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Abstract

Starting with the reaction of 2H-cyclohepta[b]furan-2-ones with an enamine, which was prepared from 4-tert-butylcyclohexanone and pyrrolidine, benz[a]azulenes having both formyl and tert-butyl groups were obtained in the three-step sequence. Subsequently, both the formyl and tert-butyl groups were eliminated by heating the benz[a]azulene derivatives in 100% H₃PO₄ to give benz[a]azulenes without these substituents in high yields. In terms of the product yield, this method is the best one ever reported for the synthesis of the parent benz[a]azulene so far. The conversion of the benz[a]azulene derivatives with a formyl group into cyclohept[a]acenaphthylen-3-one derivatives was also investigated via Knoevenagel condensation with dimethyl malonate, followed by Brønsted acid-mediated intramolecular
cyclization. The structural features including the bond alternation in the benz[a]azulene derivatives were revealed by NMR studies, NICS calculations, and a single-crystal X-ray structural analysis. The optical and electrochemical properties of a series of benz[a]azulene derivatives were evaluated by UV/Vis, fluorescence spectroscopy and voltammetry experiments. As a result, we found that some benz[a]azulene derivatives showed remarkable luminescence in acidic media. In addition, the benz[a]azulene derivatives with the electron-withdrawing group and cyclohept[a]acenaphthylen-3-one derivative displayed good reversibility in the spectral changes under the electrochemical redox conditions.

**Introduction**

Aromatic hydrocarbon skeletons with various functional groups and/or extended $\pi$-conjugated systems are expected to be promising resources for novel functional materials with attractive electronic structures. Particularly, polycyclic aromatic hydrocarbons show interesting properties such as near-infrared absorption, reversible redox activity, and high electrical conductivity, and are used in a variety of practical applications such as near-infrared responsive dyes, organic semiconductors, electrodes for rechargeable batteries, and so on.\(^1\)

Azulene is one of the non-alternate aromatic hydrocarbons that has fascinated many chemists because of its unique reactivity and properties.\(^2\) In recent years, the properties of azulene derivatives have been continuously evaluated in various practical applications, such as organic electronics,\(^3\) photovoltaics,\(^4\) electrochromism,\(^5\) and stimuli-responsive materials.\(^6\) Benz[a]azulene, a structural isomer of anthracene, is one of polycyclic aromatic
compounds, which has also been of much interest in terms of its structural and optical properties. In this regard, several research groups have reported the preparation of benz[a]azulenes and their derivatives for a long time, but the synthetic method for the parent compound is still limited (Scheme 1). To the best of our knowledge, the synthesis of the parent benz[a]azulene has firstly been achieved in 1948 by Plattner et al. and Treibs, independently, in a similar manner, i.e., the reaction of fluorene with ethyl diazoacetate, but the products yield was not available in the literature. After a while, Wege et al. reported the synthesis of benz[a]azulene in two or three steps via reactive intermediates such as carbene and benzyne, but the overall yield was low. In a more practical approach, Hansen and Sperandio reported the preparation of the parent benz[a]azulene starting from 2-iodobenzyl alcohol in six steps in an overall yield of 44%, and a year later, the same group continuously evaluated its reactivity, structural and optical properties. However, the yield in the synthesis of the parent benz[a]azulene still remains insufficient, and the reactivity, structural and optical properties of itself and its derivatives have not been fully evaluated.
In this paper, we report an efficient method for the synthesis of benz[a]azulenes, which were difficult to synthesize by using previously reported methods, as well as the reactivity of these compounds obtained in this study. As a result, we found that a benz[a]azulene derivative can be converted into cyclohept[a]acenaphthylen-3-one derivative by several step synthesis. The optical properties of the newly prepared benz[a]azulenes and cyclohept[a]acenaphthylen-3-one derivative were characterized by UV/Vis and fluorescence spectroscopy. We found that these derivatives exhibit a remarkable spectral change and emission in an acidic solution compared to those under neutral conditions. The electrochemical features of these derivatives have been investigated by both voltammetry and spectroelectrochemical experiments, revealing that some benz[a]azulene derivatives
exhibited electrochromism with good reversibility, despite the observation of irreversible cyclic voltammograms.

Results and Discussion

Synthesis of benz[a]azulene derivatives

As the first trial of the facile synthesis of benz[a]azulenes, we have attempted the conversion of tetrahydrobenz[a]azulenes,\textsuperscript{15} which are considered as a useful precursor, by the oxidative aromatization reaction using 2,3-dichloro-5,6-dicyano-\textit{p}-benzoquinone (DDQ) as the oxidant (Scheme 2). However, this reaction did not give the desired benz[a]azulenes at all, but resulted in only immediate decomposition of the precursors. Thus, it is necessary to develop a new synthetic route for the preparation for benz[a]azulenes.

![Scheme 2. An attempt to the synthesis of benz[a]azulenes by the oxidation with DDQ.](image)

Azulene derivatives are known to form charge transfer complexes with electron-deficient molecules such as picric acid and DDQ.\textsuperscript{8b,16} Based on this fact, we believed that the above decomposition was caused by the formation of charge-transfer (CT) complexes, which might take precedence over the oxidation reaction. Based on this hypothesis, we decided to introduce a bulky substituent, a \textit{tert}-butyl group, into the starting materials, tetrahydrobenz[a]azulenes, to inhibit the formation of the CT complexes.

As a result of this investigation, we established a four-step synthesis of benz[a]azulene derivatives starting from 2\textit{H}-cyclohepta[\textit{b}]furan-2-ones. The overview of the synthetic pathway of the benz[a]azulene derivatives appeared in Scheme 3.
Tetrahydrobenz[a]azulene 2a was prepared by the [8 + 2] cycloaddition of 1a with enamine prepared from 4-tert-butylcyclohexanone and pyrrolidine in 87% yield. The reaction of 2a with DDQ showed remarkable decomposition as described above, so no obvious product was obtained by this reaction. This result was considered as an overreaction in the oxidation reaction owing to the high reactivity of 2a induced by the higher HOMO level by the condensation of the cyclohexane ring. Therefore, 2a was transformed by the Vilsmeier reaction to the formyl derivative 3a in 99% yield, followed by aromatization of 3a with DDQ as an oxidant at room temperature, resulted in 10-formylbenz[a]azulene 4a in 98% yield. This success may be attributed to the synergistic effect of stabilization of the compound, arising from the moderate electron-withdrawing nature of the formyl group and inhibition of CT-complex formation by the steric hindrance of the substituted tert-butyl group. Treatment of 4a with 100% H₃PO₄ at 140 °C resulted in the one-pot elimination of both the formyl and tert-butyl groups to afford 5a in 71% yield. The overall yield (4 steps, 60%) of this synthetic procedure is the highest one among those of the previously reported synthesis for 5a. It should also be noted that the simultaneous removal of the formyl and tert-butyl groups of 4a with 100% H₃PO₄ can only be successful under the diluted conditions because the decomposition reaction is more pronounced at the higher concentration. Benz[a]azulenes 5b and 5c having an isopropyl group at the seven-membered ring in 49% and 41% yields, respectively, could also be prepared in the same manner as in the preparation of 5a. Heating of 4a and 4b in 100% H₃PO₄ for a shorter time (3–4 h) gave 6a (91%) and 6b (81%), in which only the tert-butyl group was removed. Thus, the elimination of the formyl group should correspond to the rate-determining step in the formation of benz[a]azulenes by treatment with 100% H₃PO₄. Vilsmeier reaction of 5a was also investigated. In this reaction, the reaction did not proceed in the fused benzene ring, yielding 6a with a formyl group on the azulene moiety in 81% yield. This result implies that the reactivity of the benzene moiety is not significantly improved even when the ring is fused in the electron-rich five-membered
ring of azulene. The carbonyl function attached to the azulene ring at the 1-position is successively reduced to a methylene group by NaBH₄ in the presence of BF₃·OEt₂. Thus, under the similar conditions the formyl group of 4b was reduced to give 7 with a methyl function at the 10-position in 19% yield (Scheme 3).


Introduction of various functional groups to benz[a]azulene derivatives at the 10-position was also examined to evaluate their reactivity toward electrophiles. Considering both stability and solubility, 2b with both a tert-butyl group at the 3-position and an isopropyl group at the 8-position were selected as starting materials. An overview of the synthetic pathway is illustrated in Scheme 4.

The trifluoroacetylation of 2b with trifluoroacetic anhydride in CHCl₃ and pyridine at
room temperature afforded 8 in 95% yield. In this reaction, the product yield was significantly reduced in the absence of pyridine, probably due to the inactivation towards the electrophilic substitution by the protonation of the substrate. Aromatization of 8 to 9 (86%) was readily established by the oxidation with DDQ. However, unlike the reduction from 4b to 7, the reaction of 9 with NaBH₄ in the presence of BF₃·OEt₂ produced diazulenylmethane derivative 10 in 72% yield, instead of a methylene compound. This reaction probably proceeds by a similar mechanism for the formation of diazulenyl- and triazulenylmethane derivatives that we have reported so far.¹⁹

Benz[a]azulene derivative 12 with a methyl ester function was prepared in a two-step yield of 40% by exchanging the trifluoromethyl group of 8 to methoxy function with MeONa in MeOH at the reflux temperature, followed by DDQ-oxidation of the intermediary obtained 11. Treatment of 12 with 100% H₃PO₄ at 100 °C produced 13, where only the methyl ester group at the 10-position was removed.

A methyl sulfide group was introduced in three steps from 2b at the 10-position to synthesize 15: In the presence of dimethylsulfoxide (DMSO) and trifluoroacetic anhydride (TFAA), 2b is rapidly converted to the corresponding dimethylsulfonium ion, which is readily eliminated a methyl group upon the treatment with triethylamine to generate 14 in 95% as the two-step yield (to be precise, this reaction is an S_N2 reaction in which triethylamine attacks the methyl group of the dimethylsulfonium ion to eliminate the azulenyl sulfide).²⁰ The oxidative aromatization of 14 with DDQ proceeded smoothly to afford the desired product 15 in high yield (95%).

The preparation of 18a,b with an aryl group at the 10-position was also established by utilizing the Suzuki-Miyaura cross-coupling. The precursor, the iodo derivative 16, was prepared by the reaction of 2b with N-iodosuccinimide (NIS) in the presence of a small amount of triethylamine in CH₂Cl₂ as the solvent. However, as similar to the iodoazulenes that we have reported previously, compound 16 was unstable and was used for the next
Suzuki-Miyaura cross-coupling without further purification. Cross-coupling reaction of 16 with phenylboronic acid or 4-tert-butylphenylboronic acid in the presence of Pd(dppf)Cl2 as a catalyst furnished the corresponding products 17a and 17b in 84% and 79% yields, respectively. Aromatization of the cyclohexane moiety of 17a and 17b to the fused benzene ring was achieved by the treatment with DDQ giving 18a and 18b, but the yields became slightly lower due to the competing decomposition (18a, 67%; 18b, 53%). The low yield of the products was probably due to the instability of 18a and 18b, showing significant decomposition during the storage under the ambient conditions.
Scheme 4. Synthesis of 3-tert-butyl-8-isopropylbenz[a]azulene derivatives with various functions at the 10-position.

The aromatization of 19 was unsuccessful by the treatment with DDQ. The ester derivative 19 was found to be converted to 20 by the treatment with NBS in CHCl₃, but the product was bromine-substituted at the 3-position (Scheme 5). Furthermore, the compound 20 was transformed to 21 by the decarboxylation reaction by heating in 100% H₃PO₄ at 100 °C, but in rather low yield (21%).


Synthesis of cyclohept[a]acenaphthylen-3-one derivatives

The expansion of the π-conjugated system is expected to enhance the optical properties based on a decrease in the HOMO-LUMO energy gap of the compound. Thus, the synthesis of cyclohept[a]acenaphthylen-3-one, an kind of naphthazulene, was investigated starting from 4a,b and 6a,b. As shown in Scheme 6, we planned a two-step synthesis of cyclohept[a]acenaphthylen-3-one via Knoevenagel condensation of 4a,b and 6a,b with dimethyl malonate, followed by intramolecular cyclization in the presence of Brønsted acid.

The Knoevenagel reaction of 4b with malononitrile in the presence of excess alumina catalyst gave the corresponding dicynovinyl derivatives in 98% yield. Based on the results, the reaction of dimethyl malonate with the formyl derivatives 4a,b and 6a,b was carried out under the similar conditions, but the reaction did not proceed, and the starting
materials were completely recovered. Therefore, the condensation reaction with dimethyl malonate were carried out under general Knoevenagel conditions by using piperidine as a base, resulting in the corresponding vinyl derivatives $23a,b$ and $24a,b$ from $4a,b$ and $6a,b$ in moderate to good yields. Polyphosphoric acid (PPA) mediated intramolecular cyclization of $4a,b$ and $6a,b$ was investigated, but the reaction of $23a,b$ and $24b$ showed the decomposition to afford no identified product. On the other hand, the cyclization reaction of $24a$ took place to yield cyclohepta[\text{a}]acenaphthylen-3-one $25$ in 36% yield, along with an unidentified mixture. By using Eaton's reagent the reaction produced the same product in an improved yield of 66%. Comparing PPA and Eaton's reagent, the latter has advantages of the improvement of product yield, less formation of an unidentified mixture, and easier purification process. Furthermore, the product $25$ obtained by the cyclization reaction with Eaton's reagent can be easily separated by silica gel chromatography, since the unidentified mixture formed by the reaction are highly polar materials, which making it suitable for the preparation of cyclohepta[\text{a}]acenaphthylen-3-one $25$ from the viewpoint of the easier purification process.

Compound $25$ showed high solubility in water, even though it had no hydrophilic functional group. The high hydrophilicity of $25$ should be ascribed to the contribution of bipolar structure involving both azulenium and phenoxide ions as illustrated by the resonance structure of $25'$ in Scheme 6. Furthermore, when $K_2CO_3$ was added to the aqueous solution, crystals of $25$ were precipitated immediately, suggesting that the contribution of $25'$ was reduced owing to the instability of the azulenium ion form under the basic conditions.
Scheme 6. Knoevenagel reaction of 4a,b and 6a,b, and the synthesis of cyclohept[a]acenaphthylene-3-one derivative 25; PPA = polyphosphoric acid, Eaton’s reagent = 7.7 wt.% phosphorus pentoxide in methanesulfonic acid.

Spectroscopic Properties

All the new compounds prepared in this study were well characterized on the basis of spectral data as described in the experimental section. High-resolution mass spectra of the reported compounds ionized by MALDI-TOF showed the correct molecular ion peaks. The assignment of the proton signals of the compounds observed in the $^1\text{H}$ NMR spectra was confirmed by COSY experiments. Benz[a]azulenes prepared in this study showed the pronounced bond-length alternation at the seven-membered ring. This manifested itself as a difference in the coupling constants in the $^1\text{H}$ NMR spectra as shown in Figure 1. For example, the coupling constants $^3J(H^5,H^6)$ and $^3J(H^7,H^8)$ at the seven-membered ring of 5a are both $J = 8.3$ Hz, suggesting that these parts exhibit single bond characters. On the other
hand, a large coupling constant of $J = 11.0$ Hz was observed between the vicinal protons $H^6$-$H^7$ and $H^8$-$H^9$, showing the double bond characters of these parts. Similar bond-length alternations were also observed in the $^1$H NMR spectra of 5b and 13. Therefore, these observations indicate that the aromaticity of the azulene moiety of benz[a]azulenes is reduced by the fused benzene ring in the five-membered ring.

