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## SYNTHESIS AND REDOX BEHAVIOR OF CYANOVINYLSUBSTITUTED 2*H*-CYCLOHEPTA[*b*]FURAN-2-ONES<sup>†</sup>

Taku Shoji,<sup>a\*</sup> Junya Higashi,<sup>b</sup> Shunji Ito,<sup>c</sup> Mitsunori Oda,<sup>a</sup> Masafumi Yasunami,<sup>d</sup> and Noboru Morita<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto, 390-8621, Japan

e-mail address: tshoji@shinshu-u.ac.jp

<sup>b</sup> Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

<sup>c</sup> Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

<sup>d</sup> Department of Materials Chemistry and Engineering, College of Engineering, Nihon University, Koriyama 963-8642, Japan

**Abstract** – Cyanovinyl-substituted 2*H*-cyclohepta[*b*]furan-2-ones **3**, **4**, **5** and **7** were prepared by the Wittig, Knoevenagel and electrophilic substitution reaction, respectively. The intramolecular charge-transfer (ICT) interactions between the 2*H*-cyclohepta[*b*]furan-2-one ring and cyanovinyl acceptor moiety were investigated by UV/Vis spectroscopy and theoretical calculations. The redox behavior of these novel compounds was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Significant color changes in these compounds were observed under electrochemical reduction conditions by visible spectroscopy.

## INTRODUCTION

2*H*-Cyclohepta[*b*]furan-2-one is known as a heteroazulene, a versatile precursor for azulene derivatives.<sup>1</sup> Although unusual reactivity of the compound including its derivatives has already been revealed by many research groups,<sup>2</sup> there are few derivatives for the application to the advanced materials with potentially useful electronic properties.

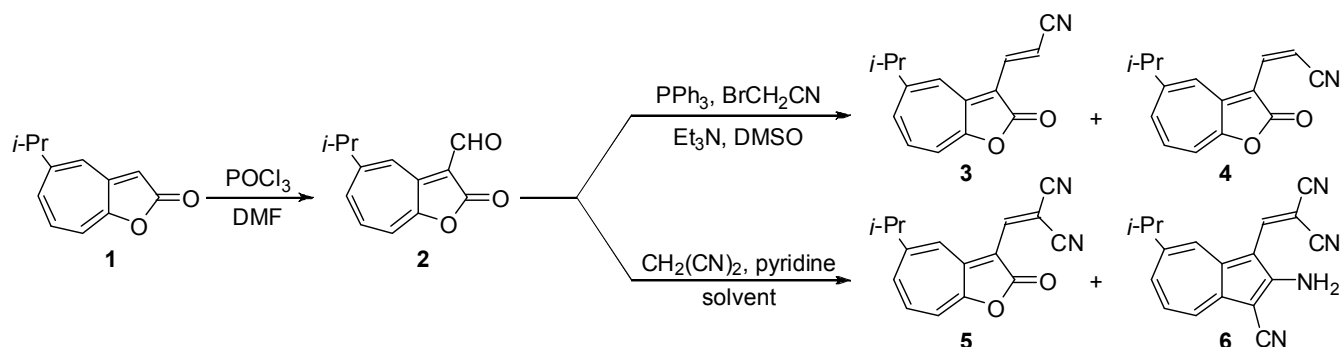
<sup>†</sup> Dedicated to Prof. Ei-ichi Negishi on the occasion of his 77th birthday.

Recently, we have reported the reaction of mono-, bis-, and tris(1-azulenylethynyl and 2*H*-cyclohepta[*b*]furan-2-on-3-ylethynyl)benzene and thiophene derivatives with tetracyanoethylene (TCNE) to give the tetracyanobutadiene (TCBD) substituted chromophores in excellent yield. We have also revealed that these new chromophores exhibit multistep reduction waves on CV and DPV. Moreover, significant color changes are also observed by the electrochemical reduction of these new derivatives.<sup>3,4</sup> However, synthesis and properties of cyanovinyl-substituted, which is unit of the TCBD, 2*H*-cyclohepta[*b*]furan-2-ones were never investigated. To clarify the substituent effect toward the spectroscopic and electrochemical property is an important clue to the design of organic materials. Herein, we describe the synthesis of mono-, di-, tricyanovinyl-2*H*-cyclohepta[*b*]furan-2-one derivatives by the Wittig, Knoevenagel and electrophilic substitution reaction, respectively. Electronic properties of the new 3-cyanovinyl-2*H*-cyclohepta[*b*]furan-2-one derivatives obtained by the reaction are characterized by CV, DPV, and absorption spectroscopy.

