A versatile and efficient method for the synthesis of benz[*a*]azulenic enones starting from readily available *o*-(2-furyl)cycloheptatrienylbenzenes[1]

Misako Sasabe,[a] Yuuko Houda,[a] Hideki Takagi,[a] Takashi Sugane,[b] Xu Bo[a] and Kimiaki Yamamura*[b]

[a] *Graduate School of Science and Technology, Kobe University, Nada, Kobe 657-8501, Japan*
[b] *Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657-8501, Japan*

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A facile, one-pot synthesis of β-(benz[*a*]azulen-10-yl)-α,β-unsaturated ketones from the corresponding *o*-(2-furyl)cycloheptatrienylbenzenes is reported. A mechanism involving a novel ring-opening cyclisation reaction by the intramolecular attack of the tropylium ion to the 2-position of the furan ring is proposed.

Introduction

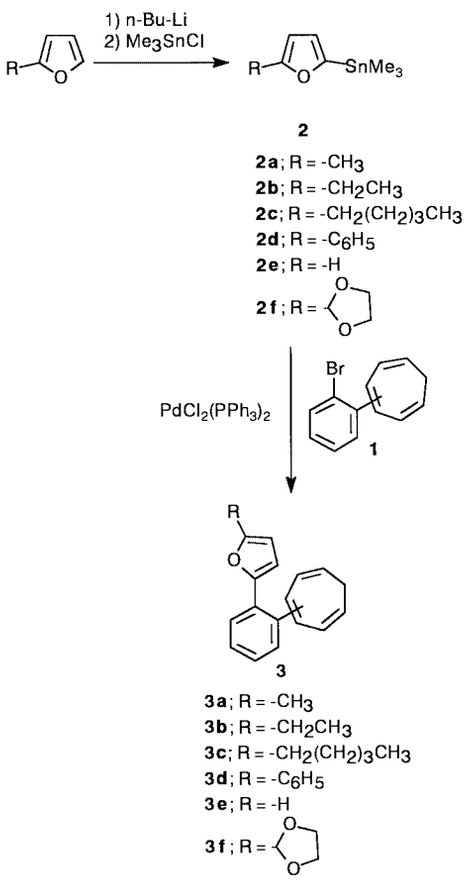
Azulene and its derivatives, which are typical non-benzenoid aromatic hydrocarbons, have been investigated extensively from the chemical, physical, pharmaceutical and physiological points of view, since the first isolation of azulene derivatives from the distillation of chamomile oil in about the middle of the 19th century. Moreover, from the viewpoint of advanced materials with special optical and electrical properties,[2] increasing interest has recently been focussed on azulenoid compounds.

Benz[*a*]azulene and its derivatives, annelated with a benzene ring on the five-membered ring of the azulene ring, are also interesting compounds. In spite of the fundamental significance of benz[*a*]azulene, synthetic difficulties, particularly for substituted systems, have impeded progress in these areas.[3] We report in this paper on a novel, one-pot synthesis of β-(benz[*a*]azulen-10-yl)-α,β-unsaturated ketones from the corresponding *o*-(2-furyl)cycloheptatrienylbenzenes. This method should provide efficient access to a variety of α,β-unsaturated carbonyl derivatives of benz[*a*]azulene.

Results and discussion

Synthesis of the precursors, *o*-(2-furyl)cycloheptatrienylbenzenes 3

The synthetic sequence leading to the precursors for the title benz[*a*]azulenic enones **4** is depicted in Schemes 1 and 2. The common starting material for the synthesis of the title benz[*a*]azulenic enones, *o*-cycloheptatrienylbromobenzene **1**, was prepared[4] as an isomeric mixture from commercially available cyclohepta-1,3,5-triene and *o*-bromoiodobenzene utilising Heck arylation.[5] As shown in Scheme 1, the palladium(II)-catalysed Stille reaction[6] of **1** with 5-substituted 2-trimethylstannylfurans **2a**–**f**, prepared according to the known procedure,[7] gave the corresponding *o*-(2-furyl)cycloheptatrienylbenzenes **3a**–**f**, in 60.0–81.8% yields. As shown in Scheme 2, the other desired precursors for **4h** and **i** were synthesized from **3f** utilising a Wittig reaction. Thus, **3f** was treated with pyridinium toluene-*p*-sulfonate (PPTS)[8] in acetone to afford *o*-(5-formyl-2-furyl)cycloheptatrienylbenzene **3g** in almost quantitative yield. Then, treatment of **3g** with an equimolar amount of the requisite Wittig reagent, benzyltriphenylphosphonium bromide or cinnamyltriphenylphosphonium chloride,[9] in the presence of 18-crown-6 and potassium hydroxide in benzene gave the corresponding *o*-(2-furyl)cycloheptatrienylbenzenes **3h** and **3i**, respectively, in good



