A Divergent Method for Preparing 1-Aryl- and 1,3-Diarylazulenes from Ethyl 3-(Cyclohepta-1,3,5-trien-1-yl)-3-oxopropionate

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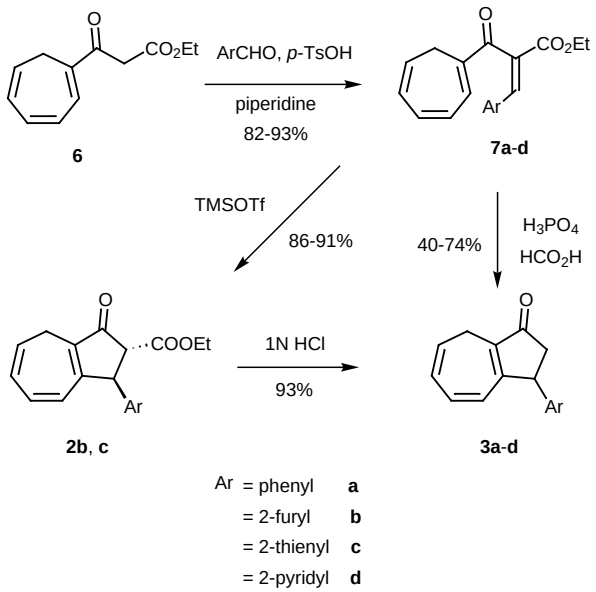
Abstract: The 3-aryl substituted 1,2,3,8-tetrahydroazulen-1-ones **3**, prepared by the Knoevenagel condensation of ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-3-oxopropionate (**6**) with arylaldehydes and subsequent Nazarov cyclization, were efficiently transformed into 1-aryl- and 1,3-diarylazulenes in a few steps.

Key words: azulenes, azulenones, Nazarov cyclization, dehydrogenation

Although tetrahydroazulen-1-ones[1] can be used as synthetic intermediates for azulenes,[2] homoazulenes,[3] bridged homotropylium cations,[4] and guaiazulene-type sesquiterpenes,[5] there are only a few convenient methods for their preparation.[2,6,7] We reported a synthetic pathway from 1-acryloylcyclohepta-1,3,5-triene, prepared from commercially available cyclohepta-1,3,5-triene (**1**) in four steps, to the tetrahydroazulen-1-ones.[6] The method involves the Nazarov cyclization[8] as a key step for constructing the bicyclic carbon framework. Also, we extended its application to synthesis of the substituted derivatives,[7] that makes it possible to obtain 3-aryl-2-ethoxycarbonyl-1,2,3,8-tetrahydroazulen-1-ones **2** from **1** quite easily. Herein we wish to report the synthesis of 3-aryl-1,2,3,8-tetrahydroazulen-1-ones **3** and their efficient transformations into 1-aryl- and 1,3-diarylazulenes **4** and **5** which may be used to synthesize π-conjugated oligomers and polymers.[9] These materials, particularly ones containing heterols and azulene as a monomeric unit, are of significant interest because of their electric and optical properties.[10]

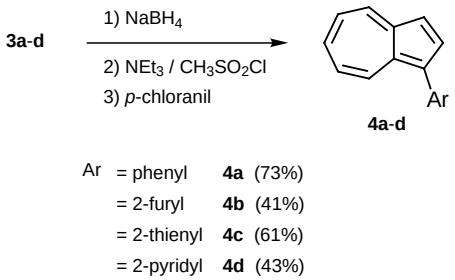
The starting material, ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-3-oxopropionate (**6**), for this work can be prepared from **1** in good yield by the Friedel–Crafts acetylation and subsequent ethoxycarbonylation.[7] Reaction of **6** with aryl aldehydes under the influence of piperidine and *p*-toluenesulfonic acid gave the arylidene derivatives **7a–d** in good yields (82−93%).[11,12] While heating **7a** and **7d** in a mixture of phosphoric acid and formic acid at 90 °C for 2 h gave the tetrahydroazulen-1-ones **3a** and **3d** in moderate yields, the reaction of **7b** and **7c** under the same conditions afforded an intractable reaction mixture, probably because of the acid-sensitive nature of the electron-rich heteroles. Thus, **3b** and **3c** were obtained from **7b** and **7c** via **2b** and **2c**, respectively, in good yields. The Nazarov cyclization of **7b** and **7c** with trimethylsilyl triflate at room temperature gave the esters **2b** and **2c**,[13] which were



Scheme 1

then hydrolyzed and decarboxylated in methanolic hydrochloric acid (70 °C, 5 h) to give **3b** and **3c** (Scheme 1).