![Figure 1](image-url)

**Figure 1.** Coupling constants of each proton observed by $^1$H NMR spectra of 5a, 5b, and 13.

To clarify the aromaticity for each ring of 5a, 5b, and 13 in terms of theoretical calculations, nucleus-independent chemical shift (NICS) calculations were performed at the GIAO/HF/6-311+G(d,p) level. The NICS(0) and NICS(1) values for 5a, 5b, and 13, and those of the parent azulene calculated in the same level as a reference are summarized in Table 1. The NICS(0) and NICS(1) values for A and B rings of 5a, 5b, and 13 showed distinct down-field shifts compared to those of the parent azulene. For example, the seven-membered A ring of 5a exhibited the values of $-2.92$ ppm for NICS(0) and $-5.50$ ppm for NICS(1), which are lower than those of the parent azulene [NICS(0) = $-8.25$ ppm, NICS(1) = $-9.90$ ppm]. Thus, these results confirm that the seven-membered A ring shows the reduced aromaticity as predicted from the $^1$H NMR experiments. The lower aromaticity of the azulene moieties of 5a, 5b, and 13, relative to that of parent azulene, should be accounted by the less contribution of the more unstable ortho-quinoid structures in the resonance form in order to retain the aromaticity of the fused benzene ring (Scheme 7).
Table 1. The NICS(0) and NICS(1) of 5a, 5b, and 13, and those of azulene as a reference at the GIAO/HF/6-311+G(d,p) level

<table>
<thead>
<tr>
<th>ring</th>
<th>NICS (X)</th>
<th>5a</th>
<th>5b</th>
<th>13</th>
<th>Azulene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>−5.50</td>
<td>−5.33</td>
<td>−4.77</td>
<td>−9.90</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>−2.92</td>
<td>−2.83</td>
<td>−2.21</td>
<td>−8.25</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>−12.73</td>
<td>−11.79</td>
<td>−11.37</td>
<td>−21.03</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>−11.32</td>
<td>−10.25</td>
<td>−9.74</td>
<td>−21.55</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>−12.43</td>
<td>−12.25</td>
<td>−12.46</td>
<td>−</td>
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<tr>
<td></td>
<td>0</td>
<td>−11.07</td>
<td>−10.91</td>
<td>−11.32</td>
<td>−</td>
</tr>
</tbody>
</table>

Scheme 7. Plausible resonance structures of 5a, 5b, and 13.

The suitable single crystal of 6a was obtained from CHCl3/MeOH mixed solvent by slow evaporation. Thus, the structure of 6a was confirmed by X-ray structural analysis (Figure 2). Similar to the benz[a]azulene derivatives reported so far, the alternating arrangement of long and short bonds, i.e., bond-length alternation, was identified in the seven-membered ring of 6b by the X-ray structural analysis. The analysis also revealed that the complete planarity in the structure of 6b and the oxygen atom of the formyl group was oriented toward the H9 proton side. Furthermore, the H9 proton signal of 6b showed a remarkable downfield shift in the 1H NMR spectrum, suggesting the presence of the intramolecular hydrogen bond between the H9 proton and the carbonyl oxygen atom.
Absorption maxima and their coefficients in the visible region of benz[a]azulenes in CH$_2$Cl$_2$ and in 10% CF$_3$CO$_2$H (TFA)/CH$_2$Cl$_2$ are summarized in Table 2. Most of the derivatives displayed the absorption bands at around 600 nm originating from the π-π* transition of azulene ring itself, whereas their maximal absorption wavelengths depended on the electronic nature of the substituted functional groups. The maximal absorption wavelengths of the most benz[a]azulene derivatives displayed a bathochromic shift compared to that of the parent azulene ($\lambda_{\text{max}} = 574$ nm in CH$_2$Cl$_2$), attributed to the extension of the conjugated system due to the fused benzene ring.

**Table 2. Absorption Maxima and Their Coefficients in the Visible Region of benz[a]azulenes in CH$_2$Cl$_2$ and in 10% TFA/CH$_2$Cl$_2$.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max}}$ (log $\varepsilon$) in CH$_2$Cl$_2$</th>
<th>$\lambda_{\text{max}}$ (log $\varepsilon$) in 10% TFA/CH$_2$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>434 (3.99), 540 (2.81), 586 (2.82)</td>
<td>390 (4.21), 430 sh (3.96)</td>
</tr>
</tbody>
</table>
In the visible region, compound 5a showed absorption maximum at $\lambda_{\text{max}} = 612$ nm with the largest molar absorption coefficient in the visible region (Figure 3). The absorption maximum of the UV/Vis spectra of 5b ($\lambda_{\text{max}} = 616$ nm) and 5c ($\lambda_{\text{max}} = 592$ nm) with an isopropyl group showed bathochromic shift by only 4 nm for the former and hypsochromic shift by 20 nm for the latter, respectively, compared to that of 5a. On the other hand, the UV/Vis spectrum of 13 ($\lambda_{\text{max}} = 628$ nm), which has both an isopropyl and a tert-butyl groups,
displayed an absorption band at the longest wavelength region among that of 5a–5c and 13.

**Figure 3.** UV/Vis spectra of 5a (blue line), 5b (red line), 5c (light-green line) and 13 (purple line) in CH$_2$Cl$_2$ (solid line) and in 10% TFA/CH$_2$Cl$_2$ (dotted lines); The spectrum in the visible region in CH$_2$Cl$_2$ is magnified ×50.

The effect in the absorption wavelength by the substituents on the azulene ring can be explained by an empirical rule proposed by Plattner et al. in the early days of azulene chemistry.$^{24}$ According to this rule, an alkyl group substituted at the odd-numbered positions (i.e., 1-, 3-, 5-, or 7-positions) of the azulene ring shows a red-shift in the absorption maximum in the UV/Vis spectrum, compared to that of the parent azulene. Conversely, the substitution of an alkyl group at the even-numbered positions (i.e., 2-, 4-, 6-, and 8-positions) exhibits a hypsochromic shift in the absorption maximum. Extending this principle, when the electron-withdrawing group is substituted at the odd-numbered position of the azulene ring, the absorption maximum is hypsochromic, and vice versa with the electron-donating group. Plattner's rule was also found to be applicable to benz[a]azulenes (Figure 4); a bathochromic shift of the absorption maximum was observed for 7 and 18a,b with methyl
and aryl groups, compared that of 13. Contrary, the absorption maximum of 9 and 12, where trifluoroacetyl and ester groups were substituted, showed a hypsochromic shift, compared to that of 13.

Figure 4. UV/Vis spectra of 7 (red line), 9 (light-green line), 12 (purple line), 13 (blue line), and 15 (orange line) in CH₂Cl₂; The spectrum in the visible region in CH₂Cl₂ is magnified ×50.

The compound 22 with a dicyanovinyl group presented a broad and strong absorption band in the visible region centered at \( \lambda_{\text{max}} = 515 \) nm originating from its push-pull structure. Similarly, 23b showed a relatively strong absorption band at around \( \lambda_{\text{max}} = 449 \) nm, but its molar absorption coefficient was smaller than that of 22. This result could be attributed to the less effective intramolecular charge transfer in 23b, compared with that of 22, since the electron-withdrawing nature of the ester group is lower than that of the cyano group. In contrast to the usual azulene derivatives, cyclohepta[c]acenaphthylene-3-one derivative 25 showed a strong absorption band, where the end absorption reached to the near-infrared region.
Under acidic conditions, azulene derivatives are known to exhibit the color change associated with the formation of azulenium ions.25 Most of benz[a]azulenes prepared in this study change in the absorption bands, which was observed in the UV/Vis spectra in the acidic medium as compared to that in CH2Cl2. The compound of 5a developed a new absorption band at \( \lambda_{\text{max}} = 398 \) nm on the UV/Vis spectrum in 10% TFA/CH2Cl2 solution. And then the absorption band in the visible region arising from the azulene derivatives observed in CH2Cl2 disappeared (Figure 3). The absorption maximum in the visible region of 5b (\( \lambda_{\text{max}} = 397 \) nm) and 5c (\( \lambda_{\text{max}} = 397 \) nm) was almost identical to that of 5a, while 13 bearing a tert-butyl group at the 3-position exhibited a slight bathochromic shift (\( \lambda_{\text{max}} = 406 \) nm).

Comparing the absorption spectra of a series of 3-tert-butyl-8-isopropylbenz[a]azulenes with a function at the 10-position in 10% TFA/CH2Cl2, there were no considerable differences among each other, implying that the electronic properties of the substituent at the 10-position are not significantly responsible for their absorption wavelengths.

For the detailed study of the protonated species, \(^1\)H NMR of 13 was measured in both CDCl3 and 10% CF3CO2D/CDCl3. The \(^1\)H NMR spectrum of 13 in 10% CF3CO2D/CDCl3 showed the disappearance of the proton signal at the 10-position due to the proton-deuterium exchange reaction with CF3CO2D. The chemical shifts of all proton signals in the azulene moiety of 13 shifted to the downfield in 10% CF3CO2D/CDCl3, compared to those in CDCl3, but the chemical shifts in the fused-benzene ring were not significantly affected. Furthermore, the bond-length alternation of the azulene moiety observed in CDCl3 was disappeared in acidic media attributed to the formation of aromatic tropylium ionic substructure. That is, the azulenium ionic species produced in the acidic medium is given by the structure in Figure 5 (bottom).
Figure 5. $^1$H NMR spectra of 13 in CDCl$_3$ (top) and 10% CF$_3$CO$_2$D/CDCl$_3$ (bottom).

Azulene derivative does not represent luminescence from the $S_1 \rightarrow S_0$ transition due to the rapid internal conversion in the $S_1$ state, but in contrast to Kasha's rule, anomalous luminescence from the $S_2 \rightarrow S_0$ transition is observed. However, it is difficult to observe visually because the light emission is very weak. Recently, several researchers, including our group, have reported that azulene derivatives exhibit relatively strong fluorescence under acidic conditions due to the formation of azulenium ions by the protonation of the azulene ring. Previously, Yamaguchi, Yasunami, and their co-workers investigated the luminescence behavior of 5b, 5c, 13, and 21 in cyclohexane. In the study, they found that these derivatives exhibit weak fluorescence from the $S_2 \rightarrow S_0$ transition, similar to that of normal azulenes, with a quantum yield ($\Phi_{flu}$) of 0.038 to 0.13%. In contrast to the results of
Yamaguchi and Yasunami et al., we found that a series of benz[a]azulene derivatives in acidic medium (i.e., 10% TFA/CH₂Cl₂) exhibit relatively stronger emission and higher quantum yields than in a neutral state.

The emission wavelengths of 5a, 5b, 5c, and 13 showed slight differences; 5b (λflu = 446 nm) and 5c (λflu = 443 nm) with an isopropyl group at the seven-membered ring exhibited a slight hypsochromic shift of the emission maximum compared to that of 5a (λflu = 459 nm), while the opposite phenomenon was detected for 13 (λflu = 493 nm) with a tert-butyl group at the 3-position. These results indicate that the tert-butyl group at the 3-position is responsible for the bathochromic shift of the emission wavelength. On the other hand, the substituent at the 10-position of the benz[a]azulene skeleton had a significant negative effect on the quantum yield (Φflu), except for 13. For example, the fluorescence quantum yields of the formyl derivative 4b (Φflu < 1%) and the ester derivative 12 (Φflu < 1%) were much lower than that of 13 (Φflu = 10.0%), and their values were below the measurement limit of the instrument. The derivatives other than 4b and 12 also resulted in lower quantum yields than that of 13, probably due to non-radiative deactivation by rotation or vibration of the substituent at the 10-position. The emission maxima of 18a (λflu = 506 nm) and 18b (λflu = 550 nm) with an aryl group displayed a bathochromic shift compared to that of 13, which may be ascribed to a decrease in the energy gap between the excited and ground states due to the expansion of the conjugated system. Furthermore, 18b was shifted the emission wavelength to a longer wavelength region than that of 18a, indicating that the substituent at the para-position of the benzene ring may affect the electronic properties of the molecule.

<table>
<thead>
<tr>
<th>Sample</th>
<th>λflu (λex) in 10% TFA/CH₂Cl₂</th>
<th>Φflu [%]</th>
<th>τflu [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>498 (371)</td>
<td>&lt; 1</td>
<td>1.0</td>
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Table 3. Fluorescent properties of benz[a]azulenes in 10% TFA/CH₂Cl₂.
<p>| | | | | |</p>
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<tbody>
<tr>
<td>5a</td>
<td>459</td>
<td>(398)</td>
<td>7.4</td>
<td>2.6</td>
</tr>
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<td>5b</td>
<td>446</td>
<td>(397)</td>
<td>13.0</td>
<td>2.9</td>
</tr>
<tr>
<td>5c</td>
<td>443</td>
<td>(397)</td>
<td>10.0</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>490</td>
<td>(412)</td>
<td>8.7</td>
<td>5.0</td>
</tr>
<tr>
<td>9</td>
<td>492</td>
<td>(366)</td>
<td>2.6</td>
<td>5.3</td>
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<td>10</td>
<td>490</td>
<td>(406)</td>
<td>4.6</td>
<td>5.2</td>
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<td>12</td>
<td>489</td>
<td>(410)</td>
<td>&lt; 1</td>
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<tr>
<td>13</td>
<td>493</td>
<td>(407)</td>
<td>10.0</td>
<td>5.1</td>
</tr>
<tr>
<td>15</td>
<td>464</td>
<td>(402)</td>
<td>1.5</td>
<td>5.5</td>
</tr>
<tr>
<td>18a</td>
<td>506</td>
<td>(423)</td>
<td>5.0</td>
<td>7.0</td>
</tr>
<tr>
<td>18b</td>
<td>550</td>
<td>(388)</td>
<td>4.4</td>
<td>5.0</td>
</tr>
<tr>
<td>22</td>
<td>483</td>
<td>(416)</td>
<td>1.3</td>
<td>5.0</td>
</tr>
<tr>
<td>23b</td>
<td>531</td>
<td>(385)</td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>25</td>
<td>553</td>
<td>(481)</td>
<td>6.0</td>
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**Electrochemical properties**