Scheme 1

yields. The structures of the obtained *o*-(2-furyl)cycloheptatrienylbenzenes **3a**–**i** were determined by their ^{1}H NMR, IR and mass spectra as well as elemental analysis. Since **3a**–**i** were isolated as isomeric mixtures, their ^{1}H NMR spectra were not completely assigned, but they did show the expected spectra features.

Conversion of 3 to benz[*a*]azulenic enones 4

Conversion of **3** to the title benz[*a*]azulenic enones **4** was successfully carried out as follows, and is illustrated in Scheme 3. The results are shown in Table 1.

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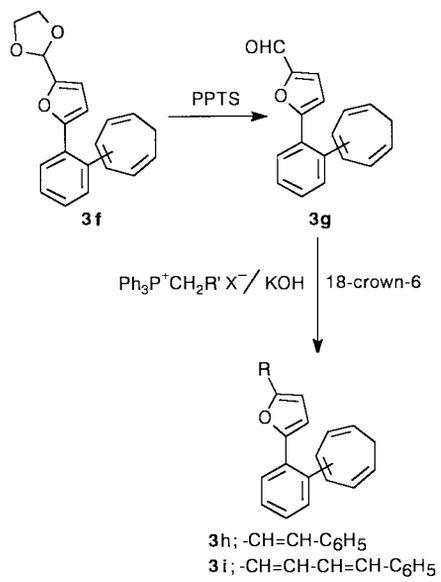
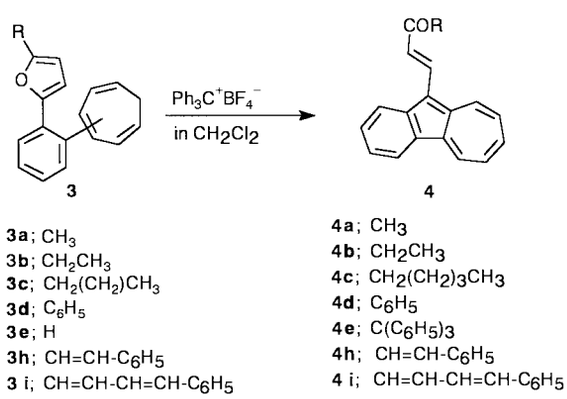
Table 1

Entry	*o*-(2-Furyl)cycloheptabenzene		Benz[*a*]azulenic enone		Yield (%)[a]
1	R = -CH_3	**3a**	R = -CH_3	**4a**	40.0
2	R = -CH_2CH_3	**3b**	R = -CH_2CH_3	**4b**	39.3
3	R = -$CH_2(CH_2)_3CH_3$	**3c**	R = -$CH_2(CH_2)_3CH_3$	**4c**	32.9
4	R = -C_6H_5	**3d**	R = -C_6H_5	**4d**	48.6
5	R = H	**3e**	R = -$C(C_6H_5)_3$	**4e**	41.3[b]
6	R = 1,3-Dioxolan-2-yl	**3f**	—	—	—
7	R = -CHO	**3g**	—	—	—
8	R = -CH=CH-C_6H_5	**3h**	R = -CH=CH-C_6H_5	**4h**	32.4
9	R = -(CH=CH)$_2$-C_6H_5	**3i**	R = -(CH=CH)$_2$-C_6H_5	**4i**	41.3

[a] Yields are of isolated and purified products. [b] Double the molar quantity of trityl tetrafluoroborate was used.

