A Convenient and Simple Synthesis of Densely Functionalized Cyclopenta[*cd*]azulenes and Cyclopenta[*ef*]heptalenes

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Syntheses of novel cyclopenta[*cd*]azulenes, **5**, **8**, and **13**, 1,2-dihydrocyclopenta[*cd*]azulenes, **6** and **12**, and cyclopenta[*ef*]heptalenes, **10**, **15**, and **16**, by simple procedures starting from tropolone in 6–8 steps are described.

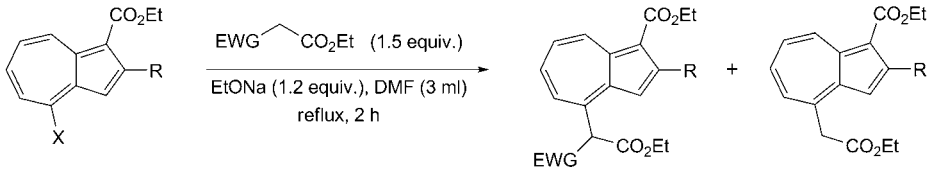
Introduction. – Azulenes constitute a class of polycyclic non-benzenoid aromatic hydrocarbons that have abidingly attracted interest of chemists [1] because of their occurence in a variety of natural products [2] and bioactive molecules [3]. These important compounds are used in various applications including cosmetics, dyes, pigments, co-polymers, and molecular materials [4]. Methods for syntheses of cyclopenta[*cd*]azulenes and cyclopenta[*ef*]heptalenes are very limited, due to its unique reactivity arising from the polarized π-electron system [5]. In 1974, *Richarz* and co-workers reported the synthesis of cyclopenta[*cd*]azulene, and 1,2-dihydrocyclopenta[*cd*]azulene derivatives from 2-azulenyl-4-acetic acid [5b]. Subsequently, *Toda et al.* developed the methodology of electrophilic substitution reactions for the synthesis of benz[*a*]indeno[1,2,3-*cd*]azulenes [5f]. However, new azulene transformation techniques are highly desirable for the future development of this class of compounds.

As a part of our research program aimed at developing a unified synthetic way toward azulene derivatives of carbo- and heterocyclic molecules [6], we have recently reported various 2-substituted azulene derivatives, and their applications in the syntheses of densely functionalized benz[*a*]azulene and multisubstituted azulene-furan frameworks [6c]. Recently, we have also developed a method for synthesis, characterization, and applications of densely functionalized pyridazines and fulvene-type compounds containing azulene moieties [6d]. On the basis of this experience, we herein report a facile and convenient methodology for densely functionalized cyclopenta[*cd*]-azulenes and cyclopenta[*ef*]heptalenes starting from tropolone in 6–8 steps. To the best of our knowledge, syntheses of such frameworks derived from 4-substituted azulene derivatives have not been properly reported in the literature, and all these products presented in this work are new in the azulene chemistry.

Results and Discussion. – We first directed our studies toward the transformation of ethyl 4-chloroazulene-1-carboxylate (**1a**, prepared from commercially available

tropolone in four steps) [6a] to ethyl 4-(1-cyano-2-ethoxy-2-oxoethyl)azulene-1-carboxylate (**3a**; 70%) by treatment with ethyl 2-cyanoacetate and EtONa in DMF under reflux for 2 h (*Table 1*, *Entry 1*) [6a]. We also extended this synthetic procedure by diethyl malonate, which provided a mixture of diethyl 2-(1-ethoxycarbonyl)azulen-4-yl)malonate (**3d**) and ethyl 4-(2-ethoxy-2-oxoethyl)azulene-1-carboxylate (**4a**) in yields of 50 and 20%, respectively (*Table 1*, *Entry 4*). Further, we achieved the generalization of this synthetic method with **2**, and all products were well characterized by their spectral data (*Table 1*).

Table 1. *Reactions of Ethyl Azulene-1-carboxylate Derivatives* **1** *and* **2**[a])[b])



1, **2** **3** **4**

Entry	Reactants **1**, **2**	X	R	EWG[c])	Products	Yield [%][d])
1	**1a**	Cl	H	CN	**3a**	70
2	**1b**	Cl	Me	CN	**3b**	86
3	**1c**	Cl	EtO	CN	**3c**	72
4	**1a**	Cl	H	CO_2Et	**3d**/**4a**	50/20
5	**1b**	Cl	Me	CO_2Et	**3e**/**4b**	60/25
6	**1c**	Cl	EtO	CO_2Et	**3f**/**4c**	38/28
7	**2a**	EtO	H	CN	**3a**	81
8	**2a**	EtO	H	CO_2Et	**3d**/**4a**	30/11

[a]) All reactions were carried out on a 2-mmol scale of reactants. [b]) Except **3a** and **3b** [6a], all compounds are new. [c]) EWG, Electron-withdrawing group. [d]) Yields of isolated products after column chromatography on silica gel.

After the successful synthesis of 4-substituted azulene derivatives, **3a**–**3f** and **4a**–**4c**, we focused our attention on the syntheses of various densely functionalized cyclopenta[*cd*]azulenes. First, for a model study, we selected **3a**, which was treated with $POCl_3$ in DMF at 0° for 2 h to provide diethyl cyclopenta[*cd*]azulene-1,4-dicarboxylate (**5a**) in a yield of 94% after purification by column chromatography (*Table 2*, *Entry 1*). The reaction proceeds *via Vilsmeier–Haack* formylation [7], more selectively at C(3), followed by intramolecular cyclization, which was confirmed by spectral analysis. To examine the scope of this reaction, we employed various 4-substituted azulene derivatives, **3b**–**3f**, **4a** and **4b**, to obtain the desired cyclopenta[*cd*]azulenes **5a**–**5c** in low-to-high yields (*Table 2*, *Entries 2–8*). Particularly, we noticed that the reactions of esters **3d**–**3f**, and **4a** and **4b** gave relatively low yields. However, this one-pot methodology demonstrated the potential in the construction of multisubstituted cyclopenta[*cd*]azulenes; a plausible mechanism for their formation is proposed in *Scheme 1*.

Scheme 1. *Proposed Mechanism for the Formation of Cyclopenta[*cd*]azulene-1,4-dicarboxylate Derivatives* **5**

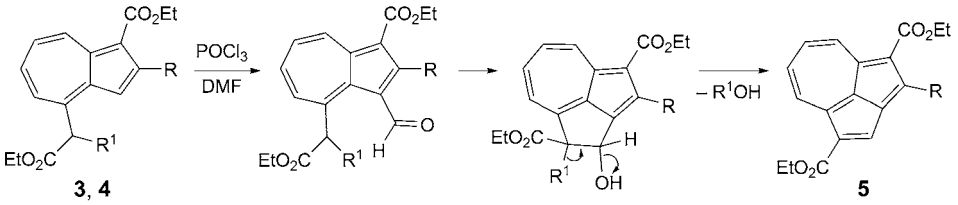
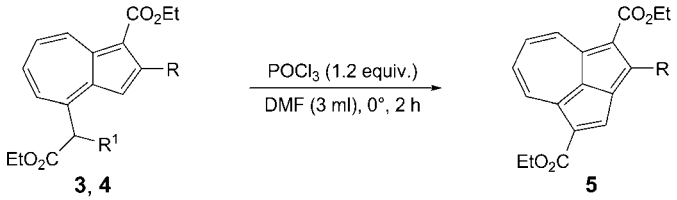


Table 2. *One-Pot Synthesis of Cyclopenta[*cd*]azulene-1,4-dicarboxylate Derivatives* **5**[a])

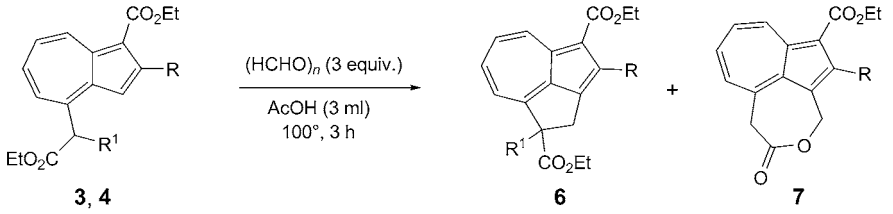


Entry	Reactants	R	R^1	Products	Yield [%][b])
1	**3a**	H	CN	**5a**	94
2	**3b**	Me	CN	**5b**	90
3	**3c**	EtO	CN	**5c**	82
4	**3d**	H	CO_2Et	**5a**	55
5	**3e**	Me	CO_2Et	**5b**	48
6	**3f**	EtO	CO_2Et	**5c**	27
7	**4a**	H	H	**5a**	42
8	**4b**	Me	H	**5b**	51

[a]) All reactions were carried out on a 1-mmol scale of reactants. [b]) Yields of isolated products after column chromatography on silica gel.

