 141.5 (C-4'), 142.0 (C-2'), 143.5 (C-6'), 152.2 (C-8a'), 158.7 (C-4), 167.8 (C-2, C-6) ppm; ir (KBr): 625 (m), 685 (m), 780 (m), 940 (m), 1100 (m), 1230 (m), 1270 (m), 1390 (m), 1500 (m), 1540 (m), 1625 (m), 2375 (m) cm^{-1}; ms (20 eV): m/z (%) 360 (33) [M^+ + 1], 359 (100) [M^+].

Anal. Calcd. for $C_{27}H_{19}O_5Cl$: C, 70.67; H, 4.17; Cl, 7.73. Found: C, 70.53; H, 4.35; Cl, 7.69.

4-(3-Methyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = Me).

Brown powder; violet (in acetone), m. p. 258°C; uv-vis (MeOH): λ_{max} (log ε) 216 (4.49), 256 (4.49), 278 (4.52), 386 (4.26), 543 (4.38); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.70 (s, 3 H, Me), 7.76 (t, 4 H, 3"-H, 5"-H, *J* = 7.2 Hz), 7.80 (t, 2 H, 4"-H, *J* = 7.1 Hz), 8.03 (t, 1 H, 5'-H, *J* = 10.1 Hz), 8.13 (t, 1 H, 7'-H, *J* = 10.1 Hz), 8.28 (t, 1 H, 6'-H, *J* = 10.1 Hz), 8.47 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.76 (s, 2 H, 3-H, 5-H), 8.77 (d, 1 H, 4'-H, *J* = 10.3 Hz), 8.78 (s, 1H, 2'-H), 9.50 (d, 1 H, 8'-H, *J* = 10.1 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 12.85 (Me), 113.9 (C-3, C-5), 124.1 (C-1), 128.7 (C-2", -6"), 130.6 (C-3", C-5"), 131.0 (C-1"), 131.8 (C-3), 134.4 (C-5'), 134.7 (C-7', C-4"), 139.0 (C-8'), 142.0 (C-4'), 143.4 (C-2'), 144.8 (C-3a'), 145.0 (C-6'), 150.0 (C-8a'), 157.1 (C-4), 167.1 (C-2, C-6) ppm; ir (KBr): 625 (m), 685 (m), 750 (m), 780 (m), 940 (m), 1105 (m), 1220 (m), 1300 (m), 1315 (m), 1450 (m), 1500 (m), 1625 (m), 2375 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 373 (100) [M^+].

Anal. Calcd. for $C_{28}H_{21}O_5Cl$: C, 71.11; H, 4.48; Cl, 7.50. Found: C, 71.23; H, 4.50; Cl, 7.55.

4-(6-Methyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 6' Me; R = X = H).

Brown powder, pink (in acetone), m. p. 257°C; uv-viz (MeOH): λ_{max} (log ε) 221 (4.36), 238 (4.42), 270 (4.49), 387 (4.21), 525 (4.40); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.87 (s, 3 H, Me), 7.66 (d, 1 H, 3'-H, *J* = 4.5 Hz), 7.77 (t, 4 H, 3"-H, 5"-H, *J* = 7.1 Hz), 7.81 (t, 2 H, 4"-H, *J* = 7.1 Hz), 7.96 (t, 1 H, 5'-H, *J* = 9.7 Hz), 8.06 (t, 1 H, 7'-H, *J* = 10.5 Hz), 8.49 (d, 4 H, 2"-H, 6"-H, *J* = 7.2 Hz), 8.74 (d, 1 H, 4'-H, *J* = 10.3 Hz), 8.76 (s, 2 H, 3-H, 5-H), 8.79 (d, 1 H, 2'-H, *J* = 4.4 Hz), 9.41 (d, 1 H, 8'-H, *J* = 10.5 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 28.12 (Me), 113.9 (C-3, C-5), 123.8 (C-1'), 125.0 (C-3'), 128.7 (C-2", C-6"), 130.7 (C-3", C-5"), 130.9 (C-1"), 134.7 (C-4"), 135.7 (C-5'), 135.9 (C-7'), 138.6 (C-8'), 140.5 (C-4'), 140.7 (C-2'), 143.2 (C-3a'), 149.0 (C-8a'), 151.1 (C-6'), 157.3 (C-4), 167.4 (C-2, C-6) ppm; ir (KBr): 625 (m), 685 (m), 780 (m), 940 (m), 1100 (m), 1215 (m), 1295 (m), 1390 (m), 1500 (m), 1625 (m), 2375 (m) cm^{-1}; ms (20 eV): m/z (%) 373 (100) [M^+].

Anal. Calcd. for $C_{28}H_{21}O_5Cl$: C, 71.11; H, 4.48; Cl, 7.50. Found: C, 71.15; H, 4.60; Cl, 7.45.

4-(4,8-Dimethyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 4',8' Me_2; R = X = H).

Brown powder, violet (in acetone), m. p. 267°C; uv-vis (MeOH): λ_{max} (log ε): 220 (4.36), 251 (4.45), 282 (4.44), 388

(4.21), 543 (4.41); ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 3.05 (s, 3 H, 4'-Me), 3.08 (s, 3 H, 8'-Me), 7.65 (d, 1 H, 3'-H, *J* = 4.4 Hz), 7.76 (t, 4 H, 3"-H, 5"-H, *J* = 7.5 Hz,), 7.79 (t, 2 H, 4"-H, *J* = 7.0 Hz), 7.89 (d, 1 H, 5'-H, *J* = 10.0 Hz), 7.92 (d, 1 H, 7'-H, *J* = 10.4 Hz), 8.05 (t, 1 H, 6'-H, *J* = 10.1 Hz,), 8.47 (s, 2 H, 3-H, 5-H), 8.48 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.62 (d, 1 H, 2'-H, *J* = 4.7 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 25.52 (8'-Me), 29.87 (4'-Me), 116.2 (C-3, C-5), 121.0 (C-3'), 128.0 (C-1'), 128.7 (C-2", C-6"), 130.7 (C-3", C-5"), 130.9 (C-1"), 134.7 (C-4"), 135.3 (C-5'), 136.4 (C-7'), 141.4 (C-3a'), 142.0 (C-2'), 149.5 (C-8'), 151.3 (C-4'), 139.3 (C-6'), 149.5 (C-8a'), 160.0 (C-4), 166.7 (C-2, C-6) ppm; ir (KBr): 625 (m), 685 (m), 780 (m), 950 (m), 1100 (m), 1210 (m), 1295 (m), 1325 (m), 1450 (m), 1500 (m), 1625 (m), 3080 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 387 (100) [M$^+$].

Anal. Calcd. for $C_{29}H_{23}O_5Cl$: C, 71.53; H, 4.76; Cl, 7.28. Found: C, 71.60; H, 4.86; Cl, 7.25.

4-(4,6,8-Trimethyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 4',6',8'-Me_3, R = X = H).

Brown powder, violet (in acetone), m. p. 276°C; uv-vis (MeOH): λ_{max} (log ε) 219 (4.26), 250 (4.43), 281 (4.43), 388 (4.21), 543 (4.41); ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 2.82 (s, 3 H, 6'-Me), 3.01 (s, 3 H, 4'-Me), 3.04 (s, 3 H, 8'-Me), 7.57 (d, 1 H, 3'-H, ^{3}*J* = 4.8 Hz), 7.76 (t, 4 H, 3"-H, 5"-H, *J* = 7.6 Hz), 7.79 (t, 2 H, 4"-H, *J* = 7.1 Hz), 7.88 (s, 1 H, 5'-H), 7.90 (s, 1 H, 7'-H), 8.40 (s, 2 H, 3-H, 5-H), 8.47 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.51 (d, 1 H, 2'-H, *J* = 4.4 Hz) ppm; ^{13}C-nmr (100.28 MHz, acetone-d_6, 25°C): δ 25.76 (8'-Me), 29.49 (6'-Me), 30.23 (4'-Me), 115.6 (C-3, C-5), 121.1 (C-3'), 128.2 (C-1'), 128.5 (C-2", C-6"), 130.6 (C-3", C-5"), 130.9 (C-1"), 134.6 (C-4"), 137.5 (C-5'), 137.8 (C-7'), 140.7 (C-2'), 141.5 (C-3a'), 148.5 (C-8'), 149.5 (C-8a'), 150.0 (C-4'), 152.1 (C-6'), 159.1 (C-4), 166.0 (C-2, C-6) ppm; ir (KBr): 625 (m), 680 (m), 780 (m), 950 (m), 1100 (m), 1210 (m), 1295 (m), 1325 (m), 1450 (m), 1500 (m), 1540 (m), 1625 (m), 2375 (m), 3080 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) = 401 (100) [M$^+$], 391 (14).

Anal. Calcd. for $C_{30}H_{25}O_5Cl$: C, 71.93; H, 5.03; Cl, 7.08; found: C, 71.95; H, 5.06; Cl. 7.05.

4-(2-*t*-Butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 2'-tBu,6'-Me, R = X = H).

Brown powder, violet (in acetone), m. p. 248 °C; uv-viz (dioxane): λ_{max} (log ε) 243 (4.34), 299 (4.42), 393 (4.19), 543 (3.86); uv-viz (MeOH): λ_{max} (log ε) 219 (4.36), 239 (4.45), 294 (4.45), 393 (4.21), 553 (4.40); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.59 (s, 9 H, tBu), 2.73 (s, 3 H, Me), 7.48 (d, 1 H, 7'-H, *J* = 10.0 Hz), 7.57 (d, 1 H, 5'-H, *J* = 10.4 Hz), 7.67 (s, 1 H, 3'-H), 7.84 (t, 4 H, 3"-H, 5"-H, *J* = 8.0, 1.2 Hz), 7.91 (dt, 2 H, 4"-H, *J* = 8.0, 1.2 Hz), 8.41 (d, 1 H, 8'-H, *J* = 10.0 Hz), 8.52 (d, 1 H, 4'-H, *J* = 10.0 Hz), 8.59 (d, 4 H, 2"-H, 6"-H, *J* = 8.0 Hz), 8.78 (s, 2 H, 3-H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 28.2 (6'-Me), 33.9 and 36.3 (2'-tBu), 122.3 (C-3, C-5), 125.0 (C-1'), 127.9 (C-3'), 130.1 (C-2", C-6"), 130.8 (C-7'), 130.9 (C-1"), 131.0 (C-5'), 131.7 (C-3", C-5"), 136.0 (C-8'), 136.5 (C-4"), 138.6 (C-4'), 140.7 (C-8a'), 143.3 (C-3a'), 153.8 (C-6'), 162.5 (C-4), 162.8 (C-2'), 169.8 (C-2, C-6) ppm; ir (KBr): 625 (m), 655 (m), 687 (m), 780 (m), 950 (m), 1095 (m), 1285 (m), 1420 (m), 1475 (m), 1515 (m), 1575 (m), 1615 (m), 2865 (m), 2960 (m), 3065 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) = 359 (100) [M$^+$].

