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Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary

AZULENE DERIVATIVES SOLUBLE IN POLAR SOLVENTS. 1-(AZULEN-1-YL)-2-(THIEN-2- or 3-YL)-ETHENES

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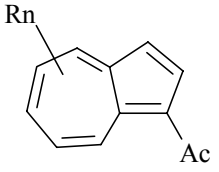
(Azulen-1-yl)carboxylic acids 3-substituted by 2-(thiazol-2- or 3-yl)-ethenyl groups and their esters were synthesized starting either from the corresponding 1-azulenyl-2-thiazolyl-ethenes, **3**, or from methyl 3-formyl-azulen-1-yl carboxylate, **7**. The ethenes **3** were phosgenated in an electrophylic reaction followed by the reaction with water or alcohol. The aldehyde **7** was transformed in Schiff base which was reacted with corresponding thienylacetic acid to generate the ester **6**b. The products characterization and considerations about the obtained compounds structure are reported.

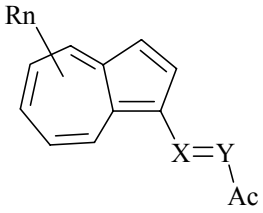
INTRODUCTION

The study of organic push-pull systems have been, and still remain, an outstanding target due to their valuable technical properties such as non-linear optical responses, electrochemical behavior or coloring properties. The good electron donor effect of azulene moiety[1] encouraged the research of push-pull compounds that contain this fragment directly bounded to an electron acceptor (Scheme 1, formula **A**) or through a conjugated bridge (Scheme 1, formula **B**).[2] Taking into account the large variety of azulene groups and electron moieties which can be used, as such as the nature of the X=Y bridge, a high number of compounds with various properties can be generated.



A

Ac = electron acceptor
Rn = alkyls



B

Series 1: X = Y = N
Series 2: X = CH; Y = N
Series 3: X = Y = CH

Scheme 1

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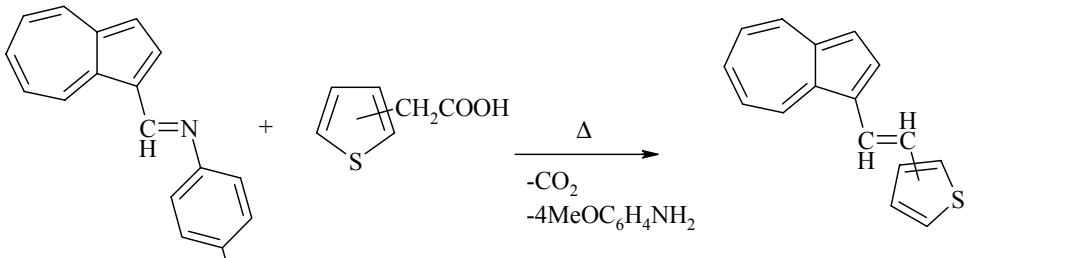
Our research group has been interested in the synthesis and properties of the azulene-containing compounds belonging to all series of compounds with general formula **B**, namely, azo derivatives,[3] imines[4] and ethenes.[5] Some of the obtained compounds showed significant NLO properties[6] whereas others showed interesting electrochemical properties[7]. Despite the high variety of the existing azulene derivatives, all the reported compounds are insoluble in water or in polar solvents. In general, the compounds with push-pull properties have to show a good solubility in polar organic solvents for immediate technical applications. Therefore, we report herein the synthesis and properties of such azulenic compounds.

RESULTS AND DISCUSSION

Synthesis. Based on our early results regarding the electrochemical behavior of 2[(*E*)-2-azulen-1-yl-vinyl]-thiophene, **3**a, as a new material for modification of electrode surfaces,[8] we have proposed to develop new similar compounds with good solubility in water or in other polar solvents. Therefore, compounds of type **3**a and its isomer **3**b were chosen as starting materials, whereas CO_2H and SO_3H were introduced as hydrophilic groups.