Next, we directed our attention to the development of an alternative methodology for the syntheses of cyclopenta[*cd*]azulenes using 4-substituted azulene derivatives. For these studies, we selected ethyl 4-(1-cyano-2-ethoxy-2-oxoethyl)azulene-1-carboxylate (**3a**), which was treated with paraformaldehyde in AcOH at 100° for 3 h to provide diethyl 1-cyano-1,2-dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylate (**6a**) in 80% yield. The reaction apparently proceded *via* a substitution, and a subsequent intramolecular condensation (*Table 3*, *Entry 1*). Encouraged by these results, we successfully transformed representative 4-substituted azulene derivatives **3b**–**3e** to 1,2-dihydrocyclopenta[*cd*]azulenes **6b**–**6e**. Interestingly, we noticed that the ester derivatives of 4-substituted azulenes **3d** and **3e** furnished mixtures of 1,2-dihydrocyclopenta[*cd*]azulenes **6d** and **6e**, and novel type of azulenolactone frameworks **7a** and **7b** in good yields. Similarly, compounds **4a** and **4b** afforded exclusively azulenolactones **7a** and **7b**, respectively, in high yields (*Table 3*). Subsequently, 1,2-dihydrocyclopenta[*cd*]azulene derivatives **6a**–**6e** were further treated with 2,3-dichloro-5,6-dicyano-1,4-benzoqui-

Table 3. *One-Pot Synthesis of 1,2-Dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylates and Lactone Derivatives,* **6** *and* **7**[a]), Respectively



3, **4** **6** **7**

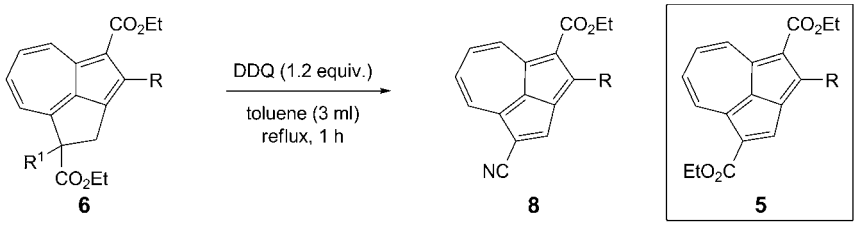
Entry	Reactants	R	R^1	Products	Yield (%)[b])
1	**3a**	H	CN	**6a**	80
2	**3b**	Me	CN	**6b**	96
3	**3c**	EtO	CN	**6c**	92
4	**3d**	H	CO_2Et	**6d**/**7a**	38/52
5	**3e**	Me	CO_2Et	**6e**/**7b**	35/54
6	**4a**	H	H	**7a**	85
7	**4b**	Me	H	**7b**	78

[a]) All reactions were carried out on a 1-mmol scale of reactants. [b]) Yields of isolated products after column chromatography on silica gel.

none (DDQ) in toluene under reflux for 1 h to give fully aromatized cyclopenta[*cd*]-azulenes, **8a**–**8c**, **5a** and **5b**, in good-to-excellent yields (*Table 4*). All the products were well-characterized by their spectral data. By this alternative method, cyclopenta[*cd*]-azulenes were obtained in lower yields as compared to those of the direct *Vilsmeier–Haack* formylation method.

Subsequently, we concentrated our efforts on the construction of cyclopenta[*ef*]-heptalene frameworks. For this purpose, we selected ethyl 4-(2-ethoxy-2-oxoethyl)-3-(3-oxobutyl)azulene-1-carboxylate (**9a**), which was prepared from the reaction of ethyl 4-(2-ethoxy-2-oxoethyl)azulene-1-carboxylate (**4a**), methyl vinyl ketone, and TsOH in EtOH at room temperature for 1 h (*Scheme 2*). Compound **9a** was further transformed to the desired densely functionalized diethyl 5-methyl-3,4-dihydrocyclopenta[*ef*]heptalene-1,6-dicarboxylate (**10a**) under various conditions. The best result was obtained *via* the intramolecular aldol pathway in the presence of EtONa in refluxing EtOH (62% yield). Encouraged by these promising results, we converted ethyl 4-(2-ethoxy-2-oxoethyl)azulene-1-carboxylate derivatives **4b** and **4c** to the desired 3,4-dihydrocyclopenta[*ef*]heptalene-1,6-dicarboxylates **10b** and **10c**, respectively, in good yields (*Scheme 2*). Compounds **9a**–**9c** were also transformed into multisubstituted dihydrocyclopenta[*cd*]azulenes **12a**–**12c** in good yields (64–82%) *via* intramolecular cyclization of compounds **11a**–**11c**, respectively. Compounds **12a**–**12c** were further oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to afford fully aromatized cyclopenta[*cd*]azulenes **13a**–**13c** in excellent yields (*Scheme 2*). A plausible mechanism for the syntheses of cyclopenta[*ef*]heptalenes **10** is depicted in *Scheme 3*. Subsequently, we also synthesized other interesting derivatives of cyclopenta[*ef*]heptalenes **15a** and **16a** from ethyl 4-(1-ethoxy-1,5-dioxohexan-2-yl)azulene-1-carboxylate

Table 4. *Oxidations of 1,2-Dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylate Derivatives* **6**[a])



Entry	Reactant	R	R^1	Products	Yield [%][b])
1	**6a**	H	CN	**8a**	78
2	**6b**	Me	CN	**8b**	86
3	**6c**	EtO	CN	**8c**	80
4	**6d**	H	CO_2Et	**5a**	56
5	**6e**	Me	CO_2Et	**5b**	41

[a]) All reactions were carried out on a 1-mmol scale of reactants. [b]) Yields of isolated products after column chromatography on silica gel.

(**14a**), which, in turn, was obtained from the reacion of **4a** with $POCl_3$ in DMF at 0° to room temperature for 2 h. The reaction presumably proceded by a *Vilsmeier–Haack* formylation and subsequent cyclization reactions. To evaluate the generality of this reaction, we converted compounds **4b** and **4c** into the desired cyclopenta[*ef*]heptalenes **15b**, **15c**, and **16b**, and **16c**, respectively, in good yields (*Scheme 2*).

Finally, we have also developed an alternative methodology for the synthesis of ethyl 4-acetyl-5,6-dihydrocyclopenta[*ef*]heptalene-1-carboxylate (**16a**) from ethyl 4-(1-ethoxy-1,5-dioxohexan-2-yl)-3-formylazulene-1-carboxylate (**19**), generated from ethyl 4-(1-ethoxy-1,5-dioxohexan-2-yl)-3-methylazulene-1-carboxylate (**18**), which, in turn, was prepared from ethyl 4-(2-ethoxy-2-oxoethyl)-3-methylazulene-1-carboxylate (**17**) [6a] with EtONa in EtOH under reflux for 5 min, in 86% yield. Compound **17** was also treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene under reflux for 20 min to furnish cyclopenta[*cd*]azulene **5a** in 42% yield. The structures of all these compounds were confirmed by spectral analyses (*Scheme 4*).

