

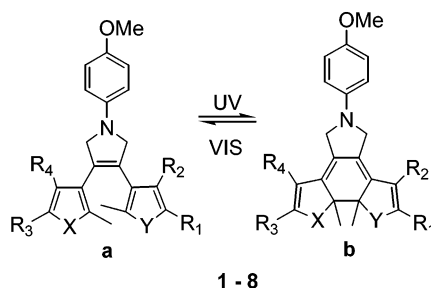
Study on Photochromism of Diarylethenes with a 2,5-Dihydropyrrole Bridging Unit: A Convenient Preparation of 3,4-Diarylpyrroles from 3,4-Diaryl-2,5-dihydropyrroles

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Symmetric and nonsymmetric diarylethenes with a 2,5-dihydropyrrole bridging unit have been prepared, and the photochromic properties are investigated. Both symmetric and nonsymmetric diarylethenes with 2,5-dihydropyrrole bridging units undergo reversible ring-opening and ring-closing photoisomerization reactions in nonpolar solvents with UV/vis light, and some of them exhibit good fatigue resistance and no marked degradation detected after 10 cycles via an on/off switch. In polar solvents, however, photochromic diarylethenes with 2,5-dihydropyrrole bridging units produce 3,4-diarylpyrrole derivatives instead of the ring-closing isomer of diarylethenes with UV light irradiation. A class of N-substituted 3,4-diphenylethenes with 2,5-dihydropyrrole bridging units were prepared and used as templates to investigate the conversion reactions. The mechanism of photoconversion of 3,4-diaryl-2,5-dihydropyrroles to 3,4-diarylpyrroles was explored as well.

Introduction

The design and synthesis of photochromic molecules is an area of intense research because of the widespread use in photonic device applications such as memory media and optical switching.^{1,2} Among various photochromic compounds, photochromic diarylethenes are the most promising organic photochromic compounds³ for

photoelectronic applications because of their fatigue resistance and thermally irreversible properties. To date, four kinds of diarylethenes with different bridge units have been reported, that is diarylethenes with a perfluorocyclopentene moiety,⁴ diarylethenes with maleic anhydride and maleimide moieties,⁵ diarylethenes with a cyclopentene moiety,⁶ and diarylethenes with a 2,5-dihydrothiophene moiety.⁷ Each kind of diarylethene has its advantages and disadvantages. Diarylethenes with a perfluorocyclopentene bridging unit, for instance, exhibit excellent photochromic properties. However, the expen-

