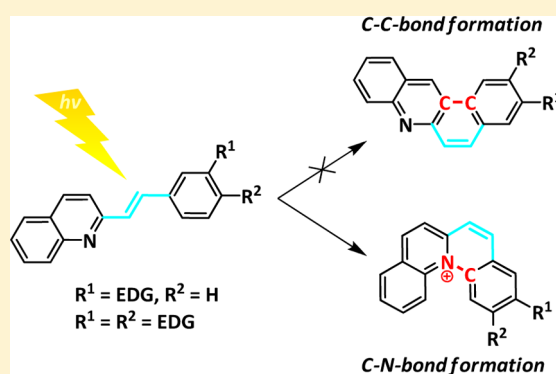# Regiospecific C−N Photocyclization of 2-Styrylquinolines

Elena N. Gulakova, Daria V. Berdnikova,* Tseimur M. Aliyeu, Yuri V. Fedorov, Ivan A. Godovikov, and Olga A. Fedorova

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S *Supporting Information*

ABSTRACT: Regiospecific C−N photocyclization of 2-styrylquinolines resulting in formation of potentially biologically active quino[1,2-a]quinolizinium derivatives was investigated. The presence of strong electron-donating groups in the phenyl ring reveals to be a crucial factor managing photocyclization effectiveness. Introduction of a crown ether moiety allows changing the photoreaction parameters by means of complexation with $Mg(ClO_4)_2$.

INTRODUCTION

Biological activity of polycondensed heteroaromatic compounds recently has been the focus of considerable interest due to high potential in developing new anticancer, antibacterial, and fungicidal drugs.[1] The main reason for the chemotherapeutic effect of the molecules possessing an extended heteroaromatic π-system is effective interaction with DNA,[2] which causes changes in the physiological functions of the nucleic acid and subsequently leads to the cell death. Significant difficulties of obtaining polycyclic aromatics by classical organic synthesis encouraged chemists to search for alternative approaches. One of the most powerful, however, not extensively studied methods is the photocyclization of stylbenes and their heterocyclic analogues.[3] The range of hetarylphenylethenes suitable for photochemical synthesis of biologically active heteroaromatic compounds is constantly expanding. Thus, photocyclization products of styryl-substituted benzimidazoles,[4,5] benzopyrroles, naphthofurans, naphthothiophenes,[6] phenanthridines,[7] and imidazopyridines[8] demonstrated high potential as anticancer and fungicidal agents. Interestingly, photocyclization of hetarylphenylethenes may lead to the formation of either neutral or charged products, which possess different biological activity. Particularly, fused heteroaromatics bearing a permanent positive charge are typical DNA-intercalators and, therefore, are of interest as potential DNA-targeting drugs.[2] From this point of view, the investigation of a phototransformation mechanism plays an important role in the development of practical applications of hetarylphenylethenes in biology and medicine.

Recently, we described novel oxidative photocyclization of indolinylphenylethenes and benzothiazolylphenylethenes leading to polycyclic heteroaromatic cations involving formation of a new C−N bond.[9,10] This photochemical transformation includes 6π-electron conrotatory electrocyclic ring closure, followed by oxidation of an intermediary dihydroelectrocycle, resulting in formation of fused products.[11−13] Moreover, we used the photocyclization reaction of 2-(3,4-dimethoxystyryl)-benzothiazole for in situ generation of a DNA-binding photoproduct directly in the presence of the nucleic acid, thus realizing photocontrolled binding with DNA.[14] In this paper, we extend our research to the phototransformations of 2-styrylquinolines **1a−1f** containing various substituents in the phenyl ring (Scheme 1). Compound **1f** was additionally modified with 15-crown-5 ether residue, providing the possibility to influence the photoreaction by complexation with a Mg^{2+} cation. Styrylquinolines **1a−1f** were prepared by condensation of quinaldine with the corresponding benzaldehyde derivatives in the presence of KOBu[t] in DMF according to published protocols.[15,16]
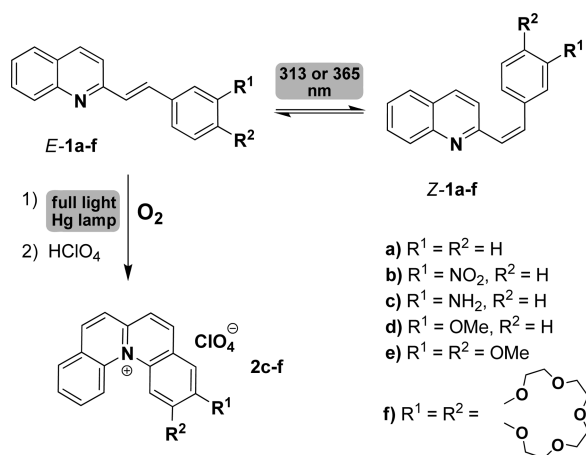
RESULTS AND DISCUSSION

