HETEROCYCLES, Vol. 62, 2004, pp. 463 - 478
Received, 31st July, 2003, Accepted, 8th September, 2003, Published online, 27th October, 2003

PREPARATION AND STRUCTURE OF DI(2-AZULENYL)KETENE ADDUCTS. γ-LACTONE AND β-LACTAM DERIVATIVES

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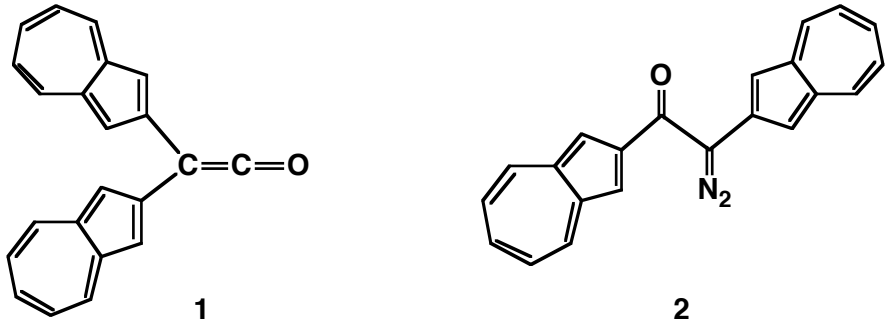
Abstract — Di(2-azulenyl)ketene (**1**) generated by thermal decomposition of diazodi(2-azulenyl)ethanone (**2**) *via* Wolff rearrangement of carbonyl carbene (**8**), and the reactive intermediate were confirmed by trapping reagents, such as azobenzene and cyclopentadienes. The reaction of **1** with tropone or imines afforded the corresponding γ-lactone (**12**) and β-lactams (**15**), respectively.

Since the first recorded[1] ketene derivative, diphenylketene, was obtained by Staudinger in 1905, the chemistry of ketenes has become of interest for chemists. In particular, ketenes have a strained heterocumulene structure, are very reactive even at low temperature, and undergo [2+2] cycloaddition to give four-membered ring such as β-lactams.

We report here on the first generation and trapping of di(2-azulenyl)ketene (**1**) by the thermal decomposition of diazodi(2-azulenyl)ethanone (**2**).



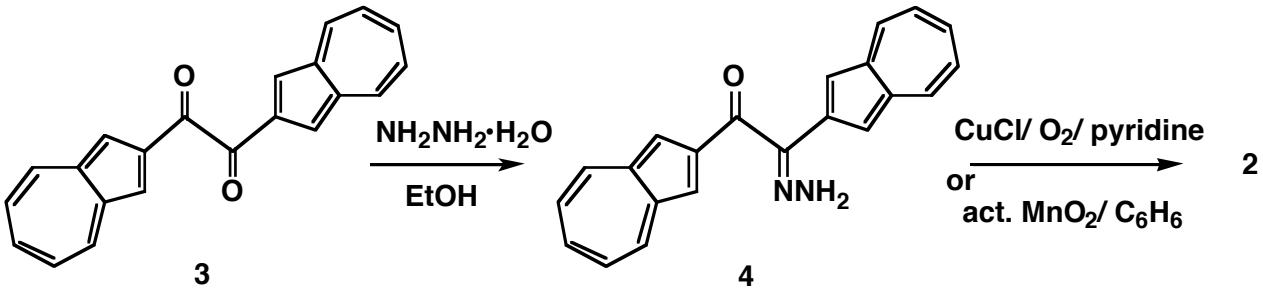
1 **2**

Chart 1

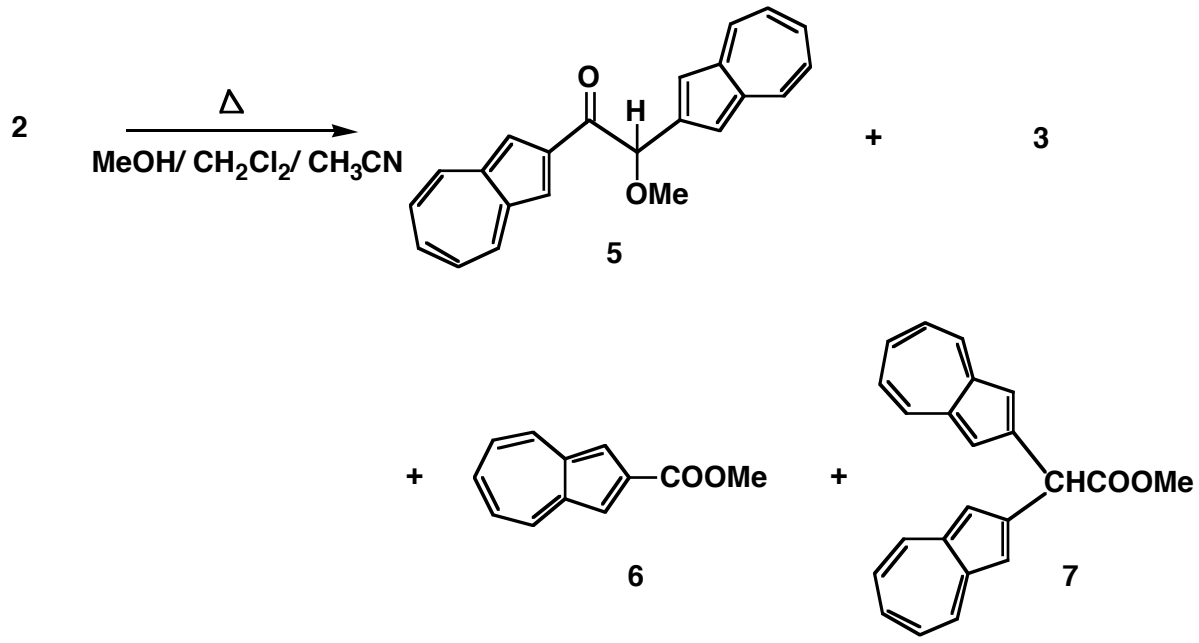
The □□diazo ketone (**2**) was obtained by the oxidation of di(2-azulenyl)ethanedione[2] monohydrazone (**4**) with copper(I) chloride/ O_2/ pyridine or activated manganese dioxide in 55% and 91% yields, respectively

(Scheme 1). The IR spectrum of **2** exhibits a strong characteristic absorption band at 2054 cm^{-1} and indicates the presence of a diazo group. The compound (**2**) is sensitive to light or heat.

