PREPARATION AND STRUCTURE OF DI(2- AZULENYL) KETENE ADDUCTS. \( \gamma \)-LACTONE AND \( \beta \)-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 \( \gamma \)-lactone (12) and \( \beta \)-lactams (15), respectively.

Since the first recorded 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 \( \beta \)-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).

![Chart 1](image-url)

The diazo ketone (2) was obtained by the oxidation of di(2-azulenyl)ethanedione\(^2\) monohydrazone (4) with copper(I) chloride/ \( \text{O}_2 \)/ pyridine or activated manganese dioxide in 55% and 91% yields, respectively.
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\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\) gave 2-azuloin methyl ether (5) (10%), methyl 2-azulencarboxylate (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 trapped ketocarbene (8) in the presence methanol (Scheme 3). The ketocarbene intermediate (8) has been also confirmed by a laser flash photolysis study.\(^4\)
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 \(^{13}\text{C}\)-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.
Recently, Machiguchi and co-workers have been proposed a new interesting feature that ketenes take part in 1,4-cycloaddition with 1,3-dienes, followed by subsequent [3,3] sigmatropic (Claisen) rearrangement to give [2+2] cycloadducts 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 \textit{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).

\[ \text{MeCN/ CH}_2\text{Cl}_2 \quad 40^\circ\text{C}, 90 \text{ h} \]

![X-Ray molecular structure of 12.](image)

The formation of the lactone (12) can be explained by considering the new two-step reaction mechanism,\(^6\) \textit{i.e.} the [2+2] addition and the subsequent [1,7] sigmatropic rearrangement (Scheme 6).
**β-Lactam derivatives:** [2+2] Cycloaddition of ketenes with imines is one of the effective synthetic method of β-lactam derivatives. Imines (14a-g) were obtained by the reaction of 2-formylazulene (13) with amines in almost quantitative yields (Scheme 7 and Table 1).

![Scheme 7](image)

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

<table>
<thead>
<tr>
<th>entry</th>
<th>primary amines</th>
<th>solvents</th>
<th>reaction conditions</th>
<th>products</th>
<th>physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>aniline</td>
<td>EtOH</td>
<td>rt, 30 min</td>
<td>14a</td>
<td>green plates mp 107-108°C</td>
</tr>
<tr>
<td>2</td>
<td>p-fluoroaniline</td>
<td>EtOH</td>
<td>rt, 1 h</td>
<td>14b</td>
<td>green plates mp 146-147°C</td>
</tr>
<tr>
<td>3</td>
<td>p-methoxyaniline</td>
<td>EtOH</td>
<td>rt, 30 min</td>
<td>14c</td>
<td>green plates mp 167-168°C</td>
</tr>
<tr>
<td>4</td>
<td>tert-butylamine</td>
<td>—</td>
<td>rt, 1.5 h</td>
<td>14d</td>
<td>blue plates mp 41-42°C</td>
</tr>
<tr>
<td>5</td>
<td>isopropylamine</td>
<td>—</td>
<td>rt, 1 h</td>
<td>14e</td>
<td>blue plates mp 53-54°C</td>
</tr>
<tr>
<td>6</td>
<td>methylamine</td>
<td>40% in water</td>
<td>rt, 1 h</td>
<td>14f</td>
<td>blue needles mp 51-52°C</td>
</tr>
<tr>
<td>7</td>
<td>2-aminothiazole</td>
<td>benzene</td>
<td>ZnCl₂, reflux, 1 h</td>
<td>14g</td>
<td>green plates mp 113-114°C</td>
</tr>
</tbody>
</table>

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-benzylideneaniline, 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).
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 \(\phi\)-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. The reaction mixture was poured in water and extracted with CH₂Cl₂. 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 C₂₂H₁₆N₂O: 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 CH₂Cl₂ (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 CH₂Cl₂ yielded 2 as green crystals (30 mg, 55%).

b) **Oxidation using activated manganese dioxide** A mixture of 4 (72 mg, 0.22 mmol) and activated manganese 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-CH₂Cl₂ 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⁺-N₂, 36), 265 (100), 155 (AzCO⁺, 98). Anal. Calcd for C₂₂H₁₄N₂O: 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/CH₂Cl₂** A solution of 2 in MeOH/MeCN/CH₂Cl₂ (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. ¹H-NMR (90 MHz, CDCl₃) δ : 3.67 (3H, s, OCH₃), 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’). ¹³C-NMR (22.5 MHz, CDCl₃) 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**: Blue plates, mp 112-113 °C (from hexane). **7**: Purple needles, mp 110-111 °C (from hexane). H-NMR (90 MHz, CDCl₃) δ: 3.87 (3H, s, OCH₃), 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’). C-NMR (22.5 MHz, CDCl₃) 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⁺-COOCH₃, 100), 265 (84), 127 (27). Anal. Calcd for C₇₅H₁₈O₂: C, 84.63; H, 5.56. Found: C, 84.30; H, 5.53.