Theoretically, the photocyclization of 2-styrylquinolines **1a−1f** may occur via C−C and/or C−N bond formation (Scheme 2). C−C photocyclization reveals to be the most common pathway for structurally related hetarylphenylethenes.[17] It should be noted, however, that products of C−C cyclization for 2-styrylquinolines were not reported up to now. At the same time, 4-styrylquinoline derivatives undergo quite effective C−C photocyclization.[18] On the other hand, C−N photocyclization of 2-styrylazines was described by a few authors earlier.[19] Nevertheless, in the cases reported so far, all the studied

Scheme 1. Photochemical Transformations of 2-Styrylquinolines

compounds contained a halogen in the *ortho*-position of the phenyl ring, thus resulting in the intramolecular nucleophilic substitution mechanism. In our study, we suppose the electrocyclic mechanism of the C−N bond formation that allows avoiding modification of the phenyl ring *ortho*-position without loss in C−N regiospecificity.

To develop the possible phototransformation pathways of 2-styrylquinolines, first, we examined the photoreaction of **1a−1f** in acetonitrile upon irradiation with filtered light at 313 or 365 nm (Figure 1a, Figures S1−S6, Supporting Information) in air-saturated solutions. In these experiments, photostationary equilibria of *E*- and *Z*-isomers were reached. Detailed characterization of the photolysis products was performed by NMR spectroscopy. Thus, comparison with the authentic spectra of *E*-**1a−1f** showed that all obtained photostationary mixtures consisted of two species, namely, initial isomers *E*-**1a−1f** and photoisomerization products *Z*-**1a−1f** (Figures S7−S12, Supporting Information).