Conclusions. – We have synthesized 4-substituted azulenes **3** and **4** from ethyl 4-chloroazulene-1-carboxylate (**1**) and its ethoxy derivative **2**. These derivatives were further used in the syntheses of novel derivatives of various cyclopenta[*cd*]azulenes, **5**, **8**, and **13**, 1,2-dihydrocyclopenta[*cd*]azulenes, **6** and **12**, and cyclopenta[*ef*]heptalenes, **10**, **15**, and **16**, by simple procedures. Utilization of these methodologies for the synthesis of biologically important molecules is in progress.

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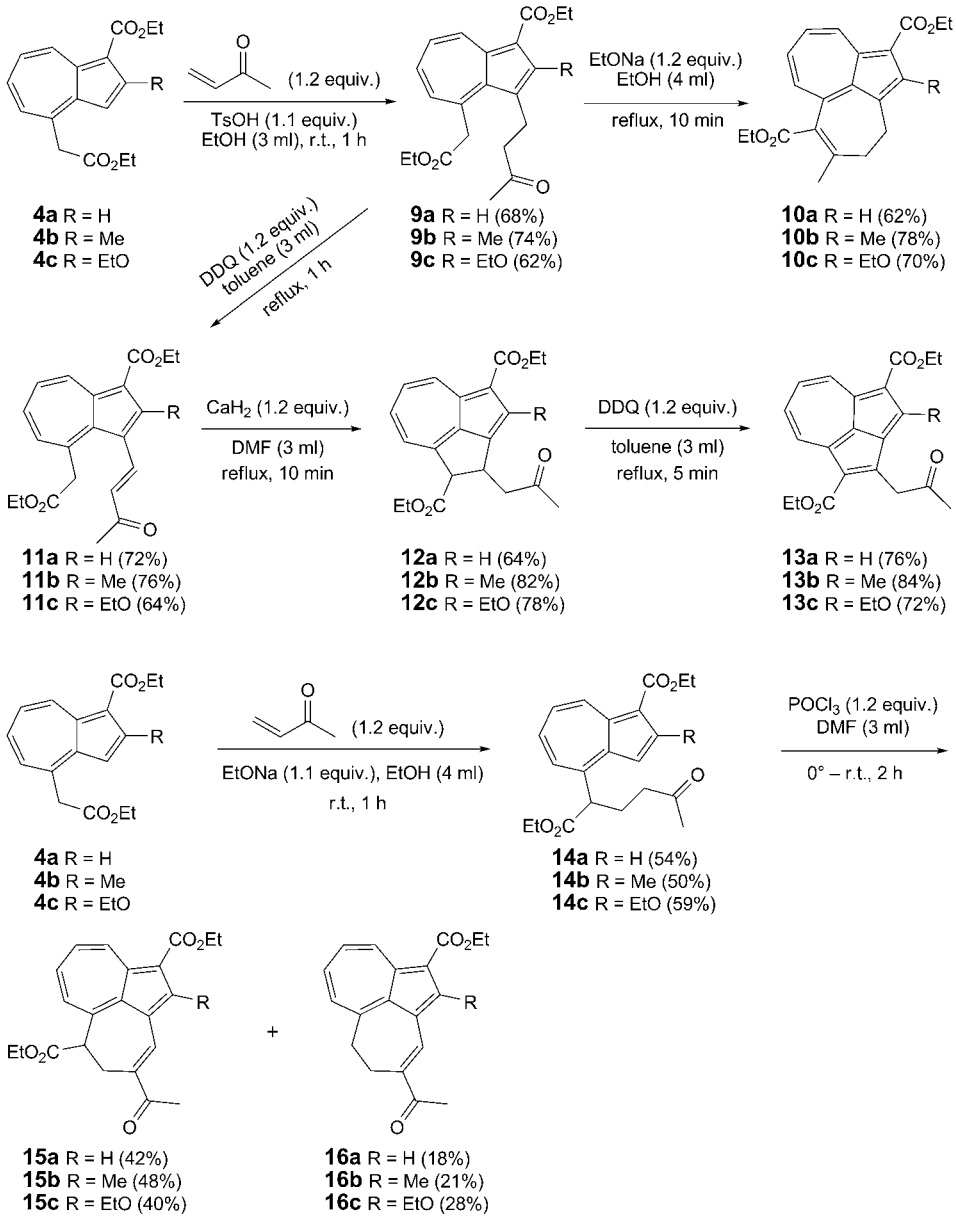
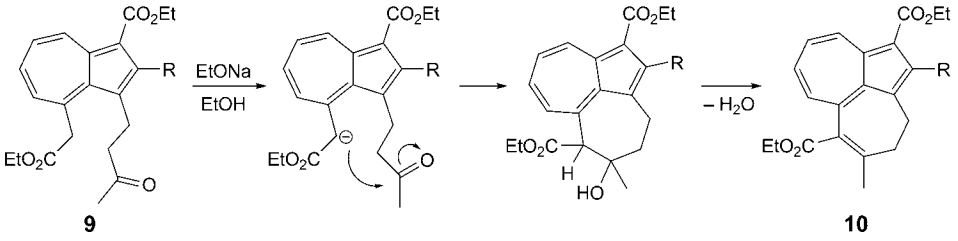
Scheme 2. *Syntheses of Cyclopenta- and Cyclohepta[*cd*]azulenes from Compounds* **4**



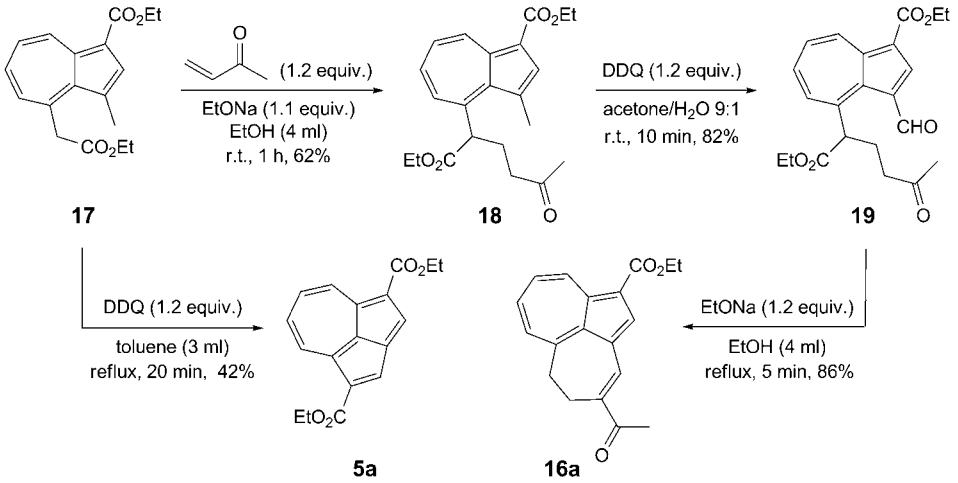
Experimental Part

General. Unless stated otherwise, reagents were obtained from commercial sources and used without further purification. Unless indicated otherwise, yields were calculated after flash column chromatography (CC). TLC: *Merck 5735 DC-Alufolien Kiesegel 60* F_{254}. CC: *Art. 9385 Kiesegel 60 H* silica gel

Scheme 3. *A Plausible Mechanism for the Synthesis of Dihydrocyclohepta[*cd*]azulene-1,6-dicarboxylates* **10**



Scheme 4. *Syntheses of Cyclopenta- and Cyclohepta[*cd*]azulenes from Compound* **17**



(SiO_2; 230–400 mesh, *Merck*). IR Spectra: *JASCO FT/IR-460*; as thin film on KBr plates; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker ACE-300* FT-NMR; δ referenced to $CDCl_3$, *J* in Hz. MS and HR-EI-MS: *Shimadzu-LC/MS-2010A* and *JEOL-JMS-HX-100* mass spectrometers, resp.; in *m/z* (rel. %).

