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Alexandru C. Razus [a] , Simona Nica [a] & Eugenia Andreea Dragu [a]
[a] Romanian Academy , Institute of Organic Chemistry , Bucharest, Romania
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Pyranylium Salts as Synthones in the Synthesis of Substituted Benzenes

Alexandru C. Razus, Simona Nica, and Eugenia Andreea Dragu
Romanian Academy, Institute of Organic Chemistry, Bucharest, Romania

Abstract: Starting from 4-(azulen-1-yl)-pyranylium perchlorates, several azulenyl-substituted phenols as well as nitrobenzene and acetophenone derivatives were synthesized. The products were characterized, and the correlations between the compound structures and NMR spectra were investigated.

Keywords: Acetophenone, azulene-1-yl-benzene, nitrobenzenes, phenols

INTRODUCTION

Recently, π-conjugated aromatic molecules have attracted much attention as a result of their numerous applications in material science[1] for optical data storage and optical switching and in biological fields as imaging fluorescence agents.[2] Among the variety of molecules studied, azulene-containing compounds have emerged as promising candidates for constructing nonlinear optical materials.[3] Azulene is a stable nonalternant aromatic hydrocarbon, which can serve either as electron donor or electron acceptor depending on the nature of the substituent and the substituted position.

In the course of our pursuit of novel azulene-based nonlinear optical materials, we have started to study the azulene-substituted pyranylium salts.[4] Pyranylium salts represent a nodal point for many synthetic routes, functioning as versatile synthones for a large variety of organic

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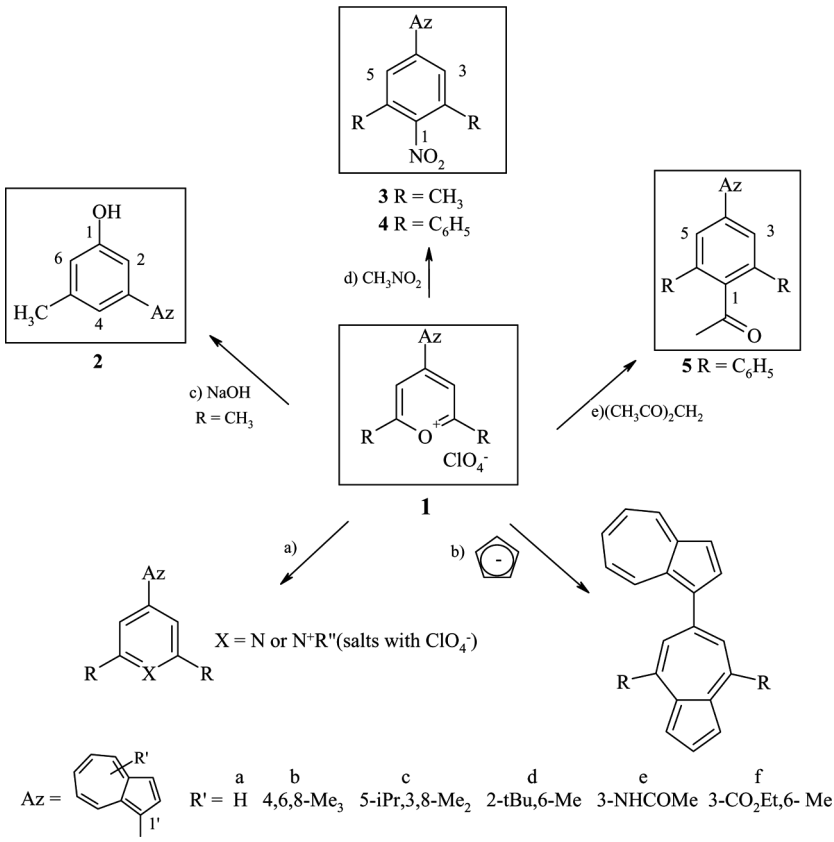
Address correspondence to Alexandru C. Razus, Romanian Academy, Institute of Organic Chemistry, Spl. Independentei, 202B, 060023 Bucharest, 35, P. O. Box 108, Romania. E-mail: acrazus@cco.ro

compounds.[5] On the other hand, pyranylium salts themselves are known to possess interesting technical properties.[6] Hence, their association with an azulene moiety may lead to organic molecules that possess valuable properties. In this framework, we focused our attention on studying the synthesis and the reactivity of azulene-substituted pyranylium salts. Several syntheses starting from pyranylium salts have already been accomplished and are described in Scheme 1 (routes a and b).[7]

An important target of our study regarding the use of pyranylium salts as building blocks was the synthesis of azulene-substituted benzenes, which are also important because of their technical properties.[8] The C–C bond formation between azulene and phenyl was first reported by Arnolds and Pahls and involved radical reaction of N-nitroso-acetanilide



Scheme 1. 4-Azulenylpyranylium salts as synthones for Az-Ar compounds generation.

with azulene (with 15% yield).[9] 1-Arylazulenes were also obtained with good conversions and yields through photoarylation of azulene with aryl iodides.[10] The metal-catalyzed coupling reaction is particularly suitable for the C–C bond formation between two aryl moieties. Thus, when palladium-catalyzed Suzuki reaction was performed using 1-azulene triflate and aryl halides, arylazulenes were obtain with around 5% yield.[11] Nevertheless, the 1-azulene triflate is unstable and decomposes in the appropriate solvents for palladium-catalyzed reactions. An intermolecular palladium acetate–catalyzed arylation of the unfunctionalized azulene with benzene was accomplished by Dyker and coworkers.[12] After 3 days at 100°C in the presence of Bu_4NBr, the yield of 1-phenylazulene was 13%. Further improvement of the reaction yields has been achieved by using azulen-1-yl boronate as starting material in an asymmetric Miyaura–Suzuki reaction using Pd(0) as catalysts.[13] However, the metal-catalyzed coupling reaction is limited by the use of substituted aromatic halides, which sometimes require excess synthetic strategies and costly catalysts. Moreover, this reaction is not suitable for all functionalized aromatic derivatives. The synthetic pathway proposed herein for 1-arylazulenes starts from azulene-substituted pyranylium salts with common reactants and mild conditions. The developed synthesis was directed mainly for the preparation of azulenyl-substituted phenols and nitrobenzene derivatives (routes c and d in Scheme 1) and with rather modest yields for acetophenone **5** (route e). The attempts to obtain azulene-substituted benzonitriles starting from acetonitrile failed. The use of ethyl cyanoacetate might be a solution for their generation.