*Anal.*Calcd. for $C_{32}H_{29}O_5Cl$: C, 72.65; H, 5.53; Cl, 6.70. Found: C, 72.62; H, 5.60; Cl, 6.75.

4-(3,8-Dimethyl-5-*iso*-propyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 5' *i*-Pr, 3',8' Me_2; R = X = H).

Blue powder, blue (in acetone), m. p. 292°C (lit 292°C)[7]; uv-vis (MeOH): λ_{max} (log ε) 215 (4.42), 247 (4.42), 279 (4.50), 388 (4.21), 576 (4.40); ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 1.47 (d, 6 H, *Me*CH, *J* = 6.8 Hz], 2.68 (s, 3 H, 3'-Me), 3.08 (s, 3 H, 8'-Me), 3.41 (hep, 1 H, Me*CH*, *J* = 6.8 Hz,), 7.75 (t, 4 H, 3"-H, 5"-H, *J* = 7.6 Hz,), 7.78 (t, 2 H, 4"-H, *J* = 7.0 Hz,), 7.99 (d, 1 H, 7'-H, *J* = 11.0 Hz), 8.16 (t, 1 H, 6'-H, *J* = 11.0 Hz), 8.36 (s, 2 H, 3'-H, 5'-H), 8.46 (d, 4 H, 2"-H, 6"-H, *J* = 7.1 Hz), 8.53 (s, 1 H, 2'-H), 8.60 (s, 1 H, 4'-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25 °C): δ 13.06 (8'-Me), 24.41 (*Me*CH), 29.9 (3'-Me), 39.08 (Me*CH*), 115.2 (C-3, C-5), 125.7 (C-1'), 128.4 (C-2", C-6"), 130.6 (C-3", C-5"), 132.1 (C-1", C-3'), 134.4 (C-4"), 136.4 (C-4'),138.5 (C-7'), 139.6 (C-6'), 142.6 (C-2'), 143.5 (C-3a'), 149.6 (C-8a'), 151.0 (C-5'), 154.0 (C-8'), 156.4 (C-4), 165.2 (C-2, C-6) ppm; ir (KBr): 625 (m), 635 (m), 685 (m), 780 (m), 940 (m), 1100 (m), 1220 (m), 1315 (m), 1345 (m), 1450 (m), 1540 (m), 1625 (m), 2375 (m), 2970 (m), 3080 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 429 (100) [M$^+$].

*Anal.*Calcd. for $C_{32}H_{29}O_5Cl$: C, 72.65; H, 5.53; Cl, 6.70. Found: C, 72.60; H, 5.63; Cl, 6.65.

4-(3-*tert*-Butyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = *t*-Bu).

Brown powder, violet (in acetone), m. p. 254°C; uv-vis (MeOH): λ_{max} (log ε) 226 (4.42), 258 (4.51), 282 (4.51), 386 (4.15), 541 (4.44); ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 1.69 (s, 9 H, t-Bu), 7.78 (t, 4 H, 3"-H, 5"-H, *J* = 7.2 Hz), 7.83 (t, 2 H, 4"-H, *J* = 7.1 Hz,), 8.09 (t, 1 H, 5'-H, *J* = 10.1 Hz,), 8.11 (t, 1 H, 7'-H, *J* = 10.1 Hz), 8.29 (d, 1 H, 4'-H, *J* = 10.3 Hz), 8.32 (t, 1 H, 6'-H, *J* = 10.1 Hz), 8.49 (d, 4 H, 2"-H, 6"-H, *J* = 7.1 Hz), 8.81 (s, 1 H, 2'-H), 8.85 (s, 2 H, 3'-H, 5'-H), 9.54 (d, 1 H, 8'-H, *J* = 10.1 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25 °C): δ 31.50 (Me), 34.09 (*C*Me_3), 114.5 (C-3', C-5'), 123.9 (C-1'), 128.8 (C-2", C-6"), 130.6 (C-3", C-5"), 131.0 (C-1"), 132.0 (C-3'), 133.0 (C-5'), 134.3 (C-7'), 134.7 (C-4"), 139.0 (C-8'), 139.7 (C-2'), 140.5 (C-4'), 143.4 (C-6'), 146.3 (C-3a'), 148.0 (C-8a'), 157.7 (C-4), 167.3 (C-2, C-6) ppm; ir (KBr): 625 (m), 685 (m), 780 (m), 950 (m), 1100 (m), 1230 (m), 1340 (m), 1400 (m), 1450 (m), 1500 (m), 1540 (m), 1625 (m), 2375 (m), 2965 (m), 3060 (m) cm^{-1}; es-ms (in the solid state): m/z (%) 415 [M$^+$, 100], 281 (22), 219 (23), 205 (20), 149 (58), 105 (56), 91 (38), 73 (45).

Anal. Calcd. for $C_{31}H_{27}O_5Cl$: C, 72.30; H, 5.28; Cl, 6.88. Found: C, 72.23; H, 5.35; Cl, 6.95.

4-(3-Acetylamino-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = Ac).

Brown powder, blue-violet (in acetone), m. p. 185°C; uv-vis (MeOH): λ_{max} (log ε) 219 (4.38), 241 (4.42), 286 (4.58), 381 (4.25), 556 (4.39); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.33 (s, 3 H, Me), 7.75 (t, 4 H, 3"-H, 5"-H, *J* = 8.0 Hz), 7.81 (t, 2 H, 4"-H, *J* = 7.2 Hz), 7.89 (t, 1 H, 5'-H, *J* = 9.2 Hz,), 8.01 (t, 1 H, 7'-H, *J* = 10.0 Hz), 8.23 (t, 1 H, 6'-H, *J* = 10.0 Hz), 8.48 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.77 (s, 2 H, 3-H, 5-H), 9.15 (s, 1 H, 2'-H), 8.88 (d, 1 H, 4'-H, *J* = 10.0 Hz), 9.45 (d, 1 H, 8'-H, *J* = 10.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 23.7 (Me), 113.4 (C-3, C-5), 126.0 (C-3'), 126.0 (C-1'), 127.9 (C-2", C-6"),

129.7 (C-3", C-5"), 131.0 (C-1", C-2'), 131.8 (C-5'), 133.0 (C-7'), 133.8 (C-4"), 135.8 (C-4'), 138.1 (C-8a'), 138.7 (C-8'), 143.2 (C-6'), 156.1 (C-4), 166.1 (C-2, C-6), 168.6 (CO) ppm; ir (KBr): 625 (m), 685 (m), 750 (m), 780 (m), 945 (m), 1105 (s), 1220 (m), 1325 (m), 1450 (m), 1485 (m), 1550 (m), 1625 (s), 1680 (m), 2375 (m), 3400 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 416 (100) [M^+], 374 (24).

Anal. Calcd. for $C_{29}H_{22}O_6NCl$: C, 67.51; H, 4.30; Cl, 6.87; N, 2.71. Found: C, 67.47; H, 4.33; Cl, 6.75; N, 2.65.

4-(3-Methoxycarbonyl-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = CO_2Me).

Brown powder, violet (in acetone), m. p. 154°C; uv-vis (MeOH): λ_{max} (log ε) 210 (4.44), 256 (4.44), 289 (4.51), 380 (4.24), 514 (4.40); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 4.01 (s, 3 H, Me), 7.79 (t, 4 H, 3"-H, 5"-H, *J* = 8.0 Hz), 7.86 (t, 2 H, 4"-H, *J* = 7.2 Hz), 8.29 (t, 1 H, 5'-H, *J* = 9.4 Hz), 8.30 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.50 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.59 (d, 4 H, 2"-H, 6"-H, *J* = 7.6 Hz), 9.07 (s, 2 H, 3'-H, 5'-H), 9.32 (s, 1 H, 2'-H), 9.67 (d, 1 H, 8'-H, *J* = 10.3 Hz,), 9.98 (d, 1 H, 4'-H, *J* = 10.3 Hz,) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 52.09 (Me), 116.1 (C-3, C-5), 121.1 (C-3'), 123.3 (C-1'), 129.2 (C-2", C-6"), 130.7 (C-3", C-5"), 131.0 (C-1"), 134.8 (C-7'), 135.3 (C-4"), 135.8 (C-5'), 140.5 (C-8'), 141.3 (C-4'), 144.9 (C-3a', C-2'), 145.0 (C-6'), 148.5 (C-8a'), 158.1 (C-4), 164.9 (CO), 167.8 (C-2', C-6') ppm; ir (KBr): 685 (m), 780 (m), 950 (m), 1100 (m), 1190 (m), 1235 (m), 1265 (m), 1395 (m), 1450 (m), 1620 (m), 1650 (m), 1690 (m), 2375 (m), 2935 (m), 3065 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 419 (100) [M^+].

Anal. Calcd. for $C_{29}H_{21}O_7Cl$: C, 67.38; H, 4.09; Cl, 6.86. Found: C, 67.40; H, 4.13; Cl, 6.76.

4-(3-Benzoyloxy-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = $PhCO_2$).

Brown powder, violet (in acetone), m. p. 181°C, uv-vis (MeOH): λ_{max} (log ε) 219 (4.49), 235 (4.58), 275 (4.45), 297 (4.45), 378 (4.22), 526 (4.35); ^{1}H-nmr (400. MHz, acetone-d_6, 25°C): δ 7.70 (t, 2 H, 3"'-H, 5"'-H, *J* = 7.6 Hz), 7.76 (t, 4 H, 3"-H, 5"-H, *J* = 7.7 Hz), 7.82 (t, 3 H, 4"-H, 4"'-H, *J* = 7.2 Hz), 8.02 (t, 1 H, 5'-H, *J* = 9.4 Hz), 8.15 (t, 1 H, 7'-H, *J* = 10.0 Hz), 8.35 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.37 (d, 2 H, 2"'-H, 6"'-H, *J* = 7.3 Hz,), 8.51 (d, 4 H, 2"-H, 6"-H, *J* = 7.1 Hz), 8.84 (s, 2 H, 3-H, 5-H), 8.92 (d, 1 H, 4'-H, *J* = 9.8 Hz), 8.94 (s, 1 H, 2'-H), 9.61 (d, 1 H, 8'-H, *J* = 9.7 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 113.5 (C-3, C-5), 120.3 (C-1), 128.0 (C-2", C-6"), 128.7 (C-1"'), 129.1 (C-3"', C-5"'), 129.7 (C-2'), 129.8 (C-3", C-5"), 130.2 (C-2"', C-6"'), 132.4 (C-1"), 132.9 (C-5'), 133.7 (C-7'), 134.0 (C-4"), 134.4 (C-4"'), 136.2 (C-4'), 139.0 (C-3a'), 139.3 (C-3'), 139.9 (C-8'), 142.2 (C-8a'), 143.9 (C-6'), 157.1 (C-4), 163.9 (CO), 166.7 (C-2, C-6) ppm; ir(KBr): 625 (m), 685 (m), 710 (m), 745 (m), 950 (m), 1100 (m), 1235 (m), 1255 (m), 1410 (m), 1450 (m), 1575 (m), 1620 (m), 1735 (m), 2375 (m), 3065 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 479 (100)[M^+].