As mentioned in the Introduction section, benz[a]azulene derivatives have been prepared by various researchers, however, their electrochemical properties have not yet been evaluated. Our group has previously reported that diazuleno[2,1-a:1,2-c]naphthalenes, an analog of benz[a]azulene, exhibits reversible redox waves on cyclic voltammograms.29 Therefore, the benz[a]azulene derivatives prepared in this study may also show the reversible redox wave based on the stabilization of the radical species generated by the electrochemical reactions. Thus, to clarify the electrochemical behavior, redox potentials of benz[a]azulenes were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox potentials of these compounds determined by DPV are summarized in Table 4.
Table 4. Redox Potentials\textsuperscript{a} of benz[a]azulenes determined by DPV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{1\text{ox}}$ [V]</th>
<th>$E_{2\text{ox}}$ [V]</th>
<th>$E_{1\text{red}}$ [V]</th>
<th>$E_{2\text{red}}$ [V]</th>
</tr>
</thead>
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<tr>
<td>4b</td>
<td>+0.68</td>
<td>–</td>
<td>−1.49</td>
<td>–</td>
</tr>
<tr>
<td>5a</td>
<td>+0.44</td>
<td>–</td>
<td>−1.79</td>
<td>–</td>
</tr>
<tr>
<td>5b</td>
<td>+0.37</td>
<td>–</td>
<td>−1.83</td>
<td>–</td>
</tr>
<tr>
<td>5c</td>
<td>+0.42</td>
<td>+0.63</td>
<td>−1.90</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>+0.25</td>
<td>–</td>
<td>−1.95</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>+0.85</td>
<td>–</td>
<td>−1.36</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>+0.46</td>
<td>+0.63\textsuperscript{b}</td>
<td>−1.83</td>
<td>–</td>
</tr>
<tr>
<td>12</td>
<td>+0.64</td>
<td>–</td>
<td>−1.62</td>
<td>−1.94</td>
</tr>
<tr>
<td>13</td>
<td>+0.32</td>
<td>+0.56</td>
<td>−1.88</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>+0.29</td>
<td>+0.66\textsuperscript{c}</td>
<td>−1.79</td>
<td>–</td>
</tr>
<tr>
<td>18a</td>
<td>+0.39</td>
<td>+0.96</td>
<td>−1.83</td>
<td>–</td>
</tr>
<tr>
<td>18b</td>
<td>+0.36</td>
<td>+0.89\textsuperscript{d}</td>
<td>−1.87</td>
<td>–</td>
</tr>
<tr>
<td>22</td>
<td>+0.76</td>
<td>+1.56</td>
<td>−1.23</td>
<td>−1.94</td>
</tr>
<tr>
<td>23b</td>
<td>+0.52</td>
<td>+1.45</td>
<td>−1.48</td>
<td>−1.94</td>
</tr>
<tr>
<td>25</td>
<td>+0.82</td>
<td>–</td>
<td>−1.13</td>
<td>−1.93</td>
</tr>
</tbody>
</table>

\textsuperscript{a} V vs Ag/AgNO\textsubscript{3}, 1 mM in benzonitrile containing Et\textsubscript{4}NClO\textsubscript{4} (0.1 M), Pt electrode (internal diameter = 1.6 mm), scan rate = 100 mVs\textsuperscript{−1}, and external reference (Fc/Fc\textsuperscript{+} = +0.15 V); \textsuperscript{b} $E_{3\text{ox}}$ was observed at +0.79 V. \textsuperscript{c} $E_{3\text{ox}}$ was observed at +1.12 V. \textsuperscript{d} $E_{3\text{ox}}$ was observed at +1.32 V.

Contrary to our predictions, most of benz[a]azulenes exhibited irreversible reduction waves on CV, indicating the formation of unstable cation or anion species under the electrochemical oxidation or reduction conditions. Relatively high reversibility was observed
under the electrochemical oxidation conditions of 15, 18a, and 18b. Previously, we have reported that 1-azulenyl sulfides show the reversible redox waves originating from the one-electron oxidation of sulfur atom was observed under the oxidation conditions on CV.\textsuperscript{20} The relatively high reversibility of the redox wave for 15 should be attributed to the one-electron oxidation of the sulfur atom, since the half-wave potential under the oxidation conditions is similar to those of 1-azulenyl sulfides reported by us, previously. Whereas the reversible waves under the electrochemical oxidation conditions observed in 18a and 18b might be explained by the delocalization of the generated radical cationic species which were stabilized by the extension of the conjugation by the substituted aryl group.

Most of benz[a]azulenes showed irreversible redox waves on CV. Especially, 9 and 22 with an electron-withdrawing group exhibited large differences in the redox waves between anodic ($E_{pa}$) and cathodic ($E_{pc}$) processes under the reduction conditions, which might be ascribed to changes in the molecular conformation or subsequent reaction of the radical ionic species generated by the redox reaction. If the cause of the irreversibility of the cyclic voltammogram is the slow electron transfer and/or the structural change of the molecule caused by the redox reaction, the reversibility can be improved by reducing the scan rate. On the other hand, if the irreversibility is due to the instability of the generated radical ions, it is expected that the reversibility will be improved by increasing the scan rate (Figure 6). Therefore, the electrochemical reduction of 22 was measured by CV at different scan rates, but the reversibility of the redox wave was not improved in any case.

A continuous measurement of 40 cycles of CV for 22 was also investigated. If the redox reaction are produced new species, the voltammograms should change gradually from the first cycle. However, there was no significant difference between the first and 40th cycles of the voltammogram in the case of 22 (Figure 7). These results indicate the series of the redox reactions regenerate eventually the neutral species of 22. The regeneration of the neutral species was also supported by the results obtained by the spectroelectrochemical
measurements described later.

Figure 6. Cyclic voltammograms for the reduction of 22 in benzonitrile (1 mM) containing Et₄NClO₄ (0.1 M) as the supporting electrolyte at different scan rates.

Figure 7. Cyclic voltammograms for the reduction of 22 in benzonitrile (1 mM) containing Et₄NClO₄ (0.1 M) as the supporting electrolyte during the 40 times continuous
measurements; scan rate = 100 mVs\(^{-1}\).

To elucidate the electrochromic behavior of a series of benz[a]azulenes, the spectral changes were monitored by visible spectroscopy under the constant voltage redox conditions. As expected by the voltammetry experiments, most of the derivatives did not show reversible spectral changes under the redox conditions with the exception of some compounds. Despite the good reversibility seen in CV under the electrochemical oxidations, spectroelectrochemical measurements did not yield reversible electrochromism at 15, 18a, and 18b. These results imply that the radical cationic species produced by the electrochemical oxidation of 15, 18a, and 18b are not stable enough to be observed by the spectroelectrochemical measurements.

Spectroelectrochemical measurements of 9 and 22 under the reduction conditions showed relatively good reversible electrochromic behavior, even though the CV measurements did not show complete reversibility. For example, electrochemical reduction of 9 developed a new absorption band at around 420 nm along with the disappearance of the original band at ca. 455 nm. The reverse oxidation of the reduced species of 9 decreased the newly generated absorption bands, and the original spectrum was recovered with a relatively good reversibility (74% recovery). Similarly, electrochemical reduction of 22 with a dicyanovinyl group produced a new absorption band at around 460 nm together with a decrease in the original absorption band at 510 nm (Figure 8, top). The reverse oxidation of the reduced species of 22 regenerated the parent spectrum with a high recovery of 83% (Figure 8, bottom). Given the comprehensive results of CV and spectroelectrochemical measurements, the reversibility of 22 in the electrochromism may be explained by the subsequent reaction of the reduced species to produce another stable species. That is, the cathodic peak potential (\(E_{pc}\)) of 22 detected at \(-1.33\) V in CV could be ascribed to the generation of radical anion, which is transformed into a more stable chemical species. The
reverse peak for the anodic process \( (E_{pa}) \) of 22 could be considered as the regeneration of the original neutral species from the newly generated species in the cathodic process, but it was not perfect.

**Figure 8.** Continuous change in the visible spectrum of 22: constant voltage electrochemical reduction at \(-1.60\) V (top) and reverse oxidation of the reduced species at ±0 V (bottom) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.
The redox cycle of 25 also revealed good reversibility under the spectroelectrochemical measurement conditions. Electrochemical reduction of 25 at −1.60 V resulted in the disappearance of the absorption bands between 450–700 nm with an isosbestic point at $\lambda = 445$ nm accompanied by the appearance of a new band at 500 nm (Figure 9, top). The reverse oxidation of the reduced species for 25 regenerated the original absorption band with a recovery ratio of 73% (Figure 9, bottom). As with 9 and 22, the cyclohexenone moiety serves as an electron-withdrawing group, so the reversibility of 25 might also be derived from the formation of stable anionic species, followed by the reactions under the electrochemical reduction conditions.
Figure 9. Continuous change in the visible spectrum of 25: constant voltage electrochemical reduction at −1.60 V (top) and reverse oxidation of the reduced species at ±0 V (bottom) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

Conclusion

In conclusion, we have described a new procedure for the synthesis of benz[a]azulenes from readily available 2H-cyclohepta[b]furan-2-one derivatives. This method should provide a new synthetic pathway for benz[a]azulenes, which are difficult and/or laborious to prepare by traditional methods. In this method, the azulene ring was constructed by [8 + 2] cycloaddition of 2H-cyclohepta[b]furan-2-ones with enamines prepared by the reaction of 4-tert-butylcyclohexanone with pyrrolidine. The resulting azulene derivatives were subsequently transformed into benz[a]azulenes via the Vilsmeier reaction, followed by the deformylation and elimination of the tert-butyl group with 100% H₃PO₄, and the final aromatization with DDQ. This four-step method of 5a provided the highest yield among the methods reported so far. The formyl derivative 6a was also transformed to cyclohept[a]acenaphthylene-3-one derivative 25 by Knoevenagel condensation with dimethyl
malonate, followed by intramolecular cyclization with Brønsted acid.

The decrease in aromaticity of the azulene moiety in benz[a]azulenes was suggested by the results of $^1$H NMR spectra, NICS calculations, and single-crystal X-ray structure analysis. The optical and electrochemical properties of the parent benz[a]azulene and their functionalized derivatives were evaluated by UV/Vis and fluorescence measurements, voltammetry experiments, and spectroelectrochemistry, which revealed that the substituents on the azulene ring directly affected their properties. As previously reported, benz[a]azulenes did not show the strong emission in neutral media, but under acidic conditions, protonation of azulenes at the five-membered ring led to the formation of an azulenium ion, providing the remarkable fluorescence.

Most of benz[a]azulenes did not show reversible redox waves on CV, but those with electron-withdrawing groups showed a remarkable spectral change under the electrochemical reduction conditions. Furthermore, the reverse oxidation of these species regenerated the parent spectrum with a high recovery, which may be explained by the stability of the generated species.

As noted in the Introduction section, the construction of novel polycyclic aromatic compounds is expected for the application to the promising organic electronic materials. Hence, further functionalization and extension of the conjugated system of benz[a]azulenes may lead to the optical and electrochemical properties required for practical electronic materials. The preparation of novel π-electron systems based on benz[a]azulene frameworks and the elucidation of their properties are currently underway in our laboratory.

**EXPERIMENTAL SECTION**

**General Methods:** $^1$H and $^{13}$C NMR spectra were measured at 500 MHz ($^1$H NMR) and 125 MHz ($^{13}$C NMR), respectively. The fluorescence quantum yield was obtained with an absolute photoluminescence quantum yield spectrometer. The fluorescence lifetimes were
obtained with a time-resolved fluorescence spectrometer based on a streak camera. The time resolution was about 500 ps. The excitation wavelength was 400 nm (second harmonic of the output from a Ti: sapphire laser). The repetition rate of the oscillator was reduced from 80 to 8 MHz with a pulse selector. Voltammetry measurements were carried out in benzonitrile as a measurement solvent, with Pt working and auxiliary electrodes and a reference electrode formed from Ag/AgNO₃ (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M).

**Compound 2a**: To a solution of 1a (1.49 g, 10.2 mmol) in EtOH (30 mL) was added pyrrolidine enamine of 4-tert-butylcyclohexanone (8.29 g, 40.0 mmol). The resulting mixture was refluxed for 6 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with hexane as an eluent to give 2a (2.06 g, 85%) as a blue solid. M.p. 42–43 °C; IR (AT-IR): ν max = 2959 (w), 2910 (w), 1572 (w), 1537 (w), 1493 (w), 1453 (w), 1425 (w), 1389 (m), 1365 (m), 1318 (w), 1298 (w), 1242 (w), 941 (w), 830 (w), 797 (m), 787 (s), 765 (w), 739 (m), 729 (s), 708 (w), 671 (w), 659 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δH = 8.14 (m, 2H, 5-H, 9-H), 7.46 (t, J = 9.7 Hz, 1H, 7-H), 7.13 (s, 1H, 10-H), 7.02–7.10 (m, 2H, 6-H, 8-H), 3.22–3.31 (m, 2H, c-Hex), 3.01–3.07 (m, 1H, c-Hex), 2.74 (m, 1H, c-Hex), 2.14–2.18 (m, 1H, c-Hex), 1.62 (m, 1H, c-Hex), 1.49–1.56 (m, 1H, c-Hex), 1.05 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 150.5, 140.2, 136.2, 135.5, 134.3, 130.9, 126.7, 122.2, 121.5, 114.8, 45.6, 32.9, 27.71, 27.65, 25.3, 24.5 ppm; HRMS (MALDI–TOF, positive) calcd for C₁₈H₂₂⁺ [M]+ 238.1716, found 238.1729.

**Compound 2b**: To a solution of 1b (5.64 g, 30.0 mmol) in EtOH (90 mL) was added pyrrolidine enamine of 4-tert-butylcyclohexanone (20.7 g, 99.8 mmol). The resulting mixture was refluxed for 22.5 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on alumina with hexane as an eluent to give 2b
(5.76 g, 68%) as a blue solid. M.p. 70–72 °C; IR (AT-IR): \( \nu_{\text{max}} = 2957 \text{ (s)}, 2912 \text{ (m)}, 1574 \text{ (w)}, 1520 \text{ (w)}, 1490 \text{ (w)}, 1465 \text{ (m)}, 1445 \text{ (w)}, 1395 \text{ (m)}, 1363 \text{ (s)}, 1329 \text{ (w)}, 1302 \text{ (w)}, 1265 \text{ (w)}, 1242 \text{ (w)}, 1189 \text{ (w)}, 1088 \text{ (w)}, 1033 \text{ (w)}, 978 \text{ (w)}, 936 \text{ (w)}, 916 \text{ (w)}, 879 \text{ (w)}, 833 \text{ (w)}, 780 \text{ (s)}, 713 \text{ (w)}, 702 \text{ (w)}, 681 \text{ (w)}, 661 \text{ (w)} \text{ cm}^{-1}; \) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 8.12 \text{ (s, 1H, 9-H)}, 8.02 \text{ (d, } J = 9.8 \text{ Hz, 1H, 5-H)}, 7.41 \text{ (d, } J = 9.8 \text{ Hz, 1H, 7-H)}, 7.26 \text{ (s, 1H, 10-H)}, 7.05 \text{ (t, } J = 9.8 \text{ Hz, 1H, 6-H)}, 3.19–3.26 \text{ (m, 2H, c-Hex)}, 3.02–3.06 \text{ (m, 2H, i-Pr, c-Hex)}, 2.69 \text{ (m, 1H, c-Hex)}, 2.14 \text{ (m, 1H, c-Hex)}, 1.60–1.61 \text{ (m, 1H, c-Hex)}, 1.48 \text{ (m, 1H, c-Hex)}, 1.35 \text{ (d, } J = 6.9 \text{ Hz, 6H, i-Pr)}, 1.04 \text{ (s, 9H, t-Bu)} \text{ ppm}; \) \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 150.5, 142.1, 140.3, 135.8, 134.5, 133.9, 129.6, 125.7, 121.3, 113.3, 45.7, 38.6, 32.9, 27.69, 27.65, 25.4, 24.7, 24.4 \text{ ppm}; \) HRMS (MALDI–TOF, positive) calcd for C\(_{21}\)H\(_{28}\)\([\text{M}]^+\) 280.2186, found 280.2204.