The 1-arylazulenes **4a–d** were obtained from the corresponding tetrahydroazulen-1-ones **3a–d** in moderate to good yields by a sequence involving reduction with $NaBH_4$, dehydration with methanesulfonyl chloride and triethylamine, and dehydrogenation with *p*-chloranil (Scheme 2).

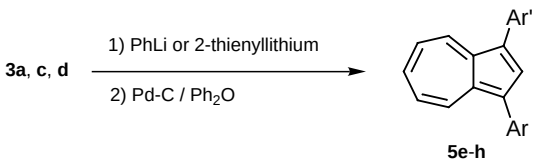


Scheme 2

The new 1-arylazulenes **4b–d** were fully characterized by spectroscopic and elemental analyses and the 1-phenyl-

azulene (**4a**)[14] was confirmed by comparison with authentic data. It is noteworthy that the dehydration of the intermediary secondary alcohols with phosphoryl chloride and pyridine, thionyl chloride and triethylamine, and only acids, such as *p*-toluenesulfonic acid or trifluoroacetic acid, gave lower yields of **4**. While Scott et al. reported a one-pot procedure from 1,2,3,4-tetrahydroazulen-1-one to azulene simply by warming with phosphorous pentaoxide in methanesulfonic acid,[2b] application of this method for **3** resulted in formation of a gummy polymeric material and none of **4**. Furthermore, the Shapiro reaction[15] of the tosylhydrazones of **3** and subseqent dehydrogenation with *o*- or *p*-chloranil were carried out; however, the yields of **4** were less than 10%.

On the other hand, the 1,2,3,8-tetrahydroazulen-1-ones **3a**, **3c**, and **3d** were reacted with phenyl- or 2-thienyllithium[16] to give the intermediary tertiary alcohols which were treated with a catalytic amount of Pd-C in refluxing diphenyl ether[17] to produce the 1,3-diarylazulenes **5e–h** as the sole isolable products in 31–68% yields (Scheme 3). The yields of **5e–h** are greater than those of 1-methyl- and 1,6-dimethylazulenes which were obtained by CH_3MgCl addition to 1,2,3,4-tetrahydroazulen-1-one and its 6-methyl derivative and subsequent vapor-phase reaction with Pd–C, reported by Scott et al.[2b] The sole production of **5e–h** in the dehydration–dehydrogenation is contrary to the case in which the secondary alcohols obtained by $NaBH_4$ reduction of **3a-d** gave a mixture of 1- and 2-arylazulenes under the same reaction conditions of this dehydration-dehydrogenation reaction. Although a phenyl group migration of 1- and 2-phenylazulenes above 300 °C has been documented,[18] the reluctance of 1,3-diarylazulenes to rearrange under similar conditions has been disclosed for the first time. Daub et al.[9c] have recently reported that **5e** could be synthesized by palladium-catalyzed coupling of phenylboronic acid and a mixture of azulene, 1-bromoazulene and 1,3-dibromoazulene, prepared by *N*-bromosuccimide bromination of azulene, in 32% yield, along with a 27% yield of 1-phenylazulene. However, this method is not suitable for synthesizing unsymmetrical 1,3-disubstituted azulenes. In contrast to Daub's method, our pathway provides the desired 1,3-diarylazulenes from the ester **6** simply by choosing an arylaldehyde for the Knoevenagel condensation and an aryllithium in the addition reaction to the 3-aryl-1,2,3,8-tetrahydroazulen-1-ones.



Ar = Ar' = phenyl	**5e**	(68%)
Ar = phenyl, Ar' = 2-furyl	**5f**	(31%)
Ar = phenyl, Ar' = 2-thienyl	**5g**	(42%)
Ar = Ar' = 2-thienyl	**5h**	(38%)

Scheme 3

In conclusion, we have shown that it is possible to convert commercially available cyclohepta-1,3,5-triene (**1**) into 1-aryl-1,2,3,8-tetrahydroazulen-1-ones **3** in four- or five-step reactions involving the Nazarov cyclization as a key step for constructing the bicyclic skeleton and that these azulenones serve as versatile synthetic intermediates for a wide variety of 1-aryl- and 1,3-diarylazulenes. In comparison with other synthetic approaches, our method offers a divergent way to unsymmetrical 1,3-disubstituted azulenes. Oligomerizations and polymerizations of these azulenes are the focus of current investigation.