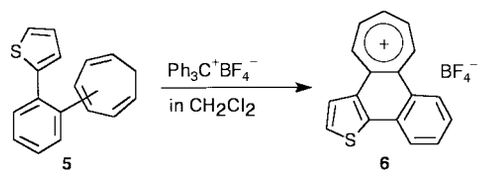


Scheme 2

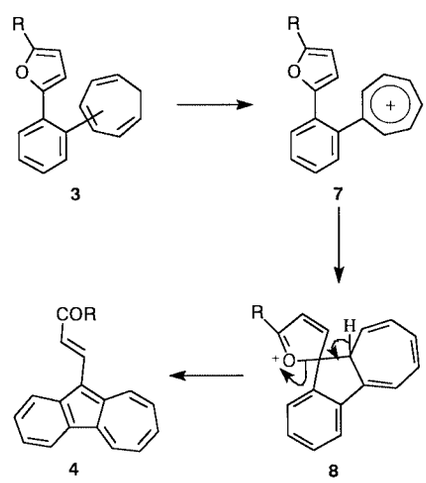


Scheme 3

A mixture of **3** with an equimolar amount of triphenylmethyl (trityl) tetrafluoroborate in dichloromethane solution (*ca.* 0.05 mol L^{-1}) was allowed to stand overnight at ambient temperature. After usual work-up, the corresponding benz[*a*]azulenic enones could be isolated as deep-coloured crystals (entries 1–5, 8 and 9). The structures of the obtained benz[*a*]azulenic enones **4** were confirmed by their ^{1}H NMR, IR, UV–Vis and MS spectra as well as elemental analysis. The structures of **4e** and **4i** were also established by X-ray crystallography.[10] When *o*-(2-thienyl)cycloheptatrienylbenzene **5**, which is an analogue of **3**, was treated with trityl tetrafluoroborate in dichloromethane for 70 h, tetracyclic cyclohepta[3,4]naphtho[1,2-*b*]thiophenylium ion **6**, which is an isoelectronic cation of triphenylene, was obtained (Scheme 4).[11] Thus, a markedly different result was obtained between the furan derivative and the thiophene derivative.



Scheme 4



Scheme 5

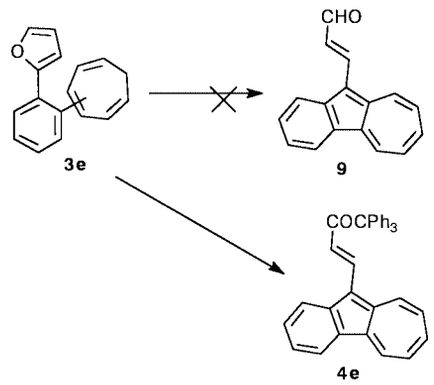
The formation of **4** from **3** can best be rationalised by the mechanism given in Scheme 5.

It is well-known that the 2-position of the furan ring is much more reactive towards the electrophiles than the 3-position, and that the furans bearing electron-donating groups on their 2(5)-positions are readily ring-opened to 1,4-diketones under acidic conditions.[12] The intramolecular electrophilic attack of the initially formed trityl substituted cation **7** on the 2-position of the furan ring gives a five-membered spiro-type intermediate **8**, which can be converted to the final product by a ring unraveling reaction and aromatisation. In fact, when **3a** was treated with an equimolar amount of trityl tetrafluoroborate in dichloromethane for 5 minutes at 0 °C, followed by addition of dry ether, a cationic reddish precipitate was obtained. Although its ^{1}H NMR spectrum was not completely assigned because it changed rapidly into a mixture including **4a**, this reddish precipitate could be assigned to be *o*-tropylio(5-ethyl-2-furyl)-benzene **7** as inferred from its UV–Vis and IR spectra. When a dichloromethane or acetonitrile solution of **7** was allowed to stand for 10 h, **4b** was obtained in 35.0% yield, together with a small amount of 1-(benz[*a*]azulen-10-yl)butan-3-one.

If this mechanism is correct, the carbonyl group and the benz[*a*]azulene ring should be *cis* to each other. However the coupling constants of *ca.* 16 Hz between the olefinic protons on **4** indicate a *trans* configuration between the carbonyl group and benz[*a*]azulene ring. This can be explained by the assumption that the initially formed *cis* isomer changes spontaneously into

the more stable *trans* isomer by the acid generated in the course of the reaction.

With **3e**, which has no substituent on the 5-position of its furan ring, one may expect the formation of α,β-unsaturated aldehyde **9**. However, when **3e** was treated with trityl tetrafluoroborate in a similar manner, the expected aldehyde **9** was not obtained,[13] and 1,1,1-triphenyl-4-(benz[*a*]azulen-10-yl)but-3-en-2-one **4e** was obtained in 25% yield (Scheme 6).