Anal. Calcd. for $C_{34}H_{23}O_7Cl$: C, 70.53; H, 4.00; Cl, 6.12. Found: C, 70.45; H, 4.08; Cl, 6.06.

4-(3-Methoxy-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H; X = MeO).

Brown crystals, blue (in acetone), dec. without melt.; uv-vis (MeOH): λ_{max} (log ε) 219 (4.35), 260 (4.37), 313 (4.38), 392 (4.23), 587 (4.40); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 4.23 (s, 3 H, MeO), 7.74 (t, 4 H, 3"-H, 5"-H, *J* = 7.7 Hz), 7.77 (t, 1 H, 5'-H, *J* = 9.4 Hz), 7.78 (t, 2 H, 4"-H, *J* = 7.2 Hz), 7.93 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.25 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.41 (d, 4 H, 2"-H, 6"-H, *J* = 7.1 Hz), 8.41 (s, 1 H, 2'-H), 8.62 (s, 2 H, 3-H, 5-H), 8.68 (d, 1 H, 4'-H, *J* = 9.2 Hz), 9.45 (d, 1 H, 8'-H, *J* = 9.7 Hz) ppm; ei-ms (in the solid state): m/z (%) 389 (100) [M^+].

Anal. Calcd. for $C_{28}H_{21}O_6Cl$: C, 68.79; H, 4.33; Cl, 7.25. Found: C, 68.73; H, 4.25; Cl, 7.31.

4-(3-Bromo-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H, X = Br).

Brown crystals, pink (in acetone), m. p. 163°C; uv-vis (MeOH): λ_{max} (log ε) 220 (4.36), 251 (4.45), 282 (4.44), 375 (4.23), 519 (4.36); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.81 (t, 4 H, 3"-H, 5"-H, *J* = 7.2 Hz), 7.87 (t, 2 H, 4"-H, *J* = 7.1 Hz), 8.22 (t, 1 H, 7'-H, *J* = 10.1 Hz), 8.19 (t, 1 H, 5'-H, *J* = 10.1 Hz), 8.44 (t, 1 H, 6'-H, *J* = 10.1 Hz), 8.57 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.86 (d, 1 H, 4'-H, *J* = 10.3 Hz), 8.94 (s, 2 H, 3-H, 5-H), 9.05 (s, 1 H, 2'-H), 9.61 (d, 1 H, 8'-H, *J* = 10.1 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 111.5 (C-3'), 115.8 (C-3, C-5), 124.9 (C-1'), 129.7 (C-2", C-6"), 131.4 (C-1", C-3", C-5"), 134.6 (C-5'), 135.3 (C-7'), 135.9 (C-4"), 140.6 (C-8'), 140.9 (C-4'), 142.9 (C-2'), 143.3 (C-3a'), 145.5 (C-6'), 146.9 (C-8a'), 159.2 (C-4), 169.3 (C-2, C-6) ppm; ir (KBr): 625 (m), 680 (m), 750 (m), 775 (m), 865 (m), 945 (m), 1100 (s), 1270 (m), 1345 (m), 1445 (m), 1475 (m), 1500 (m), 1615 (s), 2375 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 437 (100) [M^+], 439 (100) [M^++2].

Anal. Calcd. for $C_{27}H_{18}O_5BrCl$: C, 60.30; H, 3.37; Cl, 6.59; Br, 14.86. Found: C, 60.23; H, 3.35; Cl, 6.49; Br, 14.75.

4-(3-Nitro-azulen-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = R = H, X = NO_2).

This product can not be purified in order to obtain correct elemental analysis or mass spectrum; ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.82 (t, 4 H, 3"-H, 5"-H, *J* = 7.2 Hz), 7.91 (t, 2 H, 4"-H, *J* = 7.1 Hz), 8.46 (t, 1 H, 7'-H, *J* = 10.4 Hz), 8.49 (t, 1 H, 5'-H, *J* = 10.0 Hz), 8.64 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.65 (t, 1 H, 6'-H, *J* = 10.0 Hz), 9.18 (s, 2 H, 3-H, 5-H), 9.51 (s, 1 H, 2'-H), 9.77 (d, 1 H, 8'-H, *J* = 10.0 Hz), 10.00 (d, 1 H, 4'-H, *J* = 10.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 118.5 (C-3, C-5), 122.8 (C-1'), 130.0 (C-2", C-6"), 131.2 (C-1"), 131.3 (C-3", C-5"), 136.8 (C-4"), 139.3 (C-2'), 141.9 (C-5', C-7'), 142.0 (C-3'), 143.5 (C-4'), 143.8 (C-8'), 144.9 (C-6'), 171.2 (C-2, C-6) ppm.

4-(Azulen-1-yl)-2,6-diphenyl-3-metyl-pyranylium perchlorate (**6**) (Rn = X = H, R = Me).

Brown powder, pink (in acetone), dec. without melt.; uv-vis (MeOH): λ_{max} (log ε) 250 (4.24), 275 (4.15), 381 (3.79), 506 (3.76); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.71 (s, 3 H, 3-Me), 7.74 (tt, 2 H, 3"-H, 5"-H, J = 7.6, 1.6 Hz), 7.78 (d, 1 H, 3'-H, J = 4.4 Hz), 7.80 (tt, 2 H, 3"'-H, 5"'-H, J = 7.6, 1.6 Hz), 7.81 (t, 1 H, 4-H", J = 7.6 Hz), 7.82 (t, 1 H, 4-H", J = 7.6 Hz), 7.88 (t, 1 H, 5'-H, *J* = 10.0 Hz), 7.93 (t, 1 H, 7'-H, J = 10.0 Hz), 8.20 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.23 (dd, 2 H, 2"-H, 6"-H, *J* = 8.0, 1.8 Hz), 8.42 (dd, 2 H, 2"'-H, 6"'-H, J = 8.0, 1.8 Hz), 8.55 (d, J = 4.4 Hz, 1 H, 2'-H), 8.80 (s, 1 H, 5-H), 8.87 (d, 1 H, 4'-H, J = 9.6 Hz), 9.03 (d, 1 H, 8'-H, J = 10.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 19.81 (3-Me), 120.0 (C-3), 123.0 (C-3'), 126.4 (C-5), 126.4 (C-1'), 129.3 (C-1"', C-1"), 129.6 (C-2", -6"),

130.7 (C-3", C-5"), 131.4 (C3'", C-5'"), 131.7 (C-5'), 131.9 (C-7'), 132.2 (C-2'", C-6'"), 134.3 (C-4'"), 135.7 (C-4"), 139.2 (C-8'), 141.5 (C-4'), 142.2 (C-2'), 142.3 (C-3a'), 143.1 (C-6'), 148.7 (C-8a'), 165.2 (C-4), 168.2 (C-6), 170.9 (C-2) ppm; ir (KBr) 692 (m), 705 (m), 748 (m), 780 (m), 890 (m), 1175 (m), 1295 (m), 1395 (m), 1450 (m), 1490 (m), 1535 (m), 1570 (m), 1580 (m), 3025 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 373 (100) $[M^+]$.

Anal. Calcd. for $C_{28}H_{21}O_5Cl$: C, 71.11; H, 4.48; Cl, 7.50. Found: C, 71.08; H, 4.56; Cl, 7.41.

4-(4,6,8-Trimethyl-azulen-1-yl)-2,6-diphenyl-3-methyl-pyranylium perchlo-rate (**6**) (Rn = 4',6',8' Me_3; R = Me; X = H).

Brown powder, violet (in acetone), dec. without melt.; uv-vis (MeOH): λ_{max} (log ε) 242 (4.24), 290 (4.18), 372 (3.74), 532 (3.77); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.65 (s, 3 H, 3-Me), 2.81 (s, 3 H, 6'-Me), 2.86 (s, 3 H, 4'-Me), 3.03 (s, 3H, 8'-Me), 7.58 (d, 1 H, 3'-H, *J* = 4.4 Hz), 7.72 (m, 1 H, 4"-H), 7.73 (s, 1 H, 7'-H), 7.73 (t, 2 H, 3"-H, 5"-H, *J* = 7.6 Hz), 7.80 (tt, 1 H, 4"'-H, *J* = 7.6, 2.0 Hz), 7.82 (t, 2 H, 3"'-H, 5"'-H, *J* = 7.6 Hz), 7.83 (s, 1 H, 5'-H), 8.16 (d, 1 H, 2'-H, *J* = 4.8 Hz), 8.24 (d, 4 H, 2"-H, 6"-H, *J* = 7.0 Hz), 8.40 (d, 4 H, 2"'-H, 6"'-H, *J* = 7.0 Hz), 8.46 (s, 2 H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 19.71 (3-Me), 26.49 (8'-Me), 29.11 (6'-Me), 30.60 (4'-Me), 119.8 (C-3'), 120.7 (C-5), 127.9 (C-1'), 128.9 (C-3), 129.5 (C-2"', C-6'"), 130.8 (C-3", C-5"), 131.1 (C-1'"), 131.4 (C-3'",C-5'"), 132.2 (C-2", C-6"), 132.8 (C-1"), 134.3 (C-4'"), 135.2 (C-5'), 135.7 (C-4"), 135.8 (C-7'), 138.8 (C-3a'), 140.0 (C-2'), 145.4 (C-8a'), 150.2 (C-8'), 151.3 (C-4'), 151.9 (C-6'), 159.1 (C-4), 167.1 (C-2), 168.2 (C-6), 170.1 (C-4) ppm; ei-ms (in the solid state): m/z (%) 415 (100) $[M^+]$.

Anal. Calcd. for $C_{31}H_{27}O_5Cl$: C, 72.30; H, 5.28; Cl, 6.88. Found: C, 72.25; H, 5.36; Cl, 6.77.

4-(2-*t*-Butyl-6-methyl-azulen-1-yl)-2,6-diphenyl-3-methyl-pyranylium perchlorate (**6**) (Rn = 2' t-Bu, 6' Me; R = Me; X = H).