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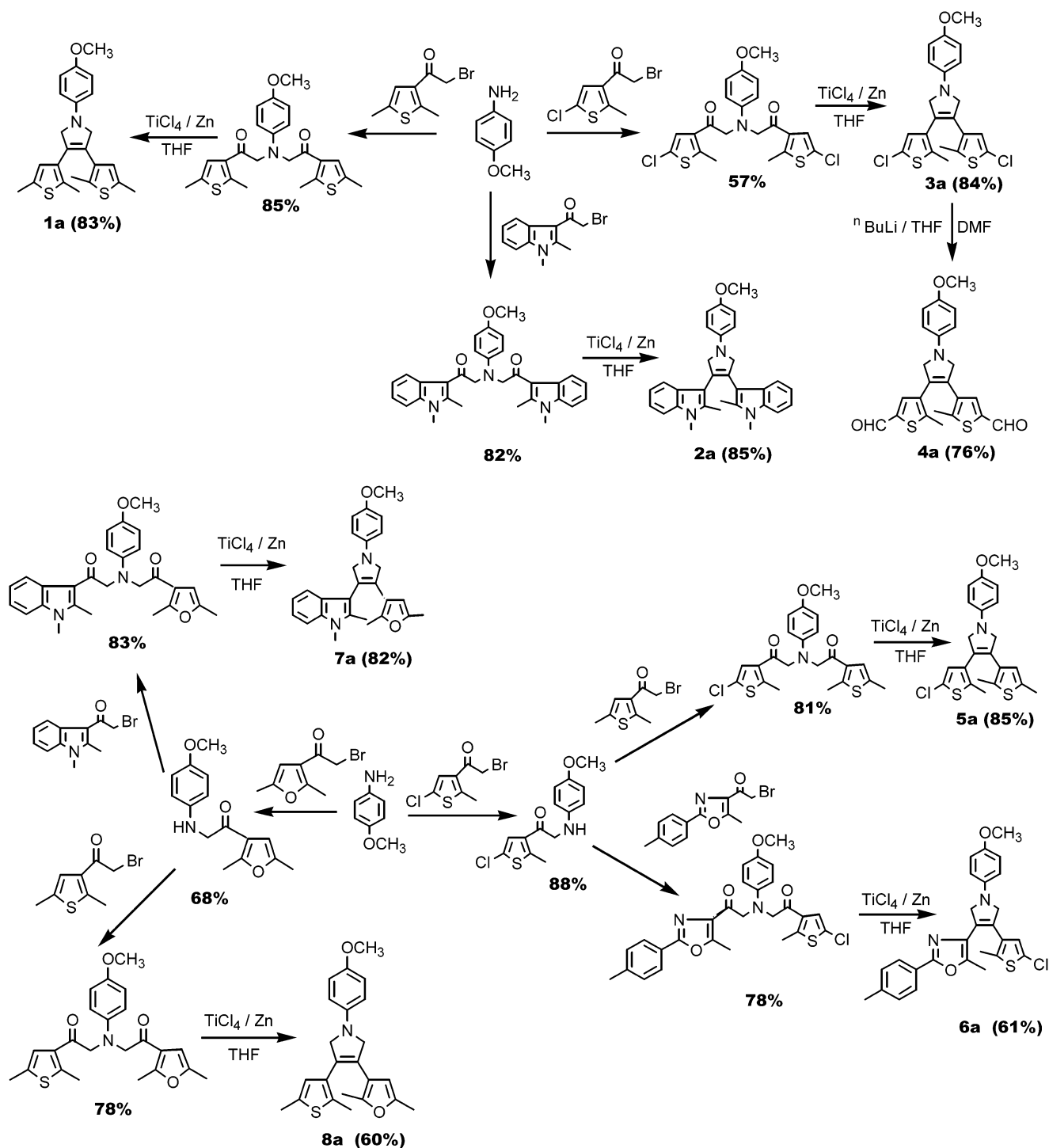
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SCHEME 1. Synthesis of Diarylethenes with a 2,5-Dihydropyrrole Bridging Unit



sive and rather volatile starting material octafluorocyclopentene poses a major disadvantage. Both diaryl-maleic anhydrides and diarylmaleimides are readily accessible but are sensitive to acidic conditions. Diarylethenes with a cyclopentene moiety and with a 2,5-dihydrothiophene moiety are facile to obtain from cheap starting materials. The major disadvantage is that non-symmetric diarylethenes are not easily prepared.

One of our research goals is to develop novel photochromic diarylethene derivatives that show good photochromic behavior. We report herein a new class of

diarylethenes with a 2,5-dihydropyrrole moiety and a novel synthetic route to preparing symmetric and non-symmetric diarylethenes. The photochromic properties of these new compounds are also presented. Compared with reported synthetic methods and properties of photochromic diarylethenes, the merits of this system are based on (1) a class of novel photochromic diarylethenes with a 2,5-dihydropyrrole moiety, (2) cheap starting materials, (3) a facile preparation, and (4) a variety of symmetric and nonsymmetric photochromic diarylethene molecules.