## RESULTS AND DISCUSSION

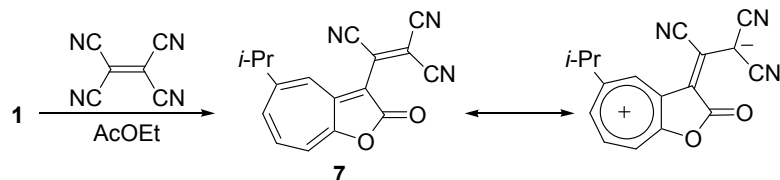
**Synthesis:** Prior to the cyanovinylation of 2*H*-cyclohepta[*b*]furan-2-one, the key intermediate formyl derivative **2** was prepared by Vilsmeier formylation of **1**, which can readily be prepared by the decarboxylation of 5-isopropyl-3-methoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one with 80% sulfuric acid.<sup>2</sup> The reaction of **1** with POCl<sub>3</sub> in DMF afforded **1** in 94 % yield, as similar with the literature (Scheme 1).<sup>5</sup> We applied the Wittig<sup>6</sup> and Knoevenagel<sup>7</sup> reaction of **2** for the preparation of the corresponding cyanovinyl derivatives. Reaction of **2** with bromoacetonitrile in the presence of triphenylphosphine in mixed solvent of DMSO/Et<sub>3</sub>N gave **3** (47% yield) and **4** (51% yield), respectively. Although the reaction afforded a mixture of **3** and **4**, these were easily separated by reversed-phase chromatography (ODS gel with 80% MeOH). For the purpose of preparation for dicyanovinyl derivative, we examined similar Wittig reaction of **2** using the 2-bromomalononitrile. However, reaction of **2** with 2-bromomalononitrile formed an insoluble complex mixture. This result might be attributable to the instability of compound in this condition. Thus, synthesis of **5** was established by the reaction of **2** with malononitrile under Knoevenagel condition. The yield of the products in this reaction was directly affected by the solvent and amount of the reagent. The reaction of **2** with equimolar amounts of malononitrile in the presence of pyridine in CH<sub>2</sub>Cl<sub>2</sub> afforded the dicyanovinyl derivative **5** in 51% yield as sole product. The reaction of **2** with the 2 equiv. of malononitrile in CH<sub>2</sub>Cl<sub>2</sub> gave **5** in 10% yield, along with 2-aminoazulene derivative **6** in 34% yield, respectively. When the solvent was changed to EtOH, compound **6** was obtained in 83% yield as sole product. In the early days of troponoid chemistry, Nozoe *et al.* reported the reaction between 2*H*-cyclohepta[*b*]furan-2-one and malononitrile in EtOH gave 2-amino-1-cyanoazulene derivatives in high yield.<sup>8</sup> Therefore, the reaction between **2** and malononitrile

should be proceeded through the similar reaction mechanism reported by Nozoe *et al.*



**Scheme 1.** Synthesis of 2*H*-cyclohepta[*b*]furan-2-one derivatives 2–6.

Tricyanovinyl-derivative **7** was synthesized by the electrophilic substitution reaction of **1** with TCNE (Scheme 2). TCNE is known as a strong organic electron acceptor, and the high reactivity of TCNE toward nucleophiles or electron-rich reagents is frequently used to introduce strong acceptor moieties into organic molecules.<sup>9</sup> Previously, Hafner *et al.* reported the reaction between azulene and TCNE, giving 1-(1,2,2-tricyanoethenyl)azulene *via* CT complex between azulene and TCNE.<sup>10</sup> We also reported the reaction of 1,6-di-*tert*-butylazulene with TCNE afforded the corresponding tricyanovinyl-derivative in excellent yield.<sup>11</sup> Similar with azulene derivatives, the reaction of **1** with TCNE in ethyl acetate at 50 °C yielded the expected tricyanovinyl-derivative **7** in 80% yield.

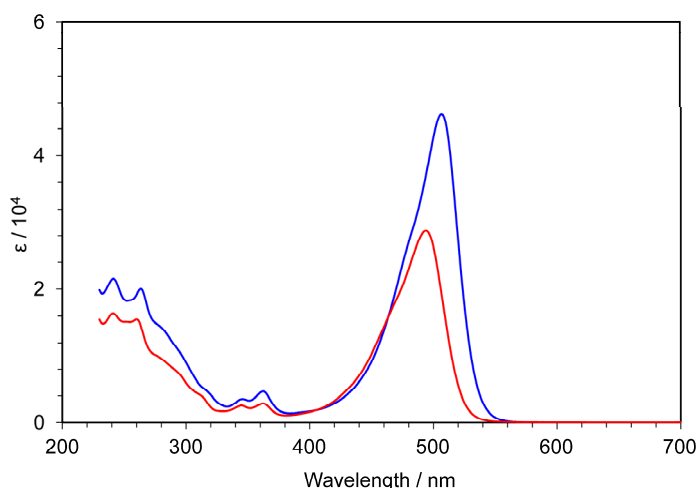


**Scheme 2.** Reaction of **1** with TCNE.

**Properties:** The new compounds **2–7** were fully characterized by the spectral data as shown in the Experimental Section. Mass spectra of **2–7** ionized by ESI showed the correct molecular ion peaks, respectively. The stereochemistry for vinyl moiety of **3** and **4** was confirmed by NOE experiment. The characteristic stretching vibration band of the carbonyl group of **2–7** was observed at  $\nu=1742\text{--}1773\text{ cm}^{-1}$  in their IR spectra, except for azulene derivative **6**. Compounds **3–7** also exhibited characteristic  $\text{C}\equiv\text{N}$  stretching at  $\nu=2197\text{--}2218\text{ cm}^{-1}$  in their IR spectra. These results are consistent with the structure of these products.