Irradiation of **1a−1f** in the presence of air oxygen with unfiltered output of a high-pressure Hg vapor lamp resulted in more complicated behavior. Under these conditions, unsubstituted 2-styrylquinoline **1a** and its nitro derivative **1b** underwent photodestruction of the molecular skeleton (Figures S1 and S2, Supporting Information). At the same time, the photochemical transformation of amino-, methoxy-, and crown-substituted styrylquinolines **1c−1f** upon irradiation with full
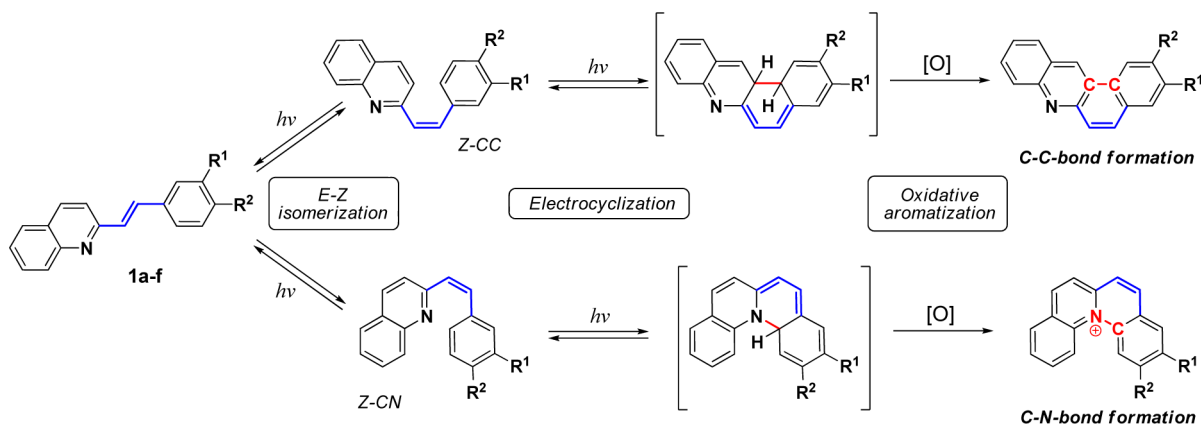
light showed sharp contrast with the previous experiments. In these cases, the photoreaction resulted in the appearance of new absorption bands in the spectral region of 400−500 nm, which were assigned to heteroaromatic species **2c−2f** (Figure 1b, Figures S3−S6 and S13, Supporting Information). The exclusive formation of C−N photocyclization products has been unambiguously proven by NMR data (Figure 2, Figures S14−S28, Supporting Information). Moreover, no positional isomerism for the substituents was detected for **2c−2f**. Heteroaromatic compounds **2d−2f** were successfully isolated as perchlorate salts by recrystallization from MeOH with a small addition of HClO$_4$ with moderate-to-good yields: **2d**, 52%; **2e**, 70%; **2f**, 45%. Characterization of the amino derivative **2c** required purification by HPLC under special conditions (injection of NaClO$_4$ solution to elute the desired species), thus leading to a very reduced amount of the obtained product. However, according to the raw NMR data, the yield of **2c** after ion exchange to perchlorate was 80%.
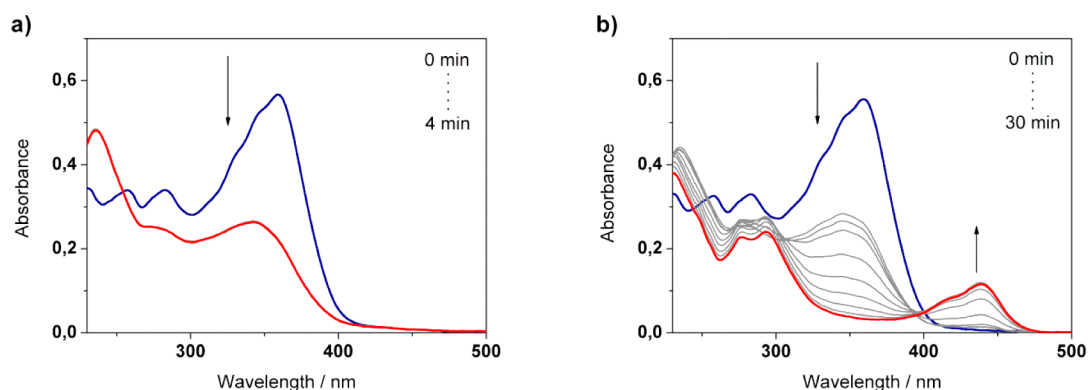
It is important to note that, for the oxidative aromatization stage, other mild oxidants may be applied such as iodine and Dess−Martin reagent. However, in these cases, we run into significant difficulties during isolation of the photocyclization products due to the presence of hardly separable iodine-containing species. At the same time, irradiation of the initial styryl derivatives upon bubbling pure oxygen through the solution led to the complete photodegradation of organic molecules.