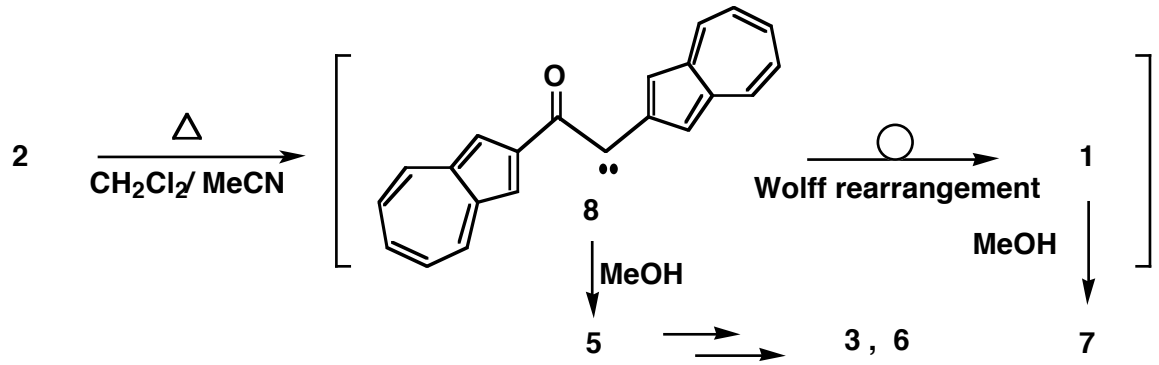
Ketene (**1**) was generated from **2** effectively on heating in dry CH_2Cl_2 (MeOH free)-MeCN (2 : 1) at 40 °C under an inert atmosphere. Ketene (**1**) has not been isolated, but confirmed by using trapping reagents as shown below. Thermal decomposition of the α-diazo ketone (**2**) in MeOH/MeCN/CH_2Cl_2 gave 2-azuloin methyl ether (**5**) (10%), methyl 2-azulenecarboxylate (**6**) (35%), methyl di(2-azulenyl)acetate (**7**) (46%) *via* the Wolff rearrangement, and diketone (**3**) (trace) (Scheme 2). It is generally accepted that the Wolff rearrangement proceeds *via* ketocarbene.[3] The O-H insertion product (**5**) is surely formed by being traped ketocarbene (**8**) in the presence methanol (Scheme 3). The ketocarbene intermediate (**8**) has been also confirmed by a laser flash photolysis study.[4]



Scheme 1

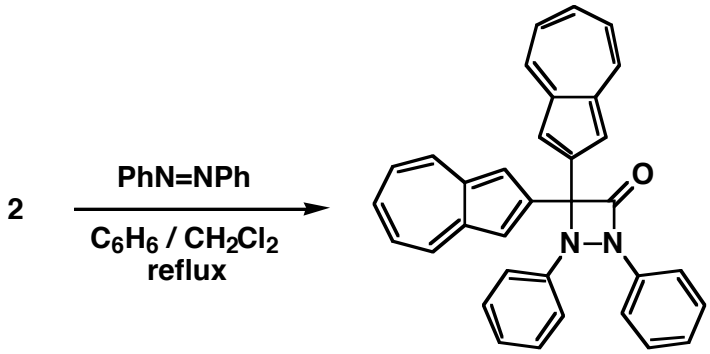


Scheme 2



Scheme 3

The thermal reaction of **2** in the presence of azobenzene gave a cycloadduct (**9**) in 57% yield. The spectral data of **9** were well consistent with the assigned structure of [2+2] cycloadduct of the expected ketene (**1**) with azobenzene. The carbonyl absorption band in the IR spectrum of **9** was observed at 1777 cm^{-1}, and a signal at 166.5 ppm in the ^{13}C-NMR spectrum was assigned as carbonyl carbon in the 1,2-diazetidin-3-one ring.



Scheme 4

Cycloaddition of 1 with cyclopentadienes: The thermal reaction of **2** in the presence of cyclopentadiene gave a cycloadduct (**10**) in 54% yield. Further, the thermal decomposition of **2** in the presence of methylcyclopentadienes under the same condition gave adducts as a mixture of **11a** and **11b** (25 : 3) in 28% yield.

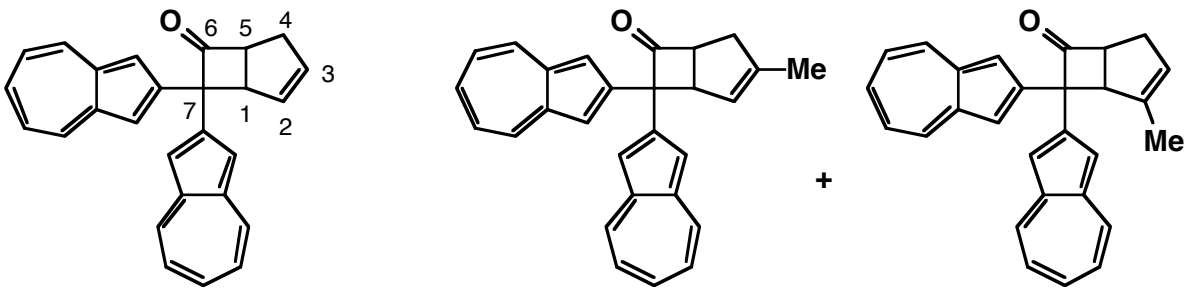
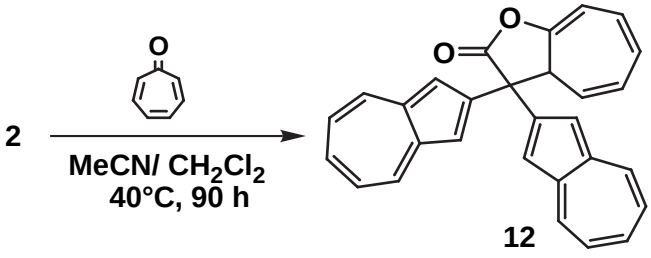


Chart 2

Recently, Machiguchi and co-workers have been proposed a new interesting feature that ketenes take part in 1,4-cycloaddtion with 1,3-dienes, followed by subsequent [3,3] sigmatropic (Claisen) rearrangement to give [2+2] cycloaddcts as a result of a systematic study.[5] It is presumed that the cycloaddition of **1** with cyclopentadienes proceeded by similar mechanism that reported by Machiguchi *et al*.

Cycloaddition of 1 with tropone: Thermolysis of **2** in the presence of tropone gave a cycloadduct (**12**) in 87% yield. The spectral data of **12** were well consistent with the assigned structure as a [8+2] cycloadduct of the expected ketene (**5**) with tropone. The C=O stretching absorption band in the IR spectrum of **12** was observed at 1799 cm^{-1} and the absorption band at relatively high frequencies was assigned to carbonyl absorption band in five-membered lactone. The structure of **12** was also confirmed by X-Ray analysis (Figure 1).



Scheme 5

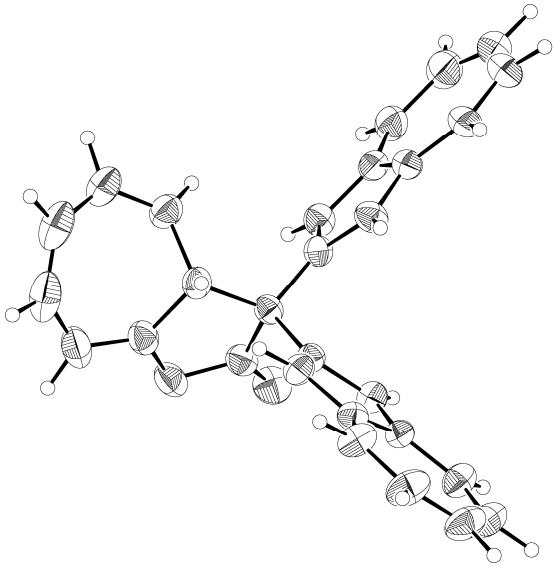
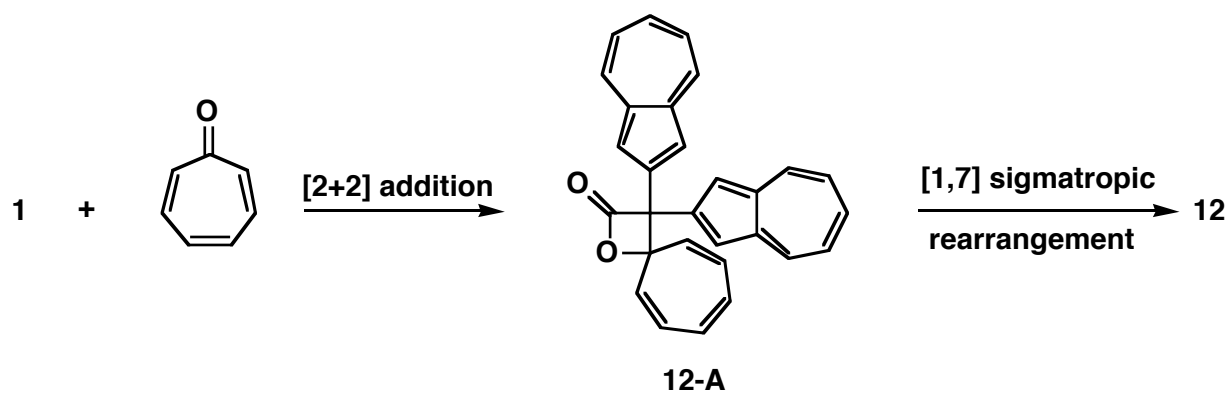