Mps were uncorrected. IR spectra were recorded on a JASCO IR-810 spectrometer; ^1H (400 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Jeol A400 spectrometer by use of $CDCl_3$ as solvent and TMS as internal standard; Mass spectra were recorded by Jeol JMS-D-300 and JMS-GC Mate spectrometers. Ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-3-oxopropionate (**6**), ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-2-arylidene-3-oxopropionates **7a**, and **7b**, and 2-ethoxycarbonyl-3-furyl-1,2,3,8-dihydroazulen-1-ones **2b** were prepared by the reported method.[7] A solution of phenyllithium in cyclohexane–diethyl ether was purchased from Aldrich and titrated before use. A solution of 2-thienyllithium in diethyl ether was prepared from thiophene and BuLi by the literature method.[15] A solution of BuLi in hexane was purchased from Merck and titrated before use.

The Knoevenagel Condensation of 6 with Aldehydes; Typical Procedure

A mixture of **6** (20 mmol), the aldehyde (20 mmol), piperidine (0.8 mL), and TsOH (0.02 g) in benzene (20 mL) was refluxed with a Dean–Stark apparatus until water was not trapped. The mixture was poured into water and extracted with benzene (3 × 30 mL). The combined organic layer was washed with brine and dried ($MgSO_4$). The solvent was removed and the residual oil was purified by silica gel chromatography (hexane/EtOAc, 8:2) to give **7c** and **7d**.

***(E)*-Ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-2-(2-thienyl)methylene-3-oxopropionate (7c)**

Yield 94%; a pale yellow oil.

IR (liq. film): ν = 1720s, 1655s, 1620s, 1250s, 1205s cm^{-1}.

^1H NMR: δ = 1.21 (t, *J* = 7.2 Hz, 3H), 2.86 (d, *J* = 6.8 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 5.68 (dt, *J* = 8.8, 6.8 Hz, 1H), 5.82 (dd, *J* = 9.2, 5.6 Hz, 1H), 6.59 (dd, *J* = 11.2, 6.0 Hz, 1H), 6.84 (dd, *J* = 11.2, 6.0 Hz, 1H), 7.00 (ddd, *J* = 4.8, 3.6, 1.6 Hz, 1H), 7.04 (d, *J* = 5.6 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.41 (d, *J* = 4.8 Hz, 1H), 7.91 (s, 1H).

^{13}C NMR: δ = 14.1, 25.1, 61.4, 126.0, 127.4, 127.7, 128.6, 129.1, 130.9, 131.3, 133.7, 134.1, 135.8, 136.4, 136.7, 165.0, 194.5.

UV-Vis (MeOH): λ (logε) = 274 (4.10), 316 (4.31) nm.

MS (EI): *m/z* (%) = 300 (M^+, 28), 254 (66), 226 (14), 198 (15), 186 (20), 149 (24), 137 (13), 118 (100), 90 (51), 65 (23).

HRMS calcd. for $C_{17}H_{16}O_3S$ *m/z* 300.0820; found 300.0775.

***(E)*-Ethyl 3-(cyclohepta-1,3,5-trien-1-yl)-2-(2-pyridyl)methylene-3-oxopropionate (7d)**

Yield 86%; an orange oil.

IR (liq. film): ν = 1715s, 1660s, 1255s, 1210s, 760s cm^{-1}.

^1H NMR: δ = 1.24 (t, *J* = 7.2 Hz, 3H), 2.87 (d, *J* = 6.8 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 5.65 (dt, *J* = 9.6, 6.8 Hz, 1H), 6.22 (dd, *J* = 9.6, 5.6 Hz, 1H), 6.52 (dd, *J* = 11.2, 6.0 Hz, 1H), 6.74 (dd, *J* = 11.2, 5.6

Hz, 1H), 6.85 (d, *J* = 6.0 Hz, 1H), 7.15 (ddd, *J* = 7.6, 4.8, 0.8 Hz, 1H), 7.35 (dm, *J* = 7.6 Hz, 1H), 7.64 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.74 (s, 1H), 8.44 (dm, *J* = 4.0 Hz, 1H).