Our efforts to stop the reaction in the electrocyclization stage and isolate the intermediary noncharged dihydrocyclic derivatives were not successful. Thus, formation of the electrocyclization products was not detected upon irradiation of 2-styrylquinolines in the deaerated solutions under argon. Most likely, dihydrocyclic intermediates are highly unstable and rapidly rearrange back into initially formed *Z*-isomers of **1a−1f** in the absence of oxidants (Scheme 2).
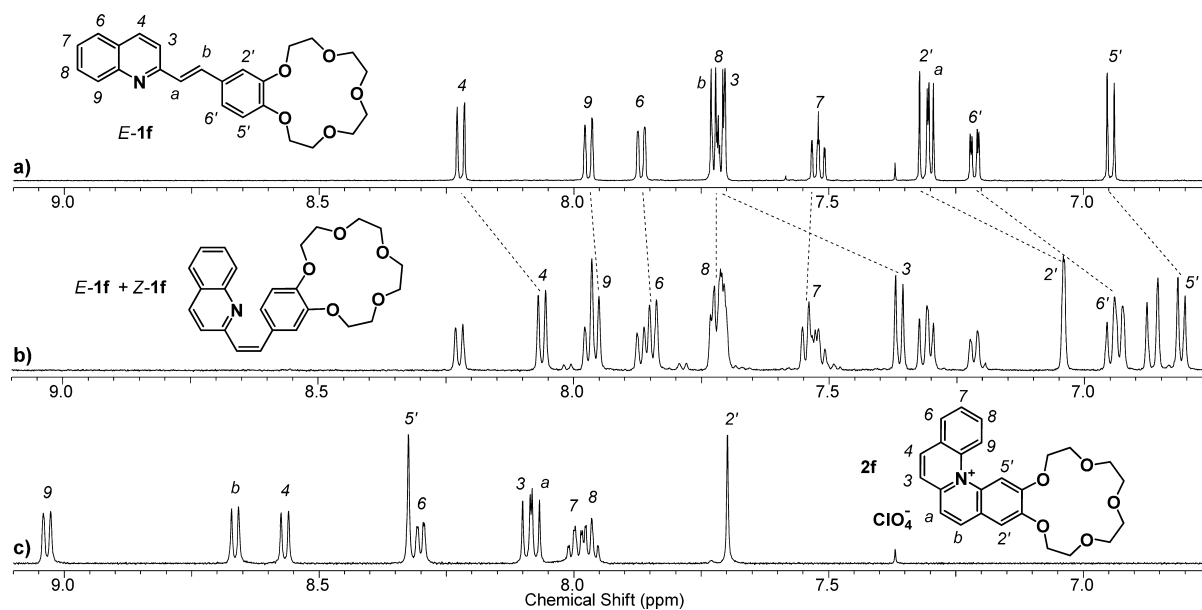
For a better understanding of the remarkable C−N regiospecificity of the studied reaction, quantum chemical calculations were carried out. Thus, geometry optimization (PM6, MOPAC) of unsubstituted 2-styrylquinoline **1a** showed that the most stable conformation of the *Z*-isomer possesses a nonplanar structure with the phenyl ring located close to protons H-3 and H-4 of the quinoline moiety (*Z-CC*) (Figure 3, Scheme 2). Stability of this conformation is also supported by NMR data (Figure 2). Thus, upon *E−Z* isomerization, signals of protons H-3 and H-4 undergo a significant upfield