Scheme 6

Apparently, the trityl salt acts as both an electrophile and a hydride abstraction reagent in the reaction. When 2.5 equivalent of trityl salt was employed, the yield of **4e** reached 41.3% (entry 5). DDQ,[14] phosphorus pentachloride,[15] ammonium nitrate–trifluoroacetic acid,[16] 1,3-benzodithiolylium salt[17] and tris(*p*-bromophenyl)amminium salt[18] were tried as hydride abstraction reagents in order to obtain the α,β-unsaturated aldehyde **9**, however satisfactory results were not obtained.

When the substituent on the furan ring is alkyl, phenyl or alkenyl, the desired α,β-unsaturated ketones were thus obtained. However, attempted conversion of formyl derivative **3g** to the corresponding α,β-unsaturated ketone **4** was unsuccessful (entry 7). The starting material **3g** was recovered unchanged even after prolonged reaction times at elevated temperatures. Presumably, the non-reactivity of **3g** is a reflection of the decrease of nucleophilicity of the 2-position in the furan ring due to the electrophilicity of the formyl group.

With **3f**, since the 1,3-dioxolane ring reacted with trityl salt,[19] a complex mixture was obtained instead of the desired benz[*a*]-azulenic enone (entry 6).

Although a few tropylium ion-mediated azulene syntheses have been reported,[20] to our knowledge, this is the first case of a tropylium ion-mediated furan-ring-opening reaction to give benz[*a*]azulene derivatives. Since 2-substituted furans are readily available and the procedure is simple, and further, the formation of benz[*a*]azulenic enones is difficult by other synthetic methods, it is considered that this is a valuable general synthetic methodology leading to various benz[*a*]-azulenic enones.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ on Hitachi R-1500 (60 MHz) and/or Bruker DPX-250 (250 MHz) Fourier Transform spectrometers. All chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. UV–Vis spectra were determined in dichloromethane on a Shimadzu UV2200 spectrometer. Mass spectra were determined on a Shimazdu GCMS QP2000A instrument.

General procedure for the synthesis of 2-trimethylstannylfurans 2

Furan (112 mmol) was dissolved in 75 ml of dry ether and cooled to −78 °C. After addition of a hexane solution of *n*-butyllithium (75 ml, 1.6 mol, 120 mmol), the solution was stirred under N_2 at −78 °C for 1 h. The mixture was then stirred for 3 h at 20 °C, and then cooled to −78 °C. Trimethylstannyl chloride (23.7 g, 120 mmol) in 20 ml of dry ether was added dropwise *via* a syringe and stirred for 2 h at −78 °C. The mixture was stirred overnight at room temperature. The reaction mixture was quenched with aqueous NH_4Cl and extracted with 2 × 80 ml of ether. The combined ether layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by distillation to give the 2-trimethylstannylfuran **2**.

2-Methyl-5-trimethylstannylfuran 2a. 2-Methyl-5-trimethylstannylfuran was isolated as a colourless oil; yield: 82.1%; bp 60 °C/8 mmHg; δ_H (60 MHz) 6.44 (1H, d, J = 3.0 Hz, furan), 5.95 (1H, d, J = 3.0 Hz, furan), 2.30 (3H, s, methyl), 0.27 (9H, s, Me) ppm.

2-Ethyl-5-trimethylstannylfuran 2b. 2-Ethyl-5-trimethylstannylfuran was isolated as a colourless oil; yield: 48.4%, bp 82 °C/11 mmHg; δ_H (60 MHz) 6.67 (1H, d, J = 3.0 Hz, furan), 6.16 (1H, d, J = 3.0 Hz, furan), 2.88 (2H, q, J = 7.5 Hz, methylene), 1.44 (3H, t, J = 7.5 Hz, methyl), 0.30 (9H, s, Me) ppm.

2-*n*-Pentyl-5-trimethylstannylfuran 2c. 2-*n*-Pentyl-5-trimethylstannylfuran was isolated as a pale yellow oil; yield: 42.5%; bp 73 °C/9 mmHg; δ_H (60 MHz) 6.47 (2H, d, J = 3.0 Hz, furan), 5.99 (1H, d, J = 3.0 Hz, furan), 2.65 (2H, t, J = 7.6 Hz, methylene), 1.70–0.80 (9H, m, methylene), 0.30 (9H, s, Me) ppm.