Brown crystals, violet (in acetone), m. p. 216°C; uv-vis (MeOH): λ_{max} (log ε) 243 (4.33), 290 (4.40), 297 (4.43), 385 (3.94), 548 (3.13); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.48 (s, 9 H, tBu), 2.43 (s, 3 H, 6'-Me), 2.69 (s, 3 H, 3-Me), 7.29 (d, 1 H, 7'-H, *J* = 10.4 Hz), 7.44 (d, 1 H, 5'-H, *J* = 10.0 Hz), 7.61 (s, 1 H, 3'-H), 7.79 (t, 2 H, 3"'-H, 5"'-H, *J* = 8.0 Hz), 7.83 (t, 2 H, 3"-H, 5"-H, *J* = 8.0 Hz), 7.87 (t, 1 H, 4"'-H, *J* = 8.0 Hz), 7.89 (t, 1 H, 4"-H, *J* = 8.0 Hz), 7.92 (d, 1 H, 8'-H, *J* = 10.0 Hz), 8.29 (d, 2 H, 2"-H, 6"-H, *J* = 8.0 Hz), 8.46 (d, 1 H, 4'-H, *J* = 10.0 Hz), 8.50 (d, 2 H, 2"'-H, 6"'-H, *J* = 8.0 Hz), 8.94 (s, 1 H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): 18.31-(3-Me), 28.67 (6'-Me), 33.15 (2'-Me), 36.0 (*C*Me_3), 118.6 (C-3'), 122.5 (C-1'), 124.3 (C-5), 128.8 (C-5', C-7'), 132.2 (C-2", C-6"), 130.5 (C-3", C-5"), 132.8 (C-1"), 133.9 (C-3), 134.4 (C-8'), 135.0 (C-4"), 137.6 (C-3a'), 138.0 (C-4'), 141.2 (C-8a'), 152.8 (C-6'), 161.0 (C-2'), 172.5 (C-2), 174.6 (C-4, C-6) ppm; ei-ms (in the solid state): m/z (%) 373 (100) $[M^+]$.

Anal. Calcd. for $C_{33}H_{31}O_5Cl$: C, 72.99; H, 5.75; Cl, 6.53. Found: C, 72.95; H, 5.76; Cl, 6.58.

4-(3,8-Dimethyl-5-*iso*-propyl-azulene-1-yl)-2,6-diphenyl-3-methyl-pyranylium perchlorate (**6**) (Rn = 5' *i*-Pr, 3',8' Me_2; R = Me; X=H).

Brown powder, blue (in acetone), dec. without melt.; uv-vis (MeOH): λ_{max} (log ε) 254 (4.38), 273 (4.35), 306 (4.17), 380 (4.07), 571 (4.01); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.49 (d, 6 H, *Me*$_2$CH, *J* = 6.8 Hz,), 2.71 (s, 3 H, 3'-Me), 2.74 (s, 3 H, 3-Me), 2.90 (s, 3 H, 8'-Me), 3.39 (heptet, 1 H, 5'-CH, *J* = 6.8 Hz), 7.38 (s, 1 H, 2'-H), 7.80 (t, 2 H, 4"'-H, *J* = 7.6 Hz), 7.81 (t, 2 H, 4"-H, *J* = 7.6 Hz), 7.73 (t, 2 H, 3"'-H, 5"'-H, *J* =7.5 Hz), 7.84 (t, 2 H, 3"-H, 5"-H, *J* =7.5 Hz), 7.80 (d, 1 H, 7'-H, *J* = 11.2 Hz), 8.06 (dd, 1 H, 6'-H, *J* = 11.2, 2.2 Hz), 8.23 (d, 2 H, 2"-H, 6"-H, *J* = 8.0 Hz), 8.40 (s, 1 H, 5'-H), 8.41 (d, 2 H, 2"'-H, 6"'-H, *J* = 8.0 Hz), 8.63 (d, 1 H, 4'-H, *J* = 2.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 19.73 (3-Me), 19.92 (3'-Me), 29.93 (CH*Me*$_2$), 30.79 (8'-Me), 39.67 (*C*HMe_2), 120.7 (C-5), 125.4 (C-1'), 128.2 (C-3), 129.4 (C-2"', C-6'"), 130.3 (C-3'), 130.8 (C-3", C-5"), 131.3 (C-1'"), 131.4 (C-3'", C-5'"), 132.2 (C-2", C-6"), 133.0 (C-1"), 134.2 (C-4'"), 135.5 (C-4"), 136.1 (C-7'), 137.1 (C-4"), 139.6 (C-6'), 140.0 (C-2'), 141.5 (C-3a'), 146.4 (C-8a'), 150.8 (C-8'), 151.5 (C-5'), 165.9 (C-2), 166.3 (C-6), 169.4 (C-4) ppm; ir (KBr): 595 (m), 645 (m), 692 (m), 730 (m), 760 (m), 770 (m), 785 (m), 815 (m), 880 (m), 920 (m), 1000(m), 1010 (m), 1030 (m), 1085 (m), 1165 (m), 1200 (m), 1360 (m), 1415 (m), 1440 (m), 1492 (m), 1535 (m), 1570 (m), 1580 (m), 2865 (m), 2925 (m), 2955 (m), 3030 (m), 3060 (m), 3075 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 443 (100) $[M^+]$.

Anal. Calcd. for $C_{33}H_{31}O_5Cl$: C, 72.99; H, 5.75; Cl, 6.53. Found: C, 72.89; H, 5.86; Cl, 6.43.

4-(Azulen-1-yl)-2,3,6-triphenyl-pyranylium perchlorate (**6**) (Rn = H; R = Ph; X = H).

Brown powder, red (in acetone), m. p. 265°C; uv-vis (MeOH): λ_{max} (log ε) 300 (4.24), 305 (4.30), 378 (4.09), 525 (4.09); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.28 (d, 1 H, 3'-H, *J* = 4.4 Hz), 7.40 (d, 1 H, 2'-H, *J* = 4.4 Hz), 7.40 (d, 2 H, 2^{IV}-H, 6^{IV}-H, *J* = 8.0 Hz), 7.42 (t, 2 H, 3^{IV}-H, 5^{IV}-H, *J* = 7.8 Hz), 7.48 (t, 1 H, 4"'-H, *J* =7.8 Hz), 7.53 (t, 2 H, 3"-H, 5"-H, *J* = 7.8 Hz), 7.64 (tt, 1 H, 4"-H, *J* = 7.6, 1.2 Hz), 7.74 (d, 2 H, 2"-H, 6"-H, *J* = 7.6 Hz), 7.80 (tt, 2 H, 3"'-H, 5"'-H, *J* = 7.6, 1.2 Hz), 7.89 (t, 1 H, 5'-H, *J* = 9.4 Hz), 7.89 (tt, 1 H, 4^{IV}-H, *J* = 7.6, 1.2 Hz), 7.94 (t, 1 H, 7'-H, *J* = 9.6 Hz), 8.21 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.51 (dd, 2 H, 2"'-H, 6"'-H, *J* = 7.6, 1.2 Hz), 8.72 (d, 1 H, 4'-H, *J* = 9.2 Hz), 8.99 (s, 1 H, 5-H), 9.27 (d, 1 H, 8'-H, *J* = 9.6 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 120.0 (C-5), 123.2 (C-3'), 126.4 (C-3, C-1'), 129.5 (C-2"', C-6'"), 129.9 (C-1'"), 130.4 (C-2^{IV}, C-6^{IV}), 130.9 (C-3^{IV}, C-5^{IV}), 131.1 (C-1"), 131.6 (C-3", C-5"), 131.8 (C-3'", C-5'"), 132.0 (C-5'), 132.3 (C-7'), 132.6 (C-2", C-6", C-4^{IV}), 133.2 (C-1^{IV}), 133.4 (C-4"), 135.9 (C-4'"), 139.4 (C-8'), 140.6 (C-4'), 141.8 (C-2'), 143.2 (C-6'), 144.0 (C-3a'), 149.0 (C-8a'), 162.8 (C-4), 168.3 (C-6), 169.5 (C-2) ppm; ir (KBr): 621 (m), 634 (m), 689 (m), 721 (m), 780 (m), 850 (m), 970 (m), 1090 (m), 1180 (m), 1220 (m), 1250 (m), 1355 (m), 1390 (m), 1430 (m), 1470 (m), 1490 (m), 1530 (m), 1565 (m), 1600 (m), 2855 (m), 2875 (m), 2920 (m), 2955 (m), 3050 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 394 (37), 393 (100) $[M^+]$.

Anal. Calcd. for $C_{33}H_{23}O_5Cl$: C, 74.09; H, 4.33; Cl, 6.63. Found: C, 74.19; H, 4.52; Cl, 6.43.

4-(3-Methyl-azulene-1-yl)-2,3,6-triphenyl-pyranylium perchlorate (**6**) (Rn = H; R = Ph; X = Me).

Brown powder, blue (in acetone), m. p. 272°C; uv-vis (MeOH): λ_{max} (log ε) 250 (4.31), 295 (4.30), 385 (4.04), 546

(4.10);. ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 2.45 (s, 3 H, Me), 7.10 (s, 1 H, 2'-H), 7.37 (d, 2 H, 2^{IV}-H, 6^{IV}-H, *J* = 8.0 Hz), 7.42 (t, 2 H, 3^{IV}-H, 5^{IV}-H, *J* = 7.8 Hz), 7.51 (t, 1 H, 4^{IV}-H, *J* =7.8 Hz), 7.52 (t, 2 H, 3"-H, 5"-H, *J* = 7.8 Hz), 7.62 (tt, 1 H, 4"-H, *J* = 7.6, 1.2 Hz), 7.73 (d, 2 H, 2"-H, 6"-H, *J* = 7.6 Hz,), 7.79 (tt, 2 H, 3"'-H, 5"'-H, *J* = 7.6, 1.2 Hz), 7.86 (t, 1 H, 5'-H, *J* = 9.4 Hz), 7.87 (tt, 1 H, 4"'-H, *J* = 7.6, 1.2 Hz), 7.88 (t, 1 H, 7'-H, *J* = 9.6 Hz), 8.16 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.48 (dd, 2 H, 2"'-H, 6"'-H, *J* = 7.6, 1.2 Hz), 8.63 (d, 1 H, 4'-H, *J* = 9.2 Hz), 8.89 (s, 1 H, 5-H), 9.19 (d, 1 H, 8'-H, *J* = 9.6 Hz,) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 13.30 (Me), 125.2 (C-1'), 125.4 (C-3), 129.8 (C-2"', C-6"'), 129.9 (C-1"'), 130.3 (C-3", C-5"), 130.9(C-2^{IV}, C-6^{IV}, C-3^{IV}, C-5^{IV}), 131.1 (C-1"), 131.5 (C-3"', -5"'), 131.8 (C-2", C-6", C-3'), 132.6 (C-4^{IV}), 133.3 (C-1^{IV}), 133.6 (C-4"), 135.4 (C-5'), 135.5 (C-7'), 135.9 (C-4"'), 138.5 (C-4'), 139.0 (C-8'), 142.0 (C-2'), 143.1 (C-3a'), 143.2 (C-6'), 146.8 (C-8a'), 162.8 (C-4), 168.2 (C-6), 169.5 (C-2) ppm; ir (KBr): 625 (m), 645 (m), 695 (m), 723 (m), 760 (m), 805 (m), 860 (m), 895 (m), 925 (m), 1040 (m), 1075 (m), 1095 (m), 1185 (m), 1220 (m), 1240 (m), 1260 (m), 1310 (m), 1380 (m), 1410 (m), 1435 (m), 1455 (m), 1480 (m), 1565 (m), 1605 (m), 3055 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 407 (100) [M$^+$].