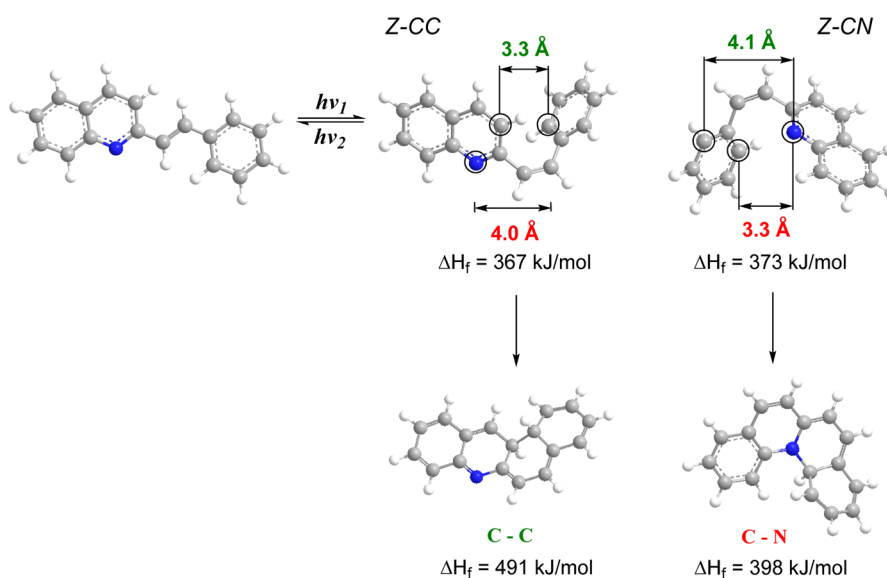**Scheme 2. Possible Photocyclization Pathways for 2-Styrylquinolines**

Figure 1. Spectral changes during the photolysis of the **1f** acetonitrile solution: (a) filtered light, $\lambda = 365$ nm; (b) full light. In both cases: $c = 2 \times 10^{-5}$ M, high-pressure Hg lamp, 20 °C.

Figure 2. ^{1}H NMR spectra in CD$_3$CN: (a) *E*-**1f**; (b) photostationary mixture of *E*-**1f** and *Z*-**1f** obtained after irradiation of the *E*-**1f** solution with filtered light, $\lambda = 365$ nm; (c) isolated photocyclization product **2f**.
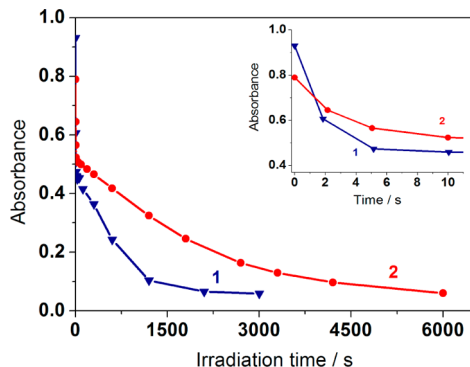

Figure 3. Optimized geometries (PM6, MOPAC) of unsubstituted 2-styrylquinoline *E*-**1a**, its *Z*-isomers, and C−C/C−N electrocyclic intermediates including calculated enthalpy of formation.

shift, whereas the positions of the rest of the quinoline proton signals remain almost unchanged. This pattern of the spectral changes discloses a strong anisotropic effect provided by the phenyl ring, which, therefore, is located in the close proximity to the aforementioned quinoline protons in the most stable conformation of the *Z*-isomer (*Z*-CC).

In terms of interatomic distances, formation of a new C—C bond (3.3 Å) in the *Z*-CC conformation is more favorable than formation of a C—N bond (4.0 Å). Therefore, formation of a C—N bond takes place from the other conformation of the *Z*-isomer (*Z*-CN), where the distance between the reacting C and N atoms is short enough (3.3 Å) to ensure bond formation. Conformation *Z*-CN was found to be 6 kJ/mol less stable in comparison to conformation *Z*-CC (Figure 3). Nevertheless, the calculated enthalpy of C—N cyclization product formation was found to be ~90 kJ/mol less than that of the C—C cyclization product, which completely matches with the experimental C—N regiospecificity of this reaction.

The next point to be discussed is the influence of the substituents in the styryl moiety of **1a**−**1f** on the occurrence of the cyclization. Apparently, effective photocyclization requires the presence of the electron donors in the phenyl ring, whereas an electron-withdrawing group (NO_2) does not favor the photocyclization. Additional evidence for the crucial role of donor substituents was provided in the experiments with crown-derived 2-styrylquinoline **1f**. Thus, complexation with a Mg^{2+} cation reduces the donor strength of crown ether oxygen atoms, which leads to pronounced deceleration of the cyclization reaction in the **1f**-Mg^{2+} complex in comparison with free **1f** (Figure 4).