^{13}C NMR: δ = 14.0, 25.4, 61.6, 123.8, 125.7, 125.9, 127.0, 129.1, 132.1, 133.1, 135.2, 135.5, 136.5, 139.6, 149.4, 151.5, 164.9, 193.9.

UV-Vis (MeOH): λ (logε) = 256sh (4.10), 295 (4.20), 453 (1.82) nm.

MS (EI): *m/z* (%) = 295 (M^+, 11), 248 (19), 221 (24), 217 (100), 193 (50), 145 (56), 91 (50).

HRMS calcd. for $C_{18}H_{17}NO_3$ m/z 295.1209; found 295.1209.

The Nazarov Cyclization of 7 in a Mixture of Phosphoric Acid and Formic Acid; Typical Procedure

A solution of **7** (10.0 mmol) in phosphoric acid (85%, 40 mL) and formic acid was stirred at 90 °C for 2 h, and then was poured into H_2O and extracted with Et_2O (3 × 100 mL). The combined organic layer was washed with sat. $NaHCO_3$ and brine, and was dried ($MgSO_4$). The solvent was removed and the residue was purified by chromatography on silica gel (hexane/EtOAc, 8:2) to give **3a** and **3d**.

(±)-3-Phenyl-1,2,3,8-tetrahydroazulen-1-one (3a)
Yield 74%; colorless oil.

IR (liq. film): ν = 1690s, 700s cm^{-1}.

^{1}H NMR: δ = 2.48 (dd, *J* = 18.8, 2.4 Hz, 1H), 2.71 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.93 (dd, *J* = 14.4, 6.8 Hz, 2H), 3.03 (dd, *J* = 18.8, 6.8 Hz, 1H), 4.05 (d, *J* = 6.8 Hz, 1H), 5.69 (dt, *J* = 10.0, 6.4 Hz, 1H), 6.15 (dd, *J* = 9.6, 6.0 Hz, 1H), 6.35 (d, *J* = 11.2 Hz, 1H), 6.67 (dd, *J* = 11.2, 6.0 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR: δ = 21.9, 45.4, 46.6, 127.1, 127.5, 127.79 (2C), 127.84, 128.9, 133.2, 136.7, 142.2, 165.9, 206.7.

UV-Vis (MeOH): λ (logε) = 216 (4.31), 296 (3.78) nm.

MS (EI): *m/z* (%) = 222 (M^+, 100), 179 (49).

HRMS calcd. for $C_{16}H_{14}O$ m/z 222.1045; found 222.1064.

(±)-3-(2-Pyridyl)-1,2,3,8-tetrahydroazulen-1-one (3d)
Yield 40%; yellow needles; mp = 60-61 °C.

IR (KBr): ν = 1675s, 750s cm^{-1}.

^{1}H NMR: δ = 2.70 (dd, *J* = 18.8, 2.4 Hz, 1H), 2.72 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.93 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.02 (dd, *J* = 18.8, 7.2 Hz, 1H), 4.27 (dm, *J* = 5.2 Hz, 1H), 5.68 (dt, *J* = 10.0, 6.4 Hz, 1H), 6.15 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.38 (d, *J* = 11.2 Hz, 1H), 6.68 (dd, *J* = 11.2, 6.0 Hz, 1H), 7.05 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.18 (ddd, *J* = 7.6, 5.2, 1.2 Hz, 1H), 7.64 (td, *J* = 7.6, 2.0 Hz, 1H), 8.56 (dm, *J* = 4.8 Hz, 1H).

^{13}C NMR: δ = 22.0, 44.6, 47.6, 122.0, 122.1, 127.4, 127.8, 127.9, 133.4, 136.8, 136.9, 149.8, 161.3, 164.6, 206.4.

UV-Vis (MeOH): λ (logε) = 257sh (3.74), 264 (3.79), 270 (3.76), 302 (3.62) nm.

MS (EI): *m/z* (%) = 223 (M^+, 26), 194 (78), 180 (100).

Anal. Calc. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 81.01; H, 5.98; N, 6.17.