RESULTS AND DISCUSSION

Synthesis of Benzenes Substituted with Azulene-1-yl Moiety

Synthesis of Phenols

Conversion of azulene-substituted pyranylium salts to phenol derivatives starts from (azulen-1-yl)-2,6-dimethylpyranylium perchlorate, **1**, R=Me, and occurs in aqueous ethanol solution in the presence of sodium hydroxide at reflux (route c in Scheme 1). The reaction takes place by incorporating one carbon atom of the 2(6)-methyl group via intramolecular condensation of an intermediate pseudobase.[15] The pseudobase is formed as a consequence of the nucleophilic attack of the OH^- anion on the α-position of pyranylium oxygen followed by ring opening.

The reaction yield is strongly influenced by the experimental conditions. The solubility of the pyranylium salt, **1**, is the determining

factor for the reaction yield. By performing the reaction with a suspension of pyranylium salt **1a**, the corresponding 3-(azulen-1-yl)-5-methyl-phenol, **2a**, was obtained only in 5% yield. Instead, the complete dissolution of the pyranylium salt increased the yield in phenol to about 39% when an excess of 5 equivalents of sodium hydroxide was used. The amount of sodium hydroxide also played a very important role for the final yield of the reaction. Thus, an excess of 7 equivalents reported to the pyranylium salt proved to be the ideal amount (exp. 4 in Table 1), whereas a larger excess (11 equivalents) leads to a severe decrease of the reaction yield. At the same time, with the greater excess of sodium hydroxide, a large number of unidentified compounds are formed.

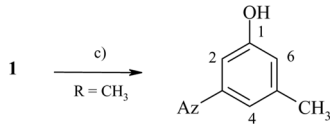
With these optimum reaction conditions (exp. 4 in Table 1), azulene-substituted phenols have been obtained. As was expected, the influence of the azulenyl moiety substituents upon reaction yields is obvious. For instance, the alkylated azulenyl from the 4-position in the pyranylium salts favors the generation of the corresponding phenols (Table 2). The possible explanation consists in the decrease in stabilization of the starting pyranylium salts because of the deviation from coplanarity of azulene and pyranylium moieties caused by the steric requirement of the bulky alkyl groups. Thus, the presence of *tert*-butyl in 2-position of the azulenyl group leads to the formation of the corresponding phenol **2d** in about 90% yield. Here, it is worth mentioning that unsubstitued azulene ring was reported to be unstable in very strong basic media[14] and this fact is reflected in the moderate yield in phenol **2a**.

It is interesting that the influence of the substituent from the 3-position of the azulenyl moiety is small. The presence of the electron-donating group $-NHCOCH_3$, **1e**, as well as the electron-withdrawing substituent $-CO_2Et$, **1f**, diminishes the yields of **2e** and **2f**, respectively.

Table 1. Influence of the experimental conditions on the reaction of 4-(azulen-1-yl)-2,6-dimethyl-pyranylium perchlorate, **1a**, in the presence of NaOH

Exp.	Starting compound	Ethanol (ml)	NaOH (mmol)	Yield in **2** (%)
1	**1a** (1 mmol)	7	5	5
2		14	5	12
3		30	5	39
4		43	7	55
5		43	12	34

Table 2. Influence of the azulenyl substituents on reaction c of pyranylium perchlorate, **1** (reaction conditions used according to Table 1, exp. 4)



2

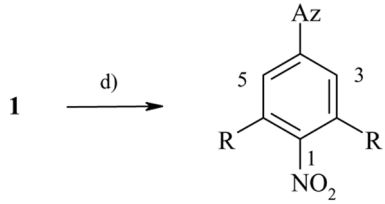
Reactions	Yield (%)
1a → **2a**	55
1b → **2b**	70
1c → **2c**	75
1d → **2d**	90
1e → **2e**	40
1f → **2f**	36

Synthesis of Nitrobenzene Derivatives

Another preparative conversion of the azulene-substituted pyranylium perchlorates **1**, namely to nitro-substituted benzenes, has also been developed. Thus, otherwise difficult accessible azulene-substituted nitrobenzenes could be easily generated. In this case, the pyranylium salt was reacted with nitromethane in the presence of potassium *tert*-butoxide (3 equivalents), yielding the 2,6-disubstituted-4-(azulen-1-yl)-nitrobenzenes **3** or **4**. The reaction took place by loss of one proton of the nitromethane followed by the attack of the generated carbanion on the 2(6) position of pyranylium salt. After the heterocyclic opening, the methylene bound to nitro group was incorporated in the new aromatic ring with the formation of nitrobenzene derivatives.[5] Contrary to the synthesis of azulenyl-phenols, in the case of nitro-substituted benzenes, 2,6-diphenyl-4-(azulen-1-yl)-pyranylium perchlorates could be also used as starting materials besides the corresponding 2,6-dimethyl compounds. The reaction yields vary from satisfactory to very good, being greater when 2,6-diphenyl-4-(azulen-1-yl)-pyranylium perchlorate has been reacted with nitromethane (Table 3) despite the longer reaction time needed for the reaction. In this case, the stabilizing effect of the two phenyl groups on the obtained benzene could be the driving force for the good yields obtained.