Anal. Calcd. for $C_{34}H_{25}O_5Cl$: C, 74.38; H, 4.59; Cl, 6.46. Found: C, 74.48; H, 4.69; Cl, 6.56.

4-(2-*t*-Butyl-6-methyl-azulen-1-yl)-2,3,6-triphenyl-pyranylium perchlorate (**6**) (Rn = 2'-*t*-Bu, 6' Me; R = Ph; X = H).

Brown powder, blue-violet (in acetone), m. p. 230°C; uv-vis (MeOH): λ_{max} (log ε) 245 (4.26), 298 (4.22), 399 (3.64), 573 (3.12); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.37 (s, 9 H, tBu), 2.63 (s, 3 H, 6-Me), 7.15 (d, 2 H, 2^{IV}-H, 6^{IV}-H, *J* = 8.0 Hz,), 7.15 (t, 3 H, 3^{IV}-H, 4^{IV}-H, 5^{IV}-H, *J* =7.8 Hz), 7.20 (d, 1 H, 7'-H, *J* = 10.0 Hz), 7.33 (d, 1 H, 5'-H, *J* = 10.0 Hz), 7.45 (s, 1 H, 3'-H), 7.53 (t, 2 H, 3"-H, 5"-H, *J* = 7.8 Hz), 7.68 (t, 1 H, 4"-H, *J* = 7.6 Hz), 7.77 (d, 2 H, 2"-H, 6"-H, *J* = 7.6 Hz), 7.83 (t, 2 H, 3"'-H, 5"'-H, *J* = 7.6 Hz), 7.93 (t, 1 H, 4"'-H, *J* = 7.6 Hz), 8.03 (d, 1 H, 8'-H, *J* = 9.6 Hz), 8.30 (d, 1 H, 4'-H, *J* = 9.2 Hz), 8.57 (d, 2 H, 2"'-H, 6"'-H, *J* = 7.6 Hz), 9.04 (s, 1 H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 28.1 (6'-Me), 33.6 (2'-Me), 118.6 (C-3'), 122.5 (C-1'), 128.8 (C-5', C-7'), 130.1 (C-2"', C-6"'), 130.3 (C-2^{IV}, C-6^{IV}), 130.5 (C-3", C-5"), 131.1 (C-1"'), 131.8 (C-2", C-6"), 132.0 (C-3"', C-5"'), 132.5 (C-3^{IV}, C-5^{IV}), 132.7 (C-4^{IV}), 132.8 (C-1"), 133.3 (C-1^{IV}), 134.4 (C-4"), 136.0 (C-3), 137.0 (C-4"'), 138.0 (C-3a'), 138.5 (C-4'), 141.2 (C-8a'), 152.0 (C-6'), 161.8 (C-2'), 170.0 (C-4, C-6), 172.2 (C-2) ppm; ei-ms (in the solid state): m/z (%) 463 (100) [M$^+$].

Anal. Calcd. for $C_{38}H_{33}O_5Cl$: C, 75.42; H, 5.50; Cl, 5.86. Found: C, 75.49; H, 5.55; Cl, 5.79.

4-(4,6,8-Trimethyl-azulene-1-yl)-2,3,6-triphenyl-pyranylium perchlorate (**6**) (Rn = 4',6',8' Me_3; R = Ph; X = H).

Brown powder, blue (in acetone), m. p. 278°C; uv-vis (dioxane): λ_{max} (log ε) 247 (4.26), 282 (4.19), 391 (3.68), 556 (3.78); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.76 (m, 3 H, 8'-Me), 2.89 (s, 3 H, 6'-Me), 3.08 (s, 3 H, 4'-Me), 7.13 (d, 1 H, 3'-H, *J* = 4.8 Hz,), 7.18 (d, 1 H, 2'-H, *J* = 4.8 Hz,), 7.37 (t, 1 H, 4^{IV}-H, *J* = 7.8 Hz,), 7.39 (t, 2 H, 3^{IV}-H, 5^{IV}-H, *J* = 7.8 Hz), 7.42 (d, 2 H, 2^{IV}-H, 6^{IV}-H, *J* = 8.0 Hz), 7.48 (t, 2 H, 3"-H, 5"-H, *J* = 7.8 Hz), 7.59 (tt, 1 H, 4"-H, *J* = 7.6, 1.2 Hz), 7.69 (s, 1 H, 5'-H), 7.70 (d, 2 H, 2"-H, 6"-H, *J* = 7.6 Hz), 7.71 (tt, 2 H, 3"'-H, 5"'-H, *J* = 7.6, 1.2 Hz), 7.71 (s, 1 H, 7'-H), 7.80 (tt, 1 H, 4"'-H, *J* = 7.6, 1.2 Hz), 8.31 (s, 1 H, 5-H), 8.39 (dd, 2 H, 2"'-H, 6"'-H, *J* = 7.6, 1.2 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ = 26.35 (6'-Me), 29.03 (8'-Me), 31.85 (4'-Me), 119.9 (C-3'), 120.5 (C-3), 122.2 (C-5'), 128.1 (C-1'), 129.6 (C-2"', C-6"'), 130.3 (C-3", C-5"), 130.7 (C-2^{IV}, C-6^{IV}), 130.9 (C-3^{IV}, C-5^{IV}), 131.1 (C-1^{IV}), 131.5 (C-3"', C-5"'), 131.9 (C-2", C-6"), 132.9 (C-4^{IV}), 133.2 (C-1"'), 133.6 (C-4"), 135.9 (C-4"'), 136.1 (C-5'), 136.7 (C-7'), 138.5 (C-1"), 140.0 (C-2'), 140.3 (C-3a'), 146.2 (C-8a'), 150.0 (C-8'), 151.6 (C-4'), 152.0 (C-6'), 165.5 (C-4), 166.6 (C-6), 169.5 (C-2) ppm; ir (KBr): 623 (m), 650 (m), 683 (m), 705 (m), 835 (m), 860 (m), 870 (m), 885 (m), 980 (m), 1030 (m), 1090 (m), 1190 (m), 1210 (m), 1250 (m), 1270 (m), 1325 (m), 1340 (m), 1365 (m), 1390 (m), 1430 (m), 1445 (m), 1460 (m), 1480 (m), 1570 (m), 1600 (m), 2950 (m), 3060 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 435 (100) [M$^+$].

Anal. Calcd. for $C_{36}H_{29}O_5Cl$: C, 74.93; H, 5.07; Cl, 6.14. Found: C, 74.99; H, 5.15; Cl, 6.16.

4-(3,8-Dimethyl-5-*iso*-propyl-azulene-1-yl)-2,3,6-triphenyl-pyranylium perchlorate (**6**) (Rn = 5' i-Pr, 3',8' Me_2; R = Me; X=H).

Brown powder, blue (in acetone), m. p. 287°C; uv-vis (dioxane): λ_{max} (log ε) 252 (4.20), 278 (4.20), 389 (3.71), 584 (3.77); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.46 (d, 6 H, Me_2CH, *J* = 6.8 Hz,), 2.39 (s, 3 H, 3'-Me), 3.13 (s, 3 H, 8'-Me), 3.36 (hep, 1 H, 5'-CH, *J* = 6.8 Hz), 7.06 (s, 1 H, 2'-H), 7.43 (d, 2 H, 2^{IV}-H, 6^{IV}-H, *J* = 8.0 Hz), 7.50 (t, 5 H, 3^{IV}-H, 4^{IV}-H, 5^{IV}-H, 3"-H, 5"-H, *J* =7.5 Hz), 7.61 (tt, 1 H, 4"-H, *J* = 7.6, 1.2 Hz), 7.73 (d, 2 H, 2"-H, 6"-H, *J* = 7.6 Hz), 7.74 (tt, 2 H, 3"'-H, 5"'-H, *J* = 7.6, 1.2 Hz), 7.81 (tt, 1 H, 4"'-H, *J* = 7.6, 1.2 Hz), 7.85 (d, 1 H, 7'-H, *J* = 11.2 Hz), 8.05 (dd, 1 H, 6'-H, *J* = 11.2, 2.0 Hz), 8.22 (s, 1 H, 5-H), 8.41 (d, 2 H, 2"'-H, 6"'-H, *J* = 7.6 Hz), 8.46 (d, 1 H, 4'-H, *J* = 2.0 Hz) ppm; ^{13}C NMR (100.62 MHz, acetone-d_6, 25 °C): δ 13.58 (3'-Me), 25.76 (CHMe_2), 30.79 (8'-Me), 39.70 (*C*HMe_2), 121.9 (C-5), 125.7 (C-1'), 127.5 (C-3), 129.4 (C-2"', C-6"'), 130.3 (C-2^{IV}, C-6^{IV}), 130.7 (C-3'), 130.9 (C-3^{IV}, C-5^{IV}), 131.3 (C-1"'), 131.5 (C-3", C-5", C-4^{IV}), 131.8 (C-3"', -5"'), 132.9 (C-2", C-6"), 133.4 (C-4"), 135.6 (C-4"'), 135.8 (C-1^{IV}), 136.3 (C-1"), 136.8 (C-4'), 137.2 (C-7'), 139.7 (C-6'), 142.4 (C-2'), 143.1 (C-3a'), 147.3 (C-8a'), 151.2 (C-8'), 152.8 (C-7'), 162.8 (C-2), 165.7 (C-6), 168.5 (C-4) ppm; ir (KBr): 625 (m), 635 (m), 665 (m), 685 (m), 725 (m), 755 (m), 765 (m), 860 (m), 970(m), 1030 (m), 1095 (m), 1185 (m), 1225 (m), 1250 (m), 1350 (m), 1390 (m), 1420 (m), 1460 (m), 1490 (m), 1525 (m), 1565 (m), 1605 (m), 2870 (m), 2930 (m), 2960 (m), 3060 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 463 (100) [M$^+$].

Anal. Calcd. for $C_{38}H_{33}O_5Cl$: C, 75.42; H, 5.50; Cl, 5.86. Found: C, 75.48; H, 5.55; Cl, 5.76.

3-Bromo-4-(azulene-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = H; R = Br; X = H).