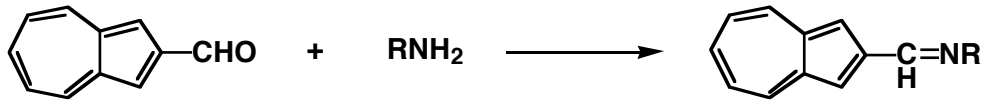
Figure 1. X-Ray molecular structure of **12**.

The formation of the lactone (**12**) can be explained by considering the new two-step reaction mechanism,[6] *i. e*. the [2+2] addition and the subsequent [1,7] sigmatropic rearrangement (Scheme 6).



Scheme 6

β -Lactam derivatives: [2+2] Cycloaddtion of ketenes with imines is one of the effective synthetic method of β -lactam derivatives.[7] Imines (**14a-g**) were obtained by the reaction of 2-formylazulene (**13**) with amines in almost quantitative yields (Scheme 7 and Table 1).



13 **14**

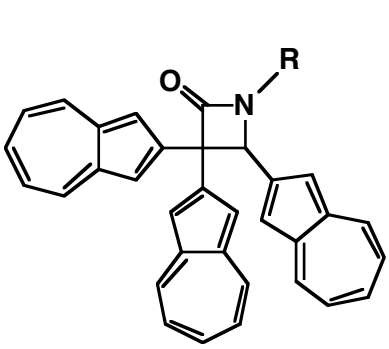
a: R= phenyl, b: R= *p*-fluorophenyl
c: R= *p*-methoxyphenyl, d: R= *tert*-butyl
e: R= isopropyl, f: R= methyl
g: R= 2-thiazolyl

Scheme 7

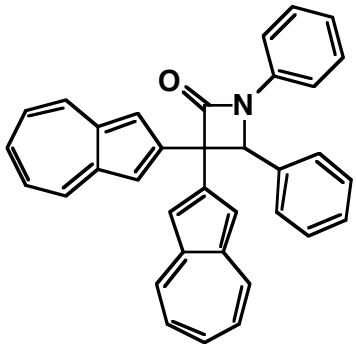
Table 1 Reaction of 2-formylazulene (13) with primary amines

entry	primary amines	solvents	reaction conditions	products	physical properties
1	aniline	EtOH	rt, 30 min	**14a**	green plates mp 107-108°C
2	*p*-fluoroaniline	EtOH	rt, 1 h	**14b**	green plates mp 146-147°C
3	*p*-methoxyaniline	EtOH	rt, 30 min	**14c**	green plates mp 167-168°C
4	*tert*-butylamine	—	rt, 1.5 h	**14d**	blue plates mp 41-42°C
5	isopropylamine	—	rt, 1 h	**14e**	blue plates mp 53-54°C
6	methylamine	40% in water	rt, 1 h	**14f**	blue needles mp 51-52°C
7	2-aminothiazole	benzene	$ZnCl_2$, reflux, 1 h	**14g**	green plates mp 113-114°C

Thermolysis of **2** in the presence of the imines (**14a-g**) gave β -lactam derivatives (**15a-g)** in 32% - 61% yields. Similarly 3,3-di(2-azulenyl)-1,4-diphenylazetidin-2-one (**16**) was obtained from diazoketone (**2**) and *N*-benzylideneaniline in 11% yield (Chart 2). All the spectral data and elemental analyses of **15a-g** and **16** supported the structures of the [2+2] cycloadduct of ketene (**1**) with imines (**14a-g**) and *N*-bendylideneaniline, respectively. The carbonyl stretching absorption bands of the lactams (**15a-f**) were observed in the range from 1751 to 1736 cm^{-1}, while that of **15g** appeared at a slightly lower frequency (1714 cm^{-1}).



15



16

a: R= phenyl, b: R= *p*-fluorophenyl
c: R= *p*-methoxyphenyl, d: R= *tert*-butyl
e: R= isopropyl, f: R= methyl
g: R= 2-thiazolyl

Chart 2

The X-Ray molecular structures of **15d** and **15e** are shown in Figure 2. In both cases, the azetidin-2-one moieties are almost planar. While the N(1)–C(5) bond in **15e** is nearly in the plane of the azetidinone unit, the *tert*-butyl group in **15d** deviates slightly from the four-membered ring to avoid the steric interaction with the vicinal azulenyl group (the angles between the N(1)–C(5) bond and the β-lactam ring: **15d**, 18.2°; **15e**, 4.3°).

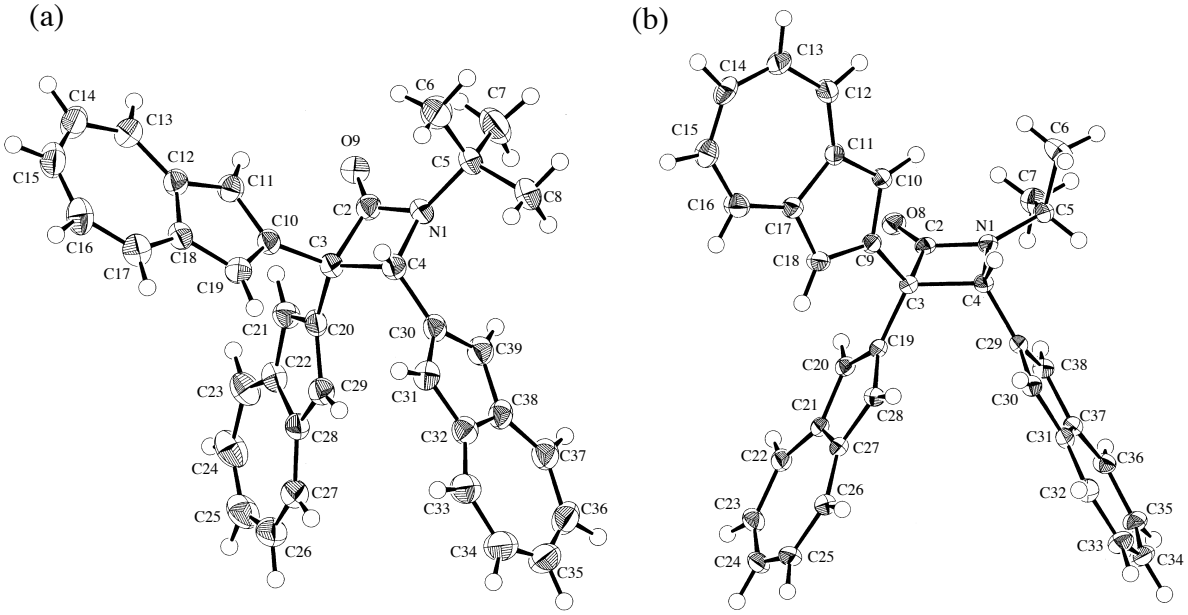


Figure 2. X-Ray molecular structures of (a) **15d** and (b) **15e**.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Spectral data were obtained on the following instruments: ^{1}H-NMR: JEOL-JNM-LA300 (300 MHz), –LA400 (400 MHz) and -FX90Q (90 MHz); ^{13}C-NMR; JEOL-JNM-LA300 (75.5 MHz), –LA400 (100

MHz) and –FX90Q (22.5 MHz); IR: JEOL JIR-Diamond20 and Hitachi model 345; MS spectroscopy: Shimadzu GCMS-QP1000EX; UV-VIS: Hitachi model 200. Elemental analyses were performed on a Perkin-Elmer model 240.