For the reaction with nitromethane, the influence of the azulenyl substitution is not as evident as for the previously discussed phenol

Table 3. Reaction of pyranylium salts **1** with nitromethane (reaction d) in the presence of *t*BuOK and n-BuLi



3 R = CH_3; **4** R = C_6H_5

Compound	**3a**[a]	**3b**[a]	**3c**[a]	**3d**[a]	**3f**[a]	**4a**[b]	**4b**[b]
Yield (%) in *t*BuOK	52	53	43	83	37	87	89
Yield (%) in n-BuLi	41	42	33	56	—	—	—

[a]Reaction time 2 h.
[b]Reaction time 18 h.

synthesis. However, the presence of a *tert*-butyl group in the 2-position of the azulenyl moiety enhanced the yield of compound **3d**. However, when the azulenyl moiety was substituted in the 3-position with CO_2Et, the yield of compound **3f** decreased.

Replacement of potassium *tert*-butoxide with a stronger base such as *n*-BuLi did not lead to an improvement of the reaction yield (Table 3). The nitrobenzene derivatives were obtained in lesser yields because of degradation of the reaction intermediates, as it has been observed by, thin-layer chromotography (TLC) monitoring of the reaction.

Acetophenone Derivative Synthesis

The versatility of the pyranylium salts **1** to function as synthones in organic synthesis was proven by isolation of 2,6-disubstituted-4-(azulen-1-yl)-acetophenone derivatives **5** when these salts were reacted with acetylacetone. The reaction occured in the presence of an excess of potassium *tert*-butoxide.[15] Because the 2,6-diphenyl substitution of the starting pyranilium salt was proven to have a favorable effect on the reaction yield as has been described for nitrobenzene derivatives, the reaction was performed for isolation of azulenyl-acetophenone **5** in 51% yield. Further investigations on the reaction mechanism as well as the influence of the azulenyl-substitution are under way in our laboratories.

NMR and Electronic Spectra

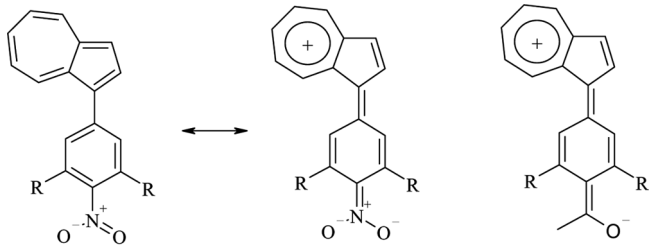
During our early investigations, we outlined the interdependence between structure and NMR or electronic spectra for several (azulene-1-yl)-aryl or heteroaryl compounds. Two main factors are determinant for the chemical shifts of the protons, namely the electron-donating effect of the azulene-1-yl group and the change in anisotropy of the magnetic field with the variation of the dihedral angle formed by the two coupled moieties. The first factor is important for the azulenyl-heteroaryl molecules with an electron acceptor heteroatom as the pyranylium salt **1a**. The coplanarity of the coupled moieties allows the electron transfer from azulenyl to heterocycle. The loss in electron density results in the strong deshielding of azulenyl protons as compared to the parent azulene (Table 4). For such compounds, the deviation from coplanarity causes a decrease in proton deshielding. This decrease is also accentuated by the inductive effect exerted by the alkyl substituents to the azulenyl moiety. The tendency of the phenyl group to polarize is very low. Therefore the substitution of 1-position of azulene with phenyl occurs without a dramatic change in the shift of the azulenic protons (Table 4).[4a] As expected, the presence of the hydroxyl group in the 3-position of the phenyl has no influence on the azulenyl protons as can be observed by comparison of the proton shifts of 1-phenylazulene with the chemical shifts of compound **2a**. Some tendency for shielding of these protons can be observed for the alkylated azulene, despite some increase of the dihedral angle formed by the coupled moieties by this substitution.

We have expected that when the 4-position of the phenyl moiety is occupied by NO_2 or $COCH_3$, which are good electron-acceptor groups, as in compounds **3**–**5**, a greater polarization of the molecule takes place with consequences in the azulenyl protons shifts. However, very similar values for the proton shifts of 1-phenylazulene and for these compounds

Table 4. Chemical shifts for azulenyl protons in compounds **2** and **3**

Compound	H-2′	H-3′	H-4′	H-5′	H-6′	H-7′	H-8′	H-3(5)
AzH	7.81	7.30	8.23	7.05	7.45	7.05	8.23	—
1a (R = Me)[6]	8.55	7.78	8.86	7.88	8.20	7.93	9.03	—
PhAz[4a]	8.02	7.43	8.34	7.14	7.58	7.14	8.55	—
2a	7.99	7.41	8.33	7.15	7.58	7.15	8.57	—
3a	7.97	7.43	8.38	7.21	7.64	7.21	8.52	7.34
4a	8.07	—[a]	8.41	7.24	7.60	7.24	8.60	7.62
5	8.08	—[a]	8.36	7.18	7.61	7.18	8.62	7.63

[a]The signal is included in a multiplet.



Scheme 2. Donor (azulenyl)-π spacer-acceptor structures.

can be observed. That means that structures **3** (II) or **5** (II) in Scheme 2 contribute to a small extent to the real electron density in the ground state of the molecule. The possible explanation for the reduced contribution of these structures consists in the difficulty of nitro or acetyl group to adopt a coplanar structure with the rest of the molecule because of the neighboring groups situated in 2 and 6 positions.