*Diethyl Cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**5a**). To a soln. of *ethyl 4-(1-cyano-2-ethoxy-2-oxoethyl)azulene-1-carboxylate* (**3a**; 1 mmol, 0.311 g) in DMF (3 ml) at 0° was added $POCl_3$ (1.2 mmol, 0.1 ml) slowly within 10 min and the reaction continued for 2 h. Then, the mixture was diluted with H_2O (10 ml), the reacion was quenched with aq. KOH soln., and the mixture was extracted with AcOEt. The combined org. layers were dried ($MgSO_4$), concentrated, and chromatographed (SiO_2; hexane/AcOEt 2:1) to afford **5a** (0.278 g, 94%). Brown solid. M.p. 144–145°. IR (KBr): 1690, 1460, 1420, 1289. ^{1}H-NMR: 1.43 (*t*, *J* = 7.0, 6 H); 4.39 (*q*, *J* = 7.0, 4 H); 8.22 (*s*, 2 H); 8.31–8.34 (*m*, 2 H); 9.27–9.30 (*m*, 2 H). ^{13}C-NMR: 14.6; 60.0; 124.8; 130.3; 135.0; 136.9; 143.5; 145.2; 164.7. LC/MS: 297 (17, M^+), 296 (100, M^+), 268 (14), 251 (45), 240 (18), 224 (20), 223 (72), 195 (20), 178 (20), 150 (54). HR-EI-MS: 296.1056 (M^+, $C_{18}H_{16}O_4^+$; calc. 296.1044).

*Diethyl 2-Methylcyclopenta[*cd*]azulene-1,4-dicarboxylate* (**5b**). As described for **5a**; from **3b**. Yield: 90%. Green solid. M.p. 115–116°. IR (KBr): 2980, 2920, 1670, 1450, 1400, 1255, 1250. ^{1}H-NMR: 1.37 (*t*, *J* = 7.1, 3 H); 1.39 (*t*, *J* = 7.2, 3 H); 2.77 (*s*, 3 H); 4.33 (*q*, *J* = 7.2, 2 H); 4.35 (*q*, *J* = 7.1, 2 H); 8.13 (*s*, 1 H); 8.14–8.16 (*m*, 2 H); 9.10–9.12 (*m*, 2 H). ^{13}C-NMR: 14.6; 16.6; 29.7; 59.6; 59.9; 120.2; 124.0; 133.5; 133.7;

135.1; 135.2; 135.3; 137.0; 141.1; 143.7; 146.9; 160.1; 164.7; 165.4. LC/MS: 311 (16, M^+), 310 (100, M^+), 265 (35), 253 (18.7), 237 (40), 208 (25), 192 (9). HR-EI-MS: 310.1200 (M^+, $C_{19}H_{18}O_4^+$; calc.310.1205).

*Diethyl 2-Ethoxycyclopenta[*cd*]azulene-1,4-dicarboxylate* (**5c**). As described for **5a**; from **3c**. Yield: 82%. Green solid. M.p. 98–99°. IR (KBr): 2960, 1683, 1660, 1490, 1450, 1162, 1080, 780. ^{1}H-NMR: 1.43 (*t*, *J* = 7.0, 3 H); 1.44 (*t*, *J* = 7.2, 3 H); 1.68 (*t*, *J* = 7.0, 3 H); 4.39 (*q*, *J* = 7.0, 2 H); 4.40 (*q*, *J* = 7.2, 2 H); 4.67 (*q*, *J* = 7.0, 2 H); 8.06 (*dd*, *J* = 4.9, 10.4, 1 H); 8.11 (*s*, 1 H); 8.22 (*dd*, *J* = 4.9, 10.4, 1 H); 9.14 (*d*, *J* = 9.6, 1 H); 9.23 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 14.6; 59.3; 60.0; 70.0; 103.2; 118.5; 124.3; 132.2; 133.0; 134.8; 135.4; 137.8; 140.1; 141.0; 147.8; 164.3; 164.7; 172.7. LC/MS: 340 (100, M^+), 295 (22), 268 (54), 266 (52), 238 (26), 221 (97), 194 (44). HR-EI-MS: 340.1306 (M^+, $C_{20}H_{20}O_5^+$; calc. 340.1305).

*Diethyl 1-Cyano-1,2-dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylate* (**6a**). To a soln. of **3a** (1 mmol, 0.311 g) in AcOH (3 ml) at r.t. was added paraformaldehyde (3 mmol, 0.090 g), and the mixture was heated at 100° for 3 h. Then, the mixture was allowed to cool to r.t., diluted with H_2O (10 ml), and extracted with AcOEt. The combined org. layer was dried ($MgSO_4$), concentrated, and subjected CC (SiO_2; hexane/AcOEt 2 : 1) to afford **6a** (0.258 g, 80%). Blue solid. M.p. 90–91°. IR (KBr): 2895, 2850, 2200, 1740, 1680, 1600, 1450, 1200, 790. ^{1}H-NMR: 1.30 (*t*, *J* = 7.1, 3 H); 1.42 (*t*, *J* = 7.1, 3 H); 3.95 (*d*, *J* = 16.5, 1 H); 4.21(*d*, *J* = 16.5, 1 H); 4.32 (*q*, *J* = 7.1, 2 H); 4.42 (*q*, *J* = 7.1, 2 H); 7.40 (*t*, *J* = 10.0, 1 H); 7.48 (*d*, *J* = 9.7, 1 H); 7.75 (*t*, *J* = 10.0, 1 H); 8.05 (*s*, 1 H); 9.11 (*d*, *J* = 9.8, 1 H). ^{13}C-NMR: 13.8; 14.5; 39.0; 50.0; 58.4; 63.9; 118.0; 121.4; 121.6; 127.0; 131.9; 132.8; 133.6; 139.0; 139.5; 148.4; 150.4; 165.0; 166.1. LC/MS: 324 (13.5, M^+), 323 (41.5, M^+), 278 (11.9), 250 (74.7), 222 (15.2), 204 (16.7), 177 (100), 150 (17.4). HR-EI-MS: 323.1150 (M^+, $C_{19}H_{17}NO_4^+$; calc. 323.1153).

*Diethyl 1-Cyano-3-methyl-1,2-dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylate* (**6b**). As described for **6a**; from **3b**. Yield: 96%. Blue solid. M.p. 133–134°. IR (KBr): 2210, 1730, 1680, 1440, 1210. ^{1}H-NMR: 1.35 (*t*, *J* = 7.2, 3 H); 1.45 (*t*, *J* = 7.1, 3 H); 2.78 (*s*, 3 H); 3.90 (*d*, *J* = 16.3, 1 H); 4.15 (*d*, *J* = 16.3, 1 H); 4.31 (*q*, *J* = 7.1, 2 H); 4.40 (*q*, *J* = 7.2, 2 H); 7.38 (*t*, *J* = 10.0, 1 H); 7.45 (*t*, *J* = 9.7, 1 H); 7.70 (*t*, *J* = 10.0, 1 H); 9.05 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 13.9; 14.6; 16.4; 38.1; 57.8; 59.8; 63.9; 118.2; 119.3; 121.5; 127.1; 133.2; 134.7; 137.3; 137.6; 146.3; 146.7; 148.4; 165.8; 166.3. LC/MS: 338 (19.7, M^+), 337 (88.2, M^+), 293 (4.8), 264 (100), 236 (5.7), 191 (97). HR-EI-MS: 337.1285 (M^+, $C_{20}H_{19}NO_4^+$; calc. 337.1309).