Brown powder, red (in acetone), m. p. 251°C; ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.32 (t, 1 H, 5'-H, *J* = 10.0 Hz), 7.34 (t, 1 H, 7'-H, *J* = 9.8 Hz), 7.38 (t, 1 H, 4"'-H, *J* = 7.2 Hz), 7.40 (t, 2 H, 3"-H, 5"-H, *J* = 7.2 Hz), 7.50 (s, 1 H, 5-H), 7.55 (t, 1 H, 4"-H, *J* = 7.2 Hz), 7.57 (t, 2 H, 3"'-H, 5"'-H, *J* = 7.2 Hz), 7.75 (t, 1 H, 6'-H, *J* = 9.8 Hz), 7.91 (dd, 2 H, 2"'-H, 6"'-H, *J* = 7.6, 0.8 Hz), 7.99 (d, 2 H, 2"-H, 6"-H, *J* = 7.6, 0.8 Hz), 8.13 (s, 1 H, 2'-H), 8.46 (d, 1 H, 8'-H, *J* = 9.2 Hz), 8.50 (d, 1 H, 4'-H, *J* = 10.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 112.8 (C-5), 118.6 (C-3'), 122.2 (C-1'), 125.5 (C-5'), 125.7 (C-7'), 126.6

(C-2"', C-6"'), 129.5 (C-3", C-5"), 130.7 (C-2", C-6", C-3'", C-5"'), 130.9 (C-1", C-4"), 131.1 (C-1'"), 133.4 (C-4"'), 137.2 (C-8'), 137.4 (C-3a'), 138.7 (C-4'), 140.4 (C-2', C-6'), 143.8 (C-8a'), 148.3 (C-4), 151.1 (C-2), 157.9 (C-6) ppm; ir (KBr): 640 (m), 660 (m), 685 (m), 775 (m), 815 (m), 955 (m), 985 (m), 1030(m), 1035 (m), 1080 (m), 1135 (m), 1225 (m), 1300 (m), 1375 (m), 1395 (m), 1425 (m), 1445 (m), 1490 (m), 1515 (m), 1565 (m), 3020 (m), 3045 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) = 397/399 (100) $[M^+]$.

Anal. Calcd. for $C_{27}H_{18}O_5BrCl$: C, 60.30; H, 3.37; Cl, 6.59; Br, 14.86. Found: C, 60.28; H, 3.39; Cl, 6.60; Br, 14.89.

3-Bromo-4-(4,6,8-trimethyl-azulene-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 4',6',8' Me_3; R = Br; X = H).

Brown powder, violet (in acetone), m. p. 280°C (lit 280°C)[12]; uv-vis (dioxane): λ_{max} (log ε) 250 (4.17), 282 (4.19), 339 (3.76), 396 (3.81), 568 (3.81); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.59 (s, 3 H, 6'-Me), 2.62 (s, 3 H, 4'-Me), 2.83 (s, 3 H, 8'-Me), 7.40 (t, 2 H, 3"-H, 5"-H, *J* = 7.8 Hz), 7.57 (t, 2 H, 3"'-H, 5"'-H, *J* = 7.2 Hz), 7.06 (s, 1 H, 5'-H), 7.16 (s, 1 H, 7'-H), 7.38 (t, 1 H, 4"-H, *J* = 8.0 Hz), 7.55 (t, 1 H, 4"'-H, *J* = 8.0 Hz), 7.91 (dd, 2 H, 2"-H, 6"-H, *J* = 7.2, 1.2 Hz), 7.50 (d, 1 H, 2'-H, *J* = 4.8 Hz), 7.99 (d, 4 H, 2"'-H, 6"'-H, *J* = 7.0 Hz), 7.50 (s, 1 H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 26.09 (8'-Me), 28.51 (6'-Me), 29.02 (4'-Me), 118.8 (C-3'), 114.0 (C-5), 126.5 (C-2"', C-6"'), 132.9 (C-4"), 129.0 (C-5'), 130.3 (C-3", C-5"), 130.5 (C-7'), 126.5 (C-3"', C-5"'), 130.8 (C-4"'), 112.8 (C-3), 130.9 (C-2", C-6"), 134.5 (C-3a'), 137.9 (C-2'), 139.8 (C-8a'), 130.8 (C-1'"), 132.5 (C-1"), 147.0 (C-8'), 148.2 (C-4'), 148.7 (C-6'), 149.0 (C-4), 157.0 (C-6), 157.2 (C-2) ppm; ir (KBr): 622 (m), 660 (m), 675 (m), 685 (m), 740 m), 745 (m), 770 (m), 775 (m), 845 (m), 870 (m), 900 (m), 935 (m), 960 (m), 980 (m), 1030 (m), 1090 (m), 1190 (m), 1215 (m), 1230 (m), 1270 (m), 1325 (m), 1440 (m), 1470 (m), 1490 (m), 1515 (m), 1568 (m), 1595 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 439/437 (100) $[M^+]$.

Anal. Calcd. for $C_{30}H_{24}O_5BrCl$: C, 62.14; H, 4.17; Cl, 6.11; Br, 13.78. Found: C, 62.25; H, 4.29; Cl, 6.20; Br, 13.89.

3-Bromo-4-(3,8-dimethyl-5-*iso*-propyl-azulene-1-yl)-2,6-diphenyl-pyranylium perchlorate (**6**) (Rn = 5' i-Pr, 3',8' Me_2; R = Br; X = H).

Brown powder, blue (in acetone), m. p. 195°C; uv-vis (dioxane): λ_{max} (log ε) 251 (4.29), 287 (4.30), 333 (3.90), 389 (3.89), 595 (3.92); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.38 (d, 6 H, Me_2CH, *J* = 6.8 Hz), 2.60 (s, 3 H, 3'-Me), 2.64 (hep, 1 H, 5'-CH, *J* = 6.8 Hz), 3.14 (s, 3 H, 8'-Me), 7.01 (d, 1 H, 7'-H, *J* = 11.2 Hz), 7.27 (s, 1 H, 5-H), 7.28 (t, 2 H, 3"-H, 5"-H, *J* =7.5 Hz), 7.40 (t, 1 H, 4"-H, *J* = 7.6 Hz), 7.47 (dd, 1 H, 6'-H, *J* = 11.2, 2.0 Hz), 7.48 (t, 1 H, 4"'-H, *J* = 7.6 Hz), 7.55 (s, 1 H, 2'-H), 7.56 (t, 2 H, 3"'-H, 5"'-H, *J* =7.5 Hz), 7.76 (d, 2 H, 2"-H, 6"-H, *J* = 8.0 Hz,), 7.98 (d, 2 H, 2"'-H, 6"'-H, *J* = 8.0 Hz), 8.20 (d, 1 H, 4'-H, *J* = 2.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 13.46 (3'-Me), 25.58 (CHMe_2), 27.56 (8'-Me), 39.13 (*C*HMe_2), 114.1 (C-5), 119.6 (C-1'), 125.7 (C-3'), 126.5 (C-2"', C-6"'), 128.8 (C-7'), 129.2 (C-3", C-5"), 130.2 (C-2", C-6"), 130.7 (C-3"', C-5"'), 130.8 (C-1'"), 130.9 (C-1"), 132.9 (C-4"), 135.0 (C-4'), 135.2 (C-6'), 136.4 (C-4"'), 139.8 (C-3a'), 140.5 (C-8a'), 141.5 (C-2'), 142.2 (C-5'), 146.9 (C-8'), 149.2 (C-4), 156.6 (C-6), 157.0 (C-2) ppm; ir (KBr): 625 (m), 632 (m), 655 (m), 688 (m), 730 (m), 745 (m), 780 (m), 845 (m), 895 (m), 985 (m), 1035 (m), 1110 (m), 1190 (m), 1220 (m), 1280 (m), 1335 (m), 1355 (m), 1390 (m), 1440 (m), 1465 (m), 1490 (m), 1530 (m), 1565 (m), 1600 (m), 2860 (m), 2960 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) 467/465 (100) $[M^+]$.

Anal. Calcd. for $C_{32}H_{28}O_5BrCl$: C, 63.22; H, 4.64; Cl, 5.83; Br, 13.14. Found: C, 63.34; H, 4.65; Cl, 5.78; Br, 13.22.

4-(Azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate (**9**) (Rn = H).

Brown crystals, plum (in acetone), m. p. 202°C; uv-vis (MeOH): λ_{max} (log ε): 242 (4.22), 296 (4.16), 336 (3.83), 359 (3.83), 466 (4.28); ^{1}H-nmr (500 MHz, DMSO-d_6, 25°C): δ 2.56 (s, 6 H, 2-Me, 6-Me), 7.51 (d, 1 H, 3'-H, *J* = 4.5 Hz), 7.77 (t, 1 H, 5'-H, *J* = 9.6 Hz), 7.80 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.06 (s, 2 H, 3-H, 5-H), 8.07 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.45 (d, 1 H, 2'-H, *J* = 4.5 Hz), 8.65 (d, 1 H, 4'-H, *J* = 9.1 Hz), 9.12 (d, 1 H, 8'-H, *J* = 9.9 Hz) ppm; ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 2.87 (s, 6 H, 2-Me, 6-Me), 7.73 (d, 1 H, 3'-H, *J* = 4.8 Hz,), 8.02 (t, 1 H, 5'-H, *J* = 9.8 Hz), 8.07 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.29 (s, 2 H, 3-H, 5-H), 8.30 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.67 (d, 1 H, 2'-H, *J* = 4.4 Hz), 8.89 (d, 1 H, 4'-H, *J* = 9.6 Hz), 9.44 (d, 1 H, 8'-H, *J* = 10 Hz) ppm; ^{13}C-nmr (125.78 MHz, DMSO-d_6, 25°C): δ 20.98 (Me), 116.0 (C-3, C-5), 122.3 (C-1'), 123.8 (C-3'), 133.1 (C-5'), 133.2 (C-7'), 138.7 (C-8'), 141.0 (C-4'), 141.2 (C-2'), 142.5 (C-3a'), 143.1 (C-6'), 150.7 (C-8a'), 157.5 (C-4), 173.1 (C-2, C-6) ppm; ei-ms (in the solid state): m/z (%) = 235 (100) $[M^+]$.

Anal. Calcd. for $C_{17}H_{15}O_5Cl$: C, 61.00; H, 4.52; Cl, 10.59. Found: C, 61.14; H, 4.66; Cl, 10.69.

4-(Azulen-1-yl)-2,6-dimethyl-pyranylium tetrafluoroborate (**9**) (Rn = H, $[BF_4]$).

Brown crystals, plum (in acetone), m. p. 198-199°C;. ^{1}H-nmr (300 MHz, DMSO-d_6, 25°C): δ 2.78 (s, 6 H, 2-Me, 6-Me), 7.74 (d, 1 H, 3'-H, *J* = 4.5 Hz), 7.99 (t, 1 H, 5'-H, *J* = 9.6 Hz), 8.02 (t, 1 H, 7'-H, *J* = 9.8 Hz), 8.29 (s, 2 H, 3-H, 5-H), 8.29 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.67 (d, 1 H, 2'-H, *J* = 4.5 Hz), 8.86 (d, 1 H, 4'-H, *J* = 9.63 Hz), 9.34 (d, 1 H, 8'-H, *J* = 9.8 Hz) ppm.