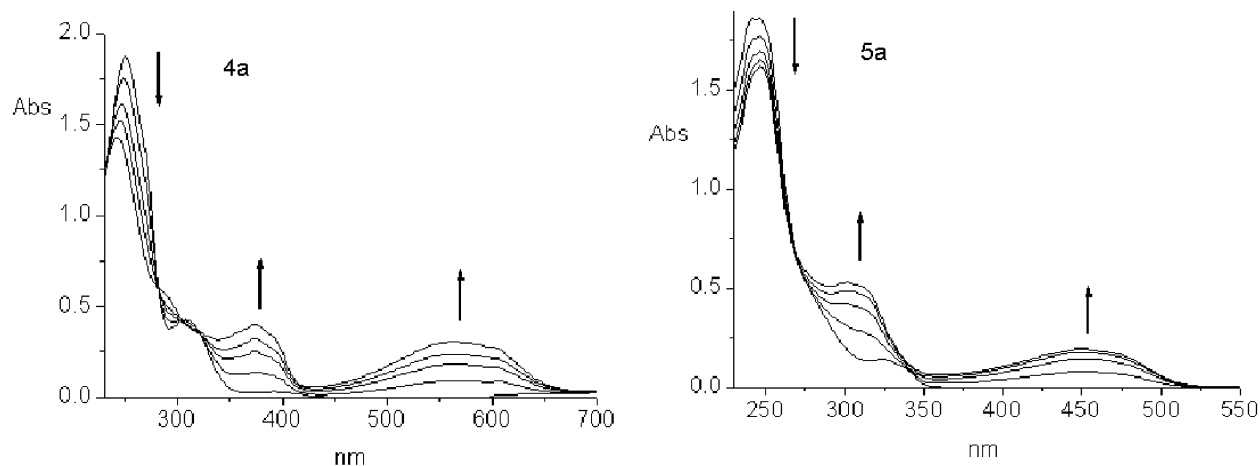
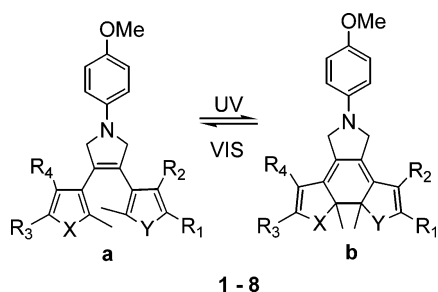


FIGURE 1. Absorption spectral changes of **4a** and **5a** ($5 \times 10^{-5} \text{M}$) in cyclohexane upon irradiation at 254 nm. Irradiation periods were 20, 40, 60, and 80 s.

SCHEME 2. Photoisomerization of Diarylethenes with a 2,5-Dihydropyrrole Bridging Unit



Results and Discussion

Photochromic diarylethenes (**1a–8a**) with a 2,5-dihydropyrrole bridging unit were prepared according to Scheme 1. The detailed synthetic procedures and characteristics of compounds can be found in the Experimental Section and Supporting Information.

Photoisomerization of diarylethenes with a 2,5-dihydropyrrole bridging unit are illustrated in Scheme 2. All synthesized diarylethenes **1a–8a** undergo reversible photochromic reactions in cyclohexane by alternating irradiation with 254 nm UV light and visible light with different wavelength cutoff filters. The changes in absorption of symmetric diarylethene **4a** and nonsymmetric diarylethene **5a** in cyclohexane at 254 nm are shown in Figure 1. Two new absorption bands appear at 380 and 583 nm, respectively, when **4a** was irradiated with 254 nm light in cyclohexane. Similar results were obtained when **5a** was irradiated under the same conditions. Two new bands appeared at long wavelengths along with a decreased band at around 250 nm. Both **4a** and **5a** show the typical absorption spectral changes of diarylethene derivatives in solution. In addition, both ring-closing isomers **4b** and **5b** can be bleached completely back to ring-opening isomers with visible light ($\geq 410 \text{ nm}$) irradiation.

The UV–vis data of other compounds for the ring-open and ring-closed isomers are listed in Table 1. Compared to the known diarylethene derivatives, all compounds showed the typical absorption spectral changes of photochromic diarylethene derivatives upon irradiation in cyclohexane. The results in Table 1 also show that the

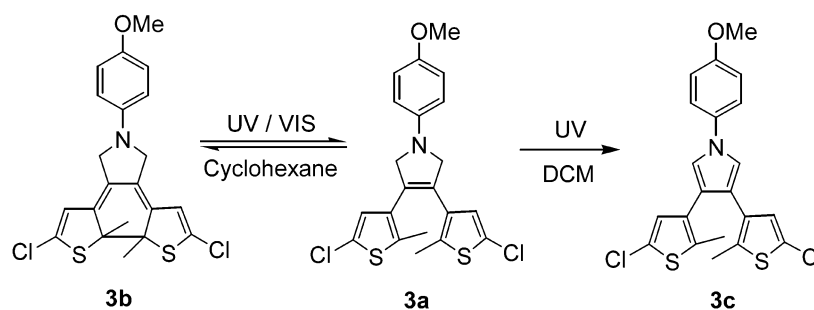
TABLE 1. UV–Vis Data of Compounds in Cyclohexane

compd	$\lambda_{\text{max}}/\text{nm}(\epsilon \times 10^4)$ (open)	$\lambda_{\text{max}}/\text{nm}$ (closed)
1	240(3.58)	450
2	234(5.65)	500
3	242(4.36)	496
4	248(3.80)	583
5	244(3.71)	450
6	286(2.69)	440
7	250(4.38)	458
8	250(3.35)	424