*Diethyl 1-Cyano-3-ethoxy-1,2-dihydrocyclopenta[*cd*]azulene-1,4-dicarboxylate* (**6c**). As described for **6a**; from **3c**. Yield: 92%. Blue solid. M.p. 128–129°. IR (KBr): 2200, 1729, 1680, 1410, 1178. ^{1}H-NMR: 1.32 (*t*, *J* = 7.1, 3 H); 1.36 (*t*, *J* = 7.2, 3 H); 1.48 (*t*, *J* = 7.0, 3 H); 3.70 (*d*, *J* = 16.2, 1 H); 3.99 (*d*, *J* = 16.2, 1 H); 4.09 (*q*, *J* = 7.0, 2 H); 4.28 (*q*, *J* = 7.2, 2 H); 4.47 (*q*, *J* = 7.0, 2 H); 7.06 (*t*, *J* = 10.4, 1 H); 7.56 (*t*, *J* = 10.0, 1 H); 7.68 (*t*, *J* = 10.4, 1 H); 9.14 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 14.1; 14.8; 16.2; 32.3; 59.4; 60.3; 61.6; 63.2; 117.7; 121.0; 122.2; 122.5; 126.1; 129.9; 131.4; 144.0; 145.6; 147.1; 147.9; 164.7; 166.2. LC/MS: 367 (100, M^+), 262 (54), 221 (46), (97). HR-EI-MS: 367.1076 (M^+, $C_{21}H_{21}NO_5^+$; calc. 367.1081).

*Triethyl Cyclopenta[*cd*]azulene-1,1,4(2*H*)-tricarboxylate* (**6d**). As described for **6a**; from **3d**. Yield: 38%. Blue solid. M.p. 130–131°. IR (KBr): 1720, 1680, 1400, 1130. ^{1}H-NMR: 1.25 (*t*, *J* = 7.1, 6 H); 1.45 (*t*, *J* = 7.0, 3 H); 4.05 (*s*, 2 H); 4.25 (*q*, *J* = 7.1, 4 H); 4.41 (*q*, *J* = 7.0, 2 H); 7.40 (*t*, *J* = 10.0, 1 H); 7.60 (*d*, *J* = 9.7, 1 H); 7.72 (*t*, *J* = 10.0, 1 H); 8.05 (*s*, 1 H); 9.10 (*d*, *J* = 9.8, 1 H). ^{13}C-NMR: 14.0; 14.6; 29.7; 36.2; 59.8; 62.4; 120.3; 124.8; 126.8; 130.9; 133.6; 138.1; 138.6; 150.9; 165.6; 169.2. LC/MS: 370 (35, M^+), 325 (10), 296 (38), 251 (100), 224 (34.5), 196 (33.8), 179 (58).

*Triethyl 3-Methylcyclopenta[*cd*]azulene-1,1,4(2*H*)-tricarboxylate* (**6e**). As described for **6a**; from **3e**. Yield 35%. Blue solid. M.p. 70–71°. IR (KBr): 1740, 1720, 1680, 1440, 1400, 1210. ^{1}H-NMR: 1.25 (*m*, 6 H); 1.45 (*t*, *J* = 7.1, 3 H); 2.75 (*s*, 3 H); 3.9 (*s*, 2 H); 4.25 (*q*, *J* = 7.1, 4 H); 4.40 (*q*, *J* = 7.1, 2 H); 7.35 (*dd*, *J* = 2.3, 9.6, 1 H); 7.61 (*t*, *J* = 9.3, 1 H); 7.62 (*t*, *J* = 9.3, 1 H); 9.00 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 13.9; 14.6; 16.3; 35.4; 59.5; 62.3; 136.4; 136.8; 145.4; 148.6; 149.6; 166.2; 169.4. LC/MS: 384 (56.5, M^+), 339 (12.9), 311 (44.3), 265 (100).

*Ethyl 3,4-Dihydro-3-oxo-1*H*-azuleno[1,8-*cd*]oxepine-9-carboxylate* (**7a**). As described for **6a**; from **3e**. Yield: 52%. Red solid. M.p. 169–170°. IR (KBr): 1740, 1680, 1420, 1220, 1060, 1010. ^{1}H-NMR: 1.40 (*t*, *J* = 7.1, 3 H); 4.28 (*q*, *J* = 7.1, 2 H); 4.50 (*s*, 2 H); 5.60 (*s*, 2 H); 7.25 (*d*, *J* = 9.9, 1 H); 7.40 (*t*, *J* = 9.7, 1 H); 7.65 (*t*, *J* = 9.9, 1 H); 8.12 (*s*, 1 H); 9.45 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 14.4; 45.2; 59.9; 66.5; 115.7; 122.6; 127.6; 130.1; 139.0; 139.3; 139.4; 140.6; 142.1; 164.8; 170.6; 175.8. LC/MS: 270 (15, M^+), 269 (82, $[M-H]^+$), 224 (24.8), 180 (71.9), 152 (100). HR-EI-MS: 270.0898 (M^+, $C_{16}H_{14}O_4^+$; calc. 270.0888).

*Ethyl 3,4-Dihydro-10-methyl-3-oxo-1*H*-azuleno[1,8-*cd*]oxepine-9-carboxylate* (**7b**). As described for **6a**; from **3e**. Yield: 54%. Red solid. M.p. 144–145°. IR (KBr): 1740, 1680, 1410, 1220, 1130. ^{1}H-NMR: 1.45 (*t*, *J* = 7.1, 3 H); 2.70 (*s*, 3 H); 4.42 (*q*, *J* = 7.1, 2 H); 4.50 (*s*, 2 H); 5.62 (*s*, 2 H); 7.21 (*d*, *J* = 9.9, 1 H); 7.41 (*t*, *J* = 9.8, 1 H); 7.55 (*t*, *J* = 9.8, 1 H); 9.46 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 14.7; 14.8; 45.3; 60.0; 63.9; 115.6; 122.1; 127.6; 130.2; 137.2; 137.6; 138.4; 139.6; 140.5; 149.9; 165.8; 171.0. LC/MS: 284 (17.7, M^+), 283 (100, $[M-H]^+$), 238 (30), 210 (17.6), 194 (52.8), 164 (81.2). HR-EI-MS: 284.1042 (M^+, $C_{17}H_{16}O_4^+$; calc. 284.1044).

*Ethyl 4-Cyanocyclopenta[*cd*]azulene-1-carboxylate* (**8a**). To a stirred soln. of (**6a** (1 mmol, 0.323 g) in toluene (3 ml) was added DDQ (1.2 mmol, 0.272 g), and the mixture was refluxed for 1 h. The mixture was allowed to cool to r.t., diluted with H_2O (10 ml), and extracted with AcOEt. The combined org. layer was dried ($MgSO_4$), concentrated, and subjected to CC (SiO_2; hexane/AcOEt 2 : 1) to afford **8a** (0.194 g, 78%). Green solid. M.p. 139–140°. IR (KBr): 2950, 2200, 1695, 1460, 1255, 1090. ^{1}H-NMR: 1.43 (*t*, *J* = 7.1, 3 H); 4.41 (*q*, *J* = 7.1, 2 H); 7.98 (*s*, 1 H); 8.27 (*s*, 1 H); 8.41 (*t*, *J* = 9.6, 2 H); 8.66 (*d*, *J* = 9.6, 1 H); 9.38 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 14.5; 60.2; 103.0; 116.3; 126.0; 130.7; 132.4; 134.5; 135.5; 136.4; 138.0; 143.8; 144.7; 144.9; 145.6; 164.4. LC/MS: 250 (34.8, M^+), 249 (100, M^+), 221 (52.6), 204 (96.5), 177 (67.6), 149 (22.2). HR-EI-MS: 249.0803 (M^+, $C_{16}H_{11}NO_2^+$; calc. 249.0771).