The shift of the two phenyl protons that are near the azulene moiety in both compound series is not influenced by the azulenyl substitution. However, the replacement of methyl groups in 2 and 6 positions by phenyls cause a deshielding of these protons.

The low tendency toward molecular polarization is also in agreement with the small differences observed between the absorption maxima of the low-energy charge-transfer transitions for the studied compounds. As expected, a small bathochromism took place in compound series **2, 3, 4**, and **5**.

Studies to extend the use of pyranylium salts as starting compounds for generating other azulenyl-substituted benzenes are in progress in our laboratory.

EXPERIMENTAL

General Procedures

Melting points were measured on a Kofler apparatus (Reichert Austria). Elemental analyses used a Perkin-Elmer CHN 240B. Ultraviolet (UV)/Vis spectra were recorded in methanol and dichloromethane (DCM) using a Varian Cary 100 Bio spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Gemini 300 (^{1}H NMR: 300 MHz; ^{13}C NMR: 75.45 MHz), Bruker Avance DRX4 (^{1}H NMR: 400 MHz; ^{13}C NMR: 100.62 MHz),

and Bruker ARX 500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 127.75 MHz) instruments; δ are expressed in parts per million (ppm) and *J* in hertz. Tetramethylsilane (TMS) was used as internal standard in $CDCl_3$ at room temperature; ^{1}H-^{1}H and ^{1}H-^{13}C COSY correlation spectroscopy experiments were used for the structure assignment. Mass spectra (MS) were recorded on a Varian 1200 L Quadrupole/MS/MS spectrometer using direct injection in electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mode. Infrared (IR) spectrum was recorded on a Bruker Vertex 70 instrument. Column chromatography used alumina [activity BII–III (Brockmann)] and silica gel [70–230 mesh (ASTM)]. DCM was distilled over CaH_2, and ethyl acetate was distilled over anhydrous sodium carbonate. Pyranylium perchlorates are obtained as described in the literature.[4]

General Procedure for the Synthesis of Compounds 2

A solution of NaOH (196 mg, 4.9 mmol) in 20 mL of H_2O was added to a solution of pyranylium perchlorate **1** (0.7 mmol) in ethanol (the amount of ethanol used for the salt dissolution is shown in Table 1). The resulting mixture was stirred under reflux for a period of 2 h. After cooling at room temperature, concentrated HCl was added for neutralization, followed by extraction of the mixture with DCM (3×50 mL) for **2a, 2b, 2c**, and **2d** and AcOEt (3×25 mL) for **2e** and **2f**. The combined organic phases were washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on the supports and elution mixture indicated in Table 5. After the first fraction containing unidentified compounds, the desired phenol was eluted.

General Procedure for the Synthesis of Compounds 3 and 4 by Reaction of the Pyranylium Perchlorates with Nitromethane

In the Presence of Potassium *tert*-Butoxide

Under an inert atmosphere (N_2), a solution of potassium *tert*-butoxide (157 mg, 1.4 mmol) in *tert*-butyl alcohol (2.5 mL) was added to a solution of pyranylium perchlorate **1** (0.7 mmol) in nitromethane (the amount of nitromethane used for the salt dissolution is shown in Table 6), and the resulting mixture was stirred under reflux for 1 h. An additional quantity of potassium *tert*-butoxide (78 mg, 0.7 mmol) in *tert*-butyl alcohol (1 g) was than used, and the stirring and reflux were continued for the time reported in Table 6. After cooling to room temperature, the reaction

Table 5. Amount of ethanol used as solvent in the reactions and the conditions for products separation

Obtained compound	EtOH used in reaction (mL)[a]	Conditions for columns chromatography	
		Support	Elution mixture
2a	30	Alumina	DCM/petroleum ether/EtOH = 2:1:0.2
2b	30	Alumina	DCM/petroleum ether/EtOH = 2:1:0.2
2c	20	Silica gel	DCM/petroleum ether = 2:1
2d	30	Silica gel	DCM/petroleum ether/EtOH = 2:1:0.2
2e	35	Silica gel	AcOEt/cyclohexane = 2:1
2f	40	Silica gel	DCM/petroleum ether = 2:1

[a]For 0.7 mmol of reacted salts.

mixture was diluted with water and repeatedly extracted with DCM (4×50 mL). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography as indicated in Table 6. After the first fraction containing unidentified compounds, the desired nitroderivative was eluted.

In the Presence of *n*-Butyllithium

n-Butyllithium (0.44 mL, 1.4 mmol) was slowly added to 0.5 mL nitromethane at 0°C under an inert atmosphere (N_2). After 5 min of stirring, a solution of pyranylium perchlorate (0.7 mmol) in nitromethane was

Table 6. Amount of nitromethane used as solvent in the reactions and the conditions for product separation

Obtained compound	CH_3NO_2 used in reaction (mL)[a]	Reaction time (h)	Conditions for column chromatography	
			Support	Elution mixture
3a	4	2	Alumina	DCM petroleum ether = 1:5
3b	3			DCM/petroleum ether = 1:5
3c	4			DCM/petroleum ether = 1:4
3d	3			DCM/petroleum ether = 1:5
3e	5		Silica gel	DCM/petroleum ether = 1:7
4a	4	18	Alumina	DCM/petroleum ether = 1:7
4b	4			DCM/petroleum ether = 1:7

[a]For 0.7 mmol reacted salt.

added. The reaction mixture was stirred for 15 min at room temperature and then refluxed for 2 h. After cooling to room temperature, water (50 mL) was added, and the formed mixture was worked up as described previously.