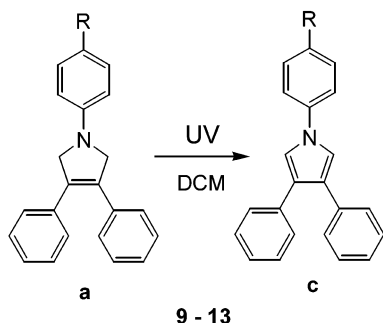
absorption maxima of ring-closed isomers arise in the region between 440 and 583 nm. In the viewpoint of application to high-density optical memory media, it was desired to develop photochromic compounds that have sensitivity in the region between 407 and 532 nm. The photochromic bleaching shows that all ring-closed isomers can be easily reversed back to ring-open isomers upon irradiation ($\geq 410 \text{ nm}$) in cyclohexane. The fatigue resistance experiments show that compounds **2**, **3**, **5**, and **7** perform very well. After 10 cycles, no marked degradation was detected by UV–vis absorption. However, there is a ca. 10% decrease in absorption (optical density) for compounds **1**, **4**, and **8** and a 25% decrease for **6** after one cycle. In addition, preliminary investigation shows that all compounds are thermally stable at ambient temperature.

It is worth noting that the solvent plays a key role in photoreactions of diarylethenes with a 2,5-dihydropyrrole bridging unit. It has been demonstrated that **3a** undergoes photochromic behavior in cyclohexane with UV/vis irradiation. The solution of **3a** in dichloromethane (DCM) with UV light irradiation produces, however, 3,4-bis(5-chloro-2-methyl)thiophene pyrrole **3c** instead of the ring-closed isomer **3b** (Scheme 3). The former cannot be reversed back to **3a** with visible light irradiation.

Compound **3c** was isolated in a yield of 70% and identified by $^1\text{H NMR}$ and MS. By comparing the $^1\text{HNMR}$ spectra of **3a** with that of **3c**, it was found that the typical signal at 4.41 ppm arising from the 2,5-dihydropyrrole bridging unit of **3a** disappeared and a new signal at 6.60 ppm, corresponding to protons in pyrrole ring, appeared in the $^1\text{HNMR}$ spectra of **3c**. Furthermore, the mass spectral analysis of **3a** and **3c** showed the relative abundance of the molecular ion (**3a**, $m/z = 436$; **3c**, m/z

SCHEME 3. Photocyclization of **3a** in Cyclohexane and Dichloromethane with UV Light

SCHEME 4. Preparation of 3,4-Diphenylpyrroles from 3,4-Diphenyl-2,5-dihydropyrroles



9 (R = H), **10** (R = CH₃), **11** (R = OCH₃), **12** (R = OH), **13** (R = Cl)

= 434) was 100%, respectively. Moreover, the absorption maximum band of **3c** ($\lambda_{\text{max}} = 270$ nm, in cyclohexane) was red shifted as much as 28 nm ($<\lambda_{\text{max}} = 270\text{--}242$ nm) and blue shifted as much as 226 nm ($<\lambda_{\text{max}} = 496\text{--}270$ nm), respectively, via comparison with **3a** and **3b**. Similar results were obtained by irradiation of other diarylethenes with 2,5-dihydropyrrole in dichloromethane and suggest that 3,4-diarylpyrroles are obtained from 3,4-diaryl-2,5-dihydropyrroles by photoreaction in DCM.