*Ethyl 4-Cyano-2-methylcyclopenta[*cd*]azulene-1-carboxylate* (**8b**). As described for **8a**; from **6b**. Yield: 86%. Green solid. M.p. 159–160°. IR (KBr): 2200, 1680, 1660, 1520, 1440, 1220, 1120. ^{1}H-NMR: 1.45 (*t*, *J* = 7.0, 3 H); 2.85 (*s*, 3 H); 4.41 (*q*, *J* = 7.0, 2 H); 8.00 (*s*, 1 H); 8.25 (*t*, *J* = 10.5, 1 H); 8.35 (*t*, *J* = 10.2, 1 H); 8.60 (*d*, *J* = 8.4, 1 H); 9.25 (*d*, *J* = 9.0, 1 H). ^{13}C-NMR: 12.8; 14.2; 60.1; 99.0; 119.2; 124.0; 128.3; 131.8; 134.9; 136.2; 136.8; 138.3; 144.0; 144.7; 145.2; 145.6; 165.2. LC/MS: 263 (100, M^+), 235 (50), 218 (92), 191 (84), 162 (44). HR-EI-MS: 263.0943 (M^+, $C_{17}H_{13}NO_2^+$; calc. 263.0927).

*Ethyl 4-Cyano-2-ethoxycyclopenta[*cd*]azulene-1-carboxylate* (**8c**). As described for **8a**; from **6c**. Yield: 0.234 g (80%). Green solid. M.p. 180–181°. IR (KBr): 2952, 2185, 1676, 1650, 1480, 1290, 796. ^{1}H-NMR: 1.39 (*t*, *J* = 7.2, 3 H); 1.68 (*t*, *J* = 7.0, 3 H); 4.39 (*q*, *J* = 7.2, 2 H); 4.64 (*q*, *J* = 7.0, 2 H); 7.79 (*s*, 1 H); 8.10 (*t*, *J* = 10.0, 1 H); 8.31 (*t*, *J* = 10.0, 1 H); 8.52 (*d*, *J* = 10.0, 1 H); 9.18 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.0; 14.5; 59.6; 70.4; 103.0; 104.4; 116.2; 118.9; 132.5; 132.6; 132.8; 133.0; 138.8; 140.8; 141.0; 148.3; 164.0; 173.1. LC/MS: 294 (M^+, 9), 293 (46, M^+), 220 (19), 219 (100), 193 (13), 164 (14). HR-EI-MS: 293.1060 (M^+, $C_{18}H_{15}NO_3^+$; calc. 293.1048).

*Diethyl 3,4-Dihydro-5-methylcyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**10a**). To a soln. of *ethyl 4-(2-ethoxy-2-oxoethyl)-3-(3-oxobutyl)azulene-1-carboxylate* (**9a**; 1 mmol, 0.356 g) in EtOH (4 ml) at r.t. was added EtONa (1.2 mmol, 0.081 g). The mixture was heated at 100° under reflux for 10 min. Then, the mixture was allowed to cool to r.t., diluted with H_2O (10 ml), and extracted with AcOEt. The combined org. layer was dried ($MgSO_4$), concentrated, and subjected to CC (SiO_2; hexane/AcOEt 2 : 1) to afford **10a** (0.209 g, 62%). Dark blue, viscous liquid. IR (KBr): 2980, 1710, 1685, 1562, 1468, 1073, 792. ^{1}H-NMR: 1.20 (*t*, *J* = 7.1, 3 H); 1.38 (*t*, *J* = 7.1, 3 H); 2.26 (*s*, 3 H); 2.62 (*t*, *J* = 5.6, 2 H); 3.10 (*t*, *J* = 6.1, 2 H); 4.18 (*q*, *J* = 7.2, 2 H); 4.32 (*q*, *J* = 7.2, 2 H); 7.06 (*d*, *J* = 10.1, 1 H); 7.22 (*t*, *J* = 9.6, 1 H); 7.40 (*t*, *J* = 9.6, 1 H); 8.14 (*s*, 1 H); 9.32 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 14.0; 14.2; 16.8; 22.6; 27.3; 34.2; 60.2; 114.2; 125.4; 127.8; 129.3; 131.4; 134.8; 135.2; 135.9; 141.9; 143.0; 148.8; 151.3; 165.6; 169.4. LC/MS: 338 (100, M^+).

*Diethyl 3,4-Dihydro-2,5-dimethylcyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**10b**). As described for **10a**; from **9b**. Yield: 78%. Dark-blue, viscous liquid. IR (KBr): 2979, 1713, 1687, 1563, 1460, 1413, 1382, 1262, 1210, 1093, 1073, 792. ^{1}H-NMR: 1.15 (*t*, *J* = 7.2, 3 H); 1.42 (*t*, *J* = 7.2, 3 H); 2.16 (*s*, 3 H); 2.60 (*t*, *J* = 5.7, 2 H); 2.64 (*s*, 3 H); 3.08 (*t*, *J* = 6.3, 2 H); 4.15 (*q*, *J* = 7.2, 2 H); 4.42 (*q*, *J* = 7.2, 2 H); 7.09 (*d*, *J* = 10.2, 1 H); 7.25 (*t*, *J* = 9.6, 1 H); 7.44 (*t*, *J* = 9.6, 1 H); 9.36 (*d*, *J* = 9.6, 1 H). ^{13}C-NMR: 13.9; 14.5; 15.1; 23.6; 27.3; 35.2; 59.8; 60.8; 114.9; 126.0; 128.4; 129.6;132.4; 134.5; 135.0; 135.6; 142.3; 142.8; 148.0; 151.0; 166.3; 169.7. LC/MS: 352 (100, M^+), 279 (66), 233 (33), 213 (63), 206 (66), 205 (38), 191 (43), 189 (69), 185 (45), 165 (64), 152 (45).

*Diethyl 2-Ethoxy-3,4-dihydro-5-methylcyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**10c**). Yield: 70%. Dark-blue, viscous liquid. IR (KBr): 2980, 1715, 1689, 1561, 1462, 1212, 1102, 1072, 793. ^{1}H-NMR: 1.21 (*t*, *J* = 7.1, 3 H); 1.48 (*t*, *J* = 7.1, 3 H); 1.68 (*t*, *J* = 7.0, 3 H); 2.62 (*t*, *J* = 5.8, 2 H); 2.72 (*s*, 3 H); 3.18 (*t*, *J* = 6.2, 2 H); 4.18 (*q*, *J* = 7.2, 2 H); 4.40 (*q*, *J* = 7.2, 2 H); 4.39 (*q*, *J* = 7.2, 2 H); 7.00 (*d*, *J* = 10.0, 1 H); 7.20 (*t*, *J* = 9.4, 1 H); 7.40 (*t*, *J* = 9.4, 1 H); 9.26 (*d*, *J* = 9.2, 1 H). ^{13}C-NMR: 14.2; 14.8; 15.4; 24.3; 27.9; 36.2; 59.6; 62.8;

71.4; 115.2; 125.8; 128.9; 129.9; 133.4; 134.9; 135.5; 136.4; 143.3; 143.8; 148.1; 151.4; 166.1; 169.9. LC/MS: 382 (100, M^+).

