# Extended π-conjugated Chromophores based on Pyrilium Core Linked to Guiazulenyl Vinyl Moieties

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*Novel pyrylium perchlorates featuring guaiazulen-ylvinyl substituents have been synthesized and fully characterized. Careful selection of the reaction conditions made possible modular approach towards synthesis of mono-, bis- and tris-(guiazulen-1-yl)vinyl pyrylium salts. Comparative studies between conventional condensation reactions with or without piperidine and microwave-assisted protocol are discussed. The microwave-assisted synthesis afforded higher selectivity in 2,4,6-tris(guiazulen-1-yl)vinyl)pyrylium perchlorate in a short reaction time. Upon replacement of the azulenyl group with guiazulenyl moiety a strong bathochromic effect was induced, the electronic spectra showing strong absorption maxima in visible for all guiazulen-1-ylvinyl pyrilium perchlorates. The $^1$H-NMR spectra confirmed the structure of the compounds, an upfield move of the chemical shifts belonging to the pyrilium and vinylene protons being observed.*

*Keywords: Guiazulen-1-ylvinyl pyrylium salts; classical condensation reaction; microwave-assisted condensation*

Organic molecules with π-conjugated structures are extensively studied for both scientific and application reasons. Such compounds found use as nonlinear optical (NLO) materials, liquid crystal displays, solar cells and organic light emitting diodes (OLEDs) [1]. For non linear optics, organic compounds are appropriate systems because they show fast electronic responses to external stimuli, flexible chemical design and good processability in devices. Electron donor–acceptor systems (D-π-A) are typical example of molecules that exhibit second-order NLO features [2]. The disadvantage of these molecules is given by commonly found centrosymmetry inactivating thus, the second harmonic generation response [3]. Hence, multipolar molecules such as quadrupoles and octupoles have been proposed as alternatives to the more conventional dipolar push-pull chromophores [4]. These NLO chromophores suppose the expanding of the charge transfer from one to two or three dimensions by connecting donor and acceptor groups with a variety of spatially extended π-conjugation bridges [5]. For example, conjugated phenylvinylene and phenylacetylene compounds showed remarkable optical and electronic properties due to the multiple conjugation pathways [6]. It has been reported that molecules with $C_{2v}$ symmetry show a significant octupole contribution to the nonlinear second-order optical susceptibility depending on the number and location of the donor/acceptor groups [7]. In this direction, pyrylium salts, compounds with $C_{2v}$ symmetry,[8] showed peculiar photophysical and electrochemical properties, reason why they found broad practical applications [9]. During the past few decades, we started to investigate the chemistry of azulenyl-substituted heterocyclic compounds [10] in order to extend our research interest in the design of azulenyl based push-pull chromophores [11]. Azulene is an isomer of naphthalene with a striking blue color resulting from the electronic transition between the $S_0$ and $S_1$ state,[12] as a consequence of low energy frontier molecular orbital transitions [13]. The dipole moment of this nonbenzoid hydrocarbon is 1.08 D, [14] astoundingly large in comparison to that of naphthalene ($\mu$ = 0 D). This can be rationalized by a significant contribution of cyclopentadienyl anion/tropylium cation resonance structure formed by the electron drift from the seven-membered ring toward the five-membered ring of azulene skeleton [13].