The Nazarov Cyclization of 7 Using Trimethylsilyl Triflate; Typical Procedure

Trimethylsilyl triflate (10.5 mmol) was added dropwise to a solution of **7** (10.0 mmol) in CH_2Cl_2 (100 mL) at r.t. This mixture was stirred at the same temperature for 0.5 to 2 h under N_2, and then was poured into sat. $NaHCO_3$ (150 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was washed with brine. After drying (Na_2SO_4) and removal of the solvent, the residue was purified by silica gel chromatography (hexane/EtOAc, 8:2) to give **2c**.

(±)-(2R*,3S*)-2-Ethoxycarbonyl-3-(2-thienyl)-1,2,3,8-tetrahydroazulen-1-one (2c)
Yield 91%; yellow prisms; mp 66-67 °C.

IR (KBr): ν = 1730s, 1690s, 1610s, 1540s, 1250s, 1150s, 720s cm^{-1}.

^{1}H NMR: δ = 1.30 (t, *J* = 7.2 Hz, 3H), 2.79 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.84 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.56 (d, *J* = 2.8 Hz, 1H), 4.22 (m, 2H), 4.80 (d, *J* = 2.8 Hz, 1H), 5.69 (dt, *J* = 10.0, 6.4 Hz, 1H), 6.18 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.50 (d, *J* = 11.2 Hz, 1H), 6.76 (dd, *J* = 11.2, 6.0 Hz, 1H), 6.85 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.94 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.21 (dd, *J* = 4.8, 1.2 Hz, 1H).

^{13}C NMR: δ = 14.2, 22.2, 44.4, 61.9, 63.3, 125.1, 125.6, 127.0, 127.1, 127.9, 128.0, 130.6, 137.9, 143.7, 164.5, 168.0, 198.0.

UV-Vis (MeOH): λ (logε) = 228 (4.28), 308 (3.75) nm.

MS (EI): *m/z* (%) = 300 (M^+, 100), 225 (12), 226 (55), 198 (32), 165 (26), 115 (18), 60 (81).

Anal. Calc. for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.87. Found: C, 67.86; H, 5.37.

Removal of the Ethoxycabonyl Group of 2 with Hydrochloric Acid; Typical Procedure

A solution of **2** (5.00 mmol) in a mixure of 1N HCl (100 mL) and CH_3OH (100 mL) was refluxed for 5 h, and then the solvent was removed. The residue was poured into H_2O and extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with sat. $NaHCO_3$ and brine, and was dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography on silica gel (hexane/ EtOAc, 8:2) to give **3b** and **3c**.

(±)-3-(2-Furyl)-1,2,3,8-tetrahydroazulen-1-one (3b)
Yield 93%; a pale yellow oil.

IR (liq. film): ν = 1710s, 1620s, 1280s, 750s, 710s cm^{-1}.

^{1}H NMR: δ = 2.667 (dd, *J* = 18.8, 2.4 Hz, 1H), 2.670 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.90 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.92 (dd, *J* = 18.8, 7.2 Hz, 1H), 4.17 (dd, *J* = 7.2, 2.4 Hz, 1H), 5.65 (dt, *J* = 10.0, 6.4 Hz, 1H), 6.08 (dd, *J* = 2.8, 0.8 Hz, 1H), 6.16 (d, *J* = 10.0, 6.0 Hz, 1H), 6.31 (dd, *J* = 2.8, 2.0 Hz, 1H), 6.56 (d, *J* = 11.2 Hz, 1H), 6.74 (dd, *J* = 11.6, 6.06 Hz, 1H), 7.34 (dd, *J* = 2.0, 0.8 Hz, 1H).

^{13}C NMR: δ = 21.9, 38.7, 42.7, 106.3, 110.3, 127.3, 127.7, 127.8, 132.8, 136.8, 142.1, 154.2, 162.8, 205.7.

UV-Vis (MeOH): λ (logε) = 221 (4.34), 303 (3.68) nm.

MS (EI): m/z (%) = 212 (M^+, 100), 183 (14), 170 (16), 155 (18), 141 (52), 128 (14), 115 (34).

HRMS calcd. for $C_{14}H_{12}O_2$ m/z 212.0837, found 212.0857.

(±)-3-(2-Thienyl)-1,2,3,8-tetrahydroazulen-1-one (3c)
Yield 93%; an yellow oil.

IR (liq. film): ν = 1700s, 1620s, 1280s, 700s cm^{-1}.