**Compound 2c:** To a solution of 1c (941 mg, 5.00 mmol) in EtOH (15 mL) was added pyrrolidine enamine of 4-tert-butylcyclohexanone (4.15 g, 20.0 mmol). The resulting mixture was refluxed for 3.5 h and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on alumina with hexane as an eluent to give 2c (610 mg, 44%) as blue oil. IR (AT-IR): \( \nu_{\text{max}} = 2959 \text{ (s)}, 2869 \text{ (w)}, 1698 \text{ (w)}, 1578 \text{ (s)}, 1548 \text{ (w)}, 1496 \text{ (w)}, 1464 \text{ (w)}, 1397 \text{ (m)}, 1364 \text{ (s)}, 1326 \text{ (w)}, 1274 \text{ (w)}, 1239 \text{ (w)}, 1173 \text{ (w)}, 1093 \text{ (w)}, 1041 \text{ (m)}, 957 \text{ (w)}, 908 \text{ (w)}, 836 \text{ (s)}, 779 \text{ (w)}, 759 \text{ (s)}, 733 \text{ (w)}, 705 \text{ (w)}, 668 \text{ (m)} \text{ cm}^{-1}; \) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 8.06 \text{ (m, 2H, 5-H, 9-H)}, 7.02–6.97 \text{ (m, 3H, 6-H, 8-H, 10-H)}, 3.17–3.26 \text{ (m, 2H, c-Hex)}, 2.97–3.04 \text{ (m, 2H, i-Pr, c-Hex)}, 2.69 \text{ (m, 1H, c-Hex)}, 2.11–2.15 \text{ (m, 1H, c-Hex)}, 1.44–1.63 \text{ (m, 2H, c-Hex)}, 1.33 \text{ (d, } J = 6.9 \text{ Hz, 6H, i-Pr)}, 1.03 \text{ (s, 9H, t-Bu)} \text{ ppm}; \) \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 157.2, 149.0, 138.9, 134.9, 134.0, 130.7, 126.5, 121.4, 120.5, 114.4, 45.7, 39.7, 32.9, 27.65, 27.57, 25.4, 24.5, 24.4 \text{ ppm}; \) HRMS (MALDI–TOF, positive) calcd. for C\(_{21}\)H\(_{28}\)\([\text{M}]^+\) 280.2186, found 280.2182.

**Compound 3a:** POCl\(_3\) (330 mg, 2.15 mmol) was added at 0 °C to a solution of 2a (155 mg,
0.582 mmol) in DMF (20 mL). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was poured into K₂CO₃ aq., extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with AcOEt as an eluent to give 3a (134 mg, 86%) as a purple solid. M.p. 79–80 °C; IR (AT-IR): \( \nu_{\text{max}} = 2956 \text{ (w)}, 2868 \text{ (w)}, 1638 \text{ (s)}, 1592 \text{ (w)}, 1536 \text{ (w)}, 1521 \text{ (w)}, 1438 \text{ (s)}, 1407 \text{ (m)}, 1394 \text{ (m)}, 1380 \text{ (m)}, 1363 \text{ (s)}, 1295 \text{ (w)}, 1244 \text{ (w)}, 1227 \text{ (w)}, 1175 \text{ (w)}, 1118 \text{ (w)}, 1031 \text{ (w)}, 998 \text{ (w)}, 979 \text{ (w)}, 942 \text{ (w)}, 896 \text{ (w)}, 845 \text{ (w)}, 785 \text{ (w)}, 737 \text{ (s)}, 702 \text{ (w)}, 676 \text{ (w)} \text{ cm}^{-1}; ^1\text{H NMR} (500 \text{ MHz, CDCl}_3): \delta_H = 10.45 \text{ (s, 1H, CHO)}, 9.27 \text{ (d, } J = 9.7 \text{ Hz, 1H, 9-H)}, 8.22 \text{ (d, } J = 9.7 \text{ Hz, 1H, 5-H}), 7.68 \text{ (t, } J = 9.7 \text{ Hz, 1H, 7-H}), 7.48 \text{ (t, } J = 9.7 \text{ Hz, 1H, 8-H}), 7.42 \text{ (t, } J = 9.7 \text{ Hz, 1H, 6-H}), 3.58 \text{ (m, 1H, c-Hex)}, 3.09–3.12 \text{ (m, 2H, c-Hex)}, 2.55–2.60 \text{ (m, 1H, c-Hex)}, 2.21–2.17 \text{ (m, 1H, c-Hex)}, 1.54–1.57 \text{ (m, 1H, c-Hex)}, 1.46–1.40 \text{ (m, 1H, c-Hex)}, 1.03 \text{ (s, 9H, t-Bu)} \text{ ppm}; ^{13}\text{C NMR} (125 \text{ MHz, CDCl}_3): \delta_C = 185.0, 154.6, 142.7, 141.2, 137.8, 134.6, 133.2, 129.2, 128.3, 127.5, 120.5, 44.9, 32.7, 27.5, 26.4, 24.6, 24.0 \text{ ppm}; \text{ HRMS (MALDI–TOF, positive) calcd for C}_{19}\text{H}_{22}\text{O} + \text{H}^+ [M + H]^+ 267.1743, found 267.1735; \text{ HRMS (MALDI–TOF, positive) calcd for C}_{19}\text{H}_{22}\text{O} + \text{Ag}^+ [M + Ag]^+ 373.0716, found 373.0735.

**Compound 3b:** POCl₃ (5.91 g, 38.5 mmol) was added at 0 °C to a solution of 2b (3.54 g, 12.6 mmol) in DMF (40 mL). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was poured into K₂CO₃ aq., extracted with hexane/AcOEt, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with hexane/AcOEt (1:1) as an eluent to give 3b (3.86 g, 99%) as a purple solid. M.p. 99–101 °C; IR (AT-IR): \( \nu_{\text{max}} = 2957 \text{ (m), 2902 \text{ (w)}, 1632 \text{ (s)}, 1599 \text{ (w)}, 1530 \text{ (w)}, 1465 \text{ (m)}, 1441 \text{ (s)}, 1402 \text{ (w)}, 1375 \text{ (s)}, 1362 \text{ (m)}, 1329 \text{ (w)}, 1301 \text{ (w)}, 1227 \text{ (w)}, 1176 \text{ (w)}, 1001 \text{ (w)}, 978 \text{ (w)}, 956 \text{ (w)}, 942 \text{ (w)}, 802 \text{ (m)}, 727 \text{ (w)}, 668 \text{ (w)} \text{ cm}^{-1}; ^1\text{H NMR} (500 \text{ MHz, CDCl}_3): \delta_H = 10.42 \text{ (s, 1H, CHO)}, 9.42 \text{ (s, 1H, 9-H)}, 8.15 \text{ (d, } J = 10.0 \text{ Hz, 1H, 5-H}), 7.67 \text{ (d, } J = 10.0 \text{ Hz, 1H, 7-H}), 7.43 \text{ (t, } J = 10.0 \text{ Hz, 1H, 6-H}), 3.61–3.57 \text{ (m, 1H, c-Hex), 3.20
Compound 3c: POCl₃ (335 mg, 2.18 mmol) was added at 0 °C to a solution of 2c (201 mg, 0.717 mmol) in DMF (30 mL). The resulting mixture was stirred at room temperature for 16.5 h. The reaction mixture was poured into K₂CO₃ aq., extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with AcOEt as an eluent to give 3c (204 mg, 92%) as red oil. IR (AT-IR): ν max = 2960 (w), 1637 (s), 1581 (m), 1441 (m), 1401 (m), 1379 (m), 1364 (m), 1304 (w), 1240 (w), 1046 (w), 997 (w), 975 (w), 957 (w), 923 (w), 840 (m), 754 (s), 675 (m), 664 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δH = 10.44 (s, 1H, CHO), 9.23 (d, J = 10.3 Hz, 1H, 9-H), 8.20 (d, J = 10.3 Hz, 1H, 5-H), 7.45 (dd, J = 10.3, 1.2 Hz, 1H, 8-H), 7.39 (dd, J = 10.3, 1.2 Hz, 1H, 6-H), 3.61–3.56 (m, 1H, c-Hex), 3.15–3.07 (m, 3H, i-Pr, c-Hex), 2.62–2.56 (m, 1H, c-Hex), 2.21–2.17 (m, 1H, c-Hex), 1.62–1.56 (m, 1H, c-Hex), 1.51–1.42 (m, 1H, c-Hex), 1.36 (d, J = 6.9 Hz, 6H, i-Pr), 1.03 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 185.0, 160.2, 153.2, 141.5, 140.1, 134.5, 133.0, 128.4, 128.0, 127.0, 120.5, 45.1, 39.7, 32.8, 27.6, 26.3, 24.8, 24.4, 24.0 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₂H₂₈O + H⁺ [M + H]⁺ 309.2213, found 309.2219, HRMS (MALDI–TOF, positive) calcd for C₂₂H₂₈O + Ag⁺ [M + Ag]⁺ 415.1186, found 415.1172.

Compound 4a: DDQ (337 mg, 1.48 mmol) was added at 0 °C to a solution of 3a (134 mg, 0.503 mmol) in toluene (15 mL). The resulting mixture was stirred at room temperature for 2
The reaction mixture was poured into K₂CO₃ aq., extracted with toluene/EtOAc, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/AcOEt (4:1) as an eluent to give 4a (130 mg, 99%) as a green solid. M.p. 125–126 °C; IR (AT-IR): ν max = 2970 (w), 2954 (w), 1635 (s), 1607 (w), 1491 (w), 1468 (m), 1449 (w), 1410 (w), 1391 (m), 1365 (m), 1329 (w), 1293 (w), 1274 (w), 1244 (w), 1212 (w), 1187 (w), 1153 (w), 1094 (w), 1076 (w), 1031 (w), 1018 (w), 992 (w), 939 (w), 876 (w), 861 (w), 841 (w), 825 (m), 776 (w), 766 (w), 741 (w), 709 (s), 655 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ max (log ε) = 240 (4.36), 284 (4.52), 337 (4.44), 350 (4.52), 391 sh (3.73), 412 (3.85), 434 (3.93), 541 (2.69), 587 (2.67), 643 sh (2.53), 716 sh (2.28) nm; UV/Vis (10% TFA/CH₂Cl₂): λ max (log ε) = 307 (4.50), 293 sh (4.45), 372 (4.25), 431 (3.96) nm; ¹H NMR (500 MHz, CDCl₃): δH = 10.81 (s, 1H, CHO), 9.24 (d, J = 10.6 Hz, 1H, 9-H), 8.84 (dd, J = 8.9, 0.9 Hz, 1H, 5-H), 8.57 (d, J = 8.6 Hz, 1H, 1-H), 8.41 (d, J = 1.4 Hz, 1H, 4-H), 7.91 (dd, J = 8.6, 1.4 Hz, 1H, 2-H), 7.73–7.69 (m, 1H, 7-H), 7.58 (dd, J = 10.6, 9.3 Hz, 1H, 8-H), 7.53 (dd, J = 10.7, 8.9 Hz, 1H, 6-H), 1.50 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 184.8, 147.1, 145.9, 143.0, 139.1, 138.1, 134.5, 132.7, 130.7, 130.6, 130.0, 129.3, 120.4, 119.5, 116.7, 35.3, 31.8 ppm; HRMS (MALDI–TOF, positive) calcd for C₁₉H₁₈O + H⁺ [M + H]⁺ 263.1430, found 263.1418, HRMS (MALDI–TOF, positive) calcd for C₁₉H₁₈O + Ag⁺ [M + Ag]⁺ 369.0403, found 369.0417.

**Compound 4b:** DDQ (1.02 g, 4.48 mmol) was added at 0 °C to a solution of 3b (454 mg, 1.47 mmol) in toluene (30 mL). The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into K₂CO₃ aq., extracted with toluene/EtOAc, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/EtOAc (4:1) as an eluent to give 4b (443 mg, 99%) as a green solid. M.p. 119–121 °C; IR (AT-IR): ν max = 2959 (m), 2867 (w), 1636 (s), 1618 (m), 1509 (w), 1475 (s), 1416 (m), 1386 (m), 1368 (s), 1306 (w), 1276 (w), 1254 (w),
Compound 4c: DDQ (468 mg, 2.06 mmol) was added at 0 °C to a solution of 3c (308 mg, 1.00 mmol) in toluene (15 mL). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with toluene. The organic layer was washed with brine and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/EtOAc (2:1) as an eluent to give 4c (289 mg, 95%) as a green solid. M.p. 104 °C; IR (AT-IR): ν_max = 2966 (w), 2875 (w), 1628 (s), 1604 (m), 1585 (m), 1525 (w), 1490 (w), 1458 (s), 1419 (m), 1404 (m), 1369 (s), 1333 (w), 1283 (w), 1265 (w), 1244 (w), 1231 (w), 1220 (m), 1196 (w), 1154 (w), 1132 (w), 1084 (w), 1052 (w), 1033 (m), 976 (m), 924 (w), 908 (w), 870 (w), 857 (w), 843 (m), 828 (m), 780 (w), 719 (m), 653 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ_max (log ε) = 243 (4.36), 286 (4.51), 341 (4.44), 354 (4.53), 410 sh (3.83), 436 (3.95), 528 (2.86), 563 (2.85), 623 sh (2.68) nm; UV/Vis (10% TFA/CH₂Cl₂): λ_max (log ε) = 261 (4.27), 290 sh (4.38), 308 (4.48), 371 (4.28), 395 sh (4.18), 450 sh (3.86) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 10.81 (s, 1H, CHO), 9.21 (d, J = 11.5 Hz, 1H, CHO), 9.21 (d, J = 11.5 Hz,
1H, 9-H), 8.78 (d, J = 9.5 Hz, 1H, 5-H), 8.54 (d, J = 8.5 Hz, 1H, 1-H), 8.37 (d, J = 1.7 Hz, 1H, 4-H), 7.86 (dd, J = 8.5, 1.7 Hz, 1H, 2-H), 7.48–7.50 (m, 2H, 6-H, 8-H), 3.14 (sept, J = 6.9 Hz, 1H, i-Pr), 1.49 (s, 9H, t-Bu), 1.39 (d, J = 6.9 Hz, 6H, i-Pr) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\)C = 185.0, 160.5, 146.7, 145.0, 140.9, 138.8, 134.2, 132.7, 131.5, 130.7, 128.6, 127.4, 120.3, 119.2, 116.4, 39.6, 35.2, 31.8, 24.1 ppm; HRMS (MALDI–TOF, positive) calcd for C\(_{22}\)H\(_{24}\)O + H\(^+\) [M + H]\(^+\) 305.1900, found 305.1881.