The synthesis procedure of ethenes **3**a and **3**b has been previously reported and is based on the condensation between Schiff base of type **1** and thienylacetic acids.[9]

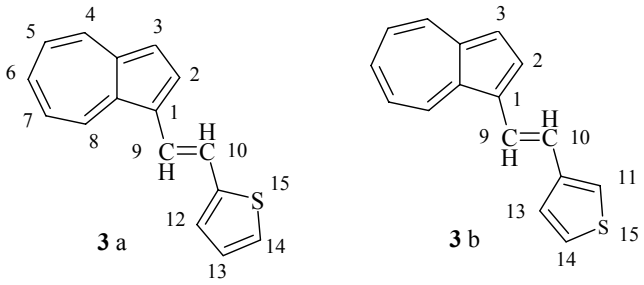
The incorporation of the above mentioned hydrophilic groups requires an attack at the nucleophilic center in compounds **3,** therefore we have calculated the net charges of different sites in these molecules (Table 1). The small obtained values for the ethylenic atoms explain their low reactivity. Despite the higher net charges at the atoms placed in the near vicinity of the heteroatom, these positions are not substituted, most likely due to low placed HOMO orbital of azulene moiety.



1 **2** a = thien-2-yl, b = thien-3-yl

3 a; recovered **1**, 5 % ;yield, 98 %
3 b; recovered **1**, 20 %; yield; 90 %

Scheme 2



3 a **3** b

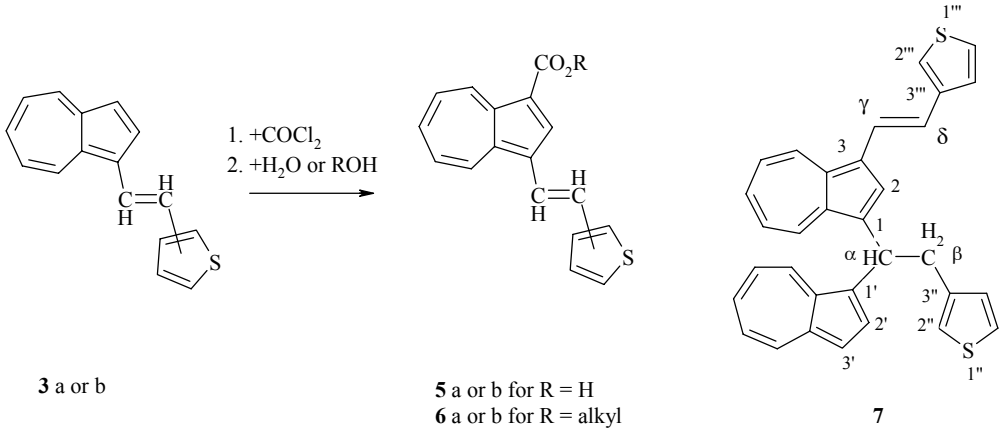
Table 1

Net charges[10] for the representative atoms of compounds **3**

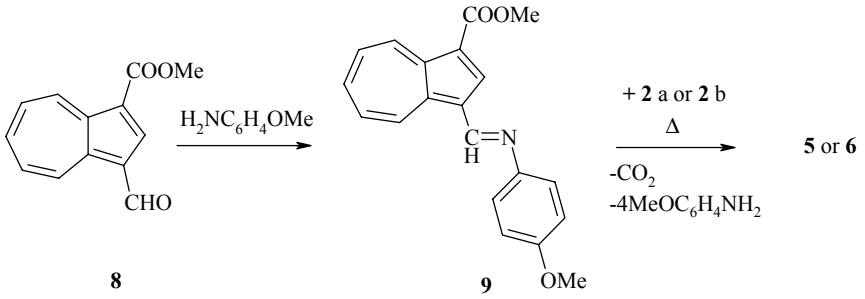
Compd	Atom number						
	2	3	4	5	6	7	8
3a	-0.0952	-0.1860	-0.0362	-0.1578	-0.0602	-0.1588	-0.0206
3b	-0.0974	-0.1846	-0.0373	-0.1581	-0.0614	-0.1578	-0.0231
Compd	Atom number						
	9	10	11	12	13	14	15(S)
3a	-0.1003	-0.0987	-0.3283	-0.1533	-0.1538	-0.4397	-0.5466
3b	-0.0923	-0.1075	-0.4415	-0.0650	-0.1421	-0.4413	-0.5613

Although, in the literature, the electrophyle reaction at 3-position in 1-vinyl-azulene derivatives was considered as impossible,[11] we have phosgenated this position in both compounds of type **3** (Scheme 3). The hydrolysis or the reaction with alcohols of the intermediary compounds led to acids **5** or esters **6,** respectively. Together with the main products, oligomers and polymers were also generated. In this respect, we have separated and characterized the dimmer **7** which resulted in the case of compound **3**b (Scheme 3).