^{1}H NMR: δ = 2.58 (dd, *J* = 18.8, 2.4 Hz, 1H), 2.68 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.92 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.06 (dd, *J* = 18.8, 7.6 Hz, 1H), 4.37 (dm, *J* = 7.2 Hz, 1H), 5.66 (dt, *J* = 10.0, 6.0 Hz, 1H), 6.16 (dd, *J* = 10.0, 6.4 Hz, 1H), 6.51 (d, *J* = 11.2 Hz, 1H), 6.72 (dd, *J* = 11.2, 6.0 Hz, 1H), 6.82 (dm, *J* = 3.2 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.18 (dm, *J* = 5.2 Hz, 1H).

^{13}C NMR: δ = 21.6, 40.4, 49.9 124.4, 124.8, 127.0, 127.4, 127.7, 127.8, 132.5, 137.0, 145.7, 164.7, 205.6.

UV-Vis (MeOH): λ (logε) = 225 (4.34), 303 (3.77) nm.

MS (EI): *m/z* (%) = 228 (M^+, 100), 185 (25), 144 (11). 115 (14), 60 (42).

HRMS calcd. for $C_{14}H_{12}OS$ m/z 228.0609; found 228.0576.

Transformation of 3-Aryl-1,2,3,8-tetrahydroazulen-1-ones (3) into 3-Arylazulenes (4); Typical Procedure

A solution of **3** (1.00 mmol) in MeOH (10 mL) was added dropwise to a suspension of $NaBH_4$ (1.20 mmol) in MeOH (5 mL) at 0 °C. This mixture was stirred at the same temp. for 1 h, and then was poured into sat. $NaHCO_3$ and extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with brine and was dried ($MgSO_4$). The solvent was removed and the residue was dissolved in CH_2Cl_2 (20 mL). To this solution at 0 °C was added Et_3N (6.00 mmol), followed by dropwise addition of methanesulfonyl chloride (1.20 mmol). This reaction solution was stirred at r.t. for 3 h. Then, *p*-chloranil (1.20 mmol) was added to this mixture which was further stirred at r.t. for 10 to 15 h. The resulted dark-colored reaction mixture was poured into water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with brine and was dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography on silica gel (hexane or hexane/EtOAc, 8:2) to give **4a–4d**.

1-Phenylazulene (4a)[14]

Yield 73%; blue leaflets; mp 56-57 °C (lit. 58 °C).

^{1}H NMR: δ = 7.15 (t, *J* = 10.0 Hz, 1H), 7.16 (t, *J* = 10.0 Hz, 1H), 7.35 (tm, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 1H), 7.50 (tm, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 10.0 Hz, 1H), 7.62 (dm, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 4.0 Hz, 1H), 8.36 (d, *J* = 10.0 Hz, 1H), 8.56 (d, *J* = 10.0 Hz, 1H).

^{13}C NMR: δ = 117.4, 123.0, 123.3, 126.3, 128.6, 129.8, 131.3, 135.2, 135.6, 137.1, 137.3, 137.5, 138.2, 141.7.

1-(2-Furyl)azulene (4b)

Yield 41%; a green oil.

IR (liq. film): ν = 1580s, 1400, 740s cm^{-1}.

^{1}H NMR: δ = 6.47 (m, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.97 (t, *J* = 9.6 Hz, 1H), 7.05 (t, *J* = 9.6 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.43 (t, *J* = 9.6 Hz, 1H), 7.49 (dd, *J* = 1.6, 0.8 Hz, 1H), 8.08 (d, *J* = 4.0 Hz, 1H), 8.13 (d, *J* = 9.6 Hz, 1H), 8.86 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR: δ = 105.4, 111.4, 118.2, 119.8, 123.5m 123.6, 133.4, 135.1, 136.2, 137.1, 138.4, 141.1, 142.3, 152.6.

UV-Vis (hexane): λ (logε) = 243 (4.43), 288 (4.38), 299sh (4.34), 309 (4.37), 321 (4.32), 328sh (4.27), 335 (4.17), 363sh (3.78), 385 (3.97), 401 (3.90), 407 (3.91), 586sh (2.35), 610sh (2.39), 637 (2.42), 675sh (2.31), 702sh (2.26), 751sh (1.83), 798 (1.62) nm.

MS (EI): *m*/*z* (%) = 194 (M$^+$, 76), 165 (100).

4b·1,3,5-trinitrobenzene Complex

Black leaflets, mp 102-104 °C.