*Diethyl 1,2-Dihydro-2-(2-oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**12a**). To a soln. of *ethyl 4-(2-ethoxy-2-oxoethyl)-3-(3-oxobut-1-enyl)azulene-1-carboxylate* (**11a**; 1 mmol, 0.354 g) in DMF (3 ml) at r.t. was added CaH_2 (1.2 mmol, 0.050 g), and the mixture was heated at 170° under reflux for 10 min. Then, the mixture was allowed to cool to r.t., diluted with H_2O (10 ml), and extracted with AcOEt. The combined org. layer was dried ($MgSO_4$), concentrated, and submitted to CC (SiO_2; hexane/AcOEt 4:1) to afford **12a** (0.227 g, 64%). Dark-blue, viscous liquid. IR (KBr): 2978, 2931, 1734, 1683, 1454, 1406, 1210, 791. ^{1}H-NMR: 1.26 (*t*, *J* = 7.1, 3 H); 1.40 (*t*, *J* = 7.1, 3 H); 2.18 (*s*, 3 H); 2.66–2.69 (*m*, 1 H); 3.18–3.21 (*m*, 1 H); 4.24 (*d*, *J* = 7.1, 2 H); 4.36 (*q*, *J* = 7.1, 4 H); 7.23 (*d*, *J* = 10.0, 1 H); 7.28 (*t*, *J* = 10.0, 1 H); 7.59 (*t*, *J* = 10.0, 1 H); 8.08 (*s*, 1 H); 8.98 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 13.8; 14.8; 15.4; 29.8; 37.9; 48.2; 60.2; 64.2; 118.1; 122.4; 126.2; 134.2; 136.9; 137.2; 137.9; 144.8; 149.1; 150.1; 166.4; 171.9; 207.8. LC/MS: 355 (23, M^+), 354 (100, M^+).

*Diethyl 1,2-Dihydro-3-methyl-2-(2-oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**12b**). As described for **12a**; from **11b**. Yield: 82%. Dark-blue, viscous liquid. IR (KBr): 2979, 2932, 1732, 1685, 1595, 1545, 1513, 1455, 1407, 1207, 1164, 1130, 1069, 783. ^{1}H-NMR: 1.29 (*t*, *J* = 7.1, 3 H); 1.43 (*t*, *J* = 7.1, 3 H); 2.15 (*s*, 3 H); 2.69–2.72 (*m*, 1 H); 2.74 (*s*, 3 H); 3.20–3.22 (*m*, 1 H); 4.26 (*d*, *J* = 7.1, 2 H); 4.41 (*q*, *J* = 7.1, 4 H); 7.25 (*d*, *J* = 10.0, 1 H); 7.32 (*t*, *J* = 10.0, 1 H); 7.54 (*t*, *J* = 10.0, 1 H); 8.95 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.2; 14.6; 15.9; 30.1; 38.9; 48.6; 59.5; 61.4; 64.0; 118.0; 122.8; 126.0; 134.1; 136.8; 137.4; 138.2; 144.9; 148.9; 150.4; 166.2; 171.6, 207.3. LC/MS: 368 (100, M^+), 311 (53), 310 (25), 238 (19). HR-EI-MS: 368.4298 (M^+, $C_{22}H_{24}O_5^+$; 368.4324).

*Diethyl 3-Ethoxy-1,2-dihydro-2-(2-oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**12c**). As described for **12a**; from **11b**. Yield: 0.310 g (78%). Dark-blue, viscous liquid. IR (KBr): 2979, 2930, 1732, 1684, 1593, 1455, 1207, 1162, 1069, 78. ^{1}H-NMR: 1.26 (*t*, *J* = 7.2, 3 H); 1.40 (*t*, *J* = 7.2, 3 H); 1.72 (*t*, *J* = 7.2, 3 H); 2.70–2.73 (*m*, 1 H); 2.75 (*s*, 3 H); 3.21–3.23 (*m*, 1 H); 4.24 (*d*, *J* = 7.1, 2 H); 4.40 (*q*, *J* = 7.1, 4 H); 4.68 (*q*, *J* = 7.1, 2 H); 7.24 (*d*, *J* = 10.1, 1 H); 7.30 (*t*, *J* = 10.1, 1 H); 7.52 (*t*, *J* = 10.1, 1 H); 8.92 (*d*, *J* = 10.2, 1 H). ^{13}C-NMR: 14.0; 14.5; 16.1; 30.4; 38.7; 48.9; 60.2; 61.1; 64.4; 71.4; 117.8; 122.2; 125.8; 134.2; 136.1; 137.0; 138.1; 144.7; 148.6; 150.0; 166.1; 171.9; 207.4. LC/MS: 398 (100, M^+), 341 (52), 340 (20).

*Diethyl 2-(2-Oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**13a**). As described for **8**; from **12a**. Yield: 0.267 g (76%). Dark-green, viscous liquid. IR (KBr): 2986, 2361, 1772, 1686, 1457, 1375, 1054. ^{1}H NMR ($CDCl_3$, 300 MH_Z): 1.42 (*t*, *J* = 7.2, 6 H); 2.28 (*s*, 3 H); 4.48 (*q*, *J* = 7.1, 4 H); 4.50 (*s*, 2 H); 8.04 (*s*, 1 H); 8.12–8.22 (*m*, 2 H); 9.11–9.20 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 75 MH_Z): 14.4; 16.6; 29.4; 30.3; 44.6; 59.6; 120.2; 120.9; 134.2; 134.6; 134.9; 135.5; 135.7; 136.4; 143.5; 145.6; 153.4; 159.7; 165.2; 165.1; 204.0. LC/MS: 352 (100, M^+).

*Diethyl 2-Methyl-3-(2-oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**13b**). As described for **8**; from **12b**. Yield: 0.307 g (84%). Green solid. M.p. 112–113°. IR (KBr): 2987, 2362, 1770, 1683, 1457, 1378, 1243, 1168, 1110, 1056. ^{1}H-NMR: 1.44 (*t*, *J* = 7.1, 6 H); 2.29 (*s*, 3 H); 2.85 (*s*, 3 H); 4.45 (*q*, *J* = 7.1, 4 H); 4.53 (*s*, 2 H); 8.10–8.20 (*m*, 2 H); 9.10–9.20 (*m*, 2 H). ^{13}C-NMR: 14.5; 16.3; 29.6; 30.1; 44.8; 59.7; 59.9; 120.6; 120.7; 133.8; 134.0; 134.3; 135.0; 135.6; 136.6; 143.9; 145.8; 153.4; 159.5; 165.1; 165.4; 204.2. LC/MS: 366 (100, M^+), 324 (22), 320 (21), 248 (26), 177 (23). HR-EI-MS: 366.01289 (M^+, $C_{22}H_{22}O_5^+$; 366.01342).

*Diethyl 2-Ethoxy-3-(2-oxopropyl)cyclopenta[*cd*]azulene-1,4-dicarboxylate* (**13c**). As described for **8**; from **12c**. Yield: 0.285 g (72%). Green liquid. IR (KBr): 2985, 2366, 1772, 1684, 1450, 1110. ^{1}H-NMR: 1.40 (*t*, *J* = 7.2, 6 H); 1.69 (*t*, *J* = 7.2, 3 H); 2.30 (*s*, 3 H); 4.38 (*q*, *J* = 7.2, 4 H); 4.48 (*s*, 2 H); 4.68 (*q*, *J* = 7.1, 2 H); 8.06–8.16 (*m*, 2 H); 9.16–9.24 (*m*, 2 H). ^{13}C-NMR: 14.4; 17.2; 30.1; 30.4; 44.4; 59.1; 64.4; 71.2; 122.6; 122.9; 133.2; 134.1; 134.3; 135.3; 135.2; 135.9; 143.8; 145.9; 152.9; 160.1; 165.3; 165.2; 204.6. LC/MS: 396 (100, M^+).