Recently, we have reported an improved synthetic strategy to isolate threefold substituted pyrylium salts featuring azulen-1-ylvinyl substituents [15]. We showed that, using microwave-assisted synthetic protocol, the reactivity of the starting 2,4,6-trimethyl pyrylium perchlorate can be conducted towards three-condensation product. These compounds posses interesting electronic properties with absorption maxima in the visible region, therefore they are suitable synthons for generation of interesting π-conjugated pyridinium based NLO-phores connected with azulenyl-donor moieties. We now report herein, the synthesis and spectroscopic characterization of olygo-vinyl-guiazulenyl substituted O-containing heterocycles. Guaiazulene (7-isopropyl-1,4-dimethylazulene) is a naturally occurring azulene derivative [16] and has been widely used clinically as anti-inflammatory and anti-ulcer agent [17] as well as in a wide range of cosmetic formulations [18]. Although is a cheap azulene-based compound, it is less involved in material science mainly due to its sensibility in the presence of air. Considering the improved impact of $C_{2v}$ symmetric push-pull chromophores as NLO materials, especially for electro-optic applications, we now direct our attention towards synthesis of cheaper highly π-conjugated pyrylium salts based on guiazulen-1-ylvinyl-substituted moieties. Hence, we report herein the synthesis and full characterization of novel pyrylium chromophores with different degree of guaiazulen-1-ylvinyl substitution.

## Experimental part

### *Methods and techniques*

Melting points: Koehler Automatic Melting Point Range Apparatus (K90190). Elemental analyses: Perkin Elmer

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CHN 240B. UV-Vis spectra: Varian Cary 100 spectrophotometer. NMR spectra in DMSO-d6: Bruker Avance DRX4 (1H: 400 MHz) spectrometer; chemical shifts (δ) are expressed in ppm, and *J* values are given in Hz. Mass spectra were recorded on Varian 1200L Quadrupole/MS/MS spectrometer by direct injection in ESI or APCI. Microwave irradiation was carried out using a Biotage Initiator 2.0 EXP – ED instrument. For the column chromatography silica gel (70-230 mesh ASTM) was used. Dichloromethane (DCM) was dried over $CaH_2$. Numbering of the atoms in the herein described compounds is given in schemes 1. RT denotes room temperature. Guiazulen-1-carbaldehyde and 2,4,6-trimethylpyrylium perchlorate were prepared following reported synthetic procedures [13,20]

*General procedure for the condensation of 2,4,6-trimethylpyrylium perchlorates with guiazulen-1-carbaldehyde*

Conventional condensation reaction

Guiazulen-1-carbaldehyde (1 mmol) and 2,4,6–trimethylpyrylium perchlorate (0.33 mmoles) were dissolved in acetic anhydride (10 mL) and the reaction mixture was stirred at 100 °C, under inert atmosphere. The reaction mixture was maintained at this temperature for 5 min. After cooling to room temperature, the mono-condensation product, **3m**, was obtained by precipitation with diethyl ether. The formed solid compound was filtered under reduced pressure and washed several times with the same solvent. High purity of the compound was accomplished by column chromatography on silica gel using DCM/acetone (6 /1) as eluting solvents.

The same procedure was repeated at 160° C, for 15 min. After several column chromatography on silica gel using the DCM/acetone (6 /1) as eluting solvents, the divinyl and trivinyl products, **3d** and **3t** were isolated.

When 3 drops of piperidine were added at the reaction mixture, at the beginning of the heating process, the compound **3t** was isolated as major compound following the above mentioned workup.

Microwave synthesis

The guiazulen-1-carbaldehyde (1 mmol) and 2,4,6–trimethylpyrylium perchlorate (0.33 mmoles) were introduced in a 2-5 mL reaction vial and acetic anhydride (5 mL) was added. The reaction vial was sealed and irradiated for two minutes at 200 °C. The reaction mixture was poured in diethyl ether and the formed precipitate was filtered off and washed several times with the same organic solvent. The tris(guiazulen-1-ylvinyl)pyrylium salt **3t**, along with traces of bis condensation product (**3d**) was filtered through a pad of silicagel using DCM/acetone (6 / 1) as solvent mixture.

The results for both procedures are reported in table 1.