The UV/Vis spectra of cyanovinyl derivatives **3**, **4**, **5** and **7** in  $\text{CH}_2\text{Cl}_2$  exhibited strong absorptions in the visible region, which may be attributable to the charge-transfer (CT) absorption band from the 2*H*-cyclohepta[*b*]furan-2-one ring to the substituted cyanovinyl moiety. Compound **3** exhibited two absorptions at  $\lambda=420$  (sh) and 436 nm, respectively. Compound **4** showed broad absorptions at  $\lambda=426$  nm. The longest wavelength absorption of **3** and **4** showed a bathochromic shift of 47 and 37 nm compared to

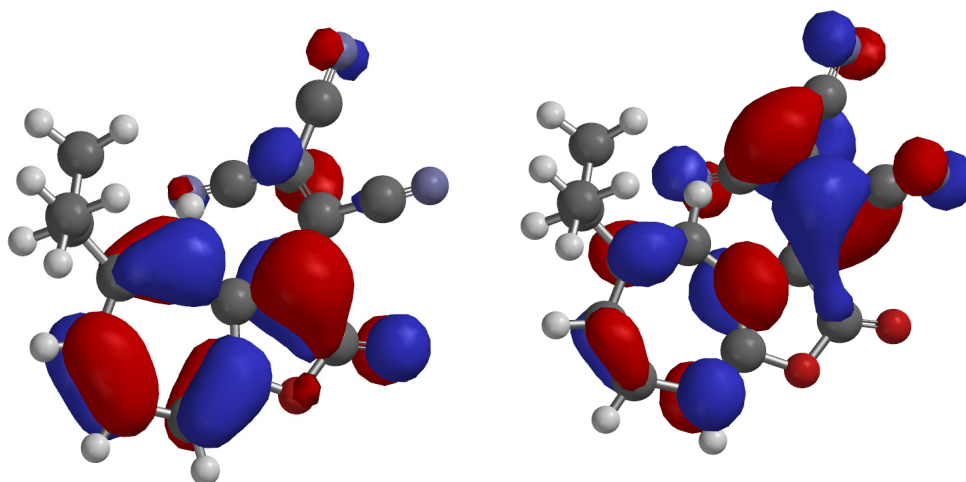
that of **1** ( $\lambda=389$  nm), probably due to expansion of the  $\pi$ -conjugation system by the cyanovinyl moiety. In compound **5**, relatively strong absorptions were observed at  $\lambda=471$  nm, which exhibited a further bathochromic shift compared to those of **3** and **4**. Compound **7** also showed a strong absorption at  $\lambda=507$  nm, compared to that of **5**. The longest absorption of **3**, **4**, **5** and **7** displayed a bathochromic shift as the number of cyano group increased. This indicates that electron-withdrawing property of cyano group reduces the HOMO-LUMO gap of the molecule.



**Figure 1.** UV/Vis spectra of **7** in  $\text{CH}_2\text{Cl}_2$  (blue line) and in 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).

Solvatochromism is observed as a characteristic feature of dipolar molecules.<sup>12</sup> A noticeable spectral feature of **7** is the presence of distinct absorption band at 507 nm in  $\text{CH}_2\text{Cl}_2$ , which blue-shifts to 494 nm in less polar hexane, suggesting the intramolecular CT nature of this band (Figure 1). It is assumed that the first excited-state has a larger dipole moment compared with that in the ground state due to the intramolecular CT character from the 2*H*-cyclohepta[*b*]furan-2-one to the tricyanovinyl unit as illustrated in Scheme 2. To

elucidate the nature of the absorption bands of **7**, density functional theory (DFT) calculation at the B3LYP/6-31G\*\* level was carried out on optimized structure of **7**.<sup>13</sup> The frontier Kohn–Sham orbitals of **7** are shown in Figure 2. Judging from a comparison between the experimental and the theoretical UV/Vis spectra, the ICT of **7** originated from the HOMO located on 2*H*-cyclohepta[*b*]furan-2-one to the LUMO



**Figure 2.** The Kohn–Sham orbitals of HOMO (left) and LUMO (right) for optimized structure of **7** calculated at the B3LYP/6-31G\*\* level.

that was mainly located on the tricyanovinyl moiety.

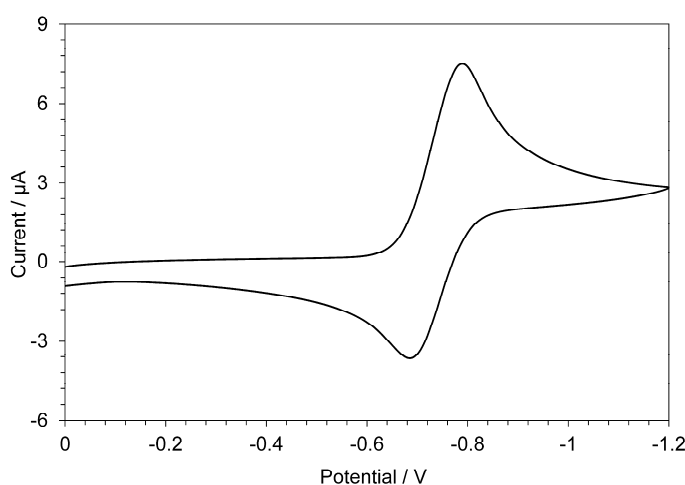
**Electrochemistry:** To clarify the electrochemical behavior of cyanovinyl derivatives **3**, **4**, **5** and **7**, redox potentials of these products were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Measurements were carried out with a standard three-electrode configuration.

Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire auxiliary and platinum disk working electrodes, respectively. All measurements were carried out under an argon atmosphere, and potentials were related to an Ag/Ag<sup>+</sup> reference electrode and Fc/Fc<sup>+</sup> as an internal reference, which discharges at +0.15 V. The redox potentials are summarized in Table 1.

**Table 1.** Redox potentials of cyanovinyl derivatives **3**, **4**, **5** and **7**.<sup>14</sup>

Sample	Method	$E_1^{\text{red}}$ [V]	$E_2^{\text{red}}$ [V]	$E_3^{\text{red}}$ [V]	$E_1^{\text{ox}}$ [V]
<b>3</b>	(DPV)	(−1.44)			(+1.02)
<b>4</b>	(DPV)	(−1.48)			(+1.03)
<b>5</b>	(DPV)	(−1.07)	(−1.86)		(+1.25)
<b>7</b>	CV	−0.75			
	(DPV)	(−0.73)	(−1.72)	(−1.80)	(+1.46)

Electrochemical reduction of **3** exhibited irreversible reduction wave at −1.44 V upon DPV. This result indicates the formation of unstable radical anionic states in the compound. Electrochemical oxidation of **3** also showed irreversible oxidation wave at +1.02 V due to the generation of radical cationic species upon DPV. Irreversible reduction and oxidation waves were observed in **4** at −1.48 V and +1.03 V upon DPV, respectively. Electrochemical reduction and oxidation of **5** also showed irreversible reduction and oxidation waves at −1.07 V and +1.25 V, respectively, owing to the generation of instable radical anionic



**Figure 3.** Cyclic voltammograms of the reduction of **7** (1 mM) in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M) as a supporting electrolyte; scan rate = 100 mVs<sup>−1</sup>.

and cationic species. Electrochemical reduction of **7** showed a reversible reduction wave at the half wave potential of −0.75 V by CV (Figure 3), probably due to the formation of a stabilized radical anion species. The electrochemical reduction also exhibited irreversible waves at −1.72 and −1.80 V by DPV, probably due to the reduction of the substituted 2H-cyclohepta[*b*]furan-2-one ring. The first reduction potential of **7** was less negative compared with those of **3**, **4**, and **5**. These

results reflect that the cyano-substituent on the vinyl moiety directly exerts for decrease of LUMO level of the molecule.

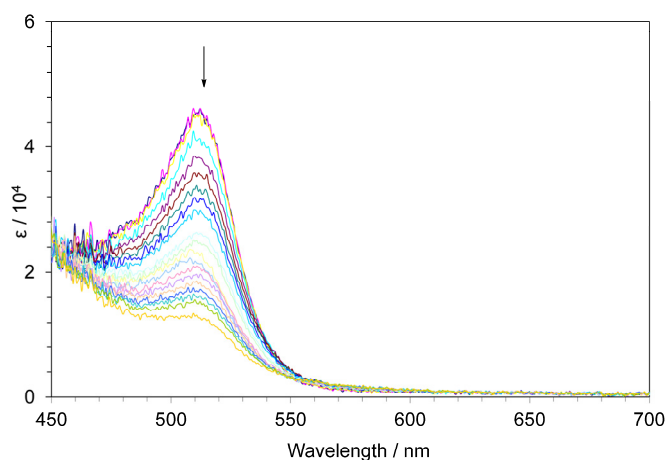
To examine the color changes during the electrochemical reactions, the spectral changes of cyanovinyl derivatives **3**, **4**, **5** and **7** were monitored by visible spectroscopy. Constant-current reduction was applied to solutions of **3**, **4**, **5** and **7**, with a platinum mesh as the working electrode and a wire counter electrode, and visible spectra were measured in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte at room temperature under electrochemical reduction conditions.

The colors of the solutions of **3** and **4** changed from orange to pale yellow during the electrochemical reduction. These changes were accompanied by increases in the broad absorption bands up to the near-infrared region. Reverse oxidation of these orange-colored solutions did not regenerate the visible spectra of the orange-colored **3** and **4**, according to irreversibility upon CV. When the UV/Vis spectra of **5** were measured under electrochemical reduction conditions, the absorption of **5** at  $\lambda=470$  nm in the visible region also gradually decreased, along with color-change from orange to yellow color. However, reverse oxidation did not regenerate the absorptions of **5**, similar with **3** and **4**. The longest absorption of **7** at  $\lambda=507$  nm gradually decreased and thus the color of the solution gradually changed from red to

yellow during electrochemical reduction (Figure 4).

Reverse oxidation of the yellow-colored solution did not regenerate the spectrum of **7**, although good reversibility was observed in the cyclic voltammogram. Recently, we reported the TCBD-substituted 2*H*-cyclohepta[*b*]furan-2-one exhibited a reversible color change between electrochemical reduction and oxidation.<sup>4</sup> Thus, these irreversibility of color change suggest that cyanovinyl moiety is less stable toward the electrochemical reaction, compared to the TCBD group.