4-(4,6,8-Trimethyl-azulen-1-yl)-2,6-dimethyl-pyrylium tetrafluoroborate [25] (**9**) (Rn = 4',6',8'-Me_3).

Brown powder, red (in acetone), m. p. 158°C; uv-viz (MeOH): λ_{max} (log ε) 216(4.05), 249(4.22), 268(4.10), 293(4.13), 374(3.81), 500(4.03); ^{1}H-nmr (500 MHz, $CDCl_3$, 25°C): δ 2.73 (s, 6 H, 2-Me, 6-Me), 2.76 (s, 3 H, 6'-Me), 2.87 (s, 3 H, 8'-Me), 2.89 (s, 3 H, 4'-Me), 7.28 (bs [26], 1 H, 3'-H), 7.35 (s, 2 H, 3-H, 5-H), 7.59 (s, 1 H, 5'-H), 7.74 (s, 1 H, 7'-H), 8.03 (bs, 1 H, 2'-H) ppm; ^{13}C-nmr (125.78 MHz, $CDCl_3$, 25°C): δ 21.56 (2-Me, 6-Me), 26.16 4'-Me), 28.79 (6'-Me), 30.89 (8'-Me), 117.7 (C-3, C-5), 120.5 (C-3'), 126.1 (C-1'), 137.2 (C-5'), 137.6 (C-7'), 140.0 (C-2'), 140.6 (C-3a'), 148.3 (C-4'), 149.1 (C-8'), 151.6 (C-6'), 158.1 (C-4), 170.9 (C-2, C-6) ppm; ir (KBr): 645(m), 740(m), 790 (m), 940 (m), 1090 (m), 1215 (m), 1275 (m), 1325 (m), 1497 (m), 1540 (m), 1580 (m), 1630 (m), 3070 (m) cm^{-1}; ms (ESI, m/z): 277 $[M^+]$, 100.

Anal. Calcd. for $C_{20}H_{21}BF_4O$: C, 65.96; H, 5.81. Found: C, 65.75; H, 5.97.

4-(2-*t*-Butyl-6-methyl-azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate (**9**) (Rn = 2'-*t*-Bu,6'-Me).

Brown crystals, red (in acetone), m. p. 154°C; uv-vis (MeOH): λ_{max} (log ε) 215 (4.07), 238 (4.22), 292 (4.40), 343 (3.74), 385

(3.59), 500 (3.96); ^{1}H-nmr (500 MHz, DMSO-d_6, 25 °C): δ 1.44 (s, 9 H, tBu), 2.68 (s, 3 H, 6'-Me), 2.91 (s, 6 H, 2-Me, 6-Me), 7.38 (d, 1 H, 7'-H, *J* = 10.4 Hz), 7.47 (d, 1 H, 5'-H, *J* = 10.0 Hz), 7.55 (s, 1 H, 3'-H), 8.07 (d, 1 H, 4'-H, *J* = 10.0 Hz), 8.08 (s, 2 H, 3-H, 5-H), 8.43 (d, 1 H, 8'-H, *J* = 10.4 Hz) ppm; ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 1.49 (s, 9H, tBu), 2.72 (s, 3H, 6-Me), 3.05 (s, 6 H, 2-Me, 6-Me), 7.45 (d, 1 H, 5'-H, *J* = 10.4 Hz), 7.53 (d, 1 H, 7'-H, *J* = 10.4 Hz), 7.59 (s, 1 H, 3'-H), 8.11 (s, 2 H, 3-H, 5-H), 8.23 (d, 1 H, 8'-H, *J* = 10.0 Hz,), 8.46 (d, 1 H, 4'-H, *J* = 10.4 Hz) ppm; ^{13}C-nmr (125.78 MHz, DMSO-d_6, 25°C): δ 21.44 (2-Me, 6-Me), 27.75 (6'-Me), 34.93 and 39.4 (2'-t-Bu), 113.4 (C-3, C-5), 119.2 (C-3'), 124.1 (C-1'), 128.7 (C-5'), 129.1 (C-7'), 134.5 (C-4'), 138.6 (C-3a'), 138.7 (C-8'), 151.7 (C-8a'), 153.9 (C-6'), 160.7 (C-4), 166.0 (C-2'), 176.0 (C-2, C-6) ppm; ir (KBr): 623 (m), 675 (m), 780 (m), 792 (m), 830 (m), 1000 (m), 1035 (m), 1090 (m), 1100 (s), 1210 (m), 1230 (m), 1305 (m), 1340 (m), 1355 (m), 1420 (m), 1465 (m), 1525 (m), 1563 (m), 1625 (m), 2862 (m), 2910 (m), 2935 (m), 2960 (m), 3080 (m) cm^{-1}; ei-ms (in the solid state): m/z (%) = 305 (100)[M$^+$].

Anal. Calcd. $C_{22}H_{25}O_5Cl$: C, 65.27; H, 6.22; Cl, 8.76. Found: C, 64.91; H, 6.02; Cl, 8.84.

4-(2-*t*-Butyl-6-methyl-azulen-1-yl)-2,6-dimethyl-pyranylium tetrafluoroborate (**9**) (Rn = 2'-t-Bu, 6'-Me $[BF_4]^-$).

^{1}H-nmr (300 MHz, DMSO-d_6, 25°C): δ 1.46 (s, 9H, tBu), 2.51 (s, 3 H, 6-Me), 2.68 (s, 6 H, 2-Me, 6-Me), 7.38 (d, 1 H, 5'-H, *J* = 10.0 Hz), 7.46 (d, 1 H, 7'-H, *J* = 10.0 Hz), 7.55 (s, 1 H, 3'-H), 8.06 (d, 1 H, 4'-H, *J* = 9.6 Hz), 8.08 (s, 2 H, 3-H, 5-H), 8.43 (d, 1 H, 8'-H, *J* = 10.0 Hz) ppm.

4-(4,6,8-Trimethyl-azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate (**9**) (Rn = 4',6',8'-Me_3).

Brown crystals, red (in acetone); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.79 (s, 3 H, 6'-Me), 2.82 (s, 6 H, 2-Me, 6-Me), 2.91 (s, 3 H, 8'-Me), 2.98 (s, 3 H, 4'-Me), 7.49 (d, 1 H, 3'-H, *J* = 4.8 Hz), 7.76 (s, 2 H, 3-H, 5-H), 7.83 (s, 2 H, 5'-H, 7'-H), 8.23 (d, 1 H, 2'-H, *J* = 4.8 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 21.55 (2-Me, 6-Me), 26.38 (4'-Me), 28.84 (6'-Me), 30.89 (8'-Me), 119.1 (C-3, C-5), 121.2 (C-3'), 127.1 (C-1'), 137.6 (C-5'), 137.8 (C-7'), 141.0 (C-2'), 148.6 (C-4'), 150.68 (C-8'), 152.61 (C-6'), 160.6 (C-4), 173.16 (C-2, C-6) ppm; ^{1}H-nmr (400 MHz, DMSO-d_6, 25 °C): δ 2.71 (s, 6 H, 2-Me, 6-Me), 2.75 (s, 3 H, 6'-Me), 2.82 (s, 3 H, 8'-Me), 2.93 (s, 3 H, 4'-Me), 7.49 (d, 1 H, 3'-H, *J* = 4.8 Hz), 7.76 (s, 2 H, 3-H, 5-H), 7.79 (s, 1 H, 5'-H), 7.80 (s, 1 H, 7'-H), 8.19 (d, 1 H, 2'-H, *J* = 4.4 Hz,) ppm; ^{1}H-nmr (400 MHz, $CDCl_3$, 25°C): δ 2.73 (s, 6 H, 2-Me, 6-Me), 2.76 (s, 3 H, 6'-Me), 2.87 (s, 3 H, 8'-Me), 2.89(s, 3 H, 4'-Me), 7.29 (d, 1 H, 3'-H, *J* = 4.8 Hz), 7.32 (s, 2 H, 3-H, 5-H), 7.59 (s, 1 H, 5'-H), 7.74 (s, 1 H, 7'-H), 7.99 (d, 1 H, 2'-H, *J* = 4.8 Hz) ppm; ei-ms (in the solid state): m/z (%) 277 (100) [M$^+$].

4-(3,8-Dimethyl-5-*iso*-propyl-azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate (**9**) (Rn = 5'*i*-Pr, 3',8'-Me_3).

Brown crystals, pink (in acetone), m. p. 173°C; uv-vis (MeOH): λ_{max} (log ε) 213 (4.08), 239 (4.22), 265 (4.29), 294 (4.15), 374 (3.74), 519 (4.27); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 1.44 (d, *J* = 6.8 Hz, 6 H, *Me*CH), 2.63 (s, 3 H, 3'-Me), 2.79 (s, 6 H, 2-Me, 6-Me), 2.93(s, 3 H, 8'-Me), 3.40 [hep, *J* = 6.8 Hz, 1 H, Me*CH*], 7.67 (s, 2 H, 3-H, 5-H), 7.92 (d, 1 H, 7'-H, *J* = 10.8 Hz), 8.11 (dd, 1 H, 6'-H, *J* = 11.0, 1.8 Hz), 8.23 (s, 1 H, 2'-H), 8.55 (d, 1 H, 4'-H, *J* = 2.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 13.61 (3'-Me), 21.45 (2-Me, 6-Me), 25.10 (*Me*CH), 31.0 (8'-Me), 39.62 (Me*CH*), 118.4 (C-3, C-5), 124.3 (C-1'), 131.8 (C-3'), 137.0 (C-4'), 138.3 (C-7'), 140.1 (C-6'), 143.0 (C-2'), 143.6 (C-3a'), 149.6 (C-8a'), 152.1 (C-8'), 154.6 (C-5'), 158.0 (C-4), 172.1 (C-2, C-6) ppm; ^{1}H-nmr (400 MHz, DMSO-d_6, 25°C): δ 1.39 (d, *J* = 6.8 Hz, 6 H, *Me*CH), 2.59 (s, 3 H, 3'-Me), 2.68 (s, 6 H, 2-Me, 6-Me), 2.83 (s, 3 H, 8'-Me), 3.33 (hep, *J* = 6.8 Hz, 1 H, Me*CH*), 7.66 (s, 2 H, 3-H, 5-H), 7.86 (d, 1 H, 7'-H, *J* = 11.2 Hz), 8.09 (dd, 1 H, 6'-H, *J* = 11.2, 2.0 Hz), 8.20 (s, 1 H, 2'-H), 8.47 (d, 1 H, 4'-H, *J* = 2.0 Hz) ppm; ^{13}C-nmr (100.62 MHz, DMSO-d_6, 25°C): δ 12.41 (3'-Me), 20.0 (2-Me, 6-Me), 23.72 (*Me*CH), 28.68 (8'-Me), 37.22 (Me*CH*), 116.6 (C-3, C-5), 121.95 (C-1'), 129.4 (C-3'), 135.2 (C-4'), 136.26 (C-7'), 138.21 (C-6'), 141.03 (C-2'), 141.0 (C-3a'), 146.88 (C-8a'), 150.2 (C-8'), 152.2 (C-5'), 155.5 (C-4), 170.0 (C-2, C-6) ppm; ei-ms (in the solid state): m/z (%) 305 (100) [M$^+$].