Anal. Calc. for $C_{20}H_{13}N_3O_7$: C, 58.97; H, 3.22; N, 10.32. Found: C, 59.01; H, 3.26; N, 10.23.

1-(2-Thienyl)azulene (4c)

Yield 61%; greenish blue plates; mp 34-35 °C.

IR (KBr): ν = 790s, 740s, 690s cm^{-1}.

^{1}H NMR: δ = 7.14 (t, *J* = 9.6 Hz, 1H), 7.17 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.18 (t, *J* = 9.6 Hz, 1H), 7.28 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.34 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.59 (t, *J* = 9.6 Hz, 1H), 8.04 (d, *J* = 3.6 Hz, 1H), 8.30 (d, *J* = 9.6 Hz, 1H), 8.74 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR: δ = 117.8, 123.5, 123.58, 123.63, 124.4, 124.5, 127.7, 135.0, 135.7, 137.3, 137.4, 138.5, 139.7, 142.2.

UV-Vis (hexane): λ (logε) = 204 (4.30), 248 (4.37), 295sh (4.39), 305 (4.43), 327sh (4.15), 382 (3.84), 414sh (3.16), 618 (2.44), 675sh (2.31), 757sh (1.72) nm.

MS (EI): *m*/*z* (%) = 210 (M$^+$, 100), 165 (20), 76 (36), 69 (53), 64 (79), 60 (68), 54 (40).

Anal. Calc. for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 79.88; H, 4.93.

1-(2-Pyridyl)azulene (4d)

Yield 43%; a purple oil.

IR (liq. film): ν = 1590s, 1515s, 1480s, 1400s, 780s cm^{-1}.

^{1}H NMR: δ = 7.14 (dd, *J* = 4.8, 4.0 Hz, 1H), 7.22 (t, *J* = 9.6 Hz, 1H), 7.31 (t, *J* = 9.6 Hz, 1H), 7.42 (d, *J* = 4.0 Hz, 1H), 7.65 (t, *J* = 9.6 Hz, 1H), 7.73 (dm, *J* = 3.6 Hz, 2H), 8.25 (d, *J* = 4.0 Hz, 1H), 8.37 (d, *J* = 9.6 Hz, 1H), 8.74 (dm, *J* = 5.2 Hz, 1H), 9.56 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR: δ = 117.8, 120.2, 123.1, 124.1, 125.2, 128.0, 136.30, 136.34, 136.7, 137.5, 137.7, 138.6, 143.2, 149.4, 156.6.

UV-Vis (hexane): λ (logε) = 217sh (4.20), 232 (4.28), 243 (4.27), 294 (4.43), 311 (4.43), 317sh (4.39), 324 (4.35), 379 (4.11), 398sh (3.87), 547sh (2.41), 564sh (2.45), 590 (2.52), 613sh (2.44), 646sh (2.42), 684sh (1.99), 703 (1.84), 718 (1.98) nm.

MS (EI): *m*/*z* (%) = 205 (M$^+$, 54), 204 (100), 60 (33).

HRMS calcd. for $C_{15}H_{11}N$ *m*/*z* 205.0892, found 205.0896.

Transformation of 3-Aryl-1,2,3,8-tetrahydroazulen-1-ones (3) into 1,3-Diarylazulenes (5); Typical Procedure

A solution of either PhLi or 2-thienyllithium (1.05 mmol) in cyclohexane-diethyl ether or THF was added to a solution of **3** (1.00 mmol) in THF (15 mL) at 0 °C. This mixture was stirred at r.t. for 1 h under N_2, and then was poured into H_2O and extracted with Et_2O (3 × 30 mL). The combined organic layer was washed with brine and was dried ($MgSO_4$). The solvent was removed and the residue was dissolved in diphenyl ether (5 mL). To this solution was added a catalytic amount of 5% Pd–C (0.05 g), and this mixture was refluxed on an oil bath for 1 h under N_2. After being cooled to r.t., the resulted mixture was filtrated to remove solids. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane) to give **5e–5h**.

1,3-Diphenylazulene (5e)[9c]

Yield 68%; mp 117-118 °C (lit. 100-102 °C).

^{1}H NMR: δ = 7.12 (t, *J* = 10.0 Hz, 2H), 7.37 (tm, *J* = 7.6 Hz, 2H), 7.51 (tm, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 10.0 Hz, 1H), 7.65 (dm, *J* = 7.6 Hz, 4H), 8.12 (s, 1H), 8.55 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR: δ = 123.5, 126.5, 128.7, 129.9, 130.6, 136.2, 136.7, 137.17, 137.22, 139.0.