**Compound 5a:** A solution of 4a (394 mg, 1.50 mmol) in 100% H\(_3\)PO\(_4\) (35 mL) was stirred at 140 °C for 19 h. After cooling to room temperature, the reaction mixture was poured into water, and neutralized with KOH aq. The precipitate was collected by filtration and dissolved in CHCl\(_3\). The crude product was purified by silica gel column chromatography with hexane/toluene (10:1) as an eluent to give 5a (190 mg, 71%) as green crystals. M.p. 150 °C; IR (AT-IR): \(\nu\)max = 3046 (w), 1698 (w), 1601 (m), 1586 (w), 1558 (w), 1523 (w), 1448 (w), 1433 (w), 1397 (w), 1377 (w), 1324 (w), 1308 (w), 1264 (w), 1240 (w), 1206 (w), 1159 (w), 1046 (w), 1012 (w), 975 (w), 934 (w), 910 (w), 885 (w), 870 (w), 855 (w), 811 (m), 763 (m), 740 (m), 682 (s), 653 (w) cm\(^{-1}\); UV/Vis (CH\(_2\)Cl\(_2\)): \(\lambda\)max (log \(\varepsilon\)) = 247 (4.03), 256 sh (4.00), 306 (4.68), 320 sh (4.39), 345 (3.47), 363 (3.60), 381 (3.65), 402 (3.47), 475 sh (2.54), 517 sh (2.61), 561 (2.69), 612 (2.70), 673 (2.60), 764 sh (2.41) nm; UV/Vis (10% TFA/CH\(_2\)Cl\(_2\)): \(\lambda\)max (log \(\varepsilon\)) = 274 (4.32), 398 (4.37) nm; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\)H = 8.39 (dd, J = 8.0, 0.9 Hz, 4-H), 8.32 (dd, J = 8.3, 0.6 Hz, 1H, 5-H), 7.96 (d, J = 11.0 Hz, 1H, 9-H), 7.87 (d, J = 8.0 Hz, 1H, 1-H), 7.69–7.66 (m, 1H, 2-H), 7.50–7.47 (m, 1H, 3-H), 7.33 (s, 1H, 10-H), 7.20 (dd, J = 11.0, 8.3 Hz, 1H, 7-H), 7.04 (dd, J = 11.0, 8.3 Hz, 1H, 8-H), 6.85 (dd, J = 10.9, 8.6 Hz, 1H, 6-H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\)C = 142.5, 140.7, 139.3, 136.1, 134.8, 131.5, 128.6, 128.0, 125.5, 123.8, 121.9, 120.9, 120.4, 116.2 ppm; HRMS (MALDI–TOF, positive) calcd for C\(_{14}\)H\(_{10}\) [M]\(^+\) 178.0777, found 178.0771.
**Compound 5b**: A solution of 4b (549 mg, 1.80 mmol) in 100% H₃PO₄ (40 mL) was stirred at 140 °C for 14 h. After cooling to room temperature, the reaction mixture was poured into water and neutralized with KOH aq. The precipitate was collected by filtration and dissolved in CHCl₃. The crude product was purified by silica gel column chromatography with hexane as an eluent to give 5b (194 mg, 49%) as green crystals. M.p. 140 °C; IR (AT-IR): ν max = 2953 (w), 2928 (w), 2865 (w), 1601 (w), 1509 (w), 1464 (w), 1451 (w), 1430 (w), 1384 (w), 1362 (w), 1312 (w), 1248 (w), 1122 (w), 1065 (w), 1011 (w), 932 (w), 915 (w), 905 (w), 881 (w), 819 (s), 793 (m), 762 (s), 747 (m), 704 (s), 656 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ max (log ε) = 248 (4.06), 306 (4.75), 346 (3.57), 362 (3.68), 380 (3.71), 401 (3.48), 519 sh (2.55), 568 (2.66), 616 (2.68), 679 (2.54), 774 sh (2.14) nm; UV/Vis (10% TFA/CH₂Cl₂): λ max (log ε) = 275 (4.33), 397 (4.48) nm; ¹H NMR (500 MHz, CDCl₃): δ H = 8.33 (d, J = 7.7 Hz, 1H, 4-H), 8.21 (dd, J = 8.2, 0.7 Hz, 1H, 5-H), 7.85 (s, 1H, 9-H), 7.81 (d, J = 7.7 Hz, 1H, 1-H), 7.64 (dd, J = 7.7, 1.0 Hz, 1H, 2-H), 7.42 (dd, J = 7.7, 1.0 Hz, 1H, 3-H), 7.21 (s, 1H, 10-H), 7.13 (d, J = 11.7 Hz, 1H, 7-H), 7.02 (dd, J = 11.7, 8.2 Hz, 1H, 6-H), 2.93 (sept, J = 6.9 Hz, 1H, i-Pr), 1.32 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ C = 143.2, 142.7, 140.8, 139.1, 135.8, 132.6, 131.4, 128.5, 127.2, 125.2, 121.4, 120.8, 120.0, 115.2, 38.4, 23.9 ppm; HRMS (MALDI–TOF, positive) calcd for C₁₇H₁₆⁺ [M]⁺ 220.1247, found 220.1226.

**Compound 5c**: A solution of 4c (1.07 g, 3.50 mmol) in 100% H₃PO₄ (80 mL) was stirred at 140 °C for 15 h. After cooling to room temperature, the reaction mixture was poured into water and neutralized with KOH aq. The precipitate was collected by filtration and dissolved in CHCl₃. The crude product was purified by silica gel column chromatography with hexane as an eluent to give 5c (316 mg, 41%) as green crystals. M.p. 127 °C; IR (AT-IR): ν max = 2958 (w), 2868 (w), 1601 (m), 1587 (w), 1524 (w), 1464 (w), 1442 (m), 1409 (m), 1213 (w), 1097 (w), 1074 (w), 1035 (w), 935 (w), 866 (w), 836 (s), 795 (w), 761 (s), 743 (s), 703 (m), 686 (w), 668 (w), 658 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ max (log ε) = 245 (4.04), 301 sh (4.70), 309
(4.75), 324 (4.67), 346 (3.58), 363 (3.68), 383 (3.70), 402 (3.45), 501 (2.69), 548 (2.77), 592 (2.78), 660 sh (2.64), 732 sh (2.37) nm; UV/Vis (10% TFA/CH2Cl2): $\lambda_{\text{max}}$ (log $\varepsilon$) = 274 (4.26), 397 (4.46) nm; $^1$H NMR (500 MHz, CDCl3): $\delta_H = 8.34$ (d, $J = 7.8$ Hz, 1H, 1-H), 8.25 (d, $J = 8.8$ Hz, 1H, 5-H), 7.93 (d, $J = 11.4$ Hz, 1H, 9-H), 7.84 (d, $J = 7.8$ Hz, 1H, 4-H), 7.63–7.63 (m, 1H, 3-H), 7.45–7.42 (m, 1H, 2-H), 7.26 (s, 1H, 10-H), 6.95 (dd, $J = 8.8$, 1.3 Hz, 1H, 6-H), 6.81 (dd, $J = 11.4$, 1.3 Hz, 1H, 8-H), 2.93 (sept, $J = 6.9$ Hz, 1H, $i$-Pr), 1.31 (d, $J = 6.9$ Hz, 6H, $i$-Pr) ppm; $^{13}$C NMR (125 MHz, CDCl3): $\delta_C = 156.0$, 142.2, 138.8, 138.6, 135.5, 131.8, 128.1, 125.0, 122.1, 121.7, 120.6, 120.4, 115.7, 39.4, 23.8 ppm; HRMS (MALDI–TOF, positive) calcd for C17H16+ [M]+ 220.1247, found 220.1228.

**Compound 6a:** A solution of 4a (1.58 g, 6.03 mmol) in 100% H3PO4 (30 mL) was stirred at 140 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into water, extracted with toluene, washed with NaOH aq. and brine, and dried with Na2SO4. The crude product was purified by silica gel column chromatography with CHCl3/AcOEt (5:1) as an eluent to give 6a (1.14 g, 92%) as a brown solid. M.p. 97 °C; IR (AT-IR): $\nu_{\text{max}} = 1637$ (s), 1604 (m), 1596 (m), 1556 (w), 1523 (m), 1475 (m), 1451 (m), 1424 (m), 1408 (w), 1395 (m), 1374 (m), 1340 (w), 1313 (w), 1263 (w), 1243 (w), 1201 (m), 1074 (m), 1026 (w), 956 (w), 938 (m), 871 (w), 860 (w), 767 (s), 705 (s), 670 (m), 660 (m) cm$^{-1}$; UV/Vis (CH2Cl2): $\lambda_{\text{max}}$ (log $\varepsilon$) = 286 (4.40), 301 (4.44), 364 (4.34), 424 (4.05) nm; $^1$H NMR (500 MHz, CDCl3): $\delta_H = 10.76$ (s, 1H, CHO), 9.13 (d, $J = 10.9$ Hz, 1H, 9-H), 8.66 (dd, $J = 8.7$, 1.0 Hz, 1H, 5-H), 8.58 (d, $J = 8.0$ Hz, 1H, 1-H), 8.31 (d, $J = 8.0$ Hz, 1H, 4-H), 7.77–7.74 (m, 1H, 2-H), 7.66–7.62 (m, 1H, 7-H), 7.54–7.43 (m, 3H, 3-H, 6-H, 8-H) ppm; $^{13}$C NMR (125 MHz, CDCl3): $\delta_C = 184.9$, 145.6, 142.6, 140.9, 138.1, 134.3, 132.8, 130.9, 130.5, 130.1, 123.6, 121.0, 120.6, 119.5 ppm; HRMS (MALDI–TOF, positive) calcd for C15H10O + H+ [M + H]+ 207.0804, found 207.0809.
**Synthesis of 6a by Vilsmeier reaction:** POCl₃ (404 mg, 2.63 mmol) was added at 0 °C to a solution of 5a (131 mg, 0.735 mmol) in DMF (30 mL). The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with toluene. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with CHCl₃/EtOAc (5:1) as an eluent to give 6a (122 mg, 81%) as a brown solid.

**Compound 6b:** A solution of 4b (779 mg, 2.56 mmol) in 100% H₃PO₄ (30 mL) was stirred at 140 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into water, extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by silica gel column chromatography with CHCl₃/ACOEt (5:1) as an eluent to give 6b (515 mg, 81%) as a greenish brown solid. M.p. 67–68 °C; IR (AT-IR): νmax = 2967 (w), 1633 (s), 1615 (m), 1602 (m), 1508 (w), 1476 (m), 1425 (m), 1385 (m), 1367 (m), 1318 (w), 1293 (w), 1266 (w), 1251 (w), 1225 (w), 1210 (w), 1189 (w), 1152 (m), 1119 (w), 1087 (w), 1044 (m), 1016 (w), 941 (w), 905 (w), 861 (m), 807 (m), 767 (s), 753 (m), 719 (m), 710 (w), 685 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λmax (log ε) = 240 (4.37), 284 (4.52), 337 (4.45), 349 (4.52), 408 sh (3.89), 430 (3.99), 536 (2.85), 575 (2.83), 632 sh (2.68), 704 sh (2.39) nm; UV/Vis (10% TFA/CH₂Cl₂): λmax (log ε) = 286 sh (4.50), 301 (4.54), 364 (4.43), 424 (4.14) nm; ¹H NMR (500 MHz, CDCl₃): δH = 10.83 (s, 1H, CHO), 9.30 (s, 1H, 9-H), 8.66 (d, J = 8.9 Hz, 1H, 5-H), 8.56 (d, J = 8.0 Hz, 1H, 1-H), 8.34 (dd, J = 8.0, 0.9 Hz, 1H, 4-H), 7.75 (t, J = 8.0 Hz, 1H, 2-H), 7.67 (d, J = 11.2 Hz, 1H, 7-H), 7.50–7.55 (m, 2H, 3-H, 6-H), 3.20 (sept, J = 6.9 Hz, 1H, i-Pr), 1.42 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 184.7, 152.6, 145.6, 142.8, 141.5, 138.7, 132.5, 132.0, 130.4, 130.3, 129.9, 123.3, 121.0, 120.2, 118.8, 39.5, 24.3 ppm; HRMS (MALDI–TOF, positive) calcd for C₁₈H₁₆O⁺ [M]⁺ 248.1196, found 248.1215.
**Compound 7**: NaBH₄ (47 mg, 1.24 mmol) was added to a solution of 4c (168 mg, 0.55 mmol) in THF (2 mL) and diglyme (0.5 mL), and the resulting mixture was stirred at room temperature for 1 h. Then, NaBH₄ (45 mg, 1.19 mmol) and BF₃·Et₂O (0.5 mL) was added to the reaction mixture and the solution was additionally stirred at the same temperature for 2 h. The reaction mixture was poured into water, extracted with hexane, washed with brine, and dried with Na₂SO₄. The crude product was purified by alumina column chromatography with hexane as an eluent to give 7 (31 mg, 19%) as green oil. IR (AT-IR): ν_max = 3567 (w), 2958 (s), 2869 (m), 2360 (m), 2342 (m), 1608 (w), 1558 (w), 1541 (w), 1507 (w), 1458 (m), 1417 (w), 1362 (m), 1338 (w), 1300 (w), 1267 (m), 1252 (m), 1201 (w), 1097 (w), 1071 (m), 1016 (w), 986 (w), 917 (m), 880 (m), 817 (s), 784 (s), 756 (w), 728 (w), 718 (w), 683 (w), 668 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_max (log ε) = 308 (4.70), 315 sh (4.68), 338 (3.64), 367 (3.66), 386 (3.69), 408 (3.50), 537 sh (2.65), 590 (2.70), 645 (2.71), 722 sh (2.64), 823 sh (2.47) nm; UV/Vis (10% TFA/CH₂Cl₂): λ_max (log ε) = 278 (4.26), 372 sh (4.08), 412 (4.31) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 8.31 (d, J = 1.7 Hz, 1H, 4-H), 8.02 (d, J = 8.2 Hz, 1H, 5-H), 7.79 (dd, J = 8.3, 1.7 Hz, 1H, 2-H), 7.73 (d, J = 8.3 Hz, 1H, 1-H), 7.66 (d, J = 0.9 Hz, 1H, 9-H), 6.96 (d, J = 11.7 Hz, 1H, 7-H), 6.85 (dd, J = 11.7, 8.2 Hz, 1H, 6-H), 2.91 (t, J = 6.9 Hz, 1H, i-Pr), 2.59 (s, 3H, Me), 1.49 (s, 9H, t-Bu), 1.33 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 144.8, 141.5, 141.1, 140.9, 134.7, 133.0, 130.4, 129.2, 126.5, 124.9, 124.7, 121.9, 117.5, 116.4, 38.7, 35.1, 32.0, 23.9, 10.2 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₂H₂₆⁺ [M]+ 290.2029, found 290.2034.