Monohydrazone (4) of di(2-azulenyl)ethanedione (3) A mixture of di(2-azulenyl)ethanedione (**3**) (223 mg, 0.72 mmol) and 80% hydrazine hydrate (135 mg, 2.12 mmol) in ethanol (40 mL) was stirred at 40 °C for 65 h. reaction mixture was poured in water and extracted with CH_2Cl_2. The organic layer was concentrated and the residue was purified by column chromatography on silica gel to afford 220 mg (94%) of **4** as dark green needles, mp 190-191 °C. IR (KBr): 3430, 3310, 3128, 1614, 1527, 1471, 1343 cm^{-1}. MS: m/z (rel. int. %) 324 (M^+, 30), 296 (M^+- CO, 18), 155 ($AzCO^+$, 98), 127 (Az^+, 100). Anal. Calcd for $C_{22}H_{16}N_2O$: C, 80.95; H, 4.94; N, 8.59. Found: C, 80.64; H, 4.81; N, 8.38.

Diazodi(2-azulenyl)ethanone (2) a) Oxidation using copper(I) chloride A solution of **4** (54 mg, 0.17 mmol) in pyridine (5 mL) was added dropwise to a solution of copper(I) chloride (33 mg, 0.17 mmol) in pyridine (5 mL) for 15 min under an oxygen atmosphere. The mixture was stirred for 45 min and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with water. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on neutral alumina with CH_2Cl_2 yielded **2** as green crystals (30 mg, 55%).

b) Oxidation using activated manganease dioxide A mixture of **4** (72 mg, 0.22 mmol) and activated manganease dioxide (113 mg, 1.3 mmol) in chloroform (29 mL) was stirred at room temp for 3 h. The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on neutral alumina with benzene-CH_2Cl_2 to give **2** (65 mg, 91%) as green crystals, mp 120 °C (decomp). IR (KBr): 2054, 1621, 1575, 1491, 1403, 1322, 1244, 1203 cm^{-1}. MS: m/z (rel. int. %) 294 (M^+-N_2, 36), 265 (100), 155 ($AzCO^+$, 98). Anal. Calcd for $C_{22}H_{14}N_2O$: C, 81.97; H, 4.38; N, 8.69. Found: C, 81.67; H, 4.39; N, 8.70.

The thermal reaction of 2 in MeOH/MeCN/CH_2Cl_2 A solution of **2** in MeOH/MeCN/CH_2Cl_2 (1:1:2, 12 mL) was warmed at 40 °C for 9.5 h under argon atmosphere. The reaction mixture was condensed to leave a residue. The residue was purified by column chromatography on silica gel with benzene to give **3** (trace), **5** 10%), **6** (35%), and **7** (46%), respectively. **3:** Green plates, mp 209-210 °C (from toluene). **5:** Dark green oil. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.67 (3H, s, $OC\underline{H}_3$), 6.00 (1H, s, =CH-), 7.12 (2H, dd, *J*= 9.8, 9.8 Hz, Az-5, 7), 7.16 (2H, dd, *J*= 9.8, 9.8 Hz, Az-5', 7'), 7.4-7.8 (2H, m, Az-6, 6'), 7.55 (2H, s, Az-1, 3), 7.96 (2H, s, Az-1', 3'), 8.33 (2H, d, *J*= 9.8 Hz, Az-4, 8), 8.41 (2H, d, *J*= 9.8 Hz, Az-4', 8'). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ: 58.0, 86.2, 116.5, 119.2, 123.5, 123.9, 128.4, 136.8, 137.2, 140.3, 140.5,

141.2, 142.8, 147.3, 196.3. MS: m/z (rel. int. %) 326 (M^+, 15), 171 (M^+-AzCO, 100), 155 ($AzCO^+$, 58), 127 (Az^+, 26). **6**[8]: Blue plates, mp 112-113 °C (from hexane). **7:** Purple needles, mp 110-111 °C (from hexane). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.87 (3H, s, OCH_3), 5.95 (1H, s, =CH-), 7.25 (4H, dd, *J*= 9.7, 9.7 Hz, Az-5, 5', 7, 7'), 7.51 (4H, s, Az-1, 1', 3, 3'), 7.54 (2H, dd, *J*= 9.7, 9.7 Hz, Az-6, 6'), 8.38 (4H, d, *J*= 9.7 Hz, Az-4, 4', 8, 8'). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ: 50.4, 52.4, 117.6, 123.4, 136.3, 136.8, 140.4, 149.3, 172.6. IR (KBr): 3000, 2941, 1740, 1575, 1479, 1400, 1271, 1155 cm^{-1}. MS: m/z (rel. int. %) 326 (M^+, 75), 267 (M^+-$COOCH_3$, 100), 265 (84), 127 (27). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.63; H, 5.56. Found: C, 84.30; H, 5.53.

4,4-Di(2-azulenyl)-1,2-diphenyldiazetidin-3-one (9) To a solution of **2** (32 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) and dry benzene (10 mL) was added azobenzene (21 mg, 0.11 mmol). The mixture was refluxed for 10 h under argon atmosphere. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with benzene to afford **9** (27 mg, 57%) as purple plates (mp 123 °C (decomp), from hexane). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 8.26 (4H, d, *J*= 9.8 Hz, Az-4, 4', 8, 8'), 6.7-7.7 (20H, m). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ: 89.9, 116.5, 118.1, 119.8, 123.5, 123.9, 124.3, 128.1, 128.4, 129.0, 137.6, 137.8, 138.6, 139.8, 145.6. 166.5. IR (KBr): 1777, 1574, 1483, 1395, 1325 cm^{-1}. MS: m/z (rel. int. %) 476 (M^+, 71), 357 (20), 356 (53), 307 (49), 268 (54), 267 (47). Anal. Calcd for $C_{34}H_{24}N_2O$: C, 85.68; H, 5.88. Found: C, 85.35; H, 5.68.