Figure 4. Dependence of the absorption of *E*-**1f** (c_{1f} = 0.03 mM) (at 358 nm) (1) and (*E*-**1f**)·Mg^{2+} (c_{1f} = 0.03 mM) (at 340 nm) (2) on the time of irradiation of the air-saturated solutions with a full light of a high-pressure Hg lamp. Inset: development of the absorption changes during the first 10 s of irradiation.

These results can be reasonably interpreted if we consider the oxidative aromatization of the dihydrocyclic intermediate as a two-step process, where an electron transfer from the substrate to the oxidant precedes or follows the hydrogen abstraction. Thus, the presence of the electron-donating groups facilitates the electron transfer and, therefore, favors formation of the desired heteroaromatic cations **2c**−**2f**. Indeed, the yield of the photoreaction increases with increasing donor strength of the substituents (cf. 52% for methoxy-derived compound **2d** vs 80% for amino-derived one **2c**). Introduction of the second donor group has the same effect on the yield increase for dimethoxy substituted product **2e** (70%) in comparison with the monomethoxy substituted one **2d**. However, the yield of

crown-containing product **2f** possessing a similar substitution pattern as dimethoxy derivative **2e** was reduced (45%), most likely, due to lower photostability of the crown ether moiety. In the absence of donor substituents (**1a**) or in the presence of the acceptor (**1b**), the electron transfer is not effective enough overall, resulting in predominant photodestruction rather than formation of the photocyclization products.

■ CONCLUSION

We have developed the regioselective C—N photocyclization of 2-styrylquinolines. It was found that irradiation of **1a**−**1f** with filtered light (λ = 313, 365 nm) results only in *E*−*Z* isomerization, whereas formation of polycyclic products **2c**−**2f** requires irradiation with full light of a Hg lamp; i.e., the presence of the shorter wavelength UV light ($\lambda < 300$ nm) is essential for the occurrence of the cyclization. The photocyclization effectiveness is strongly dependent on the electronic factors of the substituents in the styryl moiety. Thus, the process is favored only in the presence of donor groups, whereas acceptor groups or the absence of any substituents does not support formation of the polycyclic products. Tuning of the donor strength allows one to manipulate the photoreaction rate that was demonstrated by complexation of crown-modified styrylquinoline **1f** with a Mg^{2+} cation. Overall, the studied phototransformation can be used as a very simple and effective approach toward synthesis of the potentially biologically active quino[1,2-*a*]quinolizinium derivatives.

■ EXPERIMENTAL SECTION

All reagents and solvents were obtained from commercial sources and used as received. $Mg(ClO_4)_2$ for the complexation studies with crown-containing compounds was dried in vacuum at 230 °C. ^{1}H NMR spectra were recorded at 400 or 600 MHz, and ^{13}C NMR spectra were recorded at 150 MHz at ambient temperature using 5 mm tubes. Chemical shifts were determined with an accuracy of 0.01 and 0.1 ppm for ^{1}H and ^{13}C spectra, respectively, and are given relative to the residual signal of the solvent that was used as an internal reference. Spin−spin coupling constants were determined with an accuracy of 0.1 Hz. Low-resolution electrospray ionization (ESI) mass spectra were detected in the mode of full mass scanning of positive ions on a tandem dynamic mass spectrometer equipped with a mass analyzer with an octapole ionic trap. High-resolution mass spectra were recorded on a time-of-flight instrument in a positive-ion mode using electrospray ionization method. Electronic absorption spectra were measured on a fiber-optic spectrometer connected to a computer at 20 ± 1 °C. Preparation and handling of the solutions were carried out under red light. Photochemical reactions were carried out with a high-pressure Hg vapor lamp (120 W) and an immersed Hg photoreactor (125 W).