**Compound 8**: Trifluoroacetic anhydride (1.67 g, 7.95 mmol) was added at room temperature to a solution of 2b (1.04 g, 3.71 mmol) in CHCl₃ (37 mL) and pyridine (4 mL), and the resulting mixture was stirred at room temperature for 40 min. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel with CHCl₃ as an eluent to give 8 (1.33 g, 95%) as a brown...
solid. M.p. 54–60 °C; IR (AT-IR): $\nu_{\text{max}} = 2961$ (w), 1635 (m), 1530 (w), 1460 (w), 1429 (s), 1365 (w), 1333 (w), 1307 (w), 1248 (m), 1193 (s), 1136 (s), 1073 (w), 1041 (m), 1007 (w), 986 (w), 961 (w), 928 (w), 866 (w), 810 (w), 795 (w), 760 (m), 726 (m), 709 (w), 695 (w), 683 (w), 673 (w), 655 (w) cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 9.49$ (d, $J = 1.4$ Hz, 1H, 9-H), 8.18 (d, $J = 9.9$ Hz, 1H, 5-H), 7.72 (dd, $J = 9.9, 1.4$ Hz, 1H, 7-H), 7.50 (t, $J = 9.9$ Hz, 1H, 6-H), 3.46 (m, 1H, c-Hex), 3.20 (sept, $J = 7.0$ Hz, 1H, i-Pr), 3.12–3.06 (m, 2H, c-Hex), 2.63–2.57 (m, 1H, c-Hex), 2.19–2.16 (m, 1H, c-Hex), 1.63–1.57 (m, 1H, c-Hex), 1.41–1.39 (m, 7H, i-Pr, c-Hex), 1.03 (s, 9H, t-Bu) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 176.4$ (q, $J = 34.8$ Hz, COCF$_3$), 153.4, 152.5, 145.2, 142.8, 137.4, 136.9, 131.6, 128.8, 128.4, 117.5 (q, $J = 290.3$ Hz, CF$_3$), 115.6, 44.5, 39.6, 32.7, 28.0, 27.9, 27.4, 25.2, 24.6, 24.5, 24.3 ppm; HRMS (MALDI–TOF, positive) calcd for C$_{23}$H$_{27}$F$_3$O + H$^+$ [M + H]$^+$ 377.2087, found 377.2060.

**Compound 9:** DDQ (1.37 g, 6.04 mmol) was added at 0 °C to a solution of 8 (748 mg, 1.99 mmol) in toluene (30 mL). The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into K$_2$CO$_3$ aq., extracted with toluene, washed with brine, and dried with Na$_2$SO$_4$. The crude product was purified by column chromatography on silica gel with toluene as an eluent to give 9 (639 mg, 86%) as a brown solid. M.p. 128–130 °C; IR (AT-IR): $\nu_{\text{max}} = 2963$ (w), 1632 (m), 1611 (w), 1509 (w), 1482 (w), 1463 (m), 1419 (w), 1367 (w), 1333 (w), 1281 (w), 1265 (m), 1254 (m), 1244 (m), 1225 (w), 1191 (m), 1182 (m), 1127 (s), 1070 (m), 1049 (s), 1000 (w), 958 (m), 898 (w), 877 (w), 820 (m), 798 (m), 772 (w), 738 (w), 704 (w), 673 (w), 656 (w) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 249 (4.38), 293 (4.58), 349 sh (4.30), 362 (4.35), 454 (4.04) nm; UV/Vis (10% TFA/CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 286 (4.26), 310 sh (4.15), 366 (4.25), 406 sh (4.07), 474 sh (3.61) nm; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 9.88$ (d, $J = 1.7$ Hz, 1H, 9-H), 8.89 (d, $J = 8.3$ Hz, 1H, 5-H), 8.38 (d, $J = 2.0$ Hz, 1H, 4-H), 8.27 (d, $J = 8.6$ Hz, 1H, 1-H), 7.86–7.82 (m, 2H, 2-H, 7-H), 7.73 (dd, $J = 10.9, 8.3$ Hz, 1H, 6-H),
3.26 (sept, $J = 6.9$ Hz, 1H, $i$-Pr), 1.48 (s, 9H, $t$-Bu), 1.45 (d, $J = 6.9$ Hz, 6H, $i$-Pr) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_{C} = 176.3$ (q, $J = 35.2$ Hz, COCF$_3$), 155.7, 149.0, 146.3, 143.9, 139.9, 138.0, 136.7, 131.8, 131.1, 130.8, 129.5, 121.0, 117.8 (q, $J = 289.9$ Hz, CF$_3$), 116.8, 113.1, 39.9, 35.0, 31.7, 24.5 ppm; HRMS (MALDI–TOF, positive) calcd for C$_{23}$H$_{23}$F$_3$O$^+$ [M]$^+$ 372.1696, found 372.1690.

**Compound 10:** NaBH$_4$ (92 mg, 2.43 mmol) was added to a solution of 9 (545 mg, 1.46 mmol) in THF (6 mL) and diglyme (1.5 mL), and the resulting mixture was stirred for 1 h. Then, NaBH$_4$ (84 mg, 2.22 mmol) and BF$_3$·Et$_2$O (0.7 mL) was added to the reaction mixture, and the resulting mixture was stirred for 2 h. The reaction mixture was poured into water, extracted with toluene, washed with brine, and dried with Na$_2$SO$_4$. The crude product was purified by silica gel column chromatography with hexane/toluene (2:1) as an eluent to give 10 (376 mg, 38%) as a green solid. M.p. 128–130 °C; IR (AT-IR): $\nu_{\text{max}} = 2965$ (w), 1698 (w), 1609 (w), 1521 (w), 1463 (w), 1395 (w), 1364 (w), 1254 (w), 1216 (w), 1164 (s), 1123 (s), 1081 (m), 1002 (w), 926 (w), 883 (w), 862 (w), 836 (w), 790 (m), 758 (s), 679 (w), 665 (w) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 238 (4.15), 306 (4.55), 370 (3.59), 388 (3.61), 409 (3.51), 573 (2.66), 623 (2.66), 702 sh (2.60) nm; UV/Vis (10% TFA/CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 270 (4.24), 291 sh (4.10), 306 (4.18), 372 sh (4.03), 406 (4.14) nm; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H = 8.33 (s, 2H, 4-H), 8.21 (d, $J = 8.0$ Hz, 2H, 5-H), 8.03 (d, $J = 8.6$ Hz, 2H, 1-H), 7.75 (m, 4H, 2-H, 9-H), 7.02 (d, $J = 11.5$ Hz, 2H, 7-H), 6.93–6.97 (m, 2H, 6-H), 6.15 (q, $J = 11.8$ Hz, 1H, CH), 2.62 (sept, $J = 6.9$ Hz, 2H, $i$-Pr), 1.47 (s, 18H, $t$-Bu), 0.97 (d, $J = 6.9$ Hz, 6H, $i$-Pr), 0.92 (d, $J = 6.9$ Hz, 6H, $i$-Pr) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_{C} = 144.5$, 143.8, 141.4, 139.6, 136.0, 135.5, 130.6, 129.5, 128.1 (q, $J = 280.7$ Hz, CF$_3$), 127.4, 126.2, 125.6, 119.1, 118.0, 116.5, 42.1 (d, $J = 30.0$ Hz, CH), 38.7, 35.0, 31.9, 23.8, 23.7 ppm; HRMS (MALDI–TOF, Positive) calcd for C$_{44}$H$_{47}$F$_3$O$^+$ [M]$^+$ 632.3624, found 632.3601; HRMS (MALDI–TOF, positive) calcd for C$_{44}$H$_{47}$F$_3$ + Ag$^+$ [M + Ag]$^+$ 739.2675, found 739.2698.
**Compound 11:** 1M MeONa in MeOH (40 mL) was added to a solution of 8 (685 mg, 1.82 mmol) in MeOH (10 mL). The resulting mixture was refluxed for 23 h. After cooling to room temperature, the reaction mixture was poured into NH₄Cl aq., extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/AcOEt (4:1) as an eluent to give 11 (283 mg, 46%) as purple oil. IR (AT-IR): ν_max = 2958 (m), 1682 (m), 1525 (w), 1464 (m), 1442 (s), 1420 (m), 1389 (m), 1379 (m), 1364 (m), 1331 (w), 1299 (w), 1217 (s), 1189 (m), 1171 (m), 1117 (m), 1068 (w), 1025 (m), 957 (w), 923 (w), 885 (w), 829 (w), 781 (m), 757 (m), 735 (w), 693 (w), 675 (w), 666 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_H = 9.61 (s, 1H, 9-H), 8.13 (d, J = 10.0 Hz, 1H, 5-H), 7.61 (d, J = 10.0 Hz, 1H, 7-H), 7.32 (t, J = 10.0 Hz, 1H, 6-H), 3.95 (s, 3H, CO₂Me), 3.61–3.57 (m, 1H, c-Hex), 3.20–3.06 (m, 3H, i-Pr, c-Hex), 2.63–2.58 (m, 1H, c-Hex), 2.18–2.14 (m, 1H, c-Hex), 1.56–1.54 (m, 1H, c-Hex), 1.45–1.34 (m, 7H, i-Pr, c-Hex), 1.03 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 166.9, 153.8, 148.3, 142.2, 139.8, 136.0, 135.4, 130.8, 126.2, 125.5, 111.4, 50.7, 45.0, 39.4, 32.7, 29.0, 27.6, 25.3, 24.83, 24.81, 24.3 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₃H₃₀O₂⁺ [M]⁺ 338.2240, found 338.2222.

**Compound 12:** DDQ (254 mg, 1.12 mmol) was added at 0 °C to a solution of 11 (122 mg, 0.360 mmol) in toluene (20 mL). The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with toluene. The organic layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with toluene to give 12 (104 mg, 86%) as a green solid. M.p. 131 °C; IR (AT-IR): ν_max = 2959 (w), 2869 (w), 1678 (s), 1608 (w), 1545 (w), 1507 (m), 1468 (s), 1409 (m), 1370 (m), 1333 (w), 1301 (w), 1272 (w), 1254 (m), 1196 (s), 1173 (s), 1140 (m), 1127 (m), 1095 (m), 1065 (w), 1050 (w), 1019
Compound 13: A solution of 12 (229 mg, 0.685 mmol) in 100% H₃PO₄ (20 mL) was stirred at 100 °C for 1.5 h. After cooling to room temperature, the reaction mixture was poured into water, extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by alumina column chromatography with hexane as an eluent to give 13 (149 mg, 79%) as a blue solid. M.p. 72–75 °C; IR (AT-IR): ν_max = 2958 (s), 2925 (s), 2852 (m), 1698 (w), 1607 (w), 1508 (w), 1462 (s), 1415 (w), 1362 (m), 1253 (m), 1073 (w), 923 (w), 880 (w), 823 (m), 786 (m), 754 (w), 719 (w), 702 (w), 688 (w), 665 (w), 656 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λ_max (log ε) = 253 (4.08), 306 (4.74), 363 (3.71), 382 (3.73), 402 (3.47), 525 sh (2.65), 570 (2.74), 628 (2.78), 699 (2.70), 781 sh (2.57) nm; UV/Vis (10% TFA/CH₂Cl₂): λ_max (log ε) = 276 (4.29), 370 sh (4.12), 406 (4.38) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 8.33 (d, J = 0.9 Hz, 1H, 4-H), 8.22 (d, J = 8.3 Hz, 1H, 5-H), 7.81 (d, J = 1.7 Hz, 1H, 9-H), 7.72–7.77 (m, 2H, 1-H, 2-H), 7.18 (br s, 1H, 10-H), 7.11 (dd, J = 11.5, 1.7 Hz, 1H, 7-H), 6.99 (dd, J = 11.5, 8.3 Hz, 1H, 6-H), 2.92 (sept, J = 6.9 Hz, 1H, i-Pr), 1.47 (s, 9H, t-Bu), 1.32 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 144.5, 142.4, 140.8,
Compound 14: TFAA (256 mg, 1.22 mmol) was added to a solution of 2b (145 mg, 0.517 mmol) and in DMSO (0.5 mL) and CH₂Cl₂ (5 mL). The resulting mixture was stirred at room temperature for 15 min. After the solvent was removed under reduced pressure, Et₃N (10 mL) was added, and the resulting mixture was refluxed for 2 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/toluene (1:1) as an eluent to give 14 (160 mg, 95%) as blue oil. IR (AT-IR): νₘₐₓ = 2957 (s), 2917 (m), 2867 (m), 1576 (m), 1518 (w), 1465 (s), 1436 (m), 1419 (m), 1394 (s), 1363 (m), 1328 (w), 1303 (w), 1276 (w), 1240 (m), 1224 (w), 1161 (w), 1096 (w), 1032 (w), 963 (m), 912 (m), 870 (w), 817 (w), 785 (s), 758 (s), 736 (m), 688 (w), 679 (w), 659 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δH = 8.64 (d, J = 1.4 Hz, 1H, 9-H), 8.02 (d, J = 9.5 Hz, 1H, 5-H), 7.48 (d, J = 10.3 Hz, 1H, 7-H), 7.11 (t, J = 9.9 Hz, 1H, 6-H), 3.43–3.38 (m, 1H, c-Hex), 3.24–3.20 (m, 1H, c-Hex), 3.16 (sept, J = 6.9 Hz, 1H, i-Pr), 2.99–2.92 (m, 1H, c-Hex), 2.71–2.65 (m, 1H, c-Hex), 2.28 (s, 3H, SMe), 2.25–2.21 (m, 1H, c-Hex), 1.66–1.59 (m, 1H, c-Hex), 1.53–1.45 (m, 1H, c-Hex), 1.40 (d, J = 6.9 Hz, 6H, i-Pr), 1.05 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 153.3, 143.3, 140.7, 136.6, 135.2, 132.8, 129.8, 125.0, 122.4, 115.3, 45.7, 38.8, 32.8, 27.6, 26.9, 25.2, 24.7, 24.2, 20.6 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₂H₃₅S⁺ [M⁺] 326.2063, found 326.2040.

Compound 15: DDQ (193 mg, 0.850 mmol) was added at 0 °C to a solution of 14 (137 mg, 0.420 mmol) in toluene (10 mL). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was poured into K₂CO₃ aq. and extracted with toluene. The organic
layer was washed with brine, dried with Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with toluene/EtOAc (5:1) as an eluent to give 15 (126 mg, 93%) as green oil. IR (AT-IR): ν max = 2957 (s), 2921 (m), 2866 (m), 1608 (m), 1557 (w), 1506 (m), 1461 (s), 1415 (m), 1389 (m), 1362 (m), 1297 (m), 1268 (m), 1252 (m), 1237 (m), 1205 (m), 1065 (m), 1003 (m), 973 (m), 955 (m), 930 (m), 878 (m), 828 (m), 787 (s), 756 (m), 741 (w), 713 (m), 685 (m), 670 (m), 661 (m), 653 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λ max (log ε) = 264 (4.03), 319 (4.43), 373 (3.51), 392 (3.58), 414 (3.49), 525 sh (2.44), 580 (2.48), 627 (2.49), 694 sh (2.39) nm; UV/Vis (10% TFA/CH₂Cl₂): λ max (log ε) = 306 (3.69), 367 (4.00), 401 (4.00) nm; ¹H NMR (500 MHz, CDCl₃): δH = 8.35 (dd, J = 14.6, 1.4 Hz, 2H, 9-H, 4-H), 8.25 (dd, J = 8.4, 0.7 Hz, 1H, 5-H), 7.99 (dd, J = 8.3, 0.6 Hz, 1H, 1-H), 7.83 (dd, J = 8.3, 1.7 Hz, 1H, 2-H), 7.20 (dd, J = 11.5, 0.9 Hz, 1H, 7-H), 7.08 (dd, J = 11.5, 8.3 Hz, 1H, 6-H), 3.04 (sept, J = 6.9 Hz, 1H, t-Pr), 2.39 (s, 3H, SMe), 1.49 (s, 9H, t-Bu), 1.37 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 145.4, 144.3, 141.2, 140.9, 140.5, 136.0, 131.4, 130.2, 127.2, 126.9, 125.8, 118.6, 117.1, 116.6, 38.7, 35.1, 32.0, 24.0, 19.0 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₂H₂₆S⁺ [M⁺] 322.1750, found 322.1739.