The low obtained reaction yields (about 10 %) have been suggested the necessity of the optimization of the synthesis procedure and/or the findings of other routes for the synthesis of such compounds. Our attempts to optimize the synthesis route has failed therefore, we have performed the reaction starting from the accessible methyl 3-formyl-azulen-1-yl carboxylate, **8**.[12] As is shown in Scheme 4, the condensation of compound **8** with anisidine yields the Schiff base **9**, capable to react with thienylacetic acids when the desired compounds **5** (or **6**) are generated in 50 % yield.



Scheme 3



Scheme 4

Despite the reported sensibility of azulenic compounds which are substituted by vinyl group in position 1 towards strong acidic reagents[13], the successful sulfonation of some such azulenic derivatives has been determined us to follow this protocol also in the case of compounds of type **3**. Unfortunately, when sulfuric acid in acetic anhydride has been used as reagent, compounds **3** afforded only tar.

Products characterization. The first observation on the ^{1}H-NMR spectra consists in the difference between the resonances of the ethylenic proton in compounds of type **3** and their resonances in carboxylic derivatives, **5** and **6**. While for the first class of compounds the $\delta_{H\alpha}$-$\delta_{H\beta}$ difference was 0.2-0.3 ppm in $CDCl_3$, the chemical shifts for α and β protons in the carboxylic acids **5** were identical in $CDCl_3$ and became 0.3 ppm in acetone-d_6. The explanation consists in the influence of the strong electron acceptor effect of the carboxyl group which decreases the donor capacity of azulene moiety canceling the polarization of the double bond. The diminution of the donor effect for the ester group in compounds **6** is revealed by the increase in the $\delta_{H\alpha}$-$\delta_{H\beta}$ values. At the same time the signals belonging to the two ethylenic protons are also distinct (J = 16 Hz).

Table 2

^{1}H-Chemical shifts for the compounds **3**, **5** and **6** (in ppm TMS as internal standard)

compd	H-azulene							H-ethylene		H-thiophene			
	2	3	4	5	6	7	8	Hα	Hβ	2'	3'	4'	5'
3a[a]	8.17	7.37	8.41	7.10	7.50	7.05	8.16	7.49	7.29	-	7.07	7.00	7.15
5a[a]	8.75	-	8.56	7.44	7.77	7.50	9.58	7.39	7.38	-	7.11	7.04	7.21
6a[a]	8.69	-	8.57	7.40	7.75	7.45	9.55	7.43	7.40	-	7.10	7.03	7.20
3b[a]	8.21	7.40	8.44	7.10	7.52	7.07	8.20	7.54	7.21	7.26	-	7.45	7.34
5b[a]	8.78	-	8.61	7.45	7.78	7.50	9.59	7.31	7.31	7.36	-	7.50	7.45
5b[b]	8.80	-	8.92	7.55	7.93	7.59	9.61	7.79	7.49	7.56	-	7.69	7.54
6b[a]	8.69	-	8.57	7.40	7.75	7.45	9.54	7.46	7.26	7.26	-	7.44	7.36

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

The chemical shifts for protons of thiophene moiety in the studied compounds are not sensible to the COOR group substitution as has been expected, but, instead a dramatic modification can be observed for the azulenic protons. This effect is a consequence of both electronic and anisotropic influence of the introduced group towards the last mentioned protons. Thus, the protons of C-8 (the „*peri*"-position) are displaced by higher value, 1.4 ppm, followed by the displacement of the protons of C-2 position. More difficult seems to be to explain the deshielding effect shown by all protons when the ^{1}H-NMR spectra have been recorded in acetone. A possible explanation may be based on a charge transfer complex formation, generated between azulene-containing compounds and acetone solvent.

The carboxylic-substitution in compounds **5** or **6** has little influence on the chemical shifts of carbon atoms as can be observed from the ^{13}C-NMR spectra reported in the experimental part of this paper.