Procedure for the Synthesis of Compound 5

Under an inert atmosphere (N_2), a mixture of potassium *tert*-butoxide (68 mg, 0.6 mmol), pentane-2,4-dione (80 mg, 0.8 mmol), and *tert*-butyl alcohol (5 mL) was added to a suspension of pyranylium perchlorate **1** (92 mg, 0.2 mmol) in 5 mL of *tert*-butyl alcohol, and the resulting mixture was stirred under reflux for 1.5 h. After cooling to room temperature, the reaction mixture was diluted with water and repeatedly extracted with DCM (4×50 mL). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulted crude product was purified by column chromatography on silica gel using a mixture of petroleum ether-DCM 2:1.

Data

3-(Azulen-1-yl)-5-methylphenol **2a**

Blue oil; UV/VIS (MeOH), λ_{max} (log ε): 294 (4.59), 358 (3.81), 600 (broad). ^{1}H NMR ($CDCl_3$, 500 MHz, δ ppm): 2.39–2.40 (m, 3H, 5-CH_3), 4.73 (s, 1H, OH), 6.64–6.67 (m, 1H, 6-H), 6.88–6.91 (m, 1H, 2-H), 7.01–7.03 (m, 1H, 4-H), 7.15 (t, $^3J = 9.7$ Hz, 2H, 5′-H, 7′-H), 7.41 (d_{AB}, $^3J = 3.9$ Hz, 1H, 3′-H), 7.58 (t, $^3J = 9.8$ Hz, 1H, 6′-H), 7.99 (d_{AB}, $^3J = 3.8$ Hz, 1H, 2′-H), 8.33 (d, $^3J = 9.5$ Hz, 1H, 4′-H), 8.57 (d, $^3J = 9.8$ Hz, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 125.7 MHz, δ ppm): 21.52 (5-CH_3), 113.6 (C2), 114.07 (C6), 117.39 (C3′), 123.08 (C4), 123.28 and 123.30 (C5′ and C7′), 130.93 (Cq), 135.29 (Cq), 135.67 (C8′), 137.09 and 137.26 (C2′ and C4′), 138.18 (C6′), 138.97 (Cq), 139.94 (Cq), 141.77 (Cq), 155.64 (C–OH). MS-ESI positive (m/z, %, 20 eV): 235 ($[M+1]^+$, 75), 217 ($[M+1]^+$-H_2O, 68), 202 ($[M+1]^+$-H_2O–CH_3, 100). Anal. calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.22; H, 6.10.

3-(4,6,8-Trimethyl-azulen-1-yl)-5-methylphenol **2b**

Violet oil; UV/VIS (MeOH), λ_{max} (log ε): 97 (4.39), 368 (3.20), 565 (broad). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 2.35 (s, 3H, 5-CH_3), 2.50

(s, 3H, 6′-CH_3), 2.61 (s, 3H, 4′-CH_3), 2.91 (s, 3H, 8′-CH_3), 4.90 (bs, 1H, OH), 6.61–6.64 (m, 1H, 6-H), 6.64–6.67 (m, 1H, 2-H), 6.78–6.80 (m, 1H, 4-H), 6.96 (s, 1H, 5′-H or 7′-H), 7.05 (s, 1H, 7′-H or 5′-H), 7.35 (d_{AB}, $^3J = 4.0$ Hz, 1H, 3′-H), 7.55 (d_{AB}, $^3J = 4.0$ Hz, 1H, 2′-H). ^{13}C NMR ($CDCl_3$, 100.57 MHz, δ ppm): 21.50 (5-CH_3), 25.62 (4′-CH_3), 28.59 (6′-CH_3 and 8′-CH_3), 113.83 (CH), 114.78 (CH), 114.94 (CH), 124.55 (CH), 127.05 (CH), 128.92 (CH), 131.36 (Cq), 132.46 (Cq), 136.21 (CH), 137.24 (Cq), 138.57 (Cq), 143.68 (Cq), 145.86 (Cq), 146.27 (Cq), 147.64 (Cq), 154.71 (C-OH). MS-ESI positive (m/z, %): 277 ($[M + 1]^+$, 100). Anal. calcd. for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.88; H, 7.24.

3-(5-*Iso*propyl-3,8-dimethyl-azulen-1-yl)-5-methylphenol **2c**

Blue oil; UV/VIS (MeOH), λ_{max} (log ε): 293 (4.59), 369 (3.86), 606 (broad). ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.37 (d, $J = 6.9$ Hz, 6H, CH_3-iPr), 2.33 (s, 3H, 5-CH_3), 2.45 (s, 3H, 6′-CH_3), 2.66 (s, 3H, 8′-CH_3), 3.07 (hept, $^3J = 6.9$ Hz, 1H, CH-iPr), 4.90 (bs, 1H, OH), 6.60–6.62 (m, 1H, 6-H), 6.63–6.65 (m, 1H, 2-H), 6.76 (bs, 1H, 4-H), 6.89 (d_{AB}, $^3J = 10.7$ Hz, 1H, 7′-H), 7.36 (d_{AB}d, $^3J = 10.7$ Hz, $^4J = 2.2$ Hz, Hz, 1H, 6′-H), 7.52 (s, 1H, 2′-H), 8.19 (d, $^4J = 2.2$ Hz, 1H, 4′-H). ^{13}C NMR ($CDCl_3$, 75.47 MHz, δ ppm): 13.11 (3′-CH_3), 21.67 (5-CH_3), 24.96 (CH_3-iPr), 27.69 (8′-CH_3), 38.17 (CH-iPr), 114.01 (CH), 115.16 (CH), 124.30 (Cq), 124.92 (CH), 127.06 (CH), 129.03 (Cq), 134.00 (CH), 135.12 (CH), 138.59 (Cq), 139.98 (Cq), 140.22 (CH), 143.25 (Cq), 146.37 (Cq), 154.77 (C–OH). MS-ESI positive (m/z, %): 305 ($[M + 1]^+$, 100). Anal. calcd. for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.83; H, 7.98.