[2+2] Cycloaddition of di(2-azulenyl)ketene (1) with cyclopentadienes **a)** A mixture of **2** (50 mg, 0.16 mmol) and cyclopentadiene (31 mg, 0.47 mmol) in CH_2Cl_2 (16 mL) and dry MeCN (8 mL) was stirred at 40 °C for 115 h under argon atmosphere. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and condensed to leave a residue. The residue was purified by column chromatography on silica gel with toluene to give 7,7-di(2-azulenyl)bicyclo[3.2.0]hept-2-en-6-one (**10**) (30 mg, 54%) as purple needles (mp 120 °C (decomp) from hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.4-2.5 (1H, m, H-4a), 2.7-2.8 (1H, m, H-4b), 4.1-4.2 (1H, m, H-5), 4.4-4.5 (1H, m, H-1), 5.5-5.6 (1H, m, H-2), 5.7-5.8 (1H, m, H-3), 7.12 (2H, dd *J*= 9.8, 9.8 Hz, Az-5', 7'), 7.15 (2H, dd, *J*= 9.8, 9.8 Hz, Az-5", 7"), 7.31 (2H, s, Az-1', 3'), 7.35 (2H, s, Az-1", 3"), 7.50 (1H, dd, *J*= 9.8, 9.8 Hz, Az-6'), 7.53 (1H, dd, *J*= 9.8, 9.8 Hz, Az-6"), 8.21 (2H, d, *J*= 9.8 Hz, Az-4', 8'), 8.23 (2H, d, *J*= 9.8 Hz, Az-4", 8"). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 30.9, 34.8, 51.9, 59.5, 115.9, 116.6, 123.1, 123.6, 131.1, 133.8, 136.0, 136.3, 136.4, 136.8, 140.0, 140.4, 150.2, 151.6, 211.3. IR (KBr): 3045, 2947, 2920, 2908, 2846, 1768, 1572, 1468, 1400, 823, 739, 729 cm^{-1}. MS: m/z (rel. int. %) 360 (M^+, 19), 268 (100), 265 (61), 252 (59). Anal. Calcd for $C_{27}H_{20}O$; C, 89.97; H, 5.59. Found: C, 89.67; H, 5.81.

b) A solution of **2** (115 mg, 0.36 mmol) and methylcyclopentadiene (a mixture of 1-methylcyclopentadiene and 2-methylcyclopentadiene) (86 mg, 1.07 mmol) in CH_2Cl_2 (37 mL) and dry MeCN (18 mL) was stirred at 40 °C for 65 h under argon atmosphere. The reaction mixture was treated by a method similar to that used for method a) described above. The residue was chromatographied on silica gel with benzene to give a mixture of 7,7-di(2-azulenyl)-3-methylbicyclo[3.2.0]hept-2-en-6-one (**11a**) and 7,7-di(2-azulenyl)-4-methylbicyclo[3.2.0]hept-2-en-6-one (**11b**) as purple oil (38 mg, 28%). **11a:** ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.65(s, -CH_3), 2.5-2.6(m, H-4a), 2.7-2.8(m, H-4b), 4.1-4.2(m, H-5), 4.4-4.5(m, H-1), 5.2-5.3(m, H-2), 7.1-7.2(m, Az-5,5',7,7'), 7.3-7.4(m, Az-1,1',3,3'), 7.5-7.6(m, Az-6,6'), 8.1-8.3(m, Az-4,4',8,8'). **11b:** ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.55(s, -CH_3), 2.5-2.6(m, H-4a), 2.7-2.8(m, H-4b), 4.1-4.2(m, H-5), 4.4-4.5(m, H-1), 5.4-5.5(m, H-3), 7.1-7.2(m, Az-5,5',7,7'), 7.3-7.4(m, Az-1,1',3,3'), 7.5-7.6(m, Az-6,6'), 8.1-8.3(m, Az-4,4',8,8').

***N*-Substituted 2-azulenylmethyleneimines** ***N*-Phenyl-2-azulenylmethyleneimine (14a):** A solution of 2-formylazulene (**13**) (50 mg, 0.32 mmol) and aniline (30 mg, 0.32 mmol) in ethanol (5 mL) was stirred at rt for 30 min. The reaction mixture was diluted with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give **14a** (70 mg, 95%) as green plates (mp 107-108 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.16 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.25 (1H, dd, *J*= 7.5, 7.5 Hz, *Ph*-4), 7.30 (2H, d, *J*= 7.5, *Ph*-2,6), 7.42 (2H, dd , *J*= 7.5, 7.5 Hz, *Ph*-3,5), 7.58 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.78 (2H, s, *Az*-1,3), 8.35 (2H, d, *J*= 9.8 Hz, *Az*-4,8), 8.83 (1H, s, -CH=N-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 117.9, 121.0, 124.0, 126.2, 129.2, 138.8, 138.9, 140.8, 145.7, 152.4, 157.2. IR (KBr): 1612, 1589, 1572, 1562, 1481, 1404, 1136, 822, 748, 733, 692 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 292(4.77), 364(4.19), 381(4.11), 603(2.74), 644(2.76), 701(2.46). MS: m/z (rel. int. %) 231 (M^+, 77), 230 (100), 127 (21), 77 (35). Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06%. Found: C, 88.55; H, 5.53; N, 6.20%.

***N*-(4-Fluorophenyl)-2-azulenylmethyleneimine (14b):** A solution of **13** (150 mg, 0.96 mmol) and 4-fluoroaniline (107 mg, 0.96 mmol) in ethanol (15 mL) was stirred at rt for 1 h. The reaction mixture was treated by a method similar to that used for **14a** described above to give **14b** (235 mg, 94%) as green plates (mp 146-147 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.11 (2H, dd, *J*= 8.5, 5.0 Hz, *Ph*-3,5), 7.18 (dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.30 (2H, dd, *J*= 8.5, 5.0 Hz, *Ph*-2,6), 7.60 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.77 (2H, s, *Az*-4,8), 8.83 (1H, s, -CH=N-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 115.8, 116.0, 117.8, 122.5, 122.5, 124.1, 138.9, 139.0, 140.9, 156.9. IR (KBr): 1608, 1568, 1508, 1500, 1219, 1198, 1134, 835, 827, 796, 737 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 241(4.21), 295(4.74), 382(4.19), 394(4.18), 417(3.89), 600(2.69), 643(2.71), 703(2.40). MS: m/z (rel. int. %) 249 (M^+,99), 248 (100), 153 (11), 128 (15), 127 (34), 95 (13). Anal. Calcd for $C_{17}H_{12}NF$: C, 81.90; H, 4.85; N, 5.62. Found: C, 81.60; H, 5.17; N,

5.71.

***N*-(4-Methoxyphenyl)-2-azulenylmethyleneimine (14c):** A solution of **13** (50 mg, 0.32 mmol) and *p*-anisidine (39 mg, 0.32 mmol) in ethanol (10 mL) was stirred at rt for 30 min. The reaction mixture was treated by a method similar to that used for **14a** to give **14c** (80 mg, 95%) as green plates (mp 167-168 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.83 (3H, s, -OCH_3), 6.95 (2H, d, *J*= 8.8 Hz, *Ph*-3,5), 7.14 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.33 (2H, d, *J*= 8.8 Hz, *Ph*-2,6), 7.55 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.76 (2H, s, *Az*-1,3), 8.32 (2H, d, *J*= 9.8 Hz, *Az*-4,8), 8.85 (1H, s, -CH=N-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.4, 114.4, 117.6, 122.4, 123.9, 138.5, 140.8, 145.2, 146.1, 155.0, 158.5. IR (KBr): 1614, 1591, 1577, 1560, 1508, 1298, 1242, 1161, 1032, 835, 729 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 234(4.29), 296(4.70), 328(4.29), 398(4.23), 414(4.25), 598(2.69), 642(2.70), 701(2.38). MS: m/z (rel. int. %) 261 (M^+,100), 246 (40), 217 (39), 127 (11). Anal. Calcd for $C_{18}H_{15}ON$:C, 82.73; H, 5.79; N, 5.36. Found: C, 83.01; H, 5.81; N, 5.27.