We developed a preparative method suitable to obtain nonphotochromic diarylethenes with a 2,5-dihydropyrrole bridging unit. A class of N-substituted 3,4-diphenyl-2,5-dihydropyrroles (Scheme 4) were prepared and employed as templates. The results show that all compounds **9a**–**13a** can be converted into N-substituted 3,4-diphenyl pyrroles **9c**–**13c** in good yield (65–89%) in DCM by photoreaction. The results also show that the photoreaction is readily formed, is very reliable, and appears to be capable of tolerating different patterns. It is well-known that the syntheses of pyrroles are an attractive area in heterocyclic chemistry due to the fact that many pyrroles are subunits of natural products, pharmaceutical drugs, and agrochemicals.⁸ In particular, 3,4-disubstituted pyrroles have generated considerable interest owing to their remarkable diversity of biological activity. A number of these compounds have been shown to possess antidiabetic,⁹ fungicidal,¹⁰ herbicidal,¹¹ or antibacterial¹² properties. However, it is also noteworthy that the 3,4-

disubstituted pyrrole system is probably the most difficult to obtain since selective substitutions at one or more of the β -positions have been a challenging goal in many synthetic programs because of their tendency to react in aromatic substitution reactions at the more electronically favorable α -position of the heterocyclic ring. Many methodologies for preparing 3,4-disubstituted pyrroles have been reported in the literature, including (1) coupling of imines and nitroalkanes,¹³ (2) using Friedel–Crafts acylation with an electron-withdrawing group on the pyrrole nitrogen,¹⁴ (3) use of 3,4-silylated precursors,¹⁵ (4) use of Michael acceptors with tosylmethyl isocyanide (TOSMIC),¹⁶ (5) palladium-catalyzed cyclization of amino allenes,¹⁷ (6) reduction of 3- and 4-pyrrolin-2-ones with 9-borabicyclo[3.3.1]nonane (9-BBN),¹⁸ and (7) multicomponent coupling reactions.¹⁹ The preparation of 3,4-disubstituted pyrroles from 3,4-disubstituted 2,5-dihydropyrroles by photoreaction, as far as we know, has not been reported. The photoconversion of 3,4-diaryl-2,5-dihydropyrroles into 3,4-diarylpyrroles may present a new methodology of preparation of 3,4-disubstituted pyrroles. Similar results were obtained when other solvents such as acetonitrile, chloroform, tetrahydrofuran, and toluene were employed in reaction.

To explore the mechanism of photoconversion of 3,4-diaryl-2,5-dihydropyrroles to 3,4-diarylpyrroles, the following investigations were carried out. First, DMPO (5,5-dimethyl-1-pyrroline-1-oxide) was used as a spin trap to capture the free radical hydrogen in solution, and the result is presented in Figure 2. It is demonstrated by ESR spectroscopy that the hydrogen free radical is produced when **9a** is irradiated with UV light in acetonitrile. Second, it was also confirmed that hydrogen gas was formed during the photoconversion of 3,4-diaryl-2,5-dihydropyrroles to 3,4-diarylpyrroles by the appearance

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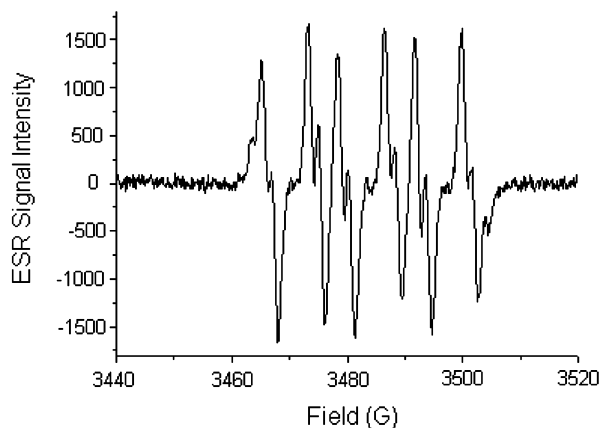


FIGURE 2. ESR spectrum of hydrogen free radical generated by irradiation of **9a** in acetonitrile.

of a singlet in the ^1H NMR spectroscopy at 5.04 ppm (H_2), and the singlet disappeared when the solution of the NMR tube was shaken with nitrogen gas. This offers a way to produce hydrogen gas by photochemistry. Additional studies of producing hydrogen from the above compounds are underway and will be reported as they become available.