Synthesis of the Photocyclization Products (2c−2f). The acetonitrile solutions (1 mM) of *E*-**1c**−**1f** (50 mg; **1c**: 0.20 mmol, **1d**: 0.19 mmol, **1e**: 0.17 mmol, **1f**: 0.12 mmol) were irradiated with the immersed Hg photoreactor (125 W) under UV−vis spectroscopy control. As soon as maximum conversion was reached, the solvent was removed in vacuum and the residue was washed with hexane and recrystallized from MeOH with addition of $HClO_4$ to give the photocyclization products **2c**−**2f** as perchlorate salts.

3-Aminoquinolino[1,2-a]quinolinium Perchlorate (2c). Yield 80% (0.16 mmol). ^{1}H NMR (CD_3CN, 600 MHz) δ: 7.28 (splitted s, 1H, H-2′, *J* = 2.7), 7.39 (dd, 1H, H-4′, *J* = 9.6, 2.7), 7.92 (t, 1H, H-7, *J* = 6.9, 7.3), 7.97 (t, 1H, H-8, *J* = 6.9, 7.3), 8.01 (d, 1H, H-3, *J* = 8.7), 8.06 (d, 1H, H-a, *J* = 8.7), 8.26 (d, 1H, H-6, *J* = 8.2), 8.47 (d, 1H, H-4, *J* = 8.7), 8.56 (d, 1H, H-b, *J* = 8.7), 8.61 (d, 1H, H-5′, *J* = 9.6), 8.83 (d, 1H, H-9, *J* = 8.2). ESI-MS **2c** in MeCN, *m/z*: calcd. 245.30; found 245.20 [2c]+. HRMS *m/z*: 245.1059 [2c]+ (calcd. for $C_{17}H_{13}N_2$, 245.1073).

3-Methoxyquinolino[1,2-a]quinolinium Perchlorate (2d). Yield 52% (0.10 mmol, 36 mg). ^{1}H NMR (CD$_3$CN, 600 MHz) δ: 4.07 (s, 3H, OCH$_3$), 7.64 (dd, 1H, H-4′, J = 9.5, 2.9), 7.77 (splitted s, 1H, H-2′, J = 2.9), 7.99−8.08 (m, 2H, H-7, H-8), 8.18 (d, 1H, H-a, J = 8.9), 8.20 (d, 1H, H-3, J = 8.6), 8.36 (d, 1H, H-6, J = 7.6), 8.71 (d, 1H, H-b, J = 8.9), 8.72 (d, 1H, H-4, J = 8.9), 8.85 (d, 1H, H-5′, J = 9.5), 8.90 (d, 1H, H-9, J = 8.3). ^{13}C NMR (CD$_3$CN, 150 MHz) δ: 56.2, 108.6, 122.5, 123.2, 123.6, 123.7, 125.4, 125.5, 129.2, 129.5, 130.1, 131.3, 132.0, 132.8, 136.3, 139.3, 139.9, 160.1. Anal. Calcd for C$_{18}$H$_{14}$ClNO$_5$: C, 60.09; H, 3.92; N, 3.89; found: C, 60.12; H, 3.98; N, 3.95. ESI-MS **2d** in MeCN, m/z: calcd. 260.31; found 260.30 [**2d**]$^+$. HRMS m/z: 260.1073 [**2d**]$^+$ (calcd. for C$_{18}$H$_{14}$NO, 260.1070).