***N-tert*-Butyl-2-azulenylmethyleneimine (14d):** A mixture of **13** (200 mg, 1.28 mmol) and *tert*-butylamine (10 mL) was stirred at rt for 1.5 h. The reaction mixture was diluted with water and extracted with ether. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give **14d** (270 mg, 99%) as blue plates (mp 41-42 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.36 (9H, s, -$C(CH_3)_3$), 7.14 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.55 (1H, dd *J*= 9.8, 9.8 Hz, *Az*-6), 7.66 (2H, s, *Az*-1,3), 8.31 (2H, d, *J*= 9.8, *Az*-4,8), 8.67 (1H, s, -CH=N-). ^{13}C-Nmr (100 MHz, $CDCl_3$) δ: 29.7, 57.8, 117.0, 123.5, 137.8, 137.9, 140.6, 147.0, 152.7.IR (KBr): 2968, 2927, 2902, 2871, 1630, 1568, 1363, 1221, 1196, 823, 727 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 238(4.18), 289(4.76), 299(4.67), 344(3.75), 356(3.83), 373(3.96), 590(2.64), 633(2.65), 691(2.33). Ms: m/z (rel. int. %) 211 (M^+,100), 196 (100), 155 (70), 127 (32). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.55; H, 8.21; N, 6.51.

***N*-Isopropyl-2-azulenylmethyleneimine (14e):** A mixture of **13** (200 mg, 1.28 mmol) and isopropylamine (5 mL) was stirred at rt for 1 h. The reaction mixture was treated by a method similar to that used for **14d** described above to give **14e** (250 mg, 98%) as blue plates (mp 53-54 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.33 (6H, d, *J*= 6.3 Hz, -$CH(C\underline{H}_3)_2$), 3.60 (1H, sep, *J*= 6.3 Hz, -$C\underline{H}(CH_3)_2$), 7.11 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.52 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.64 (2H, s, *Az*-1,3), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4,8), 8.66 (1H, s, -CH=N-). ^{13}C-Nmr (100 MHz, $CDCl_3$) δ: 24.2, 62.4, 117.2, 123.7, 138.1 x 2, 140.7, 146.2, 155.7. IR (KBr): 2956, 2920, 2841, 1630, 1572, 1402, 1373, 1196, 818, 727 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 238(4.18), 289(4.77), 301(4.65), 329(3.65), 343(3.75), 356(3.85), 373(3.99), 591(2.66), 634(2.66), 692(2.35). MS: m/z (rel. int. %) 197 (M^+,100), 182 (45), 167 (32), 155

(41), 141 (54), 127 (39). Anal. Calcd for $C_{14}H_{15}N$: C, 84.93; H, 7.66; N, 7.10. Found: C, 84.93; H, 7.77; N, 7.24.

***N*-Methyl-2-azulenylmethyleneimine (14f):** A mixture of **13** (50 mg, 0.32 mmol) and methylamine (40% aqueous solution) (10 mL) was stirred at room temperature for 1 h. The reaction mixture was treated by a method similar to that used for **14d** described above to give **14f** (52 mg, 96%) as blue needles (mp 51-52 °C, from hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.59 (3H d, *J*= 1.7 Hz, -CH_3), 7.10 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.51 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.59 (2H, s, *Az*-1,3), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4,8), 8.61 (1H, d, *J*= 1.7 Hz, -CH=N-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 48.9, 116.9, 123.7, 138.2 x 2, 140.6, 145.9, 159.2. IR (KBr): 2925, 2871, 2765, 1633, 1566, 1456, 1398, 1144, 816, 735 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 239(4.18), 289(4.76), 303(4.56), 330(3.62), 344(3.73), 356(3.82), 373(3.97), 593(2.64), 635(2.65), 691(2.32). MS: m/z (rel. int. %) 169 ($M^{+\cdot}$,75), 168 (100), 141 (60), 128 (27). Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 84.87; H, 6.85; N, 7.99.

***N*-(2-Thiazolyl)-2-azulenylmethyleneimine (14g):** To a solution of **13** (50 mg, 0.32 mmol) and 2-amino-thiazole (320 mg, 3.20 mmol) in dry benzene (10 mL) was added zinc chloride (130 mg, 0.96 mg). The mixture was refluxed for 1 h. The reaction mixture was diluted with water and extracted with benzene. Organic layer was washed with water several times, dried over anhydrous sodium sulfate, and condensed under reduced pressure to give **14g** (75 mg, 99%) as green plates (mp 113-114 °C, from hexane) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.10 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5,7), 7.22 (1H, d, *J*= 3.5 Hz, *Th*-5), 7.54 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6), 7.70 (1H, d, *J*= 3.5 Hz, *Th*-4), 7.79 (2H, s, *Az*-1,3), 8.30 (2H, d, *J*= 9.8 Hz, *Az*-4,8), 9.33 (1H, s, -CH=N-). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 118.4, 118.9, 124.2, 139.7, 139.7, 140.8, 141.5, 144.0, 159.6, 173.5. IR (KBr): 1591, 1562, 1477, 1406, 1354, 1119, 818, 735 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 249(4.18), 305(4.51), 326(4.41), 387(4.27), 402(4.32), 422(4.21), 453(3.77), 614(2.73), 658(2.76), 717(2.48). MS: m/z (rel. int. %) 238 (M^+,32), 237 (100), 127 (8). Anal. Calcd for $C_{14}H_{10}N_2S$: C, 70.56; H, 4.23; N, 11.76. Found: C, 70.26; H, 4.44; N, 11.70.

General procedure for preparing azulene-substituted β-lactams: To a solution of **2** (41 mg, 0.127 mmol) in CH_2Cl_2 (13 mL) and dry MeCN (6.5 mL) was added *N*-substituted-2-azulenylmethyleneimines (**14a-g**) (0.254 mmol). The mixture was stirred at 40 °C for 25 ~74 h under argon atmosphere. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed on silica gel with benzene to give corresponding azulene-substituted β-lactams (**15a-g**), respectively.

3,3,4-Tri(2-azulenyl)-1-phenylazetidin-2-one (15a): Purple needles, mp 226 °C (decomp) (from toluene). Yield 39%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.31 (1H, s, H-4), 6.93 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-

5', 7'), 7.03 (2H, ddm, *J*= 9.8, 9.8 Hz, *Az*-5", 7"), 7.03 (1H, dd, *J*= 7.3, 7.3 Hz, *Ph*-4), 7.11 (2H, s, *Az*-1', 3'), 7.17 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.18 (2H, s, *Az*-1'', 3''), 7.23 (1H, dd, *J*= 7.3, 7.3 Hz, *Ph*-3,5), 7.36 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.45 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.48 (2H, d, *J*= 7.3, *Ph*-2,6), 7.55 (2H, s, *Az*-1''', 3'''), 7.55 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.93 (2H, d, *J*= 9.8, *Az*-4', 8'), 8.04 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 66.5, 69.1, 116.1, 116.9, 117.5, 117.6, 122.8, 123.3, 123.7, 123.9, 128.4, 129.0, 136.2, 136.5, 136.5, 137.0, 138.1, 139.5, 140.0, 140.4, 146.5, 147.2, 151.0, 167.4. IR (KBr): 1741, 1599, 1572, 1502, 1485, 1400, 1373, 731 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max}(*log* ε): 238 (4.75), 269 (4.96), 295 (5.13), 332 (4.29), 346 (4.26), 362 (3.96), 569 (3.01), 604 (2.96), 659 (2.57) nm. MS: m/z (rel. int. %) 525 (M^+,100), 406 (25), 397 (62), 389 (36), 278 (38), 265 (20), 128 (16). Anal. Calcd for $C_{39}H_{27}NO$: C, 89.11; H, 5.18; N, 2.66. Found: C, 88.97; H, 5.23; N, 2.37.