The results reported herein showed that some electrophylic reactions can be supported by vinyilazulene compounds without dramatic damage of starting material. Other attempts to generate new azulenic compounds soluble in polar solvents are in progress.

EXPERIMENTAL PART

Melting points: Kofler apparatus (Reichert Austria). Elemental analyses: Perkin Elmer CHN 240B. ^{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 $CDCl_3$ as solvent; the signals were assigned on the basis of COSY, HETCOR and HMBC experiments. Mass spectra: JEOL JMS-DX303 spectrometer coupled to analytical gas-chromatograph Shimadzu GC-14B with a DB-1 capillary column and C-R6A integrator and Finnigan MAT 311-A/100 MS; for the spectra recording in solid state Carlo Erba QMD 1000 (EI+, 70 eV). Column chromatography: silica gel [70-230 mesh (ASTM)]. Dichloromethane (DCM) was distilled over CaH_2, ethyl acetate was distilled over Na_2CO_3. UV spectra in methanol: 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).

Synthesis

The synthesis of alkenes. An equimolar mixture of thienylacetic acid and Schiff bases **3** was placed into a flask protected against the humidity and heated at 120 °C (oil bath temperature) for 30 minutes. Thienylacetic acid was dissolved by the melted Schiff base and gradually the resulted amine from the reaction was condensed on the upper part of the flask. This has been eliminated at the end of the reaction by washing with DCM. The resulting reaction mixture was dissolved in a small amount of DCM and was chromatographed on silica gel using a mixture of *n*-pentane and DCM. The first fraction, green colored, contained the alkene that was crystallized from hexane.

The alkene phosgenation. To the alkenes dissolved in a little amount of toluene, cooled to 0 °C, under stirring, a cooled toluene solution, saturated in phosgene (~20 % phosgene) was added (at least 5 equivalent of phosgene for one equivalent of alkenes) in a well ventilated hood. The reaction mixture was kept at this temperature with magnetic stirring for 1 hour and then was heated at 80 °C for one hour. After the cooling at 0 °C, water or alcohol was added for acid or ester generation. The excess of phosgene was removed in vacuum and the toluene was partially removed in vacuum at the temperature under 80 °C. Because the poor acids solubility in toluene, a little amount of DCM was added and the organic layer was washed with water, dried on sodium sulfate and the solvent was vaporized. The chromatography on silica gel with a mixture of n-pentane and DCM afforded some amount of polymeric material without carboxylic groups in the molecules (green fractions). With DCM – ethyl acetate 10 % the acids or esters were eluted, followed by polymeric red or brown fractions.

The reaction of Schiff base 9 with thienylacetic acid.. The Schiff base **9** (obtained from the aldehyde **8** in the described conditions)[5] was condensed with thienylacetic acid in the conditions reported above for the synthesis of alkenes. The ester was purified by column chromatography and the acid was obtained by ester hydrolysis.

Product characterization

3-[(E)-2-azulen-1-yl-vinyl]thiophene, **3**b, green crystals, m. p. 160 °C (with partial sublimation). $C_{16}H_{12}S$: calcd C 81.31, H

5.12, S 13.57; found C 81.47, H 5.20, S 13.33. UV spectrum (MeOH, nm): 217 (3.24), 257 (3.23), 314 (3.44), 338 (3.25), 358 (3.08), 393 (3.08), 413 (2.92). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ = 7.07 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 5′-H), 7.10 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 7′-H), 7.21 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 2-H), 7.26 (m, 1H, 2″-H), 7.34 (ddd, $^3J_{H,H}$ = 5.0 Hz, $^4J_{2"-H,5"-H}$ = 3.0 Hz, $^4J_{2-H,5"-H}$ = 0.4 Hz, 1H, 4″-H), 7.40 (d, $^3J_{H,H}$ = 4.0 Hz, 1H, 3′-H), 7.45 (dd, $^3J_{H,H}$ = 4.8 Hz, $^4J_{H,H}$ = 3.0 Hz, 1H, 5″-H), 7.52 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 6′-H), 7.54 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 1-H), 8.20 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, 4′-H), 8.21 (d, $^3J_{H,H}$ = 4.0 Hz, 1H, 2′-H), 8.44 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, 8′-H) ppm. ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$, 25 °C): δ = 119.3 (C-3′), 121.0 (C-2), 121.1 (C-2"), 121.5 (C-1), 123.0 (C-5′), 124.0 (C-7′), 125.6 (C-4″), 126.8 (C-5″), 127.1 (C-1'), 133.2 (C-2′), 134.5 (C-8′), 135.0 (C-3a'), 135.4 (C-8a'), 137.1 (C-4′), 139.0 (C-6′), 141.3 (C-3"), 142.6 (C-3a') ppm. Mass spectrum: *m/z* (ESI): 237 (M^++1).