Anal. Calcd. for $C_{22}H_{25}O_5Cl$: C, 65.27; H, 6.22; Cl, 8.76. Found: C, 65.11; H, 6.15; Cl, 8.79.

2-(Azulen-1-yl)-4,6-dimethyl-pyranylium perchlorate (**11**) (Rn = H).

Brown crystals, plum (in acetone), dec. without melt.; uv-vis (MeOH): λ_{max} (logε) 314 (3.67), 351 (3.39), 468 (3.41); ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.72 (s, 3 H, 4-Me), 3.01 (s, 3 H, 6-Me), 7.54 (s, 1 H, 5-H), 7.69 (d, 1 H, 3'-H, *J* = 4.4 Hz), 8.02 (t, 1 H, 5'-H, *J* = 9.6 Hz), 8.13 (t, 1 H, 7'-H, *J* = 10.0 Hz), 8.31 (t, 1 H, 6'-H, *J* = 9.6 Hz), 8.47 (s, 1 H, 3-H), 8.76 (d, 1 H, 2'-H, *J* = 4.8 Hz), 8.91 (d, 1 H, 4'-H, *J* = 10.0 Hz), 9.66 (d, 1 H, 8'-H, *J* = 10.0 Hz) ppm; ^{1}H-nmr (500 MHz, DMSO-d_6, 25 °C): δ 2.68 (s, 3 H, 4'-Me), 2.95 (s, 3 H, 6'-Me), 7.28 (s, 1 H, 5-H), 7.76 (d, 1 H, 3'-H, *J* = 4.6 Hz), 8.02 (t, 1 H, 5'-H, *J* = 9.6 Hz), 8.11 (t, 1 H, 7'-H, *J* = 10.0 Hz), 8.33 (t, 1 H, 6'-H, *J* = 9.8 Hz), 8.54 (s, 1 H, 3-H), 8.81 (d, 1 H, 2'-H, *J* = 4.6 Hz), 8.92 (d, 1 H, 4'-H, *J* = 9.2 Hz), 9.54 (d, 1 H, 8'-H, *J* = 9.9 Hz) ppm; ^{13}C-nmr (125.78 MHz, DMSO-d_6, 25 °C): δ 21.65 (6-Me), 24.09 (4-Me), 117.5 (C-1'), 119.8 (C-3), 120.2 (C-5), 124.1 (C-3'), 134.0 (C-5'), 134.2 (C-7'), 140.6 (C-8'), 141.1 (C-2'), 142.1 (C-3a'), 142.3 (C-4'), 144.2 (C-6'), 150.7 (C-8a'), 168.2 (C-4), 170.7 (C-2), 171.8 (C -6) ppm; ei-ms (in the solid state): m/z (%) 235 (100) [M$^+$].

Anal Calcd. for $C_{17}H_{15}O_5Cl$: C, 61.00; H, 4.52; Cl, 10.59. Found: C, 61.09; H, 4.68; Cl, 10.68.

2-(2-*t*-Butyl-6-methyl-azulen-1-yl)-4,6-dimethyl-pyranylium perchlorate (**11**) (Rn = 2'-*t*-Bu, 6'-Me).

Brown crytals, plum (in acetone), dec. without melt.; ^{1}H-nmr (400 MHz, DMSO-d_6, 25°C): δ 1.42 (s, 9 H, tBu), 2.73 (s, 3 H, 6'-Me), 2.77 (s, 3 H, 4-Me), 2.91 (s, 3 H, 6-Me), 7.54 (s, 1 H, 5-H), 7.60 (d, 1 H, 5'-H, *J* = 9.6 Hz), 7.63 (d, 1 H, 7'-H, *J* = 9.2 Hz), 7.96 (s, 1 H, 3'-H), 8.25 (s, 1 H, 3-H), 8.49 (d, 1 H, 4'-H, *J* = 10.4 Hz), 8.53 (d, 1 H, 8'-H, *J* = 10.4 Hz) ppm; ei-ms (in the solid state): m/z (%) 305 (100) [M$^+$].

Anal. Calcd. for $C_{22}H_{25}O_5Cl$: C, 65.27; H, 6.22; Cl, 8.76. Found: C, 64.91; H, 6.02; Cl, 8.84.

2-(4,6,8-trimethyl-azulen-1-yl)-4,6-dimethyl-pyranylium perchlorate (**11**) (Rn = 4',6',8'-Me_3).

Brown crystals, plum (in acetone), dec. without melt.; uv-viz (MeOH): λ_{max} (log ε) 310 (3.62), 357 (3.33), 473 (3.60); ^{1}H-nmr (400 MHz, DMSO-d_6, 25°C): δ 2.75 (s, 3 H, 4'-Me), 2.78 (s, 3 H, 4-Me), 2.79 (s, 3 H, 8'-Me) 2.83 (s, 3 H, 6'-Me), 2.95 (s, 3 H, 6-Me), 7.51 (d, 1 H, 3'-H, *J* = 4.8 Hz), 7.57 (s, 1 H, 5'-H), 7.77 (s, 2 H, 5-H, 7'-H), 8.26 (d, 1 H, 2'-H, *J* = 4.4 Hz), 8.27 (s, 1 H, 3-H) ppm; ei-ms (in the solid state): m/z (%) 277 (100) [M$^+$].

Anal. Calcd. for $C_{20}H_{21}O_5Cl$: C, 63.75; H, 5.62; Cl, 9.41. Found: C, 63.52; H, 5.39; Cl, 9.24.

2-(3,8-Dimethyl-5-*iso*-propyl-azulen-1-yl)-4,6-dimethyl-pyranylium perchlorate (**11**) (Rn = 5' i-Pr, 3',8'-Me_2).

Brown crystals, violet (in acetone), dec. without melt.; uv-vis (MeOH): $\lambda_{max.}$ (log ε) 302 (3.93), 363 (3.57), 498 (3.83);. ^{1}H-nmr (400 MHz, DMSO-d_6 , 25°C): δ 1.38 (d, 6 H, *Me*CH, *J* = 7.2 Hz,), 2.58 (s, 3 H, 4-Me), 2.61 (s, 3 H, 3'-Me), 2.75 (s, 3 H, 6-Me), 2.83 (s, 3 H, 8'-Me), 3.33 (hep, 1 H, Me*CH,* *J* = 6.8 Hz), 7.47 (s, 2 H, 5-H), 7.82 (d, 1 H, 7'-H, *J* = 11.2 Hz), 8.05 (dd, 1 H, C(6')-H, *J* = 11.2, 2.0 Hz), 8.20 (s, 1 H, 3-H), 8.28 (s, 1 H, 2'-H), 8.50 (d, 1 H, 4'-H, *J* = 2.0 Hz,) ppm; ei-ms (in the solid state): m/z (%) 305 (100) [M^+].

Anal. Calcd. for $C_{22}H_{25}O_5Cl$: C, 65.26; H, 6.22; Cl, 8.76. Found: C, 65.04; H, 6.40; Cl, 8.56.

4-Chloro-2,6-diphenyl-pyranylium perchlorate (**3**) (R = H).

Yellow crystals, 254°C (lit 254 °C) [.27]; ^{1}H-nmr (400 MHz, acetone-d_6, 25 °C): δ 7.06-7.09 (m, 2 H, 4'-H), 7.59-7.62 (m, 4 H, 3'-H, 5'-H), 7.62 (s, 2 H, 3-H, 5-H), 8.07-8.08 (m, 2 H, 2'-H, 6'-H) ppm; ^{13}C-NMR (100.62 MHz, acetone-d_6, 25°C): δ 109.4 (C-3', C-5'), 125.7 (C-2", C-6"), 128.7 (C-3", C-5"), 130.2 (C-1"), 131.4 (C-4"), 164.0 (C-2',C-6'), 179.3 (C-4') ppm.

3-Bromo-4-chloro-2,6-diphenyl-pyranylium perchlorate (**3**) (R = Br).

Yellow crystals, m. p. 209 °C, (lit 209 °C) [3]; ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 7.97-8.00 (m, 4 H, 2'-H, 6'-H), 7.56-7.70 (m, 6 H, 3'-H, 4'-H, 5'-H), 7.04 (s, 1 H, 5-H) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 109.8 (C-5'), 115.2 (C-3'), 127.8 (C-2"', C-6"'), 130.8 (C-2", C-6"), 130.1 (C-3", C-5"), 131.0 (C-3"', C-5"'), 132.3 (C-1"'), 132.8 (C-4"), 133.4 (C-4"'), 134.1 (C-1"), 163.7 (C-6'), 165.1 (C-2'), 175.6 (C-4') ppm; ei-ms: m/z (%) 351/349 [M^++1, 30], 327 (100).

4-Chloro-3-methyl-2,6-diphenyl-pyranylium perchlorate (**3**) (R =Me).

Yellow crystals; m. p. 192°C; ^{1}H-nmr (400 MHz, acetone-d_6, 25°C): δ 2.17 (s, 3 H, Me), 7.32 (s, 1 H, 5-H), 7.61 (t, 2 H, 3"-H, 5"-H, *J* = 7.6 Hz), 7.63 (t, 2 H, 3'-H, 5'-H, *J* = 7.6 Hz), 7.65-7.68 (m, 2 H, 4'-H, 4"-H), 7.85-7.88 (m, 2 H, 2'-H, 6'-H), 8.05 (dd, 2 H, 2'-H, 6'-H, *J* = 8.0, 1.6 Hz) ppm; ^{13}C-nmr (100.62 MHz, acetone-d_6, 25°C): δ 12.26 (Me), 109.1 (C-5'), 122.5 (C-3'), 127.9 (C-2"', C-6"'), 130.4 (C-2", C-6"), 130.7 (C-3", C-5"), 130.9 (C-3"', C-5"'), 132.3 (C-1"'), 132.5 (C-4"), 133.7 (C-4"'), 133.6 (C-1"), 164.8 (C-6'), 166.6 (C-2'), 181.5 (C-4') ppm; ir (KBr): 595 (m), 625 (m), 655 (m), 680 (m), 755 (m), 810 (m), 825 (m), 1005 (m), 1100 (s), 1140 (m), 1190 (m), 1230 (m),

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