3,3,4-Tri(2-azulenyl)-1-(4-fluorophenyl)azetidin-2-one (15b): Purple needles, mp 185 °C (decomp) (from toluene). Yield 41%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.29 (1H, s, H-4), 6.92 (2H, dd, *J*= 8.7, 8.7 Hz, *Ph*-3, 5), 6.92 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 7.03 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.10 (2H, s, *Az*-1', 3'), 7.16 (2H, s, *Az*-1'', 3''), 7.17 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.35 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.43 (2H, d, *J*= 7.3, *Ph*-2,6), 7.45 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.55 (2H, s, *Az*-1''', 3'''), 7.56 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.93 (2H, d, *J*= 9.8 Hz, *Az*-4', 8'), 8.04 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 66.6, 69.3, 115.6, 115.8, 116.0, 116.7, 117.4, 118.9, 119.0, 122.8, 123.4, 123.7, 136.2, 136.5, 136.6, 136.7, 137.1, 137.2, 139.5, 140.0, 140.4, 146.1, 147.0, 150.8, 167.1. IR (KBr): 1738, 1574, 1508, 1477, 1400, 1387, 1371, 1230, 835,808 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max}(*log* ε): 236 (4.74), 268 (4.94), 295 (5.13), 332 (4.26), 346 (4.26), 361 (3.95), 568 (3.00), 605 (2.96), 665 (2.55) nm. MS: m/z (rel. int. %) 543 (M^+,100), 415 (80), 405 (44), 389 (40), 278 (55), 265 (28), 127 (8). Anal. Calcd for $C_{39}H_{26}NOF$: C, 86.16; H, 4.82; N, 2.58. Found: C, 85.88; H, 5.16; N, 2.53.

3,3,4-Tri(2-azulenyl)-1-(4-methoxyphenyl)azetidin-2-one (15c): Purple needles, mp 197 °C (decomp) (from toluene). Yield 32%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.71 (3H, s, -OCH_3), 6.27 (1H, s, H-4), 6.77 (2H, d, *J*= 9.0 Hz, *Ph*-3, 5), 6.92 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 7.02 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.11 (2H, s, *Az*-1', 3'), 7.17 (2H, s, *Az*-1'', 3''), 7.17 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.35 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.41 (2H, d, *J*= 9.0, *Ph*-2,6), 7.44 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.55 (2H, s, *Az*-1''', 3'''), 7.55 (1H, ddm, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.93 (2H, d, *J*= 9.8, *Az*-4', 8'), 8.03 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.4, 66.5, 69.1, 114.2, 116.1, 116.9, 117.5, 118.8, 122.7, 123.2, 123.7, 131.7, 136.1, 136.4, 136.4, 136.6, 137.0, 137.0, 139.5, 140.0, 140.4, 146.7, 147.3, 151.1, 156.0, 166.8. IR (KBr): 1743, 1574, 1508, 1473, 1398, 1389,

1377, 1246, 808 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 238 (4.74), 270 (4.99), 295 (5.15), 332 (4.29), 346 (4.27), 359 (3.99), 569 (3.01), 605 (2.96), 662 (2.56). MS: m/z (rel. int. %) 555 (M^+,94), 427 (64), 406 (76), 405 (100), 278 (69), 265 (29), 128 (13). Anal. Calcd for $C_{40}H_{29}NO_2$: C, 86.46; H, 5.26; N, 2.52. Found: C, 86.16; H, 5.44; N, 2.72.

3,3,4-Tri(2-azulenyl)-1-*tert*-butylazetidin-2-one (15d): Purple needles, mp 252 °C (decomp) (from toluene). Yield 42%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.40 (9H, s, -C(CH_3)$_3$), 5.83 (1H, s, H-4), 6.88 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 6.96 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.05 (2H, s, *Az*-1', 3'), 7.08 (2H, s, *Az*- 1'', 3''), 7.10 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.31 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.38 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.44 (2H, s, *Az*-1''', 3'''), 7.48 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.89 (2H, d, *J*= 9.8, *Az*-4', 8'), 7.98 (2H, d, *J*= 9.8 Hz, *Az*- 4'', 8''), 8.22 (2H, d, *J*= 9.8 Hz, *Az*- 4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 28.5, 54.9, 65.6, 67.5, 116.0, 117.3, 117.6, 122.6, 123.1, 123.5, 135.9, 136.1 x 2, 136.3, 136.7 x 2, , 139.5, 139.8, 140.3, 148.3, 149.8, 152.0, 169.7. IR (KBr): 1736, 1572, 1560, 1473, 1398, 1356, 1333, 725 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 237 (4.66), 267 (4.80), 297 (5.10), 333 (4.23), 348 (4.21), 365 (3.97), 569 (3.00), 607 (2.95), 662 (2.55). Ms: m/z (rel. int. %) 505 (M^+,55), 406 (44), 294 (98), 278 (15), 265 (100), 128 (12). Anal. Calcd for $C_{37}H_{31}NO$: C, 87.89; H, 6.18; N, 2.77. Found: C, 87.97; H, 6.17; N, 2.74.

3,3,4-Tri(2-azulenyl)-1-isopropylazetidin-2-one (15e): Purple needles, mp 208 °C (decomp) (from toluene). Yield 46%. ^{1}H-NMR(400 MHz, $CDCl_3$) δ: 1.18 (3H, d, *J*= 6.7 Hz, -CH(C$\underline{H}_3$)$_2$), 1.44 (3H, d, *J*= 6.7 Hz, -CH(C$\underline{H}_3$)$_2$), 4.01 (1H, sep, *J*= 6.7 Hz, -C$\underline{H}$(CH$_3$)$_2$), 5.84 (1H, s, H-4), 6.94 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 7.03 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.06 (2H, s, *Az*-1', 3'), 7.10 (2H, s, *Az*-1'', 3''), 7.15 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.37 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.45 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.46 (2H, s, *Az*-1''', 3'''), 7.53 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.94 (2H, d, *J*= 9.8 Hz, *Az*-4', 8'), 8.04 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), 8.26 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 20.6, 21.6, 45.6, 65.3. 68.5, 116.0, 117.3, 117.6, 122.6, 123.1, 123.5, 135.9, 136.2, 136.3, 136.4, 136.7, 136.9, 139.5, 139.8, 140.4, 148.1, 148.5, 151.7, 169.7.IR (KBr): 1751, 1572, 1468, 1398, 1383, 1335, 1325, 1319, 800, 735 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 237 (4.69), 266 (4.82), 296 (5.11), 333 (4.25), 347 (4.23), 364 (4.00), 569 (3.01), 606 (2.95), 660 (2.56). MS: m/z (rel. int. %) 491 (M^+,100), 448 (32), 406 (21), 389 (29), 363 (63), 278 (46), 265 (21), 237 (20). Anal. Calcd for $C_{36}H_{29}NO$: C, 87.95; H, 5.95; N, 2.85. Found: C, 87.91; H, 6.24; N, 2.78.