3-[(E)-2-thien-3-yl-vinyl]azulene-1-carboxylic acid, **5**b, green crystals, m. p. 213 °C (after some phase transformations). $C_{17}H_{12}O_2S$: calcd C 72.83, H 4.31, S 11.44; found C 72.66, H 4.52, S 11.33. UV spectrum (MeOH, nm): 205 (3.43), 229 (3.34), 271 (3.37), 313 (3.61), 337 (3.44), 411 (2.88). IR spectrum (solid, cm^{-1}): 608, 628, 733, 764, 829, 860, 877, 916, 939, 1026, 1042, 1149, 1232, 1317, 1386, 1438, 1506, 1533, 1571, 1590, 1644, 1644, 1949, 2561, 2719, 2849, 2915. ^{1}H NMR spectrum (400 MHz, acetone-d_6, 25 °C): δ = 7.49 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 2-H), 7.53-7.55 (m, 1H, 2″-H), 7.56 (m, 1H, 5″-H), 7.56 (t, $^3J_{H,H}$ = 10.0 Hz, 1H, 5′-H), 7.58 (t, $^3J_{H,H}$ = 10.4 Hz, 1H, 7′-H), 7.69 (m, 1H, 5″-H), 7.79 (d, $^3J_{H,H}$ = 16.4 Hz, 1H, 1-H), 7.93 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 6′-H), 8.80 (s, 1H, 2′-H), 8.92 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 4′-H), 9.61 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 8′-H) ppm. ^{13}C NMR spectrum (100.62 MHz, acetona-d_6, 25 °C): δ = 118.0 (C-1′), 120.8 (C-1), 122.7 (C-2"), 123.6 (C-2), 126.0 (C-5″), 127.0 (C-5′), 127.4 (C-3', C-7′), 128.5 (C-4″), 136.4 (C-4′), 137.5 (C-2′), 138.6 (C-8′), 140.6 (C-3a'), 141.0 (C-6′), 142.1 (C-3"), 142.9 (C-8a'), 166.4 (COO) ppm. Mass spectrum: *m/z* (ESI): 281 (M^++1).

Methyl 3-[(E)-2-thien-3-yl-vinyl]azulene-1-carboxylate, **6**b, green crystals, m. p. 126 °C. $C_{18}H_{14}O_2S$: calcd C 73.44, H 4.79, S 10.89; found C 73.56, H 4.90, S 10.75. UV spectrum (MeOH, nm): 206 (3.44), 217 (3.71), 272 (3.30), 313 (3.84), 337 (3.67), 416 (3.03). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ = 3.98 (s, 3H, Me), 7.26 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 2-H), 7.28 (m, 1H, 2″-H), 7.36 (dd, $^3J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 3.0 Hz, 1H, 5″-H), 7.40 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 5′-H), 7.44 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, 4″-H), 7.45 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 7′-H), 7.46 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 1-H), 7.75 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 6′-H), 8.57 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 4′-H), 8.69 (s, 1H, 2′-H), 9.54 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 8′-H) ppm. ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$, 25 °C): δ = 51.27 (OMe), 116.8 (C-1′), 119.9 (C-2), 121.6 (C-1), 122.7 (C-2"), 124.8 (C-4″), 126.1 (C-5″), 126.4 (C-3'), 127.9 (C-5′), 127.9 (C-7′), 134.9 (C-4′), 136.8 (C-2′), 137.9 (C-8′), 139.7 (C-6′), 140.0 (C-3a'), 140.7 (C-3"), 142.1 (C-8a'), 165.6 (COO) ppm. Mass spectrum: *m/z* (ESI): 295 (M^++1).