3-(2-*tert*-Butyl-6-methylazulen-1-yl)-5-methyphenol **2d**

Violet oil; UV/VIS (MeOH), λ_{max} (log ε): 292 (4.66), 353 (3.60), 563 (broad). ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.38 (s, 9H, CH_3-tBu), 2.37 (s, 3H, 5-CH_3), 2.59 (s, 3H, 6′-CH_3), 6.62–6.65 (m, 1H, 6-H), 6.70–6.73 (m, 1H, 2-H), 6.77–6.80 (m, 1H, 4-H), 6.90 (d_{AB}, $^3J = 9.8$ Hz, Hz, 1H, 5′-H), 7.03 (d_{AB}, $^3J = 9.8$ Hz, 1H, 7′-H), 7.31 (s, 1H, 3′-H), 7.62 (d_{AB}, $^3J = 10.2$ Hz, 1H, 4′-H), 8.13 (d_{AB}, $^3J = 9.9$ Hz, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 100.57 MHz, δ ppm): 21.52 (5-CH_3), 28.01 (6′-CH_3), 31.90 (CH_3-*t*-Bu), 34.81 (C-tBu), 113.25 (CH), 114.51 (CH), 114.75 (CH), 124.31 (CH), 125.85 (CH), 129.50 (Cq), 133.72 (CH), 134.52 (CH), 137.43 (Cq), 138.24 (Cq), 138.65 (Cq), 140.98 (Cq), 147.55 (Cq), 154.72 (Cq), 159.49 (C-OH). MS-ESI positive (m/z, %): 305

($[M+1]^+$, 100). Anal. calcd. for $C_{22}H_{24}O$: C, 86.80; H, 7.95. Found: C, 86.85; H, 8.01.

N-(3-(3-Hydroxy-5-methylphenyl)azulen-1-yl)acetamide **2e**

Green oil; UV/VIS (MeOH), λ_{max} (log ε): 297 (4.32), 377 (3.61), 613 (broad). ^{1}H NMR (acetone-D_6, 400 MHz, δ ppm): 2.27 (s, 3H, 5-CH_3), 2.37 (s, 3H, $COCH_3$), 6.68–6.73 (m, 1H, 6-H), 6.90–6.95 (m, 2H, 2-H, 4-H), 6.98 (t, $^3J = 9.7$ Hz, 1H, 7′-H), 7.03 (t, $^3J = 9.7$ Hz, 1H, 5′-H), 7.55 (t, $^3J = 9.9$ Hz, 1H, 6′-H), 8.40 (d, $^3J = 9.70$ Hz, 1H, 4′-H), 8.48 (d, $^3J = 9.53$ Hz, 1H, 8′-H), 8.55 (bs, 1H, 2′-H). Because of the small amounts of compounds **2e** and **3e** obtained, the ^{13}C NMR spectra were not recorded. MS-ESI positive (m/z, %): 292 ($[M+1]^+$, 100). Anal. calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88, N, 4.81. Found: C, 78.30; H, 5.92, N, 4.74.

Ethyl 3-(3-Hydroxy-5-methylphenyl)-6-methylazulene-1-carboxylate **2f**

Violet oil; UV/VIS (MeOH), λ_{max} (log ε): 309 (4.49), 394 (3.77), 551 (2.23). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.45 (t, $^3J = 7.2$ Hz, 3H, $C\underline{H}_3CH_2$), 2.39 (s, 3H, 5-CH_3), 2.65 (s, 3H, 6′-CH_3), 4.43 (q, 2H, $C\overline{H}_3C\underline{H}_2$), 6.71 (bs, 1H, 6-H), 6.87 (bs, 1H, 2-H), 6.95 (bs, 1H, 4-H), 7.23 ($\underline{d}_{AB}$, 1H, $^3J = 10.4$ Hz, 5′-H) 7.34 (d_{AB}, $^3J = 10.4$ Hz, 1H, 7′-H), 8.32 (s, 1H, 2′-H), 8.48 (d_{AB}, $^3J = 10.3$ Hz, 1H, 8′-H), 9.47 (d_{AB}, $^3J = 10.4$ Hz, 1H, 4′-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm): 14.73 ($\underline{C}H_3CH_2$), 21.62 (5-CH_3), 28.03 (6′-CH_3), 60.02 ($\underline{C}H_2CH_3$), 113.76, 114.69, 115.86, 123.09, 128.68, 129.28, 130.54, 136.26, 137.33, 138.10, 138.69, 138.87, 140.13, 140.37, 152.07, 156.05 (C-OH), 165.95 (CO). MS-ESI positive (m/z, %, 20 eV): 321 ($[M+1]^+$, 52), 275 ($[M+1]^+$, H-EtO, 100). Anal. calcd. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.68; H, 6.25.

1-(3,5-Dimethyl-4-nitrophenyl)azulene **3a**

Green powder, mp 115–116°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 237 (4.41), 293 (4.52), 375 (3.96), 585 (broad). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.42 (s, 6H, 3-CH_3, 5-CH_3), 7.21 (t, $^3J = 9.5$ Hz, 2H, 5′-H, 7′-H), 7.34 (s, 2H, 2-H, 6-H), 7.43 (d_{AB}, $^3J = 4.0$ Hz, 1H, 3′-H), 7.64 (t, $^3J = 9.8$ Hz, 1H, 6′-H), 7.97 (d_{AB}, $^3J = 4.0$ Hz, 1H, 2′-H), 8.38 (d, $^3J = 9.7$ Hz, 1H, 4′-H), 8.52 (d, $^3J = 9.8$ Hz, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 75.47 MHz, δ ppm): 18.1 (CH_3), 118.0 (CH), 124.0 (CH), 124.2 (CH),

129.4 (Cq), 130.1 (CH), 130.4 (Cq), 135.6 (CH), 135.9 (Cq), 137.3 (CH), 137.9 (CH), 138.7 (CH), 139.9 (Cq), 142.4 (Cq), 150.4 (C4). MS-APCI positive (m/z, %): 278 ($[M+1]^+$, 100). Anal. calcd. for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.95; H, 5.47; N, 4.93.