3,3,4-Tri(2-azulenyl)-1-methylazetidin-2-one (15f): Purple needles, mp 175 °C (decomp) (from toluene). Yield 35%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.04 (3H, s, -CH_3), 5.81 (1H, s, H-4), 6.93 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 7.06 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.08 (2H, s, *Az*-1', 3'), 7.12 (2H, s, *Az*-1'', 3''), 7.17 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.36 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.48 (1H, dd,

J= 9.8, 9.8 Hz, *Az*-6''), 7.51 (2H, s, *Az*-1''', 3'''), 7.55 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.93 (2H, d, *J*= 9.8 Hz, *Az*-4', 8'), 8.09 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), 8.28 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 27.5, 68.0, 70.4, 116.1, 116.8, 117.5, 122.7, 123.3, 123.6, 136.0, 136.3, 136.4, 136.5, 136.8, 137.1, 139.5, 140.0, 140.4, 147.0, 147.7, 151.4, 170.1. IR (KBr): 1751, 1574, 1491, 1473, 1398, 1387, 1342, 735 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 236 (4.67), 266 (4.80), 296 (5.11), 332 (4.25), 347 (4.23), 363 (3.97), 568 (3.00), 607 (2.95), 658 (2.56). MS: m/z (rel. int. %) 463 (M^+,100), 389 (20), 335 (89), 278 (31), 254 (21), 209 (23). Anal. Calcd for $C_{34}H_{25}NO$: C, 88.09; H, 5.44; N, 3.02. Found: C, 87.73; H, 5.74; N, 2.89.

3,3,4-Tri(2-azulenyl)-1-(2-thiazolyl)azetidin-2-one (15g): Purple needles, mp 216 °C (decomp) (from toluene). Yield 61%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.07 (1H, d, *J*= 5.1 Hz, *Th*-5), 6.34 (1H, s, H-4), 6.75 (2H, s, *Az*-1', 3''), 6.88 (2H, s, *Az*-1'', 3''), 6.99 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5', 7'), 7.03 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.20 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5''', 7'''), 7.29 (1H, d, *J*= 5.1 Hz, *Th*-4), 7.43 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.46 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 7.52 (2H, s, *Az*-1''', 3'''), 7.60 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'''), 7.97 (2H, d, *J*= 9.8 Hz, *Az*-4', 8'), 7.99 (2H, d, *J*= 9.8 Hz, *Az*- 4'', 8''), 8.30 (2H, d, *J*= 9.8 Hz, *Az*-4''', 8'''). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 55.7, 67.1, 105.6, 117.4, 117.7, 118.8, 124.0, 122.8, 123.0, 123.6, 136.2, 136.5, , 136.7 x 3, 137.1 137.4, 139.0, 139.7, 140.0, 148.1, 148.7, 150.4, 168.3. IR (KBr): 1714, 1631, 1574, 1468, 1400, 1358, 1323, 1230, 795 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (*log* ε): 236 (4.71), 271(4.91), 292 (5.13), 330 (4.36), 346 (4.29), 360 (4.01), 571 (3.02), 610 (2.97), 667 (2.57). MS: m/z (rel. int. %) 532 (M^+,1), 294 (27), 265 (76), 237 (100). Anal. Calcd for $C_{36}H_{24}N_2OS$: C, 81.18; H, 4.54; N, 5.26. Found: C, 80.82; H, 4.44; N, 5.14.

3,3-Di(2-azulenyl)-1,4-diphenylazetidin-2-one (16) To a solution of **2** (41 mg, 0.13 mmol) in CH_2Cl_2 (14 mL) and dry MeCN (7 mL) was added *N*-benzylideneaniline (46 mg, 0.25 mmol). The mixture was stirred at 40 °C for 74 h under argon atmosphere. The reaction mixture was treated by a method similar to that used for **14a** to give **16** (6 mg, 11%) as purple needles (mp 221 °C (decomp), recrystallized from benzene). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.92 (1H, s, H-4), 7.03 (2H, dd, *J*= 9.8, 9.8 Hz, Az-5', 7'), 7.0-7.1 (5H, m, *Ph*-2', 3', 4', 5', 6'), 7.11 (2H, s, *Az*-1', 3'), 7.17 (2H, dd, *J*= 9.8, 9.8 Hz, *Az*-5'', 7''), 7.2-7.3 (3H, m, *Ph*-3'', 4'', 5''), 7.44 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6'), 7.4-7.5 (2H, m, *Ph*-2'', 6''), 7.50 (2H, s, *Az*-1'', 3''), 7.55 (1H, dd, *J*= 9.8, 9.8 Hz, *Az*-6''), 8.04 (2H, d, *J*= 9.8 Hz, *Az*-4', 8'), 8.26 (2H, d, *J*= 9.8 Hz, *Az*-4'', 8''), ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 68.7, 69.3, 116.0, 117.5, 117.6, 123.0, 123.7, 124.0, 127.4, 128.2, 128.3, 129.1, 135.0, 136.3, 136.6, 136.7, 137.1, 137.8, 140.0, 140.4, 146.9, 150.7, 167.3. IR (KBr): 1743, 1599, 1574, 1500, 1493, 1398, 1377, 731 cm^{-1}. MS: m/z (rel. int. %) 475 (M^+,100), 398 (38), 356 (64), 278 (45). 228 (32), 128 (15). Anal. Calcd for $C_{35}H_{25}NO$: C, 88.39; H, 5.30; N, 2.95. Found: C, 88.05; H, 5.44; N, 2.95.

X-Ray structural analyses.

Reflection data were collected on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using Mo-Kα radiation (λ = 0.71069 Å) and Enraf-Nonius CAD4 diffractometer using Cu-Kα radiation (λ = 1.54178 Å). All structures were solved by direct methods and refined by full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included but not refined.

Crystal data for 12: $C_{29}H_{20}O_2$, *MW* = 400.48, monoclinic, space group $P2_1/n$, a = 10.278(1), b = 20.111(7), c = 10.763(3) Å, β = 109.22(2)°, V = 2101(1) Å^3, Z = 4, D_{calcd} = 1.266 g cm^{-3}, $F(000)$ = 840, μ(Cu Kα) = 6.15 cm^{-1}, crystal dimensions = 0.40 × 0.15 × 0.10 mm, 4515 reflections collected, 4277 independent (R_{int} = 0.0442), R_1 = 0.0533 [($I > 2\sigma(I)$), R_w = 0.1105.

Crystal data for 15d: $C_{37}H_{31}NO$, *MW* = 505.66, monoclinic, space group $P2_1/c$, a = 6.413(1), b = 9.035(2), c = 46.007(8) Å, β = 91.652(4)°, V = 2664.6(8) Å^3, Z = 4, D_{calcd} = 1.260 g cm^{-3}, $F(000)$ = 1072, μ(Mo Kα) = 0.75 cm^{-1}, crystal dimensions = 0.20 × 0.15 × 0.05 mm, 20822 reflections collected, 6112 independent (R_{int} = 0.086), R_1 = 0.053 [($I > 2\sigma(I)$), R_w = 0.096.

Crystal data for 15e: $C_{36}H_{29}NO$, *MW* = 491.63, monoclinic, space group $P2_1/n$, a = 13.4849(6), b = 10.1484(6), c = 19.8275(9) Å, β = 106.733(1)°, V = 2598.5(2) Å^3, Z = 4, D_{calcd} = 1.257 g cm^{-3}, $F(000)$ = 1040, μ(Mo Kα) = 0.75 cm^{-1}, crystal dimensions = 0.40 × 0.30 × 0.10 mm, 25051 reflections collected, 5947 independent (R_{int} = 0.042), R_1 = 0.038 [($I > 2\sigma(I)$), R_w = 0.083.

ACKNOWLEDGEMENT

The authors thank the Institute for Molecular Science for the carrying out the X-Ray analysis of **12**.

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