In summary, cyanovinyl-substituted 2*H*-cyclohepta[*b*]furan-2-one **3**, **4**, **5** and **7** were prepared by the Wittig, Knoevenagel and electrophilic substitution reaction, respectively. 2-Amino-1-cyanoazulene derivative **6** was also obtained by the reaction of **2** with malononitrile in EtOH. Analysis by CV and DPV showed that compound **7** exhibit reversible reduction wave, although compounds **3**, **4** and **5** showed irreversible waves. Although the compounds **3**, **4**, **5** and **7** did not exhibit the reversible color change during the electrochemical reduction, significant color changes were observed during the electrochemical reduction. In attempts to improve the



**Figure 4.** Continuous change in visible spectra of **7** in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M): constant-current electrochemical reduction (50  $\mu\text{A}$ ) at 30 sec intervals.

electrochromic properties, preparation of novel 2*H*-cyclohepta[*b*]furan-2-one-substituted multivalent charge-transfer chromophores with different  $\pi$ -electron cores is now in progress in our laboratory.

## EXPERIMENTAL

**General:** Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a Bruker APEX II instrument. IR and UV/Vis spectra were measured with a Shimadzu FTIR-8100M and a Shimadzu UV-2550 spectrophotometer, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker AVANCE 400 spectrometer (400 and 100 MHz). Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes, and a reference electrode formed from Ag/AgNO<sub>3</sub> (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

**3-Formyl-5-isopropyl-2*H*-cyclohepta[*b*]furan-2-one (2):** A mixture of phosphoryl chloride (2.32 g, 15.0 mmol) and DMF (10 mL) was added at room temperature to a solution of **1** (1.02 g, 5.43 mmol) in DMF (20 mL). The resulting solution was stirred at the same temperature for 2 h. The reaction mixture was poured into water and extracted with hexane. The organic layer was washed with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> to give **2** (1.10 g, 94 %) as orange crystals. Mp 169.5–170.5 °C (MeOH); HRMS (ESI): Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub> + Na<sup>+</sup> [M + Na]<sup>+</sup> 239.0679. Found: 239.0677; IR (KBr disk):  $\nu_{\text{max}}$  = 2966 (w), 2932 (w), 2872 (w), 2820 (w), 2756 (w), 1773 (s), 1746 (s), 1653 (s), 1582 (s), 1524 (m), 1485 (s), 1466 (s), 1437 (m), 1404 (m), 1375 (m), 1298 (m), 1277 (s), 1242 (m), 1200 (m), 1092 (w), 1042 (w), 1011 (w), 943 (w), 891 (w), 816 (m), 760 (w), 746 (w), 725 (w), 654 (w), 637 (m) cm<sup>-1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 254 (4.29), 283 (4.40), 427 nm (4.42);  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 10.05 (s, 1H, CHO), 9.04 (d, 1H,  $J$  = 1.6 Hz, H-4), 7.60 (t, 1H,  $J$  = 9.2 Hz, H-7), 7.55 (dd, 1H,  $J$  = 9.2, 1.6 Hz, H-8), 7.42 (dt, 1H,  $J$  = 9.2, 1.6, 1.6 Hz, H-4), 3.13 (sept, 1H,  $J$  = 6.8 Hz, *i*-Pr), 1.37 (d, 6H,  $J$  = 6.8 Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 186.09, 168.72, 165.50, 159.13, 151.71, 136.88, 136.30, 129.11, 119.94, 101.88, 39.73, 23.57 ppm; Anal. Calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>·1/10H<sub>2</sub>O: C, 71.61; H, 5.64. Found: C, 71.86; H, 5.69.

**(2*E*)-3-(5-Isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)propenenitrile (3) and (2*Z*)-3-(5-Isopropyl-2-oxo-2*H*-cyclohepta[*b*]furan-3-yl)propenenitrile (4):** A mixture of triphenylphosphine (1.21 g, 4.62 mmol) and bromoacetonitrile (505 mg, 4.21 mmol) in toluene (7 mL) was added at room temperature to a solution of **2** (438 mg, 2.03 mmol) and triethylamine (2 mL) in DMSO (6 mL). The resulting solution was

stirred at the same temperature for 15 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$  and reversed-phase chromatography (ODS gel, 80% MeOH/ $\text{H}_2\text{O}$ ) to give **3** (227 mg, 47 %) as red crystals and **4** (246 mg, 51 %) as red crystals, respectively.