1-(3,5-Dimethyl-4-nitrophenyl)-4,6,8-trimethylazulene **3b**

Brown-reddish powder, mp 197–198°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 247 (4.44), 299 (4.56), 348 (3.90), 378 (3.68), 572 (1.88). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.29 (s, 6H, 3-CH_3, 5-CH_3), 2.40 (s, 3H, 6′-CH_3), 2.54 (s, 3H, 4′-CH_3), 2.83 (s, 3H, 8′-CH_3), 6.93 (s, 1H, 5′-H), 7.01 (s, 1H, 7′-H), 7.06 (s, 1H, 2-H, 6-H), 7.27 (d_{AB}, $^3J = 4.1$ Hz, 1H, 3′-H), 7.44 (d_{AB}, $^3J = 4.1$ Hz, 1H, 2′-H). ^{13}C NMR ($CDCl_3$, 75.47 MHz, δ ppm): 17.8 (3-CH_3, 5-CH_3), 25.6 (4′-CH_3), 28.6 (6′-CH_3), 29.2 (8′-CH_3), 115.1 (Cq), 115.3 (CH), 127.6 (Cq), 127.6 (CH), 128.9 (Cq), 129.3 (CH), 130.2 (CH), 130.9 (Cq), 135.7 (Cq), 136.3 (CH), 136.4 (Cq), 146.3 (Cq), 146.7 (Cq), 147.3 (Cq), 150.1 (C4). MS-APCI positive (m/z, %): 320 ($[M+1]^+$, 100). Anal. calcd. for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.02; H, 6.61; N, 4.28.

3-(3,5-Dimethyl-4-nitrophenyl)-7-*iso*propyl-1,4-dimethylazulene **3c**

Green powder, mp 125–126°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 248 (4.48), 293 (4.53), 382 (3.85), 600 (1.92). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.30 (d, $^3J = 6.9$ Hz, 6H, CH_3–iPr), 2.28 (s, 6H, 3-CH_3, 5-CH_3), 2.36 (s, 3H, 3′-CH_3), 2.58 (s, 3H, 8′-CH_3), 3.03 (hept, 1H, CH-iPr), 6.86 (d, $^3J = 10.7$ Hz, 1H, 7′-H), 7.05 (s, 2H, 2-H, 6-H), 7.32 (dd, $^3J = 10.7$ Hz, $^4J = 2.0$ Hz, 1H, 6′-H), 7.42 (s, 1H, 2′-H), 8.14 (d, $^4J = 2.0$ Hz, 1H, 4′-H). ^{13}C NMR ($CDCl_3$, 75.47 MHz, δ ppm): 12.9 (3′-CH_3), 17.9 (3-CH_3, 5-CH_3), 24.8 (CH_3-iPr), 28.1 (8′-CH_3), 30.1 (CH-iPr), 124.6 (Cq), 127.2 (Cq), 127.5 (Cq), 128.8 (Cq), 131.0 (CH), 134.2 (CH), 135.3 (CH), 135.3 (Cq), 138.4 (Cq), 139.9 (CH), 140.7 (Cq), 143.8 (Cq), 145.9 (CH), 150.7 (C4). MS-APCI positive (m/z, %): 348 ($[M+1]^+$, 100). Anal. calcd. for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.54; H, 7.28; N, 3.98.

2-*tert*-Butyl-1-(3,5-dimethyl-4-nitrophenyl)-6-methylazulene **3d**

Violet powder, mp 106–107°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 236 (4.31), 287 (4.75), 294 (4.80), 338 (3.56), 354 (3.82), 569 (broad). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.25 (s, 9H, CH_3–tBu), 2.30 (s, 6H, 3-CH_3,

5-CH_3), 2.52 (s, 3H, 6′-CH_3), 6.86 (d_{AB}, $^3J = 10.2$ Hz, 1H, 5′-H), 6.99 (d_{AB}, $^3J = 9.9$ Hz, 1H, 7′-H), 7.02 (s, 2H, 2-H, 6-H), 7.16 (s, 1H, 3′-H), 7.40 (d_{AB}, $^3J = 10.2$ Hz, 1H, 4′-H), 8.05 (d_{AB}, $^3J = 9.8$, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ ppm): 17.8 (3-CH_3, 5-CH_3), 28.0 (6′-CH_3), 31.2 (CH_3–tBu), 34.8 (Cq–tBu), 115.0 (Cq), 124.8 (CH), 124.8 (CH), 127.4 (Cq), 128.9 (CH), 132.5 (CH), 133.4 (CH), 134.9 (CH), 137.6 (Cq), 138.24 (Cq), 142.0 (Cq), 148.0 (Cq), 150.5 (Cq), 159.5 (C4). MS-APCI positive (m/z, %): 348 ($[M + 1]^+$, 100). Anal. calcd. for $C_{23}H_{25}NO_2$: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.48; H, 7.29; N, 3.92.