Compound 17a: NIS (340 mg, 1.51 mmol) was added to a solution of 2b (280 mg, 1.00 mmol) in CH₂Cl₂ (10 mL) and Et₃N (1 mL) at 0 °C. The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into saturated Na₂SO₃ aq., extracted with CH₂Cl₂, washed with brine, and dried with Na₂SO₄. The crude product was passed though the short alumina column with hexane as an eluent to give 16. To a degassed solution of 16 (406 mg, 1.00 mmol), phenylboronic acid (193 mg, 1.58 mmol), K₃PO₄ (669 mg, 3.15 mmol) in 1,4-dioxane (5 mL) and H₂O (0.5 mL) were added PdCl₂(dppf) (56 mg, 0.07 mmol). The resulting mixture was refluxed for 18 h. The reaction mixture was poured into water, extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude
product was purified by column chromatography on silica gel with hexane as an eluent to give 17a (299 mg, 84%) as blue oil. IR (AT-IR): ν_max = 2956 (m), 2868 (w), 1599 (w), 1573 (w), 1498 (w), 1465 (m), 1444 (m), 1392 (m), 1363 (m), 1326 (w), 1241 (w), 1174 (w), 1072 (w), 1030 (w), 957 (w), 920 (w), 829 (w), 782 (m), 761 (s), 723 (w), 702 (s), 680 (w), 666 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ_H = 8.26 (s, J = 1.1 Hz, 1H, 9-H), 8.10 (d, J = 9.5 Hz, 1H, 5-H), 7.51–7.55 (m, 4H, Ph), 7.44 (d, J = 10.3 Hz, 1H, 7-H), 7.39 (td, J = 5.7, 3.0 Hz, 1H, Ph), 7.06 (t, J = 9.9 Hz, 1H, 6-H), 3.36–3.32 (m, 1H, c-Hex), 3.17–3.13 (m, 1H, c-Hex), 3.10–3.00 (m, 2H, i-Pr, c-Hex), 2.83–2.77 (m, 1H, c-Hex), 2.21–2.17 (m, 1H, c-Hex), 1.75–1.70 (m, 1H, c-Hex), 1.53–1.44 (m, 1H, c-Hex), 1.32 (d, J = 6.9 Hz, 3H, i-Pr), 1.31 (d, J = 6.9 Hz, 3H, i-Pr), 1.09 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δ_C = 148.5, 142.4, 136.9, 136.2, 135.7, 135.1, 133.1, 130.6, 129.9, 128.3, 126.1, 126.0, 124.8, 121.3, 45.7, 38.8, 32.9, 27.6, 27.4, 25.6, 24.7, 24.45, 24.37 ppm, one signal is overlapped with other signal; HRMS (MALDI–TOF, positive) calcd for C₂₇H₃₂⁺ [M]⁺ 356.2499, found 356.2519.

**Compound 18a:** DDQ (271 mg, 1.19 mmol) was added at 0 °C to a solution of 17a (110 mg, 0.312 mmol) in toluene (15 mL). The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into K₂CO₃ aq., extracted with toluene, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene as an eluent to give 18a (74 mg, 67%) as green oil. IR (AT-IR): ν_max = 3567 (w), 2960 (m), 1541 (w), 1522 (w), 1489 (w), 1472 (w), 1457 (m), 1362 (w), 1253 (w), 1001 (w), 824 (m), 787 (m), 756 (m), 731 (m), 702 (s) cm⁻¹; UV/Vis (CH₂Cl₂): λ_max (log ε) = 252 (4.27), 319 (4.59), 375 (3.72), 393 (3.80), 416 (3.70), 536 sh (2.66), 587 (2.73), 642 (2.75), 721 sh (2.69) nm; UV/Vis (10% TFA/CH₂Cl₂): λ_max (log ε) = 274 (4.24), 347 sh (3.96), 386 (4.17), 420 (4.18) nm; ¹H NMR (500 MHz, CDCl₃): δ_H = 8.40 (d, J = 1.4 Hz, 1H, 4-H), 8.26 (d, J = 8.3 Hz, 1H, 5-H), 7.98 (s, 1H, 9-H), 7.82 (d, J = 8.3 Hz, 1H, 2-H), 7.76 (dd, J = 8.3, 1.7 Hz, 1H, 1-H), 7.67 (dd, J = 8.0, 1.1 Hz, 2H, Ph), 7.56 (t, J = 7.7 Hz, 2H, Ph),
Compound 17b: NIS (337 mg, 1.50 mmol) was added to a solution of 2b (282 mg, 1.01 mmol) in CH₂Cl₂ (10 mL) and Et₃N (1 mL) at 0 °C. The mixture was stirred at room temperature for 30 min. The reaction mixture was poured into saturated Na₂SO₃ aq., extracted with CH₂Cl₂, washed with brine, and dried with Na₂SO₄. The crude product was passed through the short alumina column with hexane as an eluent to give 16. To a degassed solution of 16 (410 mg, 1.01 mmol), 4-tert-butylphenylboronic acid (269 mg, 1.51 mmol), K₃PO₄ (638 mg, 3.01 mmol) in 1,4-dioxane (5 mL) and H₂O (0.5 mL) were added PdCl₂(dppf) (41 mg, 0.05 mmol). The resulting mixture was refluxed for 14 h. The reaction mixture was poured into water, extracted with toluene, washed with brine, and dried with Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane as an eluent to give 17b (329 mg, 79%) as blue oil. IR (AT-IR): νmax = 2957 (m), 1574 (w), 1509 (w), 1464 (m), 1392 (m), 1363 (m), 1326 (w), 1268 (w), 1242 (w), 1114 (w), 1021 (w), 923 (w), 849 (m), 817 (m), 783 (m), 757 (s), 713 (w), 686 (w), 673 (w), 664 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δH = 8.26 (s, 1H, 9-H), 8.04 (d, J = 9.7 Hz, 1H, 5-H), 7.51 (d, J = 8.3 Hz, 2H, Ph), 7.39–7.42 (m, 3H, 7-H, Ph), 7.01 (t, J = 9.7 Hz, 1H, 6-H), 3.31–3.27 (m, 1H, c-Hex), 3.15–3.10 (m, 1H, c-Hex), 2.97–3.06 (m, 2H, i-Pr, c-Hex), 2.78–2.72 (m, 1H, c-Hex), 2.16–2.13 (m, 1H, c-Hex), 1.70–1.65 (m, 1H, c-Hex), 1.44–1.41 (m, 10H, t-Bu, c-Hex), 1.29 (d, J = 6.9 Hz, 3H, i-Pr), 1.28 (d, J = 6.9 Hz, 3H, i-Pr), 1.04 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 148.6, 148.5, 142.2, 136.0, 135.7, 134.9, 133.8, 133.4, 130.2, 129.8, 126.1, 125.2, 124.7, 121.2, 45.7, 38.8, 34.7, 32.9, 31.6,
27.6, 27.5, 25.6, 24.8, 24.5, 24.4 ppm; HRMS (MALDI−TOF, positive) calcd for C_{31}H_{40}^{+} [M]^{+} 412.3125, found 412.3108.

**Compound 18b**: DDQ (227 mg, 0.998 mmol) was added to a solution of 17b (205 mg, 0.498 mmol) in toluene (15 mL) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was poured into K_{2}CO_{3} aq., extracted with toluene, washed with brine, and dried with Na_{2}SO_{4}. The crude product was purified by column chromatography on silica gel with toluene as an eluent to give 18b (107 mg, 53%) as green oil. IR (AT-IR): ν_{max} = 2961 (m), 1609 (w), 1531 (w), 1462 (m), 1416 (w), 1362 (m), 1268 (w), 1200 (w), 1106 (w), 1061 (w), 1022 (w), 1001 (w), 948 (w), 927 (w), 880 (w), 863 (w), 829 (s), 787 (m), 760 (w), 703 (w), 692 (w), 682 (w), 667 (w) cm\(^{-1}\); UV/Vis (CH_{2}Cl_{2}): λ_{max} (log ε) = 265 sh (4.30), 279 sh (4.34), 320 (4.54), 375 (3.68), 395 (3.77), 418 (3.67), 543 (2.55), 591 (2.59), 657 (2.63), 734 (2.51) nm; UV/Vis (10% TFA/CH_{2}Cl_{2}): λ_{max} (log ε) = 275 (4.18), 359 sh (4.01), 388 (4.17), 434 sh (3.97) nm; \(^{1}\)H NMR (500 MHz, CDCl_{3}): δ_{H} = 8.37 (d, J = 1.5 Hz, 1H, 4-H), 8.20–8.22 (m, 1H, 5-H), 7.99 (s, 1H, 9-H), 7.84 (d, J = 8.3 Hz, 1H, 1-H), 7.73 (dd, J = 8.3, 1.5 Hz, 1H, 2-H), 7.58 (m, 4H, Ph), 7.07 (d, J = 11.7 Hz, 1H, 7-H), 6.96 (dd, J = 11.7, 8.3 Hz, 1H, 6-H), 2.85 (sept, J = 6.9 Hz, 1H), 1.48 (s, 9H, t-Bu), 1.43 (s, 9H, t-Bu), 1.25 (d, J = 6.9 Hz, 6H, i-Pr) ppm; \(^{13}\)C NMR (125 MHz, CDCl_{3}): δ_{C} = 149.5, 145.1, 142.8, 141.5, 140.2, 135.7, 133.7, 133.2, 130.9, 129.6, 126.9, 126.7, 126.6, 125.6, 125.1, 118.9, 116.6, 38.7, 35.1, 34.8, 32.0, 31.6, 23.9 ppm; HRMS (MALDI−TOF, positive) calcd for C_{31}H_{36}^{+} [M]^{+} 408.2812, found: 408.2797.

**Compound 20**: NBS (5.34 mg, 30.0 mmol) was added to a solution of 19 (2.40 g, 10.0 mmol) in CHCl_{3} (100 mL) and the resulting mixture was refluxed for 6 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel with toluene/EtOAc (5:1) as an eluent to give 20 (1.51 g, 48%)
as a green solid. M.p. 149 °C; IR (AT-IR): $\nu_{\text{max}} = 1687$ (m), 1593 (w), 1524 (w), 1487 (w), 1468 (m), 1444 (m), 1405 (m), 1378 (w), 1343 (w), 1317 (w), 1275 (w), 1256 (w), 1216 (w), 1184 (s), 1172 (s), 1132 (m), 1061 (w), 1018 (m), 962 (w), 948 (w), 915 (w), 888 (w), 864 (w), 839 (w), 816 (s), 783 (w), 740 (w), 696 (m) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 267 (4.49), 325 (4.57), 338 (4.60), 378 sh (3.74), 399 (3.86), 424 (3.91), 534 (2.71), 579 (2.73), 640 sh (2.59), 705 sh (2.30) nm; UV/Vis (10% TFA/CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 289 (4.22), 363 (4.27), 421 sh (3.78) nm; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 9.54$ (d, $J = 11.2$ Hz, 1H, 9-H), 8.61 (d, $J = 8.6$ Hz, 1H, 5-H), 8.46 (d, $J = 2.0$ Hz, 1H, 4-H), 8.40 (d, $J = 8.6$ Hz, 1H, 1-H), 7.80 (dd, $J = 8.6$, 1H, 2-H), 7.64 (dd, $J = 10.3$, 9.2 Hz, 1H, 7-H), 7.44–7.48 (m, 2H, 6-H, 8-H), 4.05 (s, 3H, CO$_2$Me) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 166.6$, 144.2, 140.8, 139.4, 138.3, 137.5, 132.7, 132.3, 131.9, 130.0, 128.9, 123.9, 123.4, 116.5, 111.9, 51.3 ppm; HRMS (MALDI–TOF, positive) calcd for C$_{16}$H$_{11}$BrO$_2$+ [M]$^+$ 313.9942, found 313.9949.

**Compound 21:** A solution of 20 (731 mg, 2.00 mmol) in 100% H$_3$PO$_4$ (40 mL) was stirred at 100 °C for 30 min. After cooling to room temperature, the reaction mixture was poured into water, neutralized with KOH aq. The precipitate was collected by filtration and dissolved in CHCl$_3$. The crude product was purified by silica gel column chromatography with hexane/toluene (1:1) as an eluent to give 21 (108 mg, 21%) as green crystals. M.p. 134–135 °C; IR (AT-IR): $\nu_{\text{max}} = 1596$ (w), 1463 (w), 1434 (m), 1387 (w), 1374 (w), 1325 (w), 1294 (w), 1272 (w), 1263 (w), 1234 (w), 1205 (w), 1118 (w), 1056 (w), 1044 (w), 973 (w), 938 (w), 918 (w), 878 (w), 859 (w), 841 (w), 826 (s), 802 (w), 785 (w), 771 (w), 743 (m), 713 (w), 690 (s), 655 (w) cm$^{-1}$; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 260 (4.12), 307 (4.74), 319 sh (4.66), 361 (3.72), 381 (3.81), 401 (3.71), 525 (2.56), 567 (2.65), 619 (2.67), 683 sh (2.56), 771 sh (2.32) nm; UV/Vis (10% TFA/CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 274 (4.29), 367 (4.16), 401 (4.11) nm; $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 8.47$ (s, 1H, 4-H), 8.24 (d, $J = 8.3$ Hz, 1H, 9-H), 7.94 (d, $J = 10.9$ Hz, 1H, 5-H), 7.72–7.74 (m, 2H, 1-H, 2-H), 7.21–7.27 (m, 2H, 7-H, 10-H), 7.04 (dd, $J = 8.6$, 1H, 5-H), 8.46 (d, $J = 2.0$ Hz, 1H, 4-H), 8.40 (d, $J = 8.6$ Hz, 1H, 1-H), 7.80 (dd, $J = 8.6$, 1H, 2-H), 7.64 (dd, $J = 10.3$, 9.2 Hz, 1H, 7-H), 7.44–7.48 (m, 2H, 6-H, 8-H), 4.05 (s, 3H, CO$_2$Me) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 166.6$, 144.2, 140.8, 139.4, 138.3, 137.5, 132.7, 132.3, 131.9, 130.0, 128.9, 123.9, 123.4, 116.5, 111.9, 51.3 ppm; HRMS (MALDI–TOF, positive) calcd for C$_{16}$H$_{11}$BrO$_2$+ [M]$^+$ 313.9942, found 313.9949.
11.2, 8.3 Hz, 1H, 8-H), 6.87 (dd, \( J = 10.9, 8.6 \) Hz, 1H, 6-H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 140.8, 139.7, 139.6, 136.5, 135.8, 132.9, 131.4, 129.2, 125.6, 124.3, 123.8, 121.7, 115.6, 115.5 \) ppm; HRMS (MALDI–TOF, positive) calcd for C\(_{14}H_9\)Br\(^+\) [M]\(^+\) 255.9882, found: 255.9890.