4,4-Di(2-azuleny1)-1,2-diphenyldiazetidin-3-one (9) To a solution of 2 (32 mg, 0.10 mmol) in CH₂Cl₂ (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). H-NMR (90 MHz, CDCl₃) δ: 8.26 (4H, d, J= 9.8 Hz, Az-4, 4’, 8, 8’), 6.7-7.7 (20H, m). C-NMR (22.5 MHz, CDCl₃) 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 C₃₈H₃₈N₂O: C, 85.68; H, 5.88. Found: C, 85.35; H, 5.68.

[2+2] Cycloaddition of di(2-azuleny1)ketene (1) with cyclopentadienes a) A mixture of 2 (50 mg, 0.16 mmol) and cyclopentadiene (31 mg, 0.47 mmol) in CH₂Cl₂ (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-azuleny1)bicyclo[3.2.0]hept-2-en-6-one (10) (30 mg, 54%) as purple needles (mp 120 °C (decomp) from hexane). H-NMR (300 MHz, CDCl₃) 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”). C-NMR (75 MHz, CDCl₃) 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 C₂₇H₂₀O: 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 CH₂Cl₂ (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 chromatographed 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: ¹H-NMR (300 MHz, CDCl₃)  δ: 1.65(s, -CH₃), 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',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: ¹H-NMR (300 MHz, CDCl₃)  δ: 1.55(s, -CH₃), 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',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-azulenylmethyleimines  N-Phenyl-2-azulenylmethyleimine (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). ¹H-NMR (400 MHz, CDCl₃)  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=). ¹³C-NMR (100 MHz, CDCl₃)  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 (CH₂Cl₂)  \( \epsilon_{\text{max}} \) (log ɛ): 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 C₁₇H₁₃N: C, 88.28; H, 5.67; N, 6.06%. Found: C, 88.55; H, 5.53; N, 6.20%.