Ethyl 3-(3,5-Dimethyl-4-nitrophenyl)-6-methylazulene-1-carboxylate **3e**

Brown-reddish powder; ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 1.46 (t, 3H, CH_3CH_2), 2.41 (s, 6H, 3-CH_3, 5-CH_3), 2.73 (s, 3H, 6′-CH_3), 4.43 (q, $^3J = 7.1$ Hz, 2H, CH_3CH_2), 7.31 (s, 2H, 2-H, 6-H), 7.35 (d, $^3J = 10.6$ Hz, Hz, 1H, 5′-H), 7.45 (d, $^3J = 10.4$ Hz, 1H, 7′-H), 8.31 (s, 1H, 2′-H), 8.41 (d, $^3J = 10.2$ Hz, 1H, 4′-H), 9.53 (d, $^3J = 10.4$ Hz, 1H, 8′-H)[18]. MS-APCI positive (m/z, %, 20 eV): 364 ($[M + 1]^+$, 17), 318 ($[M + 1]^+$-NO_2, 91), 291 ($[M + 1]^+$-CO_2Et, 17), 246 ($[M + 1]^+$-NO_2-CO_2Et, 100).

1-(3,5-Diphenyl-4-nitrophenyl)-azulene **4a**

Brown powder, mp 219–221°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 243 (4.65), 299 (4.64), 352 (3.50), 382 (3.85), 572 (2.00); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.24 (t, $^3J = 9.8$ Hz, 2H, 5′-H, 7′-H), 7.43–7.52 [m, 11H, 3′-H, phenyl (3), phenyl (5)], 7.60 (t, $^3J = 9.8$ Hz, 1H, 6′-H), 7.62 (s, 2H, 2-H, 6-H), 8.07 (d, $^3J = 4.0$ Hz, 1H, 2′-H), 8.41 (d, $^3J = 9.6$ Hz, 1H, 4′-H), 8.60 (d, $^3J = 10$ Hz, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ ppm): 118.0 (CH), 124.0 (CH), 124.4 (CH), 128.2 (CH), 128.4 (Cq), 128.5 (CH), 128.8 (CH), 130.8 (CH), 135.0 (Cq), 135.3 (Cq), 135.7 (Cq), 136.8 (CH), 137.2 (CH), 138.7 (CH), 139.7 (CH), 139.7 (Cq), 142.3 (Cq), 147.8 (C4). MS-APCI positive (m/z, %): 402 ($[M + 1]^+$, 15), 359 ($[M + 1]^+$-NO_2, 100). Anal. calcd. for $C_{28}H_{19}NO_2$: C, 83.77; H, 4.77; N, 3.49. Found: C, 83.81; H, 4.80; N, 3.52.

1-(3,5-Diphenyl-4-nitrophenyl)-4,6,8-trimethylazulene **4b**

Brown powder, mp 227–228°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 243 (4.70), 299 (4.60), 352 (3.52), 382 (3.83), 572 (2.02). ^1H NMR ($CDCl_3$, 300 MHz, δ ppm): 2.53 (s, 6H, 4′-CH_3, 8′-CH_3), 2.82 (s, 3H, 6′-CH_3), 6.95 (s, 1H, 5′-H), 7.02 (s, 1H, 7′-H), 7.27–7.39 [m, 11H, 3′-H, phenyl

(3), phenyl (5)], 7.38 (s, 2H, 2-H, 6-H), 7.55 (d, $^3J = 4{,}1$ Hz, 1H, 2′-H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz, δ ppm): 25.4 (4′-CH_3), 28.3 (6′-CH_3), 29.2 (8′-CH_3), 115.2 (CH), 127.8 (Cq), 128.1 (CH), 128.3 (CH), 128.6 (CH), 129.4 (Cq), 131.6 (CH), 133.7 (Cq), 136.3 (CH), 136.7 (Cq), 144.1 (Cq), 146.2 (Cq), 146.9 (Cq), 151.1 (C4). MS-APCI positive (m/z, %): 444 ($[M+1]^+$, 9), 398 ($[M+1]^+$-NO_2, 100). Anal. calcd. for $C_{31}H_{25}NO_2$: C, 83.95; H, 5.68; N, 3.16. Found: C, 83.98; H, 5.71; N, 3.21.

1-(5′-Azulen-1-yl-[1,1′;3,1″]terphenyl-2′-yl)-ethanone **5**

Violet powder; mp 190–192°C; UV/VIS (CH_2Cl_2), λ_{max} (log ε): 241 (4.31), 277 (4.19), 302(4.19), 373 (3.74), 582 (broad). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 1.95 (s, 3H, CH_3), 7.18 (t, $^3J = 9.8$ Hz, 2H, 5′-H, 7′-H), 7.35–7.51 (m, 11H, 3′-H and H-phenyls), 7.61 (t, $^3J = 9.8$ Hz, 1H, 6′-H), 7.63 (s, 2H, 2-H, 6-H), 8.08 (d, $^3J = 3.9$ Hz, 1H, 2′-H), 8.36 (d, $^3J = 9.8$ Hz, 1H, 4′-H), 8.62 (d, $^3J = 9.8$ Hz, 1H, 8′-H). ^{13}C NMR ($CDCl_3$, 100.62 MHz, δ ppm): 28.7 (CH_3), 116.7 (CH), 122.5 (CH), 122.9 (CH), 126.6 (CH), 127.4 (CH), 128.1 (CH), 128.7 (Cq), 129.2 (CH), 134.5 (CH), 136.2 (CH), 136.5 (CH), 137.1 (Cq), 137.4 (CH), 138.6 (Cq), 139.5 (Cq), 141.0 (Cq), 205.3 (C=O). IR (solid): selected stretching vibrations: 2957.5, 2923.7 (νCH_3), 1691 (ν**CO**). MS-ESI positive (m/z, %): 399 ($[M+1]^+$, 100), 381 ($[M\text{-}H_2O]^+$, 95). Anal. calcd. for $C_{30}H_{22}O$: C, 90.42; H, 5.56. Found: C, 90.38; H, 5.60.

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