**3**: Mp 149.0–152.0 °C (MeOH); HRMS (ESI): Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_2 + \text{Na}^+ [\text{M} + \text{Na}]^+$  262.0838. Found: 262.0837; IR (KBr disk):  $\nu_{\text{max}} = 2959$  (w), 2932 (w), 2907 (w), 2868 (w), 2212 (m), 1749 (s), 1720 (m), 1603 (s), 1585 (m), 1520 (s), 1497 (s), 1431 (w), 1408 (w), 1350 (w), 1325 (w), 1306 (w), 1261 (w), 1252 (w), 1236 (w), 964 (w), 824 (w), 800 (w), 743 (m)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\log \epsilon) = 240$  (4.32), 277 (4.28), 286 (4.29), 307 (3.91), 321 (3.79), 420 sh (4.39), 436 (4.41) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 7.43$  (d, 1H,  $J = 1.2$  Hz, H-4), 7.39 (d, 1H,  $J = 16.0$  Hz, H-Vinyl), 7.23 (dd, 1H,  $J = 11.2, 9.2$  Hz, H-7), 7.15 (dd, 1H,  $J = 9.2, 1.2$  Hz, H-8), 7.05 (dd, 1H,  $J = 11.2, 1.2$  Hz, H-6), 6.54 (d, 1H,  $J = 16.0$  Hz, H-Vinyl), 2.97 (sept, 1H,  $J = 6.8$  Hz, *i*-Pr), 1.33 (d, 6H,  $J = 6.8$  Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 166.33, 159.61, 157.36, 147.65, 136.71, 134.41, 133.89, 123.49, 119.58, 116.52, 102.41, 96.24, 39.49, 23.21$  ppm; Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_2$ : C, 75.30; H, 5.48; N, 5.85. Found: C, 75.01; H, 5.50; N, 5.81.

**4**: Mp 105.0–107.0 °C (MeOH); HRMS (ESI): Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_2 + \text{Na}^+ [\text{M} + \text{Na}]^+$  262.0838. Found: 262.0838; IR (KBr disk):  $\nu_{\text{max}} = 2980$  (w), 2958 (w), 2936 (w), 2906 (w), 2867 (w), 2212 (m), 1742 (s), 1608 (m), 1586 (m), 1520 (m), 1498 (m), 1374 (w), 1316 (w), 1283 (m), 1260 (w), 1219 (w), 793 (w), 740 (w), 731 (w), 712 (w), 649 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} (\log \epsilon) = 240$  (4.41), 272 (4.21), 307 sh (3.71), 319 (3.56), 426 (4.30) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 7.41$  (d, 1H,  $J = 1.2$  Hz, H-4), 7.25 (dd, 1H,  $J = 11.2, 9.2$  Hz, H-7), 7.17 (dd, 1H,  $J = 9.2, 1.2$  Hz, H-8), 7.16 (d, 1H,  $J = 12.0$  Hz, H-Vinyl), 7.07 (dd, 1H,  $J = 11.2, 1.2$  Hz, H-6), 5.57 (dd, 1H,  $J = 12.0$  Hz, H-Vinyl), 2.99 (sept, 1H,  $J = 6.8$  Hz, *i*-Pr), 1.35 (d, 6H,  $J = 6.8$  Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 167.06, 159.63, 158.07, 147.46, 138.71, 134.06, 133.94, 126.40, 117.21, 116.11, 103.22, 97.24, 39.55, 23.31$  ppm; Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_2 \cdot 1/4\text{H}_2\text{O}$ : C, 73.91; H, 5.58; N, 5.75. Found: C, 73.76; H, 5.51; N, 5.88.

**2-(5-Isopropyl-2-oxo-2H-cyclohepta[b]furan-3-ylmethylene)malononitrile (5)**: A mixture of malononitrile (78 mg, 1.18 mmol) and pyridine (1 mL) was added at room temperature to a solution of **1** (234 mg, 1.08 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL). The resulting solution was stirred at the same temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with  $\text{CHCl}_3$ . The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  (20 : 1) to give **5** (135 mg, 51 %) as orange crystals. Mp 183.0–186.0 °C ( $\text{CH}_2\text{Cl}_2$ ); HRMS (ESI): Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2 + \text{Na}^+$



$[M + Na]^+$  287.0791. Found: 287.0790; IR (KBr disk):  $\nu_{\max}$  = 3013 (w), 2961 (w), 2929 (w), 2871 (w), 2218 (m, CN), 2210 (m, CN), 1758 (s), 1588 (m), 1563 (m), 1523 (w), 1477 (s), 1440 (w), 1348 (m), 1312 (w), 1286 (m), 1259 (m), 1218 (m), 936 (m), 814 (w), 793 (w), 760 (w), 739 (w), 720 (w), 604 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 248 sh (4.36), 252 (4.40), 282 (4.12), 301 sh (3.89), 323 (3.83), 332 (3.81), 334 sh (3.81), 337 (3.83), 471 (4.54) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 7.77 (s, 1H, H-Vinyl), 7.75 (d, 1H,  $J$  = 1.2 Hz, H-4), 7.60 (dd, 1H,  $J$  = 10.8, 9.6 Hz, H-7), 7.51 (dd, 1H,  $J$  = 9.6, 1.2 Hz, H-8), 7.42 (dd, 1H,  $J$  = 10.8, 1.2 Hz, H-6), 3.14 (sept, 1H,  $J$  = 6.8 Hz, *i*-Pr), 1.41 (d, 6H,  $J$  = 6.8 Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 164.73, 164.18, 149.55, 147.88, 137.69, 136.26, 128.36, 120.09, 115.15, 113.21, 101.62, 100.52, 79.21, 40.15, 23.50 ppm; Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 72.72; H, 4.58; N, 10.60. Found: C, 72.68; H, 4.83; N, 10.31.