Conclusion

A facile synthetic route to the preparation of symmetric and nonsymmetric photochromic diarylethenes with a 2,5-dihydropyrrole bridging unit has been developed. This new route provides ready access to a variety symmetric, nonsymmetric, and functional diarylethenes with a 2,5-dihydropyrrole bridging unit. All photochromic diarylethenes with a 2,5-dihydropyrrole unit show photochromic behavior in nonpolar solvents. A general method for the preparation of 3,4-diarylpyrroles from 3,4-diaryl-2,5-dihydropyrroles is also demonstrated. The reactions are facile, and the procedures are reliable and appear to be capable of tolerating aryl or heteroaryl substitution patterns. Solvents have great effects on the conversion of 3,4-diaryl-2,5-dihydropyrroles to 3,4-diarylpyrroles.

Experimental Section

General Methods. ^1H NMR spectra were recorded at 300 MHz with TMS as an internal reference and CDCl_3 as a solvent. MS spectra were recorded with a Trio-2000 GC-MS spectrometer. Electron spin resonance measurements were made at ambient temperature using a Varian E-109 spectrometer. All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. All reactions were monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). A low-pressure

mercury lamp (30W) and a Xeon light (500W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively. A Pyrex vessel and a high-pressure Hg lamp (500W) were used as the light source for the preparation of 3,4-diarylpyrroles from 3,4-diaryl-2,5-dihydropyrroles.

The method of detecting H_2 by ^1H NMR spectroscopy is as follows. To a sealed, vacuum NMR tube was added 3,4-diaryl-2,5-dihydropyrrole **9a** (~5 mg) in CD_3CN (~0.5 mL). The ^1H NMR spectrum was observed after the sealed vacuum NMR tube was irradiated with a high-pressure Hg lamp (500 W) for 4 h. The sealed vacuum NMR tube was then opened, and nitrogen was added to the solution in the NMR tube for 5 min.

Materials: General Procedure for Synthesis of 1a–13a. The starting material 2-bromoacetyl aryl or heteroaryl derivatives (20 mmol), Na_2CO_3 (20 mmol), and *para*-anisidine (10 mmol) or aniline derivatives (10 mmol) were dissolved into 20 mL of EtOH (95%). The mixture was stirred for 0.5 h at ambient temperature, followed by heating to reflux for 4 h. The reaction mixture was cooled and diluted with H_2O . The solid was obtained and purified by recrystallization from EtOH. To a suspension of zinc powder (0.3 mol) in THF (350 mL) under nitrogen was added TiCl_4 (10 mL) at 0 °C by syringe. The mixture was then refluxed for 1 h. To the mixture above (15 mmol) in THF (250 mL) was added the compound very slowly at ambient temperature. The reaction mixture was stirred for another 24 h in darkness, followed by quenching with K_2CO_3 (40%, 80 mL). The solid was filtered and washed with diethyl ether (50 mL). The combined organic phases were concentrated to 50 mL under reduced pressure. Water (50 mL) was then added to the residue. The product was extracted with diethyl ether (50 mL), and the solution was dried (MgSO_4). After evaporation of the solvent, the crude product was purified by flash column chromatography. Compound **4a** was prepared as follows. To a cooled (–78 °C) solution of **3a** (2 mmol) in 40 mL of THF was added dropwise 6.5 mL of *n*-butyllithium (1.6 M in hexane) under nitrogen. The reaction mixture was stirred for 15 min, allowing the temperature to rise to –50 °C, and then cooled again to –78 °C. After the addition of DMF (0.36 mL), the reaction mixture was stirred for another 4 h, allowing the temperature to rise to 0 °C, and then poured into 50 mL of ice–water. The product was extracted with CH_2Cl_2 , and the solution was dried (Na_2SO_4). After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum/ethyl acetate as an eluent.

General Procedure for Synthesis of 3c and 9c–13c. A solution of 3,4-diaryl-2,5-dihydropyrroles (0.5 mmol) in 100 mL of dichloromethane was irradiated until the starting material was no longer detected by TLC. After rota-evaporation of the solvent, the crude products were purified by column chromatography with ether acetate/petroleum as an eluent.

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Supporting Information Available: Experimental procedures and characterization relating to the synthesis of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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