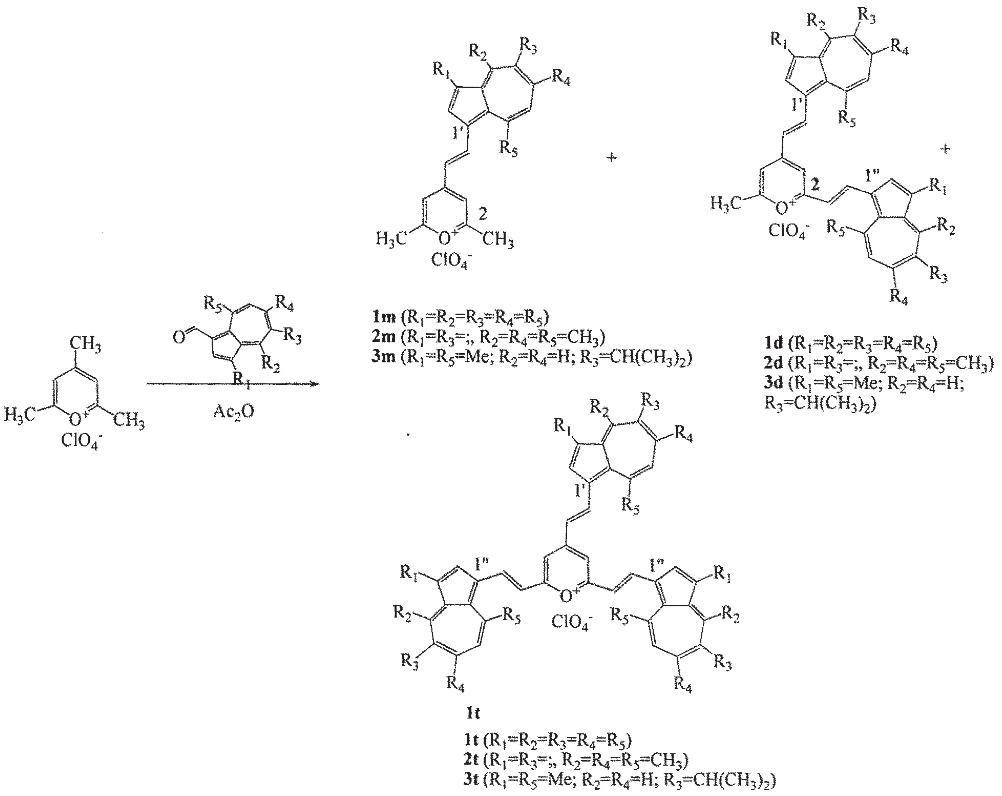
## Results and discussions

*Modular sythesis of guiazulen-1-ylvinyl substituted pyrylium perchlorates*

Encouraged by our smooth synthetic protocol described for the preparation of 2,4,6-tris-(R-azulen-1-yl)-pyrylium perchlorates, compound of type **3** (scheme 1) [15], we decided to perform the reaction with guaiazulene-carbaldehyde, a commercially available and inexpensive azulene derivative, and also to optimize the classical condensation reaction. Likewise, refluxing reaction in acetic anhydride took place step-by-step, resulting a mixture of mono-, di- and tri - vinyl derivatives. Purification of the oligo-condensation products required repetitive column chromatography and therefore time- and solvent consuming. However, precise reaction time and control of the temperature conditions make possible a modular synthesis of the condensation products. Thus, condensation reaction of 2,4,6-trimethylpyrylium perchlorate with guiazulene-1-carbaldehyde at 100° C for around five minutes, yields the corresponding mono-guiazulen-1-ylvinyl pyrilium perchlorate (**3m**) in almost quantitative yield (table 1). Just as previously observed, a prolonged reaction time and higher temperature (160° C) has given a mixture of di- and tri-guiazulen-1-ylvinyl components with the di-guiazulen-1-ylvinyl compound (**3d)** as major condensation product (50 % yield). However, addition of small amounts of piperidine (2-3 drops) provided enhanced yields and the tris-guiazulen-1-ylvinyl substituted compound (**3t**) was isolated in around 55 % yield. This is a major improvement of the classical refluxing reaction, hence without piperidine, the tri-guiazulen-1-ylvinyl compound is isolated only in small amounts (15 – 20 % yield). For comparative purpose, the reactions were performed with azulene-1-carbaldehyde and 4,6,8-trimethylazulen-1-carbaldehyde under the same conditions and it has been observed that catalytic amounts of piperidine efficiently improved the yields of the target compounds (table 1). Nevertheless, the easiest protocol to obtain the desired three-fold guiazulen-1-ylvinyl-substituted pyrylium perchlorate is the microwave-assisted reaction when, within two minutes, the target tri-guiazulen-1-ylvinyl substituted pyrylium perchlorate is obtained as unique compound, in quite pure form. The work-up of the reaction mixture consists in precipitation of the desired compound with diethyl ether and repetitive washes using the same solvent.