**2-(2-Amino-3-cyano-7-isopropyl-azulen-1-ylmethylene)malononitrile (6):** Malononitrile (133 mg, 2.01 mmol) in pyridine (2 mL) was added at room temperature to a solution of **2** (215 mg, 1.00 mmol) in EtOH (5 mL). The resulting solution was stirred at the same temperature for 24 h under an Ar atmosphere. The reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  (20 : 1) to give **6** (235 mg, 83 %) as brown crystals. Mp 260.0–263.0 °C (decomp.); HRMS (ESI): Calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_4 + \text{Na}^+$   $[M + Na]^+$  309.1111. Found: 309.1111; IR (KBr disk):  $\nu_{\max}$  = 3464 (m), 3314 (w), 3061 (m), 2972 (w), 2958 (m), 2932 (w), 2870 (w), 2214 (s), 2197 (s), 1654 (s), 1588 (s), 1538 (s), 1509 (s), 1476 (m), 1448 (m), 1437 (s), 1414 (m), 1385 (m), 1366 (w), 1348 (w), 1329 (m), 1302 (m), 1284 (m), 1254 (m), 1222 (m), 1190 (w), 1021 (w), 898 (w), 795 (m), 777 (m), 662 (w), 544 (w), 531 (w), 523 (w), 459 (w)  $\text{cm}^{-1}$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 256 (4.37), 292 (4.17), 318 (4.15), 351 sh (4.76), 365 (4.92), 399 (3.90), 425 (3.79), 446 sh (3.47), 516 sh (2.67), 559 sh (2.40) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.67 (s, 1H, H-Vinyl), 8.45 (d, 1H,  $J$  = 1.6 Hz, H-4), 8.43 (dd, 1H,  $J$  = 10.0, 1.6 Hz, H-8), 7.69 (dd, 1H,  $J$  = 10.0, 1.6 Hz, H-6), 7.64 (t, 1H,  $J$  = 10.0 Hz, H-7), 5.79 (bs, 2H,  $\text{NH}_2$ ), 3.23 (sept, 1H,  $J$  = 6.8 Hz, *i*-Pr), 1.44 (d, 6H,  $J$  = 6.8 Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 161.42, 160.60, 155.00, 150.51, 139.27, 138.90, 136.32, 134.25, 134.12, 132.75, 118.67, 117.13, 115.09, 89.98, 88.65, 39.34, 24.66 ppm; Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{N}_4$ : C, 75.50; H, 4.93; N, 19.57. Found: C, 75.30; H, 5.20; N, 19.52.

**2-Cyano-3-(5-isopropyl-2-oxo-2H-cyclohepta[b]furan-3-yl)-but-2-enedinitrile (7):** To a solution of **1** (218 mg, 1.16 mmol) in EtOAc (4 mL) was added TCNE (168 mg, 1.25 mmol). The resulting mixture was stirred at 50 °C for 2 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  (10 : 1) and

Bio-Beads with  $\text{CH}_2\text{Cl}_2$  to give **7** (268 mg, 80 %) as red crystals. Mp 150.0–152.0 °C ( $\text{CH}_2\text{Cl}_2$ ); HRMS (ESI): Calcd for  $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2 + \text{Na}$   $[\text{M} + \text{Na}]^+$  312.0743. Found: 312.0744; IR (KBr disk):  $\nu_{\text{max}} = 2978$  (w), 2961 (w), 2928 (w), 2226 (m), 2208 (w), 1767 (s), 1578 (m), 1518 (s), 1479 (s), 1439 (s), 1406 (m), 1366 (w), 1340 (m), 1317 (m), 1306 (m), 1277 (s), 1259 (m), 1238 (m), 1205 (m), 1138 (w), 1090 (w), 1022 (w), 939 (w), 912 (w), 806 (m), 766 (m), 721 (w), 673 (w), 559 (w), 500 (w)  $\text{cm}^{-1}$ ; UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 242 (4.33), 264 (4.30), 283 sh (4.14), 300 sh (3.96), 320 sh (3.62), 362 (3.67), 507 (4.66) nm; UV-Vis (hexane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 242 (4.22), 260 (4.19), 283 sh (3.96), 315 sh (3.55), 345 (3.41), 362 (3.46), 494 (4.46) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 8.04$  (d, 1H,  $J = 1.6$  Hz, H-4), 7.79 (dd, 1H,  $J = 10.4, 9.2$  Hz, H-7), 7.70 (dd, 1H,  $J = 9.2, 1.2$  Hz, H-8), 7.62 (dd, 1H,  $J = 10.4, 1.2$  Hz, H-6), 3.19 (sept, 1H,  $J = 6.8$  Hz, *i*-Pr), 1.43 (d, 6H,  $J = 6.8$  Hz, *i*-Pr) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 166.26, 162.24, 159.79, 149.31, 139.29, 138.22, 130.21, 128.61, 122.00, 112.78, 112.17, 111.11, 97.28, 89.34, 40.34, 23.68$  ppm; Anal. Calcd for  $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2$ : C, 70.58; H, 3.83; N, 14.53. Found: C, 70.45; H, 4.10; N, 14.49.