2-Phenyl-5-trimethylstannylfuran 2d. 2-Phenyl-5-trimethylstannylfuran was isolated as a colourless oil; yield: 66.0%; bp 110–113 °C/2.5 mmHg; δ_H (60 MHz) 6.53–7.68 (5H, m, phenyl), 7.52 (1H, d, J = 3.0 Hz, furan), 7.13 (1H, d, J = 3.0 Hz, furan), 0.26 (9H, s, Me) ppm.

2-Trimethylstannylfuran 2e. 2-Trimethylstannylfuran was isolated as a colourless oil; yield: 56.7%; bp 87–89 °C/55 mmHg; δ_H (60 MHz) 7.85 (1H, d, J = 2.0 Hz, furan), 7.76 (1H, d, J = 3.0 Hz, furan), 6.57 (1H, dd, J = 2.0, 3.0 Hz, furan), 0.25 (9H, s,) ppm.

2-(1,3-Dioxolan-2-yl)-5-trimethylstannylfuran 2f. 2-(1,3-Dioxolan-2-yl)-5-trimethylstannylfuran was isolated as a yellow oil; yield: 52.0%; bp 107 °C/3 mmHg; δ_H (60 MHz) 6.52 (1H, d, J = 3.0, furan), 6.44 (1H, d, J = 3.0, furan), 5.99 (1H, s, methine), 4.16–3.97 (4H, m, methylene), 0.32 (9H, s, Me) ppm.

General procedure for the synthesis of *o*-(2-furyl)cycloheptatrienylbenzenes 3

A mixture of *o*-cycloheptatrienylbromobenzene **1** (4.44 g, 18 mmol), the 2-trimethylstannylfuran **2** (23.4 mmol), bis-(triphenylphosphine)palladium(II) chloride (1.0 g, 1.42 mmol) and 70 ml of dry tetrahydrofuran was refluxed for 20 h under an N_2 atmosphere. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel using hexane as eluent to give the *o*-(2-furyl)-cycloheptatrienylbenzene **3**.

***o*-(5-Methyl-2-furyl)cycloheptatrienylbenzene 3a.** *o*-(5-Methyl-2-furyl)cycloheptatrienylbenzene was obtained as a pale yellow oil; yield: 62.8%; *m*/*z*: 248 (M^+); Found: C, 87.25; H, 6.36. Calc. for $C_{18}H_{16}O$: C, 87.06; H, 6.49%.

***o*-(5-Ethyl-2-furyl)cycloheptatrienylbenzene 3b.** *o*-(5-Ethyl-2-furyl)cycloheptatrienylbenzene was obtained as a pale yellow oil; yield: 61.0%; *m*/*z*: 262 (M^+); Found: C, 87.06; H, 6.82. Calc. for $C_{19}H_{18}O$: C, 86.99; H, 6.92%.

***o*-(5-*n*-Pentyl-2-furyl)cycloheptatrienylbenzene 3c.** *o*-(5-*n*-Pentyl-2-furyl)cycloheptatrienylbenzene was obtained as a yellow oil; yield: 91.3%; *m*/*z*: 304 (M^+); Found: C, 86.92; H, 8.12. Calc. for $C_{22}H_{24}O$: C, 86.80; H, 7.95%.

***o*-(5-Phenyl-2-furyl)cycloheptatrienylbenzene 3d.** *o*-(5-Phenyl-2-furyl)cycloheptatrienylbenzene was obtained as a pale yellow oil; yield: 60.0%; *m*/*z*: 310 (M^+); Found: C, 89.23; H, 5.98. Calc. for $C_{23}H_{18}O$: C, 89.05; H, 5.85%.

***o*-(2-Furyl)cycloheptatrienylbenzene 3e.** *o*-(2-Furyl)cycloheptatrienylbenzene was obtained as a pale yellow oil; yield: 60.0%; *m*/*z*: 234 (M^+); Found: C, 87.31; H, 6.22. Calc. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

***o*-[5-(1,3-Dioxolan-2-yl)-2-furyl]cycloheptatrienylbenzene 3f.** *o*-[5-(1,3-Dioxolan-2-yl)-2-furyl]cycloheptatrienylbenzene was obtained as a yellow oil; yield: 77.5%; *m*/*z*: 336 (M^+); Found: C, 89.47; H, 6.08. Calc. for $C_{25}H_{20}O$: C, 89.25; H, 5.99%.