2,3-Dimethoxyquinolino[1,2-a]quinolinium Perchlorate (2e). Yield 70% (0.12 mmol, 47 mg). ^{1}H NMR (CD$_3$CN, 600 MHz) δ: 4.04 (s, 3H, OCH$_3$), 4.10 (s, 3H, OCH$_3$), 7.74 (s, 1H, H-2′), 7.95−8.03 (m, 2H, H-7, H-8), 8.07 (d, 1H, H-a, J = 5.7), 8.11 (d, 1H, H-3, J = 6.4), 8.31 (d, 1H, H-6, J = 8.3), 8.36 (s, 1H, H-5′), 8.58 (d, 1H, H-4, J = 8.9), 8.69 (d, 1H, H-b, J = 8.9), 9.03 (d, 1H, H-9, J = 8.3). ^{13}C NMR (CD$_3$CN, 150 MHz) δ: 57.5, 57.6, 105.7, 108.8, 122.1, 124.1, 124.3, 126.6, 130.0, 130.6, 131.0, 132.2, 134.7, 137.1, 138.6, 140.5, 145.3, 152.5, 155.3. Anal. Calcd for C$_{19}$H$_{16}$ClNO$_6$: C, 58.55; H, 4.14; N, 3.59; found: C, 58.61; H, 4.11; N, 3.60. ESI-MS **2e** in MeCN, m/z: calcd. 290.34; found 290.20 [**2e**]$^+$. HRMS m/z: 290.1175 [**2e**]$^+$ (calcd. for C$_{19}$H$_{16}$NO$_2$, 290.1176).

11,12,14,15,17,18,20,21-Octahydro[1,4,7,10,13]pentaoxacyclo-pentadecino[2,3-g]quino[1,2-a]quinolin-24-ium Perchlorate (2f). Yield 45% (0.05 mmol, 28 mg), mp 224−226 °C. ^{1}H NMR (CD$_3$CN, 600 MHz) δ: 3.64 (m, 4H, H-δ,δ'), 3.71 (m, 4H, H-γ,γ'), 3.89 (m, 2H, H-β), 3.92 (m, 2H, H-β'), 4.31 (m, 2H, H-α), 4.36 (m, 2H, H-α'), 7.70 (s, 1H, H-2′), 7.95−8.01 (m, 2H, H-7, H-8), 8.07 (d, 1H, H-a, J = 8.7), 8.09 (d, 1H, H-3, J = 9.2), 8.30 (d, 1H, H-6, J = 7.8), 8.32 (s, 1H, H-5′), 8.56 (d, 1H, H-4, J = 8.7), 8.66 (d, 1H, H-b, J = 8.7), 9.03 (d, 1H, H-9, J = 8.7). ^{13}C NMR (CD$_3$CN, 150 MHz) δ: 69.4, 69.5, 70.1, 70.5, 70.6, 71.8, 106.8, 110.1, 122.4, 124.4, 124.6, 126.8, 130.2, 130.9, 131.3, 132.6, 134.9, 137.4, 138.9, 140.8, 145.5, 152.0, 155.0. Anal. Calcd for C$_{25}$H$_{26}$ClNO$_9$: C, 57.75; H, 5.04; N, 2.69; found: C, 57.81; H, 5.05; N, 2.74. ESI-MS **2f** in MeCN, m/z: calcd. 420.48; found 420.50 [**2f**]$^+$. HRMS m/z: 420.1799 [**2f**]$^+$ (calcd. for C$_{25}$H$_{26}$NO$_5$, 420.1805).

Photochemical Studies. The acetonitrile solutions of **1a−1f** (c = 20 μM) were irradiated either with filtered light (λ = 313, 365 nm) or with full light of a high-pressure mercury vapor lamp (120 W). Individual lines of the lamp emission spectrum (λ = 313, 365 nm) were isolated with the use of glass filters. All photoreactions were carried out in air-saturated solutions under stirring. The analysis of the reaction progress was performed by absorption spectroscopy.

Stability Constant Determination of the Complex 1f·Mg^{2+}. Complex formation of **1f** with a Mg^{2+} cation was studied by spectrophotometric titration in acetonitrile at 20 ± 1 °C. Upon addition of Mg(ClO$_4$)$_2$, the 1:1 (**1f·Mg^{2+}**) complex is formed due to the interaction of the magnesium cation with the crown ether residue. The stability constant of the complex was determined using the SPECFIT/32 program. The stability constant value is log K = 5.10 ± 0.02.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra, HRMS data for all new compounds, optical spectroscopy and photochemical studies data, and details of the computational methods. 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.

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