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## REFERENCES (AND NOTES)

- (a) P.-W. Yang, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, 1971, **12**, 4275; (b) A. Chen, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, 1974, **15**, 2581; (c) T. Nozoe, P.-W. Yang, C.-P. Wu, T.-S. Huang, T.-H. Lee, H. Okai, H. Wakabayashi, and S. Ishikawa, *Heterocycles*, 1989, **29**, 1225; (d) S. Kuroda, S. Maeda, S. Hirooka, M. Ogisu, K. Yamazaki, I. Shimao, and M. Yasunami, *Tetrahedron Lett.*, 1989, **30**, 1557; (e) T. Nozoe, H. Wakabayashi, S. Ishikawa, C.-P. Wu, and P.-W. Yang, *Heterocycles*, 1990, **31**, 17; (f) T. Nozoe, H. Wakabayashi, S. Ishikawa, C.-P. Wu, and P.-W. Yang, *Heterocycles*, 1991, **32**, 213; (g) H. Wakabayashi, P.-W. Yang, C.-P. Wu, K. Shindo, S. Ishikawa, and T. Nozoe, *Heterocycles*, 1992, **34**, 429; (h) S. Kuroda, J. Yazaki, S. Maeda, K. Yamazaki, M. Yamada, I. Shimao, and M. Yasunami, *Tetrahedron Lett.*, 1992, **33**, 2825.
- (a) N. Morita, K. Toyota, and S. Ito, *Heterocycles*, 2009, **78**, 1917; (b) K. Takase, T. Nakazawa, and T. Nozoe, *Heterocycles*, 1981, **15**, 839; (c) A. Mori, Y. Nukii, H. Takeshita, and T. Nozoe, *Heterocycles*, 1993, **35**, 863; (d) N. Morita, M. Kudo, R. Yokoyama, and S. Ito, *Heterocycles*, 2001, **54**, 679; (e) N. Morita, T. Matsuki, M. Nakashima, T. Shoji, K. Toyota, S. Kikuchi, and S. Ito, *Heterocycles*, 2006, **69**, 119; (f) N. Morita, J. Higashi, K. Okada, T. Shoji, K. Toyota, M. Watanabe, M. Yasunami, S. Kikuchi, and S. Ito, *Heterocycles*, 2007, **73**, 237; (g) J. Higashi, K.

- Okada, T. Shoji, K. Toyota, M. Watanabe, M. Yasunami, S. Kikuchi, S. Ito, and N. Morita, *Heterocycles*, 2008, **76**, 759; (h) T. Shoji, J. Higashi, S. Ito, M. Yasunami, and N. Morita, *Heterocycles*, 2011, **83**, 2271.
3. (a) T. Shoji, S. Ito, K. Toyota, M. Yasunami, and N. Morita, *Chem. Eur. J.*, 2008, **14**, 8398; (b) T. Shoji, S. Ito, K. Toyota, T. Iwamoto, M. Yasunami, and N. Morita, *Eur. J. Org. Chem.*, 2009, 4316; (c) T. Shoji, M. Maruyama, S. Ito, and N. Morita, *Bull. Chem. Soc. Jpn.*, 2012, **85**, 761.
4. (a) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, and N. Morita, *Chem. Eur. J.*, 2011, **17**, 5116; (b) T. Shoji, J. Higashi, S. Ito, T. Okujima, M. Yasunami, and N. Morita, *Org. Biomol. Chem.*, 2012, **10**, 2431.
5. M. Yokota, T. Yanagisawa, K. Kosakai, S. Wakabayashi, T. Tomiyama, and M. Yasunami, *Chem. Pharm. Bull.*, 1994, **42**, 865.
6. G. Wittig and U. Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.
7. E. Knoevenagel, *Ber. Deutsch. Chem. Ges.*, 1898, **31**, 2596.
8. (a) T. Nozoe, S. Seto, and S. Matsumura, *Proc. Japan. Acad.*, 1956, **32**, 339; (b) T. Nozoe, K. Takase, T. Nakazawa, and S. Fukuda, *Tetrahedron*, 1971, **27**, 3357.
9. (a) A. J. Fatiadi, *Synthesis*, 1986, 249; (b) A. J. Fatiadi, *Synthesis*, 1987, 749; (c) O. W. Webster, *J. Polym. Sci., Part A*, 2002, **40**, 210.
10. (a) K. Hafner and K. L. Moritz, *Angew. Chem.*, 1960, **72**, 918; (b) K. Hafner and K. L. Moritz, *Justus Liebigs Ann. Chem.*, 1961, **650**, 92.
11. T. Shoji, S. Ito, T. Okujima, J. Higashi, R. Yokoyama, K. Toyota, M. Yasunami, and N. Morita, *Eur. J. Org. Chem.*, 2009, 1554.
12. (a) P. Suppan and N. Ghoneim, *Solvatochromism, The Royal Society of Chemistry*, Cambridge, 1997; (b) P. Suppan, *J. Photochem. Photobiol. A*, 1990, **50**, 293; (c) R. Christian, In *Solvent and Solvent Effects in Organic Chemistry*; Wiley-VCH, New York, 2004.
13. The B3LYP/6-31G\*\* time-dependence density functional calculations were performed with Spartan'10, Wavefunction, Irvine, CA.
14. Redox potentials were measured by CV and DPV [in V vs. Ag/AgNO<sub>3</sub>, 1mM in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M), Pt electrode (i.d. 1.6 mm), scan rate 100 mVs<sup>-1</sup>, and Fc/Fc<sup>+</sup> = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.