Synthesis of *o*-(5-formyl-2-furyl)cycloheptatrienylbenzene 3g

A mixture of **3f** (3.4 g, 11.11 mmol), PPTS (0.871 g, 3.47 mmol), 5 ml of H_2O and 50 ml of acetone was refluxed for 1 h. After evaporating the solvent, the residue was dissolved in ether. The ether solution was washed with aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel using benzene–hexane (1 : 1) as eluent to give **3g** (2.06 g); yield: 77.5%, colourless precipite; *m*/*z*: 262 (M^+); Found: C, 89.47; H, 6.08. Calc. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

Synthesis of *o*-(5-styryl-2-furyl)cycloheptatrienylbenzene 3h

To an ice-cooled solution of benzyltriphenylphosphonium bromide (847 mg, 1.95 mmol), **3g** (501 mg, 1.91 mmol), 18-crown-6 (47 mg, 0.195 mmol), 10 ml of dichloromethane and powdered KOH (213 mg, 3.8 mmol) were added, and stirred for 2 h at ambient temperature. After diluting with 20 ml of dichloromethane, unsoluble materials were filtered off, and then the dichloromethane layer was washed with water, and dried over Na_2SO_4. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography over silica gel using hexane–ethyl acetate (4 : 1) as eluent to give **3h** (498 mg) as a yellow oil; yield: 76.8%; *m*/*z*: 336 (M^+); Found: C, 89.47; H, 6.08. Calc. for $C_{25}H_{20}O$: C, 89.25; H, 5.99%.

Synthesis of *o*-[5-(4-phenylbuta-1,3-dienyl)-2-furyl]cycloheptatrienylbenzene 3i

o-[5-(4-Phenylbuta-1,3-dienyl)-2-furyl]cycloheptatrienylbenzene was prepared as described for **3h**, using triphenylcinnamylphosphonium chloride as Wittig reagent as a yellow oil; yield: 81.8%; *m*/*z*: 362 (M^+); Found: C, 89.25; H, 6.22. Calc. for $C_{27}H_{22}O$: C, 89.47; H, 6.12%.

General procedure for the synthesis of benz[*a*]azulenic enones 4

o-(2-Furyl)cycloheptatrienylbenzene **3** (5.84 mmol) in 5 ml of dry CH_2Cl_2 was added to a solution of trityl tetrafluorobotate (1.93 g, 5.85 mmol) in 15 ml of dry CH_2Cl_2 at ambient temperature. The mixture was stirred for 5 min, and then dry CH_2Cl_2 (200 ml) was added. The solution was stirred overnight at ambient temperature. The solvent was removed *in vacuo*. The product was purified by column chromatography (silica gel, hexane–ethyl acetate (4 : 1)) and recrystallised from benzene–hexane (1 : 1).

(*E*)-4-(Benz[*a*]azulen-10-yl)but-3-en-2-one 4a. (*E*)-4-(Benz[*a*]-azulen-10-yl)but-3-en-2-one was isolated as dark-green needles; yield: 40.0%; mp 112 °C; δ_H (250 MHz) 8.47 (1H, d, *J* = 7.5 Hz, six-membered ring), 8.45 (1H, d, *J* = 11.0 Hz, seven-membered ring), 8.41 (1H, d, *J* = 11.0 Hz, seven-membered ring), 8.38 (1H, d, *J* = 16.0 Hz, olefin), 8.29 (1H, d, *J* = 8.0 Hz, six-membered ring), 7.81 (1H, t, *J* = 7.5 Hz, six-membered ring), 7.60 (1H, t, *J* = 7.5 Hz, six-membered ring), 7.42 (1H, t, *J* = 9.0 Hz, seven-membered ring), 7.28 (1H, dd, *J* = 9.0, 11.0 Hz, seven-membered ring), 7.19 (1H, dd, *J* = 9.0, 11.0 Hz, seven-membered ring), 7.11 (1H, d, *J* = 16.0 Hz, olefin), 2.49 (3H, s, methyl) ppm; *m*/*z*: 246 (M^+); Found: C, 87.66; H, 5.81. Calc. for $C_{18}H_{14}O$: C, 87.78; H, 5.73%.