1-[1-(Azulen-1-yl)-2-(thien-3-yl)-ethyl]-3-[(E)-2-(thien-3-yl-vinyl)]azulene, **7,** green crystals. Despite our attempt to purify the compound **7,** it remained contaminated with little amount of oligomers therefore the elemental analysis failed. UV spectrum (MeOH, nm): 238, 278, 367, 403, 426. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ = 3.71 (d, $^3J_{H,H}$ = 7.6 Hz, 2H, C(β)-H), 5.49 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, C(α)-H), 6.60 (m, 1H, 2"-H), 6.70 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, 4"-H), 6.86 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 5'-H), 6.97 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 7'-H), 6.98 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 7-H), 7.07 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 5-H), 7.07 (dd, $^3J_{H,H}$ = 4.8 Hz, $^4J_{H,H}$ = 6.4 Hz, 1H, 5″-H), 7.15 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, C(δ)-H), 7.24 (d, $^4J_{H,H}$ = 2.8 Hz, 1H, 2'"-H), 7.32 (dd, $^4J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 4.8 Hz, 1H, 4'"-H), 7.37 (t, $^3J_{H,H}$ = 4.0 Hz, 1H, 3'-H), 7.38 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 6'-H), 7.40 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 6-H), 7.43 (d, $^3J_{H,H}$ = 4.8 Hz, 1H, 5"'-H), 7.50 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, C(γ)-H), 7.95 (t, $^3J_{H,H}$ = 4.0 Hz, 1H, 2'-H), 8.06 (t, $^3J_{H,H}$ = 9.2 Hz, 1H, 4'-H), 8.18 (s, 1H, 2-H), 8.20 (t, $^3J_{H,H}$ = 9.2 Hz, 1H, 8-H), 8.26 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 8'-H), 8.34 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 4-H) ppm. ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$, 25 °C): δ = 37.38 (C-α), 38.82 (C-β), 117.0 (C-3'), 120.6 (C-δ), 120.9 (C-2"'), 121.3 (q), 121.4 (C-1, C-1', C-γ), 121.8 (C-2"), 122.1 (C-5, C-7'), 122.4 (C-7), 122.7 (C-5'), 124.8 (C-5"'), 124.9 (C-5"), 125.9 (C-1), 126.0 (C-4"'), 128.6 (C-4"), 132.0 (C-2), 133.1 (C-4'), 133.1 (C-4), 133.4 (C-8), 134.8 (q), 135.1 (q), 136.0 (C-2'), 136.6 (C-8'), 137.3 (C-6), 138.2 (C-6'), 138.4 (q), 140.8 (q), 141.1 (q), 141.2 (q) ppm. Mass spectrum: *m/z* (ESI): 473 (M^++1).

3-[(E)-2-thien-2-yl-vinyl]azulene-1-carboxylic acid, **5**a, green crystals, m. p. 195-200 °C (after several allotropic changes). $C_{17}H_{12}O_2S$: calcd C 72,83, H 4.31, S 11.44; found C 72.79, H 4.62, S 11.65. UV spectrum (MeOH, nm): 211 (3.81), 238 (3.85), 274 (3.93), 323 (3.99), 362 (3.92), 384 (3.79), 416sh (3.57). IR spectrum (solid, cm^{-1}): 674, 736, 772, 852, 877, 924, 1039, 1156, 1236, 1316, 1390, 1441, 1460, 1504, 1534, 1572, 1591, 1641, 1828, 2552, 2721, 2908, 3022. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C): δ = 7.04 (dd. $^3J_{H,H}$ = 4.8 Hz, $^3J_{H,H}$ = 3.6 Hz, 1H, 4″-H), 7.11 (d, $^3J_{H,H}$ = 3.5 Hz, 1H, 3″-H), 7.21 (d, $^3J_{H,H}$ = 5.2 Hz, 1H, 5″-H), 7.36 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 2-H), 7.41 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 1-H), 7.44 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 5′-H), 7.50 (t, $^3J_{H,H}$ = 9.8 Hz, 1H, 7′-H), 7.77 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 6′-H), 8.56 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 4′-H), 8.75 (s, 1H, 2′-H), 9.57 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, 8′-H) ppm. ^{13}C NMR spectrum (125.75 MHz, $CDCl_3$, 25 °C): δ = 116.1 (C-1'), 119.4 (C-2), 121.7 (C-1), 123.8 (C-5"), 125.7 (C-3"), 126.3 (C-3'), 127.0 (C-5'), 127.7 (C-4"), 128.5 (C-7'), 135.1 (C-4'), 137.7 (C-2'), 138.1 (C-8'), 139.9 (C-6'), 140.5 (C-3a'), 142.7 (C-8a'), 143.6 (C-2"), 170.4 (COO) ppm. Mass spectrum: *m/z* (ESI): 281 (M^++1).