N-(4-Fluorophenyl)-2-azulenylmethyleimine (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). ¹H-NMR (400 MHz, CDCl₃)  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=). ¹³C-NMR (100 MHz, CDCl₃)  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 (CH₂Cl₂)  \( \epsilon_{\text{max}} \) (log ɛ): 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 C₁₇H₁₂NF: 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). ¹H-NMR (400 MHz, CDCl₃) δ: 3.83 (3H, s, -OCH₃), 6.95 (2H, d, J= 8.8 Hz, Ph-H₂), 7.14 (2H, dd, J= 9.8, 9.8 Hz, Az-5,7), 7.33 (2H, d, J= 8.8 Hz, Ph-H₂), 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-). ¹³C-NMR (100 MHz, CDCl₃) 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 (CH₂Cl₂) ℓₘₐₓ (log ℓ): 234(4.29), 296(7.40), 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 C₁₅H₁₃ON: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). ¹H-NMR (400 MHz, CDCl₃) δ: 1.36 (9H, s, -C(CH₃)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-). ¹³C-Nmr (100 MHz, CDCl₃) 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 (CH₂Cl₂) ℓₘₐₓ (log ℓ): 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 C₁₅H₁₃N: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). ¹H-NMR (400 MHz, CDCl₃) δ: 1.33 (6H, d, J= 6.3 Hz, -CH(CH₃)₂), 3.60 (1H, sep, J= 6.3 Hz, -CH(CH₃)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-). ¹³C-Nmr (100 MHz, CDCl₃) 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 (CH₂Cl₂) ℓₘₐₓ (log ℓ): 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
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). ¹H-NMR (400 MHz, CDCl₃) δ: 3.59 (3H d, J= 1.7 Hz, -CH₃), 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-). ¹³C-NMR (100 MHz, CDCl₃) 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 (CH₂Cl₂) [max (log δ): 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⁺,75), 168 (100), 141 (60), 128 (27). Anal. Calcd for C₁₄H₁₁N: 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-aminothiazole (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) ¹H-NMR (400 MHz, CDCl₃) 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-). ¹³C-NMR (100 MHz, CDCl₃) 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 (CH₂Cl₂) [max (log δ): 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 C₁₄H₁₀N₅S: 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 CH₂Cl₂ (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%. ¹H-NMR (400 MHz, CDCl₃) δ: 6.31 (1H, s, H-4), 6.93 (2H, d, J= 9.8, 9.8 Hz, Az-
3,3,4-Tri(2-azulenyl)-1-(4-fluorophenyl)azetidin-2-one (15b): Purple needles, mp 185 °C (decomp) (from toluene). Yield 41%. 1H-NMR (400 MHz, CDCl₃) δ: 6.29 (1H, s, H-4), 6.92 (2H, dd, J = 8.7, 8.7 Hz, Ph-3, 5), 7.03 (2H, dd, J = 9.8, 9.8 Hz, Az-5′′, 7′′), 7.11 (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′″), 7.35 (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′″), 7.75 (1H, ddm, J = 9.8, 9.8 Hz, Az-6′′′), 7.93 (2H, d, J = 9.8, Az-4′, 8′). 13C-NMR (100 MHz, CDCl₃) 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, 136.7, 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 (CH₂Cl₂) 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 C₃₉H₂₆NO: 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-methoxyphenyl)azetidin-2-one (15c): Purple needles, mp 197 °C (decomp) (from toluene). Yield 32%. 1H-NMR (400 MHz, CDCl₃) δ: 3.71 (3H, s, -OCH₃), 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′″), 7.75 (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′′′). 13C-NMR (100 MHz, CDCl₃) 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, 136.6, 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, 1373, 1354, 1345, 1335, 1325, 1315, 1305, 1295, 1285, 1275, 1265, 1255, 1245, 1235, 1225, 1215, 1205, 1195, 1185, 1175, 1165, 1155, 1145, 1135, 1125, 1115, 1105, 1095, 1085, 1075, 1065, 1055, 1045, 1035, 1025, 1015, 1005, 995, 985, 975, 965, 955, 945, 935, 925, 915, 905, 895, 885, 875, 865, 855, 845, 835, 825, 815, 805, 795, 785, 775, 765, 755, 745, 735, 725, 715, 705, 695, 685, 675, 665, 655, 645, 635, 625, 615, 605, 595, 585, 575, 565, 555, 545, 535, 525, 515, 505, 495, 485, 475, 465, 455, 445, 435, 425, 415, 405, 395, 385, 375, 365, 355, 345, 335, 325, 315, 305, 295, 285, 275, 265, 255, 245, 235, 225, 215, 205, 195, 185, 175, 165, 155, 145, 135, 125, 115, 105, 95, 85, 75, 65, 55, 45, 35, 25, 15, 5, 1.
1377, 1246, 808 cm⁻¹. UV-VIS (CH₂Cl₂) 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 C₄₀H₂₈NO₂: C, 86.46; H, 5.26; N, 2.52. Found: C, 86.16; H, 5.44; N, 2.72.

3,3,4-Tri(2-azuleny)-1-tert-butylazetidin-2-one (15d): Purple needles, mp 252 ºC (decomp) (from toluene). Yield 42%. ¹H-NMR (400 MHz, CDCl₃) δ: 1.40 (9H, s, -C(CH₃)₃), 5.83 (1H, s, H-4), 6.88 (2H, dd, J= 9.8, 9.8 Hz, A₃₋₅’, 7’), 6.96 (2H, dd, J= 9.8, 9.8 Hz, A₃₋₅”, 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, A₃₋₅”, 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”). ¹³C-NMR (100 MHz, CDCl₃) δ: 28.5, 54.9, 65.6, 67.5, 116.0, 117.3, 117.6, 112.6, 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 (CH₂Cl₂) 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 C₁₀H₂₈NO: C, 87.89; H, 6.18; N, 2.77. Found: C, 87.97; H, 6.17; N, 2.74.