*Electronic spectra*

As a main feature, the electronic spectra of all obtained compounds show strong absorption band in the visible region. The position of the absorption maximum depends on the number of guiazulen-1-ylvinyl substitution of the pyrylium core, namely shifts bathocromically from $\lambda_{max}$ = 631 nm in compound **3m** to 766 nm in compound **3d** and at 768 nm for compound **3t** (table 2). As expected, the second guiazulen-1-ylvinyl moiety present at C-2 position induces a high bathochromic shift of the visible absorption maximum, in order: **3m** < **3d** and it is almost the same for the third grafted guiazulen-1-ylvinyl substituent. Therefore, the extension of the conjugation pathway induced a red shift of the absorption band. Moreover, comparison of the UV-Vis spectrum of the herein described three-fold substituted pyrylium salt with the UV-Vis spectrum of tris-styryl pyrylium perchlorate indicates that the electronic contribution of the guaiazulenyl moieties is dominant being observed a bathochromic shift of around 43 nm when compared with 2,4,6-tris(4-dimethyl-aminostyryl)pyrylium perchlorate [8,19]. It is also known that, the modification of a donor group in a chromophore has a large influence on the UV-Vis spectrum. Thus, within the series of tris-azulen-1-ylvinyl heterocycles, the substitution of the azulenyl moieties causes a red shift of the absorption maximum. By comparison to the azulenyl-derivative **1t**, a strong bathochromic effect is induced through alkyl substitution. This spectral pattern was already observed in the case of tris(4,6,8-trimethylazulen-1-ylvinyl) substituted heterocycle, compound **2t**, for which the absorption wavelength was observed at $\lambda_{max}$ = 734 nm**.** In the case of guiazulenyl substitution, the inductive effect is much stronger through methyl and *iso*-propyl substitution of the azulenyl skeleton and the bathochromic effect is around 78 nm as compared



Scheme 1

**Table 1**
CONDENSATION REACTION OF 2,4,6-TRIMETHYL-PYRYLIUM PERCHLORATE WITH $R_n$AZULENE-1-CARBALDEHYDES USING CONVENTIONAL CONDENSATION REACTION, (A) AND MICROWAVE SYNTHESIS, (B)

| Staring azulene | Used procedure | Products/yield (%) |
|---|---|---|
| Azulen-1-carbaldehyde | ***A.1.*** | **1m** / 90-95 |
| | ***A.2.*** | **1d** / 50-60 and **1t** / 15-20 |
| | ***A.3.*** | **1d** / 25 and **1t** / 52 |
| | ***B*** | **1t** / 50[a] |
| 4,6,8-Trimethyl-azulen-1-carbaldehyde | ***A.1.*** | **2m** / 90-95 |
| | ***A.2.*** | **2d** / 50-60 and **2t** / 15-20 |
| | ***A.3.*** | **2d** / 20 and **2t** / 54-55 |
| | ***B*** | **2t** / 55[a] |
| Guiazulen-1-carbaldehyde | ***A.1.*** | **3m** / 90-95 |
| | ***A.2.*** | **3d** / 50-60 and**3t** / 15-20 |
| | ***A.3.*** | **3d** / 15 and **3t** / 55[b] |
| | ***B*** | **3t** / 55-58[a] |

[a]Depending on used azulene, traces of **1d**, **2d** or **3d** were detected.[b]Due to the instability of the guaiazulen-derivative, the reaction requires shorter time in order to avoid the production of tar.