*Diethyl 4-Acetyl-5,6-dihydrocyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**15a**). As described for **5**; from **14a**. Yield: 0.153 g (42%). Brown liquid. IR (KBr): 2977, 1730, 1680, 1651, 1210, 1055. ^{1}H-NMR: 1.18 (*t*, *J* = 7.1, 3 H); 1.44 (*t*, *J* = 7.1, 3 H); 2.50 (*s*, 3 H); 3.98–4.10 (*m*, 3 H); 4.41 (*q*, *J* = 7.2, 2 H); 4.46 (*q*, *J* = 7.2, 2 H); 7.30 (*d*, *J* = 10.0, 1 H); 7.54 (*t*, *J* = 10.0, 1 H); 7.64 (*t*, *J* = 10.0, 1 H); 8.06 (*s*, 1 H); 8.14 (*s*, 1 H); 9.51 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.1; 14.3; 15.5; 25.7; 28.9; 55.1; 60.5; 118.2; 123.1; 129.1; 133.8; 134.3; 135.0; 136.7; 137.7; 138.9; 145.0; 148.2; 154.0; 166.2; 171.4; 196.6. LC/MS: 366 (100, M^+).

*Diethyl 4-Acetyl-5,6-dihydro-2-methylcyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**15b**). As described for **5**; from **14b**. Yield: 0.182 g (48%). Brown liquid. IR (KBr): 2979, 1731, 1685, 1652, 1455, 1211, 1056, 744. ^{1}H-NMR: 1.08 (*t*, *J* = 7.1, 3 H); 1.45 (*t*, *J* = 7.1, 3 H); 2.51 (*s*, 3 H); 2.87 (*s*, 3 H); 3.94 – 4.01 (*m*, 3 H); 4.46 (*q*, *J* = 7.1, 2 H); 4.47 (*q*, *J* = 7.1, 2 H); 7.33 (*d*, *J* = 10.0, 1 H); 7.51 (*t*, *J* = 10.0, 1 H); 7.66 (*t*, *J* = 10.0, 1 H); 8.01 (*s*, 1 H); 9.50 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.0; 14.5; 15.0; 25.2; 28.4; 55.9; 60.3; 61.0; 118.7; 123.4; 128.9; 133.3; 133.8; 134.9; 136.9; 137.3; 138.6; 144.6; 148.7; 154.3; 166.0; 171.0; 197.0. LC/MS: 380 (30, M^+), 306 (48), 219 (18), 189 (100), 165 (41).

*Diethyl 4-Acetyl-2-ethoxy-5,6-dihydrocyclopenta[*ef*]heptalene-1,6-dicarboxylate* (**15c**). As described for **5**; from **14c**. Yield: 0.164 g (40%). Brown liquid. IR (KBr): 2977, 1728, 1680, 1450, 1210, 1051, 744. ^{1}H-NMR: 1.18 (*t*, *J* = 7.1, 3 H); 1.54 (*t*, *J* = 7.1, 3 H); 1.72 (*t*, *J* = 7.2, 3 H); 2.56 (*s*, 3 H); 3.89 – 4.01 (*m*, 3 H); 4.40 (*q*, *J* = 7.1, 2 H); 4.49 (*q*, *J* = 7.1, 2 H); 4.70 (*q*, *J* = 7.1, 2 H); 7.30 (*d*, *J* = 10.0, 1 H); 7.50 (*t*, *J* = 10.0, 1 H); 7.65 (*t*, *J* = 10.0, 1 H); 8.06 (*s*, 1 H); 9.51 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.2; 14.8; 15.1; 25.4; 27.9; 56.0; 60.0; 61.2; 71.2; 118.0; 123.1; 129.0; 133.1; 133.4; 134.6; 136.7; 137.0; 138.1, 144.3; 148.2; 154.1; 166.1; 171.9; 196.8. LC/MS: 410 (100, M^+), 321 (40), 229 (12).

*Ethyl 4-Acetyl-5,6-dihydrocyclopenta[*ef*]heptalene-1-carboxylate* (**16a**). As described for **5**; from **14a**. Yield: 0.053 g (18%). Brown solid. M.p. 113 – 114°. IR (KBr): 2980, 1688, 1585, 1418, 1211, 1080, 744. ^{1}H-NMR: 1.43 (*t*, *J* = 7.1, 3 H); 2.48 (*s*, 3 H); 3.00 (*t*, *J* = 7.1, 2 H); 3.30 (*t*, *J* = 7.1, 2 H); 4.41 (*q*, *J* = 7.1, 2 H); 7.40 (*d*, *J* = 10.0, 1 H); 7.52 (*t*, *J* = 10.0, 1 H); 7.74 (*t*, *J* = 10.0, 1 H); 7.85 (*s*, 1 H); 8.38 (*s*, 1 H); 9.74 (*dd*, *J* = 1.2, 10.0, 1 H). ^{13}C-NMR: 14.5; 14.8; 25.2; 26.4; 40.3; 60.2; 118.1; 123.8; 128.2; 132.6; 133.9; 136.5; 137.9; 139.1; 143.7; 153.6; 153.7; 166.1, 197.5. LC/MS: 294 (53, M^+), 279 (42), 251 (68), 178 (88), 152 (100).

*Ethyl 4-Acetyl-5,6-dihydro-2-methylcyclopenta[*ef*]heptalene-1-carboxylate* (**16b**). As described for **5**; from **14b**. Yield: 0.064 g (21%). Brown solid. M.p. 108 – 109°. IR (KBr): 2980, 1688, 1652, 1455, 1211, 1080. ^{1}H-NMR: 1.45 (*t*, *J* = 7.1, 3 H); 2.51 (*s*, 3 H); 2.87 (*s*, 3 H); 2.98 (*t*, *J* = 7.1, 2 H); 3.24 (*t*, *J* = 7.1, 2 H); 4.46 (*q*, *J* = 7.1, 2 H); 7.33 (*d*, *J* = 10.0, 1 H); 7.43 (*t*, *J* = 10.0, 1 H); 7.61 (*t*, *J* = 10.0, 1 H); 7.99 (*s*, 1 H); 9.42 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.5; 14.8; 25.2; 26.4; 40.3; 60.2; 118.1; 123.8; 128.2; 132.6; 133.9; 136.5; 137.9; 139.1; 143.7; 153.6; 153.7; 166.1; 197.5. LC/MS: 308 (14, M^+), 294 (60), 279 (42), 223 (62), 178 (100), 152 (71).

*Ethyl 4-Acetyl-5,6-dihydro-2-ethoxycyclopenta[*ef*]heptalene-1-carboxylate* (**16c**). As described for **5a**; from **14c**. Yield: 0.094 g (28%). Brown, viscous liquid. IR (KBr): 2982, 1686, 1650, 1451, 1209. ^{1}H-NMR: 1.41 (*t*, *J* = 7.2, 3 H); 2.50 (*s*, 3 H); 1.72 (*t*, *J* = 7.2, 3 H); 2.89 (*t*, *J* = 7.1, 2 H); 3.20 (*t*, *J* = 7.1, 2 H); 4.40 (*q*, *J* = 7.1, 2 H); 4.72 (*q*, *J* = 7.1, 2 H); 7.30 (*d*, *J* = 10.0, 1 H); 7.41 (*t*, *J* = 10.0, 1 H); 7.64 (*t*, *J* = 10.0, 1 H); 8.00 (*s*, 1 H); 9.40 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR: 14.2; 14.9; 25.6; 26.0; 40.7; 57.1; 61.0; 70.2; 118.7; 123.1; 128.0; 132.1; 133.0; 136.2; 137.0; 139.9; 143.8; 153.5; 153.4; 166.0; 197.0. LC/MS: 338 (100, M^+), 224 (40), 299 (22).

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