3,3,4-Tri(2-azuleny)-1-isopropylazetidin-2-one (15e): Purple needles, mp 208 ºC (decomp) (from toluene). Yield 46%. ¹H-NMR(400 MHz, CDCl₃) δ: 1.18 (3H, d, J= 6.7 Hz, -CH(CH₃)₂), 1.44 (3H, d, J= 6.7 Hz, -CH(CH₃)₂), 4.01 (1H, sep, J= 6.7 Hz, -CH(CH₃)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”). ¹³C-NMR (100 MHz, CDCl₃) 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 (CH₂Cl₂) 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 C₁₉H₂₈NO: C, 87.95; H, 5.95; N, 2.85. Found: C, 87.91; H, 6.24; N, 2.78.

3,3,4-Tri(2-azuleny)-1-methylazetidin-2-one (15f): Purple needles, mp 175 ºC (decomp) (from toluene). Yield 35%. ¹H-NMR (400 MHz, CDCl₃) δ: 3.04 (3H, s, -CH₃), 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,
3,3,4-Tri(2-azulenyl)-1-(2-thiazolyl)azetidin-2-one (15g): Purple needles, mp 216 °C (decomp) (from toluene). Yield 61%. 1H-NMR (400 MHz, CDCl₃) : 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'''''). 13C-NMR (100 MHz, CDCl₃) : 55.7, 67.1, 105.6, 117.4, 117.7, 118.8, 124.0, 122.8, 123.0, 123.6, 132.6, 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 (CH₂Cl₂) : 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 C₃₆H₂₅N₂O₈: 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 CH₂Cl₂ (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). 1H-NMR (400 MHz, CDCl₃) : 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'''). 13C-NMR (100 MHz, CDCl₃) : 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 C₃₆H₂₅N₂O : 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-K$\alpha$ radiation ($\lambda = 0.71069$ Å) and Enraf-Nonius CAD4 diffractometer using Cu-K$\alpha$ radiation ($\lambda = 1.54178$ 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: $\text{C}_{29}\text{H}_{20}\text{O}_2$, $MW = 400.48$, monoclinic, space group $P2_1/n$, $a = 10.278(1)$, $b = 20.111(7)$, $c = 10.763(3)$ Å, $\beta = 109.22(2)^{\circ}$, $V = 2101(1)$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.266$ g cm$^{-3}$, $F(000) = 840$, $\mu$(Cu K$\alpha$) = 6.15 cm$^{-1}$, crystal dimensions = 0.40 $\times$ 0.15 $\times$ 0.10 mm, 4515 reflections collected, 4277 independent ($R_{\text{int}} = 0.0442$), $R_1 = 0.0533$ [(I > 2$\sigma$(I)), $R_w = 0.1105$.

Crystal data for 15d: $\text{C}_{77}\text{H}_{16}\text{NO}$, $MW = 505.66$, monoclinic, space group $P2_1/c$, $a = 6.413(1)$, $b = 9.035(2)$, $c = 46.007(8)$ Å, $\beta = 91.652(4)^{\circ}$, $V = 2664.6(8)$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.260$ g cm$^{-3}$, $F(000) = 1072$, $\mu$(Mo K$\alpha$) = 0.75 cm$^{-1}$, crystal dimensions = 0.20 $\times$ 0.15 $\times$ 0.05 mm, 20822 reflections collected, 6112 independent ($R_{\text{int}} = 0.086$), $R_1 = 0.053$ [(I > 2$\sigma$(I)), $R_w = 0.096$.

Crystal data for 15e: $\text{C}_{36}\text{H}_{22}\text{NO}$, $MW = 491.63$, monoclinic, space group $P2_1/n$, $a = 13.4849(6)$, $b = 10.1484(6)$, $c = 19.8275(9)$ Å, $\beta = 106.733(1)^{\circ}$, $V = 25985.2(2)$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.257$ g cm$^{-3}$, $F(000) = 1040$, $\mu$(Mo K$\alpha$) = 0.75 cm$^{-1}$, crystal dimensions = 0.40 $\times$ 0.30 $\times$ 0.10 mm, 25051 reflections collected, 5947 independent ($R_{\text{int}} = 0.042$), $R_1 = 0.038$ [(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.

REFERENCES AND NOTES
1. H. Staudinger, Ber., 1905, 38, 1735; H. Staudinger, ibid., 1907, 40, 1145; H. Staudinger, ibid., 1911, 44, 1619.
4. (a) The ketocarbene (5) has been confirmed by a laser flash photolysis of 2. The details will be reported in the other paper; (b) J. P. Toscano, M. S. Platz, V. Nikolaev, and V. Popic, J. Am. Chem. Soc., 1994, 116, 8146.