**Table 2**
ABSORPTION MAXIMA $\lambda_{max}$ in nm (log ε) FOR THE PYRYLIUM SALTS (IN ACETONE)

| Compd. | **1t** | **2t** | **3t** | **3d** | **3m** |
|---|---|---|---|---|---|
| λ (log ε) | 690 (4.94) | 734 (4.82) | 768 (4.95) | 766 (4.85) | 631 (4.85) |

to **1t** (table 2). A possible explanation is given by the stabilizing inductive effect of the alkyl groups upon the formed tropylium cation. However, from the second to the third guiazulen-1-ylvinyl no reasonable shifts are observed in the absorption maximum, reason why it is supposed that the *iso*-propyl groups hinders the extension of the π-electronic system upon the whole molecule.

### *$^1$H-NMR spectra*

As previously reported, the compounds posses a low solubility in organic solvents, reason why the recording of $^{13}$C-NMR spectra and correlation NMR experiments were very difficult. Even for the $^1$H-NMR spectra, higher temperature (60 °C) and low water content of the DMSO-$d_6$ solvent was required in order to spectroscopically characterize the compounds.

*Heterocycle protons (3- and 5-H).* Structural assignment reflects the perturbation induced by the azulen-1-ylvinyl substitution on the pyrylium protons. Comparison of the spectral data with reported tris-styryl compounds such as 2,4,6-tris(4-dimethylaminostyryl) pyrylium perchlorate indicates a strongly shielding effect induced by the azulenyl

**Table 3**
HETEROCYCLE AND ETHYLENE PROTONS (δ, ppm)

| Compound | 3-and 5-H | 2/6-(py)-CH= | 2/6-(az)-CH=[a] | 4-(py)-CH= | 4-(az)-CH=[a] |
|---|---|---|---|---|---|
| **1m** | 7.87 | - | - | 7.36 | 9.07 |
| **2m** | 7.61 | - | - | 7.25 | 9.02 |
| **3m** | 7.49 | - | - | 7.15 | 8.92 |
| **1t** | 7.81 | 7.30 | 8.65 | 7.24 | 8.75 |
| **2t** | 7.23 | 6.92 | 8.22 | 7.03 | 8.32 |
| **3t** | 6.98 | 6.88 | 8.06 | 6.67 | 8.12 |

[a] py = pyrylium.

groups [19]. In addition, alkyl substitution of the pendant azulenyl moieties further increases the upfield move of the pyrylium protons chemical shifts. Replacement of the azulenyl group with guiazulenyl substitution produces an upfield move of the pyrylium protons of around 0.38 ppm when comparing the proton NMR spectra of **1m** with **3m**, indicative of an increased degree of conjugation. This is further in agreement with observed Δδ difference of 0.58 ppm when comparing the corresponding chemical shifts in the non-substituted azulenyl compound **1t** with 4,6,8-trimethyl substituted **2t**. Additional bulky alkyl substituents in guaiazulenyl-containing pyrylium salts induces a more pronunced shield Δδ = 0.83 ppm relative to **1t** (table 3), showing the strong influence of the electron-donating effect exerted by the methyl and *iso*-propyl groups in compounds of type **3**. The shielding effect observed for the chemical shifts of the pyrylium protons in the guiazulen-1-ylvinyl series follows the order: **3m** < **3d** < **3t**.

*Vinylene protons***.** As results from table 3, the value of δ for az-C*H*= is always higher than that for py-C*H*= and this difference is higher for the ethylene at C-4 than at C-2/6. Upon alkyl substitution of the azulenyl moieties, the shielding effect of the vinyl protons placed in the neighborhood of the heterocyclic ring is slightly lower when compared to the corresponding vinylene protons close to the azulenyl magnetic field. The field anisotropy created by the azulene ring is much more intense as compared with that of pyrylium.