(*E*)-1-(Benz[*a*]azulen-10-yl)pent-1-en-3-one 4b. (*E*)-1-(Benz-[*a*]azulen-10-yl)pent-1-en-3-one was isolated as dark-green needles; yield: 39.3%; mp 85–90 °C; δ_H (250 MHz) 8.46 (1H, d, *J* = 8.4 Hz, seven-membered ring), 8.43 (1H, d, *J* = 16.0 Hz, olefin), 8.43 (1H, d, *J* = 7.9 Hz, six-membered ring), 8.41 (1H, d, *J* = 10.9 Hz, seven-membered ring), 8.29 (1H, d, *J* = 8.1 Hz, six-membered ring), 7.81 (1H, t, *J* = 7.6, six-membered ring), 7.59 (1H, t, *J* = 7.4 Hz, six-membered ring), 7.41 (1H, dd, *J* = 9.5, 10.0 Hz, seven-membered ring), 7.26 (1H, dd, *J* = 8.7, 10.0 Hz, seven-membered ring), 7.17 (1H, dd, *J* = 8.1, 11.0 Hz, seven-membered ring), 7.13 (1H, d, *J* = 16.0 Hz, olefin), 2.79 (2H, q, *J* = 7.3 Hz, methylene), 1.26 (3H, t, *J* = 7.3 Hz, methyl) ppm; *m*/*z*: 260 (M^+); Found: C, 87.78; H, 6.25. Calc. for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

(*E*)-1-(Benz[*a*]azulen-10-yl)oct-1-en-3-one 4c. (*E*)-1-(Benz-[*a*]azulen-10-yl)oct-1-en-3-one was isolated as dark-green needles; yield: 32.9%; mp 63–66 °C; δ_H (250 MHz) 8.47 (1H, d, *J* = 8.2 Hz, seven-membered ring), 8.43 (1H, d, *J* = 8.4 Hz, six-membered ring), 8.42 (1H, d, *J* = 14.8 Hz, olefin), 8.41 (1H, d, *J* = 11.6 Hz, seven-membered ring), 8.29 (1H, d, *J* = 8.1 Hz, six-membered ring), 7.82 (1H, t, *J* = 7.6 Hz, six-membered ring), 7.59 (1H, t, *J* = 7.6 Hz, six-membered ring), 7.41 (1H, dd, *J* = 9.5, 9.7 Hz, seven-membered ring), 7.26 (1H, dd, *J* = 9.0, 10.1 Hz, seven-membered ring), 7.17 (1H, dd, *J* = 9.6, 10.1 Hz, seven-membered ring), 7.13 (1H, d, *J* = 15.4 Hz, olefin), 2.75 (2H, t, *J* = 7.5 Hz, methylene), 1.80–1.74 (2H, m, methylene), 1.48–1.36 (2H, m, methylene), 0.94 (3H, t, *J* = 7.3 Hz, methyl) ppm; *m*/*z*: 302 (M^+); Found: C, 87.50; H, 7.39. Calc. for $C_{22}H_{22}O$: C, 87.38; H, 7.33%.

(*E*)-3-(Benz[*a*]azulen-10-yl)-1-phenylprop-2-en-1-one 4d. (*E*)-3-(Benz[*a*]azulen-10-yl)-1-phenylprop-2-en-1-one was isolated as dark-green needles; yield: 48.6%; mp 174 °C; δ_H (250 MHz) 8.69 (1H, d, *J* = 15.4, olefin), 8.47 (1H, d, *J* = 11.0, seven-membered ring), 8.45 (1H, d, *J* = 8.5 Hz, six-membered ring), 8.41 (1H, d, *J* = 8.1 Hz, seven-membered ring), 8.35 (1H, *J* = 8.0 Hz, six-membered ring), 8.12 (2H, dd, *J* = 1.5, 7.5 Hz, phenyl), 7.86 (1H, d, *J* = 15.5, olefin), 7.83 (1H, t, *J* = 7.6 Hz, six-membered ring), 7.57 (1H, t, *J* = 7.5, six-membered ring), 7.50–7.61 (3H, m, phenyl), 7.41 (1H, dd, *J* = 9.2, 10.3, seven-membered ring), 7.25 (1H, t, *J* = 8.9, seven-membered ring), 7.18 (1H, dd, *J* = 8.5, 10.9, seven-membered ring) ppm; *m*/*z*: 308 (M^+); Found: C, 89.45; H, 5.36. Calc. for $C_{23}H_{16}O$: C, 89.58; H, 5.23%.