Ethyl 3-[(E)-2-thien-2-yl-vinyl]azulene-1-carboxylate, **6**a, green crystals, m. p. 80 °C. $C_{19}H_{16}O_2S$: calcd C 74.00, H 5.23, S 10.40; found C 73.89, H 5.32, S 10.25. UV spectrum (MeOH, nm): 212 (3.57), 240 (3.62), 284 (3.72), 298 (3.73), 322 (3.72), 385 (3.44), 425 (3.11). ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C): δ = 1.47 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, Me), 4.45 (q, $^3J_{H,H}$ = 7.2 Hz, 2H, CH_2), 7.03 (dd, $^3J_{H,H}$ = 4.2 Hz, $^3J_{H,H}$ = 3.6 Hz, 1H, 4″-H), 7.10 (d, $^3J_{H,H}$ = 3.2 Hz, 1H, 3″-H), 7.20 (d, $^3J_{H,H}$ = 5.2 Hz, 1H, 5″-H), 7.37 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 2-H), 7.40 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 5′-H), 7.44 (d, $^3J_{H,H}$ = 16.0 Hz, 1H, 1-H), 7.45 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 7′-H), 7.75 (t, $^3J_{H,H}$ = 9.6 Hz, 1H, 6′-H), 8.57 (d, $^3J_{H,H}$ = 9.6 Hz, 1H, 4′-H), 8.69 (s, 1H, 2′-H), 9.55 (d, $^3J_{H,H}$ = 10.0 Hz, 1H, 8′-H) ppm. Mass spectrum *m/z* (ESI): 309 (M^++1).

Methyl 3–{(E)-[(4-methoxyphenyl)imino]methyl}azulene-1-carboxylate, **9,** brown crystals, m. p. 118 °C. $C_{20}H_{17}O_3N$: calcd C 75.22, H 5.37, N 4.39; found C 75.13, H 5.56, N 4.26. UV spectrum (MeOH, nm): 205 (4.68), 238 (4.74), 295 (4.88), 339 (4.57), 402 (4.42), 538 (3.12). IR spectrum (solid, cm^{-1}): 721, 735, 775, 824, 870, 900, 952, 1030, 1107, 1130, 1167, 1191, 1214, 1246, 1296, 1339, 1399, 1415, 1445, 1499, 1533,

1575, 1609, 1681, 1697, 1807, 2833, 2943. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C): δ = 3.85 (s, 3H, OMe), 3.97 (s, 3H, COOMe), 6.96 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H, 3'- and 5'-H), 7.29 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H, 2'-and 6′-H), 7.66 (t, $^{3}J_{H,H}$ = 9.8 Hz, 2H, 5- and 7-H), 7.90 (t, $^{3}J_{H,H}$ = 9.8 Hz, 1H, 6-H), 8.69 (s, 1H, 2′-H), 8.92 (s, 1H, CH=), 9.72 (d, $^{3}J_{H,H}$ = 10.0 Hz, 1H, 4′-H), 9.84 (d, $^{3}J_{H,H}$ = 9.6 Hz, 1H, 8′-H) ppm. ^{13}C NMR spectrum (100.62 MHz, $CDCl_3$, 25 °C): δ = 51.27 (COOMe), 55.50 (OMe), 114.4 (C-3′, C-5'), 116.4 (C-1'), 116.8 (C-3), 122.0 (C-2', C-6'), 124.2 (C-1), 129.9 (C-5, C-7), 138.8 (C-4, C-8), 140.6 (C-6), 141.8 (C-3a), 143.3 (C-2), 144.2 (C-8a), 146.0 (C-4'), 153.8 (CH=), 157.9 (C=N), 165.4 (CO) ppm. Mass spectrum: *m/z* (ESI): 276 (M^{+}+1), 246 (M-OMe+H), 218 (M-COOMe+H), 155 (AzCO).

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