*Azulenyl protons***.** The $^1$H NMR spectra showed the azulenyl protons are placed in the expected area. We have previously reported that, the substitution of the azulenyl system at C-1 position with positively charged heterocycle (in 2 or 4 position), strongly deshielded the azulenyl protons [10]. The chemical shifts are influenced by the alkyl substitution of the nonbenzenoid groups, namely a strong shielding effect of the proton placed at 2-position in the skeleton. In the case of compounds of type **3**, described herein, the shielding effect is also a consequence of the 3-methyl substituent found in the guiazulenyl moieties.

### *Product characterization*

*(E)-4-(2-(5-isopropyl-3,8-dimethylazulen-1-yl)vinyl)-2,6-dimethylpyrylium perchlorate* **(3m)** dark blue powder, mp > 350 °C; UV-Vis (acetone): $\lambda_{max}$ (log ε) 373 (sh), 414 (sh, 3.73), 616 (sh, 4.80), 631 (4.85) nm; $^1$H NMR (DMSO-d$_6$, 60 ° C): δ 1.38 (d, 6H, *J* = 6.6 Hz, CH$_3$'-*iso*propyl), 2.58 (s, 6H, 2-Me, 6-Me), 2.59 (s, 3H, 3'-Me), 3.23 (hept, 1H, *J* = 6.8 Hz, CH'-*iso*propyl), 3.26 (s, 3H, 8'-Me), 7.15 (d, 1H, *J* = 14.6 Hz, (py)-C*H*=), 7.49 (s, 2H, 3-H, 5-H), 7.80 (d$_{AB}$, 1H, *J* = 11.0 Hz, 7'-H), 7.93 (dd, 1H, *J* = 11.0 Hz, *J* = 2.2 Hz, 6'-H), 8.29 (s, 1H, 4'-H), 8.38 (d, 1H, *J* = 2.2 Hz, 2'-H), 8.92 (d, 1H, *J* = 14.5 Hz, (az")-C*H*=) ppm; ESI-MS: *m/z* (%) = 331.0 (100) [M$^+$]. Elemental Analysis Calcd for $C_{23}H_{25}ClO_5$: C, 66.26; H, 6.04; Found: C, 66.25; H, 6.01.

*2,4-bis((E)-2-(5-isopropyl-3,8-dimethylazulen-1-yl)vinyl)-6-methylpyrylium perchlorate* **(3d)** Dark blue powder, mp > 350 °C; UV-Vis (acetone): $\lambda_{max}$ (log ε) 412 (sh, 3.85), 569 (3.96), 766 (4.85) nm; $^1$H NMR (DMSO-d$_6$, 60 ° C): δ 1.27 (d, 6H, *J* = 6.8 Hz, CH$_3$"-*iso*propyl), 1.33 (d, 6H, *J* = 6.8 Hz, CH$_3$'-*iso*propyl), 2.55, 2.56, 2.58 (s, 9H, 6-Me, 3"-Me, 3'-Me), 3.06 (s, 3H, 8"-Me), 3.18 (s, 3H, 8'-Me), 2.92-3.12 (m, 4H, CH"-*iso*propyl, CH'-*iso*propyl), 7.09 (d, 1H, *J* = 14.8 Hz, 4-(py)-C*H*=), 7.15 (d, 1H, *J* = 14.4 Hz, 2-(py)-C*H*=), 7.32 (s, 1H, 3-H/5-H), 7.37 (d,1H, *J* = 10.4 Hz, 7"-H), 7.39 (s, 1H, 3-H/5-H), 7.56 (d, 1H, *J* = 10.4 Hz, 7'-H), 7.65 (d, 1H, *J* = 11.2 Hz, 6"-H), 7.76 (d, 1H, *J* = 10.8 Hz, 6'-H), 8.14 - 8.23 (m, 4H, 2'-H, 2"-H, 4"-H, 4'-H), 8.57 (d, *J* = 15.2 Hz, 1H, 2-(az)-C*H*=), 8.69 (d, *J* = 14.8 Hz, 1H, 4-(az)-C*H*=) ppm; ESI-MS: *m/z* (%) = 539.0 (100) [M$^+$]. Elemental Analysis Calcd for $C_{40}H_{43}ClO_5$: C, 75.16; H, 6.78; Found: C, 75.15; H, 6.73.