3-Phenyl-1-(2-furyl)azulene (5f)

Yield 31%; a green oil.

IR (liq. film): ν = 1575s, 770s, 740s, 710s cm^{-1}.

^{1}H NMR: δ = 6.55 (ddd, *J* = 3.2, 1.6, 0.8 Hz, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 7.07 (t, *J* = 9.6 Hz, 1H), 7.13 (t, *J* = 9.6 Hz, 1H), 7.36 (tm, *J* = 7.6 Hz, 1H), 7.49 (tm, *J* = 8.0 Hz, 2H), 7.56 (m, 4H), 8.21 (s, 1H), 8.43 (d, *J* = 9.6 Hz, 1H), 8.92 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR: δ = 105.9, 111.5, 119.0, 123.8, 124.1, 126.6, 128.6, 129.9, 131.3, 134.8, 135.1, 136.3, 136.9 (2C), 137.7, 139.3, 141.4, 152.3.

UV-Vis (hexane): λ (logε) = 222 (4.23), 256sh (4.28), 276sh (4.48), 292 (4.51), 300sh (4.48), 330 (4.25), 394 (3.88), 414sh (3.80), 600sh (2.33), 651 (2.42), 720sh (2.25), 812sh (1.64) nm.

MS (EI): *m*/*z* (%) = 270 (M$^+$, 100), 239 (35), 165 (15).

5f·1,3,5-trinitrobenzene Complex

Black leaflets; mp 106-107 °C.

Anal. Calc. for $C_{26}H_{17}N_3O_7$: C, 64.60; H, 3.54; N, 8.69. Found: C, 64.38; H, 3.57; N, 8.76.

3-Phenyl-1-(2-thienyl)azulene (5g)

Yield 42%, green plates, mp 88-89 °C.

IR (kBr): ν = 855s, 790s, 760s, 735s, 700s cm^{-1}.

^1H NMR: δ = 7.11 (t, *J* = 10.0 Hz, 1H), 7.15 (t, *J* = 10.0 Hz, 1H), 7.19 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.31 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.37 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 10.0 Hz, 1H), 7.62 (dm, *J* = 7.6 Hz, 2H), 8.14 (s, 1H), 8.49 (d, *J* = 9.2 Hz, 1H), 8.74 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR: δ = 122.7, 123.8, 124.0, 124.7, 124.9, 126.6, 127.7, 128.7, 129.9, 130.9, 136.28, 136.30, 136.4, 136.8, 137.2, 137.3, 139.2, 139.3.

UV-Vis (hexane): λ (logε) = 203 (4.42), 233 (4.22), 295 (4.45), 335sh (4.12), 388 (3.82), 594sh (2.32), 635 (2.39), 690 (2.29), 775 (1.74) nm.

MS (EI): *m/z* (%) = 286 (M^+, 100), 239 (11).

Anal. Calc. for $C_{20}H_{14}S$: C, 83.88; H, 4.93. Found: C, 84.28; H, 5.08.

1,3-Di(2-thienyl)azulene (5h)
Yield 38%, green plates, mp 132-133 °C.

IR (liq. film): ν = 840s, 730s, 690s cm^{-1}.

^1H NMR: δ = 7.16 (t, *J* = 9.6 Hz, 2H), 7.19 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.29 (dd, *J* = 3.2, 1.2 Hz, 2H), 7.38 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.59 (t, *J* = 9.6 Hz, 1H), 8.16 (s, 1H), 8.70 (t, *J* = 9.6 Hz, 2H).

^{13}C NMR: δ = 123.0, 124.3, 124.9, 125.1, 127.8, 136.4, 137.0, 137.3, 138.8, 139.6.

UV-Vis (hexane): λ (logε) = 206 (4.43), 239 (4.32), 289sh (4.50), 297 (4.53), 345sh (4.16), 395 (3.91), 646 (2.46), 700sh (2.35), 798sh (1.75) nm.

MS (EI): m/z (%) = 292 (M^+, 100), 258 (11).

Anal. Calc. for $C_{18}H_{14}S_2$: C, 73.94; H, 4.14. Found: C, 74.18; H, 4.37.

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