**Compound 22:** Malononitrile (69 mg, 1.04 mmol) was added to a mixture of 4b (150 mg, 0.493 mmol) and alumina (2.51 g) in CHCl\(_3\) (10 mL). The resulting mixture was stirred at room temperature for 24 h. After removing alumina by filtration, the filtrate was concentrated under reduced pressure to give 22 (170 mg, 98%) as a red solid. M.p. 163 °C; IR (AT-IR): \( \nu_{\text{max}} = 2967 \) (w), 2207 (m), 1547 (s), 1514 (w), 1480 (m), 1459 (s), 1428 (m), 1379 (m), 1363 (m), 1346 (m), 1311 (m), 1273 (m), 1243 (s), 1192 (w), 1174 (w), 1147 (w), 1127 (w), 1077 (m), 1046 (w), 1003 (w), 935 (w), 921 (w), 904 (m), 885 (w), 843 (w), 829 (m), 807 (m), 761 (w), 722 (w), 698 (w), 667 (w), 654 (w), 617 (m) cm\(^{-1}\); UV/Vis (CH\(_2\)Cl\(_2\)):\( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 275 (4.53), 327 (4.54), 372 (4.11), 389 (4.16), 481 sh (4.26), 507 (4.36) nm; UV/Vis (30\% TFA/CH\(_2\)Cl\(_2\)):\( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 277 (4.33), 328 (4.31), 373 (4.17), 390 (4.16), 513 (4.07) nm; \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta_H = 8.74 \) (d, \( J = 8.9 \) Hz, 1H, 5-H), 8.39 (s, 1H, vinyl), 8.35 (d, \( J = 1.7 \) Hz, 1H, 4-H), 8.29 (d, \( J = 1.4 \) Hz, 1H, 9-H), 8.07 (d, \( J = 8.6 \) Hz, 1H, 1-H), 7.91 (dd, \( J = 8.4, 1.9 \) Hz, 1H, 2-H), 7.75 (d, \( J = 11.2 \) Hz, 1H, 7-H), 7.65 (t, \( J = 10.9, 8.9 \) Hz, 1H, 6-H), 3.25 (sept, \( J = 6.9 \) Hz, 1H, \( i-\text{Pr} \)), 1.45–1.48 (m, 15H, \( i-\text{Pr}, t-\text{Bu} \)) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C = 153.3, 149.7, 147.5, 145.0, 144.5, 139.0, 138.0, 134.24, 134.22, 131.7, 131.3, 131.2, 129.2, 120.6, 117.3, 117.1, 115.5, 73.8, 39.8, 35.2, 31.7, 24.5 ppm; HRMS (MALDI–TOF, positive) calcd for C\(_{25}H_{24}N_2\)\(^+\) [M]\(^+\) 352.1934, found 352.1926; HRMS (MALDI–TOF, positive) calcd for C\(_{25}H_{24}N_2\) + Ag\(^+\) [M + Ag]\(^+\) 459.0985, found 459.0963.

**Compound 23a:** Piperidine (252 mg, 2.96 mmol) was added to a solution of 4a (79 mg, 0.30 mmol) and dimethyl malonate (396 mg, 3.00 mmol) in MeOH (5 mL). The resulting mixture
was stirred at room temperature for 18.5 h. The reaction mixture was poured into water, extracted with toluene/EtOAc, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/AcOEt and reversed phase column chromatography with 80% MeOH to give 23a (49 mg, 43%) as brown oil. IR (AT-IR): νₘₐₓ = 2952 (w), 1716 (m), 1587 (m), 1521 (w), 1465 (m), 1435 (m), 1415 (w), 1364 (w), 1332 (w), 1255 (s), 1239 (s), 1213 (s), 1160 (w), 1106 (w), 1070 (m), 1038 (w), 992 (w), 921 (w), 890 (w), 825 (w), 805 (w), 748 (m), 710 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 267 (4.29), 313 (4.50), 357 (4.11), 449 (4.07), 575 (2.69), 624 (2.61), 705 sh (2.44) nm; UV/Vis (10% TFA/CH₂Cl₂): λₘₐₓ (log ε) = 310 (4.63), 392 (4.11), 452 sh (3.82) nm; ¹H NMR (500 MHz, CDCl₃): δH = 8.59 (s, 1H, vinyl), 8.53 (dd, J = 8.6, 0.9 Hz, 1H, 9-H), 8.38 (d, J = 1.4 Hz, 1H, 4-H), 8.18 (d, J = 10.9 Hz, 1H, 5-H), 7.76–7.82 (m, 2H, 1-H, 2-H), 7.41 (dd, J = 10.9, 8.6 Hz, 1H, 7-H), 7.29 (dd, J = 10.9, 8.6 Hz, 1H, 8-H), 7.14 (dd, J = 10.9, 8.6 Hz, 1H, 6-H), 3.92 (s, 3H, CO₂Me), 3.55 (s, 3H, CO₂Me), 1.47 (s, 9H, t-Bu) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 167.6, 166.0, 146.4, 142.6, 140.7, 139.3, 138.6, 136.4, 134.2, 131.1, 129.8, 128.2, 128.0, 126.9, 122.8, 119.5, 119.4, 116.8, 52.6, 52.4, 35.2, 31.9 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₄H₂₄O₄⁺ [M⁺] 376.1669, found 376.1651.

**Compound 23b:** Piperidine (148 mg, 1.74 mmol) was added to a solution of 4b (52 mg, 0.17 mmol) and dimethyl malonate (256 mg, 1.94 mmol) in MeOH (5 mL). The resulting mixture was stirred at room temperature for 20 h. The reaction mixture was poured into water, extracted with toluene/EtOAc, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/AcOEt (4:1) as an eluent to give 23b (57 mg, 80%) as brown oil. IR (AT-IR): νₘₐₓ = 2960 (w), 1712 (m), 1637 (w), 1585 (w), 1508 (w), 1469 (m), 1434 (m), 1365 (w), 1303 (w), 1236 (s), 1215 (s), 1191 (m), 1159 (w), 1106 (w), 1072 (m), 1041 (w), 1004 (w), 954 (w), 915 (w), 880 (w), 864 (w), 826 (w), 795 (w), 755 (s), 666 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 250 sh (4.27), 268 (4.35), 291
Compound 24a: Piperidine (286 mg, 3.34 mmol) was added to a solution of 6a (59 mg, 0.29 mmol) in MeOH (5 mL) and dimethyl malonate (333 mg, 2.52 mmol). The resulting mixture was stirred at room temperature for 18.5 h. The reaction mixture was poured into water, extracted with toluene/EtOAc, washed with brine, and dried with Na2SO4. The crude product was purified by column chromatography on silica gel with toluene/AcOEt and reversed phase column chromatography with 80% MeOH to give 24a (42 mg, 46%) as a green solid. M.p. 110–113 °C; IR (AT-IR): νmax = 1734 (m), 1713 (m), 1592 (m), 1489 (w), 1449 (w), 1434 (m), 1353 (w), 1324 (w), 1233 (s), 1213 (s), 1181 (m), 1068 (m), 1042 (w), 990 (w), 947 (w), 932 (w), 907 (w), 881 (w), 849 (w), 766 (m), 753 (m), 691 (m) cm⁻¹; UV/Vis (CH₂Cl₂): λmax (log ε) = 242 sh (4.23), 263 (4.29), 307 (4.46), 360 (4.08), 443 (4.06), 565 (2.71), 615 (2.65), 695 sh (2.40), 773 sh (2.01) nm; UV/Vis (10% TFA/CH₂Cl₂): λmax (log ε) = 305 (4.62), 384 (4.12), 422 sh (3.97) nm; ¹H NMR (500 MHz, CDCl₃): δH = 8.59 (s, 1H, vinyl), 8.51 (dd, J = 8.6, 0.9 Hz, 1H, 9-H), 8.39 (d, J = 8.0 Hz, 1H, 1-H), 8.19 (d, J = 11.2 Hz, 1H, 5-H), 7.83 (d, J = 8.0 Hz, 1H, 4-H), 7.70–7.73 (m, 1H, 3-H), 7.52–7.55 (m, 1H, 2-H), 7.41–7.45 (m, 1H, 7-H), 7.30 (dd, J = 10.9, 8.6 Hz, 1H, 8-H), 7.18 (dd, J = 10.6, 8.9 Hz, 1H, 6-H), 3.92 (s, 3H, CO₂Me), 3.53 (s, 3H, CO₂Me), 3.06 (sept, J = 6.9 Hz, 1H, i-Pr), 1.45 (s, 9H, t-Bu), 1.35 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 169.2, 146.9, 145.9, 142.3, 140.8, 138.3, 136.7, 136.5, 131.3, 130.8, 128.4, 127.9, 127.8, 120.0, 118.9, 116.7, 113.8, 51.5, 39.3, 35.1, 31.8, 24.0 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₇H₃₀O₄⁺ [M⁺] 418.2139, found 418.2141.
Compound 24b: Piperidine (337 mg, 3.96 mmol) was added to a solution of 6b (98 mg, 0.40 mmol) and dimethyl malonate (518 mg, 3.92 mmol) in MeOH (10 mL). The resulting mixture was stirred at room temperature for 20.5 h. The reaction mixture was poured into K₂CO₃ aq., extracted with toluene/AcOEt, washed with brine, and dried with Na₂SO₄. The crude product was purified by column chromatography on silica gel with toluene/AcOEt and reversed phase column chromatography with 80% MeOH to give 24b (100 mg, 70%) as brown oil. IR (AT-IR): νmax = 2956 (w), 1713 (m), 1600 (w), 1579 (m), 1505 (w), 1482 (w), 1459 (w), 1433 (m), 1364 (w), 1315 (w), 1235 (s), 1187 (m), 1159 (w), 1072 (m), 1048 (w), 986 (w), 941 (w), 895 (w), 860 (w), 829 (w), 803 (w), 760 (s), 723 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λmax (log ε) = 246 sh (4.22), 265 (4.30), 311 (4.45), 360 (4.03), 449 (4.06), 560 (2.79), 629 (2.72), 694 sh (2.51) nm; UV/Vis (10% TFA/CH₂Cl₂): λmax (log ε) = 304 (4.55), 378 (4.09), 420 sh (3.95) nm; ¹H NMR (500 MHz, CDCl₃): δH = 8.61 (s, 1H, vinyl), 8.38 (dd, J = 8.5, 0.9 Hz, 1H, 5-H), 8.31 (d, J = 8.0 Hz, 1H, 1-H), 8.09 (s, 1H, 9-H), 7.79 (d, J = 8.0 Hz, 1H, 4-H), 7.68 (t, J = 8.0 Hz, 1H, 3-H), 7.47 (t, J = 8.0 Hz, 1H, 2-H), 7.40 (d, J = 11.4 Hz, 1H, 7-H), 7.30 (dd, J = 11.4, 8.5 Hz, 1H, 6-H), 3.93 (s, 3H, CO₂Me), 3.51 (s, 3H, CO₂Me), 3.04–3.09 (sept, J = 13.5, 1H, i-Pr), 1.35 (d, J = 6.9 Hz, 6H, i-Pr) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 167.5, 166.1, 148.0, 142.4, 140.8, 140.4, 139.6, 136.7, 131.8, 131.0, 129.4, 129.2, 128.2, 122.8, 122.3, 120.9, 119.4, 119.0, 52.6, 52.2, 39.2, 23.9 ppm; HRMS (MALDI–TOF, positive) calcd for C₂₃H₂₂O₄⁺ [M⁺] 362.1513, found 362.1510; HRMS (MALDI–TOF, positive) calcd for C₂₃H₂₂O₄ + Ag⁺ [M + Ag⁺] 469.0564, found 470.0541.
**Compound 25**: A solution of 24b (42 mg, 0.13 mmol) in Eaton’s reagent (3 mL) was stirred at 70 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into brine, extracted with CHCl₃/EtOAc, and dried with Na₂SO₄. The crude product was purified by silica gel column chromatography with EtOAc as an eluent to give 25 (25 mg, 66%) as a red solid. M.p. 133 °C; IR (AT-IR): νmax = 1712 (m), 1681 (w), 1624 (m), 1605 (w), 1574 (m), 1543 (s), 1498 (m), 1438 (m), 1416 (m), 1389 (m), 1338 (m), 1304 (m), 1261 (m), 1240 (m), 1214 (s), 1114 (m), 1065 (m), 1012 (m), 976 (w), 876 (w), 863 (w), 774 (m), 740 (m), 706 (m), 695 (m), 680 (m), 663 (w) cm⁻¹; UV/Vis (CH₂Cl₂): λmax (log ε) = 272 (3.98), 281 (4.02), 312 (4.15), 328 sh (4.15), 337 (4.19), 366 (4.11), 383 (4.19), 455 sh (3.81), 488 (4.17), 522 (4.32) nm; UV/Vis (10% TFA/CH₂Cl₂): λmax (log ε) = 271 (4.10), 289 (3.81), 340 (4.27), 351 (4.26), 481 (4.27) nm; ¹H NMR (500 MHz, CDCl₃): δH = 8.91 (s, 1H, 1-H), 8.66–8.70 (m, 2H, 4-H, 11-H), 8.53–8.57 (m, 2H, 6-H, 7-H), 7.85 (t, J = 7.6 Hz, 1H, 5-H), 7.67–7.71 (m, 1H, 9-H), 7.60–7.54 (m, 2H, 8-H, 10-H), 3.99 (s, 3H, CO₂Me) ppm; ¹³C NMR (125 MHz, CDCl₃): δC = 181.3, 168.0, 146.7, 145.7, 140.0, 139.0, 136.8, 135.0, 134.3, 132.8, 132.3, 129.4, 127.9, 126.9, 125.8, 125.5, 117.8, 52.4 ppm; HRMS (MALDI–TOF, positive) calcd for C₁₉H₁₂O₃ + H⁺ [M + H⁺]⁺ 289.0859, found 289.0852.

**Synthesis of 25 with PPA**: A solution of 24a (77 mg, 0.24 mmol) in PPA (10 mL) was stirred at 95 °C for 11 h. After cooling to room temperature, the reaction mixture was poured into brine, extracted with CHCl₃/EtOAc, and dried with Na₂SO₄. The crude product was purified by silica gel column chromatography with EtOAc as an eluent to give 25 (25 mg, 36%) as a red solid.
Supporting Information

Copies of $^1$H, $^{13}$C NMR, COSY spectra, HRMS, UV/Vis and fluorescent spectra, and cyclic and differential pulse voltammograms of reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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NOTES

The authors declare no competing financial interest.
Professor Masafumi Yasunami passed away on January 25, 2013.

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23 CCDC 1959815 (6b) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.