*2,4,6-tris((E)-2-(5-isopropyl-3,8-dimethylazulen-1-yl)vinyl)pyrylium perchlorate* **(3t)**

Dark green powder, mp > 350 °C; UV-Vis (acetone): $\lambda_{max}$ (log ε) 422 (4.46), 466 (4.46), 768 (4.95) nm; $^1$H NMR (DMSO-d$_6$, 60 ° C): δ 1.27 (d, *J* = 6.8 Hz, 12 H, CH$_3$"-*iso*propyl), 1.30 (d, *J* = 6.8 Hz, 6 H, CH$_3$'-*iso*propyl), 2.22 (s, 6H, 3"-Me), 2.25 (s, 3H, 3'-Me), 2.76 (s, 6H, 8"-Me), 2.80 (s, 3H, 8'-Me), 2.92-3.01 (m, 2H, CH"-*iso*propyl), 3.01-3.06 (m, 1H, CH'-*iso*propyl), 6.67 (d, 1H, *J* = 14.4 Hz, 4-(py)-C*H*=), 6.88 (d, 2H, *J* = 15.2 Hz, 2/6(py)-C*H*=), 6.98 (s, 2H, 3-H, 5-H), 7.08 (d$_{AB}$, 2H, *J* = 10.8 Hz, 7"-H), 7.17 (d$_{AB}$, 1H, *J* = 11.2 Hz, 7'-H), 7.45 (d$_{AB}$, 2H, *J* = 10.8 Hz, 6"-H), 7.49 (d$_{AB}$, 1H, *J* = 10.8 Hz, 6'-H), 7.76 (s, 1H, 2'-H), 7.79 (s, 2H, 2"-H), 7.85 (s, 2H, 4"-H), 7.90 (s, 1H, 4'-H), 8.06 (d, 2H, *J* = 15.2 Hz, 2H, 2/6-(az)-C*H*=), 8.12 (d, 1H, *J* = 15.6 Hz, 4-(az)-C*H*=) ppm ppm; ESI-MS: *m/z* (%) = 747.0 (100) [M$^+$]. Elemental Analysis Calcd for $C_{56}H_{59}ClO_5$: C, 79.36; H, 7.02; Found: C, 79.33; H, 7.04.

## Conclusions

New pyrylium perchlorates featuring one, two and three-guaiazulen-1-ylvinyl substitution were obtained and fully characterized. Comparative studies between conventional condensation reactions and microwave-assisted protocol showed that last synthetic pathway affords higher selectivity towards three-fold substituted guiazulen-1-ylvinyl pirilium salt. Regarding the conventional condensation reaction, the yield in 2,4,6-tris(guiazulen-1-yl)vinyl)pyrylium perchlorate was enhanced by using catalytic amounts of piperidine. Upon replacement of the azulenyl group with guiazulenyl moiety a strong bathochromic effect was induced, the electronic spectra showing strong absorption maxima in visible for all mono-, bis- and tris-guiazulen-1-ylvinyl pyrilium perchlorates. The

$^1$H-NMR spectra confirmed the structure of the compounds with an upfield shift of the pyrilium and vinylene protons chemical shifts. Taking into account the commercial availability of this azulenyl derivative, undoubtedly, these novel azulenyl substituted heterocyclic derivatives are well suited for the development of functional NLO chromophores with extended π-conjugation. Further work to transform the pyrylium salts in the corresponding pyridine and pyridinium salts, respectively, are underway in our laboratories.

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