(*E*)-1,1,1-Triphenyl-4-(benz[*a*]azulen-10-yl)but-3-en-2-one 4e. (*E*)-1,1,1-Triphenyl-4-(benz[*a*]azulen-10-yl)but-3-en-2-one was isolated as black prisms; yield: 41.3%;[21] mp 295 °C; δ_H (250 MHz) 8.45 (1H, d, *J* = 15.1, olefin), 8.45 (1H, d, *J* = 11.0 Hz, seven-membered ring), 8.42 (1H, d, *J* = 10.8 Hz, seven-membered ring), 8.39 (1H, d, *J* = 8.1 Hz, six-membered ring), 8.30 (1H, dd, *J* = 8.0, 8.3 Hz, six-membered ring), 7.80 (1H, dd, *J* = 8.0, 7.8 Hz, six-membered ring), 7.58 (1H, dd, *J* = 7.8, 8.1 Hz, seven-membered ring), 7.43 (1H, dd, *J* = 8.8, 11.0 Hz, seven-membered ring), 7.41 (15H, m, phenyl), 7.30 (1H, dd, 1H, *J* = 9.0, 10.9 Hz, seven-membered ring), 7.00 (d, 1H, *J* = 15.2 Hz, olefin) ppm; *m*/*z*: 474 (M^+); Found: C, 90.12; H, 5.48. Calc. for $C_{36}H_{26}O$: C, 89.97; H, 5.59%.

(*E*,*E*)-1-(Benz[*a*]azulen-10-yl)-5-phenylpenta-1,4-dien-3-one 4h. (*E*,*E*)-1-(Benz[*a*]azulen-10-yl)-5-phenylpenta-1,4-dien-3-one was isolated as dark-green needles; yield: 44.6%; mp 146–150 °C; δ_H (250 MHz) 8.63 (1H, d, *J* = 15.5 Hz, olefin), 8.51 (1H, d, *J* = 10.9 Hz, seven-membered ring), 8.49 (1H, d, *J* = 8.4

Hz, six-membered ring), 8.45 (1H, d, J = 8.0 Hz, six-membered ring), 8.37 (1H, d, J = 7.5 Hz, six-membered ring), 7.84 (1H, t, J = 7.5 Hz, six-membered ring), 7.81 (1H, d, J = 16.3 Hz, olefin), 7.69–7.65 (2H, m, phenyl), 7.60 (1H, t, J = 7.5 Hz, six-membered ring), 7.43 (1H, d, J = 15.2, olefin), 7.42 (1H, dd, J = 9.0, 10.4 Hz, seven-membered ring), 7.46–7.40 (3H, m, phenyl), 7.29 (1H, dd, J = 8.6, 9.1 Hz, seven-membered ring), 7.21 (1H, dd, J = 9.1, 10.5 Hz, seven-membered ring), 7.17 (1H, d, J = 16.3 Hz, olefin) ppm; *m*/*z*: 334 (M^+); Found: C, 89.90; H, 5.51. Calc. for $C_{25}H_{18}O$: C, 89.79; H, 5.43%.

(*E*,*E*,*E*)-1-(Benz[*a*]azulen-10-yl)-7-phenylhepta-1,4,6-trien-3-one 4i. (*E*,*E*,*E*)-1-(Benz[*a*]azulen-10-yl)-7-phenylhepta-1,4,6-trien-3-one was isolated as dark-green prisms; yield: 32.4%; mp 101–106 °C; δ_H (250 MHz) 8.59 (1H, d, J = 15.7, olefin), 8.53 (1H, d, J = 13.2 Hz, seven-membered ring), 8.46 (1H, d, J = 12.6 Hz, seven-membered ring), 8.45 (1H, d, J = 8.1 Hz, six-membered ring), 8.36 (1H, d, J = 8.1 Hz, six-membered ring), 7.84 (1H, d, J = 7.5 Hz, six-membered ring), 7.65–7.51 (6H, m, six-membered ring, olefin, phenyl), 7.38 (1H, d, J = 15.2, olefin), 7.33 (1H, dd, J = 11.1, 8.6 Hz, seven-membered ring), 7.21 (1H, dd, J = 11.0, 8.0 Hz, seven-membered ring), 7.43–7.26 (4H, m, seven-membered ring, phenyl), 6.78 (1H, d, J = 15.1, olefin) ppm; *m*/*z*: 360 (M^+); Found: C, 89.88; H, 5.63. Calc. for $C_{27}H_{20}O$: C, 89.97; H, 5.59%.

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